

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1934.

General, Physical, and Inorganic Chemistry.

Exchange reactions of protium (H^1) and deuterium (H^2). R. H. CRIST and G. A. DALIN (J. Chem. Physics, 1933, 1, 677).— H_2O vapour containing 1% H^2 was circulated through a tube at 800° with ordinary H_2 for several days; after drying, the gas gave a spectrum with the H^2 β line strengthened.

D. R. D.

Intensity measurements on the band spectrum of helium. R. C. JOHNSON and R. C. TURNER (Proc. Roy. Soc., 1933, A, 142, 574—587).—The intensities in the bands 4650, 3676, 3556, 3206, and 3120 Å. of the main "line series" of He have been studied. The predicted distribution is of the correct type, but agreement with observation is not complete. The temp. obtained from intensity factor considerations agree with the vals. found from the position of the max. intensity in the branches. L. L. B.

Wave functions for the ground state of lithium and three-electron ions. E. B. WILSON, jun. (J. Chem. Physics, 1933, 1, 210—218).—Improved wave functions and ionisation potentials have been obtained for the configuration $1s^2 2s$, and a simple rule is derived by which the wave function of any three-electron ion may be written down without further calculation.

A. J. M.

Effects of pressure on the visible band spectra of nitrogen. H. S. HARNED and E. R. BROWNS-COMBE (J. Chem. Physics, 1933, 1, 183—185).—The visible band spectrum of N_2 in the electrodeless discharge was studied at pressures from 0.002 to 4 mm. At the lowest pressure all lines of wave-length < 5500 Å. were due to the first negative group of N_2^- (except 5463 and 4358 Å., due to at. N). With increase of pressure, the first and second positive band systems increased in intensity up to a pressure of 0.2 mm., after which the second positive band system began to fade.

A. J. M.

Structure of the second positive group of nitrogen. A. GUNTSCHE (Z. Physik, 1933, 86, 262—272).

A. B. D. C.

Second positive group of the nitrogen spectrum. D. COSTER, F. BRONS, and A. V. D. ZIEL (Z. Physik, 1933, 86, 411—412).—A correction (cf. A., 1933, 991).

A. B. D. C.

New O_2^+ bands. Dissociation energy of O_2^- and ionisation potential of O_2 . R. S. MULLIKEN and D. S. STEVENS (Physical Rev., 1933, [ii], 44, 720—723).—Three new bands in the first negative and several in the second negative system of O_2^+

are reported. The inconsistency, between ionisation potential and band spectrum data, of vals. for the dissociation energy of O_2^+ and the ionisation potential of O_2 is discussed.

N. M. B.

Triplet spectrum of aluminium hydride. W. HOLST (Z. Physik, 1933, 86, 338—347).

A. B. D. C.

Magnetic quenching of fluorescence of diatomic sulphur. J. GENARD (Compt. rend., 1933, 197, 1402—1404; cf. A., 1933, 1095).—The fluorescence produced in S_2 vapour by Hg light in a field of 40,000 gauss is diminished to varying degrees, or enhanced, according as the exciting light is of $\lambda < \text{or} > 3126$ Å.

C. A. S.

Arc spectrum of sulphur in the ultra-violet. J. E. RUEDY (Physical Rev., 1933, [ii], 44, 757—760).—Data and term vals. are tabulated for the range 100—2600 Å., and include many new lines. S was vaporised in a modified Schuler tube with a discharge in He.

N. M. B.

Spectrum of doubly-ionised argon A III. T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 724—729; cf. A., 1932, 979).—Utilising the changes in intensity and character of the lines produced by the self-induction in the discharge, a no. of A III lines have been detected and analysed.

J. W. S.

Doppler effect in spectra of positive rays of uniform velocity in argon, neon, and helium. (Miss) A. I. MCPHERSON (Physical Rev., 1933, [ii], 44, 711—716).—The positive-ray spectra in the range 2500—5000 Å., for particles of approx. uniform energy, show Doppler effect. Data for the effect in the $\lambda 3418$ Ne arc line, the A and Ne spark lines, the He arc lines (faint), and the $\lambda 4686$ He spark line are given.

N. M. B.

Spectra of potassium in successive stages of ionisation. M. RAM (Indian J. Physics, 1933, 8, 151—161).—Data and analyses for 32 lines of K III, 30 of K IV, 5 of K V, and 27 of K VI in the extreme Schumann region below $\lambda 1100$ are tabulated.

N. M. B.

Pressure effects of nitrogen on potassium absorption lines. W. W. WATSON and H. MARGENAU (Physical Rev., 1933, [ii], 44, 748—752; cf. A., 1933, 879).—Data for the pressure effects of N_2 up to 30 atm. on the first three doublets of the principal K absorption spectrum series are given. The 4045 and 3446 Å. doublets show shifts of the

absorption max. to the red, and half-widths $>$ twice those of the resonance lines. Explanations of the non-linear increase with gas density of the shifts and half-widths are discussed. N. M. B.

Spectra of trebly- and quadruply-ionised calcium. M. RAM (Indian J. Physics, 1933, 8, 163—170).—Analyses of existing data for the spark lines of Ca, giving 14 terms with 27 lines of Ca IV and 24 terms with 36 lines of Ca V, are tabulated. N. M. B.

Absorption by thin films of copper, silver, and gold in the visible and ultra-violet regions. A. SMAKULA (Z. Physik, 1933, 86, 185—194).—All three metals show small absorption maxima between 700 and 186 m μ , and these may be ascribed to electron transitions in the lattice. No new regions of transparency were observed, and this seems consistent with the presence of an ultra-violet absorption due to bound electrons together with a long-wave absorption region due to free or conductivity electrons. A. B. D. C.

Emission constants of metals in the near infra-red. C. HURST (Proc. Roy. Soc., 1933, A, 142, 466—490).—The emissivity of Cu has been determined directly over the wave-length range 1.5—5 μ for 700° and 850°, and that of Ni over the range 1—6.5 μ for 850° and 1000°. The method of measurement is described and its advantages are discussed. A comparison of the results with the vals. predicted by the classical theory of Drude and by the quantum-mechanical theory of Kronig (A., 1931, 1209) shows that the former fits the facts better. L. L. B.

Hyperfine structure of the red line of cadmium (6438), and of the green-yellow (5649) and green (5562) lines of krypton. (Miss) M. ROMANOVA and (Miss) A. FERCHMIN (Compt. rend. Acad. Sci. U.S.S.R., 1933, 2, 57—63).—The Cd line shows 3 satellites, the 5649 Kr 6, and the 5562 line 8. A. B. D. C.

Absorption of iodine vapour in presence of other gases. H. I. AGARBICEANU (Compt. rend., 1933, 197, 1198—1199; cf. A., 1933, 880).—The absorption spectrum of I vapour has been examined in presence of O₂ and N₂ (at 1—760 mm. Hg) between $\lambda\lambda$ 4000 and 6700 Å. No new band was observed, but increased absorption occurs in all progressions ν' , increasing with ν' ; progressions with $\nu''=0$ are even more affected. O₂ is slightly more active than N₂. Other mols. apparently deactivate those of I (cf. A., 1932, 787). C. A. S.

Quenching of iodine fluorescence by iodine and argon. J. F. KOEHLER (Physical Rev., 1933, [ii], 44, 761—768; cf. Turner, A., 1932, 1183).—Absorption measurements and collision probability calculations were made for fluorescence excited by the green and yellow Hg lines. A does not alter the absorption of I; the yellow excited series is quenched $>$ the green by both I and A. The complex nature of A quenching is discussed. N. M. B.

Magnetic extinction of fluorescence of iodine vapour. J. GENARD (Compt. rend., 1933, 197, 1104—1107).—Using fields up to 42,600 gauss the fluorescence-field curve for I vapour excited by

λ 5461 of HgI supports Van Vleck's explanation (cf. A., 1932, 787). C. A. S.

Nuclear moments of xenon. E. GWYNNE JONES (Nature, 1933, 132, 781).—Hyperfine structures of Xe I confirm Kopfermann's val. (A., 1933, 1096) of $\frac{1}{2}$ for the nuclear moment (I) of Xe¹²⁹; for Xe¹³¹ (I) is $>$ $\frac{1}{2}$, and from the analogy between certain Xe and Hg lines, is probably $\frac{3}{2}$. L. S. T.

Regularities in the spectrum of doubly-ionised cerium. P. N. KALIA (Indian J. Physics, 1933, 8, 137—145).—Data and analyses for 111 lines in the range λ 3544—2203 are tabulated. 38 terms were discovered and partly identified by comparison with the closely similar La II spectrum. N. M. B.

Polarisation of fluorescence bands of mercury vapour. G. ZIELINSKI (Compt. rend., 1933, 197, 1109—1111; cf. A., 1932, 891).—Fluorescence excited in Hg vapour by non-polarised light from a Zn spark, examined perpendicularly to the direction of the exciting light, shows 5.6% polarisation. C. A. S.

Hyperfine structure intensities of the 2^3S_1 — $2^3P_{0,1,2}$ triplet in optically excited mercury vapour. M. L. POOL and S. J. SIMMONS (Physical Rev., 1933, [ii], 44, 744—747).—Photographs and data for the hyperfine structures of λ 4047, 4358, and 5461 Hg lines in the arc and in fluorescence are given. The anomalous increase in intensity of the central component in fluorescence is accounted for by the absorption coeffs. of the components of λ 4047. N. M. B.

Positive ion excitation of mercury vapour. E. J. JONES (Physical Rev., 1933, [ii], 44, 707—710).—A mixture $3X_2O-Al_2O_3-3SiO_2$ ($X=Li$ or K) was found to be a powerful source of positive ions. Intensity-velocity curves found for the Hg spectral lines resulting from the bombardment of Hg vapour by Li^+ and K^+ ions indicate that velocity rather than energy is the chief factor in the mechanism of collision processes. The spark lines λ 2847, 2260, and 2224 appear at 1000 volts for Li^+ ions. N. M. B.

Experimental test of the spin-maintaining theory for atomic collisions. R. DOREL and K. GAILER (Physikal. Z., 1933, 34, 827—831).—There was preferential excitation of Hg triplets by collision with He atoms, without triplet excitation in the He. He rays after passage through Hg vapour were not markedly ionised. In colliding with Hg, the He behaves as an elastic sphere. These results disagree with those to be expected from the theory of electronic rotation impulse maintenance. A. J. M.

Theory of hyperfine structure. S. GOLDSMIT (Conv. Fis. Nucl., 1932, 1, 33—49; Chem. Zentr., 1933, ii, 178).—A discussion. A. A. E.

Analysis of Zeeman patterns. R. A. FISHER (Physical Rev., 1933, [ii], 44, 724—726).—A simple graphical representation of the line distribution, intensities, polarisation, and g vals. for Zeeman patterns in all types of spectra, and giving identification and analysis of observed patterns, is described. N. M. B.

Configuration interaction in complex spectra. C. W. UFFORD (Physical Rev., 1933, [ii], 44, 732—739; cf. A., 1933, 5).—Mathematical. N. M. B.

Relative multiplet transition probabilities from spectroscopic stability. E. U. CONDON and C. W. UFFORD (Physical Rev., 1933, [ii], 44, 740—743; cf. A., 1932, 892).—Mathematical. N. M. B.

Relative intensity tables for spectrum lines. H. E. WHITE and A. Y. ELIASON (Physical Rev., 1933, [ii], 44, 753—756).—Calc. relative intensities are tabulated under each resultant spin from singlets to octets, to include all probable L and J vals., and can be applied to g -coupling, hyperfine structure, and related multiplets. N. M. B.

Theory of broadening of spectral lines. H. MARGENAU (Z. Physik, 1933, 86, 523—529).—Fourier and statistical methods of analysing intensity distributions in spectral lines give similar results. A. B. D. C.

Absorption spectra due to excitation of inner electrons. I. General. H. BEUTLER (Z. Physik, 1933, 86, 495—515).—Absorption series due to metal vapours were observed between 1200 and 600 Å., and transitions were obtained from electron levels below the valency level, to outer levels which "pre-dissociate" into an electron and ionised atom or mol. A. B. D. C.

Delay period in sparking. F. BATH (Z. Physik, 1933, 86, 275—296).—The time required for sparking was observed with an automatic apparatus, using well-defined conditions, with the gases CO_2 , N_2 , and H_2 at atm. pressure. A. B. D. C.

Influence of a magnetic field on a glow discharge. T. TAKAMINE, T. SUGA, and A. YANAGIHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 69—96; cf. A., 1933, 1096).—At pressures of a few mm. the luminosity of a glow discharge in Ne and He is increased generally on application of a magnetic field, the length of the cathode dark space being simultaneously shortened in the same way as by increase of pressure. J. W. S.

Diffusion theory of the positive column. R. SEELIGER and A. KRUSCHKE (Physikal. Z., 1933, 34, 883—885).—Theoretical. A. J. M.

Association of ionic oscillations with the negative glow and anode glow. K. G. EMELEUS and A. H. GREGG (Phil. Mag., 1933, [vii], 16, 1079—1082). H. J. E.

Fine structure of residual rays. M. BLACKMAN (Z. Physik, 1933, 86, 421—447).—Damping of residual ray frequencies is investigated theoretically for one- and three-dimensional lattices (cf. A., 1933, 661). A. B. D. C.

Explanation of the spectrum of the corona of the sun. R. FRERICHS (Naturwiss., 1933, 21, 849).—The 6374-72 Å. line in the corona spectrum is bound up with the other O lines, and there is no reason for its isolated occurrence in the spectrum. A. J. M.

Excess of colour and the K line of calcium in interstellar absorption. A. COLACEVICH (Atti R. Accad. Lincei, 1933, [vi], 17, 1065—1069).—The relation between the intensity, I , of the K line of Ca II

and the excess of colour, EC (the deviation of the colour index from its normal val.), in interstellar light absorption is given by $I=20EC+4.4$. O. J. W.

Spectrum of the night sky and of the zodiacal light. K. R. RAMANATHAN and J. V. KARANDIKAR (Nature, 1933, 132, 749). L. S. T.

Zeeman effect in bands of comet tails. R. SCHMID and L. GERO (Z. Physik, 1933, 86, 314—320). A. B. D. C.

X-Ray spectra in the region 50—250 Å. M. SIEGBAHN and T. MAGNUSSON (Nature, 1933, 132, 750).—The more prominent lines in the L series of the X-ray spectra of the elements 19 (K) to 12 (Mg) are recorded. L. S. T.

Satellites of the $K\beta_1$ of potassium. H. TAZAKI (J. Sci. Hiroshima Univ., 1933, A, 3, 321—325).—The position of the $K\beta_1$ line of K is independent of the state of chemical combination. With metallic K as the emitting substance, $K\gamma$, $K\beta'$, $K\beta_1$, $K\beta''$, $A\beta_5$, $K\beta'''$, $K\beta''''$, and two other lines are observed. These last lie between $K\beta''$ and $A\beta_5$, and between $K\beta_5$ and $K\beta'''$, and are denoted $K\beta^v$ and $K\beta^{vi}$, respectively. When KCl, K_2SO_4 , and K_2CO_3 were used as emitting substances, $K\beta^{vi}$ was not found, was observed faintly in the case of K_2CO_3 , and the other satellites all occurred without change of wave-length. J. W. S.

Widths and shapes of the $K\alpha$ X-ray doublet from Ca (20) to Ni (28). L. G. PARRATT (Physical Rev., 1933, [ii], 44, 695—702; cf. Allison, A., 1933, 881).—Rocking curves and full widths at half max. intensity are given. Resolution into α_1 and α_2 component lines is attempted; the relative intensities, defined as the ratio of areas under the component curves, is $2:1 \pm 2\%$. The variation of the ratio of peak intensities from element to element compensates for the variation in line width giving a constant ratio for component areas. N. M. B.

New forbidden lines in the L series. S. KAUFMAN (Physical Rev., 1932, [ii], 40, 116).—Lines corresponding with forbidden transitions in elements of at. nos. 78—90 under conditions designed to reveal the $L\beta_2$ satellites are recorded. L. S. T.

Atomic factor for X-rays as a dispersion theory problem (K shell). H. HONL (Ann. Physik, 1933, [v], 18, 625—655).—Mathematical. J. W. S.

Non-relativistic theory of the continuous X-ray spectrum. F. SAUTER (Ann. Physik, 1933, [v], 18, 486—496).—Theoretical. A. J. M.

Breakdown potentials for highly purified and dried hydrogen and oxygen at pressures from 1 to 60 tor and distances of 1—35 mm., and their deviations from Paschen's law. H. FRICKE (Z. Physik, 1933, 86, 464—478). A. B. D. C.

Calculation of emission potentials from simple material constants. F. ROTHER and H. BOMKE (Z. Physik, 1933, 86, 231—240). A. B. D. C.

Heat of volatilisation of electrons in the thermionic effect. T. FRANZINI (Nuovo Cim., 1933, 10, 57—77; Chem. Zentr., 1933, ii, 21).

Mass spectrograph study of the ionisation and dissociation by electron impact of *n*-octane. E. G. LINDER (J. Chem. Physics, 1933, 1, 129—132; cf. A., 1932, 983).—Bombardment by 120-e.v. electrons causes dissociation into fragments, the most numerous containing two or three C atoms (and some H); ions containing odd nos. of H atoms are more numerous than those containing even nos. The dissociation tendency is $>$ for C_6H_6 .

N. M. B.

Electronic interference at ground and polished surfaces. H. RAETHER (Physikal. Z., 1933, 34, 839—840).—The changes taking place when multi-cryst. metallic surfaces were scratched, ground, polished, pressed, and hammered were investigated by the electron interference method. Similar experiments were carried out with single-crystal surfaces of NaCl, $CaCO_3$, CaF_2 , FeS_2 , and graphite.

A. J. M.

Efficiency of electron emission by metastable atoms. E. W. PIKE (Physical Rev., 1932, [ii], 40, 314—315).—The results of Fould and Langmuir (A., 1932, 315) are discussed.

L. S. T.

Electron density and electron temperature in freely-burning luminous arcs. R. MANNKOPFF (Z. Physik, 1933, 86, 161—184).—Ionisation potential, electron density, and degree of ionisation were determined both from diffusion of ions and from the intensity ratio of arc and spark lines. The electron temp. and gas temp. appear to differ by $< 20^\circ$ at 1 atm.; calculations of at. and electronic collision efficiencies show that electron collisions primarily cause ionisation.

A. B. D. C.

Polarisation of diffused electrons. W. M. ELSASSER (Compt. rend., 1933, 197, 1186—1188).—Forster's proof (cf. A., 1933, 1097) that polarisation cannot be produced by reflexion of an electron jet by a unidimensionally varying potential is generalised to show that Born's method never gives as a first approximation a polarisation effect for any potential (cf. A., 1932, 441).

C. A. S.

Complex electronic impacts. L. GOLDSTEIN (J. Phys. Radium, 1933, [vii], 4, 576—593).—Mathematical. The quantum theory of perturbations is applied to the mechanism of complex inelastic impacts involving at least two at. electrons.

N. M. B.

Images of the electron microscope using photo-electrons. E. BRUCHE (Z. Physik, 1933, 86, 448—450).

A. B. D. C.

Scattering of electrons by metal vapour. II. Zinc. E. C. CHILDS and H. S. W. MASSEY (Proc. Roy. Soc., 1933, A, 142, 509—518).—Measurements have been made of the angular distributions of 4—143-volt electrons scattered elastically in Zn vapour. The scattering curves are compared with those observed for Cd and Hg.

L. L. B.

Inelastic scattering of slow electrons in gases. IV. F. H. NICOLL and C. B. O. MOHR (Proc. Roy. Soc., 1933, A, 142, 647—658; cf. A., 1932, 1185).—An extension of previous measurements to CH_4 , N_2 , Ne, and Hg vapour. The inelastic scattering observed at small angles is discussed with reference to Born's theory, and the gradual disappearance of

the diffraction effects at large angles at the lower voltages is investigated.

L. L. B.

Total secondary electron emission from metal faces. S. R. RAO (J. Annamalai Univ., 1933, 2, 249—257).—The shape of the total secondary electron emission curves for metal faces and the differences between the results for multi- and single-cryst. faces can be explained by considering the absorption of secondary electrons by the photo-electric target. The mean velocity of the secondary electrons increases with increasing potential at first rapidly, and then more slowly. The results of Petry on surfaces containing adsorbed gas are confirmed and explained.

A. J. M.

Physical properties of the positron. J. THIBAUD (Compt. rend., 1933, 197, 915—917; cf. A., 1933, 993).—By the method previously described it is shown that the sp. charge of the positron is $< 1/2$, and \approx double that of the electron. Positrons are possibly emitted as a spectrum by radon and radiothorium, resulting from internal conversion of γ -radiation. Positrons are produced by the action of γ -rays on Al, Cu, Ag, Pt, Pb, Bi, and U, the more readily the higher is the at. no. of the element acted on (cf. *ibid.*, 549). The coeff. of absorption of positrons is of the same order as that of electrons of the same average energy. The charge of the positron is considered positive, thus rendering unnecessary Dirac's conception of an electron of negative mass (cf. A., 1930, 271).

C. A. S.

Positive electron. P. KUNZE (Physikal. Z., 1933, 34, 849—857).—Various methods of production of the positive electron arc reviewed, and the possibility of regarding the particle as an unstable one in the Dirac sense is discussed.

A. J. M.

Ionisation function of argon in atomic argon radiation of a few hundred ion-volt-equivalents. O. BEECK (Physikal. Z., 1933, 34, 840—841).—A method for the production of a powerful, const. beam of at. rays has been devised, and used for determination of the ionisation function of A. The no. of electrons produced per atom, in a distance of 1 cm., under a pressure of 1 mm., and at 0° is 4.5 for 350, and 6.5 for 650 ion-volt-equivs.

A. J. M.

Polarisation of positive-ray glow. W. ROMBERG (Ann. Physik, 1933, [v], 18, 515—528).—Theoretical.

A. J. M.

Atomic mass of sodium. II. Sodium chloride-silver ratio. C. R. JOHNSON (J. Physical Chem., 1933, 37, 923—933; cf. A., 1932, 922).—Six titrimetric NaCl : Ag ratios give $Na = 22.994$ ($Cl = 35.457$, $Ag = 107.880$). The same val. is obtained from five gravimetric NaCl : AgCl ratios.

F. L. U.

At. wts. of radioactive substances. F. WESTERN and A. E. RUARK (J. Chem. Physics, 1933, 1, 717—722).—Vals. are deduced for the probable at. wts. of the Pb isotopes and from these the at. wts. of radioactive substances are calc. allowing for the mass and energy lost in disintegration. It is considered that the chemical at. wt. of Ra is too low, whilst those of Th and U are too high.

H. S. P.

Isotope of hydrogen. II. P. ZEEMAN and J. DE GIER (Proc. K. Akad. Wetensch. Amsterdam, 1933,

36, 716—717; cf. A., 1933, 1099).—Positive-ray analysis of H_2 containing 10% H^3H^2 shows additional parabolas with $m/e=6$ and 20, and ascribed to H_2^+ and $OH_2^1H_2^+$ ions, respectively. J. W. S.

Isotopes of sodium and caesium. C. B. DOLLINS and E. R. BISHOP (J. Amer. Chem. Soc., 1933, 55, 4372—4374).—The magneto-optical method shows the presence of three isotopes in Na, one heavier and one lighter than 23, and of six isotopes in Cs, three lighter and two heavier than 133. E. S. H.

Manganese isotopes. I. G. OTTO and E. R. BISHOP (J. Amer. Chem. Soc., 1933, 55, 4371—4372).—The magneto-optical method of analysis indicates that Mn has seven isotopes, three of which are lighter and three heavier than 55, the most abundant. E. S. H.

Separation of isotopes. H. EYRING and A. SHERMAN (J. Chem. Physics, 1933, 1, 345—349).—Theoretical. The relative importance of effusion processes, the half quanta due to van der Waals forces, and half quanta associated with homopolar linkings is considered with respect to the separation of isotopes. Calculations are given of the role of zero-point energy in the separation of the isotopes. Only in the neighbourhood of liquid H_2 temp. are van der Waals forces important. Processes involving the breaking of homopolar linkings at moderate or low temp. are more efficient than effusion processes. Catalysts, light, electric discharges, and electrolysis, which at low temp. provide atoms which enter into subsequent reactions, are particularly effective. J. W. S.

Name and symbol for H^2 . H. C. UREY, I. M. MURPHY, and F. G. BRICKWEDDE (J. Chem. Physics, 1933, 1, 512—513).— H^1 and H^2 , and the names protium and deuterium, respectively, are proposed. F. L. U.

Thorium- C'' . (Mlle.) C. CHAMITÉ (Compt. rend., 1933, 197, 1037—1039).—To obtain Th- C'' by the recoil method on a Au plate spread with Th active deposit a circular ring of ebonite maintained at negative potential was used; the air within the ring was freed from charged dust by laying a metal plate on the ring. This was replaced for about 10 sec. by the collecting plate for Th- C'' . Saturation was obtained with a field of about 700 volts per cm. Th- C'' free from any trace of Th- C and giving a half-life period of 3.1 min. was obtained with 270 volts per cm. Slight anomalies in the beginning of the decay curve of Th- C'' were possibly connected with the fine structure of α -rays from Th- C . C. A. S.

Interaction of hard γ -rays with atomic nuclei. C. Y. CHAO and T. T. KUNG (Nature, 1933, 132, 709).—The scattering experiments described for the action of hard γ -rays (I) on Pb are interpreted as evidence for the disintegration of Pb by (I). L. S. T.

Interaction of hard γ -rays with atomic nuclei. (LORD) RUTHERFORD (Nature, 1933, 132, 709).—The experiments described (preceding abstract) provide additional evidence of the creation of negative and positive electrons by the conversion of a hard γ -ray in the strong electric field of a nucleus, and are best interpreted as such rather than as a nuclear disintegration. L. S. T.

Nuclear γ -ray absorption. T. HEITING (Naturwiss., 1933, 21, 800; cf. A., 1933, 1100).—When bombarded with hard γ -radiation, Al, Fe, Cu, and Pb give out secondary γ -radiation of wave-length 24 X independent of at. no. The process is, therefore, not a nuclear photo-process, where the wave-length should vary with at. no. There is a second component ($\lambda = 6.6$ X) which belongs to nuclear resonance or a nuclear photo-process, and of which the intensity is very small. The secondary radiation of const. wave-length may be regarded as a recombination radiation, due to the recombination of positrons and electrons arising from the absorption of the γ -rays. A. J. M.

Absorption of penetrating γ -rays. W. GENTNER (Compt. rend., 1933, 197, 1111—1112; cf. A., 1933, 995).—The difference between the coeff. of absorption per electron of Pb and that calc. by the Klein-Nishina formula for Pb, namely μ_c — shows a much less marked min. for λ 6.6 X than the differences μ_{Pb} — or μ_{Pb} — determined by Chao (cf. A., 1932, 318). C. A. S.

Use of a high-pressure ionisation chamber for the study of γ -radiation and neutrons. P. SÁVEL (J. Phys. Radium, 1933, [vii], 4, 609—612).—Ionisation current-pressure curves for the pressure range 1—30 atm. are given for γ -rays from Ra and complex radiation emitted by Be irradiated by α -particles from Po, the chamber being successively filled, in each case, with H_2 , N_2 , and A. N. M. B.

Disintegration of lithium under proton bombardment. P. I. DEE (Nature, 1933, 132, 818—819).—The proton beam is passed into the gas of the expansion chamber through a thin mica window and then allowed to fall on a thin target of Li_2O . A dense sphere of ionisation is produced by scattering of the protons in the gas, but in addition short-range particles mostly emitted in opposite pairs, can be observed. Further work is necessary to decide whether the reaction in question is ${}^7_3Li + {}^1_1H \rightarrow {}^8_4He + {}^0_{-1}e + \gamma$ -radiation or ${}^7_3Li + {}^1_1H \rightarrow {}^8_4He + {}^2_1He$. L. S. T.

Disintegration of lead by means of penetrating radiation. B. ROSSI (Atti R. Accad. Lincei, 1933, [vi], 17, 1073—1077).—The secondary particles obtained by the action of penetrating cosmic radiation on Pb are produced not singly, but in groups of several particles at once, due to nuclear disintegrations. O. J. W.

Wave-statistical theory of radioactive disintegration. K. C. KAR and A. GANGULI (Phil. Mag., 1933, [vii], 16, 1097—1109).—A relation between the disintegration const. and the velocity of the emitted α -particle is derived, and is compared with experimental vals. H. J. E.

Mechanism of the Geiger-Muller counter. G. STETTER (Physikal. Z., 1933, 34, 886).—A criticism of the experimental conditions in the work of Christoph and Hanle (A., 1933, 996). A. J. M.

Mechanism of the Geiger-Muller counter. W. CHRISTOPH and W. HANLE (Physikal. Z., 1933, 34, 886).—A reply to Stetter (preceding abstract). A. J. M.

Neutrons and positrons. W. BOTHE (Naturwiss., 1933, 21, 825—831).—A review.

New artificial source of neutrons. H. R. CRANE, C. C. LAURITSEN, and A. SOLTAN (Compt. rend., 1933, 197, 913—915; cf. A., 1933, 1225).—Using the same apparatus, LiCl and Be were bombarded with ions (deutons and protons) from a mixture of 5% H² with 95% H¹, which yielded very many more neutrons than were obtained when bombardment was with He ions (the no. was reduced by > 50% if the internal coating of the electroscope with paraffin was omitted). Bombardment with protons has no effect on Be and but little on LiCl (cf. A., 1933, 883). The disintegrations may be assumed to be $\text{Be}^9 + \text{H}^2 \longrightarrow \text{B}^{10} + n^1$ and $\text{Li}^7 + \text{H}^2 \longrightarrow 2\text{He}^4 + n^1$.

C. A. S.

Collisions of neutrons with light nuclei. II. N. FEATHER (Proc. Roy. Soc., 1933, A, 142, 689—709; cf. A., 1932, 790, 981).—The method previously described has been applied to neutron-O₂ nucleus encounters, and series of photographs of the tracks produced in O₂-H₂ and C₂H₂-He gas mixtures have been obtained. Evidence is adduced for the presence of recoil protons due to neutrons produced in the resonance disintegration of Be, and also of C recoil atoms due to neutrons of high energy. Disintegration collisions have been observed in O₂, and one case of C-nucleus disintegration by the neutrons from Po-Be.

L. L. B.

Materialisation by interaction of photon and electron. F. PERRIN (Compt. rend., 1933, 197, 1100—1102).—The min. energy, $h\nu$, of a photon that enables it on meeting an electron of mass m to materialise as a pair of electrons, + and —, is $4mc^2$, or approx. 2×10^6 e.v., of which half appears as the two electrons and half as kinetic energy, or double that required for the photon to materialise on a nucleus; the resultant electrons (two negative and one positive) have a velocity of about $4c/5$ in the direction of the incident photon. If the energy of the photon is $> 4mc^2$ the electrons will have different velocities. The result should appear as a triple fork in an expansion chamber, and should be discernible in a gas of high at. wt., e.g., Xe.

C. A. S.

Materialisation of electrons at the time of collision of two electrons: annihilation of positive electrons. F. PERRIN (Compt. rend., 1933, 197, 1302—1304; cf. preceding abstract).—The collision between an electron of kinetic energy $> 2mc^2$ (about 10^6 e.v.) and an at. nucleus should produce a pair (+ and —) of electrons, as also should one between two electrons, one at (relative) rest, the other with kinetic energy $6mc^2$, in which case the colliding and the materialised electrons should all move in the direction of the incident electron with velocity $\sqrt{3/2}c$; if the energy of the incident electron is $> 6mc^2$ the velocities and directions will be various. Conversely, a pair (+ and —) of electrons should be dematerialisable with emission of two photons each of energy mc^2 ; if this happens in presence of a third electron, then with propulsion of the electron and emission of one photon with energies of $2mc^2/3$ and $4mc^2/3$, respectively; or if in presence of two other electrons, with propulsion of each of these with energy mc^2 . Such phenomena should be recognisable in a Wilson chamber photograph.

C. A. S.

Exchange of energy between inert gas atoms and a solid surface. J. M. JACKSON and A. HOWARTH (Proc. Roy. Soc., 1933, A, 142, 447—456).—The theory of the thermal accommodation coeff. (Jackson and Mott, A., 1932, 1074) is extended by removing the restriction that all the solid atoms should oscillate with the same frequency. Good agreement is obtained with the experimental results of Roberts for the accommodation coeff. of He on a clean surface of W (*ibid.*, 316, 680).

L. L. B.

Exchange of energy between gas atoms and solid surfaces. III. Accommodation coefficient of neon. J. K. ROBERTS (Proc. Roy. Soc., 1933, A, 142, 518—524; cf. A., 1932, 316, 680).—The accommodation coeff. of Ne with a W surface free from films of adsorbed gas is 0.07 at 295° abs., and varies little with temp. down to 79° abs. With a surface covered with adsorbed films the val. is 0.6. Applying Jackson and Mott's theory of the interchange of energy between monatomic gas atoms and the atoms of a solid surface (*ibid.*, 1074) to the experimental results for He and Ne, it is shown that the repulsive forces between W atoms and the gas atoms are not similar to the forces between elastic spheres.

L. L. B.

Energy distribution in cosmic rays. W. G. POLLARD (Physical Rev., 1933, [ii], 44, 703—706).—Mathematical. Cosmic rays probably preserve their energy distribution of original emission.

N. M. B.

System of the elements. I. Vector model of the free atom. II. Periodic classification. III, IV. Interpretation of chemical properties in terms of atomic theory. V. Investigation of the atomic nucleus. VI. Structure of atomic nuclei. A. J. RUTGERS (Chem. Weekblad, 1933, 30, 602—606, 632—635, 642—646, 654—657, 671—674, 682—684).—A lecture.

H. F. G.

Pauli's principle in nuclei. W. M. ELSASSER (J. Phys. Radium, 1933, [vii], 4, 549—556).—The addition of a neutron or proton to a nucleus is considered; it gives rise to a system from the energy distribution of which various nuclear properties are explained.

N. M. B.

Bond energies and mass defects in atomic nuclei. W. M. LATIMER and W. F. LIBBY (J. Chem. Physics, 1933, 1, 133—136).—The interpretation of the mass defect curve is discussed in reference to the coupling of protons and electrons (cf. A., 1931, 544). Gamow's equation is modified by making the attractive energies the sum of the linking energies. The calc. vals. for the mass defect of the symmetrical nuclei of O, A, Zn, Xe, and Po are in good agreement with experiment.

N. M. B.

Characteristic values of the two minima problem and quantum defects of f states of heavy atoms. T. Y. WU (Physical Rev., 1933, [ii], 44, 727—731).—Mathematical. An application of the characteristic vals., solved by an approx. method, explains the fact that the calc. quantum defects are all very close to 1.

N. M. B.

Constitutive parts of atomic nuclei. D. IVAN-
EKO (Compt. rend. Acad. Sci. U.S.S.R., 1933, 2, 52—56).—Theoretical (cf. A., 1932, 981).

A. B. D. C.

Normal state of hydrogen molecule-ion. B. N. DICKINSON (J. Chem. Physics, 1933, 1, 317—318).—Rosen's treatment for H_2 (A., 1932, 211) was found not suitable for H . D. R. D.

Lifetimes of unstable molecules. N. ROSEN (J. Chem. Physics, 1933, 1, 319—326).—The lifetime of a mol. containing surplus energy is derived from consideration of internal energy transitions and compared with data for HO_2 . D. R. D.

Lifetimes of unstable molecules. O. K. RICE (J. Chem. Physics, 1933, 1, 625—626).—A note on Rosen's paper (preceding abstract). H. J. E.

Normal state of the hydrogen molecule. S. WEINBAUM (J. Chem. Physics, 1933, 1, 593—596).—The calc. dissociation energy of normal H_2 is 4.00 e.v. H. J. E.

Quantum mechanics of seven and eight electrons with spin degeneracy. H. EYRING and G. E. KIMBALL (J. Chem. Physics, 1933, 1, 239—246).—Calculations and proofs are given for assumptions previously made (A., 1933, 213) using an extension of Slater's method (A., 1931, 548) for 3 and 4 atoms. M. S. B.

Calculation of matrix elements for Lewis electronic structures of molecules. L. PAULING (J. Chem. Physics, 1933, 1, 280—283).—A simple graphical method is developed for calculating the coeff. of the integrals occurring in the matrix elements involved in Slater's treatment (A., 1931, 1356) of the electronic structure of mols. M. S. B.

Calculation of matrix elements between linking eigenfunctions. H. EYRING and G. E. KIMBALL (J. Chem. Physics, 1933, 1, 626).—Mathematical (see above). H. J. E.

Dispersion theory in metallic conductors. II. Y. FUJIOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 202—215). R. S.

Self-forces of elementary particles. I. G. WENTZEL (Z. Physik, 1933, 86, 479—494).—Theoretical. A. B. D. C.

Density of energy in the theory of light. L. DE BROGLIE (Compt. rend., 1933, 197, 1377—1380; cf. A., 1932, 1184).—Mathematical. The classical form $(\mathcal{E}^2 + \mathcal{H}^2)/2$ for the density of electromagnetic energy is approx., as is $mv^2/2$ for the kinetic energy in relativistic dynamics. C. A. S.

Atomic eigenfunctions in the impulse space. G. RUMER (Compt. rend. Acad. Sci. U.R.S.S., 1933, 104—105). H. J. E.

Relativistic theory of the Dirac electron in a nul field. A. PROCA (Ann. Physique, 1933, [x], 20, 347—440).—Mathematical. A relativistic form of the Dirac theory is approached by the introduction of a "proper time" analogous to classical proper time. The functions and physical interpretation of a new type of ternary operator are examined. N. M. B.

Heights of nuclear potential barriers. E. W. POLLARD (Phil. Mag., 1933, [vii], 16, 1131—1141; cf. A., 1933, 443).—For Li, Be, B, N, F, C, and Al the height is a linear function of the at. no. The theoretical significance of the rule is discussed. H. J. E.

Zeeman effect in solids. F. H. SPEDDING (J. Chem. Physics, 1933, 1, 144—154; 287, errata).—Crystal photographs and microphotometer curves are given for the transverse Zeeman effect on the absorption lines of monoclinic $GdCl_3 \cdot 6H_2O$. Results can be explained on the assumption that if an electron is excited as a first approximation, only its spin can orient in a magnetic field. N. M. B.

Photochemistry of solid lithium hydride. F. BACH and K. F. BONHOEFFER (Z. physikal. Chem., 1933, B, 23, 256—264).—Solid LiH has a marked absorption max. at 2517 Å., which is taken to correspond with transfer of an electron from H' to an adjacent Li⁺ giving neutral unexcited atoms. The quantum yield, measured by the evolution of H_2 , is about 0.05, which is ascribed to the bulk of the H formed remaining in the LiH lattice. LiH becomes greyish-blue on exposure to ultra-violet light, but may be decolorised by heating or exposure to visible light of long wave-length. R. C.

Spectroscopic evidence for the molecule PN. J. CURRY, L. HERZBERG, and G. HERZBERG (J. Chem. Physics, 1933, 1, 749).—An extensive system of diat. bands in the region 2400—2900 Å. has been found when a discharge is passed through N_2 containing P. The fine structure shows that the system is a $^1\Pi \rightarrow ^1\Sigma$ transition, and so cannot be due to PO or CP. The rotational and vibrational const. point to PN. H. S. P.

Spectroscopic proof and structure of the PN molecule. J. CURRY, L. HERZBERG, and G. HERZBERG (Z. Physik, 1933, 86, 348—366).—The $^1\Pi$ band system due to PN (see above) has been analysed and the nuclear separations are 1.487 and 1.542 Å. for the $^1\Sigma$ and $^1\Pi$ levels. A. B. D. C.

New band systems in the gadolinium oxide spectrum. G. PICCARDI (Nature, 1933, 132, 714).—A correction (cf. A., 1933, 1102). L. S. T.

Band spectrum of tin oxide. F. C. CONNELLY (Proc. Physical Soc., 1933, 45, 780—791).—The emission and absorption spectra of a H_2 flame containing traces of $SnCl_4$ have been investigated, and the SnO bands have been analysed. SnO is the emitter, since the spectrum can be obtained with a Sn arc in air, but not in H_2 or N_2 . Vibrational analysis of Mahanti's A system (A., 1931, 544) is extended to $v'=8$, and approx. vals. of the vibrational const. are calc. from the band head data. The lower electronic level of this system is the ground state and its energy of dissociation is 5.7 volts. J. W. S.

Band spectrum of bismuth oxide. C. GHOSH (Z. Physik, 1933, 86, 241—248).—The vibrational structure of bands between 4300 and 6700 Å. has been analysed. A. B. D. C.

Molecular spectra of some indium and gallium halides. A. PETRIKALN and J. HOCHBERG (Z. Physik, 1933, 86, 214—230).—Absorption and emission spectra in the ultra-violet were observed for $InCl_2$, $InCl$, $InBr$, $GaCl_2$, $GaBr_2$, and GaI_2 at different temp. A. B. D. C.

Change in the absorption spectrum of cobalt chloride in aqueous solution with increasing concentration of hydrochloric acid. O. R. HOWELL

and A. JACKSON (Proc. Roy. Soc., 1933, A, 142, 587—597).—From a study of the variation of the extinction coeffs. of the four principal bands 695, 666, 626, 610 m μ of solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (12 g. per litre) with increasing concn. of HCl , it is shown that no blue constituent is formed until a crit. concn. of acid (5.0*N*) is reached, and its amount then increases rapidly with increasing concn. of acid, the relation becoming linear at 7.1*N*. The state of the Co atom is determined only by the environment and is independent of the relative concn. of the Co to the other constituents. The intensity of absorption of the blue complex ion is 92.5 times that of the red.

L. L. B.

Rotation analysis of the $^2\Sigma \rightarrow ^2\Sigma$ and $^2\Pi \rightarrow ^2\Sigma$ bands of CO^+ . R. SCHMID and L. GERO (Z. Physik, 1933, 86, 297—313).

A. B. D. C.

Spectrum of the afterglow of carbon dioxide. A. FOWLER and A. G. GAYDON (Proc. Roy. Soc., 1933, A, 142, 362—369).—The spectrum of the CO_2 afterglow differs from those given by oxides of C in vac. tubes, but resembles that given by the flame of CO burning in air or O_2 . It is probable that the bands of the CO_2 afterglow and of the CO flame are produced by the direct combination of CO and O_2 , without dissociation into atoms of C and O or mols. of C. The extreme complexity of the spectrum, as revealed by spectrographs of adequate resolving power, also suggests that the bands of the afterglow originate in CO_2 mols.

L. L. B.

Absorption spectra of uranium compounds. F. EPHRAIM and M. MEZENER (Helv. Chim. Acta, 1933, 16, 1257—1272).—Spectral absorption lines for a large no. of U compounds are given. A parallel is drawn between the spectra of U compounds and those of the rare earths. UCl_5 , the only known compound of U^{V} , gives no absorption lines even in liquid air. Heavy metal *uranates* have been prepared by digesting UO_2 salts with the metallic hydroxides, but $\text{CdO} \cdot 2\text{UO}_3$ and $\text{ZnO} \cdot \text{UO}_3$ only have been obtained as clearly defined compounds. The *uranates* do not give a linear absorption spectrum.

M. S. B.

Predissociation and the crossing of molecular potential energy curves. O. K. RICE (J. Chem. Physics, 1933, 1, 375—389; cf. A., 1931, 271, 1077, 1078).—Theoretical. The calculation of the width and shape of a line broadened on account of predissociation is extended to include perturbations of such size that the lines of given rotational quantum no. belonging to two adjacent vibrational levels do not overlap appreciably. The theory is applied to predissociation phenomena in ICl , and two groups of sharp and diffuse levels are ascribed respectively to ICl^{35} and ICl^{37} .

J. W. S.

Colours of copper salts. W. D. BANCROFT and H. W. ROGERS (J. Physical Chem., 1933, 37, 1061—1073).—The colour of Cu^{II} salts is the same in the solid, solution, and vapour states if the chromophoric groups are the same. Cu^{II} with $2\text{H}_2\text{O}$ is green and with $\leq 3\text{H}_2\text{O}$ blue. The NH_3 mol. has practically the same effect as the H_2O mol., but the blue shade is different. Anhyd. Cu^{II} is probably colourless, but may be red. The red or brown colour of CuCl_2 alone and in certain double salts is probably due to a ψ -salt. X-Ray

analysis has shown that the group $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ probably exists in some of the green double salts. Cu produces a blue colour in borate and silicate glasses. The reasons for the various colours are unknown.

H. S. P.

Ultra-violet absorption and chemical reactivity of organic compounds. M. GRUNFELD (Ann. Chim., 1933, [x], 20, 304—370).—A full account of work previously published (A., 1930, 838; 1932, 371, 444).

F. L. U.

Continuous absorption spectrum of polyatomic molecules. III. Y. HUKUMOTO (Sci. Rep. Tôhoku, 1933, 22, 868—878).—Dissociation energies of C_2Cl_4 , C_2HCl_3 , $\text{C}_3\text{H}_5\text{Cl}$, Bu^nBr , Bu^nI , CCl_4 , SiCl_4 , TiCl_4 , and SnCl_4 have been calc. from the long wavelength limits of the continuous absorption bands. Bu^nI has two regions of absorption. The shift of the absorption limits on liquefaction is attributed to changes in the unstable potential energy states of some of the mols.

J. G. A. G.

Ultra-violet absorption of aldehydes. H. CONRAD-BILLROTH (Z. physikal. Chem., 1933, B, 23, 315—318).—Measurements have been made with aliphatic aldehydes in hexane solution. With the normal aldehydes the max. is displaced by 1350 cm^{-1} compared with the corresponding ketone. With both classes of compound the position of the band seems to depend only on the no. of groups, other than $\cdot\text{CHO}$ or COMe , attached to the C atom adjacent to the $\cdot\text{CHO}$.

R. C.

Ultra-violet absorption of some organic substances. J. DABROWSKI and L. MARCHLEWSKI (Bull. Soc. chim., 1933, [iv], 53, 946—950).—The absorption spectrum of isatin (I) is very close to that of the *N*-Me ether (II) and totally different from that of the *O*-Me ether (III), the resemblance of the (I) and (II) spectra thus confirming the observations of Hartley and Dobbie (J.C.S., 1899, 75, 640). This is contrary to the statement of Morton and Rogers (cf. A., 1926, 9), and it is suggested that these authors worked with (III) which had undergone a change to a substance more closely resembling (I), since (III) is known to be unstable. It is concluded that the study of absorption spectra in this series can be used to determine the constitution of the tautomeric substance, as was stated by Hartley and Dobbie.

R. S.

Light absorption of *p*-nitrosodimethylaniline. J. F. H. CUSTERS and C. J. DIPPEL (Z. Physik, 1933, 86, 516—520).—The region investigated was 250—550 m μ before and after addition of an equiv. amount of HCl .

A. B. D. C.

Absorption spectra of diphenols in alkaline medium. A. SAINT-MAXEN and E. DUREUIL (Compt. rend., 1933, 197, 1411—1413).—The absorption spectra of quinol (I), pyrocatechol (II), and resorcinol (III) in aq. and alkaline solution have been compared for λ 2200—5800 Å. The changes in presence of alkali for the spectra of (I) and (II) indicate quinone formation; in (III), where this is impossible, they are negligible (cf. A., 1909, ii, 374).

C. A. S.

Spectral absorption of methylated xanthines and constitution of the purine nucleosides. J. M.

GULLAND and E. R. HOLIDAY (*Nature*, 1933, **132**, 782).—The ultra-violet spectral absorption of xanthine (I) and certain Me derivatives may provide a method of distinguishing between derivatives of (I) substituted in the 7 or 9 positions, and this method can be used to assign to these positions the carbohydrate radical (II) in the natural and synthetic purine glucosides. (I) and its Me derivatives can be divided into two groups: (i) the absorption curves show two bands in alkaline solution, viz., (I), 1-, 8-, and 9-methyl-, 3:9-dimethyl-, and 1:3:9-trimethyl-purine, and (ii) the curves show one band in both acid and alkaline solution, viz. 3-, 7-methyl-, 1:3-, 1:7-, 3:7-dimethyl-, and 1:3:7-trimethyl-purine. Me at position 7 thus inhibits the appearance of the second band. A comparison of the spectra of methyl-purines with those in which the H of the NH of the glyoxaline ring is unsubstituted suggests that in 3-methylpurine and in theophylline (Me at 1 and 3) this H is at position 7, whereas in (I) and 1- and 8-methylpurine it is at position 9, the reverse of the usual arrangement. The formula of (I) and of the hypothetical isopurine would therefore have to be interchanged. In xanthinose from yeast-nucleic acid it is probable that (II) is attached at position 9, whilst the synthetic arabinoside and glucoside of theophylline contain (II) in position 7 (cf. A., 1933, 838). L. S. T.

Absorption spectra of molecular organic compounds. W. H. HUNTER and E. H. NORTHEY (*J. Physical Chem.*, 1933, **37**, 875—887).—Measurement of the absorption spectra of fused chloro-, benzo-, tolu-, xylo-, and duro-quinone, and of equimol. mixtures of them with aromatic hydrocarbons, ethers, and amines permits the latter to be arranged in order of increasing effect, ranging from mere solvent action to mol. compound formation. This order is independent of the quinone used. The change in the spectrum produced by a substance capable of forming a mol. compound increases with increasing oxidation-reduction potential of the quinone.

F. L. U.

Polarisation of the fluorescent band. S. M. MITRA (*Current Sci.*, 1933, **2**, 176—177).—The fluorescence band obtained with solutions of various dyes in glycerol and in gelatin, and with solutions of Na salicylate, BzOH, and β -C₁₀H₇·NH₂ in glycerol was found to be equally polarised throughout.

A. J. M.

Structure of the ultra-violet spectrum of various proteins. F. VLES and M. PRAGER (*Arch. Phys. biol.*, 1932, **10**, 5—20; *Chem. Zentr.*, 1933, i, 2219).—Narrow bands in the region 275 m μ exist in the absorption spectra of serum and of various proteins, but not in the same band in that of COME₂. The nature of the groups responsible is considered.

A. A. E.

Spectrochemical investigation of the viscose reaction. K. ATSUKI and H. SOBUE (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 589—595B).—Absorption data are recorded for cellulose xanthate for visible and ultra-violet light. There is a max. at 3000—3100 Å. for the xanthate and at 3300 Å. for the reaction products of NaOH and CS₂ alone.

A. G.

Vibration frequencies and other constants of the H₂O molecule. J. H. VAN VLECK and P. C. CROSS (*J. Chem. Physics*, 1933, **1**, 357—361).—The calculation is based on the Slater-Pauling theory of directed valency, supplemented by data from the band spectrum of the OH mol. The heat of dissociation and valency angle agree with experiment. Two fundamentals should fall near 2.8 μ , this being in agreement with Mecke's interpretation of the H₂O spectrum, but not with that of Johnston and Walker.

J. W. S.

Infra-red absorption spectra of NO₂ and N₂O₄. R. SCHAFFERT (*J. Chem. Physics*, 1933, **1**, 507—511).—Measurements have been made between 3° and 150°. Frequencies of bands due to NO₂ and N₂O₄, respectively, are tabulated. The simplicity of the spectrum of N₂O₄ suggests a symmetrical structure of the mol.

F. L. U.

Rotation vibration spectrum of methane. H. VEDDER and R. MECKE (*Z. Physik*, 1933, **86**, 137—156).—This spectrum was photographed between 0.7 and 1 μ . The rotational structure was measured but not analysed. The known vibration bands of CH₄ can be allotted to four normal frequencies at 3015, 2945, 1530, and 1320 cm.⁻¹ The problem of the normal modes is investigated, assuming a general potential field having the symmetry of the molecule. The observed frequencies indicate that the particular case of a valency force field fits the mol., and that the force consts. for C-H, angular, and H-H displacements are as 5.5 : 1 : 0.12.

A. B. D. C.

Transmission of infra-red radiation by a thin layer of horn. J. H. TAYLOR (*Proc. Roy. Soc.*, 1933, **A**, 142, 598—605).—A layer of horn 0.022 mm. thick was used. Marked absorption was found in the region of 3.4 μ , and also in the region beyond 6 μ .

L. L. B.

Discovery of molecular diffusion of light in pure liquids. A. TURPAIN (*Compt. rend.*, 1933, **197**, 1107—1109).—The mol. diffusion of light by a pure liquid and its polarisation were described, and the Raman effect was foreshadowed, by Lallemand 65 years ago (cf. *ibid.*, 1869, **69**, 189; 1874, **79**, 694).

C. A. S.

Raman effect of aluminium salts. A. DA SILVA VEIRA (*Compt. rend.*, 1933, **197**, 1035—1037).—Raman lines of Al(NO₃)₃ and Al₂(SO₄)₃ occur between 270 and 1639 cm.⁻¹, but lines of higher frequency of the sulphate were concealed by a continuous background. NO₃' lines are at 721, 1052, 1312, and 1414, that at 819 being an inactive frequency; 721, 1312, and 1414 are forbidden; 721 is doubly and 1312 and 1414 are singly degenerate; 1639 is due to H₂O. Of the sulphate lines 461, 612, 981, and 1109 are due to SO₄²⁻; 396 in both is ascribed to Al⁺⁺⁺. There are some indications that Al⁺⁺⁺ is hydrated (cf. A., 1932, 983). The origin of nitrate lines at 446, 537, 627, 1241, and 1530 and of sulphate lines at 270, 527, and 686 is doubtful.

C. A. S.

Evidence from Raman effect for electrolytic dissociation in sulphuric acid. I. R. RAO (*Indian J. Physics*, 1933, **8**, 123—135).—A qual. study gave Raman lines 416, 742, 1043, 562, 910, 1171, and

1365 cm^{-1} . The four last-named decrease in intensity with dilution, whilst the 1043 line increases, being attributed to the HSO_4 ion, and due to dissociation on dilution. At lower concns., a new line 980 cm^{-1} , attributed to the SO_4 ion, appears; it increases in intensity with dilution, indicating further dissociation of HSO_4 into H^+ and SO_4^{2-} . The lines 562, 1171, and 1365 are stated to be evidence of mols. of the type $\text{SO}_2(\text{OH})_2$ in the pure acid. The successive dissociation stages are $\text{H}^+ + \text{HSO}_4^-$ and $2\text{H}^+ + \text{SO}_4^{2-}$. N. M. B.

Raman bands of water. G. BOLLA (Nuovo Cim., 1933, [ii], 10, 101—107; Chem. Zentr., 1933, ii, 989).—Five new bands, max. at $\Delta\nu=510$, 780, 1645, 2150, and 3990 cm^{-1} , have intensities < those at 3200 and 3435 cm^{-1} . The band at 1645 cm^{-1} is narrower and sharper than the others. A. A. E.

Raman spectrum of water vapour. D. H. RANK (J. Chem. Physics, 1933, 1, 504—506).—The displacements 1648 and 984 cm^{-1} reported by Johnston and Walker (A., 1933, 1102) were not observed. F. L. U.

Raman effect in solutions of ammonium nitrate in nitric acid. L. MEDARD and (Mlle.) T. PETITPAS (Compt. rend., 1933, 197, 1221—1222).—The Raman spectra for $\text{NH}_4\text{NO}_3 + 2\text{HNO}_3$ (i.e., 38.7% NH_4NO_3) and for solutions of 0—55% NH_4NO_3 in HNO_3 contain lines previously reported (cf. A., 1933, 1228) with variations indicating that dilution of HNO_3 with NH_4NO_3 has a similar effect to dilution with H_2O . 3100—3300 cm^{-1} is referred to vibration of H in the mol. $\text{NO}_2\cdot\text{OH}$. C. A. S.

Vibration spectra and structure of the cyanogen halides. W. WEST and (Miss) M. FARNSWORTH (J. Chem. Physics, 1933, 1, 402—405).—The Raman spectra of CN halides, in the liquid state or in EtOH solution, contain three frequencies, $\nu_1=2201$, 2187, 2158 cm^{-1} ; $\nu_2=729$, 580, 470 cm^{-1} , $\nu_3=397$, 368, 321 cm^{-1} , for CNCl, CNBr, and CNI, respectively. The order of intensity of Raman transitions is $\nu_1 > \nu_2 > \nu_3$. The relative vals. of the frequencies indicate a linear arrangement of the nuclei in the lowest electronic state of these mols., and the data accord with the structure $\text{X}\cdot\text{C}\cdot\text{N}$ rather than $\text{X}\cdot\text{N}\cdot\text{C}$. J. W. S.

Raman spectrum of tetramethylmethane. D. H. RANK (J. Chem. Physics, 1933, 1, 572—575).—Data for CMe_4 , *n*-amyl chloride, and CMe_3Cl are recorded. A vibrational frequency of 415 cm^{-1} for CMe_4 , predicted by Kohlrausch and Barnes (A., 1933, 7), was observed. H. J. E.

Complete Raman spectrum of benzene from 4100 to 5100 Å. P. GRASSMANN and J. WEILER (Z. Physik, 1933, 86, 321—337).—Using high dispersion, 41 Raman lines were observed and allocated to combinations of 10 fundamental frequencies. The displacement at 984 cm^{-1} is ascribed to C^{13} . A. B. D. C.

Raman spectra of dichlorobenzenes. J. W. SWAINE and J. W. MURRAY (J. Chem. Physics, 1933, 1, 512).—Raman frequencies for the three isomerides are given. F. L. U.

Raman spectra of ring compounds. I. Mono-substituted benzene compounds. J. W. MURRAY

and D. H. ANDREWS (J. Chem. Physics, 1933, 1, 406—413).—An improved apparatus for study of Raman spectra is described. The use of filters, e.g., PhNO_2 , NaNO_2 , or $\text{Cu}(\text{NO}_3)_2$, for removing violet, ultra-violet, and red light, respectively, is suggested, this aiding the location of the weaker lines of the spectrum. Raman spectra of *n*- C_4H_{10} , PhCl, PhBr, and PhI have been reinvestigated and the results are tabulated. Several new lines have been found. The Raman spectrum of 2-chloropyridine has been found to be analogous to that of PhCl. J. W. S.

Raman spectrum of some substituted cyclenes. M. GODCHOT, E. CANALS, and (Mlle.) G. CAUQUIL (Compt. rend., 1933, 197, 1407—1409).—The Raman spectra of seven Me and an Et derivative of cyclopentene, -hexene, or -heptene are compared with those of the corresponding unsubstituted cyclenes. The differences are slight, the chief being that in the Me derivatives the line near 800 cm^{-1} is replaced by two. 825 of cyclohexene becomes 821 and 758 in 1-methylcyclohexene; the line near 1440 is thickened in the Et derivative, and replaced by a doublet in the Me_2 and Me_3 derivatives. C. A. S.

Depolarisation of light; depolarisation by organic colloids and by kaolins. V. PETRESCU (Ann. Sci. Univ. Jassy, 1933, 18, 318—336).—Suspensions of birefringent particles > the wave-length of light can cause depolarisation. With casein, legumin, fluorescein, rhodamine, and benzopurpurin depolarisation occurs, but with kaolins the effect is irregular, probably owing to impurities. H. S. P.

Diffusion of light and rotations of molecules in liquids. A. ROUSSET (Compt. rend., 1933, 197, 1033—1035).—The depolarisation factor ρ , measured at the centre of the spectrum, has been determined for C_6H_6 , CS_2 , AcOH, and SO_2 , as a function of the width (25—2500 μ) of the slit of the spectrograph, whence are deduced the relative intensities of the *P*, *Q*, and *R* branches, the distribution of intensities in *P* and *R*, and also ρ_0 , the depolarisation factor of the *Q* branch. The differences between the results and those previously obtained are discussed (cf. A., 1932, 107, 898; 1933, 446, 448). C. A. S.

Quenching of light from flames produced by various chemicals. C. D. CHILD (Phil. Mag., 1933, [vii], 16, 1141—1150).—Addition of salts and acid (e.g., HNO_3 or AlCl_3) to aq. Ca, Sr, Na, or K salts sprayed into otherwise non-luminous flames generally diminishes the characteristic radiation. Results are attributed to dissociation of the added mols. in the flames. H. J. E.

Theory of the phosphorogen. A. A. GUNTZ (Compt. rend., 1933, 197, 1030—1033).—The conclusion (cf. A., 1931, 998; 1932, 11; 1933, 579) that in the production of phosphorescent ZnS total absence of any phosphorogen may be compensated by the high temp. (about 3000°) of prep. is disputed on the ground that solid ZnS could not exist at a temp. >1500°, and that a concn. of 10^{-5} Cu is the optimum at 2000°. Some factor other than temp. must intervene (cf. A., 1926, 885). C. A. S.

Thermo-luminescence spectra of fluorites. I. Thermo-luminescence spectra of fluorites from

Obira. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 234—241).—Specimens showing greater no. of thermo-luminescence bands in the short-wave region have greater photo-sensitivity and rare-earth content.

R. S.

Triboluminescence of mercurous halides. J. H. KRÉPELKA and D. F. NOVOTNY (Časopis českoslov. Lék., 1933, 13, 26—35, 85—95; Chem. Zentr., 1933, i, 3542).—Pure, solid Hg^{I} halides, but not complex Hg compounds, exhibit triboluminescence; the sensitivity is $>$ that of ultra-violet fluorescence. Hg^{II} compounds free from Hg^{I} cannot be obtained by direct synthesis from Hg and Cl_2 ; crystallisation in the dark in an inert atm. is necessary. The intensity of the phenomenon depends on degree of dispersion, presence of impurities, temp., and H_2O content.

A. A. E.

Ionisation potentials and energies of formation of non-polar molecules. J. SAVARD (Compt. rend., 1933, 197, 1122—1123, and J. Phys. Radium, 1933, [vii], 4, 650—664).—The relation $D=2n(I_m-I_a)$ or $2nI_m-n_aI_a$, according as D is the energy of dissociation of the mol. A_2 or AB_p (provided that in AB_p the no. of linking electrons is even and they are in one envelope), where $2n$ is the no. of linking electrons in the mol., n_a the no. of electrons in A, I_m the first ionisation potential of the mol., and I_a that of the atom, is deduced theoretically, and verified for H_2 , N_2 , O_2 , C_2 , Cl_2 , Br_2 , HCl , HBr , CO , CO_2 , SO_2 , H_2O , CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , and C_2N_2 , and also for the energies of the single, double, and triple linkings of C.

C. A. S.

Photo-electric sensitisation of caesium. W. KLUGE (Physikal. Z., 1933, 34, 844—846).—By means of a special photo-cell experiments were carried out with compact Cs layers down to -39° , and studied at 600 m μ . Experiments in the ultra-violet were made with cells of the type M-Cs₂O-Cs, where M is the carrier metal (Ag, Cu, Ni, or Au). In all cases two short-wave max. were observed. The electronic emission from a cell of this type comes from the immediate surface (adsorbed Cs layer) in the visible and infra-red, but in the ultra-violet from the intermediate layer.

A. J. M.

External photo-electric effect at low temperatures. R. SUHRMANN (Physikal. Z., 1933, 34, 877).—The sensitivity curve at low temp. deviates considerably from expectation based on the classical theory, and agrees with the theory of Sommerfeld.

A. J. M.

Power loss phenomena in liquid dielectrics. W. JACKSON (Proc. Roy. Soc., 1933, A, 142, 606—620).—A series of dielectric loss measurements have been made on samples of C_6H_6 , PhMe, PhCl, and PhNO_2 , for frequencies of 2×10^5 to 2×10^6 cycles per sec., before and after the application of d.c. voltage. The dielectric loss over this frequency range can be accounted for in terms of ionic conduction. On the application of steady voltage an "electrical cleaning" process occurs which affects the magnitude of this loss. A theory is proposed to explain the phenomena observed.

L. L. B.

Influence of surface charge on conductivity measurements for poor conductors. F. SEIDL

(Z. Physik, 1933, 86, 274).—Former results (A., 1932, 899) agree with those of Goldhammer (cf. A., 1933, 888).

A. B. D. C.

Diffusion and electrolytic conduction in crystals. (Ionic semi-conductors.) W. JOST (J. Chem. Physics, 1933, 1, 466—475; cf. A., 1933, 353).—Theoretical. Calculations based on the assumption that atoms or ions are displaced to metastable positions in the interlattice space agree in order of magnitude with observed data regarding the influence of polarisation and the energy of activation.

F. L. U.

Dielectric constant and ionisation potential of gases. A. GUNTHER-SCHULZE (Z. Physik, 1933, 86, 249—252).—A logarithmic relation between ionisation potential and dielectric const. is shown to hold with great accuracy for inert gases, and mol. gases lie irregularly about this relation.

A. B. D. C.

Dependence of the dielectric constants of gases on temperature and density. H. H. UHLIG, J. G. KIRKWOOD, and F. G. KEYES (J. Chem. Physics, 1933, 1, 155—159).—Data for the dielectric consts. of CO_2 , CH_4 , H_2 , N_2 , and NH_3 over a wide range of temp. and density are tabulated. Molar polarisation, plotted as a function of the density, increases slowly for CO_2 and NH_3 , but is quite independent for the others. For CO_2 , CH_4 , H_2 , and N_2 it is independent of the temp., indicating that these mols. have no permanent dipoles; for NH_3 it varies widely. The calc. dipole moment of NH_3 is 1.48×10^{-18} c.s.u.

N. M. B.

Dielectric constant of $\text{H}^2\text{H}^2\text{O}$. G. N. LEWIS, A. R. OLSON, and W. MARONEY (J. Amer. Chem. Soc., 1933, 55, 4731).—The ratio of the dielectric const. of $\text{H}^2\text{H}^2\text{O}$ to that of $\text{H}^1\text{H}^1\text{O}$ at 25° is 0.990. The divergence increases with falling temp.

E. S. H.

Dielectric constant of liquid sulphur. H. J. CURTIS (J. Chem. Physics, 1933, 1, 160—165).—The dielectric const. and power factor were measured for the temp. range 118 — 350° ; the former at 118° was 3.520 ± 0.010 . Polarisation curves show that liquid S is non-polar, whereas absorption bands in the infra-red spectrum indicate polar mols. No explanation is available.

N. M. B.

Dielectric constants of substances containing water. J. TAUSZ and H. RUMM (Kolloid-Beih., 1933, 39, 58—104).—The dielectric consts., ϵ , of several powders and fibrous materials (including sugar, starch, silicic acid, borax, and tobacco) have been determined by an isodielectric method, and the influence of temp., frequency, structure, and H_2O content has been examined. The vals. obtained for dry sugar and starch (3.71 and 4.01, respectively) are $<$ those in the literature. The presence of H_2O increases ϵ , whilst the variation of ϵ with temp. shows in some cases that the H_2O is in two different states; a portion of the H_2O (bound) has little influence, whilst the remainder (free) renders ϵ sensitive to temp. In starch at 0° most of the H_2O appears to be bound, whilst in SiO_2 gel a considerable proportion is free. The proportion of free to bound H_2O varies with temp. and with the structure.

E. S. H.

Electric moment as a measure of the ionic nature of covalent linkings. J. G. MALONE (J. Chem. Physics, 1933, 1, 197—199).—The two-electron

linking with H has the following vals. for the electric moment ($\mu \times 10^{18}$): H-As 0.10; H-P 0.36; H-I 0.38; H-S 0.63; H-Br 0.78; H-Cl 1.03; H-N 1.04; H-O 1.32. These vals. give the position of the elements on an electronegativity scale (Pauling, A., 1932, 1191). The moments of SbCl_3 (3.1×10^{-18}) and of SbBr_3 (2.4×10^{-18}) and of other inorg. halides give vals in agreement with those calc. from the scale. It is predicted that all the trihalides of elements of group V should give appreciable moments, except PI_3 and NCl_3 , which should have zero moment. A. J. M.

Dipole moments of mercaptans and sulphides. W. S. WALLS and C. P. SMYTH (J. Chem. Physics, 1933, 1, 337—340).—Measurements are reported for thi-anthrene, Et_2S , *n*-amyl sulphide, Bu°SH , and *n*-amyl mercaptan in C_6H_6 at 25° and 50°. The polarisation of the sulphides is dependent on concn., as with the mercaptans. D. R. D.

Induction between linking moments in some halogenated methanes. C. P. SMYTH and K. B. McALPINE (J. Chem. Physics, 1933, 1, 190—196).—The dielectric consts. of vapours of CHCl_2F , CHClF_2 , CCl_3F , and CCl_2F_2 were measured. To explain the results it is necessary to consider the effects of induction and 'widening of valency angles by repulsion. Knowing the induction effect, the dipole moments of CH_2Cl_2 and CHCl_3 can be calc.; they agree with experiment. The val. of a linking moment is treated as a function of its environment. Whilst it seems probable that there is a widening of valency angle due to repulsion in all the unsymmetrically substituted methanes, induction is much more important than this in deciding the moments of the CH_4 derivatives considered. A. J. M.

Dipole moments and structures of certain long-chain molecules. C. P. SMYTH and W. S. WALLS (J. Chem. Physics, 1933, 1, 200—204).—The dipole moments of isoprene, $\text{Br}[\text{CH}_2]_6\text{Br}$, $\text{Br}[\text{CH}_2]_9\text{Br}$, and $\text{Br}[\text{CH}_2]_3\text{Br}$, have been determined. That of isoprene is almost zero, and can therefore play no part in causing this substance to polymerise. Comparison of the vals. obtained with those for other long-chain dibromides shows that the moment of $\text{Br}[\text{CH}_2]_3\text{Br}$ may be increased by a van der Waals attractive force between the two Br atoms. This effect is not important with other long-chain dibromides, since the force varies inversely as the sixth power of the distance. The moments do not enable a decision to be made between an extended zig-zag C chain and one in which there is free rotation about the C-C linking. A combination of both fits the results, the chain being generally of zig-zag form, but often bent by rotation about certain links in the chain. A. J. M.

Rotation of polar groups in organic compounds. J. M. STURTEVANT (J. Amer. Chem. Soc., 1933, 55, 4478—4485).—Theoretical. Quantum methods and classical theory give approx. the same results in certain cases of strong dipole interaction between polar groups capable of rotation about a single linking in org. mols. E. S. H.

Relation between dipole moment and cohesive forces. IV. A. E. VAN ARKEL (Rec. trav. chim.,

1933, 52, 1013—1027).—A discussion, with special reference to *cis-trans* isomerism. H. F. G.

Orientation of non-polar molecules by dipoles. J. WEIGLE (Helv. phys. Acta, 1933, 6, 68—81; Chem. Zentr., 1933, ii, 508—509).—The effect of the electric field of a dipole on non-polar solvent mols. is calc. If the non-polar mols. are anisotropic they are oriented by the dipole and produce an electric moment which increases that of the dipole. The induced moment is about 1% of that of the original dipole. If the polar mol. is not spherical, polarisation of the neighbouring mols. produces a considerable opposing moment. A. A. E.

Atomic polarisation. C. P. SMYTH (J. Chem. Physics, 1933, 1, 247—250).—New vals. of at. polarisation have been calc. from the temp. variations of the dielectric consts. in the vapour state. The vals. are small, but not so small as determined from infra-red intensity data, and the absence of negative vals. indicates that they should not be attributed to experimental errors. The large vals. previously reported for several alkyl halides are probably incorrect, except in the case of complex mols., where dipole orientation may occur within the mol. as indicated by the dielectric const. of the substance in the solid state. M. S. B.

Relation between apparent at. vol. and the co-ordination centres of insoluble complex compounds. G. GUTZEIT (Arch. Sci. phys. nat., 1933, [v], 15, 409—417).—If the radius of the atoms is plotted against at. no., only metals lying below a line joining Be, Mg, Ca, Sr, Ba, and Ra form insol. co-ordination compounds, and of these metals, those lying above a line joining Be, Sc, Zr, and Hf form co-ordination compounds with O (in :CO , -CHO , etc.) but not with N in NH_3 and its derivatives. The interpretation of these facts is discussed. H. F. G.

Calculation of the refractive indices of sodium hydrogen carbonate from the atomic arrangement. W. H. ZACHARIASEN (J. Chem. Physics, 1933, 1, 640—642).—Vals. calc. from the author's X-ray data (this vol., 16) agree with observed figures to within 0.02. D. R. D.

Refractive indices of ethylene chloride, *s*-tetra-chloroethane, and of their mixture and the molar refractions of these substances. S. HAMAI (Bull. Chem. Soc. Japan, 1933, 8, 297—308).—*n* shows linear dependence on reciprocal of abs. temp. in every case. Mol. refractions are 20.82 and 31.23, respectively. The dipole moment of $\text{C}_2\text{H}_4\text{Cl}_2$ is calc. as 1.375×10^{-18} e.s.u. R. S.

Analysis of rotatory dispersion curves of configurationally related fatty acids. P. A. LEVENE, A. ROTHEN, and R. E. MARKER (J. Chem. Physics, 1933, 1, 662—676).—Rotatory dispersion curves are given in the visible and ultra-violet for twelve acids and Et esters, and limited rotation measurements on ten other acids, all of the type $\text{CH}_3\text{-CHR-}[\text{CH}_2]_x\text{-CO}_2\text{H}$ either pure or in *n*- C_6H_{14} . Increase of *x* does not alter the direction of the contribution due to R, but reverses that due to the CO_2H between $x=0$ and $x=1$. Change of R between Et and $\text{C}_{10}\text{H}_{21}$ causes no change in sign of contributions. D. R. D.

Rotatory power of very dilute solutions. I. PEYCHES (J. Phys. Radium, 1933, [vii], 4, 594—608).—A method for the polarimetric measurement of α of solutions of the order 10^{-3} mol. per litre is applied to the alkali tartrates. α of Ru, Cs, and K tartrates increases linearly with concn., but the curves for Na and Li show a max. In all cases the curves converge near the origin, indicating the individuality of the tartrate ion of $[\alpha] + 45.7^\circ$. It is concluded that the variation of α is a linear function of the ionic potential.

N. M. B.

Influence of neutral salts on rotatory power of *d*- α -phenylethylamine hydrochloride. YEU-KI-HENG (Compt. rend., 1933, 197, 1316—1318).— $[\alpha]$ of *d*- α -CHPhMe·NH₂·HCl increases rapidly with concn.; it is further increased by addition of a neutral salt. With the same anion the effect depends solely on the concn. of the anion; for different anions it depends on the charge, mass, and composition, large for phthalate or ferrocyanide, smaller for citrate, and still smaller for halides in the order I⁻, Br⁻, Cl⁻, F⁻; that of LiI is abnormally large (cf. A., 1928, 1320).

C. A. S.

Photo-electric measurement of magnetic rotatory dispersion in the ultra-violet. G. BRUHAT and A. GUINIER (Compt. rend., 1933, 197, 1028—1030; cf. A., 1933, 448).—The magnetic rotatory dispersion, $m = \alpha/\rho_{4358}$, has been determined for H₂O for 11 vals. of λ (5893—2482 Å.) (cf. A., 1916, ii, 280; 1927, 295), and for heptane, heptene, and heptinene for 8 vals. (5893—2804 Å.). Verdet's consts. and the mol. rotatory powers of the hydrocarbons in the liquid and gaseous states are, for the yellow Hg line, respectively, 1.28, 1.47, and 1.56×10^{-2} ; 1.87, 2.07, and 2.03; and 1.52, 1.66, and 1.62, giving rotations of 27 and 35×10^{-2} for the double and triple linkings, respectively (cf. A., 1933, 1001).

C. A. S.

Magnetic rotatory dispersion and absorption of the cerous ion in solution. R. W. ROBERTS, L. A. WALLACE, and I. T. PIERCE (Nature, 1933, 132, 782).—Previous results are confirmed for higher concns. of Ce₂(SO₄)₃. The rotation of Ce⁺⁺⁺ throughout the range 5780—3341 Å. is controlled by the two absorption bands 2960 and 2540 Å. The calc. strengths (*f* vals.) for certain transitions agree with estimates made directly from absorption data for dil. solutions of Ce₂(SO₄)₃.

L. S. T.

Comparison of quantum theoretical formulæ and experimental results for electrical double refraction. T. NEUGEBAUER (Z. Physik, 1933, 86, 392—410).—Quantum theory gives an interpretation of the Kerr effect for symmetrical mols. where the Kerr const. is not related to degree of depolarisation. This theory also gives an estimate of the internal crystal field in solids.

A. B. D. C.

Influence of substituents in bases and anions on the co-ordination number of a metal. A. ABLOV (Ann. Sci. Univ. Jassy, 1933, 18, 297—317).—Co-ordination compounds of Cu salts of various acids with NH₃, C₅H₅N, β -picoline, and C₂H₄(NH₂)₂ (en) have been studied. There is a parallelism between the strength of the acid and the no. of mols. co-ordinated, but the base itself also has influence

on the co-ordination no. The following compounds are described: (NHPh·SO₃)₂[Cu(C₅H₅N)]; (C₆H₅Br₂·NH·SO₃)₂[Cu(C₅H₅N)₄]; (C₆H₅Br₂·NH·SO₃)₂[Cu(NH₃)₄], H₂O; (OAc)₂[Cu(NH₃)₂·2½H₂O]; (CH₂Cl CO₂)₂[Cu(NH₃)₄], H₂O; (CH₂Cl·CO₂)₂[Cu en₂], 2H₂O; (CN·CH₂·CO₂)₂[Cu(C₅H₅N)₃], 2H₂O; [N(CH₂·CO₂)₃]₂Cu₃·6H₂O; [Cu(C₆H₄N)₄]Cl₂.

H. S. P.

Theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions. J. D. BERNAL and R. H. FOWLER (J. Chem. Physics, 1933, 1, 515—548).—Theoretical. Three arrangements of H₂O mols. in liquid water are postulated: an ice-tridymite form below 4°; a quartz-like form (4—200°); an NH₃-like close-packed form (200—340°). These forms pass continuously into each other. The theory accounts for the observed crystal structure of ice, the X-ray diffraction curve of water, the total energy of water and ice, the degree of hydration of + and - ions in water, and the heats of dissolution of ions. The abnormally high mobilities of H⁺ and OH⁻ are due to transfer of H⁺ from (OH₃)⁺ to OH₂ and to transfer of H⁺ from OH₂ to OH⁻, respectively. Density changes and dielectric properties of water, and the viscosities of dil. ionic solutions and conc. acids are explained qualitatively. The mobility of (H⁺) is about five times that of (H²) in aq. solutions.

H. J. E.

Theory of structure of CH₄ and related molecules. I. J. H. VAN VLECK (J. Chem. Physics, 1933, 1, 177—182).—The Slater-Pauling and Hund-Mulliken theories of the structure of the CH₄ mol., based on localised linkings (electron pairs), are compared with the Heitler-London theory. Both the former, whilst of equal importance, are useful only quantitatively when higher approximations are made.

A. J. M.

Theory of structure of CH₄ and related molecules. II. J. H. VAN VLECK (J. Chem. Physics, 1933, 1, 219—238).—Calculations are made which show that, according to both the Hund-Mulliken and the Slater-Pauling schemes (see above), the tetrahedral model of CH₄ is the most stable. Also in compounds CH₂X₂, CHX₃, and CH₃X the most stable models are tetrahedra of less symmetry than the regular tetrahedron unless the C-H and C-X linkings are of equal intensity. The predicted deviations of the valency angles from 109.5° agree with X-ray diffraction data for CH₂Cl₂ and CHCl₃. With *s*-*p* hybridisation and electron pairing two linking axes do not necessarily set themselves at 109.5°. The angle can be anything between 90° and 180°, depending on the relative intensities of the *s* and *p* linkings. If the *s* linking power is not negligible, the angle between an NH axis and the pyramidal axis in NH₃ should be somewhat $> 54.7^\circ$, the val. when the 3 NH axes are orthogonal, characteristic of pure *p* linking. This is in general agreement with experimental data. CH₄⁺ should be a flattened rather than a regular tetrahedron, or might even be a plane. CH₃ should also be a flatter pyramid than NH₃.

M. S. B.

Allotropy of liquid nitrobenzene. E. L. LIND and T. F. YOUNG (J. Chem. Physics, 1933, 1, 266—269).—No discontinuities indicating allotropy were found in the density and surface tension curves for PhNO_2 , whether intensively dried or otherwise, between 6° and 20°. No evidence of delayed transition was observed even on keeping the cooled samples at 6° for 24 hr. M. S. B.

Occurrence of univalency among the elements. H. SCHMID (Angew. Chem., 1933, 46, 691—695).—A lecture. H. F. G.

Theory of multiple linkings. A. BURAWOY (Z. physikal. Chem., 1933, 166, 393—400; cf. A., 1933, 590).—The proportion of biradical mols. in various org. compounds containing multiple linkings has been calc. from the intensity and width of the R bands. The difference in energy content between the biradical mol. and the "saturated" mol. represented by the usual formula, which is the energy of rupture of the second or third linking of the multiple linking, is 2.5—9.0 kg.-cal. This small val. accounts for the high reactivity of unsaturated compounds. R. C.

Electronic structures of polyatomic molecules and valency. V. MOLECULES RX_n . R. S. MULLIKEN (J. Chem. Physics, 1933, 1, 492—503; cf. A., 1933, 339).—The approx. construction, for shared electrons in mols. RX_n , of mol. orbitals as linear combinations of at. orbitals is discussed and illustrated by equations for RX_2 , RX_3 , and RX types. F. L. U.

Absolute magnetic susceptibility of water and its variation with temperature. H. AUER (Ann. Physik, 1933, [v], 18, 593—612).—The susceptibility of H_2O as measured by an improved method, which is described in detail, is $0.72183 \times 10^{-6} \pm 0.067\%$ at 20°, and its temp. coeff. $(d\chi_i/dt)/\chi_i$ changes from 2.9×10^{-4} at 5° to 0.62×10^{-4} at 70°. J. W. S.

Magnetic susceptibility of MnO as a function of temperature. R. W. TYLER (Physical Rev., 1933, [ii], 44, 776—777; cf. Li. A., 1932, 900).—The susceptibility-temp. curve for the range 26° to -202° showed a sharp discontinuity at -156°, corresponding with that in the sp. heat-temp. curve, and another at -188°. Mass susceptibility data are given. N. M. B.

Magnetic permeability of ferromagnetic metals at very high frequency. G. POTAPENKO and R. SANGER (Naturwiss., 1933, 21, 818—819).—A modification of the usual parallel-wire method for determining the permeability of ferromagnetic metals with short waves, requiring only a small quantity of the metal, is described. The permeability of Fe calc. from ohmic resistance agrees with that of Arkadiev (Ann. Physik, 1919, 58, 105), and from self-induction with that of Hoag and Jones (A., 1933, 117). Both vals. decrease with increasing frequency. Similar results are obtained for Ni. Co has a very small permeability, < 5 for waves of λ 120 cm. A. J. M.

Effect of magnetic field on the energy transfer in paramagnetic gases. H. SENFTLEBEN and J. PIETZNER (Physikal. Z., 1933, 34, 834—835).—To investigate further the effect of a magnetic field on the heat-conductivity of a paramagnetic gas (A., 1931, 31;

1933, 559), experiments were carried out to discover whether the effect is bound up with each single mol. of O_2 , or whether the conjunction of two mols. by collision is necessary. The variation of the effect by the addition of diamagnetic gases to O_2 was studied. The O_2 -He curve is similar to that for pure O_2 , but the effect is greatly weakened and is not necessarily bound up with the collision of O_2 mols. The field exerts an influence on the energy transfer between O_2 and the mols. of the foreign gas. A. J. M.

Magnetic susceptibility of ions. K. KIDO (Sci. Rep. Tôhoku, 1933, 22, 835—867; cf. A., 1932, 1077; 1933, 340).—Observed susceptibilities of "inert-gas-like" ions diverge markedly from calc. vals. (cf. A., 1932, 795) and the corresponding differences of paramagnetic susceptibility increase with the no. of valency electrons. Mol. susceptibilities of inorg. compounds are calc. from the observed vals. of the constituent ions. In general, the additive law applies to homopolar and org. compounds, but double linkings depress diamagnetic susceptibility. J. G. A. G.

Is there a strictly reversible process in the magnetisation of ferromagnetic substances by extremely small alternating currents? H. WITTKE (Ann. Physik, 1933, [v], 18, 679—700).—For small changes of a magnetic field of finite magnitude, the ratio of the resulting loss to the change in magnetic energy is proportional to the change in field strength, and such small changes give rise to a reversible process. For zero field strength, however, the process is irreversible. J. W. S.

Magnetisation curve of a ferromagnetic material for very small fields. R. GANS (Ann. Physik, 1933, [v], 18, 701—704).—Theoretical. J. W. S.

Thermodynamic relationships. I. I. PLACINTEANU (Ann. Sci. Univ. Jassy, 1933, 18, 10—12).—Formulae are deduced for the influence of temp. on surface tension and for the velocity of propagation of sound in fluids. H. S. P.

Exchange of energy between polyatomic molecules and a metallic surface. F. R. WHALEY (J. Chem. Physics, 1933, 1, 186—189; cf. Rice and Byke, A., 1931, 1001).—It has been shown that when fairly complicated mols. (CHCl_3 , COMe_2 , MeOH , CCl_4 , EtOAc) strike a hot surface (Pt) the efficiency of energy transfer from the solid surface to the vibrational degrees of freedom of the impinging mol. is in any case low, and possibly zero. The impinging mols. appear to behave as regards energy transfer like hypothetical gases with six degrees of freedom, translational and rotational. A. J. M.

Virial and molecular structure. J. C. SLATER (J. Chem. Physics, 1933, 1, 687—691).—When the total internal energy of a mol. is known, the virial theorem may be used to find the kinetic and potential energies for all configurations of the nuclei. These data may be applied to give an explanation of the formation of a covalent linking. H. S. P.

Binding forces in alkali and alkaline-earth metals according to the free electron theory. O. K. RICE (J. Chem. Physics, 1933, 1, 649—655).—The conception of intrinsic ionic vol. is introduced into the free electron theory. Energies of sublimation

calc. from at. vol. data agree well with experiment for alkali metals, but less well for alkaline earths. An extended relationship gives compressibilities in poor agreement with experiment, but the difference is attributed to magnification of small errors rather than to weakness of the theory. D. R. D.

Dispersion and polarisability and the van der Waals potential in the alkali halides. J. E. MAYER (J. Chem. Physics, 1933, 1, 270—279).—The ultra-violet absorption of NaCl, KCl, and KI is in agreement with the dispersion of these salts and can be used to calculate the dipole-dipole potential const. for the van der Waals attraction between negative ions. The same const. can also be estimated for the other alkali halides as well as the quadrupole-dipole const. A much greater val. is thus found for the van der Waals potential than previously, and this accounts for the stability of the CsCl type of lattice. The assumption that the polarisability of a given ion varies inversely as the "main frequency" of the crystal is shown to be in approx. agreement with experiment. M. S. B.

Lattice energies of silver and thallium halides. J. E. MAYER (J. Chem. Physics, 1933, 1, 327—334).—Theoretical lattice energies calc. from electrostatic considerations agree with experiment, supporting the view that the linking is entirely ionic. Discrepancies with AgI are ascribed to homopolar linking. D. R. D.

Lattice energies of cuprous halides. J. E. MAYER and R. B. LEVY (J. Chem. Physics, 1933, 1, 647—648; cf. preceding abstract).—Comparison of theoretical and experimental lattice energies leads to the conclusion that the linking is not entirely ionic, particularly for CuI. D. R. D.

Nature of the chemical linking. V. Quantum-mechanical calculation of the resonant energy of benzene and naphthalene and the hydrocarbon free radicals. L. PAULING and G. W. WHELAND (J. Chem. Physics, 1933, 1, 362—374; cf. A., 1932, 561, 1191).—It is concluded that the principal contributions to the structure of C_6H_6 are made by the two Kekule forms, resonance between them stabilising the mol. to the extent of about 1.35 v.e. over a ring with three double linkings. The excited structures also contribute appreciably both to the energy and to the eigenfunction. The structure of $C_{10}H_8$ is similar. Dissociation of certain substituted ethanes into free radicals is attributed to the stabilisation of the free radicals resulting from resonance among structures in which the unpaired electron is located on the Me C atom and those in which it is on other atoms. The calc. tendencies towards dissociation are in agreement with experiment, the fact that dissociating power of β - $C_{10}H_7$ is < that of α - $C_{10}H_7$ and that of $\cdot C_6H_5$ is < that of Ph , being explained. J. W. S.

Nature of the chemical linking. VI. Calculation from thermochemical data of the energy of resonance of molecules among several electronic structures. L. PAULING and J. SHERMAN (J. Chem. Physics, 1933, 1, 606—617).—When the normal state of a mol. is represented by only one electronic structure, the total energy of formation of

the mol. equals the sum of the linking energies. If these two energies are unequal, the difference is interpreted as the resonance energy of the mol. among several electronic structures. Data for various aliphatic, aromatic, and heterocyclic mols. are used to calculate the resonance energy. H. J. E.

Nature of the chemical linking. VII. Calculation of resonance energy in conjugated systems. L. PAULING and J. SHERMAN (J. Chem. Physics, 1933, 1, 679—686).—The extra resonance energy of conjugation is calc. for dihydronaphthalenes and -anthracenes, C_2H_3Ph , stilbene, isostilbene, C_2HPh_3 , C_6Ph_4 , Ph_2 , *o*-, *m*-, and *p*- $C_6H_4Ph_2$, and $C_6H_5Ph_3$. The calc. vals. agree approx. with the empirical vals. from thermochemical data and enable rules to be deduced for the relative energy of conjugation in various cases. H. S. P.

Vibration in three-particle systems with special applications to the ethyl halides and ethyl alcohol. P. C. CROSS and J. H. VAN VLECK (J. Chem. Physics, 1933, 1, 350—356).—The vibrational potential of polyat. mols. is discussed in the light of the theory of directed valency, and the results are applied to the Et halides and EtOH by considering the CH_3 , CH_2 , and OH groups as dynamic units. Calc. force consts. give approx. the experimental frequencies. J. W. S.

Statistical theory of low-frequency intermolecular forces. J. G. KIRKWOOD (J. Chem. Physics, 1933, 1, 597—605).—Mathematical. H. J. E.

Activation energies for reactions of atoms in different states. G. K. ROLLEFSON and J. C. POTTS (J. Chem. Physics, 1933, 1, 400—401).—Calculations of activation energy, by a modification of Eyring's method, indicate that normal Cl atoms are much more reactive with respect to ICl than are Cl atoms excited to the $^2P_{1/2}$ state, in agreement with experiment (A., 1930, 1135; 1931, 578). J. W. S.

Deflexion of molecular rays in an electric field: electric moment of hydrogen chloride. I. ESTERMANN and R. G. J. FRASER (J. Chem. Physics, 1933, 1, 390—399).—The mol.-beam method has advantages over the dielectric-const. method for determination of dipole moments in that low gaseous pressures only are required, it is independent of solubility of the compounds in non-polar solvents, and it can detect the effects of relative motions, and especially of the higher rotational states of non-gyroscopic mols. on the moment. Also deviation of the dipolar axis by other than 90° from the axis of rotation is readily detectable, and provides a possible means of deciding between alternative mol. configurations. The application to the detection of temp. variation of the dipole moment is also suggested. An improved apparatus is described, and results for HCl are given, the moment being calc. as 1.95×10^{-18} e.s.u. J. W. S.

Densities and parachors of vinyl acetate and its liquid polymerides. C. GREEN, J. MARSDEN, and A. C. CUTHBERTSON (Canad. J. Res., 1933, 9, 396—401).—Densities of monomeric vinyl acetate have been measured from 9° to 31° . The parachor and Ramsay and Shields const. have been determined for the monomeride (I) and some liquid

polymerides (II). Assuming that the (II) are a solution of a dimeride in (I) and using Staudinger's formula to calculate the parachor of the dimeride, the parachors of (II) are calc. from the mixture law and agree with the experimental vals. H. S. P.

Hydrodynamic equations with capillary terms; theory of surface tension. Y. ROCARD (J. Phys. Radium, 1933, [vii], 4, 533—548).—Mathematical. Pressures and tensions due to non-uniform density distribution in a fluid in motion or in equilibrium are considered. From the results obtained the Kelvin isotherm theorem, the Ramsay-Shields relation, and the law of corresponding states are deduced.

N. M. B.

Inherent limitation of Soller multiple slits. T. N. WHITE (Rev. Sci. Instr., 1933, [ii], 4, 590—592).—The characteristic X-rays reflected from a crystal may, at certain deviations from the Bragg angle, be partly obstructed by the separating strips of the multiple slits, resulting in min. which give to a single line the appearance of a multiplet.

N. M. B.

Effect of absorption by the crystal on interference phenomena with X-rays according to the dynamic theory. M. KOHLER (Physikal. Z., 1933, 34, 839).—Theoretical.

A. J. M.

Lattice constants. M. C. NEUBURGER (Z. Krist., 1933, 86, 395—422; cf. A., 1931, 1217).

C. A. S.

Second principle of crystal chemistry. A. KAPUSTINSKI (Z. Krist., 1933, 86, 359—369; cf. A., 1933, 1001).—The validity of the equation $U = 256\eta_1\eta_2\Sigma n/(r_K + r_A)$ is demonstrated by plotting $U/\eta_1\eta_2\Sigma n$ against $1/(r_K + r_A)$ for many compounds, deviations occurring only with Ag^I , Cu^I , and Tl^I . Accordingly, as the second principle of crystal chemistry, it is enunciated that the lattice energy of a crystal, U , and the properties depending thereon are determined by the no. (Σn), dimensions (r_K , r_A), valencies (η_1 , η_2), and in some cases also the polarisation properties of the constituent ions (or atoms). The above equation is applied to the energetics of a morphotropic series, the calculation of the ionic radius of Sn^{II} (1.04 ± 0.02), and heats of reaction, formation, and dissolution (cf. A., 1927, 611).

C. A. S.

Regularities in the transformation of metals in the solid state. U. DEHLINGER (Metallwirt., 1933, 12, 207—210; Chem. Zentr., 1933, ii, 493—494).—The transformations (tempering, hardening, and recrystallisation) are discussed in relation to lattice changes.

A. A. E.

Investigations of amorphous metal layers. H. ZAHN and J. KRAMER (Z. Physik, 1933, 86, 413—420).—Electrolytically deposited Sb and Pt are transformed into the cryst. state at a definite temp., which is independent of the method of formation of the amorphous layer.

A. B. D. C.

Submicroscopic distinctions between metals after casting and after recrystallisation. U. DEHLINGER (Physikal. Z., 1933, 34, 836—838).—Experiments were carried out with 99.8% Al to ascertain if there is any difference in nuclear size between the cast and recryst. metal. It is shown that there is some difference in texture.

A. J. M.

Molecular structure of ice and liquid water. E. L. KINSEY and O. L. SPONSLER (Proc. Physical Soc., 1933, 45, 768—779).—The structure proposed regards ice as a lattice of H^+ cations and complex double pyramidal H_3O_2^- anions, which form neutral chains parallel to the c axis. At the m.p. rearrangement occurs, producing large nos. of H_2O mols., in temp. equilibrium with the H_4O_2 mols., which are prevented from dissociating into H^+ and H_3O_2^- by the large polarising fields present in the liquid state. The theory permits a qual. explanation of many abnormal properties of water and ice.

J. W. S.

Lattice constant of carborundum. G. BORRMANN and H. SEYFARTH (Z. Krist., 1933, 86, 472—473; cf. A., 1926, 562).—Modification II of SiC has a 3.076, c 15.07 Å.

C. A. S.

X-Ray structure of silver amalgam. A. WERYHA (Z. Krist., 1933, 86, 335—339).— Ag_3Hg_4 prepared by Reinders' method (cf. A., 1906, ii, 219) or by long immersion of Ag wire in Hg is cubic, a 10.09 Å., with 4 mols. in unit cell, space-group O_h^2 ; the point groups of the 12 Ag and 16 Hg atoms are respectively C_{3v} and C_{3v} , the former with no parameter, the latter with $u=0.192$.

C. A. S.

X-Ray investigation of MgZn and MgZn_5 . L. TARSCHISCH (Z. Krist., 1933, 86, 423—438).—The existence of MgZn (cf. A., 1929, 873) is established; it has d 4.24, a 5.33, c 8.58 Å., with 6 mols. in the unit cell; the structure closely resembles that of MgZn_2 , which is hexagonal with 4 mols. in the unit cell (cf. A., 1927, 190), Mg atoms replacing Zn_2 in each cell. MgZn_5 , d 6.60, has a 9.92, c 16.48 Å., with 16 mols. in the unit cell, space-group D_6^h .

C. A. S.

Interatomic distances in crystals of the alkali halides. M. L. HUGGINS and J. E. MAYER (J. Chem. Physics, 1933, 1, 643—646).—Ionic radii for Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , F^- , Cl^- , Br^- , and I^- are calc. from the lattice consts. of the alkali halides.

D. R. D.

"Alternating" structure of cadmium bromide. J. M. BIJVOET and W. NIEUWENKAMP (Z. Krist., 1933, 86, 466—470; cf. A., 1929, 1369).—A powder photograph of a crystal of CdBr_2 from aq. solution implies a unit cell with a 2.30, c 6.23 Å., and containing $1/3$ mol.; a structure in which layers of CdCl_2 and CdI_2 types alternate, or one due to repeated twinning, is deduced. Long-continued trituration alters the structure, and heating at about 400° produces the CdCl_2 type alone.

C. A. S.

Crystal lattice of sodium hydrogen carbonate. W. H. ZACHARIASEN (J. Chem. Physics, 1933, 1, 634—639).— NaHCO_3 forms monoclinic prismatic crystals with 4 mols. in the unit cell, with a 7.51 ± 0.04 , b 9.70 ± 0.04 , c 3.53 ± 0.03 Å., β $93^\circ 19'$, space-group $P2_1/n$, d_{calc} 2.16, and d_{obs} 2.20—2.22. The orientation of the constituent atoms is deduced.

D. R. D.

Crystal structure of potassium dithionate. M. L. HUGGINS (Z. Krist., 1933, 86, 384—388).—Two errors in the original paper (cf. J. Min. Soc. Amer., 1931, 16, 580) are corr., but the criticisms of Hagg and Helwig (cf. A., 1932, 1079; 1933, 33) are not accepted.

C. A. S.

Potassium pentacalcium sulphate. F. KRULL and O. VETTER (Z. Krist., 1933, 86, 389—395).— $\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$, "penta-salt," d^{25} 2.897, is monoclinic, n_a 1.550, n_β 1.585, $n_\gamma - n_a$ 0.033, i.e., intermediate between anhydrite and syngenite (n_a 1.500, n_β 1.517, $n_\gamma - n_a$ 0.019). It is slowly decomposed by H_2O , leaving pseudomorphous but porous gypsum (cf. A., 1904, ii, 561; 1905, ii, 319; 1917, ii, 176). C. A. S.

Crystal structure of thallium silicofluoride. M. TABET (Gazzetta, 1933, 63, 679—680).— Tl_2SiF_6 has a structure of the K_2PtCl_6 type with a 8.60, d_{calc} 5.72. O. J. W.

Rhodonitrites of ammonium, potassium, rubidium, calcium, thallium, barium, and lead. A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1933, [vi], 18, 45—52; cf. A., 1933, 666).—The following vals. of a (Å.) and d_{calc} , respectively, have been obtained for the compounds of the general formula $\text{M}_3[\text{Rh}(\text{NO}_2)_6]$, where M=metal atom or NH_4 : NH_4 , 10.91 ± 0.02 , 2.214; K, 10.63 ± 0.02 , 2.744; Rb, 10.83 ± 0.02 , 3.321; Cs, 11.30 ± 0.02 , 3.357; Tl, 10.91 ± 0.02 , 5.073. They all have a structure of the $\text{K}_3\text{Co}(\text{NO}_2)_6$ type. $\text{Ba}_3[\text{Rh}(\text{NO}_2)_6]$ and $\text{Pb}_3[\text{Rh}(\text{NO}_2)_6]$, which are isomorphous with the above salts, are probably cubic with a 10.70 and 10.53 Å., respectively. The Rb, Cs, Tl, and Pb compounds are new. O. J. W.

Structure and swelling of montmorillonite. U. HOFMANN, K. ENDELL, and D. WILM (Z. Krist., 1933, 86, 340—348).—Montmorillonite being readily hydrolysed occurs in quantity only in arid regions. Analysis: SiO_2 49.0, Al_2O_3 23.0, Fe_2O_3 0.3, CaO 1.6, MgO 2.9, H_2O 23%, of which all but 4 is removed over H_2SO_4 or at moderate temp., leaving $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ (cf. A., 1909, ii, 736). The crystals are rhombic, a 5.095, b 8.83, c 15.2 Å., and consist of alternate layers of $\text{AlO}(\text{OH})$ and SiO_2 extending in the a - b plane exactly as in kaolin, from which it differs only in dimension along the c axis. The H_2O occurs between the layers, the c dimension varying with its amount, thus explaining the swelling on hydration. C. A. S.

Transformation points and softening of glasses. E. RENCKER (Compt. rend., 1933, 197, 1049—1051; cf. A., 1928, 354; 1933, 1247).—Differential dilatation-temp. curves for B_2O_3 , Pollopass, Pyrex, and a glass containing 87% SiO_2 + 9% Na_2O + 4% BeO show that the transformation point coincides with that of the commencement of softening. C. A. S.

X-Ray investigation of tridymite glass. M. E. NAHMIA (Nature, 1933, 132, 857—858).—X-Ray analysis of a devitrified glass (78% SiO_2 , 12% CaO , and 10% Na_2O) gives a pattern of tridymite (I). The use of thermal expansion curves in deciding between (I) and cristobalite is untrustworthy. L. S. T.

X-Ray diffraction of vitreous silica. B. E. WARREN (Z. Krist., 1933, 86, 349—358).—In vitreous SiO_2 each Si is tetrahedrally surrounded by 4 O, being 3.1 Å. from each of the four nearest, and 5.0 Å. from each of the twelve nearest Si; each O is shared by two tetrahedral groups. The orientation of such

groups of 16 Si and attendant O is random (cf. A., 1931, 550; 1933, 12). The structure of Pyrex glass is similar. C. A. S.

Crystal morphology of quartz. I. Vicinal faces of quartz and their significance as regards interpenetrating twins of the Brazil and Dauphinee laws. II. Crystal morphology of α -(high-temperature) quartz. III. Morphological constants of β -quartz. G. KALB (Z. Krist., 1933, 86, 439—452, 453—457, 458—465).—With the exception of quartz occurring in hollows in effusive rocks all quartz crystals on which vicinal faces occur are of the β (low-temp.) variety. The vicinal faces are of two types: (I) an older, in which the three pyramidal faces are of approx. equal size, and (II) a younger, of recent hydrothermal formation, in which one face is markedly smaller than the others (cf. A., 1933, 140). C. A. S.

X-Ray and electron diffraction of iodine and the di-iodobenzenes. S. B. HENDRICKS, L. R. MAXWELL, V. L. MOSLEY, and M. E. JEFFERSON (J. Chem. Physics, 1933, 1, 549—565).— $p\text{-C}_6\text{H}_4\text{I}_2$ is orthorhombic bipyramidal (a 17.004, b 7.381, c 6.210 Å.). $m\text{-C}_6\text{H}_4\text{I}_2$ is rhombic pyramidal (a 17.20, b 7.08, c 6.21 Å.). $o\text{-C}_6\text{H}_4\text{I}_2$ is monoclinic prismatic (a 8.29, b 12.23, c 7.91 Å.; 4 mols. $\text{C}_6\text{H}_4\text{I}_2$ per unit cell in each case). From X-ray and electron diffraction measurements the I—I distances are 6.85, 5.97—5.92, and 4.00 Å., respectively. The I—I distance in I vapour is 2.64 Å. The electron diffraction results for $o\text{-C}_6\text{H}_4\text{I}_2$ require the I—C valency directions to be bent by about 10° from symmetrical positions in the plane of the C_6 ring. H. J. E.

X-Ray studies of fatty acids. F. B. SLAGLE and E. OTT (J. Amer. Chem. Soc., 1933, 55, 4396—4404).—Interplanar distances of the (001) planes have been determined for pure n -fatty acids containing C_{10} — C_{19} . Slight variations with the method of prep. were observed, and a new modification of the C_{14} acid was found to be produced by pressing. E. S. H.

X-Ray studies of mixed fatty acids. F. B. SLAGLE and E. OTT (J. Amer. Chem. Soc., 1933, 55, 4404—4418; cf. preceding abstract).—Data are given for several two-component mixtures of the n -fatty acids C_{10} — C_{18} , and for complex mixtures containing up to nine components. The existence of solid solutions was established in each case. E. S. H.

Fine structure of structurally isomeric hydrocarbons didiphenyl and triphenylbenzene. E. HERTEL and G. H. ROMER (Z. physikal. Chem., 1933, B, 23, 226—234).—Didiphenyl has I_a 8.14, I_b 5.64, I_c 18.4 Å., β 97° , space-group C_{2h}^2 , and 2 mols. in the unit cell. $s\text{-C}_6\text{H}_5\text{Ph}_3$ has I_a 11.2, 19.8, I_c 7.6 Å., space-group V_h^h , and 4 mols. in the unit cell. R. C.

Structure of chrysene and 1:2:5:6-dibenzanthracene in the crystalline state. J. IBALL and J. M. ROBERTSON (Nature, 1933, 132, 750—751).—Chrysene crystallises in the monoclinic system with a 8.34, b 6.18, c 25.0 Å., β 115.8° ; space-group C_{2h}^2 , or, less probably, C_2^2 ; 4 mols. per unit cell. Orientation is discussed. 1:2:5:6-Dibenzanthracene has a face-centred pseudo-orthorhombic lattice, but the

system is actually monoclinic with a 6.59, b 7.84, c 14.17 Å., and β 103.5°; space-group C_{2h}^2 or C_2^2 with 2 mols. per unit cell.
L. S. T.

Structure of chrysene and 1:2:5:6-dibenzanthracene in the crystalline state. J. D. BERNAL (Nature, 1933, 132, 751).—Chrysene shows the forms (001), (110), and (100) with a marked tendency to twinning on the c face. The optic axial plane is (010) with γ making 10° to the c axis in the obtuse angle: birefringence (I) is high and negative with a fairly large optic axial angle (II). Dibenzanthracene has a high (I), negative, with (II) 78°; α lies along b and ν almost or quite perpendicular to (001).
L. S. T.

Reflexion of X-rays from anthracene crystals. B. W. ROBINSON (Proc. Roy. Soc., 1933, A, 142, 422—447).—The abs. intensity of reflexion of X-rays from anthracene crystals for the (001) planes has been measured for the wave-lengths 1.539 and 0.709 Å. The method of measurement is described and the necessary corrections (in particular for extinction in the crystals) are investigated. The final vals. of the structure factor F for the (001) planes are 30.5 and 32.8, respectively.
L. L. B.

Fourier analysis of the durene structure. J. M. ROBERTSON (Proc. Roy. Soc., 1933, A, 142, 659—674).—A double Fourier analysis has been applied to the structure factors for the three principal crystallographic zones of durene (cf. A., 1933, 1108). The deduced structure shows a regular plane hexagon C_6 ring with the 4 Me groups in the plane of the ring, but slightly displaced towards the unsubstituted positions. The orientation of the mol. in the crystal is given. The C—C distance in the C_6 ring is 1.41 Å.; the distance between the centre of the Me group and the adjacent C atom in the C_6 ring is 1.47 Å.; the shortest distance between the Me groups in neighbouring mols. is 3.93 Å.
L. L. B.

Crystalline structure of naphthalene. Quantitative X-ray investigation. J. M. ROBERTSON (Proc. Roy. Soc., 1933, A, 142, 674—688).—A double Fourier analysis of the experimental data has been carried out for the zones about the a , b , and c crystal axes. The deduction of the orientation and structure of the mols. closely follows that given for anthracene and durene (A., 1933, 216, 558, and preceding abstract). The C rings are in the form of two regular plane hexagons, with the C—C distance 1.41 Å., and the closest distance of approach between the centres of atoms in adjacent mols. 3.60 Å. The structure differs from that of anthracene chiefly in the larger inclination of the long axis of the mol. to the (010) plane.
L. L. B.

Crystallographic study of sucrose. IV. G. VAVRINECZ (Magyar Chem. Fol., 1933, 39, 40—49; Chem. Zentr., 1933, ii, 210).—The effect of 91 org. and inorg. compounds on the morphology of sucrose crystallised from 70% aq. solution at room temp. has been studied; in most cases small effects are produced.
A. A. E.

Transformation of cyclopentadiene into its dimeride. E. G. V. BARRETT and L. J. BURRAGE (J. Physical Chem., 1933, 37, 1029—1035).—V.p. measurements have been made at various temp. of a

cyclopentadiene during its change from pure monomeride (I) to pure dimeride (II), and also of known mixtures of (I) and (II). Liquid crystals have been noted.
H. S. P.

Liquid crystals produced by evaporation or cooling of an aqueous solution of tartrazine. P. GAUBERT (Compt. rend., 1933, 197, 1436—1438).—Evaporation of a drop of an aq. solution of tartrazine (I) at room temp. produces an outer ring of solid crystals surrounding a birefringent liquid of the unstable nematic and smectic phases (Friedel, A., 1923, ii, 223). In contact with a little H_2O (I) does not pass into the mesomorphic state.
J. W. B.

Electron scattering experiments on the change of semi-conducting crystal surfaces on electron bombardment. R. SUHRMANN (Physikal. Z., 1933, 34, 878).—Rupp's method was used. Bombardment with electrons causes the disappearance of the crystal lattice for PbS. The bombarding electrons do not form a double layer at the surface. This would require only the shifting of the scattering max. The change in contact potential, and possibly also in the unidirectional effect of electron bombarded surfaces of this type, is due to strong distortion of the lattice.
A. J. M.

Investigation of the orientations of thin evaporated metallic films by the method of electron diffraction. K. R. DIXIE (Phil. Mag., 1933, [vii], 16, 1049—1064).—Vac.-evaporated deposits of Ag on Mo, SiO_2 , and glass, and Al or Zn on Mo, show different orientations according to the temp. (10—650°), and independently of the support. The deposits behave as a two-dimensional gas.
H. J. E.

Diffraction of electrons by mica. J. A. DARBYSHIRE (Z. Krist., 1933, 86, 313—324; cf. A., 1932, 797).—Changes in the diffraction pattern of muscovite with thickness are described (cf. A., 1928, 1174; 1932, 3), and also those in the reflexion pattern with changes in angle of incidence and azimuth (cf. A., 1932, 979). The pseudo-symmetrical effects occur when the incident beam travels along the more important of the zone axes that lie in the cleavage plane.
C. A. S.

Electron diffraction and molecular structure. R. W. DORRTE (J. Chem. Physics, 1933, 1, 566—571).—Data for *cis*- and *trans*- $C_2H_2Br_2$, C_2HBr_3 , vinyl bromide, C_2Cl_4 , and C_2HCl_3 are recorded. The structures are planar, with interat. distances C—C 1.3, C—Br 2.0, and C—Cl 1.8 Å.
H. J. E.

Determination of the structures of methane derivatives by the electron diffraction method. R. W. DORRTE (J. Chem. Physics, 1933, 1, 630—633).—In CM_3Br , the angular distribution of the 3 Me groups and the Br atom around the central C is tetrahedral; the C of the Me is at 1.55 Å. and the Br 2.06 Å. from the central C. The distance between C and halogen is 2.06 Å. in $MeBr$ and 2.28 Å. in MeI . In CH_2Br_2 and CH_2I_2 , the angle between the C—halogen linkings is 125° and the interat. distances are C—Br 2.03, Br—Br 3.61, C—I 2.28, and I—I 4.06 Å. In $CHBr_3$, the angle between the C—Br linkings is 115° and the interat. distances are C—Br 2.05 and Br—Br 3.46 Å.
D. R. D.

Electron diffraction by hydrocarbons. H. R. NELSON (Physical Rev., 1933, [ii], 44, 717—719).—Diffraction patterns for 25—50-kv. electrons reflected from thin films of vaseline, paraffin, and tap grease indicate that the films are mainly cryst. with the long axes perpendicular to the plane of the film.

N. M. B.

Variation with temperature of the resistance of nickel wire to stretching. S. ARZYBASCHEV and V. JUSHAKOV (Z. Physik, 1933, 86, 521—522).—The resistance was investigated between 350° and —190°; it decreased with falling temp. to —83° but at —190° showed an increase.

A. B. D. C.

Electrical resistance and heat in metals. C. R. UNDERHILL (J. Franklin Inst., 1933, 216, 629—634).—A method is indicated for a general equation for the temp. coeff. of the resistance of metals for all temp. up to the m.p., starting from determination of the equation of the R_m/T curve, where R_m is the mean resistance over the temp. range 0— T .

A. G.

Fluctuations of molecular field and magnetic equation of state of nickel. L. NÉEL (Compt. rend., 1933, 197, 1310—1312; cf. following abstract).—Magnetic isotherms of Ni calc. on the assumption of a fixed no. of groups of carriers of magnetic moment give results in accord with experiment near the Curie point, but with still better accord when quantum mechanics is applied. The magnetic equation of state for Ni is consistent with the theory that the no. of magnetic electrons varies with the magnetisation (e.g., 0.83 per atom for $\sigma=0$, 0.61 at saturation). (Cf. A., 1932, 901.)

C. A. S.

Susceptibility of nickel near the Curie point. L. NÉEL (Compt. rend., 1933, 197, 1195—1197).—A quant. method is described to support the qual. agreement between the magnetisation curves based on the hypothesis of fluctuations of the mol. field and on experimental results previously demonstrated (cf. A., 1932, 901). The $1/\chi$ - T curves thus calc. for the interval 919.5—634.14° abs., during which the susceptibility varies in the ratio 1:265, agree with experiment (cf. A., 1926, 339).

C. A. S.

Magnetic anisotropy of crystals of trans-dinitrotetramminocobaltic chloride. L. W. STROCK (Z. physikal. Chem., 1933, B, 23, 235—238).—On crystallising out in a magnetic field crystals of 1:6- $[\text{Co}(\text{NO}_2)_2, 4\text{NH}_3]\text{Cl}$ orient themselves with $\beta = [100]$ parallel to the lines of force. The crystals are magnetically anisotropic and the unit cell contains 16 mols.

R. C.

Volume magnetostriction for poly- and single crystals. O. VON AUWERS (Physikal. Z., 1933, 34, 824—827).—Single crystals of the Fe-Ni series and polycryst. specimens of Fe-Co-Ni alloys were investigated. 15 polycryst. Fe-Co-Ni alloys were investigated, including permivar, which has smaller vol. magnetostriction than others.

A. J. M.

Electronic conduction of cuprous oxide. W. SCHOTTKY and F. WAIBEL (Physikal. Z., 1933, 34, 858—864).—The Hall effect was investigated for Cu_2O (a) for plates of the substance containing free O_2 , at low temp. (—180° to 20°), and (b) for outgassed plates at 18—855°. A reversal of the sign of the

Hall potential was found between 400° and 500°, showing that there is an increase of the electron defect conduction over the electron excess conduction with rising temp. The potential increases with decreasing conductivity in both (a) and (b). For (b) there was a very rapid decrease of the Hall const. with fall of temp. The theory is discussed.

A. J. M.

High strength of thin filaments, the Joffé effect and associated phenomena according to Griffith's theory of rupture. E. OROWAN (Z. Physik, 1933, 86, 195—213).

A. B. D. C.

Propagation of sound in nitrogen tetroxide. W. T. RICHARDS and J. A. REID (J. Chem. Physics, 1933, 1, 737—748).—An extension of previous work (A., 1933, 217). Expressions for the adsorption of sound by dissociating gases are derived from Einstein's theory, and it appears that measurements of the absorption max. should show whether an absorptive region is due to failure of the dissociation reaction or of the heat capacity to follow the adiabatic cycle of the sound wave. Experiments to detect the absorption max. with N_2O_4 failed owing to inaccuracy of measurement. The acoustical properties of such gases are better investigated by dispersion measurements.

H. S. P.

Selenium compound of high thermoelectric power. M. A. LEVITSKAJA and V. J. DLUGAČ (Compt. rend. Acad. Sci. U.R.S.S., 1933, 109—110).—The properties of Cu_2Se are described.

H. J. E.

New effect at the occurrence of superconductivity. W. MEISSNER and R. OCHSENFELD (Naturwiss., 1933, 21, 787—788).—The effect of lowering the temp. below the transition point to superconductivity on the distribution of the lines of force in a cylindrical superconductor placed in a homogeneous magnetic field has been investigated. Although the magnetic field is kept const. the distribution of the lines of force in the external neighbourhood of the conductor changes on lowering the temp. below the transition point. In the interior of a long Pb tube the magnetic field remains the same as it was before lowering the temp. If the field is removed while the Pb is superconducting the field inside the tube remains the same, and the field strength outside does not become quite zero. If the magnetic field is started after the Pb is superconducting the field inside the tube remains zero.

A. J. M.

Wiedemann-Franz number, thermal conductivity, and thermoelectric force of tellurium. C. H. CARTWRIGHT (Ann. Physik, 1933, [v], 18, 656—678).—A method is described for the simultaneous measurement of Wiedemann-Franz no. (I), thermal conductivity (II), and thermo-electric force (III). These properties have been examined for single- and poly-crystal 99.99% Te at room temp. and at liquid O_2 temp. (I) is > 100 times the normal figure, but it is shown that this is not contradictory to the theory of electrical conductivity by electrons. At room temp. (III) is greater when (I) is greater. Cooling to liquid O_2 temp. causes a decrease in (III) and an increase in (I). (II) and (III) for pure Te are unaffected by heat-treatment.

J. W. S.

Purification and physical properties of chemical compounds. IV. Theoretical basis for the behaviour of controlled time-temperature curves. E. L. SKAU and W. H. LANGDON (Proc. Nat. Acad. Sci., 1933, 19, 943—947; cf. A., 1933, 667).—Mathematical. J. G. A. G.

Low-temperature specific heats. I. Improved calorimeter for use from 14° to 300° abs. Heat capacity and entropy of naphthalene. J. C. SOUTHARD and F. G. BRICKWEDDE. II. Calibration of the thermometer and the resistance of platinum, platinum-10% rhodium, and constantan between -259° and -190°. J. C. SOUTHARD and R. T. MILNER (J. Amer. Chem. Soc., 1933, 55, 4378—4384, 4384—4391).—I. The adiabatic calorimeter described has a precision of about 0.1% and is particularly suitable for studying slow transitions and thermal changes. The molal heat capacity of $C_{10}H_8$ increases almost linearly from 1.411 g.-cal. per mol. at 15.14° abs. to 39.55 at 294.68° abs. The entropy and free energy of formation at 298.16° abs. are 39.89 ± 0.12 e.u. and $+48.5$ kg.-cal., respectively.

II. A const.-vol. gas thermometer for the calibration of resistance thermometers between 14° and 90° abs. is described. The electrical resistances of Pt, Pt-10% Rh, and constantan have been determined over this range with an error of about $\pm 0.02^\circ$.

E. S. H.

M.p. of potassium nitrite. B. VON LENGYEL (Naturwiss., 1933, 21, 848).— KNO_2 has m.p. $419 \pm 3^\circ$.

A. J. M.

Physical constants of thioxan, selenoxan, and dithian. J. D. A. JOHNSON (J.C.S., 1933, 1530).—Vals. of b.p. (corr.) at various pressures and n_D^{20} are given.

H. B.

Determination of internal heat of rotation of ethane. A. EUCKEN and K. WEIGERT (Z. physikal. Chem., 1933, B, 23, 265—280).—The mol. heat has been determined down to 140° abs. by measurements of the thermal conductivity relative to C_2H_4 . From the results the variation with temp. of that part of the mol. heat due to the restricted rotation of the Me groups relative to each other ("internal heat of rotation") has been deduced and the difference in potential energy between the two positions where the H atoms of the Me groups are opposite to each other and where they are twisted through 60° calc. to be 315 g.-cal. $\pm 20\%$.

R. C.

Free rotation in monosilane lattice. K. CLU-SIUS (Z. physikal. Chem., 1933, B, 23, 213—225).—Measurements of the sp. heat of SiH_4 from 10° abs. to the b.p. have revealed the occurrence of a rotational transformation at 63.4° abs., signalled by a peak on the sp. heat-temp. curve. The peak is unsymmetrical, the fall being much the more abrupt on the higher temp. side, which is ascribed to strong coupling of the rotators in the solid. The solid is weakly doubly refracting above the transition point and strongly doubly refracting below it.

R. C.

Investigations in the critical region. IV. Critical isotherm and Joule effect of nitrogen tetroxide. K. BENNEWITZ and J. J. WINDISCH (Z. physikal. Chem., 1933, 166, 416—427; cf. A.,

1929, 873).—With apparatus permitting the measurement of the isothermal Joule effect at high temp. with corrosive substances the crit. Joule isotherm of N_2O_4 has been determined and found to correspond below the crit. d with the curve deduced from the universal ideal Joule curve and the vals. of K_p . At higher d there are deviations ascribed to non-ideality. It is concluded that the ideal Joule curve is valid even for associated mixtures and that van der Waals forces and the chemical forces of association are separable and inherently different.

R. C.

Vapour pressures of propane and propylene. A. W. FRANCIS and G. W. ROBBINS (J. Amer. Chem. Soc., 1933, 55, 4339—4342).—An all-glass apparatus for determining v.p. > 1 atm. is described. Data are given for C_3H_8 over the range 27—64° and for C_3H_6 between 29° and 46°.

E. S. H.

Densities of organic crystals. A. MUKHERJEE (Indian J. Physics, 1933, 8, 147—149).—The limiting densities of 24 org. crystals determined by the immersion method (cf. Krishnan, A., 1933, 340) are tabulated, and are in good agreement with vals. from X-ray data.

N. M. B.

Determination of density of corrosive liquids under high pressure, particularly the critical density of nitrogen tetroxide. K. BENNEWITZ and J. J. WINDISCH (Z. physikal. Chem., 1933, 166, 401—415).—By means of a new apparatus depending on the buoyancy principle, utilising a magnetically controlled float, the orthobaric densities of N_2O_4 have been determined from 17.6° up to the crit. temp. (158.20°). The extrapolated crit. d is 0.570.

R. C.

Simplified formulas for the calculation of expansion coefficients and compressibilities of gases at low pressures from the Beattie-Bridgeman equation of state. J. B. M. COPPOCK (J. Physical Chem., 1933, 37, 995—999).—Simple forms of the Beattie-Bridgeman virial equation have been used to calculate the thermal expansion coeffs. of various gases and also the low-pressure compressibility of N_2 and CO. Agreement with experimental data is good.

H. S. P.

Viscosity of H^2H^2O . G. N. LEWIS and R. T. MACDONALD (J. Amer. Chem. Soc., 1933, 55, 4730—4731).—Viscosity vals., determined by a capillary method over the range 5—35°, are given. The vals. do not agree with those of Selwood and Frost (A., 1933, 1233).

E. S. H.

Vapour viscosities and the Sutherland equation. J. H. ARNOLD (J. Chem. Physics, 1933, 1, 170—176).—Vals. of the Sutherland const., in the equation for the temp. variation of the viscosity of a gas, calc. by the use of mol. diameters and viscosity determinations at a single temp. are compared with available data obtained by various methods for the variation of viscosity with temp. for a no. of org. substances.

N. M. B.

Theory of liquid viscosity. D. SILVERMAN (Trans. Faraday Soc., 1933, 29, 1285—1294).—Theoretical. Maxwell's equation (Phil. Mag., 1868, [iv], 35, 133) is evaluated, and the resulting expressions are compared with experimental data.

H. J. E.

Effect of a magnetic field on diffusion of paramagnetic gases. H. SENFTLEBEN (Physikal. Z., 1933, 34, 835—836).—There is a marked effect on the diffusion of various gases into O_2 , but not for diffusion of one diamagnetic gas into another. A sensitive method for determining the effect is described.

A. J. M.

Complex formation due to polarisation. I. System krypton and hydrogen chloride. G. GLOCKER, C. P. ROE, and D. L. FULLER. **II. System propane and hydrogen chloride.** G. GLOCKER, D. L. FULLER, and C. P. ROE (J. Chem. Physics, 1933, 1, 703—708, 709—713).—I. The rare gases may form loose compounds with dipoles due to polarisation forces. If the p - v - T relation for a mixture of gases is determined, evidence of interaction may be deduced from a study of the second virial coeff. This method has been used to show that interaction occurs between Kr and the dipole HCl.

II. Saturated hydrocarbons resemble the rare gases and evidence of interaction between C_3H_8 and HCl has been obtained by the above method. H. S. P.

Refractive index of liquid mixtures containing pyridine. N. A. PUSHIN and P. G. MATAVULJ (Bull. Soc. Chim. Yougoslav., 1933, 4, 63—69).—The n -composition curves of the systems C_5H_5N -PhOH, o - and p - C_6H_4Cl -OH, o -, m -, and p -cresol, thymol, and guaiacol indicate formation of 1:1 compounds in every case.

R. T.

Partial vapour pressures and refractivities of mixtures of benzene with nitrobenzene, phenol, benzyl alcohol, or -dichlorobenzene. A. R. MARTIN and C. M. GEORGE (J.C.S., 1933, 1413—1416).—The partial v.p. at 70° and the refractivities at 25° of the binary mixtures are recorded and discussed in reference to inter-dipole and van der Waals forces. The OH-compounds are associated to a much greater degree than the others, but p - $C_6H_4Cl_2$ appears to be slightly associated.

H. F. G.

Application of Henglein's equation to liquid mixtures and solutions. V. A. KIREEV (J. Gen. Chem. Russ., 1933, 3, 622—627).—The v.p. calc. from Henglein's equation (A., 1920, ii, 732) agree with the experimental data for aq. $COMe$, and H_2SO_4 .

R. T.

Rapid determination of vapour-pressure isotherms of liquid mixtures and solutions. V. A. KIREEV, E. N. SERPIONOVA, and N. S. MATJUSCHIN (J. Appl. Chem. Russ., 1933, 6, 769—771).—Measured vols. of one component are added at const. temp. to a fixed vol. of the other, and the v.p. is measured after each addition.

R. T.

Binary systems. IV. Ethane systems. F. E. C. SCHEFFER and J. SMITTENBERG (Rec. trav. chim., 1933, 52, 982—986).—Temp.-pressure data are recorded for C_2H_6 + p - $C_6H_4Cl_2$ (I), 1:3:5- $C_6H_3Cl_3$ (II), p - C_6H_4ClBr (III), and p - C_6H_4Cl (IV). For (I) the miscibility is complete throughout the range studied (5 — 78°), whereas (II) is only partly miscible between about 40° and 50° . For (III) the 3-phase line intersects the heterogeneous area, the quadruple point being at about 40° and 52 atm.

(IV) exhibits very limited miscibility, and dP/dt for the 3-phase line is negative throughout. H. F. G.

Boiling of fused reciprocal salt-pairs. System (NaK)(ClI). E. JANECKE (Z. anorg. Chem., 1933, 215, 49—65).—A space model is constructed from the experimental data of Greiner and Jellinek (A., 1933, 770).

F. L. U.

Investigation of the gold-copper system by determination of resistance at low temperatures. V. POSPIŠIL (Ann. Physik, 1933, [v], 18, 497—514).—Alloys containing 10—100% Au have been investigated in the chilled and tempered conditions by finding the ratio of their resistances at -195° and -252.4° to that at 0° (the r -val. method). This method is regarded as more trustworthy than the determination of sp. resistance. The concn.-resistance curves for the chilled alloys are similar to those for a binary system with a complete series of mixed crystals. The curves for the tempered alloys, however, show sharp min. at 25 and 50% Au, corresponding with $AuCu_3$ and $AuCu$. At 75% Au the curve for the tempered alloy rises above that for chilled alloys, showing that some modification of the mixed crystal system in the former is brought about by the tempering in this region. The results agree with those of Grube (A., 1931, 1364). No indication of Au_2Cu_3 was found.

A. J. M.

Compounds of aluminium with silver. F. E. TISCHTSCHENKO (J. Gen. Chem. Russ., 1933, 3, 549—557).—A study of the fusion diagram and of the microcryst. structure of ordinary and chilled alloys affords evidence of the compound α - $AlAg_3$ (I) which is formed at the peritectic temp. 771° , and undergoes transformation into β - $AlAg_3$ (II) at 606° , and of the compound Al_2Ag , m.p. 751° , which decomposes below 711° to yield $AlAg_2$ (III). (I) does not form solid solutions, but (II) can dissolve $\approx 10.2\%$ Al (at 722°), and (III) can dissolve $\approx 1.3\%$ Ag or 3.2% Al.

R. T.

Iron-rich iron-silicon alloys. C. P. YAP (J. Physical Chem., 1933, 37, 951—967; cf. A., 1932, 1206).—Thermoelectric characteristics, electrode potentials, and X-ray photographs of Fe-Si alloys containing 13—32% Si suggest that Fe_3Si (ϕ) is present. The existence of Fe_3Si_2 and $FeSi$ is also indicated. A study of existing f.-p. data indicates that ϕ should be formulated as Fe_6Si_2 .

F. L. U.

Electrical conductivity and equilibrium diagram of binary alloys. VIII. System lithium-zinc. G. GRUBE and H. VOSSKUEHLER (Z. anorg. Chem., 1933, 215, 211—224).—The complete equilibrium diagram has been examined by thermal analysis and transformations in the solid state determined by temp.-resistance measurements. There are five series of homogeneous mixed crystals: α , 0—1.5% Li; β , 8.5—24%; γ , 26.5—29%; δ , 33—50%; ϵ , 98—100%. The existence of Li_2Zn_3 has been confirmed. With excess of Li or Zn it forms δ mixed crystals. On cooling it changes at 174° into another form which gives δ' mixed crystals with either component. A new compound, $LiZn_2$, is formed at 93° from γ' and δ' mixed crystals. The existence of a compound $LiZn$ is doubtful.

M. S. B.

Conclusions from rules on concentration of valency electrons in binary intermetallic alloys. H. PERLITZ (J. Chem. Physics, 1933, 1, 335—336).—The empirical rules governing the formation of intermetallic phases of the types of β -, γ -, and ϵ -brass are expressed algebraically. These phases are not to be expected when the metals have the same no. of valency electrons, but may be expected if the concn. of valency electrons of one component is $>$, and of the other $<$, $3/2$, $21/13$, or $7/4$ electrons per atom. Since the same conditions govern the appearance of β -, γ -, and ϵ -phases, all these may be expected when any one is found. D. R. D.

Magnesium-zinc-silicon alloys rich in magnesium. E. ELCHARDUS and P. LAFFITE (Compt. rend., 1933, 197, 1125—1127).—The thermal diagram of the system Mg-Zn-Si has been determined within the limits Mg-Mg₂Si-MgZn₂. Over most of the range the melt forms two phases, the limit for ternary solid solution having the composition 94.5 Mg+5.25 Zn+0.25% Si; that of the ternary eutectic, m.p. 335°, is 53.3 Mg+43.5 Zn+3.2% Si (cf. B., 1923, 892; A., 1929, 398). C. A. S.

Solubility of cupric chloride in water and transition points of its hydrates. The tetrahydrate. E. BOYE (Z. anorg. Chem., 1933, 215, 75—80).—Equilibria in the system CuCl₂-H₂O have been determined. The tetrahydrate forms blue needles, the colour of which is not changed by H₂O. The cryohydric point is at -43.4°. Transition temp. are as follows: $4 \rightleftharpoons 3$, 15.0°; $3 \rightleftharpoons 2$, 25.7°; $2 \rightleftharpoons 1$, 42.2°. F. L. U.

Solubility of thallous iodate and thallous chloride in the presence of amino-acids. C. F. FAILEY (J. Amer. Chem. Soc., 1933, 55, 4374—4378).—The solubility of TlIO₃ and TlCl in H₂O in presence of glycylglycine, glycine, α -alanine, α -amino-*n*- and -*iso*-butyric acid, α -amino-*n*-valeric acid, carbamide, and diketopiperazine, respectively, has been determined. For TlIO₃ the logarithm of the solubility is approx. a linear function of the concn. of the added substance. The dielectric consts. of the solutions do not explain the differences observed among the NH₂-acids. E. S. H.

Rule for the expression of the partition of associating substances. M. J. ALMQUIST (J. Physical Chem., 1933, 37, 991—994).—A distribution equation agreeing with experimental data and having a theoretical basis is given. The degree of association is assumed to be equal in both solvents. H. S. P.

Fractional crystallisation of radiferous barium chloride. (MME.) B. E. MARQUES (Compt. rend., 1933, 197, 1314—1315; cf. A., 1933, 562).—The relative quantities of Ra⁺⁺ and of Ba⁺⁺ in the solution before and after crystallisation are slightly different. C. A. S.

Diffusion of hydrogen through platinum and nickel and through double layers of these metals. W. R. HAM (J. Chem. Physics, 1933, 1, 476—481).—Direct experiments on double layers of Pt and Ni show that the temp. coeff. of flow depends wholly on the outgoing surface. The work of Borelius (A., 1927, 195, 727) is confirmed for single sheets. F. L. U.

Sorption of oxygen by nickel catalysts. W. W. RUSSELL and L. G. GHERING (J. Amer. Chem. Soc., 1933, 55, 4468—4474; cf. A., 1932, 332).—Considerable amounts of O₂ are instantaneously and irreversibly adsorbed by Ni catalysts even at -190°. The degree of irreversible adsorption increases with rising temp.; considerable reversible adsorption occurs only at -190°. The rates of slow sorption increase with rising temp. Activated adsorption probably occurs at -190° and accounts for most of the O₂ sorbed at 0°. E. S. H.

Possible magnitude of the sorption error in measurements involving easily sorbable gases at low pressures. M. FRANCIS (J. Physical Chem., 1933, 37, 1019—1027).—Measurements with SO₂ at <0.1 mm. show that the amount of gas sorbed on the walls of a simple apparatus may exceed that in the free space. Care must therefore be taken in interpreting pressure changes with a sorbable gas at low pressures. H. S. P.

Sorption of iodine vapour by various inorganic substances. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1933, 63, 99—116).—Although sorptive power (*s*) is widely observed, the velocity of sorption of I vapour at room. temp. by numerous inorg. powders (not previously evacuated) from all groups of the periodic table is, in general, small, but is increased (1) by trituration with I, (2) by previous heating of the powder, and (3) by heating with I, and is therefore hindered by the absorbed air. *s* depends on the surface area of the sample and hence on its method of prep.; with ZnO there is a definite relation between *s* and the nature of the compound from which it is prepared by thermal decomp. Vigorous grinding of the powder sometimes increases (fibrous Al₂O₃) and sometimes hinders (SiO₂ gel) sorption. Most rapid sorption occurs with MgO, ZnO (from basic ZnCO₃ at 300°), Ca(OH)₂, and Sb₂O₃. The colour (*c*) of the sorbate varies from yellow to red, becoming almost black for high I content (*i*), the relation of *c* to *i* varying with different substances and samples. Optical analysis of the reflected light and of the absorption curves for different thicknesses of I shows that *c* is related to the light transmission of the (thin) layers of adsorbed I, and is also influenced by the optical behaviour of the sorbing material. J. W. B.

Adsorbabilities of ions. K. S. G. DOSS (J. Indian Chem. Soc., 1933, 10, 503—508).—Theoretical. E. S. H.

Adsorption of thorium-B by thallium halide crystals in presence of ions. II. J. F. KING and P. R. PINE (J. Physical Chem., 1933, 37, 851—874; cf. A., 1933, 899).—Adsorption of Th-B⁺⁺ on TlBr and TlI is increased by I⁻, CrO₄²⁻, CNS⁻, and Br⁻, the effect decreasing in the order named. It is diminished by Cl⁻ and C₂O₄²⁻, and by Pb⁺⁺, Cu⁺⁺, Ag⁺, and Tl⁺. Anions are adsorbed on the crystal surfaces, conferring a negative charge on them, and the subsequent adsorption of Th-B⁺⁺ is favoured by insolubility of the salt formed by it with the ion concerned. This rule is strictly followed among the halide anions, but the effectiveness of other ions is partly determined by their deformability. Cations

diminish adsorption of Th-B⁺⁺ by competing with it. In the latter case Tl⁺ is most effective because it is more readily attached than foreign ions to the Tl halide lattice. No "neutral" (*i.e.*, non-adsorbing) specimen of TlBr or TlI could be prepared.

F. L. U.

Effect of alkali and alkaline-earth ions on the adsorption of thorium-B by silver bromide crystals. J. F. KING and U. T. GREENE (*J. Physical Chem.*, 1933, 37, 1047—1059).—The adsorption (I) of Th-B ions on AgBr crystals in presence of alkali and alkaline-earth bromides has been measured. At const. [Br⁻] and with different cations, the (I) of Th-B changes as a result of the simultaneous (I) of the cations. A relation appears to exist between the adsorbability of the cations and their heats of hydration, ionic size, and the solubility of the bromides.

H. S. P.

Adsorption systems of kaolins and clays with liquids in relation to plasticity. E. GRUNER (*Z. anorg. Chem.*, 1933, 215, 1—18).—V.p.-composition isotherms have been determined for systems of kaolins and clays with various liquids. Liquids which do not form plastic mixtures give a v.p. curve consisting of vertical and horizontal parts with a sharply curved connecting portion, whilst those which confer plasticity show a gradual transition. Parallelism exists between the degree of plasticity and the extent of the inclined part of the curve. The latter group includes only those liquids which possess asymmetric dipoles, such as H₂O, NH₃, and their simple derivatives. Liquid NH₃ dehydrates allophane present in clays but is without action on kaolinite. The results are discussed with reference to the chemical constitution of kaolinite. F. L. U.

Elementary deduction of Gibbs' adsorption theorem. F. O. KOENIG and R. C. SWAIN (*J. Chem. Physics*, 1933, 1, 723—730).—Theoretical. An exact elementary deduction of Gibbs' adsorption theorem and of related equations is given.

H. S. P.

Preparation and properties of thin lead sulphide layers, with special reference to their detector action. II. G. BRUCKMANN (*Kolloid-Z.*, 1933, 65, 148—161; cf. A., 1933, 1113).—The layers have a stoichiometric composition and well-defined crystal structure; their optical properties depend on the film thickness. Detector action is observed with the purest PbS and is independent of the material under the PbS layer, but varies with the thickness of the film, and is favoured by a coarse cryst. structure. The existence of a solid, insulating layer at the point of contact is improbable. The electrons pass in the direction from contact material to PbS, except when contact with graphite is made; no difference is shown by various metals and alloys as contact materials. Theories of rectifying action are discussed.

E. S. H.

Surface phenomena at the interface solid-solution. Change in heats of wetting of solutions of surface-active substances on addition of electrolytes. B. ILJIN, V. SEMENTSCHENKO, and V. IVANOV (*Z. physikal. Chem.*, 1933, 166, 382—392).—The heat of wetting, *Q*, of non-activated wood charcoal in aq. solutions of NaCl, Pr³OH, and

Bu³OH is > in pure H₂O and increases with the concn. In mixed solutions of either alcohol and NaCl the increase in *Q* compared with pure H₂O is > the sum of the effects caused by the two solutes separately.

R. C.

Vaporous state of myristic acid films on aqueous solutions. S. A. MOSS and E. K. RIDEAL (*J.C.S.*, 1933, 1525—1528).—A new type of Langmuir trough is described in which the film pressure (*F*) rotates a floating barrier against the torsion of a wire. Myristic acid spread on H₂O is found to obey the equation $FA = 0.5RT$, where *A* = area of the film, and it is deduced that the mols. are associated in pairs even when *A* is large.

D. R. D.

Influence of foreign substances on the wettability of chemicals by water. L. J. WEBER and A. C. CHATTERJI (*Kolloid-Beih.*, 1933, 38, 412—438).—The wettability of C₁₀H₈, anthracene, and phenanthrene by aq. solutions of org. substances has been determined (with an accuracy of ±3%) by a simple sedimentation method. In series of fatty acids, alcohols, esters, and amines the wettability increases with increasing mol. wt. or surface activity. Traube's rule is valid for the lower homologues. Non-polar substances (paraffin, CS₂, CCl₄, pentane) have little influence on the wettability of C₁₀H₈, whilst small amounts of polar substances (oleic acid, NH₂Ph, PhOH, toluidine, xylydine, CH₂Ph·OH) increase the wettability. Similar phenomena are observed when the org. substances are added to molten C₁₀H₈. The great influence exerted by small amounts of impurities suggests that the wettability of a substance may be used as an indication of its purity. E. S. H.

Experiments with wetting agents. H. A. NEVILLE and C. A. JEANSON (*J. Physical Chem.*, 1933, 37, 1001—1008).—The surface tensions of aq. solutions of various concns. of the Na sulphonates of C₆H₅, PhMe, xylene, cymene, PhEt, PhPr², PhBu, and of a commercial wetting agent (sulphonate) have been measured. Two substituting groups increase the surface activity > a single group with the same no. of C atoms. The absorption of the wetting agents by wool runs parallel with the potential curve of the wool in acid solution and is negligible in alkali. These agents increase the sorption of dye in acid and decrease it in alkaline solution.

H. S. P.

Surface tension of film-covered liquids at saturation. H. BROWN (*J. Amer. Chem. Soc.*, 1933, 55, 4521—4523).—A discussion (cf. A., 1933, 899).

E. S. H.

New method of studying electrical properties of unimolecular films on liquids. H. G. YAMINS and W. A. ZIZMAN (*J. Chem. Physics*, 1933, 1, 656—661).—The surface potential of unimol. films of some fatty acids and glycerides on pure H₂O and 0.01N-H₂SO₄ was measured by a potentiometer and a condenser comprising the surface under study and a metal plate vibrating above it. Reproducible results are obtained which agree with those of earlier workers.

D. R. D.

Surface chemistry. Nobel lecture. I. LANGMUIR (*Angew. Chem.*, 1933, 46, 719—733).—A summary of Langmuir's published work. E. S. H.

Electrokinetic phenomena in capillaries. H. REICHARDT (Z. physikal. Chem., 1933, 166, 433—452; cf. A., 1931, 795).—Since the streaming potential, ζ , at a liquid-solid interface may change with time when the liquid remains stationary, the variability of ζ with the streaming velocity, v , at low vals. of v is explained. The field due to ζ retards the flow in the double layer. If surface conduction is predominant the transport back of the charges set free at the ends of the capillary will occur principally by backward streaming of the part of the double layer in immediate proximity to the wall, which will reduce the mean v . If the cross-section of the double layer is a not negligible fraction of the total liquid cross-section the effective resistance of the capillary to the flow of liquid under the influence of a pressure difference, p , may be considerably increased by the field due to ζ . The fundamental electrokinetic equations for narrow capillaries are deduced. The equation for the convection current is valid for wide tubes within which there is turbulent flow. Turbulence within the double layer is impossible. Saxeen's relation ζ/p —(amount of liquid transported electro-osmotically)/(current strength) is valid also for systems of capillaries where convective surface conduction plays a part. R. C.

Capillary ascension of hydrosols and solutions of dyes: influence of concentration and of electrolytes. A. BOUTARIC and M. PEYRAUD (Compt. rend., 1933, 197, 1218—1220).—When strips of filter-paper are suspended with one end dipping into various hydrosols, and sols or solutions of colloidal or semi-colloidal dyes, the H_2O rises first at a rate which is independent of the solute and is followed more slowly by the colloid etc. Decrease of humidity or rise in temp. increases the rate. When these are const. the rate is independent of concn. for negative colloids etc., but increases linearly with the concn. for positive colloids, thus affording a means of determining the electric character of the colloid. The effect of an electrolyte added to the sol varies mainly according to the cation or anion as the colloid is negative or positive, respectively. C. A. S.

Water filtration through membranes and membrane resistance. V. V. LEPESCHKIN (Kolloid-Z., 1933, 65, 184—186).—At pressures < 100 cm. H_2O the velocity of filtration of H_2O through parchment and dried collodion membranes decreases with decreasing pressure, until a pressure is reached (the "membrane resistance") at which filtration stops. Membrane resistance increases as the pore size decreases, but is practically independent of the thickness of the membrane. The observed phenomena are ascribed to the force required to overcome the attraction between the H_2O mols. and the walls of the membrane. E. S. H.

Stationary, checked, and other states of osmotic systems. II. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 717—723; cf. A., 1933, 900).—Theoretical. J. W. S.

Influence of p_H on speed of diffusion of the chlorine ion across collodion membranes. C.

HRYNKOWSKI (Bull. Soc. Chim. biol., 1933, 15, 1146—1153).—The rate of diffusion of Cl^- in solutions of KCl, NaCl, $CaCl_2$, and mixtures of these salts increases with decreasing p_H of the solutions. A higher p_H or $[Ca^{++}]$ decreases the time required for equilibrium to be established. H. D.

Mol. wts. of dissolved substances. A. W. POUND and J. R. POUND (J. Physical Chem., 1933, 37, 969—972; cf. A., 1931, 843).—Results of cryoscopic determinations of the mol. wt. of 11 substances in various org. solvents are given. F. L. U.

F.p. and osmotic pressures of lactose solutions. E. O. WHITTIER (J. Physical Chem., 1933, 37, 847—849).—Results of f.p. measurements from 4.7% to saturation are given. Since the vals. agree within 1% with those for sucrose, it is inferred that one may be substituted for the other without influence on osmotic effects. F. L. U.

Lambert-Beer law and the nature of absorbent particles in solution. E. DARMOIS (Compt. rend., 1933, 197, 1120—1121).—Absorption curves which deviate from the Lambert-Beer law, and are supposed to indicate the presence of two or more isomerides, are similar to those for rotatory power under similar circumstances, and deductions relative to the no. of isomerides present can be similarly made (cf. A., 1911, ii, 352; 1928, 589). C. A. S.

Absorption spectra of glycine solutions and their interpretation. G. A. ANSLOW, M. L. FOSTER, and C. KLINGLER (J. Biol. Chem., 1933, 103, 81—92).—Absorption spectra for H_2O , HCl, and NaOH solutions of glycine (I) have been determined for the range 6000—1850 Å. F.p. determinations before and after irradiation have also been made. The results indicate that the cation $^+NH_3 \cdot CH_2 \cdot CO_2H$ exists in both H_2O and HCl solution. Determinations of the frequency at which dissociation (II) occurs in the CO_2H group show that (I) behaves like other NH_2 -acids (cf. A., 1932, 896). Hence (II) takes place by the separation of H^+ from the mol. ion giving the zwitter-ion. In aq. NaOH the (I) cation exists as $^+NH_3 \cdot CH_2 \cdot CO_2Na$ and (II) takes place by the separation of Na^+ leaving the zwitter-ion. The energies of (II) in ergs and volts, and the heats of (II) in cal., have been calc. Polymerisation increases with increasing concn. and also with irradiation of the solutions with ultra-violet light. The results confirm the theory of the zwitter-ion structure of the (I) mol. M. S. B.

Molecular refraction in dilute solutions. II. Interferometric precision measurement of refractive indices. W. GEFFOKEN and A. KRUIS (Z. physikal. Chem., 1933, B, 23, 175—192; cf. A., 1933, 587).—By using monochromatic light with a modified form of Haber-Loewe apparatus, interferences of the order of several thousand can be observed. The difference in n between solution and solvent can be determined with an abs. precision ranging from 0.05 in the more conc. solutions to 0.03 for dil. solutions. For aq. NH_4NO_3 at 25° the apparent mol. refraction of the solute falls linearly with increasing concn., but with aq. NaCl and KCl the curve exhibits a max. R. C.

Specific influence of the solvent in electrolytic dissociation. D. J. G. IVES (J.C.S., 1933, 1360—1365).—Conductometric titration of solutions of Cu, Ni, and Zn sulphates and malonates and Cu oxalate containing C_5H_5N (which may be expected to provide a more stable solvation sheath) supports the view previously put forward (A., 1931, 1126). It is suggested that the behaviour of salts of the Cu malonate type is governed by the electron-accepting tendency of the cation and its influence on the competing co-ordinating tendencies of the anion and the solvent; if the solvent has the greater co-ordinating tendency the differences of the degrees of ionisation of a series of salts having a common anion or cation may almost completely disappear, whereas if the tendency is greater for the anion the differences due to sp. properties of the other ions will be apparent.

H. F. G.

F.p. of aqueous solutions. IV. Potassium, sodium, and lithium chlorides and bromides. G. SCATCHARD and S. S. PRENTISS (J. Amer. Chem. Soc., 1933, 55, 4355—4362; cf. A., 1932, 912).—Refinements of technique are described. The bromides show greater deviations from the limiting law than the corresponding chlorides. Deviations for salts of the same anion increase in the order $K < Na < Li$, except in very dil. solutions of LiCl.

E. S. H.

Optical determination of ionic equilibria in dilute ethyl alcoholic solution. P. GROSS, A. JAMOCK, and F. PATAT (Monatsh., 1933, 63, 117—126).—Under conditions ensuring rigid exclusion of H_2O the mol. extinction coeffs. (ϵ) of NH_4 and NET_4 picrates at 4360 Å. and 20° for dil. EtOH solutions ($c = 2.5 \times 10^{-6}$ to 2.9×10^{-3} mol. per litre) are const. (4019 ± 3 and 4026 ± 8 , respectively), indicating complete dissociation. Picric acid under such conditions gives a val. for the activity coeff. almost identical with that previously obtained (A., 1930, 992), but the thermodynamic dissociation const. (k_0) deviates slightly from the previous val. (cf. below). Measurements of ϵ for picric acid and NH_4 picrate in the visible and ultra-violet regions confirm the complete dissociation of the salt and the assumption that undissociated picric acid does not absorb between the visible region and 3600 Å. Increasing concn. of H_2O in EtOH causes a linear increase in ϵ for NET_4 picrate until at 0.8 mol. per litre it reaches the val. for the picrate ion in H_2O , but its effect on ϵ for the free acid is greater owing to alteration in the dissociation const. conditioned by the equilibrium $(EtOH, H)^+ + H_2O \rightleftharpoons H_3O^+ + EtOH$ (equilibrium const. calc. $= 0.0524 \pm 0.001$), whence the deviation in k_0 noted above would be caused by $< 0.1\%$ of H_2O in the EtOH previously used.

J. W. B.

Dielectric properties of solutions of electrolytes in a non-polar solvent. C. A. KRAUS and G. S. HOOPER (Proc. Nat. Acad. Sci., 1933, 19, 939—943; cf. A., 1933, 1120).—In harmony with the view that electrolytes in non-polar solvents are in the form of ion pairs which unite to form more complex aggregates at higher concn., the rise of dielectric const., k , at 25°, with increase of concn. of C_6H_6 solutions of tetraisoamylammonium picrate (I) and bromide (II), triisoamylammonium picrate

(III), and $AgClO_4$ (IV) is with $m-C_6H_4(NO_2)_2$ (V) in C_6H_6 . At high concn., k is related to the symmetry of the ions. Electric moments are: (I) 18.0, (II) 14.7, (III) 12.91, (IV) 11.97, and (V) 4.0×10^{-18} e.s.u.

J. G. A. G.

Investigation of influence of solute on solvent by means of infra-red absorption spectra. II. Effect of hydrogen and hydroxyl ions on state of association of water. R. SUHRMANN and F. BREYER (Z. physikal. Chem., 1933, B, 23, 193—212; cf. A., 1933, 348, 998).—Extinction coeff. measurements have been made between 0.85 and 2.3μ . The absorption max. of H_2O at 0.98, 1.20, and 1.45 are depressed by dissolved HCl or H_2SO_4 , and the absorption on the long-wave side of these bands and that at 1.96μ is increased. These effects are ascribed to the addition of H^+ to H_2O mols., and to depolymerisation of the H_2O . From the depression of the max. at 1.45 by HCl it is calc. that each H^+ binds approx. 1 H_2O mol. The absorption curve of H_3O^+ , calc. from absorption data for aq. HCl, shows no distinct banded absorption, which suggests that H^+ forms no definite compound with H_2O but merely a short-lived complex in which the at. vibrations of H_2O are modified in varying degree by the electric field of H^+ . All the absorption max. of H_2O are depressed by KOH. Here each OH^- binds approx. 2 H_2O mols. The absorption curve of H_2O mols. under the influence of OH^- is similar in character to that of H_3O^+ , and it is probable that OH^- forms no definite compound with H_2O but merely influences the H_2O to a variable extent.

R. C.

Limiting laws of the interionic attraction theory of strong electrolytes. P. VAN RYSELBERGHE (J. Chem. Physics, 1933, 1, 205—209).—The general form of the limiting laws can be obtained by combining the Gibbs-Helmholtz equation and the virial theorem of Clausius. The equations of Debye and Hückel and of Kramers represent special forms of the general laws.

A. J. M.

Influence of soluble phosphates on viscosity of kaolin suspensions. V. A. PLOTNIKOV and E. M. NATANSON (J. Appl. Chem. Russ., 1933, 6, 839—844).—The viscosity η of kaolin (I) suspensions is reduced to the same extent by 0.062N- Na_2HPO_4 (II), 0.063% Na_2SiO_3 (III), 0.36% Na_2CO_3 , 0.24% K_2CO_3 , 0.33% K_2CrO_4 , and 0.24% $(NH_4)_3PO_4$; at higher concns. η rises again in all cases. The action of the above electrolytes is due to adsorption on (I), which is at a max. at the concns. given. The p_H of the suspensions varies very little with increasing concn. of (II) or (III), owing to the buffer action of (I), and variations in η cannot be attributed to change in p_H .

R. T.

Mechanism of the formation of Kohlschütter's silver sol. H. B. WEISER and M. F. ROY (J. Physical Chem., 1933, 37, 1009—1018).—Kohlschütter's Ag sol may be obtained by the action of H_2 on suspensions of Ag_2O at 50° or 60° provided these have not been ultra-filtered. Soft glass, Pyrex, or quartz vessels may be used and the presence of alkali or sulphide is unnecessary. With Pt, deposition of Ag crystals occurs owing to the activation of H at

the Pt surface. Mirror formation on glass is due to deposition of Ag_2O by the alkali in the glass, followed by the reduction of Ag_2O by H activated at a Ag or Ag- Ag_2O surface. H. S. P.

Significance of gas phase in formation of emulsions. F. ROGOWSKI and K. SOLLNER (Z. physikal. Chem., 1933, 166, 428—432).—The formation of emulsions either by the action of supersonic waves or by shaking is promoted and the emulsions are rendered more stable by the presence of a foreign gas, the action of which is apparently not sp. R. C.

Determination of the amount of bound water in disperse systems. I. Refractometry and polarimetry. A. DUMANSKI (Kolloid-Z., 1933, 65, 178—184).—A sucrose solution of known concn. is added to the colloid system containing a known amount of total H_2O . After shaking and keeping, the solution is filtered, and sucrose is determined in the filtrate refractometrically or polarimetrically. The amount of bound H_2O is calc. from the difference between the concn. of sucrose found and the concn. it would possess if it were dissolved in the total H_2O present. E. S. H.

Composition of arsenic trisulphide sol and its variation with age and under the influence of light. V. KRESTINSKAJA and V. JAKOVLEVA (Kolloid-Z., 1933, 65, 187—191).—The micelles of As_2S_3 sols contain excess of As_2O_3 or H_2S according to the conditions of prep. Ageing phenomena are due to hydrolysis of As_2S_3 and oxidation of H_2S . By adsorption of H_2AsO_3 and loss of H_2S , the relative As content of the micelles increases. The ageing process is accelerated by light. E. S. H.

Phase volume theory and homogenisation of concentrated emulsions. J. B. PARKE (J.C.S., 1933, 1458—1459).—Emulsions containing > 74% disperse phase (I) by vol. must contain drops of non-uniform size (cf. J.C.S., 1907, 91, 2001); such emulsions of C_6H_6 and PhMe in Na and K oleate solutions are broken down by homogenisation to emulsions of about 70% (I) in which the drops are microscopically uniform, whilst more dil. emulsions are unaltered. D. R. D.

Optics of white sols. II. Diffuse side rays. T. CASPERSSON (Kolloid-Z., 1933, 65, 162—170; cf. A., 1932, 993).—The optical relations of colloidal particles of different diameters are discussed theoretically. E. S. H.

Colloid-chemical foundations of photoanisotropy. I. General problem. F. WEIGERT and J. MATULIS (Kolloid-Beih., 1933, 38, 384—411).—An introductory discussion. E. S. H.

Role of dielectric constant, polarisation, and dipole moment in colloid systems. XI. Stabilisation of metal organosols. Wo. OSTWALD, J. F. EHLERS, and H. ERBRING (Kolloid-Beih., 1933, 38, 337—383; cf. A., 1932, 462).—The sol-forming power and sol stability of Ag dispersed in org. media by the oscillating electrical discharge can be measured by the "Umschlagszeit" (U), which is the time in sec. during which dispersion can occur before the onset of coagulation. The dependence of U and the corresponding concn. of sol on the applied potential

and temp. has been investigated and the existence of a crit. temp. is confirmed. The conditions of dispersion of Hg in (a) mixtures of polar and non-polar liquids (Et_2O , PhNO_2 , MeOH, EtOH, PrOH, Bu^oOH, and COMe_2 in C_6H_6) and (b) mixtures of two polar liquids (PhNO_2 , H_2O , MeOH, EtOH, PrOH, Bu^oOH, isoamyl and *n*-hexyl alcohols in Et_2O) have been examined. In the simplest case (Et_2O - C_6H_6), U varies with the proportion of one component in the mixture c according to the relation $U = k\sqrt{c(1/\epsilon_c)}$ or $U = k_1\sqrt{c(\mu^2/\epsilon_c)}$, where ϵ_c is the dielectric const., μ the dipole moment, and k and k_1 are consts. With PhNO_2 - C_6H_6 the expression $U = k\sqrt{cP''}$ is valid, where P'' ($=k_1\mu^2$) is the orientation polarisation. U is increased when a polar liquid is added to a non-polar liquid but is not altered when a non-polar liquid is added to a polar liquid. These results are discussed in relation to the degree of dissociation of the moles. of liquid. E. S. H.

Magneto-optical investigations on ferric oxide sols. I. General. W. HELLER (Kolloid-Beih., 1933, 39, 1—57; cf. following abstract).—The variable, complex magneto-optical behaviour observed with Fe_2O_3 sols is due to the presence of several constituents (α - Fe_2O_3 , α - Fe_2O_3 , and a basic salt of unknown composition), which have different properties. α - Fe_2O_3 gives a positive effect, which increases with increasing field strength in a characteristic way. Goethite sols give at first a positive effect, changing to negative with ageing of the sol. The intermediate stage between positive and negative double refraction is isotropic when the sol is homodisperse, but gives a positive-negative (alternating) effect when heterodisperse. The change of sign with time is more rapid in sols having small particles. In general, with rise of temp. negative effects tend to diminish and positive effects to be enhanced. The temp. coeff. in very fresh positive or aged negative sols is relatively small (3—6%), but is considerable in the intermediate stage. Magnetic double refraction is reduced by all processes that bring about coagulation. E. S. H.

Transverse magneto-optic anisotropy of some colloidal solutions. II. Ferric oxide sol. (Summary.) W. HELLER and H. ZOCHER (Z. physikal. Chem., 1933, 166, 365—381; cf. A., 1933, 461).—A study of the Majorana phenomenon. α - Fe_2O_3 sols have a const. double refraction, δ , independent of the field strength, H , whilst with α - Fe_2O_3 sols δ varies with H and may become negative on keeping, a change ascribed to diminishing form anisotropy of the particles. Sols containing supposedly a colloidal basic salt have positive δ . The magneto-optical data indicate that the active substance in most Fe_2O_3 sols prepared by the usual methods at room temp. is goethite primary particles. The only types of coagulation producing anisotropic particle aggregates are coagulation by shaking or stirring and very slow pptn. by electrolytes. The double diffraction passes through a max. with increasing degree of dispersity. With fresh goethite sols δ decreases with rise of temp., T , whilst with very old sols the negative δ decreases, becomes positive, and passes through a max. These variations are ascribed to rapid decrease in the inner

anisotropy of the particles as T rises. The form of the H function of the anisotropy of goethite sols varies with T . Orientability decreases rapidly in the order $\alpha\text{-Fe}_2\text{O}_3 > \text{goethite} > \text{basic salt}$. Orientation and de-orientation in the magnetic field are extremely rapid compared with V_2O_5 sols. Under the influence of light the rate of variation of δ with time increases materially, and moderate warming has an even more marked effect. In light of short wavelength all the sols are strongly dichroic. All natural Fe_2O_3 sols exhibit a positive, usually weak, streaming double refraction.

R. C.

Change of stability of sols of various concentrations with their purity. S. GHOSH and R. N. MITTRA (J. Indian Chem. Soc., 1933, 10, 471—476).—Experiments with ThO_2 sols show that if the sol contains large amounts of stabilising electrolyte it may behave abnormally on dilution towards coagulation by univalent electrolytes, although additive effects are shown when the sol is coagulated by a mixture of electrolytes.

E. S. H.

Kinetics of slow coagulation. I, II. D. N. GHOSH (J. Indian Chem. Soc., 1933, 10, 509—516, 517—527).—I. Smoluchowski's equation is not applicable to the slow coagulation of a monodisperse S sol which is free from ionogenic impurities. The difference between rapid and slow coagulation is ascribed to the almost complete discharge which occurs in the rapid process.

II. The S-shaped slow-coagulation curves are explained on the ground that the rate at any stage depends on (a) the no. of primary particles, and (b) the no. of multiple particles. The adherence factor ϵ in Smoluchowski's theory is not a const., but is a function of time, increasing as the size of the multiple particles grows.

E. S. H.

Viscosity of cellulose solutions. (MME.) A. DOBRY and J. DUCLAUX (Compt. rend., 1933, 197, 1318—1320).—The influence of the nature of the solvent on the viscosity of cellulose nitrate solutions has been examined.

C. A. S.

Heat development and work performance in the dilution of lyophilic sols. I. OKAMURA (Kolloid-Z., 1933, 65, 175—178).—The heat of dilution and osmotic pressure of solutions of cellulose nitrate and acetate and ethylcellulose in COMe_2 and MeOAc respectively have been determined. The differential work of swelling is $>$ the differential heat of dilution.

E. S. H.

Lyophilic colloids. XIX. Influence of neutral salts and non-electrolytes on isoelectric gelatin sol. L. W. J. HOLLEMAN, H. G. B. DE JONG, and R. S. T. MODDERMAN (Kolloid-Beih., 1933, 38, 439—463; cf. A., 1933, 23).—Determinations of the viscosity of isoelectric gelatin sols show that $(\eta_r - \eta_0)/\eta_0$ is increased by small amounts of electrolytes, the effect increasing with increasing valency of the anion. The lyotropic series is also encountered, but in the reverse order. The results are explained by assuming that the electrophoretic null point at the isoelectric point represents a compensation of two weak, opposite charges. A similar effect is observed with MeOH , EtOH , PrOH , and methane.

E. S. H.

Lyophilic colloids. XX. Capillary-electric charge and hydration as state variables of hydrophilic gels. Formation of starch paste. J. A. VAN DER HOEVE, H. G. B. DE JONG, and H. R. KRUYT (Kolloid-Beih., 1933, 39, 105—138; cf. A., 1933, 779).—The influence of electrolytes and non-electrolytes on the temp. at which potato-starch forms a paste with H_2O has been investigated. At low concns. of electrolyte the temp. rises with increasing concn., the effect being the greater the higher is the valency of the cation; at higher concns. lyotropic influences come into play. Non-electrolytes favour the formation of paste when positively adsorbed (tannin), but have the opposite effect when negatively adsorbed (EtOH). The influence of electrolytes or non-electrolytes on the formation of paste bears no relation to their influence on sols of starch. A mechanical theory of the formation of starch paste is developed.

E. S. H.

Odometer observation as an aid in the elucidation of gel structure. K. VON TERZAGHI (Kolloid-Z., 1933, 65, 129—148).—A discussion of published work on the pressure and heat of swelling of gels and the pressure-vol. relations of coarsely disperse gel models. The heat developed is due partly to the internal friction of H_2O streaming through the structure, and partly to the change of state of H_2O from the ordinary to the boundary layer state.

E. S. H.

Mol. wt. of gelatin. W. R. ATKIN (J. Soc. Leather Trades Chem., 1933, 17, 575—582).—The min. mol. wt. of gelatin (I) calc. on the assumption that the (I) mol. contains two histidine mols. is 34,500, which is $>$ that obtained by Lloyd (B., 1922, 224, 907). There are 360 NH_2 -acid groups in the (I) mol. and 80% have been allocated to individual NH_2 -acids. The remaining 20% have a higher O content and must contain OH groups. The mean mol. wt. of a (I) NH_2 -acid is 114, which agrees with X-ray data.

D. W.

Electric conductivity of gelatin. (MLE.) S. VEIL (Compt. rend., 1933, 197, 1044—1046; cf. A., 1932, 226). The current-time curve of a gelatin film shows a sharp rise to a max. in the first 0.5 hr., followed by a sharp fall in the next 1.5 hr., and then a slow decline to zero. The current-voltage curve accords initially with Ohm's law, but there is a subsequent steady decrease in the current/voltage ratio, resulting finally in a const. "saturation" current. Agar agar behaves similarly though less clearly so.

C. A. S.

Protein systems. II. Rate of freezing and shape of particle in protein solutions. H. H. WEBER and C. PULLEN (Biochem. Z., 1933, 266, 153—161).—The rate of freezing of supercooled (down to -8°) protein solutions is retarded by 10—20% when the colloidal particles are spherical (ovalbumin, myosin), but is unaffected when they are rod-shaped (ovoglobulin, Edsall's myosin). The retardation is independent of $[\text{H}^+]$ (p_H 4.9—9.4), of the extent of supercooling, and of the presence or absence of electrolytes.

W. McC.

Activity coefficient of ovalbumin in presence of ammonium sulphate. C. F. FAIRLEY (J. Phys.

ical Chem., 1933, 37, 1075—1082).—The log of the activity coeff. of ovalbumin in presence of $(\text{NH}_4)_2\text{SO}_4$ deduced from osmotic data is a linear function of the salt concn. The activity coeffs. agree with solubility measurements when the composition of the solid phase is taken into account. H. S. P.

Temperature coefficients of viscosity of liquids in relation to the structure of caoutchouc in solution. W. F. BUSSE and E. KARRER (Kolloid-Z., 1933, 65, 211—223).—The relation $1/\eta = KS^{-1}e^{-q/kT}$, where η is the viscosity, S the shearing force, r the particle radius, T the abs. temp., K and k are consts., and q is an energy factor, is derived theoretically and confirmed for solutions of caoutchouc in various org. solvents over a range of systems in which η varied in the ratio 1:10⁶. The relation is not valid when irreversible changes occur in the solution or for solutions in Et₂O near the setting point; mastication, heating, and irradiation produce irreversible changes which displace q and K in the direction of lower concn. The results suggest that there is no temp.-variable equilibrium between higher and lower polymerides. The high viscosity cannot be attributed solely to solvation, but is mainly due to the mechanical inclusion of considerable amounts of solvent in the network of the disperse phase. E. S. H.

Properties of liquid silk. D. ONGARO (Giorn. Chim. Ind. Appl., 1933, 15, 506—510).—Silk has been obtained in the liquid state direct from the sericogenic glands of the silkworm, without the aid of chemical agents. The silk solution is in unstable equilibrium and its hardening is a true coagulation, even when caused by mechanical agencies. Silk solutions from races or crosses of silkworms with coloured cocoons may sometimes ppt. their pigment some time prior to setting, the coagulum then having a white colour identical with that of coagula from races with white cocoons. The Au index and the protective power of the Au solution are almost const. for solutions from the different races. Under the ultra-microscope the fibroin solution exhibits active Brownian movement, which is much slower than that of the Au solutions. Unlike the coagula obtained by mechanical action, those formed spontaneously from the silk solution are optically inactive. In 1% solution, fibroin has $[\alpha]_D$ —39.0°. T. H. P.

Fine structure of silk. V. Swelling phenomena in fibroin threads. K. OHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 216—232).—Swelling of fibroin produced by conc. neutral salt solutions etc. is related to micellar structure. The velocity of swelling of the central zone is < that of the outer layer, resulting in the production of spherical and fan-like forms. The external membrane is semipermeable. S

Displacement of equilibrium. R. ÉTIENNE (Compt. rend., 1933, 197, 1117; cf. A., 1933, 1118).—The error suggested by Verschaftelt is non-existent. C. A. S.

Le Chatelier's principle. J. M. BIJVOET (Chem. Weekblad, 1933, 30, 742—747).—The apparently anomalous behaviour of the N₂-H₂ system on addition

of N₂ at const. pressure is explicable in terms of the le Chatelier theorem as developed by Wagner.

H. F. G.

Amino-sulphonic acids. III. Dissociation constants of taurine derivatives. B. JOSEPHSON (Biochem. Z., 1933, 266, 9—17; cf. A., 1933, 1012).—In taurine, its *N*-alkylated derivatives (Me, Me₂, Prⁿ, heptyl, Ph, CH₂Ph) and CO₂H·C₆H₄·NH·[CH₂]₂·SO₃H (I) the ·SO₃H has a very high dissociation const. (II) which varies with the nature and no. of the substituents. A similar variation occurs in the (always very low) (II) of the substituted ·NH₂. (I) distinctly exhibits two (II), but taurodeoxycholic acid, probably because its ·CO₂H is not free, exhibits only one.

W. McC.

Dissociation of water in lithium bromide solutions at 25°. J. E. VANCE (J. Amer. Chem. Soc., 1933, 55, 4518—4521).—The dissociation const. of H₂O in aq. LiBr has been calc. from e.m.f. measurements of the cells H₂|LiOH(*m*₁), LiBr(*m*₂)|AgBr|Ag and H₂|LiBr(*m*), HBr(0.01)|AgBr|Ag and from determinations of the activity coeff. of 0.01*M*-HBr. E. S. H.

Thermodynamics of ionised water in potassium and sodium bromide solutions. H. S. HARNED and W. J. HAMER (J. Amer. Chem. Soc., 1933, 55, 4496—4507).—The dissociation const. of H₂O has been derived from measurements of e.m.f. of the cells H₂|K(Na)OH(0.01), K(Na)Br|AgBr|Ag and H₂|HBr(0.01), K(Na)Br|AgBr|Ag in aq. solution at 0—60°. The vals. of the normal potential of the Ag|AgBr electrode are given with an accuracy of ±0.01 mv. by $E_0 = 0.07169 - 5.259 \times 10^{-4}(t - 25) - 3.022 \times 10^{-6}(t - 25)^2$. The total heat of dissociation of H₂O and the relative partial mol. heat content of H' and OH' in aq. KCl, KBr, and NaBr solutions at 0—60° have been calc. The results agree with data obtained from determinations of heats of neutralisation at 20°. E. S. H.

Calculation of the equilibria in keto-enol tautomerism. G. W. WHELAND (J. Chem. Physics, 1933, 1, 731—736).—Linking and resonance energies deduced from empirical data have been applied to calculate keto-enol equilibria. The method has been used for PhOH, resorcinol, phloroglucinol, CH₂Ac₂, hydroxymethylene ketones, Et acetoacetate, acetylmalonate, and malonate, CHAc₃, CH(CO₂Et)₃, 1:2-cyclohexadione, Ac₂. The results are in qual. agreement with experiment. H. S. P.

Influence of strength of base on formation of aluminotartaric complexes. PARISELLE (Compt. rend., 1933, 197, 1214—1216; cf. A., 1926, 957; 1927, 856).—KOH behaves similarly to NaOH, but with NH₃, aq. the change in rotation indicates that (NH₄)₂(AlO)C₄H₃O₆ is only partly formed even with large excess of NH₃. Piperidine behaves similarly. With C₅H₅N and quinoline no aluminotartarate is formed; excess of base produces negative rotation and these bases apparently act merely as solvents.

C. A. S.

Equilibrium constants in terms of activities derived from cryoscopic data. II. Dissociation of pyridine *o*-chlorophenoxide in *p*-dichlorobenzene. H. M. GLASS and W. M. MADGIN (J.C.S., 1933, 1431—1435).—The equilibrium const., calc. on an activity basis, is 34.78 at the f.p. of the solution.

This, combined with the previous data in C_6H_6 at its f.p. (A., 1933, 350), gives 6800 g.-cal. for the mol. heat of formation in solution, ignoring any slight variation in K due to the change of solvent. D. R. D.

Activity of ammonia in ammonium chloride solutions. H. E. MATTHEWS and C. W. DAVIES (J.C.S., 1933, 1435—1439).—The distribution of NH_3 between $CHCl_3$ and H_2O has been measured at 25° over the range 0—3*M* in the H_2O layer, and with concns. of NH_4Cl in the H_2O up to 0.2*M*. The calc. activities suggest that the salt exerts three superposed effects. D. R. D.

Application of solubility data to determination of activity coefficients of acid molecules in solutions of sodium and potassium chloride. E. LARSSON (Svensk Kem. Tidskr., 1933, 45, 236—245).—A review of the author's work. R. P. B.

Limitations of solubility method for determining dissociation constant. W. V. BHAGWAT and S. S. DOOSAJ (J. Indian Chem. Soc., 1933, 10, 477—490).—The dissociation consts. of formic, acetic, salicylic, and citric acids have been determined, using the formula $K_2 = K_1 - a(c - b + a)/(b - a)^2$ (cf. Dhar, A., 1913, ii, 565). The vals. obtained increase with increasing concn. of the acid used. The effect of dilution depends on which of two opposite factors predominates—hydrolysis of the salt and degree of dissociation. E. S. H.

"Salting-out" and "salting-in" of weak acids. I. Activity coefficients of the molecules of *o*-, *m*-, and *p*-chlorobenzoic acids in aqueous salt solutions. II. Activity coefficients of the molecules of *o*-, *m*-, and *p*-hydroxybenzoic acids in aqueous salt solutions. A. OSOL and M. KILPATRICK (J. Amer. Chem. Soc., 1933, 55, 4430—4440, 4440—4444).—I. From determinations of the solubilities of $C_6H_4Cl \cdot CO_2H$ in aq. solutions of alkali salts the mol. solubilities and activity coeffs. have been calc. Both "salting-out" and "salting-in" are observed with the same weak acid. Activity coeffs. of the mols. of $C_6H_4Cl \cdot CO_2H$ and of $BzOH$ have the same vals. at corresponding concns.

II. Similar data are given for $OH \cdot C_6H_4 \cdot CO_2H$. "Salting-out" consts. in KCl solutions decrease with transfer of OH to the *m*- and *p*-positions, respectively. E. S. H.

Activity coefficient of thallos chloride in protein systems. J. C. H. STONE and C. F. FAILEY (J. Physical Chem., 1933, 37, 935—949; cf. A., 1932, 802).—Activity coeffs. of $TlCl$ in solutions of ovalbumin, edestin, excelsin, and hæmoglobin have been calc. from solubility measurements. The changes in solubility are related to the calc. ionic strength of the solutions. F. L. U.

Binary systems in two phases. I. HCl - Kr . II. HCl - C_3H_8 . G. GLOCKER, D. L. FULLER, and C. P. ROE (J. Chem. Physics, 1933, 1, 714—716).—The *p*-*T*-*x* relations of the mixtures HCl - Kr and HCl - C_3H_8 have been measured. No mixture showed > one liquid phase and retrograde condensation was observed in all cases. H. S. P.

System lead acetate-acetic acid. A. W. DAVIDSON and W. CHAPPELL (J. Amer. Chem. Soc., 1933,

55, 4524—4525).— $Pb(OAc)_2 \cdot 0.5AcOH$ is the stable solid phase below 56° over a wide concn. range, although this phase does not appear to separate without inoculation. Above 56° $Pb(OAc)_2$ is formed. E. S. H.

System Hg_2O - N_2O_5 - H_2O . H. G. DENHEAM and C. V. FIFE (J.C.S., 1933, 1416—1419).—Schreinemakers' residue method has been applied to the system at 25°. In stable equilibrium with solution there exist $2Hg_2O \cdot N_2O_5 \cdot H_2O$, $5Hg_2O \cdot 3N_2O_5 \cdot 3H_2O$, and $4Hg_2O \cdot 3N_2O_5 \cdot H_2O$. $Hg_2(NO_3)_2 \cdot 2H_2O$ exists in two orthorhombic modifications, but the existence of other hydrates of the normal salt could not be confirmed. H. F. G.

Equilibria in the system ammonium nitrate-sodium nitrate-water. E. A. NIKITINA (J. Gen. Chem. Russ., 1933, 3, 513—518).—The equilibrium relations have been studied at 0°, 15°, 20°, 30°, 40°, 60°, 80°, and 98°. R. T.

System cadmium sulphate-sulphuric acid-water. R. ARDITTI (Compt. rend., 1933, 197, 1209—1211).—On pouring H_2SO_4 into saturated aq. $CdSO_4$ the ppt. always consists first of $CdSO_4 \cdot H_2O$ which is stable within certain limits of concn. of H_2SO_4 (varying with temp.), below which it passes slowly into $3CdSO_4 \cdot 8H_2O$, and above into $CdSO_4 \cdot H_2SO_4$. Solubility curves for 0°, 16°, 21°, and 33.5° are given. Density, refraction, conductivity, and viscosity-wt.-% H_2SO_4 curves for similar solutions show max. (or min.) at the transition point $3CdSO_4 \cdot 8H_2O \rightarrow CdSO_4 \cdot H_2O$ (cf. A., 1897, ii, 316). C. A. S.

System $Na_2S_2O_3$ - $Ag_2S_2O_3$ - H_2O at 25°. H. BASSETT and J. T. LEMON (J.C.S., 1933, 1423—1427).— $Na \cdot Ag(S_2O_3)_2 \cdot 2H_2O$, $Na_5Ag_3(S_2O_3)_4 \cdot 2H_2O$, $NaAgS_2O_3 \cdot H_2O$, and $NaAg_3(S_2O_3)_2 \cdot H_2O$ are formed. No isomerism is observed; the yellow forms reported (A., 1907, ii, 347; 1922, ii, 57) are probably partly decomposed materials. D. R. D.

Ternary system diphenyl-diphenylamine-benzophenone. H. H. LEE and J. C. WARNER (J. Amer. Chem. Soc., 1933, 55, 4474—4477; cf. A., 1933, 228).—Two stable ternary eutectics occur. One at 18.8° contains Ph_2 30.5 mol.-% and $NHPh_2$ 49.0 mol.-%. The other at 16.5° contains Ph_2 30.0 mol.-% and $COPh_2$ 52 mol.-%. Evidence for the existence of two metastable ternary eutectics is given. E. S. H.

System allyl alcohol-iodine-di-iodopropyl alcohol. F. G. CAUGHLEY and P. W. ROBERTSON (J.C.S., 1933, 1323—1326).—The dissociation of di-iodopropyl alcohol (I) in CCl_4 solution into I and allyl alcohol (II) corresponds with a gas reaction of the second type; the degree of dissociation at 25° is 28% at dilution 20 and 58% at dilution 160, and 51% at 50° and dilution 20. Light accelerates the forward and reverse reactions, without altering the equilibrium, which is almost independent also of the solvent (C_6H_6 , $PhMe$, C_6H_{14}). The dissociation is unimol. and the reverse reaction bimol., and both are but slightly influenced by catalysts. The calc. heat of formation of (I) from I and (II) is 12.3 kg.-cal. H. F. G.

Phosphoric acid and the phosphates. III. **Equilibria between phosphoric acid and the**

hydrates of calcium sulphate. A. SANFOURCHE and A. KRAPIVINE (Bull. Soc. chim., 1933, [iv], 53, 970—973).—The solubility of CaSO_4 shows a max. when the solution contains 200—300 g. P_2O_5 per litre. The composition of the solid phase is given.

R. S.

Reciprocal salt-pair $\text{Ca}(\text{NO}_3)_2 + 2\text{KCl}$ at -10° . I. KRITSCHESKI and R. K. IZKOVITSCH (Z. anorg. Chem., 1933, 215, 103—104).—Compositions of solid and liquid phases for the system $\text{Ca}(\text{NO}_3)_2\text{--KCl--H}_2\text{O}$ at -10° have been determined. The industrial production of KNO_3 at this temp. is not considered practicable.

F. L. U.

Third law of thermodynamics. V. NJEGOVAN (Coll. Czech. Chem. Comm., 1933, 5, 415—423; cf. A., 1933, 351).

D. R. D.

Attempt to express the chemical constant thermodynamically. V. NJEGOVAN (Coll. Czech. Chem. Comm., 1933, 5, 424—426).—The author's conception of "internal effect" (A., 1933, 351) is applied to calculation of the chemical const.

D. R. D.

Free energy of ozone. L. S. KASSEL (J. Chem. Physics, 1933, 1, 414—417).—The three fundamental frequencies deduced by Gerhard (A., 1933, 208) for the O_3 mol. are not in perfect agreement with experiment. From these vals., however, the free energy is calc. as $S_{298.1} = 57.0$, compared with $S_{273} = 86.5$ from e.m.f. measurements. The max. partial pressure of O_3 in equilibrium with O_2 and O at 1 atm. is 1.0×10^{-6} atm. at 3400° abs. The 1% O_3 obtained by heating filaments at 2300° abs. in liquid O_2 must be formed from at. O in the cold regions.

J. W. S.

Thermal dissociation of cyanogen into cyanide radicals. G. B. KISTIAKOWSKY and H. GERSHINOWITZ (J. Chem. Physics, 1933, 1, 432—439; cf. A., 1932, 684).—From measurement of the pressures at which absorption bands due to CN produced in the dissociation of C_2N_2 at different temp. near 1200° have equal intensities, the heat of dissociation is calc. to be 77 ± 4 kg.-cal. By using existing thermochemical data this is shown to be also the most probable energy of the C-C linking. Similarly calc. vals. for $\text{HCN} \rightarrow \text{H} + \text{CN}$ and the energy of the C-H linking are 94.5 ± 4 kg.-cal. The heat of sublimation of C (graphite) is 154 kg.-cal.

F. L. U.

Heat of dissociation of the carbon-carbon linking. J. B. CONANT (J. Chem. Physics, 1933, 1, 427—431).—Heats and free energies of dissociation of the C-C linking in a series of disubstituted dioxanths and tetraphenylethanes have been calc. on the basis of Ziegler's data for C_2H_6 (A., 1929, 1010). The effect of different substituent groups on the heat of dissociation of C_2H_6 has been estimated.

F. L. U.

Energy of dissociation of water by symmetrical vibrations and products of this dissociation. M. MAGAT (Compt. rend., 1933, 197, 1216—1218).—A revised and more accurate method of calculating the vibration frequencies of H_2O gives its energy of dissociation as 269 ± 3 kg.-cal. (cf. A., 1933, 552). The difference between this and 218 ± 1 kg.-cal., deduced from thermochemical and spectro-

scopic data, corresponds closely with the energy of activation of the O atom (45.2 kg.-cal.). Thus H_2O is dissociated into 2H and activated O (cf. A., 1929, 11; 1931, 1109).

C. A. S.

Thermodynamic properties of the H^1H^2 , H^2H^2 molecules and compounds containing the H^2 atom. H. C. UREY and D. RITTENBERG (J. Chem. Physics, 1933, 1, 137—143).—Calc. vals. for the summation of state and free energies of the mols. H^1 , H_2 , and H^1H^2 are tabulated for the temp. range $20.4\text{--}700^\circ$ abs., and their dependence on the spin and statistics of H^2 is discussed. The influence of the H isotope on equilibrium const. is illustrated for the reactions $\text{H}_2 + \text{H}^2 = 2\text{H}^1\text{H}^2$, $\text{H}_2 + 2\text{H}^2\text{Cl} = \text{H}_2 + 2\text{H}^1\text{Cl}$, and $\text{H}_2 + 2\text{H}^2\text{I} \rightarrow \text{H}_2 + 2\text{H}^1\text{I}$.

N. M. B.

Free energy of steam and carbon dioxide. A. R. GORDON (J. Chem. Physics, 1933, 1, 308—312).—Calc. equilibrium consts. for the water-gas equilibrium agree well with experimental vals. over the range $700\text{--}1259^\circ$ abs. For the producer-gas equilibrium, theory predicts greater dissociation of CO into CO_2 and graphite than is found in practice. This may be explained if graphite has zero point entropy $>$ that given by the third law of thermodynamics. Equilibrium consts. for the reaction $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$ are tabulated.

D. R. D.

Entropy of nitrous oxide and carbon dioxide. W. H. RODEBUSH (Physical Rev., 1932, [ii], 40, 113).—The calc. entropy of N_2O , based on the views of Plyler and Barker (A., 1932, 108), is 52.4 entropy units at 298° abs.; that of CO_2 , based on the data of Martin and Barker (*ibid.*, 982), is 51.0 units at 298° abs.

L. S. T.

Thermodynamic constants of iodine monochloride, iodine monobromide, and bromine monochloride in carbon tetrachloride solutions. C. M. BLAIR, jun., and D. M. YOST (J. Amer. Chem. Soc., 1933, 55, 4489—4496).—From the v.p. of ICl and Cl_2 , heats of dissolution of I and Br , and heats of formation of ICl , IBr , and BrCl , the following data have been obtained: free energy $\text{I } 2660$, $\text{Br } 389$, Cl_2 1110 , $\text{ICl } -2133$, $\text{IBr } -153$, $\text{BrCl } 393$; heat content $\text{I } 5990$, $\text{Br } 712$, Cl_2 -3720 , $\text{ICl } -2835$, $\text{IBr } 1721$, $\text{BrCl } -1882$; entropy $\text{I } 39.1$, $\text{Br } 36.8$, Cl_2 37.1 , $\text{ICl } 38.3$, $\text{IBr } 38.5$, $\text{BrCl } 36.9$. Reaction between Br and Cl_2 in CCl_4 solution is appreciably slower than between I and Cl_2 or I and Br .

E. S. H.

Free energy, entropy, and heat capacity of bromine and hydrogen bromide from spectroscopic data. A. R. GORDON and C. BARNES (J. Chem. Physics, 1933, 1, 692—695).—The equilibrium consts. for the reaction $\text{Br}_2 \rightleftharpoons 2\text{Br}$ calc. from spectroscopic data differ from Bodenstein's experimental vals. Similar calculations on the dissociation of HBr give results which agree with the e.m.f. measurements of Bodenstein and Geiger, but disagree with Falckenstein's data.

H. S. P.

Heat capacities of gaseous mono- and dimethylamine. W. A. FELSING and F. W. JESSEN (J. Amer. Chem. Soc., 1933, 55, 4418—4422).—The mol. heat capacities between 0° and 50° are given by $9.530 + 0.1108T - 1.212 \times 10^{-4}T^2$ and $5.595 - 0.1148T + 2.750 \times 10^{-4}T^2$ for NH_3 and NHMe , respectively.

The corresponding vals. of γ are 1.202 and 1.149, respectively. E. S. H.

Evaluation of the series which arise in the calculation of thermodynamic quantities from spectroscopic data. A. R. GORDON and C. BARNES (J. Chem. Physics, 1933, 1, 297—307).—Tables are given for obtaining the free energy, entropy, and heat capacity at high temp. from the mol. spectrum of a gas, and simplified methods of calculation are given for conditions outside the range of the tables. The procedure is illustrated by calculations for Cl₂, Br₂, HCl, CO, O₂, and NO. D. R. D.

Mathematical methods for computing thermodynamic functions from spectroscopic data. L. S. KASSEL (J. Chem. Physics, 1933, 1, 576—585).—Theoretical. Vals. for the entropy, heat content, and heat capacity of CO from 50° to 1400° abs. are recorded. H. J. E.

Heat capacity and entropy of silver sulphate from 14° to 300° abs. Entropy of the sulphate ion. W. M. LATIMER, J. F. G. HICKS, jun., and P. W. SCHUTZ (J. Chem. Physics, 1933, 1, 424—425).—The heat capacity of Ag₂SO₄ has been measured from 14° to 300° abs. and the entropy determined graphically as $S_{298.1} = 47.76$ e.u. Coupling this val. with the entropy of solution and the entropy of the Ag⁺ ion leads to a val. 2.8 e.u. for the entropy of the SO₄²⁻ ion at 298.1° abs. J. W. S.

Heat capacities and entropies of calcium and barium sulphates from 15° to 300° abs. Entropy and free energy of the sulphate ion. W. M. LATIMER, J. F. G. HICKS, jun., and P. W. SCHUTZ (J. Chem. Physics, 1933, 1, 620—624; cf. A., 1933, 466).—The heat capacities of BaSO₄ and CaSO₄·2H₂O have been measured from 15° to 300° abs. Vals. for CaSO₄·2H₂O vary slightly with crystal size. The entropies at 298.1° abs. are 31.51 and 46.36 e.u., respectively. The entropy and free energy of formation of SO₄²⁻ are 3.5 e.u. and -175,300 g.-cal., respectively. H. J. E.

Partial and integral heats of dilution of cadmium sulphate solutions from electromotive force measurements. V. K. LA MER and W. G. PARKS (J. Amer. Chem. Soc., 1933, 55, 4343—4355; cf. A., 1931, 912).—The e.m.f. of the cell Cd(saturated amalgam)|CdSO₄, PbSO₄|Pb (saturated amalgam) has been determined at 0°, 10°, 20°, and 30° for concns. of CdSO₄ between 0.0005 and 0.02*M*. Activity coeffs. are given and previous work is confirmed. The following thermodynamic vals. have been determined for the reaction: $E^\circ 0.00905V$, $(\partial E^\circ/\partial T)_p - 6.60 \times 10^{-4}$, $(\partial^2 E^\circ/\partial T^2)_p - 1.73 \times 10^{-5}$, $\Delta F^\circ 417.6$ g.-cal., $\Delta H^\circ - 9198$ g.-cal., $C_p^\circ - 229$ g.-cal. per degree. The calc. partial mol. heat capacity of CdSO₄ is approx. -200 g.-cal. per degree per mol. at 15°. E. S. H.

Entropy of a crystalline solution of silver bromide and silver chloride in relation to the third law of thermodynamics. E. D. EASTMAN and R. T. MILNER (J. Chem. Physics, 1933, 1, 444—456).—The free energy of formation of mixed crystals of AgCl and AgBr from the pure components has been determined by e.m.f. measurements, and the change in heat content by dissolution of the mixed crystals

and the components respectively in aq. Na₂S₂O₃. The entropy change obtained from these results is about 1.1 g.-cal. per degree. Sp. heat measurements over the range 15—298° abs. show that at no point does the change in heat capacity differ from 0. Assuming that this remains true below 15° abs., it follows that the entropy change at 0° abs. is the same as at 298° abs. The result is discussed theoretically and a restricted formulation of the third law is suggested. F. L. U.

New chemical theory: its origin and significance. A. GOSSELIN (Bull. Soc. chim., 1933, [iv], 53, 923—945).—Theoretical. An extension of Werner's theory with reference to thermochemical properties. R. S.

Electrolytic conduction in aqueous solutions. A. C. D. RIVETT (Rept. Austral. Assoc. Adv. Sci., 1933, 21, 420—431).—Liversidge Lecture. An historical review of electrolytic conduction and outline of newer conception developed by Masson. R. S.

Conductivity of mixtures of electrolytes. II. V. K. SEMENCHENKO and V. V. SERPINSKI (J. Gen. Chem. Russ., 1933, 3, 470—477).—The conductivities of the following aq. solutions at 25°: 0.000125—0.2*N*-KCl; 0.001—1.0*N*-NaNa₃; 0.000125—0.005*N*-NaBr; 0.000166—2*N*-MgSO₄; 3:1, 1:1, and 1:3 mixtures of KCl and NaNa₃ (total concn. 0.001*N* and 0.1*N*), and of KCl and MgSO₄ (total concn. 0.001—2*N*); 1:1:1 and 1:1:2 mixtures of KCl, NaBr, and MgSO₄ (total concn. 0.0005*N* and 0.005*N*) are in closer agreement with Onsager's formula than are the vals. obtained by previous authors. The vals. for mixtures are additive; this is ascribed to the reduced mobility of more, and the enhanced mobility of less, mobile ions. R. T.

Conductivity measurements of thorium and other jelly-forming systems. S. PRAKASH (J. Physical Chem., 1933, 37, 907—916; cf. A., 1932, 1202).—The electrical conductivity of systems forming jellies of Th phosphate, arsenate, and molybdate, and of Fe^{III} arsenate and Al(OH)₃ remains const. during setting, and increases after several days. The temp. coeff. is const. between 35° and 60°. F. L. U.

Conductance of bases in liquid ammonia. W. W. HAWKES (J. Amer. Chem. Soc., 1933, 55, 4422—4430).—Data are recorded for solutions of KNH₂ and NaNH₂ up to dilutions of 52,000 and 36,000 litres, respectively. An upper limit for the dissociation const. of NaNH₂ is 2.65×10^{-5} . The data deviate from the theory of Fuoss and Kraus (A., 1933, 464) and from the mass action law. E. S. H.

Electro-endosmosis and electrolytic water transport. III. Solutions of copper salts. H. C. HEPBURN (Proc. Physical Soc., 1933, 45, 755—764; cf. A., 1931, 1236; 1932, 698).—Measurements have been made of the liquid transport produced by the passage of an electric current through aq. CuCl₂ and Cu(NO₃)₂ by the parchment-paper membrane method, the results being compared with data for CuSO₄. The electro-endosmotic effect of the diaphragm is discussed in terms of the influence of the electrical charge of the diaphragm and of the thickness of the double layer formed at the diaphragm-solution

interface. For CuCl_2 the direction of liquid transport is reversed above 0.1*N*, this reversal being attributed to the effect of the electrolytic H_2O transport.

J. W. S.

Ionising powers of solvents. A. H. W. ATEN and L. BOERLAGE (*Rec. trav. chim.*, 1933, 52, 1046—1051).—Theoretically, the presence of positive and negative partial moments in a mixture of solvents should tend to increase the ionising power. This is confirmed by measurements of the conductivities of solutions of NH_4EtCl , $\text{NH}_4\text{Et}_2\text{Cl}$, $\text{NH}_4\text{Et}_3\text{Cl}$, and NEt_4Cl in mixtures of NH_4Ph with PhNO_2 , and with PhCN , but does not hold for mixtures of NH_4Ph and PhBr .

H. F. G.

Electrodes of third kind. M. LE BLANC and O. HARNAPP (*Z. physikal. Chem.*, 1933, 166, 321—342).—For the satisfactory working of such an electrode, an equilibrium must be established between two sparingly sol. salts and a solution. If the solution is dil. and there is a large difference in solubility between the solid phases, operation of the electrode is possible when the solution dissolves both solid phases. The solubility product of the solid phase having the same cation as the metal electrode must, however, be several powers of 10 < that of the other solid phase, and the ratio of the solubility of the latter to the concn. of the ion to be determined must be as small as possible. Solubilities at 18° of CaWO_4 , Hg_2WO_4 , and $\text{Hg}_2\text{C}_2\text{O}_4$ have been determined. The electrodes $\text{Hg}|\text{Hg}_2\text{WO}_4\text{--CaWO}_4\text{--Ca}^{++}$ and $\text{Hg}|\text{Hg}_2\text{C}_2\text{O}_4\text{--CaC}_2\text{O}_4\text{--Ca}^{++}$ have been studied, the second proving serviceable. In solutions containing Cl^- , Hg^+ electrodes are useless owing to separation of Hg_2Cl_2 and pptn. of the cation to be determined. The electrode $\text{Cd}|\text{Cd stearate--Ca stearate--Ca}^{++}$ is free from this objection but does not respond to changes in $[\text{Ca}^{++}]$.

R. C.

Cells with liquid ammonia or an ammoniacal solution as solvent. G. I. COSTEANU (*Compt. rend.*, 1933, 197, 1113—1114; cf. A., 1933, 29).—The e.m.f. of the cells $\text{Cd}|\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}|\text{NH}_4\text{NO}_3|\text{AgNO}_3|\text{Ag}$ and $\text{Zn}|\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}|\text{NH}_4\text{NO}_3|\text{AgNO}_3|\text{Ag}$ in liquid NH_3 containing different amounts of H_2O and at different temp. vary only a few % when the % of H_2O varies from 0 to 80, and temp. from -75° to 18°.

C. A. S.

Polarographic studies with the dropping mercury cathode. XXXIV. Suppressive effect of certain alkaloids on the maximum current due to electro-reduction of oxygen. E. HAMAMOTO (*Coll. Czech. Chem. Comm.*, 1933, 5, 427—435).—The adsorbability of five alkaloids at the Hg -aq. KCl interface is of the same order as that of org. dyes (cf. A., 1931, 914).

D. R. D.

Electromotive force due to the movement of electrodes in different solutions. Variation of the phenomenon with concentration, time, and pressure of the dissolved gas. V. G. GEORGHU (*Ann. Sci. Univ. Jassy*, 1933, 18, 335—384).—The e.m.f. has been measured with electrodes of various metals in H_2O and in solutions of acids, bases, and salts. The e.m.f. may be positive or negative and may increase or decrease with time. It depends also on the nature and pressure of the gas above the liquid.

H. S. P.

Effect of the solvent on the potential of the chloranil electrode. B. O. HESTON and N. F. HALL (*J. Amer. Chem. Soc.*, 1933, 55, 4729—4730).—The accepted val. (+0.664 volt) for the potential of the saturated chloranil electrode against the H_2 electrode has been confirmed for 50% aq. EtOH , but +0.680 and +0.715 volt have been obtained in AcOH and 50% aq. dioxan, respectively. The potential may be assumed independent of the solvent only if the electrode materials remain unsolvated.

E. S. H.

Hydrolysis and the oxidation-reduction potential of the system $\text{Fe}^{+++}\text{--Fe}^{++}$. P. A. KRIUKOV and G. P. AVSEJEVITSCH (*Z. Elektrochem.*, 1933, 39, 884—891; cf. A., 1933, 909).—The oxidation-reduction potential of Fe solutions is correlated with the p_{H} of the solution, measured with a glass electrode, for p_{H} 3.5—6. From the results, and from titration curves, vals. derived for the solubility product of $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are $3.2\text{--}9.3 \times 10^{-14}$ and 0.1×10^{-36} to 3.45×10^{-35} , respectively.

H. J. E.

Oxidation-reduction potential of system hypoxanthine uric acid. (MILLER) S. FILITTI (*Compt. rend.*, 1933, 197, 1212—1213).—Three different methods give the normal oxidation-reduction potential of this system [in presence of diastase, with 1 : 1'-dimethyl-4 : 4'-dipyridylum chloride (cf. A., 1932, 1102) as indicator, and p_{H} 7.24—7.34] at 38° as 0.031 ± 0.002 volt, whence $\Delta F = +2861 \pm 180$ g.-cal. The heat of reaction at const. pressure is -1700 g.-cal.

C. A. S.

Buffer intensities of milk and milk constituents.—See A., 1933, 1319.

Overvoltage of metals. N. THON (*Compt. rend.*, 1933, 197, 1312—1314).—Deductions made from the view that the relation between current and overvoltage is linear (cf. A., 1932, 700) are not in accord with experiment. The hypothesis of energies of activation (cf. A., 1928, 1088) applied to cryst. metal deposits, e.g., Pb , Zn , Cd , Bi , Cu , and Ag , leads to unsatisfactory conclusions; that of active centres (cf. A., 1930, 1376) affords a better explanation. The reverse holds for Fe , Co , and Ni , and complex salts of other metals (cf. A., 1913, ii, 287). In a gaseous cathode (see below) the absence of active centres explains the high overvoltage.

C. A. S.

Electrolysis of metallic salt solutions with rarefied gas cathode. N. THON (*Compt. rend.*, 1933, 197, 1114—1117).—The (metal) cathode is separated from the surface of the electrolyte by a variable distance d , the space containing only vapour from the solution. With a.c. the system electrolyte|rarefied gas|Pt has a rectifying effect, a positive current passing from liquid to metal. With d.c. at 1000 volts metal is deposited on the surface of the solution only when this contains a salt of a noble metal, e.g., Ag , Au , Pt . In all other cases, including Hg and Cu , H_2 is evolved. Corbino's contrary observation (cf. A., 1927, 523) appears to have been due to the close proximity of the electrode to the surface of the electrolyte, or to the wall of the containing vessel. The facts support Volmer's theory (cf. A., 1932, 24).

C. A. S.

Electrolytic growth of metallic crystals. T. ERDEY-GRUZ (*Naturwiss.*, 1933, 21, 799—800).—The growth of single crystals of Ag by electrolysis of solutions of various Ag salts has been examined. The development lacks uniformity in solutions of AgNO_3 , AgClO_4 , AgF , or $\text{KAg}(\text{NO}_2)_2 + \text{KNO}_2$. In these cases development occurs at selected points on the cryst. surface, whilst the greater part of the surface appears to be passive. Uniformity is favoured by solutions of $\text{KAg}(\text{CN})_2 + \text{KCN}$, $\text{AgI} + \text{KI}$, $\text{Ag}_2\text{O} + \text{NH}_3$, $\text{AgCl} + \text{NH}_3$, $\text{AgBr} + \text{NH}_3$. Complex salts give the best results because the great adsorption of their anions tends to cover the regions of high energy development (sharp points etc.) on the surface.

A. J. M.

Electrochemistry of chromium. IV. O. S. FEDEROVA (*J. Gen. Chem. Russ.*, 1933, 3, 636—640).—Theoretical.

R. T.

Theory of passivity phenomena. XIX. Destruction of natural oxide film of iron on rusting. W. J. MULLER and W. MACHU (*Z. physikal. Chem.*, 1933, 166, 357—364; cf. A., 1933, 787).—In the removal of the oxide film in the rusting of a protected Fe electrode the amount of surface bare at any particular moment can be determined directly from the difference in optical behaviour between the bare surface and the surface still covered. The results agree with those obtained indirectly from the i_0/t_p curve. The rate of disappearance of the film is at any moment proportional to the amount of surface still covered at that moment.

R. C.

Theory of passivity. XX. Passivity of nickel. W. J. MULLER and E. LÖW (*Z. Elektrochem.*, 1933, 39, 872—879).—Criticisms of the film theory (Georgi, A., 1932, 1093) are answered. Photomicrographs are given showing oxide films on a passive Ni anode.

H. J. E.

Theory of passivity. XXI. W. J. MULLER (*Z. Elektrochem.*, 1933, 39, 880—883).—Polemical against E. Muller and Schwabe (cf. A., 1933, 785). The film theory of passivity is supported.

H. J. E.

Theory of passivity. E. MULLER and K. SCHWABE (*Z. Elektrochem.*, 1933, 39, 884; cf. preceding abstract).—A reply.

H. J. E.

Anodal passivation of lead. P. PORFIROV (*J. Gen. Chem. Russ.*, 1933, 3, 590—595).—Passivation of Pb anodes in aq. H_2SO_4 is due to deposition of a PbSO_4 film (I) on the surface, with consequent increase in c.d. on the free areas; this leads to the formation of colloidal PbSO_4 , involving increased resistance to the passage of current, and resulting in still greater increase in c.d. at the anode to a crit. val. above which (I) is converted into PbO_2 , corresponding with complete passivation of the anode. In anhyd. H_2SO_4 passivation is due to (I) alone.

R. T.

Thermodynamics and kinetics of gaseous reactions. W. H. RODEBUSH (*J. Chem. Physics*, 1933, 1, 440—443).—Theoretical.

F. L. U.

Calculation of reaction velocity as a function of temperature. A. SKRABAL (*Monatsh.*, 1933, 63, 23—38).—Theoretical. Mathematical methods for the rapid evaluation of the various constns. in the

formulae of (1) Arrhenius, (2) Harcourt and Esson, (3) Berthelot, (4) van 't Hoff, (5) Kooij, and (6) Bodenstein, relating velocity coeffs. with temp., are deduced and the formulae tested. Two-const. formulae (1)—(3) are unsatisfactory, but the three-const. formulae (4) and (5) are satisfactory as extrapolation formulae, and the magnitudes of the extrapolation errors are determined.

J. W. B.

Relation between molecular activation energy and isokinetic temperature. H. DAMIANOVICH (*An. Inst. Invest. cient. tecnol.*, 1930, 1, No. 3, 15—29; *Chem. Zentr.*, 1933, ii, 818).—In absence of accelerating factors, and when the van 't Hoff-Arrhenius equation is applicable, the mol. activation energy (I) is approx. proportional to the abs. temp. In isothermal changes (I) behaves like $\log 1/\text{velocity coeff.}$, and in unimol. reactions is proportional to the mean life of the mol.

A. A. E.

Limits of inflammation of mixture $2\text{H}_2 + \text{O}_2$. P. TAUZEN (*Compt. rend.*, 1933, 197, 1046—1049).—The lower (a) and upper (b) limits of temp. of inflammation at varying pressures (0—120 mm. Hg) have been plotted as pressure-temp. curves, (a) by allowing the mixture contained in a vessel outside the furnace to expand into one inside it and at the desired temp.; (b) by passing into this second vessel the desired amount of the mixture at a low temp., and then heating rapidly. For (a) pressure is almost const. from 420° to 520° ; for (b) the curve rises with increasing rapidity until it becomes asymptotic to the ordinate of temp. = 560° approx. The min. temp. of inflammation in a heating tube 2.5×10 cm. (424°) was < in one 5×20 cm. (450°), but the curves intersect at about 520° ; in the former temp. of inflammation was lowered, in the latter raised a few degrees, by heating the mixture for some time at a temp. 15 — 35° below that of inflammation when directly heated thereto.

C. A. S.

Mechanism of the reaction of hydrogen atoms with oxygen. J. R. BATES (*J. Chem. Physics*, 1933, 1, 457—465; cf. A., 1933, 358).—Theoretical. The mechanism previously suggested (*ibid.*, 236) affords a satisfactory interpretation of observations on velocity-concn. relations, quantum yield, and temp. coeff.

F. L. U.

Kinetics of the reaction between hydrogen and nitrous oxide. I. H. W. MELVILLE (*Proc. Roy. Soc.*, 1933, A, 142, 524—545).—The kinetics of the reaction between H_2 and N_2O have been studied at 50—400 mm. and 550 — 700° in SiO_2 bulbs. The final products are mainly N_2 and H_2O . The rate is directly proportional to the pressure of N_2O and nearly independent of that of H_2 , except when the N_2O pressure is high. N_2 and A have no effect. The apparent energy of activation is 32 kg.-cal. Explosions may occur on raising the pressure and temp. The suggested mechanism of the reaction is as follows: the reaction is of the chain type, initiated by O atoms derived from the thermal dissociation of N_2O mol. and propagated by H atoms and OH radicals. Termination occurs mainly in the gas by combination of H atoms, but some may take place on the walls.

L. L. B.

Mechanism of explosive combustion of gaseous hydrocarbons. A. W. FRANCIS (Chem. and Ind., 1933, 926—927).—The nature of the products of explosive combustion is determined primarily by the flame temp. Probably free C results from thermal decomp. of part of the original hydrocarbon rather than by hydroxylation. R. S.

[Mechanism of combustion.] W. A. BONE (Chem. and Ind., 1933, 928—929; cf. preceding abstract).—A criticism. R. S.

Rate of dissociation of nitrogen tetroxide. C. E. TREETER, jun. (J. Chem. Physics, 1933, 1, 251—265; cf. A., 1932, 1209).—No measurable dispersion of sound has been found in N_2O_4 up to 53.8 kc. At higher frequencies no evidence of transmission could be observed up to 860 kc., this absorption indicating dispersion. It was not possible, however, to determine whether dissociation, time lag, or a combination of both was responsible. Thus the sonic method for measuring rates of dissociation of gases appears to fail. M. S. B.

Oxidation of nitric oxide to nitric anhydride by ozone, and under the influence of the silent electrical discharge. N. KOBOZEV, M. TEMKIN, and S. FRAIBERG (J. Gen. Chem. Russ., 1933, 3, 534—539).—NO reacts with O_3 as follows: $NO + O_3 \rightarrow NO_2 + O_2$; $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$. The velocity of reaction is considerably > that of O_2 with NO, and the smallest traces of O_3 are removed from air by NO. The above reactions do not take place if mixtures of air and NO are passed through an ozoniser, as the O_2 necessary for O_3 formation is combined as NO_2 . O_3 has no action on N_2O . R. T.

Ignition temperatures of mixtures of hydrogen sulphide, carbon disulphide, and air. F. D. LEICESTER (J.S.C.I., 1933, 52, 341—346r).—Ignition temp. have been determined up to 500°. A 60% H_2S -air mixture ignites at 487°. From this point the ignition temp. falls to a min. at 12—13% H_2S , and then rises again with falling H_2S content. A 32% CS_2 -air mixture ignites at 332°; the ignition temp. falls smoothly with decreasing CS_2 content, a mixture containing 0.5% CS_2 having an ignition temp. of 81°. The results for H_2S - CS_2 -air mixtures are complex, but addition of H_2S to CS_2 -air mixtures always causes, at first, a rise in the ignition temp. The whole field of mixtures up to 32% CS_2 and 60% H_2S , having ignition temp. up to 500°, has been explored.

Kinetics of the thermal decomposition of methyl ethyl ether. E. W. R. STEACIE (J. Chem. Physics, 1933, 1, 618—619).—The heat of activation is 54,500 1500 g.-cal, which harmonises with vals. for other ethers, and is > Hinshelwood and Glass' val. (A., 1929, 1148). H. J. E.

Factor independent of temperature in unimolecular reactions. G. SALOMON (Helv. Chim. Acta, 1933, 16, 1354—1360).—From available data it is shown that in the Arrhenius equation for reactions of the first order, $K = Z \cdot e^{-E/RT}$, Polanyi and Wigner's theoretical conclusion (A., 1929, 404) that $Z = 10^{14}$ approx. is valid where the mol. contains only atoms of approx. equal wt., there is no steric interference,

and any solvent required has no influence. Where, however, the velocity of reaction varies with the solvent any val. may be found for Z and for the heat of activation E . M. S. B.

Facility of ring-formation in cyclic imino-compounds. G. SALOMON (Helv. Chim. Acta, 1933, 16, 1361—1373).—From known data for the velocity of ring closure of the halogenoalkylamines to cyclic imines at different temp. the heat of activation E and factor Z (cf. preceding abstract) have been calc. The reaction can take place only if an activated mol. happens to be in the "ring position" and the statistical equilibrium, ring position chain position, influences the val. of Z . The length of the chain and hence the deviation of valency linkings in forming the ring influences the velocity of ring formation. 3- and 4-membered rings require a higher heat of activation than 5- and 6-membered rings. On the other hand, the 7-membered ring also requires a large heat of activation, possibly because the space arrangement of the solute mol. in the solvent favourable to reaction depends on the length of the chain. The influence of substituents is discussed and illustrated by the behaviour of the Ph- and Me-substituted chloro- and bromo-ethylamines. The influence of the solvent on the ring and chain equilibrium is discussed and it is shown that the ring position of the solute mol. probably predominates when the solvent differs most, physically, from the solute. This is in agreement with the behaviour of ϵ -chloroamylamine and of $CH_2Br \cdot CH_2 \cdot NH_2$ in H_2O and in org. solvents, since Z in the former solvent may be as much as 10^{5-6} times > in the latter. The effect is balanced to some extent by the fact that E is about 5 kg.-cal. lower in the org. solvents than in H_2O . There is no simple connexion between the dipole moment of the solvent and reaction velocity. M. S. B.

Effect of ethyl radicals on the thermal decomposition of azomethane. Kinetics of the thermal decomposition of lead tetraethyl. Ethyl radicals and hydrogen. J. A. LEERMAKERS (J. Amer. Chem. Soc., 1933, 55, 4508—4517).—The thermal decomp. of $PbEt_4$ at 245—275° and initial pressures of 13—52 mm. is unimol. and 96—97% homogeneous. The rate coeffs. are given by $k_1 = 1.2 \times 10^{12} e^{-36,900/RT}$ sec⁻¹. Experiments on the decomp. of $PbEt_4$ in presence of azomethane (I) show that the Et radical does not react with (I) at about 275°. Et radicals do not react appreciably with H_2 at 275°. The calc. activation energies of bimol. reactions of Et radicals with H_2 or (I) are > 15 kg.-cal. E. S. H.

Thermal decomposition of ethylene iodide. L. B. ARNOLD, jun., and G. B. KISTIAKOWSKY (J. Chem. Physics, 1933, 1, 166—169; 287, errata).—Investigation of the homogeneous gaseous decomp. in the temp. range 205—230° indicates two simultaneous reactions giving the same final products, C_2H_4 and I_2 . One is a reaction, similar to that in solution, catalysed by I atoms; the other is a unimol. decomp. Activation energies are 30,200 and 36,600 g.-cal., respectively. Results for the catalysed reaction in solution and in the gas phase are in agreement, indicating negligible solvent influence. N. M. B.

Cross-activation in the unimolecular decomposition of mixtures of gaseous methyl and ethyl ether. E. W. R. STEACIE (J. Chem. Physics, 1933, 1, 313—316).—Repetition of previous work (A., 1932, 576) with more accurate temp. control indicates that the cross-activation efficiency of collisions between Me_2O and Et_2O mols. is 40—60%, confirming Kassel's result (*ibid.*, 1209) qualitatively but not quantitatively. D. R. D.

Quantum mechanics of chemical reactions involving conjugate double linkings. H. EYRING, A. SHERMAN, and G. E. KIMBALL (J. Chem. Physics, 1933, 1, 586—592).—Theoretical. The addition of Br to butadiene occurs most readily in the $\alpha\delta$ position, and when the additive mol. approaches in the plane of the C atoms. The activation energy is 30—60 kg.-cal., and the homogeneous reaction would be very slow at room temp. Actually it is fairly rapid, and the addition reaction must therefore occur at a surface. The surface reaction mechanism is discussed.

H. J. E.

Influence of substituents on heat of activation of a simple addition reaction. E. HERTEL and J. DRESSEL (Z. physikal. Chem., 1933, B, 23, 281—290).—The velocity of addition of NPhMe , and its derivatives to trinitroanisole and its derivatives has been determined at various temp. These reactions follow the bimol. law and involve the transfer of the Me group of the anisole to the NH_2 -group of the aniline. In respect of their effect on the heat of activation, Q , substituents follow the same order as for their effect on basicity and their auxochromic action. Q is an additive property which is influenced by a fixed amount by a given substitution. R. C.

Mechanism of substitution reactions. A. R. OLSON (J. Chem. Physics, 1933, 1, 418—423).—For many reactions of the type $AB+C$ — the strength of the linking between A and B is too great to account for the rate of reaction, so addition or simultaneous additions and dissociations must occur. From the quantum mechanical conception of linkings a spatial inversion of A must occur for every such substitution. The theory is applied to the Walden inversion, and a correlation is obtained between the rotational and configurative changes. Its application to the Beckmann rearrangement and to *cis-trans*-isomerism is also indicated. J. W. S.

Thermal decomposition of ethyl mercaptan and ethyl sulphide.—See this vol., 56.

Rate of bromate formation in aqueous solutions containing hypobromous acid and its anion. H. A. LIEBHAFSKY and B. MAKOWER (J. Physical Chem., 1933, 37, 1037—1046).—At low $[\text{Br}^-]$, solutions of HOBr are more stable than accords with the rate of the reaction $5\text{HOBr}=\text{BrO}_3'+2\text{Br}_2+\text{H}^++2\text{H}_2\text{O}$. The rate-determining step appears to be $2\text{HOBr}+\text{OBr}'\rightarrow\text{BrO}_3'+2\text{Br}'+2\text{H}^+$. The reaction probably does not result from triple collisions, but the mechanism is not understood. The reactions for ClO_3' , BrO_3' , and IO_3' formation are analogous.

H. S. P.

Temperature coefficient of the decomposition of hydrogen peroxide in presence of potassium

iodide. W. C. K. HENDER and R. A. ROBINSON (Trans. Faraday Soc., 1933, 29, 1300—1305).—The reaction at 15—45° in 0.01—0.06N-aq. KI is unimol. with respect to H_2O_2 , and proportional to $[\text{KI}]$. The observed rate is accounted for by a triple collision mechanism involving the H_2O mol. Similar results are found in MeOH and $(\text{CH}_2\text{OH})_2$ as solvent. In EtOH bimol. collisions between H_2O_2 and KI will account for the observed rate. Neutral salts influence the temp. coeff. slightly in aq. KI. H. J. E.

Velocity of esterification of alcohols in acetic acid. II. A. KAILAN and S. SCHWEBEL (Monatsh., 1933, 63, 52—78; cf. A., 1932, 1210).—The velocity of esterification (v) of $\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ (I), $\text{CH}_2\text{Ph}\cdot\text{OH}$, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, and *o*-, *m*-, and *p*-nitrobenzyl alcohols in AcOH containing initially 0.128 or 1.068 mol. H_2O per kg. 100% acid (w_0) has been determined by the f.p. method (A., 1929, 605) ($w=0.2460\Delta+0.02512\Delta^2-0.001061\Delta^3$). Esterification is complete in all cases. In the absence of HCl w_0 has little influence on v , the ratio of the unimol. k_0 for $w_0=0.128$ and 1.068 varying between 0.72 and 1.20 according to the alcohol. With HCl catalysis (k_c for HCl concn. c) increase in w_0 accelerates esterification, $(k_c-k_0)/c$ being increased by 16—49% as w_0 increases from 0.128 to 1.068: v is approx. proportional to c and with 1 mol. HCl per kg. 100% AcOH is 4000—6000 times > its val. for the uncatalysed reaction under otherwise similar conditions. In these primary alcohols a double linking has a retarding effect, v for (I) being only about 54% of its val. for Pr^nOH . Substitution of H by Ph in the α , β , and γ positions to the OH reduces v to, respectively, 31, 69, and 59% of its original val., whereas the ratio of v for $\text{CH}_2\text{Ph}\cdot\text{OH}$ and its *o*-, *m*-, and *p*- NO_2 -derivatives is 1:0.32:0.58:0.48. These results are compared with the effect of similar substitution in the corresponding acids. J. W. B.

Velocity of hydrolysis of simple ethers. A. SKRABAL and A. ZAHORKA (Monatsh., 1933, 63, 1—22).—By determination of the alcohols formed, on hydrolysis, by the method of Fischer and Schmidt (A., 1926, 632; apparatus modified), the velocity coeffs. for the acid hydrolysis ($p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ as catalyst) of highly purified samples of Et_2O (k_1), Pr^n_2O (k_2), and Pr^nOEt (k_m) in H_2O at 55°, 65°, 75°, 85°, and 95°, are found to be, respectively; k_1 —, 0.0435, 0.200, 0.776, 2.63; k_2 0.312, 1.605, 7.10, 26.16, —; k_m 0.0725, 0.385, 1.821, 7.11, —, $\times 10^{-6}$. The effect of temp. is given by: $\log k_1 = -14535/T - 0.0574767T + 55.069$; $\log k_2 = -14592/T - 0.0601507T + 57.711$, and $\log k_m = -13445.6/T - 0.0481207T + 49.6355$, whence extrapolated vals. of k at 25° and 125° are obtained. The half-val. period for Et_2O in N -acid solution at 25° is 4.75×10^{10} min. The ratio $k_m:k_2$ = approx. 1:10:33. The val. of k_m lies between $\sqrt{(k_1k_2)}$ and $\frac{1}{2}(k_1+k_2)$, being nearer to the geometric mean at lower temp. and to the arithmetic mean at higher temp. Hence the presence of each group modifies the contribution of the other towards the velocity of hydrolysis. Cases where $k_{RR'}$ is < or < $\frac{1}{2}(k_{2R}+k_{2R'})$ are discussed on a theoretical basis for ethers ROR' when R and R' are both alkyl, both

acyl, or mixed alkyl and acyl groups, and examples of each type are cited. J. W. B.

Velocity of decomposition of diazo-compounds in water. XII. E. YAMAMOTO, R. GOSHIMA, and J. HASHIMA (J. Soc. Chem. Ind. Japan, 1933, 36, 609—613B).—The decomp. velocities, between 0° and 80°, of 1:4- and 1:5-NH₂-C₁₀H₆·SO₃H and Cleve's acid are recorded. R. S.

Velocity of diazotisation of aromatic amines. S. UENO and T. SUZUKI (J. Soc. Chem. Ind. Japan, 1933, 36, 615—619B).—With 47 aromatic amines the velocity of diazotisation is increased by increasing the HCl concn. (0.05—4*N*), by the presence of NaCl or KCl, and by negative substituents in the order Cl < CO₂H < SO₃H < NO₂, and at 10° is 3—4 times > at 0°. In the NH₂Ph series it is greater with *o*- than with *p*- or *m*-substituted derivatives (except that strongly negative substituents, *e.g.*, SO₃H or NO₂, are equally effective in the *o*- and *p*-position), is scarcely affected by alkyl and decreased by alkoxy-groups. In the C₁₀H₇NH₂ series the effects of substitution are irregular. Diazotisation is very much more rapid in HBr, but slow in HNO₃, H₂SO₄, or 1:5-C₁₀H₆(SO₃H)₂. R. S. C.

Hydrolysis of ethylene bromide with alcoholic alkali hydroxide. A. L. BERNOUILLE and W. KAMBLI (Helv. Chim. Acta, 1933, 16, 1187—1200).—By hydrolysis of C₂H₄Br₂ with aq. K₂CO₃ a yield of > 90% (·CH₂·OH)₂ may be obtained. With K₂CO₃ in H₂O—EtOH mixtures the chief product is CH₂:CHBr. With EtOH—NaOH the only product is CH₂:CHBr and the reaction has been followed kinetically at 21—31°. The reaction is bimol. and the reaction velocity is much reduced by the addition of H₂O. The dependence of the velocity coeff. on temp. follows the same exponential law whether H₂O is present or not. M. S. B.

Kinetics of reaction of alkaline-earth metals with nitrogen and other gases. II. Kinetics of reaction of alkaline-earth metals with nitrogen. III. Action of sodium and other substances as "exciters" of reaction between calcium and nitrogen. A. VON ANTROPOFF and K. H. KRUGER. IV. Kinetics of reaction between calcium and nitrogen in presence of argon. A. VON ANTROPOFF and H. KLINGEBIEL (Z. physikal. Chem., 1933, 167, 49—53, 54—61, 62—70; cf. A., 1929, 34).—II. Sr and Ba are considerably more active towards N₂ than is Ca, and are never passive, *i.e.*, nitride formation occurs throughout the mass of the metal instead of being confined to a surface film. Reaction begins with Sr at 350° and with Ba at 200°; in each case the velocity rises continually with temp. With Sr, but not with Ba, the reaction is accelerated by Na or NaOH.

III. At 700° the passivity of Ca is not eliminated by Na. At lower temp. Na initiates the reaction between Ca and N₂, but the reaction once started proceeds more rapidly if the Na, which has a retarding action similar to that of an indifferent gas, is removed. Li, K, NaOH, Na₂O, Na₂O₂, and NH₄NO₃ also serve as "exciters", the action of the Na compounds possibly depending on the formation of Na by reaction with

the Ca. Na can effect activation independently of the presence of NaOH.

IV. The rate of reaction with a mixture of N₂ and A of a Ca rod the end face of which is activated with a grain of Na first rises rapidly as reaction proceeds, owing to increase in the reacting surface area, then falls rapidly, on account of accumulation of A in the porous nitride layer, and finally decreases slowly and linearly after attainment of a stationary state in which the velocity is determined by the rate of diffusion of N₂ through the nitride layer. In the removal of N₂ from A by means of hot Ca turnings the Ca should be activated with NaOH. The reaction velocity is greatly enhanced and spectrally-pure A is readily obtained. R. C.

Influence of fluid velocity on heterogeneous reactions. II. Dissolution velocity of metallic copper in ammoniacal cupric solutions. S. UCHIDA and I. NAKAYAMA (J. Soc. Chem. Ind. Japan, 1933, 36, 635—642B).—Cu^{II}-NH₃ solution, saturated with O₂, and circulated through Cu tubes of various diameters, dissolves Cu in accordance with the theory of heterogeneous reactions involving fluid films (cf. A., 1933, 911). The variation is analogous to the case of heat transfer. R. S.

Dissolution of magnesium in aqueous salt solutions. III. L. WHITBY (Trans. Faraday Soc., 1933, 29, 1318—1331; cf. A., 1933, 1017).—The initial rates of dissolution of Mg in aq. KCl, KBr, KI, and K₂SO₄ (*N* and 0.001*N*), in saturated aq. Mg(OH)₂, and in 0.001*N*-aq. KOH were of the same order, irrespective of the solute or its dilution. Smaller Mg surfaces give a disproportionately high rate in relation to larger surfaces. Results support the theory of primary preferential OH discharge. The solubility of Mg(OH)₂ in the *N*-salt solutions, in 0.001*N*-KOH, and in H₂O has been measured. H. J. E.

Validity of the mass-action law in the reaction of proteins with acids and bases. G. ETTISCH and G. V. SCHULZ (Biochem. Z., 1933, 265, 338—369).—The combination of serum-globulin and -albumin with bases can be divided into two reactions, one primary and immediate, the other secondary and requiring several hr. With acids the secondary reaction is insignificant. The primary reaction is purely ionic, and follows the zwitterion scheme; the equilibrium between bound and free H⁺ and OH⁺ obeys the mass law. Three alkali- and two acid-binding groups may be distinguished in terms of their dissociation consts. and the amounts of each are determined. The isoelectric point of albumin is calc. from the dissociation consts. P. W. C.

Homogeneous catalysis of stereoisomeric change in oximes. T. W. J. TAYLOR and D. C. V. ROBERTS [with P. JULIFF and (Miss) M. S. MARKS] (J.C.S., 1933, 1439—1444).—The determination of the rate of transformation, *α*, at 55°, of 0.04—0.054*M*-*α*- to *β*-benzilmonoxime in EtOH is based on the observation that whereas the *β*-oxime reacts only very slowly with Cu(OAc)₂ the *α* isomeride rapidly forms an insol. Cu complex in EtOH. *α* is unimol. with respect to *α*-oxime and is strongly catalysed by LiCl (I) and NMe₄Cl but not by KOAc (II) and KEtSO₄.

Catalysis by HCl is greatly diminished by H_2O . Analogous qual. results are recorded for the effects of (I) and (II) on the transformation of β - into α -benzaloxime. It is probable that the catalysis involves an interaction between the electronic systems of the ion-pair (or undissociated mol.) of the electrolyte and the C:N linking of the oxime. J. G. A. G.

Kinetics of reaction between potassium persulphate and potassium ferrocyanide in neutral solution. J. HOLLUTA and W. HERRMANN (Z. physikal. Chem., 1933, 166, 453—467).—The reaction has been studied at 15° . All the classical methods of determining the order fail. The second-order velocity coeff. remains const. throughout a given experiment but varies with the initial concn., whilst the third-order coeff. rises as reaction proceeds. These anomalies are due to the presence of a powerful electrostatic ionic field, and to K^+ having a strong sp. accelerating action. In conc. aq. K_2SO_4 the second-order velocity coeff. ceases to vary with the initial concn. and the reaction becomes a normal second-order reaction. Diffused daylight does not affect the reaction. A possible reaction mechanism is outlined. R. C.

Chemical kinetics. Temperature dependence of energy of activation. Entropy and free energy of activation. V. K. LA MER (J. Chem. Physics, 1933, 1, 289—296).—Published data for the decomp. of $\text{CO}(\text{CH}_2\text{CO}_2\text{H})_2$ by H_2O , the reaction between NaOPh and various alkyl iodides, and the decomp. of diacetone alcohol by aq. and aq.-MeOH solutions of NaOH indicate that the energy of activation, as calc. from the temp. coeff. of the reaction velocity, varies with temp. The theoretical foundation of the Arrhenius and Bronsted equations is discussed, and it is deduced that the Hinshelwood-Moelwyn-Hughes collision theory can be true only in the improbable event of the entropy of activation being zero. D. R. D.

Catalytic oxidations. II. Oxidation of benzaldehyde. III. Oxidation of pyruvic acid. K. MEYER (J. Biol. Chem., 1933, 103, 25—37, 39—49).—II. PhCHO, when purified by distillation and fractional crystallisation, is not autoxidised in C_6H_6 , but in the presence of small amounts of Fe it absorbs O readily without an induction period. As catalyst pyridine-hæmochromogen is more effective than Fe^{++} , and Fe^{+++} than Fe^{++} . If purified by distillation alone, PhCHO appears to be accompanied by substances which inhibit activation by a heavy metal such as Fe, Cu, or Ni. PhOH inhibits the catalytic activity of 10 times its equiv. of Fe. A greater effect is achieved by adding the PhOH before the Fe rather than after. In presence or absence of PhCHO, BzO_2H is immediately decomposed in acid solution with liberation of O_2 , but with PhCHO in non-aq. solution the per-acid is stable even in the presence of hæmin.

III. The autoxidation of AcCO_2H in alkaline solution is catalysed by hæmin and, to a much greater extent, by certain fluorescent dyes, the latter requiring the presence of light. It is probably the enolic form of the acid which is oxidised and the principal product is $\text{H}_2\text{C}_2\text{O}_4$. The speed of the photochemical reaction is proportional to the concn. of AcCO_2H and to the

log. of the concn. of fluorescent dye. Fluorescence seems a necessary property of the photosensitiser, but chemical constitution is evidently important also. The reaction is not inhibited by PhOH. M. S. B.

Pseudo-atoms and isosteric compounds. III. Comparative studies with benzene, thiophen, and furan. H. ERLLENMEYER and M. LEO (Helv. Chim. Acta, 1933, 16, 1381—1389).—The catalytic action of C_6H_6 , $\text{C}_4\text{H}_4\text{S}$, and $\text{C}_4\text{H}_4\text{O}$ on the reaction $\text{EtI} + \text{NEt}_3 = \text{NEt}_4\text{I}$ has been compared. The velocity coeff. for $\text{C}_4\text{H}_4\text{S}$ is much $>$ for either of the other two. This has led to a comparison of all the known physical data for the three compounds and their derivatives. There is a remarkable similarity between the physical data for C_6H_6 and $\text{C}_4\text{H}_4\text{S}$, but $\text{C}_4\text{H}_4\text{O}$ shows considerable deviations. This is attributed to a similarity between the outer electron systems of S and the group $\cdot\text{CH}:\text{CH}\cdot$ so that the latter group behaves as a pseudo-S atom. It is also significant that the resonance potentials of S and C_2H_2 are the same, 6.5 volts, whilst that of O is 9.1 volts. It thus appears that C_6H_6 and $\text{C}_4\text{H}_4\text{S}$ have a similar mol. field, and this similarity is not shared by $\text{C}_4\text{H}_4\text{O}$. M. S. B.

Catalysed reaction of hydrogen with water. J. HORRUTI and M. POLANYI (Nature, 1933, 132, 819).—The exchange of atoms between H_2 and H_2O previously observed (A., 1933, 1233) is catalysed by Pt black. This may be due to the ionisation of H_2 corresponding with the electromotive process of the H_2 electrode, and if the H_2 contains heavy H_2 (I) leads to the replacement of (I) by H. The slow at. exchange between H and H_2O previously observed may be due to some catalyst, possibly the walls of the vessel, acting in a similar way. H_2O containing (I) reacts with Fe more slowly than ordinary H_2O . L. S. T.

Effect of salts on the catalytic decomposition of hydrogen peroxide by colloidal platinum. M. A. HEATH and J. H. WALTON (J. Physical Chem., 1933, 37, 977—990).—The decomp. of H_2O_2 by colloidal Pt at 25° in presence of various concns. of NaCl, BaCl_2 , AlCl_3 , ThCl_4 , NaNO_3 , $\text{Al}(\text{NO}_3)_3$, and $\text{Th}(\text{NO}_3)_4$ has been investigated. A relation exists between the rate of decomp. and the rate of migration of the Pt particles in an electric field, but this is less marked with Th salts. Anions except NO_3^- affect the decomp., due possibly to substitution of OH groups in $\text{Pt}(\text{OH})_6^{--}$ (I). A possible mechanism for the decomp. of H_2O_2 due to (I) is given. H. S. P.

Kinetics of contact oxidation of SO_2 . G. K. BORESKOV and V. P. PLIGUNOV (J. Appl. Chem. Russ., 1933, 6, 785—796).—Taylor and Lenher's formula (A., 1931, 1246) is applicable to the reaction $2\text{SO}_2 + \text{O}_2 \longrightarrow 2\text{SO}_3$ catalysed by a V catalyst (I) of the approx. composition $8\text{SiO}_2 \cdot 2\text{SnO}_2 \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{O} \cdot \text{BaO}$. The apparent heat of activation is 55 kg.-cal. at $< 440^\circ$, and 20 kg.-cal. at $> 440^\circ$; in the latter case identical results are obtained using Pt catalyst. At $< 440^\circ$, the velocity of reaction is proportional to that of elimination of SO_3 from the active surface of (I). Formulae are given connecting yield of SO_3 with temp., velocity of flow, and concn. of substrates. R. T.

Dissolution of metals in acids. M. SCHUNKERT (Z. physikal. Chem., 1933, 167, 19—28; cf. A., 1931,

576).—Such substances as albumin, dextrin, gelatin, and saponin reduce the rate of dissolution of Fe and Zn in dil. and conc. aq. H_2SO_4 , the retarding action running parallel with the adsorbability as measured by the Au no. Me-violet and methylene-blue retard the dissolution of Fe in conc. H_2SO_4 and accelerate the dissolution of Zn in dil. H_2SO_4 . Salts may have either a retarding or an accelerating action. The above foreign substances are effective only if they are deposited on the metal itself, and have no effect if they are deposited on the impurities responsible for local action. The variable effect of salts is attributed to changes in the degree of dissociation on addition to the acid. R. C.

Catalytic polymerisation of propylene.—See B., 1933, 997.

Catalytic high-pressure hydrogenation of aromatic hydrocarbons.—See B., 1933, 1046.

Influence of traces of oxygen on decomposition of acetaldehyde by heat. LETORT (Compt. rend., 1933, 197, 1042—1044).—The decomp. of MeCHO at 477° and 225 mm. Hg pressure was examined in a SiO_2 vessel so designed as to exclude all trace of O_2 in excess of 10^{-4} mm. Hg, alone, and with addition of definite amounts of O_2 \times 0.034 mm. Hg. In absence of O_2 the reaction is of order 2.2; in presence thereof (e.g., 0.0135 mm. Hg pressure) the reaction occurred as in its absence after 17.8% of the MeCHO had been decomposed, by which time 6 vols. of O_2 had caused decomp. of an additional 9800 vols. of MeCHO . The irregularities previously noted (cf. A., 1926, 804; 1931, 1001; 1933, 910) are due to the presence of traces of O_2 . C. A. S.

Catalytic activity of liquid and solid surfaces. Decomposition of methyl alcohol on solid and liquid zinc. E. W. R. STEACIE and E. M. ELKIN (Proc. Roy. Soc., 1933, A, 142, 457—465).—There is no discontinuity at the m.p. of Zn when the metal is used as a catalyst for the thermal decomp. of gaseous MeOH between 360° and 440°. It is concluded that the whole surface of the metal is uniformly active, and that the catalytic activity of a solid cannot be limited to a part of the surface. L. L. B.

Concentration of deuterium by electrolysis. D. H. RANK (J. Chem. Physics, 1933, 1, 750).—The low concn. of "deuterium" [H^2] in commercial electrolytic cells run hot is due to losses of H_2O vapour with the electrolytic gases and to evaporation. H. S. P.

Current distribution at the anode in the electrolytic formation of sodium persulphate. O. ESSIN and E. ALFIMOWA (Z. Elektrochem., 1933, 39, 891—894; cf. A., 1933, 34, 468).—The previous equation for the division of current between the various anode processes is applicable to the electrolytic formation of $\text{Na}_2\text{S}_2\text{O}_8$ when changes are made in the type of cathode and in the e.d. The addition of HF is also without influence. H. J. E.

Polarographic studies with the dropping mercury cathode. XXXV. Electrolysis of aqueous solutions of beryllium salts. W. KEMULA and M. MICHALSKI (Coll. Czech. Chem. Comm., 1933, 5,

436—442).—The deposition of Be at the dropping Hg cathode is preceded by H_2 evolution, the effect being reduced by higher Be concns. The close similarity between the deposition potentials of Be and Al makes it impossible to separate these metals. D. R. D.

Anodic dissolution of copper-tin alloys.—See B., 1933, 1013.

Anodic behaviour of copper in alkali chloride and hydrogen chloride solutions. Z. SZABO (Magyar Chem. Fol., 1933, 39, 1—19; Chem. Zentr., 1933, ii, 345).—In 1—6M solutions in H_2 the Cu dissolves as Cu^+ and forms CuCl_3^- . The potential of the Cu electrode depends on $[\text{Cu}]$ and $[\text{Cl}^-]$ of the solution. Lewis' law holds for complex anions. Activity coeff. and equilibrium const. for CuCl_3^- are calc.; the latter is 0.145×10^{-5} . A. A. E.

Electrolysis of acetates in absolute alcohol. F. FICHTER and R. E. MEYER (Helv. Chim. Acta, 1933, 16, 1408—1412).—The electrolysis of NaOAc and AcOH in MeOH and in H_2O , respectively, has been carried out under exactly similar conditions in order to investigate the character of the Kolbe hydrocarbon synthesis. The output of CO_2 and C_2H_6 in MeOH is slightly $>$ in H_2O , whilst H_2 is somewhat less. A little C_2H_4 is always present in the anode gases, but in larger amount from the H_2O solution, and a very little O_2 in both cases. The results are considered to favour the view that Ac_2O_2 is an intermediate product in the Kolbe hydrocarbon synthesis and that O_2 itself takes part in the electrochemical oxidation. Experiments show that $\text{Mg}(\text{OAc})_2$ in MeOH is of little use for the Kolbe synthesis, for, although a considerable quantity of C_2H_6 is obtained from the H_2O together with some C_2H_4 , O_2 , and CO_2 , the MeOH solution gives very little gas at the anode and no C_2H_6 at either electrode, pure H_2 only being formed at the cathode. Variation of the NaOAc or KOAc concn. whilst the AcOH concn. remains const. at 20% gives a max. yield of C_2H_6 at an intermediate concn. of salt. The max. for KOAc is at 1.44N. M. S. B.

Electrolytic oxidation of anthracene to anthraquinone. N. S. DROZDOV and S. S. DROZDOV (J. Appl. Chem. Russ., 1933, 6, 897—902).—Anthracene (I) in COMe_2 — H_2SO_4 solution combines directly with O at the anode to yield anthraquinone (II); this does not take place with suspensions of (I) in H_2SO_4 , when the agency of a catalyst is necessary for the transference of O. The velocity of oxidation using $\text{Ce}_2(\text{SO}_4)_3$ catalyst is $>$ with $\text{K}_2\text{Cr}_2\text{O}_7$, but the product is considerably more contaminated with products of further oxidation of (II). The nature of the above reactions is not affected by varying c.d. at the anode. Anthraquinol is not an intermediate product in the above processes. R. T.

Recombination of atomic hydrogen in the tungsten arc. F. J. HAVLICEK (Helv. phys. Acta, 1933, 6, 165—197; Chem. Zentr., 1933, ii, 832).—Recombination is unimol., and an intermediate state is probably involved. The temp. coeff. of the velocity coeff. is given by $189e^{-2040/RT}$. Hence the higher is the temp., the greater is the velocity of recombina-

ation. At room temp. the half-val. period is approx. 0.175 sec. A. A. E.

Electrolysis in the glow discharge. IV. A. KLEMENC and H. F. HOHN (Z. physikal. Chem., 1933, 166, 343—356; cf. A., 1931, 805).—The products in this electrolysis are qualitatively independent of the polarity of the discharge vessel. The current yield, A , is greater in the cathode than in the anode fall. In the reduction of HClO_3 and HClO_4 , A is much $>$ corresponds with Faraday's law. It is concluded that in electrolysis in the glow discharge "active" uncharged substances participate in the electrochemical processes. These include such substances as at. H and also substances formed in ordinary electrolysis on discharge of the ions. The production of $\text{H}_2\text{S}_2\text{O}_8$ in the electrolysis of aq. H_2SO_4 shows that the mechanism of formation cannot be $2\text{HSO}_4' + 2\oplus \rightarrow \text{H}_2\text{S}_2\text{O}_8$; possibly it is $2\text{HSO}_4' + \text{O} + \text{H}_2\text{O} = \text{H}_2\text{S}_2\text{O}_8 + 2\text{OH}'$. R. C.

Reactions of the hydroxyl radical in the electrodeless discharge in water vapour. W. H. RODEBUSH and M. H. WAHL (J. Chem. Physics, 1933, 1, 696—702).—When the electrodeless discharge is produced in a stream of H_2O vapour at 0.1—0.2 mm. pressure, about 50% of the H_2O is converted into H_2O_2 which may be frozen out. The formation of H_2O_2 is attributed to dissociation of H_2O into H' and OH' followed by $2\text{OH} = \text{H}_2\text{O}_2$. H_2O_2 is not obtained in tubes with electrodes owing to the catalytic action of the spluttered metal. Spectroscopic examination showed two new bands with heads at 3564 and 3326 Å. which are attributed to OH' . H. S. P.

Chemical action of the [electric] spark on gases at low pressure. H. LEFÉVRE (Chim. et Ind., 1933, 29, Spec. No., 427—431).—Pure CO_2 , at pressures of 0.1—18 mm. of Hg, was subjected to electric discharges (I) from condensers; the effect of varying the initial pressure of the gas, the energy of (I), and the no. of sparks, on the reaction $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ is described. "Asymmetric" (I) of low energy, having the nature of Geissler tube discharges, produced very little, and (I) of higher energy ("symmetrical"), relatively great (e.g., 15%), decomp. of CO_2 . The decomp. of CH_4 by (I), mainly into C_2H_2 and H_2 , is discussed, and is concluded to be too small to be of industrial interest. A. L. R.

Heterogeneous chemical reactions in the silent electric discharge. VI. S. MIYAMOTO (J. Sci. Hiroshima Univ., 1933, A, 3, 347—366; cf. A., 1933, 33, 682).—The following salts are reduced by gaseous H_2 in the silent discharge; $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, KNO_3 , KNO_2 , AgNO_3 , $\text{Mn}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, and $\text{Cd}(\text{NO}_3)_2$. Details of the reaction products are given; in no case did they include azides, hyponitrites, or NH_2OH . J. W. S.

Inertness and chemical activity of the rare gases. H. DAMIANOVICH (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 30—44; Chem. Zentr., 1933, ii, 847).—When a discharge is passed in He between Pt electrodes the product contains 15% of a substance insol. in HCl-HNO_3 and considered to be a compound. Products obtained in He, O_2 , N_2 , and H_2 are compared. A. A. E.

Density of the product of the action of helium on platinum. H. DAMIANOVICH and J. PIAZZA (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 45—48; Chem. Zentr., 1933, ii, 847).—The product has d 15, or after 3 months in He 16.8. A. A. E.

Action of nitrogen at low pressure on platinum under the influence of the electric discharge. H. DAMIANOVICH and G. BERRAZ (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 58—63; Chem. Zentr., 1933, ii, 848).—A dark grey substance, d 18.3, having a metallic lustre is obtained; 7.7% is sol. in dil. HCl-HNO_3 . A. A. E.

Action of oxygen at low pressure on platinum under the influence of the electric discharge. H. DAMIANOVICH and J. PIAZZA (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 49—53; Chem. Zentr., 1933, ii, 847).—The product obtained from O_2 at 2—0.08 mm. and 380—1500 volts has d 15.4. 32.6% is sol. in HCl-HNO_3 . The composition corresponds with the formula Pt_2O_3 . A. A. E.

Action of hydrogen at low pressure on platinum under the influence of the electric discharge. H. DAMIANOVICH and C. CHRISTEN (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 54—57; Chem. Zentr., 1933, ii, 847).—With pure Pt and H_2 at 0.1—4 mm. and 500—550 volts slow absorption of H_2 and sputtering of Pt occur. A. A. E.

Effect of electric discharges on hydrocarbons at low pressure. C. C. CHRISTEN (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 71—81; Chem. Zentr., 1933, ii, 850).—With C_7H_{16} , using Ni electrodes and 300—600 volts, partial condensation, independent of temp., occurs. The product is a non-volatile yellowish-brown mass; the portion insol. in light petroleum and sol. in Et_2O is attacked by conc. H_2SO_4 , HNO_3 , and Br. The product slowly absorbs atm. O_2 . A. A. E.

Weigert effect. (Effect of dye concentration on photodichroism.) W. KEMULA (Z. physikal. Chem., 1933, B, 23, 305—314).—The variation with the type of gelatin and colour of light of the Weigert effect in gelatin films coloured with various dyes and exposed to white and monochromatic linearly polarised light has been studied. With increasing dilution of dye the photodichroic sensitivity shifts more and more from the subsidiary max. towards the principal max. of extinction at longer wave-lengths, whilst the short-wave subsidiary max. diminishes and the long-wave principal max. is scarcely affected. It is suggested that the dye occurs in two photosensitive forms having different extinction curves, and that with decreasing dye concn. the concn. of the form with the short-wave extinction max. decreases more rapidly than the concn. of the form with the long-wave max. The gelatin film also exerts a filter action. The phenomena of photoanisotropy are due to photochemical changes in the particles of binding medium, the fibres being coloured dichroically by adsorption of dye. R. C.

Physico-chemical study of the function of sodium sulphite in photographic developers. K. M. PANDALAI and G. G. RAO (Z. anorg. Chem., 1933, 215, 23—32).—From experiments on the

reduction of AgCl by quinol and metol developers, it is concluded that normal development is an induced reaction in which Ag halide is the actor, the org. reducing agent the inductor, and Na_2SO_3 the acceptor. Quinol reacts primarily with AgCl, and the quinone formed is then reduced by the Na_2SO_3 . Photographic plates treated with a mixture of Na_2SO_3 and quinone or quinhidrone undergo slow but otherwise normal development. F. L. U.

Actinometry with uranyl oxalate at λ 278, 253, and 208 m μ , including a comparison of periodically intermittent and continuous radiation. F. P. BRACKETT, jun., and G. S. FORBES (J. Amer. Chem. Soc., 1933, 55, 4459—4466).—The gross quantum yield, in moles of $\text{H}_2\text{C}_2\text{O}_4$ per quantum, in the photolysis of solutions containing 0.05M- $\text{H}_2\text{C}_2\text{O}_4$ and 0.01M- UO_2SO_4 is 0.48 ± 0.01 when λ is 208 m μ , 0.63 ± 0.03 for 253 m μ , and 0.59 ± 0.01 for 278 m μ . The light source was a Zn spark of high constancy. The absorption coeffs. involved are given. Periodically intermittent and const. radiation are photochemically equiv. E. S. H.

Photochemical studies. XVI. Chlorination of benzene. H. P. SMITH, W. A. NOYES, jun., and E. J. HART (J. Amer. Chem. Soc., 1933, 55, 4444—4459; cf. A., 1932, 349).—The reaction in the gaseous phase proceeds by a short chain reaction. At the beginning of the reaction the rate of change of pressure is proportional to the square root of the light intensity, the pressure of the Cl_2 , and the pressure of the C_6H_6 . The main initial reaction is addition, but substitution also occurs. The mechanism is discussed. E. S. H.

Reaction mechanism of photochemical conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in ultra-violet light. K. G. ZIMMER (Z. physikal. Chem., 1933, B, 23, 239—255).—The infra-red absorption of $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-CHO}$ (I) at various temp. gives no indication that (I) is a mixture of tautomerides. Observations on the dichroism of crystals for wave-lengths 436 and 405 m μ give a possible explanation of the dependence of the yield in the cryst. state on the plane of polarisation of the incident light. There is no appreciable photo-electric effect or fluorescence. The primary process in the photochemical reaction is dissociation of (I) into $\text{o-NO-C}_6\text{H}_4\text{-CHO}$ and O. These products by re-combination may either form $\text{o-NO-C}_6\text{H}_4\text{-CO}_2\text{H}$ acid or re-form (I), which explains the low quantum yield, although other causes, particularly energy dissipation, may contribute. The temp. coeff. between 45° and 70° is < 1 . R. C.

Solarisation of glass by soft X-rays. H. KERSTEN and C. H. DWIGHT (J. Chem. Physics, 1933, 1, 627—629).—The intensity of the brown coloration and the rate of fading have been investigated under various conditions of temp., tube current, etc. D. R. D.

Decomposition of sodium azide by controlled electron bombardment and by ultra-violet light. R. H. MULLER and G. C. BROUS (J. Chem. Physics, 1933, 1, 482—491).—Cryst. NaN_3 is decomposed by electrons possessing energies > 11.5 volts. The reaction velocity has been studied in relation to the

voltage. The threshold wave-length for photochemical decomp. is about 405 m μ , and the rate \propto light intensity. There is no apparent relation between the energies needed for the two types of decomp. F. L. U.

Effect of a wave-capturing oscillating circuit on chemical reactions. A. DE P. FORJAZ (Compt. rend., 1933, 197, 1124—1125).—Exposure to a Lakhovsky oscillating circuit ($\lambda=1.256$ m.) catalyses certain reactions, e.g., it accelerates the interaction of EtOH and AcOH, the ageing of wine, ionisation, and allotropic change, and lowers the acidity of an oil or of vinegar. C. A. S.

Decomposition of chloroform by radiations from radon. G. HARKER (J. Proc. Roy. Soc. New South Wales, 1933, 67, 96—117).— CHCl_3 is decomposed by γ -radiation to give Cl_2 and, by subsequent reaction, CCl_4 and HCl . The effect of various metal filters has been measured. Minute traces of impurities affect the amount of decomp.; the presence or accumulation of the reaction products decreases the amount of decomp. Secondary radiation has no effect. 29.8 and 251.3 g.-cal. of X- and γ -radiation, respectively, are needed for decomp. of 1 mol. of CHCl_3 . R. S. C.

Physiological effects of radio waves. J. L. DONNELLY (Science, 1933, 78, 290).—The heating effect of short radio waves on solutions of various electrolytes previously observed (A., 1930, 1376) has been confirmed. Dil. solutions of purified glucose and a solution of HCl in C_6H_6 are not heated by high-frequency currents (I). PhOH was partly liquefied, but no temp. change was observed. The system H_2O -PhOH shows no temp. increase on irradiation. The therapeutic use and physiological effect of (I) are discussed in the light of the above results. L. S. T.

Use of liquid air for the purification of radium emanation. N. MORTARA (Atti R. Accad. Lincei, 1933, [vi], 17, 1069—1072).—The use of freshly prepared liquid air or liquid N_2 is recommended for the condensation of Rn owing to the lower temp. obtainable. With liquid O_2 the loss of Rn is considerable. O. J. W.

Heavy water. K. F. BONHOEFFER (Angew. Chem., 1933, 46, 776—779).—A lecture.

Concentration of H^2 isotope. G. N. LEWIS and R. T. MACDONALD (J. Chem. Physics, 1933, 1, 341—344; cf. A., 1933, 442).—By electrolysing 20 litres of H_2O from an old commercial electrolytic cell in four stages until only 0.5 c.c. remained, H_2O of d 1.073 was obtained. No large accumulations of heavy O isotopes occurred and, assuming the d to vary linearly with the fraction of H^2 , 2/3 of the H in this H_2O was H^2 . Further reduction of the vol. to 0.25 would give 99% H^2 . In electrolysis the % loss of H^1 : % loss of $\text{H}^2=5:1$. Provisionally it is found that the concn. of H^2 in ordinary H_2O is 1 in 6500. J. W. S.

Isotopic fractionation of water. E. W. WASHBURN, E. R. SMITH, and M. FRANDSEN (J. Chem. Physics, 1933, 1, 288).—By the isotopic fractionation of H_2O electrolytically (A., 1932, 894) the d , f.p., and

b.p. of the residual H_2O rise continuously as electrolysis proceeds, whilst n decreases. By successive recombination of the electrolytically obtained O and H and re-electrolysis it should be possible to obtain isotopically pure H_2O of composition $H^{16}O^{16}H^{16}$.

M. S. B.

Isotopic fractionation of water by distillation and by adsorption. E. W. WASHBURN and E. R. SMITH (J. Chem. Physics, 1933, 1, 426; cf. preceding abstract; A., 1932, 793).—A difference of 64.9 p.p.m. was found between the d of the initial distillate and final residue on distillation of 10 litres of H_2O through a 35-ft. fractionating column, the residue having increased by 53.3 p.p.m. After 300 g. of charcoal had been immersed in 500 g. H_2O for 3 weeks the d of the supernatant H_2O had decreased by 6.5 p.p.m. and that of the absorbed water increased by 6.7 p.p.m. Fractionation of H_2O can therefore be carried out both by distillation and by adsorption.

J. W. S.

Decomposition of water by metalloids [and non-metals]. J. CAMPARDOU (Bull. Soc. chim., 1933, [iv], 53, 986—992).—A preliminary discussion.

R. S.

Complex periodides. G. SPACU and P. SPACU (Bul. Soc. Stiinte Cluj, 1932, 7, 154—159; Chem. Zentr., 1933, ii, 686).—The following compounds have been prepared: $[Cu en_2]I_2 \cdot 2I_2$, $[Cd en_2]I_2 \cdot I_2$, $[Zn en_2]I_2 \cdot I_2$, $[Ni en_2]I_2 \cdot I_2$, $[Cu pn_2]I_2 \cdot I_2$. Attachment of I_2 prevents dissociation of $[M en_2]^+$.

A. A. E.

Complex thiocyanate amines. II, III. G. SPACU and G. GRECU (Bul. Soc. Stiinte Cluj, 1931, 6, 238—254, 1932, 7, 13—24; Chem. Zentr., 1933, ii, 685).—II. The following compounds have been prepared:

$[Ag(SCN)_4][Co en_3]$, $[Ag(SCN)_4][Cr en_3]$, $[Ag(SCN)_3][Cr(NH_3)_6]Cl$, $[Zn(SCN)_4][Co en_3]SCN$, $[Hg(SCN)_4]_2[Cr en_3]_2$, $[Hg(SCN)_4]_2[Co(NH_3)_6]_2$, $[Hg(SCN)_2Cl][Co en_2Cl_2](1:6)$, $[Cr(SCN)_6]_2[Zn en_2]_3$, $[Cr(SCN)_6][Co en_3]$, $[Cr(SCN)_6]_3[Co en_2Cl_2]_3(1:6)$, $[Cr(SCN)_4(NH_3)_2]_2[Cu en_2]$.

$[Cr(SCN)_4(NH_3)_2]_2[Ni en_2] \cdot 2H_2O$, $[Cr(SCN)_4(NH_3)_2][Cd en_2]$, $[Cr(SCN)_4(NH_3)_2][Co en_3]$, $[Cr(SCN)_4(NH_3)_2][Co en_2Cl_2](1:6)$, $[Cr(SCN)_4(NH_3)_2][Co en_2Cl_2](1:2)$.

$[Cr(SCN)_4(NH_3)_2]_3[Cr en_2]$, $[Mn(SCN)_4][Cu en_2]$, $[Mn(SCN)_4][Cd en_2] \cdot 2H_2O$, $[Mn(SCN)_6][Ni en_2]_2$.

III. $[Bi(SCN)_6][Co en_3]$, $[Bi(SCN)_6][Cr en_3]$, $[Cr(SCN)_6][Co(NH_3)_6] \cdot 2H_2O$, $[Cr(SCN)_6][Co en_2(SCN)_2](1:6)$ and $(1:2)_3 \cdot 2H_2O$, $[Cr(SCN)_6][Co en_2Br_2](1:6)_3$.

$[Cr(SCN)_6][Co en_2(NO_2)_2](1:6)$ and $(1:2)_3$, $[Cr(SCN)_4(NH_3)_2][Co en_2(SCN)_2](1:6)$ and $(1:2)_2$, $[Cr(SCN)_4(NH_3)_2][Co en_2Br_2](1:6)$, $[Cr(SCN)_4(NH_3)_2][Co en_2(NO_2)_2](1:6)$ and $(1:2)_2$.

A. A. E.

Homogeneous and heterogeneous complex salts in solution. V. G. SPACU and P. SPACU (Bul. Soc. Stiinte Cluj, 1932, 7, 95—103; Chem. Zentr., 1933, ii, 685—686).—The following compounds have been prepared (pn=propylenediamine): $[HgI_4][Cu pn_2]$, $[AgI_2][Cu pn_2]$ (suitable for gravimetric determination of Ag in presence of Cu), $[Ni en_3]S_2O_3$ (suitable for determination of $S_2O_3^{2-}$ in presence of SO_4^{2-} , SO_3^{2-} , S^{2-} , SCN^- , and $S_4O_6^{2-}$).

$[HgI_3][Co en_2(SCN)_2] \cdot 4H_2O$, $[PbI_4][Co en_2(SCN)_2]_2$, $[AgI_2][Co en_2Cl_2](1:2)$ and $(1:6)$.

A. A. E.

Hydrated calcium aluminates. J. LEFOL (Compt. rend., 1933, 197, 919—921).—Curves relating the no. of mols. of H_2O remaining to the temp., obtained by Guichard's method (cf. A., 1926, 1021), for (1) $Al_2O_3 \cdot 4CaO \cdot 12H_2O$, (2) $Al_2O_3 \cdot 3CaO \cdot 21H_2O$ (needles), (3) $Al_2O_3 \cdot 3CaO \cdot 6H_2O$ (cubic), and (4) $Al_2O_3 \cdot 2CaO \cdot 7H_2O$ (cf. A., 1930, 162, 436, 872) indicate the formation of the following hydrates from (1) with 10.5—11 H_2O at 95°, and 6 H_2O at 175°; (2) with 8—8.5 H_2O at 135° (3) with 1.5 H_2O at 260—310°, (3) itself being stable to about 250°; and (4) with 5 H_2O at 150°, dehydration beginning at 65°, up to which temp. 0.5—1 mol. H_2O had been absorbed.

C. A. S.

Purification of mercury.—See B., 1933, 1062.

Purification of mercury by an electrolytic method. M. E. HANKE and M. JOHNSON (Science, 1933, 78, 414—415).—The Hg is made the positive pole of a 110-volt d.c., first in presence of 10% H_2SO_4 (I), and then in presence of 5% NaCl. Finally, it is made negative in presence of (I). Scum is removed by filtration between the steps. 500 c.c. of Hg can be purified in 1.5 hr.

L. S. T.

Decomposition of mercurous iodide into mercury and mercuric iodide. Equilibrium states. Crystallisation of the compound. M. FRANÇOIS (Ann. Chim., 1933, [x], 20, 285—303).—A full account of work previously published (A., 1896, i, 22, ii, 248, 301, 363; 1897, ii, 492; 1898, ii, 334).

F. L. U.

Crystal analysis of unstable precipitates. P. JOLIBOIS and G. FOURETIER (Compt. rend., 1933, 197, 1322—1323).—An X-ray photograph taken within 0.02 sec. of the mixing of streams of aq. $HgCl_2$ and aq. KI (cf. A., 1920, ii, 112) showed the structure of the yellow HgI_2 thus pptd. to be identical with that of yellow HgI_2 obtained at 140°.

C. A. S.

Reduction of alumina by carbon. W. D. TREADWELL and A. GYGER (Helv. Chim. Acta, 1933, 16, 1214—1225).— Al_2O_3 is reduced by C in a circulating stream of A. The resulting CO content of the A atm. is determined by measuring the heat conductivity of the gas by the changes in resistance of a heated Pt wire in the gas mixture. By rapid heating to 2000° abs. the equilibrium is represented by the equation $Al_2O_3 + 3C \rightleftharpoons 2Al + 3CO$. Al_4C_3 is probably formed either by the reaction $3CO + 6Al \rightleftharpoons Al_4C_3 + Al_2O_3$ or $2Al_2O_3 + 9C \rightleftharpoons Al_4C_3 + 6CO$ and the equilibrium condition is not reached in the apparatus. The CO pressure appears to remain const. as long as metallic Al is present. Micro-analytical methods are described for the determination of Al and Al_4C_3 in the reaction mixture, Al by reduction of $FeCl_3$ to $FeCl_2$ and Al_4C_3 by treatment with dil. HCl and combustion over CuO of the H_2 and CH_4 produced.

M. S. B.

Luminescent aluminium oxides and their crystallochemical relationships to the natural and synthetic precious stones of the corundum type and their colorations. E. TIEDE and H.

LUDERS (Ber., 1933, 66, [B], 1681—1689; cf. A., 1931, 1253).—Conditions are described which permit the sesquioxides of Cr, Rh, Ti, V, Fe, and Ga which crystallise in the corundum lattice to be mixed with Al_2O_3 to form a series of mixed crystals on a basis of isomorphism. Only those sesquioxides which are involved in the corundum lattice are capable of luminescence and all yield fluorescent systems. The fundamental crystallographic conditions of fluorophors are therefore markedly more simple than those of phosphors. The colour and luminescent powers of the mixtures melted in the H_2 - O_2 flame or cathode-ray furnace are compared with those of natural precious stones. H. W.

Artificial transformation of felspar into kaolin. R. SCHWARZ and G. TRAGESER (Z. anorg. Chem., 1933, 215, 190—200).—If felspar (I) is heated with pure H_2O the latter becomes increasingly alkaline through hydrolysis of (I). By a preliminary heating at 850° the rate of attack is reduced, owing to diminution of surface exposed by aggregation of particles. Superheated steam at 500° or 1000° , either alone or mixed with SO_2 , NH_3 , or HCl , has the same effect. By treatment with N-HCl at 330° for 250 hr. under pressure in a steel bomb (320° gives approx. 110 atm. H_2O vapour), (I) is partly transformed into kaolin (II), as shown by the dehydration curve of the product and X-ray diagram. A similar result is obtained with 0.5N-HCl at 320° for 115 hr., but not at 180° and 250° . Instead, a residue rich in SiO_2 is left ($\text{Al}_2\text{O}_3 : \text{SiO}_2 = 1 : 7-8.6$). No (II) formation has been observed with H_2SO_4 or HF . CO_2 at 190 atm. and 320° for 250 hr. produced no marked change. (II) is decomposed at 220° by 0.5N-HCl , owing to the much greater solubility of Al_2O_3 compared with SiO_2 . At 320° the greatly increased solubility of SiO_2 results in a saturated solution in which (II) is stable and from which it can separate. Hence under these conditions any suitable silicate such as orthoclase, leucite, or anorthite will form (II).

M. S. B.

Formation of silicon carbide. K. ARNDT and E. HAUSMANN (Z. anorg. Chem., 1933, 215, 66—74; cf. B., 1932, 134).—Reduction of SiO_2 by C begins at about 1600° . At 2250° SiC is decomposed, the resulting graphite retaining the form of the original crystals. No difference in behaviour was observed when using anthracite, wood C, or petrol C with quartz sand as starting material. So-called "siloxicon," reported to be formed at 1600° , is SiC in a microcryst. condition. F. L. U.

Germanium. XL. Action of ammonia on monochloromonogermane and dichloromonogermane. Action of water on monochloromonogermane. L. M. DENNIS and R. W. WORK. **XLI. New salts of fluogermanic acid.** L. M. DENNIS and B. J. STANESLOW [with W. D. FORGENG] (J. Amer. Chem. Soc., 1933, 55, 4486—4489, 4392—4396). **XL.** The reactions of GeH_3Cl and GeH_2Cl_2 with excess of liquid NH_3 are represented by $3x\text{GeH}_3\text{Cl} + 3x\text{NH}_3 \rightarrow 3x\text{NH}_4\text{Cl} + x\text{GeH}_4 + 2(\text{GeH})_2$ and $\text{GeH}_2\text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{Ge} + 2\text{NH}_4\text{Cl}$. When excess of H_2O acts on GeH_3Cl neither H_2 nor the hypothetical $(\text{GeH}_3)_3\text{O}$ is produced.

XLI. The prep., optical properties (including n), d , and solubilities in H_2O , MeOH , and EtOH of the following are described:

$(\text{NH}_4)_2\text{GeF}_6$; $(\text{NH}_4\text{OH})_2\text{H}_2\text{GeF}_6$; $(\text{N}_2\text{H}_4)_2\text{H}_2\text{GeF}_6$; $(\text{NH}_2\text{Ph})_2\text{H}_2\text{GeF}_6$; $(\text{NHPPhMe})_2\text{H}_2\text{GeF}_6$; $(\text{NPhMe})_2\text{H}_2\text{GeF}_6$. All the salts are sol. in H_2O , but are hydrolysed with separation of GeO_2 . $(\text{NH}_2\text{OH})_2\text{H}_2\text{GeF}_6$ forms a dihydrate. E. S. H.

Rapid heating of lead azide in a vacuum. W. SCHUMACHER (Compt. rend., 1933, 197, 917—918).— PbN_6 or Ag fulminate detonates on heating in vac. in the same way as in air, thus differing from Hg fulminate. C. A. S.

Nitric oxide-sulphurous acid. I, II. E. WEITZ and F. ACHTERBERG (Ber., 1933, 66, [B], 1718—1727, 1728—1733).—I. As working hypothesis, the constitution $\begin{array}{c} \text{O} \cdots \text{O} \\ | \quad | \\ \text{O} \quad (\text{NO})_2 \end{array} \text{H}$ is assigned to nitric oxide-sulphurous acid. The formation of the salts is to some extent reversible, since the alkali salts when heated decompose (sometimes "spontaneously") into SO_4^{--} and N_2O (70—80%) and SO_3^{--} and NO . In H_2O , the K salt (I) decomposes almost quantitatively into SO_4^{--} and NO , whilst in presence of alkali SO_3^{--} and N_2O appear; the Na salt (II) decomposes more readily. (II) reduces Fehling's solution more readily than does (I) in accordance with the usual greater stability of the complex salts of K. In alkaline solution the salts are slowly but quantitatively oxidised by KMnO_4 to SO_4^{--} and NO_2^+ and further in acid solution to NO_3^+ : $\text{K}_2\text{SO}_3 \cdot 2\text{NO} + 4\text{O} + \text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 2\text{HNO}_3$. Absorption of NO by aq. K_2SO_3 occurs most rapidly in presence of 0.1—0.2 mol. of KOH . Neutral solutions of (I) and (II) slowly become alkaline, $\text{K}_2\text{SO}_3 \cdot 2\text{NO} + \text{K}_2\text{SO}_3 + \text{H}_2\text{O} = \text{K}_2\text{S}_2\text{O}_6 + \text{N}_2\text{O} + 2\text{KOH}$, the change being ultimately inhibited by the KOH produced. A similar but very slow change which is finally inhibited by alkali takes place between (I) and alkali thiosulphate. The reaction $\text{K}_2\text{SO}_3 \cdot 2\text{NO} + \text{EtOH} = \text{KEtSO}_4 + \text{N}_2\text{O} + \text{KOH}$ is also arrested by the liberated alkali. Unexpectedly, these "sulphonating" actions occur more rapidly in slightly acidic than in neutral or alkaline solution. (I) and K_2SO_3 appear to react in the solid phase. Atm. oxidation of (I) occurs in presence of traces of acid (HCl or KHSO_4), $2\text{K}_2\text{SO}_3 \cdot 2\text{NO} + \text{O}_2 = 2\text{K}_2\text{SO}_4 + 4\text{NO}$. K tetroxalate is without action, whereas $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ causes development of heat and production of K_2SO_3 in addition to K_2SO_4 .

II. Treatment of (I) with FeSO_4 yields the unstable salt $\text{K}_4\text{Fe}(\text{SO}_3 \cdot 2\text{NO})_3$ which decomposes in presence of its mother-liquor into K_2SO_4 , FeSO_4 , N_2O , and a little $\text{Fe}(\text{OH})_3$ and basic Fe^{+++} salt. Under similar conditions (II) gives an intense red solution (III). Solutions of (I), FeSO_4 , and NH_3 salts give essentially the same product as without NH_3 , but it appears more stable and less definite in composition. (III) does not add NO . Rapid absorption occurs when NO is passed into FeSO_3 suspended in Na_2SO_3 ; Fe^{+++} and NH_4OH result. (I) and FeSO_3 yield the salt $\text{KFe}_3\text{S}_3(\text{NO})_6 \cdot \text{H}_2\text{O}$, NO appearing to be lost as such from (I). Co^{++} salts and (I) in neutral solution apparently afford mixtures of $\text{K}_4\text{Co}(\text{SO}_3 \cdot 2\text{NO})_3$ and $\text{K}_2\text{Co}(\text{SO}_3 \cdot 2\text{NO})_2$; in presence of NH_3 a red solution

results which rapidly evolves gas and deposits ill-defined ppts. Zn and Mn solutions give the salts $K_4Zn(SO_3,2NO)_3$ and $K_4Mn(SO_3,2NO)_3$, respectively. (II) does not yield ppts. under like conditions, but characteristic colours are developed in the solutions. (I) and La salts appear to yield a series of colourless double salts. (II) and $TiNO_3$ or $BaCl_2$ yield the respective compounds $Ti_2SO_3,2NO$ and $BaSO_3,2NO,2H_2O$. With $[Co(NH_3)_6]Cl_3$ the substance $[Co(NH_3)_6]Cl(SO_3,2NO),H_2O$ results. H. W.

Phosphoric acid and the phosphates. I. Formation of the basic alkaline-earth phosphates. A. SANFOURCHE. **II. Volumetric titration of phosphoric acid and the phosphates.** **IV. Action of water on monocalcium phosphate.** A. SANFOURCHE and B. FOCET (Bull. Soc. chim., 1933, [iv], 53, 951—963, 963—969, 974—980).—I. The composition of the ppts. formed by addition of $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ to H_3PO_4 solutions has been examined. At 100° the end products are respectively a tribasic phosphate, a hydroxyapatite (I), and a mixture of (I) and tetrabasic phosphate. The tri- and tetra-basic phosphates are regarded as salts of the acid $H_6P_2O_9$.

II. (a) Titration with 0.1N-NaOH in presence of $CaCl_2$ ($CaCl_2 : P_2O_5$, 5—10) is recommended. Addition of excess alkali and back titration introduces errors due to formation of (I) (cf. above). (b) The solution, containing < 0.2 g. H_3PO_4 , is neutralised against Me-orange. 20 c.c. of 5% aq. $AgNO_3$ are added and the HNO_3 liberated is titrated with 0.1N-NaOH against Me-red. Near the end-point, the ppt. is allowed to settle and more indicator added. The method is not suitable for solutions containing Fe or Al.

IV. The amount of $CaHPO_4$ formed at various concns. of $CaH_4(PO_4)_2$ salt is given. No decomp. occurs in solutions containing < 1.3%. The reverse reaction between $CaHPO_4,2H_2O$ and H_3PO_4 attains the same equilibrium at once, but when the anhyd. salt is used false equilibria occur. R. S.

Oxidation of hypophosphoric acid by bromine. B. BLASER and P. HALPERN (Z. anorg. Chem., 1933, 215, 33—43).—Contradictory statements in the literature regarding the oxidation of $H_4P_2O_6$ by Br are attributed to the fact, now observed, that the reaction is strongly influenced by the p_H of the mixture. At p_H 8 $H_4P_2O_7$ is formed rapidly and quantitatively, whilst outside the limits 5—11 the reaction is scarcely detectable. In the alkaline range the oxidation is powerfully catalysed by Cu^{II} . The constitution of $H_4P_2O_6$ is discussed. F. L. U.

Ammoniates of vanadium halides. F. EPHRAIM and E. ANMANN (Helv. Chim. Acta, 1933, 16, 1273—1287).—The compound VBr_2 has been obtained as a light reddish-brown cryst. substance by the reduction of VBr_3 with H_2 . The action of liquid NH_3 at or below room temp. on this and other V halides has been investigated. VCl_2 , VCl_3 , VBr_2 , and VBr_3 form ammines, but not VCl_4 , although it combines readily with NH_3 . Decomp. curves are given for the various ammines. Except VBr_2 they all take up rather > $6NH_3$, probably as the result of absorption, and on raising the temp. this is gradually given up until the pentammine is formed. For this there is a well-

defined decomp. temp. at which the triammine is obtained: VCl_2 171—178°, VCl_3 178—179°, and VBr_2 210—214°. The decomp. of $VBr_3,5NH_3$ takes place above 240°, but is less clearly defined and does not go quite so far as the triammine. The ammines are all readily attacked by atm. O_2 and by H_2O . This contrasts with the behaviour of the corresponding Cr^{III} and Co^{III} compounds, although, from the fact that V^{III} has the same no. of electrons in the outside shell as Cr^{III} , it might have been expected that the corresponding ammines would display a similar behaviour. Densities have been determined for the different halides and ammines and the % contraction on the formation of the V^{II} is compared with those for the halides and ammines of bivalent Cr, Mn, Fe, Co, and Ni and shown to be similar. M. S. B.

Heteroplex compounds containing antimony tribromide. A. C. VOURNASOS (Praktika, 1932, 7, 227—232; Chem. Zentr., 1933, ii, 522).—The following compounds are described: $K_2Sb_3Br_9I_3$, $HgSb_6Br_{18}I_2$, $K_2Sb_3Br_9F_2$, $SrSb_6Br_{18}Cl_2,6H_2O$, $K_2Sb_3Br_9(SCN)_2$, $K_2Sb_3Br_9(NO_3)_2$, $NaSb_3Br_9N_3$. A. A. E.

Complex bromo-compounds of antimony. W. PETZOLD (Z. anorg. Chem., 1933, 215, 92—102; cf. A., 1933, 1258).—The following compounds are described: $(NMe_4)_3Sb_2Br_{11}$, $(C_5H_6N)_3Sb_2Br_{12}$, $RSbBr_6$ (NH_2Me_2 , NH_2Et_3 , NEt_4 , guanidinium, 2:4:6-collidinium, 5:7-dibromohydroxyquinolinium), $(NHMe_3)_2SbBr_8$, $RSbBr_7$, and $R_2Sb_2Br_{15}$ (2:4:6-collidinium), R_2SbBr_9 (α - and β -picolinium, 2:4-lutidinium). F. L. U.

Sulphur monoxides. III. Formation of sulphur monoxide in some chemical decompositions. P. W. SCHENK and H. PLATZ (Z. anorg. Chem., 1933, 215, 113—128).—In the decomp. of $SOCl_2$ vapour by heating with metals a large yield of SO is obtained with Ag, Sb, Na, and Sn, for which the heat of formation of the chlorides is > that of the oxides, but little or none with Mg, Al, and Zn, for which the contrary is the case. The amount of SO present in the vapour can be determined spectroscopically. SO cannot be separated from $SOCl_2$ by cooling to -60° , since it dissolves in the latter with decomp. into S and SO_2 . No SO is obtained by the thermal decomp. of $SOCl_2$ alone, nor by that of $H_2S_2O_3$ and $H_2S_2O_4$ or their Na salts. SO is not an intermediate product in the reaction between H_2S and SO_2 in presence of H_2O to form $H_2S_2O_6$. At room temp. S_2O_3 gives the orange substance regarded as S_2O_2 , the anhydride of $H_2S_2O_3$, but no SO is found in the vapour (cf. Wohler and Wegwitz, A., 1933, 919). No SO is formed by the thermal dissociation of SO_2 , but it is formed on combustion of S vapour present in excess. M. S. B.

Oxidation of chromic oxide in aqueous solution by atmospheric oxygen under pressure. V. V. IPATIEV, jun., and V. G. TRONEV (J. Appl. Chem. Russ., 1933, 6, 832—838).—Conversion of $Cr(OH)_3$ into CrO_3 does not occur in media of p_H < 3, under pressures of 75—100 atm.; in 4N- Na_2CO_3 100% conversion is attained. Aq. CrO_3 is quantitatively reduced to $Cr(OH)_3$ when heated with > N-acids, at 1—100 atm. R. T.

Reduction of chromic oxide to chromium.—See B., 1933, 1014.

Fluorine. O. RUFF (Angew. Chem., 1933, 46, 739—742).—Published data on the fluorides of Cl, Br, I, O, S, N, and C are reviewed. The prep. and properties of the following are described: ReF_6 [m.p. 18.8° , b.p. 47.6° , d (liquid) 3.61], ReOF_4 [m.p. 39.7° , b.p. 62.7° , d (liquid) 3.72], O_2F_2 (m.p. -160° , b.p. -57° , d 1.45). E. S. H.

Fluorine polyhalides of organic amines. H. S. BOOTH, W. C. MORRIS, and G. D. SWARTZEL (J. Amer. Chem. Soc., 1933, 55, 4466—4468).—The prep. and properties of the following are described: $\text{NH}_3\text{MeF}, \text{ICl}_3$, m.p. $35-40^\circ$; $\text{NH}_3\text{Et}_2\text{F}, \text{ICl}_3$, m.p. $60-63^\circ$; $\text{NHMe}_2\text{F}, \text{ICl}_3$, m.p. $121-145^\circ$; $\text{NMe}_3\text{F}, \text{ICl}_3$, m.p. $267-270^\circ$; $\text{C}_5\text{H}_5\text{NHF}, \text{ICl}_3$, m.p. $187-190^\circ$. Thermal dissociation occurs on heating. The stability increases with the no. of Me groups. E. S. H.

Rhenium tribromide. H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1933, 215, 111—112).— ReBr_3 is formed as a greenish-black sublimate when Re is heated at 500° in Br vapour. In presence of O_2 a dark blue distillate, probably containing oxybromide, is formed at 400° . F. L. U.

Oxygen and halogen compounds of rhenium. I. NODDACK and W. NODDACK (Z. anorg. Chem., 1933, 215, 129—184).— Na rhenite , Na_2ReO_3 , is a brown powder insol. in H_2O and aq. NaOH but slowly attacked by acids with separation of ReO_2 in H_2SO_4 and green H_2ReCl_6 in conc. HCl . K_2ReO_3 is similar. BaReO_3 can only be obtained mixed with Na_2ReO_3 . Rhenites behave similarly to manganites. By the fusion of NaOH with NaReO_4 under suitable conditions Na hyporhenate , probably either as the pyro-salt, $\text{Na}_4\text{Re}_2\text{O}_7 \cdot \text{H}_2\text{O}$, or the ortho-salt Na_3HReO_4 , is obtained in light, sand-yellow, hexagonal plates or prisms stable under aq. or EtOH-NaOH , in which it is almost insol. The K salt has not been obtained in the solid state, but probably as a deep yellow solution. The Ba salt has been obtained mixed with Na salt. Ba rhenate , BaReO_4 , an unstable leaf-green salt formed by the fusion of ReO_2 with $\text{Ba}(\text{ReO}_4)_2$ and NaOH , cannot be freed from $\text{Ba}(\text{ReO}_4)_2$. The corresponding Na compound, also impure, is readily attacked by H_2O . By fusion of colourless NaReO_4 with NaOH in air the product is red when hot and yellow when cold, and the Ba mesoperrhenate , $\text{Ba}_3(\text{ReO}_5)_2$, is similarly obtained, and can also be prepared by pptn. of $\text{Ba}(\text{OH})_2$ by NaReO_4 in aq. NaOH . It is citron-yellow when cold, but red at 800° , and is decomposed by H_2O into $\text{Ba}(\text{ReO}_4)_2$ and $\text{Ba}(\text{OH})_2$. $\text{K}_4\text{Re}_2\text{OCl}_{10}$ forms mixed crystals with the corresponding Ru compound, $\text{K}_4\text{Ru}_2\text{OCl}_{10}$. No evidence of salts of the composition $\text{X}_n\text{Re}(\text{OH})\text{Cl}_5$ or $\text{X}_2\text{Re}(\text{OH})\text{Br}_5$ has been obtained. From the deep green solution of H_2ReCl_6 salts of K, Rb, Cs, Tl, Ag, Hg^I , NH_4 , MeN (?), and of $\text{C}_5\text{H}_5\text{N}$, quinine, and nitron, are pptd. The double chlorides of the alkali metals form deep green solutions which are fairly stable. Solubility data are given for K_2ReCl_6 , Cs_2ReCl_6 , and $\text{K}_4\text{Re}_2\text{O}_4\text{Cl}_{10}$ in HCl and H_2SO_4 , and comparative electrical conductivities for K_2PtCl_6 , K_2ReCl_6 , and $\text{K}_4\text{Re}_2\text{OCl}_{10}$. H_2ReCl_6 is a very weak acid. H_2ReBr_6 forms a deep yellow solu-

tion by boiling ReO_2 with conc. HBr and gives cryst. ppts. of X_2ReBr_6 with K, Rb, and Cs salts, and $\text{C}_5\text{H}_5\text{N}$ and nitron. These are stable in solutions containing $> 15\%$ HBr . The properties of ReCl_3 have been more extensively studied, and a double salt, $\text{C}_5\text{H}_5\text{N}, \text{HCl}, \text{ReCl}_3$, has been obtained. ReBr_3 has also been prepared as black crystals and the double salt $\text{C}_5\text{H}_5\text{N}, \text{HBr}, \text{ReBr}_3$. In alkaline solutions any compound containing Re of intermediate valency tends to split up, giving compounds of Re in different stages of oxidation, the proportion of each depending on conditions. By this means a strongly reducing solution containing Re^{II} has been prepared. It gives a brown ppt. on dilution with H_2O or treatment with bases and a black sulphide with H_2S . By reduction of an ice-cold acid solution of ReCl_3 with Zn or Na amalgam the solution becomes red and then bluish-violet, with strong reducing properties, and apparently contains Re^I . A brown cryst. ppt. of K_2ReOCl_6 can be obtained, but it is very unstable, like the original ReOCl_4 . Another compound of Re^{VI} , of the probable composition $\text{C}_5\text{H}_5\text{N}, \text{HCNS}, \text{ReO}(\text{CNS})_4$, has also been obtained. A method is described for determining the valency of Re in its different compounds by oxidising to Re^{VII} with chromate and determining gravimetrically the Cr_2O_3 formed. M. S. B.

Mesoperrhenates. B. SCHARNOW (Z. anorg. Chem. 1933, 215, 185—189; cf. preceding abstract).—The conditions of formation of $\text{Ba}_3(\text{ReO}_5)_2$ by evaporation of aq. $\text{Ba}(\text{ReO}_4)_2$ with excess of aq. $\text{Ba}(\text{OH})_2$ and with exclusion of atm. CO_2 have been investigated. The formation takes place at a lower $\text{Ba}(\text{OH})_2$ concn. the higher is the concn. of $\text{Ba}(\text{ReO}_4)_2$, but there must always be a considerable excess of $\text{Ba}(\text{OH})_2$. It forms small yellow hexagonal prisms and is readily decomposed in the moist state by CO_2 forming $\text{Ba}(\text{ReO}_4)_2$ and BaCO_3 . The corresponding Sr compound is not formed because the solubility of $\text{Sr}(\text{OH})_2$ is not sufficiently high. Conductivity data are given for perrhenic acid. λ diminishes rapidly with increasing concn. M. S. B.

Corrosion of iron. E. TOPORESCU (Compt. rend., 1933, 197, 1040—1041).—Corrosion, ordinarily attributed to "differential aeration," is due to the depolymerisation and consequent increased chemical activity caused by surface tension on liquids (e.g., H_2O or 6% aq. NaCl) drawn up by such tension, e.g., between two plates of Fe placed at an angle of 7° . The corrosion product shows rhythmic growth similar to Liesegang rings. C. A. S.

Complex platinum compounds with ter- and quinque-valent platinum. VI. P. C. RAY and N. N. GHOSH (Z. anorg. Chem., 1933, 215, 201—204).—By the action of bases on $\text{PtBrEt}_3\text{S}_2$ (cf. A., 1933, 476) a series of compounds has been built up in which there are always 2 atoms of Br and the no. of Pt atoms is 2 or a multiple of 2. These are: $\text{Pt}_2\text{Br}_2\text{Et}_2\text{S}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, m.p. 205° ; $\text{Pt}_2\text{Br}_2\text{Et}_2\text{S}_2 \cdot 2\text{C}_6\text{H}_5\text{N}$, m.p. 240° (decomp.); $\text{Pt}_4\text{Br}_2(\text{Et}_2\text{S}_2)_3 \cdot \text{NH}_4\text{Et}$; $\text{Pt}_6\text{Br}_2(\text{Et}_2\text{S}_2)_5 \cdot 2\text{CH}_3\text{Ph} \cdot \text{NH}_4$; $\text{Pt}_{10}\text{Br}_2(\text{Et}_2\text{S}_2)_9 \cdot 2\text{NHPh} \cdot \text{NH}_4$; $\text{Pt}_{10}\text{Br}_2(\text{Et}_2\text{S}_2)_9 \cdot \text{NPr}_3$. M. S. B.

Electrometric studies of the precipitation of hydroxides. XII. Reaction of sodium hydroxide on platinum chloride in solution. Reaction

of potassium cyanide on platinic chloride. H. T. S. BRITTON and E. N. DODD (J.C.S., 1933, 1429—1431).— PtCl_4 hydrolyses slowly in aq. solution, thus: $\text{PtCl}_4 + x\text{H}_2\text{O} = \text{Pt}(\text{OH})_x\text{Cl}_{4-x} + x\text{HCl}$. In presence of NaOH , x may be as high as 3, and the resultant complex has no conductivity, but combines with NaCl forming a feebly conducting complex containing Pt in the anion. Aq. PtCl_4 reacts with KCN , liberating HCN by virtue of the acid formed by hydrolysis. The $\text{Pt}(\text{OH})_3\text{Cl}$ is not decomposed by excess of KCN and no platinicyanide is formed. D. R. D.

Sulphides, selenides, and tellurides of the six platinum metals. L. WOHLER, K. EWALD, and H. G. KRALL (Ber., 1933, 66, [B], 1638—1652).—The metal chloride is intimately mixed with excess of metalloid and heated in a porcelain boat in CO_2 until reaction commences. The cold mass is powdered and transferred to a hard glass tube, which is evacuated, sealed, and heated until reaction is complete. Excess of S, Se, or Te is removed by treating the product with CS_2 followed by boiling 5% Na_2S , hot 0.5*N*- KCN , and boiling 2*N*- HNO_3 followed by dil. KOH , respectively. The products obtained are such as contain the highest % of metalloid possible under the conditions. The existence of lower compounds is investigated by their isothermal decomp. at lower temp. in H_2 or, preferably N_2 . Several sulphides are prepared from the metallic chloride and H_2S (free from H_2) at high temp. The following are described: IrS_3 and IrS_2 degraded to IrS ; IrSe_2 whence IrSe_2 ; IrTe_3 whence IrTe_2 ; Rh_2S_5 , Rh_2Se_5 , and RhTe_2 ; RuS_2 , RuSe_2 , and RuTe_2 ; OsS_2 , OsSe_2 , and OsTe_2 ; PdS_2 , PdS , PdSe_2 , PdTe_2 ; PtS_2 , PtS , PtSe_2 , PtTe_2 . A stable intermediate between OsS_2 and Os or between RuS_2 and Ru probably does not exist. The stability of the compounds towards chemical reagents diminishes with increasing at. wt. of the metalloid. H. W.

[Indirect volumetric determinations.] C. V. BORDEIANU (Arch. Pharm., 1933, 271, 514).—A reply to Eisenbrand (A., 1933, 686). R. S. C.

Determination of moisture.—See B., 1933, 1039.

Detection of chloride in presence of other halides. W. BRASH (Analyst, 1933, 58, 686).—The mixed halides are pptd. with AgNO_3 ; the ppt. is suspended in H_2O , and treated with $\text{K}_3\text{Fe}(\text{CN})_6$ and a few drops of dil. aq. NH_3 . A brown ppt. of $\text{Ag}_3\text{Fe}(\text{CN})_6$ indicates Cl' . E. C. S.

Determination of available chlorine in bleach liquor.—See B., 1933, 1008.

Determination of bromide by conversion into cyanogen bromide. S. I. SCHODTSEV (J. Appl. Chem. Russ., 1933, 6, 991—994).—Aq. Cl_2 is added to 50—100 c.c. of solution containing ≤ 2 mg. Br' , 10 c.c. of *N*- KCN are added, excess of Cl_2 is removed by aspiration, 2 g. of KI are added, and liberated I is titrated with aq. $\text{Na}_2\text{S}_2\text{O}_3$. The advantages of the use of Cl_2 as oxidant rather than KMnO_4 , KIO_3 , or KBrO_3 consist in the facility of removal of excess of oxidant, and in that the method is applicable in presence of org. impurities. R. T.

Determination of small amounts of iodine and bromine in presence of chlorine, especially in

mineral waters. G. LOCKEMANN and T. KUNZMANN (Z. anal. Chem., 1933, 94, 385—396).—(a) I' , liberated by FeCl_3 , is determined colorimetrically. (b) The total halogen is determined by titration with AgNO_3 . (c) Addition of a known, insufficient vol. of *N*- AgNO_3 ppts. $\text{AgI} + \text{AgBr} + \text{some AgCl}$. From the wt. of this, with (a), the amount of Br is calc. The amount of Cl is evaluated from (a), (b), and (c).

J. S. A.

Argentometric determination of iodides using cinchonine and bismuth nitrates as indicator. R. UZEL (Coll. Czech. Chem. Comm., 1933, 5, 383—395).—A mixture of cinchonine nitrate and $\text{Bi}(\text{NO}_3)_3$ may be used as internal indicator in the titration of I' with AgNO_3 in presence of HNO_3 . The orange-red compound $\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot \text{HBI}_4$ (I) is formed and is decomposed by AgNO_3 . The results are 0.5% low. Most common ions do not interfere. If PO_4''' or AsO_4''' is present, excess of the Bi reagent must be added to ppt. these. The titration may be performed in presence of Cl' and Br' . If $[\text{Br}'] > 4[\text{I}']$, an equal vol. of Pr^0OH should be added to suppress the ionisation of the bromide and lower the solubility of (I). If $[\text{Cl}'] > 20[\text{I}']$ or $[\text{CNS}'] > [\text{I}']$, the I' must be pptd. as AgI from NH_3 solution, reduced by Zn and acid, and then titrated as described above. In presence of CN' the titration must be carried out in strongly acid solution. $\text{Fe}(\text{CN})_6'''$ and $\text{Co}(\text{CN})_6'''$, if present in considerable quantity, should first be pptd. by means of $\text{Zn}(\text{NO}_3)_2$. The method may also be employed for the determination of Ag' by titration with KI . D. R. D.

Volumetric determination of small quantities of inorganic iodine. J. F. SADUSK, jun., and E. G. BALL (Ind. Eng. Chem. [Anal.], 1933, 5, 386—389).—Under the prescribed conditions, Winkler's method gives trustworthy results for < 1 mg. I . Cl' and SO_4'' do not interfere, unless present in high concn., $[\text{Br}']$ should not exceed $20 \times [\text{I}']$, NO_2' should be absent, and $[\text{Fe}''']$ should be $< 0.1 \times [\text{I}']$. E. S. H.

Determination of small quantities of fluorine. Steiger-Merwin reaction. I. Optimum conditions and interference. II. Procedure. H. J. WICHMANN and D. DAHLE (J. Assoc. Off. Agric. Chem., 1933, 16, 612—619, 619—624).—(1) The yellow colour of H_2O_2 -peroxidised Ti develops only at $p_{\text{H}} > 4$ and the bleaching action of F, which is the basis of the above determination, increases with increasing p_{H} to a max. at approx. 1.5 and then decreases almost to zero at 2.5. The bleaching per unit of F increases with increase in concn. of F and decrease in Ti, the sensitiveness being greatest for 0.02—0.01 mg. F, which is the lower limit of the reaction if a polarising photometer is used. Curves show the effects on the reaction of various quantities of inorg. substances (especially Al , SO_3 , P_2O_5), org. matter from apple skins, and colouring matters of fruits, and indicate that complexes are formed which invalidate the reaction because the effects on the Ti of the foreign substance and the F are not additive.

II. A procedure based on the above data is described in which the equiv. of 0.01—0.05 mg. of F is used and the p_{H} adjusted to 1.00 ± 0.02 by 1:10 HCl ; a mixture of 2 c.c. of 20% TiCl_3 and

20 c.c. of HCl is diluted to 1 litre and 2 c.c. are used. The max. errors for samples of apple peelings, cabbages, and rat-feeds containing 0.0006—0.1% NaF and 0—0.5 mg. F were -0.01% and -0.03 mg., respectively. F occurs as a natural ingredient of drinking- H_2O (0.45—3.9 p.p.m.); in manufactured phosphates as a remnant of that originally present in the rock (256—307 p.p.m.); in spray residues of apples and vegetables (1.7—135.3 p.p.m.); and in strawberry juice used as preservative (141 p.p.m.). J. G.

Determination of fluorides. I. M. KORENMAN (J. Appl. Chem. Russ., 1933, 6, 986—987).—Small quantities of F are determined with an error of $\pm 6\%$ by comparing the coloration given by the solution with 5 c.c. of 0.045% $Ti(SO_4)_2$, 3 c.c. of 3% H_2O_2 , and H_2O to 25 c.c. with that given by a standard solution. < 0.002 mg. HF per litre of air can be detected by the change in colour from violet to yellow of a test-paper dipped in Zr alizarin lake and HCl. R. T.

Fluorometry. I. I. TANANAEV (J. Appl. Chem. Russ., 1933, 6, 939—944).—Excess of SiO_2 is added to 10 c.c. of aq. NaF, the solution is made acid to Me-orange with conc. HCl, and then neutral with 0.5N-KOH (I), when 10 c.c. of 4N- $CaCl_2$ are added, and the solution is titrated with (I) (phenolphthalein); 1 equiv. of (I) is used per equiv. of F. Directions are given for the fluorometric titration of Ca, Al, Fe, and SiO_2 ; these determinations can be performed in 30 min., and are as accurate as the usual methods. R. T.

Determination of fluorine in insoluble fluorides. A. A. BORKOVSKI and N. A. PORFIREV (J. Appl. Chem. Russ., 1933, 6, 984—985).—F in fluor-spar or cryolite is determined with an error of $\pm 1\%$ by the following modification of Tananaev's method: 0.2—0.5 g. of substance is ground with 1 g. of SiO_2 and added to 40 c.c. of 25% H_2SO_4 , H_2SiF_6 is distilled off into H_2O , the distillate is made neutral with 0.25N-NaOH, and F is determined titrimetrically according to I. Tananaev (cf. preceding abstract). R. T.

Titration of sodium sulphide with potassium ferricyanide. A. A. VASSILIEV and M. E. SCHUB (J. Appl. Chem. Russ., 1933, 6, 988—990).—20 c.c. of aq. Na_2S (I) are titrated with 0.1N- $K_3Fe(CN)_6$ (II) to the appearance of a red coloration with 0.4% Na nitroprusside (III). 20 c.c. of (I), 10 c.c. of 0.5N-NaOH, 5 c.c. of (III), and 50 c.c. of H_2O are then added to the vol. of (II) used in the first titration, and the mixture is titrated further with (II), adding ≤ 1 drop every 10 sec. The Na_2S content so found is $>$ that by direct titration, during which part of the Na_2S undergoes oxidation, and is practically identical with that found iodometrically. R. T.

Flask oxidation in determination of sulphurous acid by distillation. P. F. NICHOLS and H. M. REED (Ind. Eng. Chem. [Anal.], 1933, 5, 398—399).—No means of entirely preventing oxidation in the distillation flask was discovered. E. S. H.

Inhibiting effect of certain substances on oxidation of sulphurous acid. J. S. MITCHELL, G. A. PITMAN, and P. F. NICHOLS (Ind. Eng. Chem. [Anal.],

1933, 5, 415—416).—Numerous substances, known to inhibit the oxidation of Na_2SO_3 and $NaHSO_3$ solutions, are found to inhibit the oxidation of H_2SO_3 . None of these was found effective in increasing the yield of H_2SO_3 distilled from dried fruits. E. S. H.

Direct titration of sulphate. Tetrahydroxyquinone as an internal indicator. W. C. SCHROEDER (Ind. Eng. Chem. [Anal.], 1933, 5, 403—406).— SO_4^{--} (2—20 mg. in 25 c.c.) is determined by direct titration with aq. $BaCl_2$, with tetrahydroxyquinone as indicator. The error is ± 0.2 mg. SO_4^{--} . The max. amounts of other ions permissible in the solution are: CO_3^{--} 7.5, Al^{+++} 5, SiO_3^{--} 25, Mg^{++} 15, Fe^{++} 0.1 mg.; Ca^{++} , OH^- , and Cl^- have no effect. E. S. H.

Sodium rhodizonate as an indicator for determination of sulphate ions in acid mixtures. M. N. MARUSCHKIN (J. Appl. Chem. Russ., 1933, 6, 951—962).—The results obtained by Strebing and Zombory's method (A., 1930, 53) are high, owing to adsorption of Ba and H_2SO_4 salts from the solution. In determination of pure H_2SO_4 , $BaSO_4$ adsorbs exclusively $BaCl_2$, in presence of HNO_3 $Ba(NO_3)_2$ is very strongly adsorbed, and in presence of alkali sulphates K_2SO_4 is adsorbed $>$ is Na_2SO_4 . R. T.

Determination of small amounts of selenium in pyrites.—See B., 1933, 1055.

Determination of nitrogen by burning in the flaming arc. W. D. TREADWELL and T. ZURRER (Helv. Chim. Acta, 1933, 16, 1180—1187).—The gas, containing \approx a few % N_2 and a large and therefore practically const. proportion of O_2 , is allowed to flow, at about 1 litre per min., through a flaming arc, requiring about 20 watts, between Pt electrodes. The gases are absorbed in aq. NaOH at a rate proportional to their concn. and the amount of NaOH neutralised is determined by conductometric titration. A formula from which the concn. of N_2 may be determined is deduced. The results are in good agreement with those obtained by other methods. M. S. B.

Titration of ammonia in presence of boric acid. Macro- and micro-Kjeldahl procedures. E. W. MEEKER and E. C. WAGNER (Ind. Eng. Chem. [Anal.], 1933, 5, 396—398).—The end-point is determined by colour matching with Mc-red. E. S. H.

Accurate semimicro-Kjeldahl determination. D. I. HITCHCOCK and R. C. BELDEN (Ind. Eng. Chem. [Anal.], 1933, 5, 402).—Northrop's method (A., 1933, 94) is modified by using Hg and Se simultaneously as catalysts; the mean error is 0.2%. E. S. H.

Determination of small quantities of nitrous acid by the esterification method. I. J. SCHAFERSCHTEIN (J. Appl. Chem. Russ., 1933, 6, 995—997).—Fischer and Schmidt's method (A., 1929, 667) serves for determining 0.025—5 mg. of $NaNO_2$, with certain modifications, viz., air is substituted for CO_2 for aspiration of $MeNO_2$, and Bernoulli's reagent for KI in determining $MeNO_2$. If EtOH is used in place of MeOH, the results should be multiplied by 1.075. The results are 40% low if impure MeOH is used. R. T.

Determination of nitrates in water.—See B., 1933, 1088.

Mould-growth test for minute amounts of arsenic. H. R. SMITH and E. J. CAMERON (Ind. Eng. Chem. [Anal.], 1933, 5, 400—401).—The sample is added with *Scopulariopsis brevicaulis* (Sacc.), Bainier, to a synthetic medium of Czapek's solution and agar. Small amounts of As (1 p.p.m. in a 1-g. sample) are detected by the odour of AsMe_3 , which develops within 2—5 hr. E. S. H.

Determination of traces of arsenic by Cribier's method. I. Mechanism of the method. H. GRIFFON and M. BUISSON (J. Pharm. Chim., 1933, [viii], 18, 422—437).—The method (cf. A., 1921, ii, 653) is extremely sensitive, but is essentially comparative, so that the experimental details must be followed exactly and fresh standard stains made for new reagents. With 10^{-4} to 10^{-7} g. As, the stain reaches its max. length in 20 min., when the rate of AsH_3 formation is at a max. The max. rate at which H_2 is evolved is proportional to the amount of As present. Only about 30% of the As is liberated as AsH_3 , which produces the stain. The success of the method in analysis depends entirely on the prep. of the standard stains. S. C.

Determination of silicon in sea-water. T. G. THOMPSON and H. G. HOULTON (Ind. Eng. Chem. [Anal.], 1933, 5, 417—418).— $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and H_2SO_4 are added to the sample and the colour is compared with a picric acid standard. E. S. H.

Colorimetric determination of carbon dioxide in gas mixtures. P. W. WILSON (Science, 1933, 78, 462—463).—The method previously described (A., 1932, 1222) is modified for routine analyses so that p_{H} is determined colorimetrically. L. S. T.

Distillation of hydrocyanic acid from sulphuric acid solutions. Determination [of cyanides]. S. MORRIS and V. G. LILLY (Ind. Eng. Chem. [Anal.], 1933, 5, 407—408).—The presence of Cl' does not adversely affect the distillation. Rubber stoppers and corks absorb HCN and should be protected by Sn foil. In absence of $\text{Fe}(\text{CN})_6^{4-}$ and taking the prescribed precautions the method of Pagel and Carlson (A., 1933, 137) is accurate to 0.05%. E. S. H.

Determination of alkalis as silicofluorides. W. D. TREADWELL and W. KONIG (Helv. Chim. Acta, 1933, 16, 1201—1208).—If hydrated SiO_2 containing NaCl is evaporated to dryness on the H_2O -bath with HF, Na passes quantitatively into Na_2SiF_6 and can thus be accurately determined. Na_2SiF_6 gives an acid reaction in solution, owing to the formation of HF, and the result obtained gravimetrically may be checked by treating the solution of Na_2SiF_6 with CaCl_2 . CaF_2 , hydrated SiO_2 , and free acid are formed, and the acid may be titrated electrometrically or by using an indicator such as bromocresol-purple, since there is a sharp end-point at p_{H} 5.7. By combining the gravimetric and electrometric methods, binary mixtures of the alkalis may be determined. If Mg is present it is first removed by pptn. with hydroxyquinoline. The method is also suitable for micro-determinations. M. S. B.

Separation of alkalis in silicate analysis and the titrimetric determination of potassium. P. N. GRIGORIEV (Sprechsaal Keram., 1933, 66, 162—

163; Chem. Zentr., 1933, i, 3766).—After opening up with $\text{HF} + \text{H}_2\text{SO}_4$ the excess of acid is removed by gentle ignition until fumes of SO_3 are no longer evolved. $\text{Ba}(\text{OH})_2$ is added instead of BaCl_2 and the excess, together with basic constituents other than alkalis, removed with $(\text{NH}_4)_2\text{CO}_3$ and aq. NH_3 , or by passing CO_2 into the alkaline solution. K is determined by a modification of the cobaltinitrite method. A. A. E.

Titrimetric determination of perchlorates: microanalysis of potassium. A. BOLLIGER (Z. anal. Chem., 1933, 94, 403—408).—The perchlorate (I) and picrate of methylene-blue (II) are sol. in CHCl_3 . To the solution of the perchlorate to be determined is added 0.001N-(II) in slight excess, $+\text{NaH}_2\text{PO}_4$ as buffer $+\text{CHCl}_3$ to extract (I). Excess of (II) is determined by titration with 0.001N-picric acid, the picrate being extracted with CHCl_3 from the H_2O layer until colourless. When > 1 mg. ClO_4^- is present, (I) may be removed by centrifuging before extraction. 0.025 mg. KClO_4 may be determined to within 5% in presence of SO_4^{2-} or PO_4^{3-} . J. S. A.

Comparison of colorimetric methods for determining potassium. F. ALTEN, H. WEILAND, and K. KURMIES (Z. Pflanz. Düng., 1933, 32, A, 171—182).—The cobaltinitrite ppt. obtained by the methods of Wrangell (B., 1933, 162), of Herzner (A., 1931, 1259), and of Fischer (*ibid.*) contains more Na than is required by $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$. By pptn. in presence of saturated NaCl solution, $\text{K}_3[\text{Co}(\text{NO}_2)_6] \cdot \text{Na}_3[\text{Co}(\text{NO}_2)_6]$ (I) is invariably produced. In the Wrangell colorimetric method the colour intensity is proportional to the concn. only in the range $(10—300) \times 10^{-6}$ g. N_2O_3 in 100 c.c. Moreover, the nitrosoindole solution is unstable. Riegler's naphthol reagent is suitable for concns. $> 15 \times 10^{-6}$ g. N_2O_3 in 100 c.c. The colour obtained by Griess' reagent is suitably permanent and is applicable over wide ranges of $[\text{NO}_2^-]$. Details are given of a modified method involving pptn. of K as (I). A. G. P.

Determination of sodium as sodium triuranyl magnesium acetate. F. ALTEN, H. WEILAND, and E. HILLE (Z. Pflanz. Düng., 1933, 32, A, 129—140).—The methods of Blanchetiere (A., 1923, ii, 579) (1), of Weiland (A., 1928, 383) (2), and of Kahane (A., 1930, 726, 880) (3) are compared. In (1) and (2), the use of BaCl_2 instead of $\text{Ca}(\text{OH})_2$ and uranyl acetate is recommended for the removal of PO_4^{3-} prior to the pptn. of the Na salt. Excessive amounts of K are pptd. by tartaric acid instead of EtOH. In (3) the inclusion of EtOH in the reagent solution is impracticable in the presence of K^+ , Ba^{2+} , NH_4^+ , or CaSO_4 . Details are given for the analysis of fertiliser materials, plant ash, and soil extracts, and for the recovery of U from wash liquors etc. A. G. P.

Direct determination of sodium in presence of large amounts of calcium, magnesium, and ammonium. T. NODA (J. Soc. Chem. Ind. Japan, 1933, 36, 635B).—The uranyl Mg acetate method (cf. A., 1930, 726) gave an accuracy of 1% in the determination of Na (1—2 mg. NaCl) in presence of CaCl_2 , MgCl_2 , or NH_4Cl (2.0 g.) at the dilutions (per c.c.) 0.1 g. Ca, 0.07 g. Mg, or 0.04 g. NH_4 . R. S.

Microchemical detection of rubidium in presence and absence of caesium. N. A. TANANAEV, A. G. KANKANJAN, and M. V. DARBINJAN (*J. Appl. Chem. Russ.*, 1933, 6, 980—983).—The min. concn. in which Rb can be detected as $\text{Rb}_2\text{AuPdCl}_7$ (I) is 0.3 mg. per c.c. in absence, and 0.2 mg. in presence, of Cs and other cations; Cs can similarly be detected as $\text{Cs}_2\text{AuPdCl}_7$ (II) in $< 0.0004N$ solutions. The crystals of (I) and (II) are octahedral when pptd. from 0.1N and cruciform when pptd. from $< 0.1N$ solutions. Rb cannot be detected by the above method in solutions in which $[\text{Rb}]:[\text{Cs}] > 1:4$. Cs may be separated by pptn. as CsBiF_4 (A., 1932, 1010).

R. T.

Iodometric determination of silver. (MILLER.) M. L. JOSSEN (*Compt. rend.*, 1933, 197, 1324—1326; cf. A., 1928, 1391; 1931, 1023).—The reactions consequent on mixing an I-iodide solution with one of AgNO_3 are: (a) $\text{KI} + \text{AgNO}_3 = \text{AgI} + \text{KNO}_3$; (b) $\text{I}_2 + \text{H}_2\text{O} + \text{AgNO}_3 = \text{AgI} + \text{HOI} + \text{HNO}_3$; (c) $\text{HOI} + \text{KI} = \text{I}_2 + \text{KOH}$; and (d) $3\text{HOI} + 3\text{AgNO}_3 = 2\text{AgI} + 3\text{HNO}_3 + \text{AgIO}_3$ (pptd.); the pptn. of AgIO_3 vitiates the result. The change of tint (starch being present) occurs when the no. of mols. of AgNO_3 added equals that of mols. of KI + half the no. of atoms of I [(a) and (b) above]. For accurate work aq. AgNO_3 should be poured into aq. KI with addition of only one drop of EtOH —I, thus avoiding the difficulty resulting from (d). C. A. S.

Silver electrodes "of the second kind" as comparison and indicator electrodes. W. HILTNER (*Z. anal. Chem.*, 1933, 95, 37—43; cf. A., 1933, 1027).— AgCl , AgBr , AgI , or Ag_2S electrodes, stabilised by addition of aq. NaCl , AgNO_3 , or Ag_2SO_4 , may be used as comparison electrodes, or as indicator electrodes in determining Ag in presence of oxidising agents, or for the respective anions. The halides may be fused on to a Pt wire. They are unsuitable for pptn. reactions with PO_4''' , CrO_4'' , or $\text{C}_2\text{O}_4''$. The Ag_2S electrode may be used in cyanometric Ni determinations.

H. J. E.

Analytical and quantitative lines of silver, arsenic, bismuth, cadmium, copper, mercury, lead, antimony, and tin in the arc spectrum, between 2330 Å. and 3400 Å. S. PINA DE RUBIES and M. A. BARGUES (*Z. anorg. Chem.*, 1933, 215, 205—210).—The substance to be examined is diluted with NaCl to concns. from 1% to 0.0001%, and 0.05 g. of the mixture is used. It also contains 0.5% Mo as reference element. Intensities obtained from spectrographs of three different resolving powers are recorded. Analytical lines are those for the 1% mixture. They are always the same if the same quantity of substance is vaporised. Quant. lines are those analytical lines the intensities of which are not changed by the electrical conditions of the arc within certain limits.

M. S. B.

Magneto-optic Nicol rotation method for quantitative analysis of calcium. E. R. BISHOP, C. B. DOLLINS, and I. G. OTTO (*J. Amer. Chem. Soc.*, 1933, 55, 4365—4370).—The procedure described is suitable for $[\text{Ca}]$ between 3.74×10^{-12} and 1×10^{-3} g. per c.c. More conc. solutions are diluted. The results are not influenced by the presence of Mg^{++} , Na^+ , NH_4^+ , H^+ , SO_4'' , NO_3' , or PO_4''' . The error in duplicate deter-

minations or in comparison with KMnO_4 titrations is about 10%. E. S. H.

Volumetric determination of the hardness of water.—See B., 1933, 1038.

Determination of calcium in lead-calcium alloys.—See B., 1933, 1062.

Determination of magnesium by the drop method. N. A. TANANAEV and P. S. SAVTSCHENK (*J. Appl. Chem. Russ.*, 1933, 6, 970—975).—1—1.5 c.c. of 2N- NH_4Cl , excess of N- Na_2CO_3 , and 2—3 drops of aq. H_2O_2 are added to 2—3 c.c. of solution (I), which is then boiled and filtered. A few drops of aq. NH_3 and of aq. Na_3PO_4 are added to the filtrate (II), where a ppt. of $\text{Mg}_2\text{P}_2\text{O}_7$ (III) indicates the presence of < 0.02 mg. of Mg per c.c. of (I). The presence of other cations does not interfere, but AsO_4''' and PO_4''' should previously be removed. Mg may be determined as (III) gravimetrically or nephelometrically, or by removing NH_4^+ from (II) by aq. CH_2O , pptg. Mg as $\text{Mg}(\text{OH})_2$ by aq. alkali, and weighing the Mg obtained by igniting $\text{Mg}(\text{OH})_2$. R. T.

Qualitative analysis of the hydrogen sulphide group without ammonium polysulphide. R. W. HUFFERD (*Ind. Eng. Chem. [Anal.]*, 1933, 5, 422). The solution is boiled with aq. Br, excess of Br is driven off, H_2S is passed, and the ppt. is treated with freshly prepared NH_4HS . E. S. H.

Qualitative analysis of small amounts of minerals. II. Detection of small amounts of zinc with dithizone. G. RIENACKER and W. SCHIEFER (*Z. anal. Chem.*, 1933, 94, 409—415; cf. A., 1932, 588).—A CCl_4 solution of dithizone gives with alkaline Zn solutions a red coloration in the H_2O layer which is sp. (limit 5×10^{-6} g.). Cd, Cu, and Hg interfere and must first be removed by H_2S . J. S. A.

Precipitation conditions of zinc sulphide and aluminium hydroxide, and the gravimetric separation of zinc from aluminium. J. N. FRERES (*Z. anal. Chem.*, 1933, 95, 1—36).— $(\text{NH}_4)_2\text{SO}_4$ is added to the solution containing Zn, preferably as ZnSO_4 and with little Cl', and H_2SO_4 added until it is just acid to Me-orange. Zn is pptd. in hot solution as ZnS by H_2S , finely-divided filter-paper being present. The ppt. is ignited in H_2S and weighed as ZnS . Factors affecting the separation and pptn. are discussed. The potentiometric determination of Zn in presence of NH_4Cl , NH_4CNS , and $(\text{NH}_4)_2\text{SO}_4$ indicates complex ion formation. H. J. E.

Determination of lead as carbonate and its separation from silver by means of carbonic acid in dilute pyridine solution. A. JILEK and J. KOŤA (*Coll. Czech. Chem. Comm.*, 1933, 5, 396—410).—The neutral solution, containing > 0.2 g. of Pb and > 0.2 g. of Ag, is diluted to 80 c.c., 5 c.c. of EtOH and 15 c.c. of 10% aq. $\text{C}_5\text{H}_5\text{N}$ are added, and CO_2 is passed for 45 min. After 2—3 hr., CO_2 is passed again for 5 min., and the ppt. is collected and washed with H_2O saturated with CO_2 and containing 4% EtOH and 0.4% $\text{C}_5\text{H}_5\text{N}$. The ppt. may be dried at 120° and weighed as PbCO_3 , or ignited and weighed as PbO . The Ag may be pptd. from the filtrate by means of HCl . D. R. D.

Spectrographic adsorption measurements with metal ion solutions at powder surfaces. E. BERL and B. SCHMITT (Kolloid-Z., 1933, 65, 264—267).—Analysis of ultimate rays allows the detection of 0.001% of Cu, Pb, Zn, or Cd in mineral powders.

E. S. H.

Use of amyl alcohol in the sodium diethyldithiocarbamate method for determination of copper. R. W. THATCHER (J. Amer. Chem. Soc., 1933, 55, 4524).—*iso*Amyl alcohol, redistilled at 129—131°, is preferred to *n*-amyl alcohol.

E. S. H.

Application of diphenylcarbazine and diphenylcarbazone to mercurimetric microtitration. J. V. DUBSKY and J. TRTÍLEK (Chem. Listy, 1933, 27, 385—388).—Diphenyl-carbazide and -carbazone give intense violet colorations in presence of Hg^{++} . Accurate results are obtained using these indicators in titration of Cl^- by 0.01*N*- $\text{Hg}(\text{NO}_3)_2$; Cu^{++} , Cd^{++} , Co^{++} , Fe^{++} , Ca^{++} , and Ba^{++} do not interfere. The solution titrated should contain a small excess of HNO_3 .

R. T.

Detection of europium, and three lines of extreme sensitivity. G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], 17, 1092—1094).—The three lines 4661, 4627, and 4594 Å. of Eu are shown very persistently in the flame spectrum of that element even when only a trace of it is mixed with Nd-Sa-Gd mixtures, and they may serve to detect Eu in such mixtures.

O. J. W.

Drop reaction for aluminium. S. N. POTSHCHINOK (J. Appl. Chem. Russ., 1933, 6, 948—950).—Al is detected in presence of other cations by adding excess of $(\text{NH}_4)_2\text{S}$, acidifying with 2*N*-HCl, boiling, and filtering. 0.05% Na alizarinsulphonate and an equal vol. of 5% $\text{Na}_2\text{S}_2\text{O}_3$ are added to the filtrate, and the solution is boiled during 1 min.: if < 0.04 mg. Al is present the ppt. of S is coloured rose to orange-red.

R. T.

Micro-analysis of aluminium. I. Determination of iron, copper, and manganese.—See B., 1933, 1062.

Tervalent manganese. VIII. Determination of MnO_2 in pyrolusite by thermal degradation to Mn_2O_3 . W. FRANKE and A. FREITAG (Z. anorg. Chem., 1933, 215, 105—110; cf. A., 1930, 179).—The thermal deoxygenation of MnO_2 in artificial "pyrolusites" is influenced by the nature of the other substances present, and no definite temp. can be prescribed for the change $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$. Determinations based on extraction with dil. H_2SO_4 are also unsatisfactory.

F. L. U.

Colorimetric determination of iron with sulphosalicylic acid. F. ALTEN, H. WEILAND, and E. HUIE (Z. anorg. Chem., 1933, 215, 81—91).—Extinction coeffs. of mixtures of sulphosalicylic acid with acid and alkaline Fe solutions in presence of various foreign substances (B., 1932, 50) have been measured. The colour is influenced by $[\text{H}^+]$, PO_4^{---} , Mn^{++} , and org. substances. Procedure is described, involving the use of citrate buffers and colour filters, whereby disturbances due to the factors named, other than Mn^{++} , may be eliminated.

F. L. U.

Antimony as an indicator electrode in potentiometric titration of iron and aluminium. E. W. KANNING and F. H. KRATLI (Ind. Eng. Chem. [Anal.], 1933, 5, 381—383).—Sb is a suitable indicator electrode for the pptn. of Fe^{+++} and Al from neutral solutions of their chlorides by adding NaOH. Mixtures of FeCl_3 and AlCl_3 can be determined approx., especially when present in equal proportions.

E. S. H.

Increased sensitivity of a microchemical reaction for Co^{++} and Cu^{++} , and the induced reaction of Fe^{++} , Fe^{+++} , and Ni^{++} . I. M. KORENMAN (Z. anal. Chem., 1933, 95, 44—48).—Co-pptn. of $\text{Co}[\text{Hg}(\text{CNS})_4]$ (blue), or $\text{Cu}[\text{Hg}(\text{CNS})_4] \cdot \text{H}_2\text{O}$ (yellowish-green), with $\text{Zn}[\text{Hg}(\text{CNS})_4]$ (white) by $(\text{NH}_4)_2[\text{Hg}(\text{CNS})_4]$ increases the sensitivity for Co^{++} and Cu^{++} 25- and 16-fold to 1:10⁵ and 1:1.3×10⁵, respectively. Salts of Fe^{++} , Fe^{+++} , and Ni^{++} give no ppt. with $(\text{NH}_4)_2[\text{Hg}(\text{CNS})_4]$ alone, but form characteristic mixed crystals in presence of Zn^{++} .

H. J. E.

Determination of small quantities of nickel in rock analysis. H. F. HARWOOD and L. S. THEOBALD (Analyst, 1933, 58, 673—682).—In ordinary routine analysis Ni is partly co-pptd. with the R_2O_3 oxides, but not completely, even in the presence of Br and NH_3 . A correction must be applied to the Al_2O_3 for the Ni co-pptd. Ni is not co-pptd. with SiO_2 , CaO, or MgO. Ni is determined directly, on a separate sample of rock, in presence of Fe, Al, Ca, Mg, and alkalis (citric acid being added to prevent pptn. of the R_2O_3 oxides) by pptn. with dimethylglyoxime (I). α -Furildioxime can replace (I) and is preferable when < 0.02% of Ni is present. 0.0025% of NiO can be detected in 2 g. of rock.

E. C. S.

Determination of nickel and small quantities of aluminium in heat-resistant alloys.—See B., 1933, 1014.

Electrolytic determination of chromium with rotating mercury electrode. P. S. TUTUNDŽIĆ (Z. anorg. Chem., 1933, 215, 19—22; cf. A., 1932, 243).—By using a rotating Hg cathode the time required for electrolytic determination of 0.1—0.2 g. of Cr may be reduced to 120 min.

F. L. U.

Application of the potential-forming system metal/metal anion to potentiometric titrations. I. Precipitation titration of chromate, molybdate, and tungstate, and of some metal ions, using chromium, molybdenum, and tungsten indicator electrodes. H. BREINTZINGER and E. JAHN (Z. anal. Chem., 1933, 94, 396—403).— CrO_4^{--} , MoO_4^{--} , and WO_4^{--} may be titrated potentiometrically, preferably at 95°, against 0.1*N*- BaCl_2 , using Cr-plated stainless steel, Mo or W wire, respectively, as electrode. Ba, Sr, Pb, Cu, Cd, and Mn may be determined similarly by titration with Na_2MoO_4 . For Sr and Mn, 30—40 vol.-% of EtOH should be added. Na_2CrO_4 and Na_2WO_4 may also be used.

J. S. A.

Electro-analytic determination of chromium at a rotating mercury electrode. P. S. TUTUNDŽIĆ (Bull. Soc. Chim. Yougoslav., 1933, 4, 101—105).—The method previously described (A., 1932, 243) gives good results for the determination of Cr.

R. T.

Determination of titanium in steel.—See B., 1933, 1060.

Determination of zirconium in steel.—See B., 1933, 1060.

Qualitative analysis of small amounts of minerals. III. Detection of tantalum and niobium. G. RIENACKER and W. SCHIFF (Z. anal. Chem., 1933, 94, 415—422; cf. this vol., 48).—Ta is detected by the pptn. of tantalic acid from acid solution. The mineral is fused with NaHSO_4 , dissolved in dil. $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$, and H_2SO_3 added. The solution is boiled, H_2SO_3 being slowly added to replace evaporated H_2O . Pptn. of Ta, but not Nb if alone, occurs in 10—15 min. Yellow WO_3 , sol. in NaOH, is also pptd. H_3PO_4 or a large excess of SiO_2 interferes. Nb in 0.5 c.c. of the dil. H_2SO_4 solution from a NaHSO_4 fusion is reduced to Nb^{III} by Zn, 0.5 c.c. of alizarin in EtOH added, then 0.4 c.c. of 10% H_2SO_4 + 1 drop of saturated aq. Na tartrate + 1 drop of saturated aq. NaOAc. In presence of Nb, a red Nb-alizarin lake of indefinite composition is pptd.

J. S. A.

Spectro-analytic investigation of purest platinum. W. GERLACH (Physikal. Z., 1933, 34, 846; cf. A., 1933, 800).—The following specifications are given: technically pure Pt, 99.5%; chemically pure, impurity 0.01—0.1%; physically pure, 0.001—0.01%; spectroscopically pure, < 0.001%.

A. J. M.

Sources of error in liquid thermometers due to the behaviour of the indicator. W. GRUNDMANN (Z. Physik, 1933, 86, 550—554).—The effect of compressibility, gas absorption, distillation, and contraction of the liquid on the accuracy of these thermometers is discussed.

A. B. D. C.

Modified design for mercury bulb of thermostat. G. B. HEISIG and A. E. CAMERON (Ind. Eng. Chem. [Anal.], 1933, 5, 420—421).—The bulb is filled with Hg, has a large surface, but uses a small amount of Hg. The device enables a 25-litre thermostat to be kept at $25 \pm 0.002^\circ$.

E. S. H.

Automatic cryostat. A. E. CAMERON (Rev. Sci. Instr., 1933, [ii], 4, 610—611).—An apparatus for the range 0° to -70° , with a max. variation of $\pm 0.1^\circ$, to operate for 12—24 hr., is described. Cooling liquid is forced from a reservoir, an equal vol. of liquid being automatically siphoned back from the bath.

N. M. B.

Determination of heat of dissolution. M. M. POPOV, K. G. CHOMJAKOV, N. N. FEODOSSJEV, and P. K. SCHIROKICH (Z. physikal. Chem., 1933, 167, 29—34).—With calorimeters so constructed as to permit thorough mixing of the contents and consisting solely of metal parts not projecting far out of the liquid the adiabatic method of operation and the usual method give the same result. The mol. heat of dissolution of KCl in 200 mols. of H_2O at 20° is $-4.376 \pm 0.1\%$ kg.-cal.₁₅

R. C.

Vacuum annealing furnace. E. F. LOWRY (Rev. Sci. Instr., 1933, [ii], 4, 606—609).—The furnace tube and heater elements are constructed of 80:20 Cr-Ni; rubber gaskets are replaced by picein wax joints.

N. M. B.

Wide-angle magnetic spectrometer. C. D. BOCK (Rev. Sci. Instr., 1933, [ii], 4, 575—580).—An instrument for focussing widely divergent ions is described. By a suitable variation in the intensity of the deflecting magnetic field, a second-order focus is obtained.

N. M. B.

Use of thermionic valves and undamped high-frequency oscillations in quantitative spectrum analysis. G. POTAPENKO (Z. anorg. Chem., 1933, 215, 44—48).—An arrangement for generating a.c. at 80—100 kv. and $>10^6$ cycles for the production of spark spectra is described. The spark is very const. and analytical results are reproducible. The spectra are practically free from air lines.

F. L. U.

Production of astigmatism in spectrographs by inclining lenses. A. COUDER (Compt. rend., 1933, 197, 1199—1201).—A method for enlarging the image of a spectral line as it falls on a photographic plate, by means of astigmatism caused by inclining the lenses by rotating them around an axis parallel to the edges of the prism, is described.

C. A. S.

Rontgengoniometer. E. SCHIEBOLD (Z. Krist., 1933, 86, 370—383).—The instrument ("rotation rontgengoniometer") resembles in principle that of Sauter (cf. A., 1933, 451, 480); anticipation is claimed.

C. A. S.

Measurement of vibration ellipse by means of elliptically polarised light of great ellipticity. C. MUNSTER (Z. Krist., 1933, 86, 325—334).

C. A. S.

Complementary colour relations. E. GENBERG (Proc. Physical Soc., 1933, 45, 836—840).—Pairs of wave-lengths have been determined which are complementary with respect to equi-energy radiation taken as white. The energy and luminosity of one of the complementaries for unit luminosity of the white are given.

J. W. S.

Nephelometry.—See B., 1933, 991.

Fluorescence testing.—See B., 1933, 1067.

Unidirectional photo-cells. F. ROTHER and H. BOMKE (Physikal. Z., 1933, 34, 865—870).—Methods are described for the improvement of the efficiency of unidirectional Cu_2O cells. A thin layer of Cu_2O is best, but there is a practical limit to this. The efficiency can be increased by preparing the Cu_2O layer in an atm. of H_2O vapour. The addition of a foreign metal to the Cu on which the Cu_2O is formed may alter the properties of the latter, owing to the presence of the foreign metal in the diffusion layer. If the Cu is alloyed with a metal which is permeable to, or dissolves, O_2 , e.g., Ag, the Cu_2O may be formed between a zone of Cu and one of the added metal. Cells with this arrangement are more efficient.

A. J. M.

Light beam of uniform intensity of cross-section. J. T. LAY and I. C. CORNOG (Rev. Sci. Instr., 1933, [ii], 4, 600—602).—For the measurement of the intensity of a beam of light at any point in its cross-section a photo-electric method is described, leading to the production of a beam varying in intensity by <0.3% over an area of 30 sq. cm.

N. M. B.

Reduction of grain effects in microphotometer readings. S. HARRIS (Rev. Sci. Instr., 1933, [ii], 4, 598—599; cf. Richtmyer, A., 1933, 800).—Grain effect is reduced by the use of a slit of adjustable width and length. N. M. B.

Microphotometer. J. WEIGLE (Rev. Sci. Instr., 1933, [ii], 4, 595—597).—The instrument embodies a simple device for controlling the movement of the photographic plate and the device for recording the galvanometer deflexions. N. M. B.

Improved design of the mechanical interval sorter and its application to the analysis of complex spectra. G. R. HARRISON (Rev. Sci. Instr., 1933, [ii], 4, 581—586).—The machine previously described (cf. A., 1933, 247) is improved to record groups of lines containing a no. of lines given by their frequency density. Motor drive is employed; the tape will record in either direction, and improved calibration of the tape eliminates errors due to stretch. Intervals up to 10,000 wave nos., accurate to ± 0.02 wave no., can be recorded. Applications to the spectra of Os, Ir, and Ce are given. N. M. B.

Apparatus for determination of p_H . W. HUTTINGER (Woch. Brau., 1933, 50, 338—339).—The circuit consists of the solution of unknown p_H connected to a standard acid solution by a KCl-agar bridge and a capillary electrometer. After addition of a little quinhydrone to each cell alkali is run into the acid until a null point is reached, and the p_H calc. from the titration val. The method is rapid and accurate. R. H. H.

Stabilising of cold-cathode X-ray tubes. I. FANKUCHEN (Rev. Sci. Instr., 1933, [ii], 4, 593—594).—Instability due to irregular gas emission from parts of the tube subjected to electrical discharges is eliminated by confining the intense electrical fields in the tube to regions where the length of the lines of force is $<$ the mean free path of the ions at the existing gas pressure. N. M. B.

Variation of electrical conductivity of dielectrics with temperature in a range from 20° to -110°. S. SHIMIZU (Sci. Rep. Tôhoku, 1933, 22, 662—686).—In general, a linear relation between the log of the conductivity and $1/T$ exists for quartz, cristobalite, kaolin, filter-paper, selenite, volcanic glass, ebonite, and mica, but with most of these, sharp changes of slope occur at sp. temp. In some cases, these anomalies are correlated with the presence of H₂O. J. G. A. G.

Simple high [electrical] resistance. I. C. JONES (Nature, 1933, 132, 823; cf. A., 1933, 1265). L. S. T.

Amplification and recording of rapid Geiger-Muller counter impulses. G. L. LOCHER (J. Franklin Inst., 1933, 216, 553—558).—A circuit which is of high sensitivity and can record up to 1400 impulses per sec. is described. The true no. of impulses is $Nx/(1 - e^{-x})$, where N is the observed no., and x is the average no. of impulses occurring in the resolving time of the apparatus. Photo-electric processes play an important part in the recovery time of counters. A. G.

Demonstration experiment. Barkhausen effect up to the Curie point. O. TESCHE (Physikal. Z., 1933, 34, 879).—A ferromagnetic wire, heated by a.c., is surrounded symmetrically by a ring-coil. The Barkhausen effect can be shown to disappear on passing through the Curie point. A. J. M.

Absolute measurement of magnetic fields. H. AUER (Ann. Physik, 1933, [v], 18, 613—624).—A method is described for measuring intense magnetic fields (about 8000 gauss) with an accuracy of $\pm 0.026\%$. J. W. S.

Use of glass filter apparatus in the determination of the adsorptive or catalytic activity of technical adsorbents. F. KRCZIL (Chem.-Ztg., 1933, 57, 803—805).—Porous glass plates (I) are useful for removing suspended solids from gas streams, for efficient scrubbing of gases by liquids, for saturating gases with the vapours of liquids, and for removing suspended liquid particles from saturated gases. (I) can also be used for absorbing indicators for detecting the presence of certain constituents in gas currents. Various types of apparatus containing (I) in different forms for the above and other purposes are illustrated. A. R. P.

Filtering device. E. B. KESTER (Ind. Eng. Chem. [Anal.], 1933, 5, 422). E. S. H.

Automatic pipette washer. E. HOWELL and F. M. FRANK (Amer. J. Public Health, 1933, 23, 1186). E. C. S.

Burette fitted with reservoir. M. CHATRON (Bull. Soc. Chim. biol., 1933, 15, 1154—1155). H. D.

Weighing burette. J. CORNOG and R. CORNOG (Ind. Eng. Chem. [Anal.], 1933, 5, 408). E. S. H.

Apparatus for microanalysis of gas. J. S. SWEARINGEN, O. GERBES, and E. W. ELLIS (Ind. Eng. Chem. [Anal.], 1933, 5, 369—370).—Blacet and Leighton's method is modified. E. S. H.

New apparatus for gas analysis. A. G. SUVOROV (J. Appl. Chem. Russ., 1933, 6, 1005—1009).—Apparatus for analysis of gases containing CO₂, O₂, CH₄, C₂H₆ and higher hydrocarbons, H₂, N₂, H₂S, NO, and NO₂ is described. R. T.

Stirring rod with fritted glass disc. J. E. S. HAN (Ind. Eng. Chem. [Anal.], 1933, 5, 421). E. S. H.

Apparatus for the determination of m.p., b.p., transition points, ignition temperatures, etc., specially for use with a small quantity of sample. S. WATANABE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 264—268).—The material is placed in a cup surrounding one of two Cu-constantan junctions connected to a recording galvanometer. The temp. of the enclosing vessel is indicated thermoelectrically and a record of the thermal changes in the material is obtained. R. S.

Instrument for rapid determination of moisture.—See B., 1933, 991.

Simplified micro-comparator. W. STIRLING (Analyst, 1933, 58, 684—686).—Apparatus for simultaneous examination of objects at distances up to 30 cm. apart is described. E. C. S.

Laboratory drain-tray. J. L. WILSON (Ind. Eng. Chem., 1933, 25, 1216).—A portable enamelled tray is illustrated. C. I.

Determination of surface and interfacial tensions. J. C. SPEAKMAN (J.C.S., 1933, 1449—1453).—The difference between the pressures required to depress to the same horizontal level the menisci in two capillary tubes of different diameter is an exact measure of the surface or interfacial tension. Data for C_6H_6 , H_2O , $C_6H_6-H_2O$, Et_2O-H_2O , and $CHCl_3-H_2O$ are recorded and the special advantages of the method are emphasised. J. G. A. G.

Recovery of iodine from metallic iodides by oxidation with technical nitric acid. R. F. McCLEARY and E. F. DEGERING (Ind. Eng. Chem. [Anal.], 1933, 5, 420).—A suitable apparatus is described. E. S. H.

Bumping prevention. J. E. S. HAN (Ind. Eng. Chem. [Anal.], 1933, 5, 362).—A sieve plate of Ag or Pt is recommended. E. S. H.

Continuous liquid extractor. A. MAZUR, R. ROSENTHAL, and B. HARROW (Ind. Eng. Chem. [Anal.], 1933, 5, 419). E. S. H.

Apparatus for filling large closed-end manometers. A. E. CAMERON (Ind. Eng. Chem. [Anal.], 1933, 5, 419). E. S. H.

Concentration gradient in the ultra-centrifuge cell. O. LAMM (Nature, 1933, 132, 820—821).—A new refraction method for determining the concentration gradient in a sedimentation equilibrium is described. L. S. T.

Ultracentrifuge. J. W. BEAMS, A. J. WEED, and E. G. PICKELS (Science, 1933, 78, 338—340).—Details of a high-speed, air-driven centrifuge are given. L. S. T.

Paper hygrometers. G. R. R. BRAY (Nature, 1933, 132, 857). L. S. T.

Paper hygrometers. P. H. PRIOR (Nature, 1933, 132, 857).—In comparatively still air the rate of change of stretch may, after an initial period, become so small that a condition resembling equilibrium is reached. Air velocity is thus an important factor. L. S. T.

Cellophane in the determination of humidity. E. SCHWEITZER (Naturwiss., 1933, 21, 784—787).—Cellophane (I) is very permeable to H_2O vapour, and could be used to cover hygrometers (II) to prevent access of dust and corroding fumes. It is also hygroscopic, and (II) could be constructed based on the gain in wt. The degree of humidity can also be found by impregnating (I) with $CoCl_2$ and noting the colour change, preferably by finding the absorption

limit in the ultra-violet. The extension which (I) undergoes on taking up H_2O can be made the basis of portable (II). The absorption of H_2O also alters the strength of (I), and the R.H. can be determined by finding the pressure required to burst a membrane of (I), and its curvature. (I) can be used in standardising hygrometers by placing a mass of (I) which has taken up H_2O in the instrument. A. J. M.

Continuously operating laboratory apparatus for high-pressure reactions. L. VON SZESZICH and H. VOLLBRECHT (Chem. Fabr., 1933, 6, 469—471).—The reaction vessel (a 25-c.c. steel tube) is connected to a pump and a compressor for introducing liquid and gas, respectively, a condenser, a separator, and a pressure gauge, and is surrounded by an electrically heated furnace. The apparatus is specially designed for small-scale studies of gas- and liquid-phase reactions of all kinds. H. F. G.

Solubility of sulphur dioxide in tap lubricants. M. FRANCIS (Rev. Sci. Instr., 1933, [ii], 4, 615—619).—Pressure-solubility curves are given for lanoline, Ramsay Fett, beeswax-vaseline grease, H_3PO_4 , Apiczon, picein, and white sealing-wax. N. M. B.

Simple agitation device. G. W. MARKS (Science, 1933, 78, 483).—An oil-can, suitably cut and suspended, is oscillated by a stream of compressed air. L. S. T.

Griffiths' sensitive manometer. P. C. VINCENT (Proc. Physical Soc., 1933, 45, 808—832).—The instrument is analogous to the H_2O U-tube manometer, but with an aq. solution of uranine in place of H_2O , and pure air-free H_2O in place of air. The accuracy is $\pm 1\%$ over the pressure range 2—20 dynes per sq. cm. J. W. S.

Griffiths' method for determining a small change in the density of a liquid. P. C. VINCENT (Proc. Physical Soc., 1933, 45, 833—835).—The dissolution of glass by H_2O and the resulting increase in d of the latter have been followed by means of the special manometer (cf. preceding abstract). The d of H_2O does not change appreciably during weeks of contact with SiO_2 . J. W. S.

Gasometric determination of density of solids. J. PIAZZA (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 64—70; Chem. Zentr., 1933, ii, 911).—The substance is placed in one of two horizontal single-bulbed capillary tubes in which the movement of a Hg meniscus caused by changes of pressure is observed. The vol. or d is determined with the aid of a graph. A. A. E.

Century of progress in chemistry. A. B. LAMB (Science, 1933, 78, 371—376).—An address. L. S. T.

Geochemistry.

Ultra- γ -radiation. E. A. SMITH and F. M. SMITH (Bul. Soc. Stiinte Cluj, 1932, 7, 104—112; Chem. Zentr., 1933, ii, 175).—Results of measurements of ultra- γ -radiation in Australia, Canada, Greenland, Spitzbergen, and India are reported. A. A. E.

Absorption of ultra-violet radiation in the lower atmosphere. L. HERMAN (Compt. rend., 1933, 197, 1342—1344).—Ten absorption bands, degraded towards the red, have been observed between λ 2400 and 2800; 8 have been measured. All are

triple, the other constituents being much fainter, and resembling those of O_2 under pressure (cf. A., 1932, 891; 1933, 759). C. A. S.

Origin of atmospheric ozone. A. DAUVILLIER (Compt. rend., 1933, 197, 1339—1341).—The O_3 content at ground level at Scoresby Sound (Greenland) was determined during each day from Nov. 1932 to Aug. 1933. The max., 57 mg. per cu. m., occurred at the end of Dec. The amount varied with the wind, being lowered by a N.E. wind to about 4—6 mg., rising when the wind dropped by 10—15 mg. per day. It was much lower (average only 6 mg.) in spring and summer. The amount also varied with the prevalence of aurora with a lag indicating that the aurora is accompanied by formation of O_3 in the upper air, whence it takes about a month to descend to ground level. Its presence in the air was further proved by the ultra-violet spectrum in the twilight of the polar night. C. A. S.

Formaldehyde in the upper atmosphere. N. R. DHAR and A. RAM (Nature, 1933, 132, 819—820).—All samples of rain- H_2O contain 0.00015—0.0012 g. of CH_2O (I) per litre, the amount being greater when the rainfall is preceded by clear sunny days. (I) may thus be the result of photo-formation from CO_2 and H_2O in the atm., at a height < that of the formation of O_3 . The absorption of solar radiations shorter than 2900 Å. may be partly due to the (I) present in the atm. L. S. T.

Calcium carbonate and carbonic acid content of sea-water according to the scientific results of the "Meteor" expedition. V. M. GOLDSCHMIDT (Naturwiss., 1933, 21, 811—817).—A report of the chemical work of the German "Meteor" Atlantic expedition, 1925—1927. The results of the determination of the solubility of $CaCO_3$ in sea- H_2O are given. The connexion between the CO_2 pressure and $[H^+]$, and the causes of H_2CO_3 distribution, are discussed. A. J. M.

Heavy metals in natural mineral waters. S. S. MIHOLIC (Bull. Soc. Chim. Yougoslav., 1933, 4, 107—120).—European mineral H_2O can be classified into three groups, according to their heavy metal content. Those containing predominately Ni and Co correspond with the Archean folding, Sn with the Hercynian, and Pb and Zn with the Alpine folding. Data for the Caledonian folding are not available. R. T.

Bacterial activity in the thermal springs of Aix and Aix-Burtscheid. A. BRUSSOFF, F. REINARTZ, and A. SCHLOEMER (Z. Unters. Lebensm., 1933, 66, 446—453).—The stony and sandy lime deposits in the thermal H_2O at Aix-Burtscheid are formed by the activity of SiO_2 , Fe, and CaO bacteria. E. C. S.

Radioactivity of springs on the massif of the Ballon d'Alsace. R. DELABY, R. CHARONNAT, and M. JANOT (Compt. rend., 1933, 197, 1140—1142; cf. A., 1933, 251).—The most radioactive springs (93.1—106.3 m μ c.) are at the source of the Savoureuse river, and derived from granite, but the variation with rainfall is the reverse of that previously stated (cf. A., 1920, ii, 727). Radioactivity of the H_2O rapidly decreases along this river, being practically zero 3 km.

from its source. Observations on the Ballon de Servance (max. 38 m μ c.) confirm the close connexion of radioactivity with the granite. C. A. S.

Beryllium and helium. I. Helium contained in beryls of varied geological age. (LORD) RAYLEIGH (Proc. Roy. Soc., 1933, A, 142, 370—381; cf. A., 1933, 692).—The He content of more than 60 specimens of beryl has been determined. Large He content is limited to specimens of great geological age. L. L. B.

Geochemistry of the alkali metals. V. M. GOLDSCHMIDT, H. BERMAN, H. HAUPTMANN, and C. PETERS (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1933, 235—244; Chem. Zentr., 1933, i, 3911—3912).—Arc spectrographic analytical methods are described. Average vals. for terrestrial rocks are: Li_2O 0.1, Rb_2O 0.03, Cs_2O 0.001%; Li:Na (atoms) 1:150. The behaviour of alkali metals in magmatic and magmatic-pneumatolytic rocks is discussed. Rb is always accompanied in minerals by much K; Cs accumulates in the sublimation products of effusive rocks. The effect of weakening and sedimentation on the distribution of alkali metals is also discussed. A. A. E.

Geochemistry of selenium. V. M. GOLDSCHMIDT and O. HEFTER (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1933, 245—252; Chem. Zentr., 1933, i, 3912).—The geochemical separation of Se from S is discussed in relation to their similar ionic dimensions and to the conditions of oxidation. The determination of Se in sulphate minerals is described. A. A. E.

Geochemistry of germanium. V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1933, 141—166; Chem. Zentr., 1933, i, 3912—3913).—Results of arc or X-ray spectroscopic determinations in many rocks and minerals are reported. A method for detecting 0.0001% is described. Ge was detected in almost all magmatic rocks and minerals except dunite; its associations are recorded. The distribution of Ge in sedimentary rocks is discussed. In meteorites Ge accumulates in the Ni-Fe rather than in the troilite. The average Ge content of silicate rocks is about 0.0006% GeO_2 . A. A. E.

Presence of gallium in sulphide ores. A. GRUNBERG, A. FILIPPOV, and I. JASVONSKIJ (Compt. rend. Acad. Sci. U.S.S.R., 1933, 2, 69—74).—Minerals and ores from Altai have been investigated for Ga, which appears most richly in Ridder Zn blende. A. B. D. C.

Apatite and nepheline from Chibinogorsk, Kola Peninsula. F. VOGEL (Metall u. Erz, 1933, 30, 191—193; Chem. Zentr., 1933, ii, 758).

Variation in electrical conductivity of hydrous minerals with temperature. S. SHIMIZU (Sci. Rep. Tôhoku, 1933, 22, 633—661).—In general, the conductivities, k , of minerals of the type $xAl_2O_3 \cdot ySiO_2 \cdot zH_2O$ (I), $Al_2O_3 \cdot xH_2O$, and $K_2O \cdot xAl_2O_3 \cdot ySiO_2 \cdot zH_2O$ increase with rise of temp. and the anomalous variations are correlated with discontinuous vol. changes and the heat effects revealed by thermal analysis. With (I), max. vals. of k at 100—200° and 450—650° correspond with the absorption of heat due to elimination of H_2O , whilst the abrupt decrease of k at 900—

1000° is correlated with evolution of heat. The dehydration of diasporite proceeds stepwise.

Age of Fitchburg granite. A. C. LANE (Science, 1933, 78, 435).—Microchemical analysis indicates an age of 36×10^7 years for the Fitchburg granite.

L. S. T.

Alkaline granite from Magasbukk, Ditrau. V. IANOVICI (Ann. Sci. Univ. Jassy, 1933, 18, 113—117).—A chemical analysis and a petrographical description are given.

H. S. P.

Talc-serpentine-chlorite rocks of south Mewar and Dungarpur. B. K. GHOSH (Rec. Geol. Surv. India, 1933, 66, 449—460).—A series of talc-serpentine-chlorite rocks occurring in Dungarpur and Mewar (Udaipur), Rajputana, is derived from intrusive peridotites or pyroxenites by the action of H_2O and CO_2 aided by faulting and folding on the magnesian minerals: $4MgSiO_3$ (enstatite) + H_2O + $CO_2 = Mg_3H_2(SiO_3)_4$ (talc) + $MgCO_3$; $CaMg_3(SiO_3)_4$ (tremolite) + H_2O + $CO_2 = Mg_3H_2(SiO_3)_4$ + $CaCO_3$; and $4Mg_2SiO_4$ (olivine) + H_2O + $5CO_2 = Mg_3H_2(SiO_3)_4$ + $5MgCO_3$. Calcite and magnesite both occur in the deposits, together with magnetite, rutile, ilmenite, chromite, etc.

C. A. S.

Olivine-gabbro from the Jocotca region, Ditrau. V. IANOVICI (Ann. Sci. Univ. Jassy, 1933, 18, 107—112).—A petrographical description and a chemical analysis of a new olivine-gabbro are given.

H. S. P.

Composition of matlockite. W. NIEUWENKAMP (Z. Krist., 1933, 86, 470—471).—The powder diagram of $PbFCl$ (cf. A., 1932, 450) is identical with that of matlockite, showing that the latter has the same composition, and not Pb_2OCl_2 . Analysis gave 6.5% F (calc. for $PbFCl$ 7.3%).

C. A. S.

New minerals. H. UNGEMACH (Compt. rend., 1933, 197, 1132—1134).—Revised measurements of the following minerals from Tierra Amarilla (Chili) are given (cf. Z. Krist., 1889, 15, 1): copiapite, triclinic, $a:b:c=0.4134:1:1.3280$, α $100^\circ 12'$, β $86^\circ 47'$, γ $90^\circ 32'$; quenstedtite, triclinic, $a:b:c=0.2621:1:0.2776$, α $94^\circ 10'$, β $101^\circ 44.5'$, γ $96^\circ 18.5'$; the coquimbite includes two distinct species, of the same composition, and often occurring together, coquimbite proper, hexagonal, $a:c=1:1.5643$; and a new rhombohedral variety, *paracoquimbite*, $a:c=1:2.3464$, pale violet. The following from the same locality are new: *amarillite*, $NaFe(SO_4)_2 \cdot 6H_2O$, pale yellow, monoclinic, $a:b:c=0.7757:1:1.1482$, β $84^\circ 23'$; *lapparentite*, $[AlFe]_2O_3 \cdot 2SO_3 \cdot 10H_2O$, monoclinic, $a:b:c=0.2919:1:0.24155$, β $85^\circ 10'$; and *leucoglaukite*, $Fe_2O_3 \cdot 4SO_3 \cdot 5H_2O$, resembling, but with less H_2O than, rhomboclase, pale greenish-blue, hexa-

gonal, $a:c=1:0.5589$. Associated with the foregoing are S, chalcantinite, natrojarosite, roemerite, fibroferite, and halotrichite.

C. A. S.

Barytes in granulite sand of Alençon (Orne). L. BERTHOIS (Compt. rend., 1933, 197, 1051—1052).—Barytes forms 0.017—0.086 (average 0.038)% of the sand bordering the granulite intrusion at Alençon, and is so distributed as to indicate its derivation from the granulite, probably by fumarole action. It also occurs in larger amounts (30—60 times) in the arkose of the Inferior Oolite in this neighbourhood, but is of similar origin, a larger proportion of the other material having been removed.

C. A. S.

Evolution of heat on contact of dry earth with water. P. HAGENE (Compt. rend., 1933, 197, 935—937; cf. A., 1933, 590).—The heat evolved on moistening dried and comminuted samples of humus from pollarded hollow willows and an ash is 18.65—23.60 g.-cal. per kg., the content of org. matter being 47.4—87.4%. That evolved by surface soils from the neighbourhood of Dijon and containing little organic matter, after similar treatment, is 4.02—8.04 g.-cal. per kg. The proportion of the evolved heat due to the mineral content of humus and of soil is about the same.

C. A. S.

Bitumen deposits and lignite field of Chalaïnov, Heilungkiang Province [China]. T. F. HOU (Bull. Geol. Survey China, 1932, 19, 51—76).—Bitumen occurring in cavities or pores in trachyte (3 specimens, 2.2, 12.8, 3.4%) contained, respectively, fixed C 42.6, 34.2, 11.4; ash 15.2, 4.4, 28.2; volatile matter 42.2, 61.4, 60.4%, and had d 1.53, 1.16, 1.16, and m.p. 70° , 55° , 100° . Bituminous matter is regarded as one of the end phases of volcanic activity and to have been deposited simultaneously with agate. Lignites from the same area contained H_2O 34.80—49.92, volatile matter 16.54—30.04, fixed C 27.22—32.26, ash 4.66—8.00, S 0.25—0.59%, and had calorific val. 3580—4784.

CH. ABS.

Vanadium in mineralised bitumens. N. A. ORLOV and V. A. USPENSKI (J. Appl. Chem. Russ., 1933, 6, 1010—1022).—A review of lit.

R. T.

Troilite nodules of meteorites. Geochemistry of chromium, nickel, and tin. V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 278—287; Chem. Zentr., 1933, ii, 849).—Ni, Cr, Sn, and Ge in troilites of meteorites have been determined by X-ray or are spectrography, and their chemical relationships in troilites are discussed.

A. A. E.

[Young's modulus and Poisson's ratio with reference to geophysical applications.] W. A. ZISMAN (Proc. Nat. Acad. Sci., 1933, 19, 989—990).—Errata are given (cf. A., 1933, 1028, 1029).

Organic Chemistry.

$\alpha\delta$ -Addition and subtraction reactions in hydrocarbon chemistry. L. S. KASSEL (J. Chem. Physics, 1933, 1, 749—750).—The mechanism of the hydrogenation and dehydrogenation of hydrocarbons is discussed.

H. S. P.

Mechanism of explosive combustion of gaseous hydrocarbons.—See this vol. 34.

Preparation and reactions of $\delta\delta$ -dimethyl- Δ^4 -pentene (neopentylethylene). F. C. WHITMORE

and A. H. HOMEYER (J. Amer. Chem. Soc., 1933, 55, 4555—4559).— MgBu^nCl and allyl bromide give a good yield of $\delta\delta$ -dimethyl- Δ^2 -pentene (I), b.p. 72.35°/760 mm., purified through its dibromide, b.p. 77—78°/9 mm. (I) and dry HBr at 0° afford $\delta\delta$ -dimethyl- n -amyl bromide, b.p. 70—71°/35 mm., 154°/730 mm.; the Grignard reagent and O_2 give $\delta\delta$ -dimethyl- n -amyl alcohol, b.p. 96°/62 mm., 158°/737 mm. (α -naphthylurethane, m.p. 80.5—81°). (I) does not react with dry HI at 0—5°. (I) and AcOH -conc. H_2SO_4 give the acetate, b.p. 92—93°/10 mm., of $\delta\delta$ -dimethylpentan-3-ol (α -naphthylurethane, m.p. 86.5—87°), and a mixture, b.p. 72—82°/740 mm., of olefines. (I) is polymerised by 85% H_2SO_4 at 5—20° to a mixture of products; 100% H_2SO_4 has little action.

H. B.

Preparation of $\beta\zeta$ -dimethylheptadiene. H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1933, 52, 1007—1012).—Methylheptenone, prepared from citral and 10% K_2CO_3 , is condensed with MgMeI , and the resulting $\beta\zeta$ -dimethylheptenol, b.p. 80—80.5°/14 mm., dehydrated with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ at 145°. $\beta\zeta$ -Dimethylheptadiene, b.p. 143.7±0.2°/762 mm. (purified over Na), which is probably a mixture of isomerides, absorbs the calc. vol. of H_2 with formation of $\beta\zeta$ -dimethyl- n -heptane. Determination of the Br val. (McIlhiney) is no criterion of its purity.

H. A. P.

Preparation of vinylacetylene by Willstätter and Wirth's method. E. A. SHILOV, A. N. MAKASHINA, A. I. SMIRNOVA, and G. I. YAKIMOV (Sintet. Kauchuk, 1933, No. 1, 4—12).—(1) $\alpha\delta$ -Butylene dibromide is obtained directly from technical butadiene by Thiele's method. (2) NMe_3 is used instead of NHMe_2 : $(\text{CH}_2\text{Br}\cdot\text{CH})_2 + 2\text{NMe}_3$ (in dry MeOH) = $[\text{CH}_2(\text{NMe}_3\text{Br})\cdot\text{CH}]_2$. The dibromide is shaken with H_2O and pptd. Ag_2O to give $[\text{CH}_2(\text{NMe}_3\cdot\text{OH})\cdot\text{CH}]_2$, which on distillation affords $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$.

CH. ABS.

Acetylene polymerides and their derivatives. XVII. **Mercury derivatives of vinylacetylene.** W. H. CAROTHERS, R. A. JACOBSON, and G. J. BERCHE (J. Amer. Chem. Soc., 1933, 55, 4665—4667).— $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$ (I) and $\text{EtOH}\text{-K}_2\text{HgI}_2$ or cold $\text{AcOH}\text{-Hg}(\text{OAc})_2$ give *Hg divinylacetylde* (II), m.p. 144—145°, which absorbs O_2 when kept in air to give an explosive compound, reacts with Br(I) in CHCl_3 to form $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CBr(I)}$, and with Na in C_6H_6 affording $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CNa}$. (I) or (II) with $\text{AcOH}\text{-Hg}(\text{OAc})_2$ at 60—70° gives $\alpha\alpha$ -di(acetoxymercuri)- β -acetoxymercurio- Δ^2 -butadiene (III), $\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{O}\cdot\text{HgOAc})\cdot\text{C}(\text{HgOAc})_2$ [corresponding tri-chloro-, -bromo-, and -iodo-mercuri-derivatives, prepared from (III) and KHal in 50% AcOH], hydrolysed (dil. HCl) to *Me vinyl ketone*. (III) and Br in CHCl_3 give *tribromomethyl vinyl ketone*, b. p. 128—130°/0.04 mm., m.p. 73—75°.

H. B.

Acetylene polymerides and their derivatives. XVIII. **α -Halogeno- β -vinylacetylenes.** R. A. JACOBSON and W. H. CAROTHERS (J. Amer. Chem. Soc., 1933, 55, 4667—4669).— α -Chloro-, b.p. 55—57°/760 mm., α -bromo-, b.p. 52—53°/217 mm., and α -iodo- (I), b.p. 78°/125 mm., β -vinylacetylenes are prepared from $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{CH}$ and aq. NaOHal in N_2 ; they

often explode in air and polymerise to explosive black solids. (I), also prepared from $\text{CH}_2\cdot\text{CH}\cdot\text{C}\cdot\text{MgBr}$ and I, with $\text{EtOH}\text{-HCl}$, CuCl , and NH_4Cl gives a compound, $\text{C}_4\text{H}_4\text{ClI}$, b.p. 73.5—74.5°/35 mm., which polymerises to a black tar.

H. B.

Decomposition of chloroform by radiations from radon.—See this vol., 40.

Hydrolysis of ethylene bromide with alcoholic alkali hydroxide.—See this vol., 36.

Preparation of trimethylene chlorobromide. I. STRUKOV (Khim. Farm. Prom., 1933, 2, 66—68).—In Bruylants' method the allyl chloride is saturated with HBr in sunlight; the yield is 95—97%. CH. ABS.

$\alpha\epsilon$ -Dibromopentane. J. D. A. JOHNSON (J.C.S., 1933, 1531—1532).— $\alpha\epsilon$ -Dibromopentane (I), prepared from 1-benzoylpiperidine and PBr_5 by (essentially) von Braun's method (A., 1904, i, 841; 1905, i, 596), contains 15—16% of PhCN . Pure (I), b.p. 95.5°/10 mm., m.p. —29.5° (lit. —35 to —34°), is obtained by dissolution of the mixture (b.p. up to 105°/10 mm.) in light petroleum (b.p. 40°) and extraction with seven successive amounts of conc. H_2SO_4 . The parachor of (I) is anomalous.

H. B.

Molecular rotations in members of homologous series. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1933, 103, 299—309).—The max. $[\text{M}]_D^{25}$ for numerous members of the series $\text{CHMeR}\cdot[\text{CH}_2]_n\text{X}$; where R is Et, Pr^a , Bu^a , n -amyl, and n -heptyl, X is Br, OH, Me, CO_2H , and CO_2Et , and $n=0\text{--}5$, are compared. The contribution of the $\text{CH}_2\cdot\text{OH}$ group approaches closely to that of Me after a certain distance from the asymmetric centre is reached (provided R contains > 2 C atoms) but never equals it.

The Grignard reagent from γ -methylhexyl bromide, $[\text{M}]_D^{25}$ —7.6° (all vals. are homogeneous), and CH_2O give δ -methylheptyl alcohol, b.p. 81°/18 mm., $[\text{M}]_D^{25}$ 0° [bromide, b.p. 80°/15 mm., $[\text{M}]_D^{25}$ —5.2° (—14.5°)]. The *d-Et* ester, b.p. 95°/25 mm., $[\text{M}]_D^{25}$ +4.18° (+12.84°), of δ -methylhepticoic acid, $[\text{M}]_D^{25}$ +3.56°, is reduced (Na, EtOH , PhMe) to *d- ϵ -methylheptyl alcohol*, b.p. 87°/20 mm., $[\text{M}]_D^{25}$ +3.9° (+12°) [bromide, b.p. 86°/14 mm., $[\text{M}]_D^{25}$ +4.81° (+14.92°)]. The *d-Et* ester, b.p. 110°/25 mm., +4.4° (+13.66°), of ϵ -methyl-octicoic acid, $[\text{M}]_D^{25}$ +3.93°, is similarly reduced to *d- ζ -methyl-octyl alcohol*, b.p. 100°/20 mm., $[\text{M}]_D^{25}$ +4° (+12.5°) [bromide, b.p. 101°/14 mm., $[\text{M}]_D^{25}$ +4.48° (+13.96°)], whilst the *l-Et* ester, b.p. 112°/30 mm., $[\text{M}]_D^{25}$ —1.21° (—5.9°), of δ -propylhexoic acid, $[\text{M}]_D^{25}$ —0.76°, gives *l- ϵ -propylhexyl alcohol*, b.p. 110°/25 mm., —0.37° (—1.72°) [bromide, b.p. 95°/12 mm., $[\text{M}]_D^{25}$ —1.53° (—7.78°)]. The *l-Et* ester, b.p. 125°/25 mm., $[\text{M}]_D^{25}$ —1.45° (—2.84°), of δ -butylhexoic acid, $[\text{M}]_D^{25}$ —0.86°, similarly affords ϵ -butylhexyl alcohol, b.p. 125°/25 mm., $[\text{M}]_D^{25}$ 0° [bromide, b.p. 112°/12 mm., $[\text{M}]_D^{25}$ —2.69° (—5.29°)], whilst the *l-Et* ester, b.p. 140°/25 mm., $[\text{M}]_D^{25}$ —0.92° (—1.69°), of δ -amylhexoic acid, $[\text{M}]_D^{25}$ —0.33°, gives *d- ϵ -amylhexyl alcohol*, b.p. 140°/25 mm., $[\text{M}]_D^{25}$ +1.03° (+1.85°) [bromide, b.p. 124°/12 mm., $[\text{M}]_D^{25}$ —1.89° (—4.02°)]. The vals. quoted in parentheses are calc. max.

H. B.

Detection of sorbitol in the presence of dulcin and saccharin. G. REIF (Z. Unters. Lebensm., 1933, 66, 408—412).—Dulcin (I), PhCHO , and H_2SO_4 give

benzylidenedulcin, m.p. 205—206°, which gives an orange-yellow colour with COMe_2 and H_2SO_4 and thus interferes with the detection of sorbitol (II). (I) also forms a cryst. acetate which interferes with the identification of sorbitol hexa-acetate. Both (I) and saccharin (III) are removed by animal C when Werder's technique (B., 1929, 619) is employed. (III) does not, however, give a CHPh compound, so does not interfere with the colour and Ac tests for (II).

E. C. S.

Preparation and significance of glyceromono-phosphoric acid. C. NEUBERG and M. KOBEL (Angew. Chem., 1933, 46, 711—713).—Hexoso diphosphate (I) solution from the fermentation of glucose, sucrose, fructose, mannose, galactose, or maltose with yeast (fresh, dry, or extract) in presence of excess of phosphate is dismutated with NaF and MeCHO (or *iso*-valeraldehyde) for 3.5 hr., yielding *l*-glycerophosphoric acid (II), which is isolated as the Ba H salt ($+2\text{H}_2\text{O}$). Phosphate goes into org. combination in both stages. With dil. yeast extract, or with lower (I) concn., the yield is less, whilst more NaF is required. (I) is also obtained from Na glyceraldehyde phosphate using extract free from carbohydrates under similar conditions, the yield being approx. halved in absence of MeCHO. The significance of (II) and its aldehyde as intermediates in the process of fermentation is discussed.

A. A. L.

Thermal decomposition of ethyl mercaptan and ethyl sulphide. W. M. MALISOFF and E. M. MARKS (J. Chem. Physics, 1933, 1, 284—284; cf. A., 1931, 1393).—Polemical. Trenner and Taylor (A., 1933, 374) carried out their investigations under conditions different from those employed by the authors.

M. S. B.

Thermal decomposition of ethyl mercaptan and ethyl sulphide. N. R. TRENNER and H. A. TAYLOR (J. Chem. Physics, 1933, 1, 286; cf. preceding abstract).—Polemical. There is no reason to suppose that mercaptan decomp. in hydrocarbon solvents will be different from that in the pure state.

M. S. B.

Composition of fatty acid mixtures. I. Relation of composition to Dalican's curve. R. N. WENZEL (Ind. Eng. Chem. [Anal.], 1933, 5, 393—396).—Limitations of the use of the curve are emphasised and illustrated.

R. S. C.

Ethyl and methyl fluoroformates. H. C. GOSWAMI and P. B. SARKAR (J. Indian Chem. Soc., 1933, 10, 537—539).—*Me*, b.p. 40°, and *Et*, b.p. 57°, *fluoroformates* are prepared from ClCO_2Alk and anhyd. TiF_4 .

H. B.

Preparation of derivatives of vinylacetic acid. L. FALAISE and R. FROGNIER (Bull. Soc. chim. Belg., 1933, 42, 427—441).—Vinylacetonitrile (I) is obtained in good yield by Breckpot's method (A., 1931, 194); allyl formate or a mixture of allyl alcohol and formate can also be used. (I) is hydrolysed rapidly by conc. HCl to vinylacetic acid (II); small amounts of β -chloro- α -butyronitrile and crotonic acid are also formed. (II) is unaffected by dry HCl; esterification (EtOH-HCl) gives 70% of *Et* vinylacetate, b.p. 124.2—124.4°/761.5 mm., which is also unaffected by dry HCl.

H. B.

Determination of the double linking [in derivatives of the butenoic acids]. R. FROGNIER and F. VAN GOETSENHOVEN (Bull. Soc. chim. Belg., 1933, 42, 391—409).—The rate of addition of Br (in CCl_4) to the following substances (in CCl_4) at room temp. in the dark is vinylacetic acid Et vinylacetate (I) vinylacetonitrile (II) > crotonic acid (III) > *trans*-crotononitrile (IV) > *cis*-crotononitrile (V). A method [based on that of Heim (A., 1931, 205)] in which the substance (in CCl_4) is treated with KBr-KBrO_3 and 10% H_2SO_4 is described; the no. of mols. of Br added are: (II) 0.99, (I) 0.99, (IV) 0.016, (V) 0.006, *Et* crotonate 0.02. In presence of sunlight, similar addition of Br to all the nitriles is rapid. (II) does not add I in CCl_4 ; reaction is rapid with ICl, but occurs more slowly with IBr (in CHCl_3 and the dark). Addition of 1 mol. of Br to most of the above compounds occurs much more rapidly in presence of H_2O . Treatment of (II) with $\text{Br-H}_2\text{O}$ gives 93.3 mol.-% of H' per mol. of Br added; addition of KBr, KCl, and KNO_3 decreases the amount of H' in the order quoted. Addition of HOBr (prepared using HgO) to (II) occurs to the extent of 97.5%; (IV) similarly adds 1% (in presence of 10% H_2SO_4 , almost quant. addition is accomplished; similar quant. addition is found with HOBr from $\text{Br-H}_2\text{O}$ and Ag_2SO_4). The question of lactone formation and the secondary reactions occurring during the decomp. of excess of Br by KI are discussed.

H. B.

Electrolytic oxidation of glycollic acid in alkaline solution. E. TONMILA (Suomen Kem., 1933, 6B, 70).—Electrolytic oxidation of $\text{OH-CH}_2\text{-CO}_2\text{H}$ (Fe, Ni, or Cu anode) affords $\text{CHO-CO}_2\text{H}$, $\text{H}_2\text{C}_2\text{O}_4$, and HCO_2H . With a Pt anode, CH_2O is the main product; some H_2 is also liberated.

J. L. D.

Apparatus for determination of lactic acid. H. J. FUCHS (Z. physiol. Chem., 1933, 221, 271—277).—A current of air introduces the KMnO_4 below the surface of the boiling reaction mixture and carries over the MeCHO through a reflux condenser into an improved absorption apparatus containing NaHSO_3 .

J. H. B.

Benzyl laevulate. P. P. T. SAK, H. H. LEI, and H. M. FANG (J. Amer. Chem. Soc., 1933, 55, 4727—4728).—Laevulic acid (52 g.), $\text{CH}_3\text{Ph-OH}$ (160 g.), HCl (7 g.), and PhMe (440 g.) are boiled for 24 hr.; subsequent distillation gives *benzyl laevulate* (65 g.), b.p. 181—183°/17 mm. (*phenyl*-, m.p. 91—92°, *p-tolyl*-, m.p. 99—100°, *p-chlorophenyl*-, m.p. 106—107°, and *p-bromophenyl*-, m.p. 103°, -hydrates).

H. B.

Polymerisation and ring formation. XVIII. Polyesters from α -hydroxydecoic acid. W. H. CAROTHERS and F. J. VAN NATTA (J. Amer. Chem. Soc., 1933, 55, 4714—4719).—A series of polyesters (M 780—25,200) of the type $\text{OH}-(\text{CH}_2)_9\text{-CO-O-}[\text{CH}_2]_9\text{-CO}_2\text{H}$ are prepared from α -hydroxydecoic acid (I) by heating under various conditions; M is determined by titration with EtOH-KOH in EtOH-CHCl_3 and the esters are hydrolysed (EtOH-NaOH) to (I). A small amount of the dimeric lactone of (I) (cf. Lycan and Adams, A., 1930, 65) is always formed in the above preps. Numerous physical data are given; strong oriented fibres (cf. A.,

1932, 601) are obtained only from the esters of $M > 9330$.

H. B.

Ether-like compounds. XI. Ether-lactone with seven-membered ring. M. H. PALOMAA and U. TOUKOLA (Ber., 1933, 66, [B], 1629—1632; cf. A., 1933, 697).— γ -Methoxypropoxyacetic acid, b.p. 140—140.5°/7 mm., is demethylated with difficulty to a Br-free product by HBr. γ -Hydroxypropoxyacetic acid, prepared from $\text{ONa}[\text{CH}_2]_3\text{OH}$ and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$, passes at 200—220°/0.1—1 mm. into the corresponding lactone, $\text{O} \begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\text{C}-\text{O}-\text{O} \end{array}$ m.p.

135.5°, which does not tend to polymerise and in $\text{COMe}_2\text{-H}_2\text{O}$ is hydrolysed by acid about 1/90 as fast as $\text{O} \begin{array}{c} \text{CH}_2\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}-\text{CO} \end{array} \text{O}$.

H. W.

Reactivity of atoms and groups in organic compounds. XIV. Influence of substituents on thermal stability of derivatives of malonic acid. J. F. NORRIS and H. F. TUCKER (J. Amer. Chem. Soc., 1933, 55, 4697—4704).—The m.p. (tube), m.p. (Dennis bar), and decomp. temp. (average val.) [determined by a modification of the method previously used (A., 1931, 197)], respectively, are given after the malonic acids, $\text{CHR}'(\text{CO}_2\text{H})_2$: R, R' = H, 129—131°, 134°, 129°; H, Pr ^{β} , 87—91°, 88°, 103°; H, CHMe:CH₂, 97—101°, 95°, 99°; H, sec.-Bu, 75—76°, 76°, 98°; H, isoamyl, 95—96°, 96°, 101°; H, Ph, 139—141°, 169°, 123°; H, *o*-C₆H₄Cl, 128—130°, 133°, 101°; H, CH₂Ph, 119—120°, 120°, 116°; Me₂, 193—194°, 195°, 150°; Et, 126—127°, 126° 126°; Me, Et, 121—122°, 121°, 123°; Me, Pr ^{α} , 102—106°, 105°, 98°; Me, Pr ^{β} , 120—124°, 126°, 110°; Me, CHMe:CH₂, 89—91°, 85°, 96°; Me, Bu ^{α} , 98—99°, 98°, 109°; Ph, Et, 153—155°, 182°, 117°; Cl, Et, 110.2°, —, 96°; Cl, Pr ^{α} , 98.8—99.3°, —, 76°; Cl, Bu ^{α} , 90.7—91.8°, —, 83°. The use of a method involving the detection of the CO₂ liberated gives vals. 1—3° higher. The decomp. temp. of $\text{CHR}(\text{CO}_2\text{H})_2$ is < that of $\text{CH}_2(\text{CO}_2\text{H})_2$. The relationship between the decomp. temp. and structure of substituents is discussed. $\text{CH}_2(\text{CO}_2\text{H})_2$ decomposes at 115—116° in presence of H₂O, AcOH, KHSO₄, Mg, Al, and ZnCl₂ at varying rates.

H. B.

Specific oxidising action of selenium dioxide. R. MULLER (Ber., 1933, 66, [B], 1668—1670).—SeO₂ oxidises $\text{CH}_2(\text{CO}_2\text{Et})_2$ in xylene at 130° to Et₂ ketomalonate, which partly decomposes into Et₂C₃O₄ and CO; the liberated H₂O causes partial hydrolysis to Et H mesoxalate. Similarly, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ affords Et α -diketobutyrate (disemicarbazone, m.p. 270°); a secondary formation of AcCHO is not observed.

H. W.

Ethylene [glycol] glutarate. Y. TSUZUKI (Bull. Chem. Soc. Japan, 1933, 8, 313—316).— $(\text{CH}_2\text{OH})_2$, glutaric acid, and ZnCl₂ (0.5 mol.) at 135—140° give a gummy *H* ester, $\text{OH}[\text{CH}_2]_2\text{O}[\text{CO}(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_2\text{O}]_3\text{CO}[\text{CH}_2]_3\text{CO}_2\text{H}$. The degree of polymerisation of this ester being < that in the succinic acid series, and that in the maleic < that in the fumaric acid series, is in agreement with stereochemical considerations.

R. S. C.

Chain abbreviation and ring formation during thermal degradation of natural polyene dyes. R. KUHN and A. WINTERSTEIN (Ber., 1933, 66, [B],

1733—1741; cf. A., 1933, 145).—Fresh analyses of the product (I), m.p. 135°, obtained in 10—12% yield by the thermal decomp. of crocetin Me₂ ester (II) (*loc. cit.*) indicate the formula C₁₅H₂₀O₄ instead of C₁₆H₂₂O₄. (I) is transformed by HI or KOH-EtOH into the dicarboxylic acid (III) C₁₃H₁₆O₄, m.p. 296° (corr.; Berl), re-transformed into (I) by CH₂N₂. (III) absorbs 4 H₂ and yields approx. 3 mols. of AcOH when oxidised by CrO₃. The absorption spectrum of (I) in *n*-C₆H₁₄ indicates that all the double linkings are conjugated among themselves and with the carboxyls. Since the difference between the mols. of (I) and (II) is C₂H₈ (corresponding with PhMe lost during degradation) (I) is Me₂ α -80-trimethyl- $\Delta^{7,9,11}$ -octatetraene- α -0-dicarboxylate. (I) does not exist preformed in natural (II); chromatographic separation of mixtures of (I) and (II) is easy. Small amounts of tricyclocrocetin (IV) are obtained by thermal decomp. of (II) hydrolysed to the dicarboxylic acid C₂₀H₂₄O₄, m.p. 263—264° (corr.; Berl), which absorbs only 4 H₂, and hence contains three rings. The absorption spectrum shows > two conjugated linkings. During the degradation of (II), 12% of (I), 1% of (IV), 10% of PhMe + *m*-xylene, and 2% of (II) are obtained.

H. W.

Vitamin-C. P. KARRER, K. SCHOPP, and F. ZEHNDER (Helv. Chem. Acta, 1933, 16, 1161—1163).—The action of MgMeI on dimethylisopropylidene-ascorbic acid leads to the development of 2OH without loss of OMe, thus confirming the lactone formula of Hirst *et al.* (A., 1933, 594) in contrast with the Me ester structure. Oxidation of ascorbic to dehydro-ascorbic acid (I) corresponds exactly with that of dialuric acid to alloxan (II). The possibility of a peroxide constitution of (I) [and also (II)] is indicated by the oxidising action and absence of colour.

Thioketonic esters. IV. S. K. MITRA (J. Indian Chem. Soc., 1933, 10, 491—495; cf. A., 1933, 698).—CH₂EtAc·CO₂Et and H₂S in EtOH-HCl at 0° give Et α -ethylthioacetoacetate (I), b.p. 85°/14 mm., hydrolysed (10% H₂SO₄) to COMePr. (I) and NHPH-NH₂ afford 1-phenyl-3-methyl-4-ethyl-5-pyrazolone (II), m.p. 108°. The Na derivative of (I) in C₆H₆ with EtBr, Bu ^{β} I, AcCl, and BzCl gives Et β -ethyl-, b.p. 95°/14 mm., β -isobutyl-, b.p. 100°/15 mm., β -acetyl- (III), b.p. 105°/12 mm., and β -benzoyl-, b.p. 185°/18 mm., -thiol- α -ethylcrotonate, respectively, all of which with NHPH-NH₂ afford (II). MgEtBr and (III) give COMeEt and (I).

H. B.

Influence of traces of oxygen on decomposition by heat of acetaldehyde.—See this vol., 38.

Unsaturated aldehydes. IV. Dicrotonaldehyde and octatrienal from crotonaldehyde. K. BERNHAUER and R. DROBNICK (Biochem. Z., 1933, 266, 197—201; cf. A., 1932, 834).—The acid C₈H₂O₄, obtained by oxidation of condensation products (I) of CHMe:CH·CHO, is dicrotonic acid. Oxidation of the fraction of (I) of b.p. 96—102°/12 mm. gives octatrienoic acid. Hence (I) probably contain dicrotonaldehyde and octatrienal.

W. McC.

Semi-acetals. SCHIMMEL & Co. (Report, 1933, 78—81; Chem. Zentr., 1933, ii, 1008—1009).—When the aldehyde has :CH₂ adjacent to :CO, what-

ever the constitution of the alcohol, semi-acetal formation is indicated by increase in d and n of the product. The reaction is exothermic. Citronellal and citronellol react, but not citral and geraniol. Aromatic aldehydes behave analogously. For optically active substances $[\alpha]$ is practically additive. n -Decaldehyde and decyl alcohol give a compound, $C_{20}H_{22}O_2$, $M[\alpha]$ 97.9° (semi-acetal, calc. 97.72°; mixture 98.29°), relatively stable towards alkali. M.p., d , n_D^{20} , and n_D for semi-acetals from aliphatic and aromatic (including optically active) aldehydes, $R\cdot CH_2\cdot CHO$ or $R\cdot CHO$, and alcohols are tabulated.

A. A. E.

Determination of small quantities of acetone in presence of other substances. I. N. KORENMAN (J. Appl. Chem. Russ., 1933, 6, 1002—1004).— $COMe_2$ (0.00025—0.001 mg. per 100 c.c.) is determined colorimetrically by the Frommer-Emilowicz reaction (salicylaldehyde and NaOH). A no. of org. solvents do not interfere.

R. T.

Hydrogenolysis of sugars. W. H. ZARTMAN and H. ADKINS (J. Amer. Chem. Soc., 1933, 55, 4559—4563).—Hydrogenation [H_2 (300 atm.), Cu—Cr oxide catalyst, EtOH at 250°] of glucose, sorbitol, mannitol, sucrose, lactose, maltose, α -methyl- d -glucoside, glucose penta-acetate, and gluconolactone (I) gives varying amounts of MeOH, EtOH, $OH\cdot CHMe\cdot CH_2\cdot OH$, and (probably) 4-hydroxy-2- α -hydroxyethylfuran, b.p. 118—125°/1 mm., $\alpha\beta\epsilon$ -trihydroxyhexane, b.p. 142—144°/1 mm., and $\alpha\beta\epsilon\zeta$ -tetrahydroxyhexane, b.p. 214—215°/1 mm. Some $(\cdot CH_2\cdot OH)_n$ is produced from (I).

H. B.

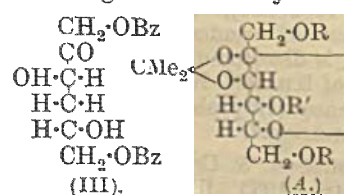
Shaffer and Hartmann combined carbonate-citrate method for determination of glucose. J. O. HALVERSON and F. W. SHERWOOD (Ind. Eng. Chem. [Anal.], 1933, 5, 418—419).—The method is accurate if the error incidental to the standard conditions used is determined.

R. S. C.

Acceleration by boric acid of the mutarotation of glucose. G. AURISICCHIO (L. Ind. Chimica, 1933, 8, 1369—1370).— H_3BO_3 accelerates the mutarotation. 0.5—3% solutions do not influence the equilibrium rotation.

H. F. G.

Derivatives of γ -fructose. New isopropylidene-fructose. L. ZERVAS and P. SESSLER (Ber., 1933, 66, [B], 1698—1703).—Fructose cyanohydrin, m.p. 114—115° (improved prep.) (Ac_6 derivative, m.p. 80—82°), is converted by $BzCl$ in anhyd. C_5H_5N into the unstable *dibenzoylfructose cyanohydrin* (I), m.p. about 150° [additive compounds with C_5H_5N (II), m.p. 128° (corr.), $[\alpha]_D^{20}$ -13.3° in C_5H_5N , and with $AcOH$, m.p. 140° (corr.)]. Inability of (I) to react with CPh_3Cl is evidence of the location of the Bz groups at 1 and 6. (II) is transformed by Ag_2CO_3 in boiling $EtOAc$ into *fructose 1:6-dibenzoate* (III),



m.p. 114—115° (corr.), $[\alpha]_D^{20}$ -7.3° to $+2.0^\circ$ in EtOH, $[\alpha]_D^{20}$ $+1.8^\circ$ in AcOH, reconverted into (II) by HCN and C_5H_5N . (III) and anhyd. $COMe_2$ containing a

little conc. H_2SO_4 afford 2:3-isopropylidene- α - d -fructofuranose 1:6-dibenzoate. (IV; A; R=Bz; R'=H), m.p. 118° (corr.), $[\alpha]_D^{20}$ $+13.5^\circ$ in EtOH, $+12.7^\circ$ in $COMe_2$, transformed by $BzCl$ in C_5H_5N into the *tribenzoate* (V) (A; R=R'=Bz), m.p. 137° (corr.), $[\alpha]_D^{20}$ -9° in $COMe_2$. (IV) is hydrolysed by $Ba(OH)_2$ to 2:3-isopropylidene- α - d -fructofuranose (VI) [A; R=R'=H], m.p. 80°, $[\alpha]_D^{20}$ $+18.9^\circ$ in H_2O , $[\alpha]_D^{20}$ $+14.1^\circ$ in $COMe_2$, which does not reduce Fehling's solution, is not oxidised by $Pb(OAc)_4$ (Criegee), and does not react with $COMe_2$ and H_2SO_4 . Benzoylation transforms (VI) into (V), whilst Ac_2O in C_5H_5N yields the *triacetate*, m.p. 55°, $[\alpha]_D^{20}$ -8° in EtOH, and CPh_3Cl affords *ditriphenylmethylisopropylidene-fructose*, m.p. 155° (corr.), $[\alpha]_D^{20}$ -5.2° in C_5H_5N .

H. W.

Action of nitric acid on sugars. S. VON MONASTERSKI (Z. ges. Schiess- u. Sprengstoffw., 1933, 28, 349—350).—*Sucrose octanitrate*, m.p. 80—82°, explodes at 169—170°, is prepared by adding HNO_3 (d 1.498), dropwise, and then oleum (17% SO_3) to a mixture of sucrose and carbamide nitrate and pouring the solution into cold H_2O ; alternatively a mixture of sugar and pinene hydrochloride is nitrated at 0° with mixed acid (H_2SO_4 50, HNO_3 38, SO_3 5, H_2O 7%), the mixture heated to 80°, and poured into cold H_2O . *Maltose octanitrate* (I), m.p. 135°, explodes at 171—180°, is prepared by heating maltose and carbamide nitrate with HNO_3 and oleum at 80°, evolution of N oxides being avoided. "Maltobenzite," explodes at 200°, is prepared by heating a mixture of (I), $m\text{-}C_6H_4(NO_2)_2$, and C_6H_6 to 70°, kneading to a plastic mass, heating to 95°, again kneading, and cooling. Heats of explosion, fall-hammer and Pb-block tests are recorded.

W. J. W.

Material synthesis of wood substance from the wood-forming plant saps. Fructose as the primitive substance in the synthesis of "lignin." H. WISLICENUS and H. HEMPEL [with (in part) K. UEBEL, H. FRIEDERICI, and H. VON ZEHMEN] (Cellulosechem., 1933, 14, 149—168).—Largely a more detailed account of work previously reviewed (A., 1930, 824; 1933, 989). Fructose (I) is readily autoxidised (sterile air), particularly in dil. alkaline solution, to colloidal products which are adsorbed by $Al(OH)_3$. Similar products are formed from (I) (much more readily and to a larger extent than from glucose) by dehydration (heat; H_2SO_4 ; Ac_2O — $ZnCl_2$). These products resemble the "primitive lignin" of the cambial sap, suggesting that lignin may arise from (I).

H. B.

Glycerolysis of sucrose. H. VOGEL (Ber., 1933, 66, [B], 1670—1672).—When heated with glycerol at 130°/11 mm., sucrose yields a syrup from which abs. EtOH causes separation of a solid giving phenylglucosazone, m.p. 204°, $[\alpha]_D^{20}$ $+52.01^\circ$ in H_2O , when treated with $NHPh\cdot NH_2$, at 100° and β -glucose pentaacetate, m.p. 132°, when boiled with Ac_2O and $NaOAc$. The non-cryst. portion yields glycerylfructoside, slowly converted by $NHPh\cdot NH_2$ in boiling H_2O into glucosazone. α -Galactosan (I), rhamnosan, and arabinosan with glycerol at 120°/12 mm. yield bitter syrups which do not reduce Fehling's solution. α -Glucosan and (I) are transformed by MeOH at 120° into α -methyl-glucoside and -galactoside, respectively.

H. W.

Glucosides of *p*-nitro- and *p*-amino-phenol and their fermentative scission.—See A., 1933, 1286.

Glucosidic azo-dyes.—See A., 1933, 1286.

Heart glucosides. IV. Deacetyldigilanids A, B, and C. A. STOLL and W. KREIS (Helv. Chim. Acta, 1933, 66, 1390—1407; cf. A., 1933, 1146).—Digilanid A in MeOH is transformed by aq. Ca(OH)₂ at room temp. into deacetyldigilanid A (I), C₄₇H₇₄O₁₈, m.p. 258° (decomp.) after softening at 255° (corr.), [α]_D²⁰ +10.4° in 75% EtOH, probably identical with purpureagluco-side A. Treatment in 95% EtOH with 2N-H₂SO₄ at 40° converts (I) into digitoxigenin, digitoxose (II), and digilanidobiose (III): C₄₇H₇₄O₁₈+3H₂O=C₂₃H₃₄O₄+2C₆H₁₂O₄+C₁₂H₂₂O₉. Hydrolysis with an enzyme prep. (IV) from the leaves of *Digitalis purpurea* leads to digitoxin. Deacetyldigilanid B, m.p. 240° (corr., decomp.), [α]_D²⁰ +20.4° in 75% EtOH, obtained in the same manner as (I), is hydrolysed by acid to gitoxigenin, (II), and (III): C₄₇H₇₄O₁₉+3H₂O=C₂₃H₃₄O₅+2C₆H₁₂O₄+C₁₂H₂₂O₉, and by (IV) to gitoxin (V). Cryst. deacetyldigilanid C, m.p. 265—268° (decomp.) after darkening at 235° (corr.) and softening at 255° (corr.), derived similarly from digilanid C, is hydrolysed by acid to digoxigenin, (II), and (III): C₄₇H₇₄O₁₉+3H₂O=C₂₃H₃₄O₅+2C₆H₁₂O₄+C₁₂H₂₂O₉, and by (IV) to (V). The physiological activity of the digilanids is retained in their deacetyl derivatives. H. W.

Emulsin. XIII. Preparation and enzymic fission of glucosides of *N*-acetylglucosamine and 2-deoxyglucose. B. HELFERICH and A. LÖFF (Z. physiol. Chem., 1933, 221, 252—258; cf. this vol., 109).—Alkaline hydrolysis of tetra-acetylphenyl-β-d-glucosaminide, m.p. 201.5—202° (corr.), decomp. from 185°, [α]_D²⁵ -10° in CHCl₃, gave *N*-acetylphenyl-β-d-glucosaminide (I), m.p. 238° (decomp.), [α]_D²⁵ -5.4° in H₂O. There is no parallelism between the hydrolysis of (I), phenyl-β-glucoside and -α-d-mannoside, indicating that the enzymes concerned differ. Bromination of triacetylglucal, elimination of Br with AgOAc, and fusion with PhOH gave triacetylphenyl-α-d-glucoside 2-bromohydrin, m.p. 104—106° (corr.), [α]_D²⁵ +60.7° in CHCl₃, converted by NaOMe in MeOH into phenyl-α-d-glucoside 2-bromohydrin (II), m.p. 122—124° (corr.), [α]_D²⁵ +88.2° in H₂O, which, with Na-Hg, gave phenyl-2-deoxy-α-d-glucoside (III), m.p. 162—163° (corr.), [α]_D²⁵ +159° in H₂O. Acetylation of 2-deoxyglucose and fusion with PhOH of the tetra-acetate, m.p. 109—110°, [α]_D²⁵ +109°, and hydrolysis of the Ac groups of the resulting tetra-acetylphenyl-2-deoxyglucoside, m.p. 87—88° (corr.), [α]_D²⁵ +146°, also gave (III). (II) is not hydrolysed by emulsin. The hydrolysis of (III) is paralleled by α-mannosidase, but not by β-glucosidase, fission.

J. H. B.

Phosphorus of potato starch. T. POSTERNAK (Compt. rend., 1933, 197, 1157—1158).—Hydrolysis of potato starch (I) with ox pancreas or malt extract and treatment of the filtrate with Pb subacetate (II) and 10% aq. NH₃ gives a ppt. containing about 80% of the original P. Dissolution of the dry ppt. in AcOH, neutralisation with aq. NH₃, and addition of EtOH affords a viscous product which gives a further ppt. with (II) in AcOH. Decomp. of this with H₂SO₄

and neutralisation with Ba(OH)₂ gives (by pptn. with EtOH) (probably) a Ba hexaoxomonophosphate, which reduces Fehling's solution and contains one reducing group (determined by NaOI) per atom of P. It is hydrolysed (2% H₂SO₄) to glucose and (probably) Ba maltose monophosphate, which is fairly resistant to hydrolysis. A biose monophosphate acid has also been isolated from the hydrolysate of (I) with 2% H₂SO₄. (I) consists of long chains of glucose residues linked through the α-position; the P is attached (as phosphate) to one of the residues. H. B.

Determination of glycogen. M. SAHYUN (J. Biol. Chem., 1933, 103, 203—208).—The use of > 50 mg. of activated C (I) or norit in the method previously described (A., 1932, 77) does not prevent hydrolysis of glycogen (II) by N-H₂SO₄; with larger amounts (100—200 mg.), results similar to those of Bancroft and Fry (A., 1933, 457) and Good *et al.* (*ibid.*, 625) are obtained. (I) adsorbs very little H₂SO₄. The pptd. (II) (cf. *loc. cit.*) is completely hydrolysed by 5N-H₂SO₄ (as little as possible to be used) at 100° in 15—20 min. H. B.

Oxycellulose. K. H. BERGMANN (Angew. Chem., 1933, 46, 713—716).—The applicability of the KMnO₄ no. method is confirmed for carbohydrates and related compounds, but requires modification when applied to oxycellulose (I) (improved prep.). (I) is extracted from the fibre by repeated treatment with hot NaOH and titrated with KMnO₄, the KMnO₄ no. being calc. by an approx. formula. The results agree with those obtained from the loss in wt. of the fibre to within 1%. The acidified (CO₂ or AcOH) extract gives a substance (C₆H₈O₆)_n, also obtained from (I) prepared by different methods. It is not glycuronolactone. Fibres containing (I) produced by different methods with cold KOH yield the K salt (sinters and reddens 135°, suddenly sinters, decomp., and partly melts 163°, sinters 183°, strong decomp. 186°) of polyglycuronic acid. The fall in strength of fibre is proportional to the increase in (I) content. A. A. L.

Chemical nature of hypochlorite oxycelluloses. R. HALLER and F. LORENZ (Helv. Chim. Acta, 1933, 16, 1165—1180).—American cotton is purified by treatment with "degomma" at 40°, followed by twice boiling with 2% NaOH in absence of air under slightly increased pressure for 8 hr. and subsequent washing with running H₂O, treatment with 0.5% H₂SO₄, and final washing. The product is soaked in NaOCl containing little NaOH, thoroughly squeezed, exposed to CO₂ for 12 hr., soured with 0.5% HCl, washed with H₂O, and dried at 50°. Extraction with H₂O (Soxhlet) shows that the degradation products of oxy- (I) are much more firmly retained than those of hydro-cellulose. Extraction with wet steam is much more effective than with H₂O. The extractions show that a portion of the reducing degradation products in (I) can be removed, and that these are in adsorptive union with (I). Fibrous structure is apparently retained by the residue, which, however, crumbles readily and is shown by acid val. and [α] to retain degradation products not removable by H₂O. Treatment of the relatively very small extract with neutral and basic Pb acetate leads to the identification of

d-saccharic acid and acids derived from higher carbohydrates which yield *d*-glucose when hydrolysed. The bulk of the residue is a neutral material which strongly reduces Fehling's solution, does not react with $\text{NHPh}\cdot\text{NH}_2$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, or $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2$; it yields a freely-sol. Ac derivative and is hydrolysed to *d*-glucose. It is considered that the oxidation of cellulose by NaOCl is initiated by hydrolytic fission of the highly-polymerised mol.

H. W.

Behaviour of hydrochlorides of organic bases towards chloroauric acid. Constitution of the abnormal auric chloride complexes. D. C. SEN (J. Indian Chem. Soc., 1933, 10, 497—501).—Complexes of the type $\text{BH}[\text{AuCl}_4]$ (I) (m.p. quoted in parentheses), where B is 1 mol. of base, are prepared by Fenner and Tafel's method (A., 1900, i, 111) from base hydrochloride and HAuCl_4 in H_2O ; in $\text{EtOH}\cdot\text{HCl}$ (cf. *loc. cit.*), the complexes $\text{BH}[\text{AuCl}_4]\cdot\text{B}\cdot\text{HCl}$ (II) (the constitutions are assigned from determinations of sp. resistance and mol. vol.) are often formed. (II) decompose in H_2O , COMe_2 , or hot EtOH to (I) and $\text{B}\cdot\text{HCl}$. The following are described: (I), where B is quinoline (238°), piperidine (206°), NH_2Et (195°), $\text{CH}_3\text{Ph}\cdot\text{NH}_2$ (168°), and NMe_3 (220°); (II), where B is quinoline (180°), piperidine (183°) (lit. 170°), and NH_2Et (70°).

H. B.

Action of formaldehyde on amines and amino-acids. H. T. CLARKE, H. B. GILLESPIE, and S. Z. WEISSHAUS (J. Amer. Chem. Soc., 1933, 55, 4571—4587).— NH_2Alk and NHAlk_2 are methylated by CH_2O (1.1 mol. per Me group introduced) in warm HCO_2H to NMe_2Alk and NMeAlk_2 , respectively; the H involved in the reduction is supplied (mainly) by the HCO_2H : $\text{NHR}_2 + \text{CH}_2\text{O} + \text{HCO}_2\text{H} \rightarrow \text{NMeR}_2 + \text{CO}_2 + \text{H}_2\text{O}$. NH_2Bu , $\text{CH}_2\text{Ph}\cdot\text{NH}_2$, piperidine (I), $(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2$, and 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NH}_2$ are thus converted into NMe_2Bu , $\text{CH}_3\text{Ph}\cdot\text{NMe}_2$ (II), 1-methyl-piperidine (III), $(\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe})_2$, and 2:4:6- $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{NMe}_2$, respectively; NH_2Ph gives a viscous product and the reaction fails with amides, $\text{CO}(\text{NH}_2)_2$, guanidine, and NH_2OH . $\text{NH}(\text{CH}_2\text{Ph})_2$ (IV) similarly affords $\text{NMe}(\text{CH}_2\text{Ph})_2$ (V) (main product), PhCHO , and (probably) (II). $\text{CH}_3[\text{N}(\text{CH}_2\text{Ph})_2]$ is converted by warm HCO_2H into (IV) and (V); $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$ is not an intermediate, since this is readily hydrolysed by HCO_2H . Methylenedipiperidine and HCO_2H similarly afford (I) and (III); in these cases, the change $\text{CH}_2(\text{NR}_2)_2 \rightarrow \text{NHR}_2 + \text{OH}\cdot\text{CH}_2\cdot\text{NR}_2$ (which is subsequently reduced) probably occurs. $(\text{C}_2\text{H}_5)_3\text{N}_4$ (VI) and warm HCO_2H give (mainly) NH_3 and NMe_3 together with small amounts of NH_2Me and NHMe_2 ; about 75% of the C of (VI) is found as Me. In all the above reactions, some of the H (for reduction) is supplied by CH_2O . MeCHO , HCO_2NH_4 , and HCO_2H give 2-methyl-5-ethylpyridine; CO_2 is not produced (cf. above).

Methylation of various NH_2 -acids is accomplished under similar conditions. Thus, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ gives 50–70% of $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (hydrochloride, m.p. 189–190°), and a little NMe_3 ; α -aminoisobutyric acid affords 80% of α -dimethylaminoisobutyric acid [hydrochloride, m.p. 264° (decomp.); Me ester, b.p. 154–155°]; $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ yields 38% of

$\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (hydrochloride, m.p. 188–191°); α -amino- α -phenylbutyric acid furnishes α -dimethylamino- α -phenylbutyric acid, m.p. 220° (decomp.), and some COPhEt (probably formed thus:



$\text{CPhEt}\cdot\text{NMe} \rightarrow \text{COPhEt}$). $\text{NH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ similarly affords some PhCHO . Alanine, leucine, and α -amino-octico and glutamic acids do not give the NMe_2 -derivatives; volatile bases are produced. *dl*-Phenylalanine (VII), CH_2O , and HCO_2H (or AcOH) give (mainly) NH_2Me and (probably) β -phenyl- α -2:3-diketo-4-phenyl-1-pyrrolidylpropionic acid (VIII), m.p. 245–246° [*Ba* salt (+3 H_2O); Me ester, m.p. 118°; anil anilide, m.p. 215°; Me ether, m.p. 75–90° (*Ba* salt; Me ester, m.p. 78°; anilide, m.p. 208°)]; *l*-phenylalanine affords a similar compound, m.p. 250–251°, $[\alpha]_D^{20} -37.6^\circ$ in *N*- NaOH . (VIII) is also obtained from (VII), $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ (IX) (which is undoubtedly an intermediate in the above reaction), and CH_2O in AcOH . *l*-*p*-Methoxyphenylalanine (X) and (IX) similarly afford (probably) β -anisyl- α -2:3-diketo-4-phenyl-1-pyrrolidylpropionic acid, m.p. 239–240°, $[\alpha]_D^{20} -135.5^\circ$ in *N*- NaOH ; with CH_2O and HCO_2H , (X) yields (probably) β -anisyl- α -2:3-diketo-4-anisyl-1-pyrrolidylpropionic acid, m.p. 231° (decomp.), $[\alpha]_D^{20} -31^\circ$ in *N*- NaOH . (VIII) is oxidised by alkaline KMnO_4 to BzOH and (probably) a little (IX) and by Ag_2O to PhCHO . (VIII) and Ac_2O give a compound, $\text{C}_{21}\text{H}_{17}\text{O}_4\text{N}$, m.p. 192–194°, whilst with BzCl and aq. NaOH a compound, $\text{C}_{26}\text{H}_{23}\text{O}_6\text{N}$, m.p. 60° (previous softening), results; these are hydrolysed to (VIII). (VIII) and NH_2OH afford a compound, $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$, m.p. 185–186° (decomp.) (yellow > 160°), also hydrolysed to (VIII).

H. B.

Mechanism of action of carbon disulphide on primary and sec. amines. H. S. FRY and W. V. CULP (Rec. trav. chim., 1933, 52, 1061–1066).—Interaction of sec. (aralkyl-)amines with excess of CS_2 in presence of I (1 equiv.) and $\text{C}_5\text{H}_5\text{N}$ (excess) gives only thiuram disulphides (44–89% of theory). Since primary amines under these conditions give only thiocarbamides (A., 1913, i, 1174), it is concluded that this latter reaction occurs in accordance with the equation $\text{NHR}\cdot\text{CS}\cdot\text{SH} + \text{NH}_2\text{R} \rightarrow \text{H}_2\text{S} + \text{NHR}\cdot\text{C}(\text{NH})\cdot\text{SH} \rightarrow \text{CS}(\text{NHR})_2$. *Bis*- α -naphthylethyl-, m.p. 166.7°, and β -naphthylethyl-thiuram disulphide, m.p. 158–159°, are described. H. A. P.

Fluorine polyhalides of organic amines.—See this vol., 44.

Action of trimethylamine on $\alpha\gamma$ -tetramethyldiamino- $\beta\gamma$ -hydroxypropane dimethiodide. L. GORINI (Gazzetta, 1933, 63, 751–756).—If in the prep. of $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_3)_2$ from $\text{OH}\cdot\text{CH}(\text{CH}_2\text{I})_2$ and NMe_3 an autoclave is used, with excess of NMe_3 , the product contains increasing quantities of $\text{OH}\cdot\text{CH}(\text{CH}_2\cdot\text{NMe}_2)_2$ (I) and $\text{NMe}\cdot\text{I}$ as the concn. of NMe_3 and the hydrolytic power of the solvent increase. (I), new b.p. 46°/2 mm., forms a di-iodide (II), m.p. 225°, and a dihydrochloride (III), m.p. 256°, which are also prepared from the iodo- and chloro-hydrins and NHMe_2 ; with Ac_2O (III) forms tetramethyldiaminoisopropyl acetate dihydrochloride, m.p. 247°. E. W. W.

Amidoxime salts. I. Hippuramidoxime. J. V. DUBSKY and J. TRTILEK (Coll. Czech. Chem. Comm., 1933, 5, 310—316).—Addition of NH_4OH in 96% EtOH to a warm solution of $\text{NHBz}\cdot\text{CH}_2\cdot\text{CN}$ in EtOH affords *hippuramidoxime* (I) $\text{NHBz}\cdot\text{CH}_2\cdot\text{C}(\text{NOH})\cdot\text{NH}_2$ (tautomeric), m.p. 123—126°, the Cu, $\text{RCu}\cdot 2\text{H}_2\text{O}$ ($\text{R} = [\text{NHBz}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{NO}]$), losing 1 H_2O at 100° to give $\text{RCuOH}\cdot\text{H}_2\text{O}$, and Ni, R_2NiOH (II) [from (I), $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, and H_2O_2 in NH_3 solution], decomp. in boiling H_2O , compounds of which are described and their constitutions discussed. According to conditions mixtures of (II) and compounds of type R_3Ni may be obtained. J. W. B.

Diamino-acid, canavanin. III. Constitution of canalin. M. KITAGAWA and S. MONOBE (J. Biochem. Japan, 1933, 18, 333—343).—Canalin (A., 1933, 382) (sulphate; *Bz*, lactam, m.p. 163—164°; *Et* ester hydrochloride) is reduced by H_2 —Pt-black to α -amino- γ -hydroxybutyric acid and NH_3 . The structure $\text{CH}_3(\text{ONH}_2)\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ is proposed. F. O. H.

Additive compounds of cystine and picric acid. G. TOENNIES (Z. physiol. Chem., 1933, 222, 1—2).—Picric acid (A) and *l*-cystine (B) form complexes AB_3 (from H_2O) and AB_6 (from MeOH). In MeOH in presence of A the $[\alpha]$ of B is 25% > the normal val. J. H. B.

Production of cysteine from cystine by irradiation. P. SZENDRO, U. LAMPERT, and F. WREDE (Z. physiol. Chem., 1933, 222, 16—20).—*l*-Cysteine is formed in 5% yield by irradiation of cystine with ultra-violet light. J. H. B.

Action of carbon monoxide on iron and cobalt complexes of cysteine. M. P. SCHUBERT (J. Amer. Chem. Soc., 1933, 55, 4563—4570).—Cysteine hydrochloride (I), $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, and KOH in H_2O and CO give after acidification (HCl) the complex (II), $\text{Fe}[\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}]_2\cdot 2\text{CO}\cdot\text{H}_2\text{O}$ (Na , salt + $2\text{H}_2\text{O}$), which is stable in air but decomposes (into its components) in warm aq. solution. K_2 cobaltobiscysteinate (A., 1933, 1039) does not give a complex analogous to (II); 1 mol. of CO is absorbed in solution and K_3 cobalttricycysteinate (III) (*loc. cit.*) and the acid $\text{H}[\text{Co}(\text{CO})_4]$ (IV) [*Ag* (+0.5 and $2\text{H}_2\text{O}$), blackens at about 90°, and *Hg*, m.p. 82° (decomp.), salts] are produced. (III) and CO in aq. KOH give K_2CO_3 and (IV). Acidification (HCl) of solutions containing (IV) affords *Co tetracarbonyl* (+0.5 H_2O), decomp. 48—50°, which with (I) and aq. KOH gives (III) and (IV). H. B.

Basis for the physiological activity of -onium compounds. XIII. Betaine-amides. R. R. RENSHAW and H. T. HOTCHKISS, jun. XIV. Aryl ethers of choline. I. R. R. RENSHAW and W. D. ARMSTRONG (J. Biol. Chem., 1933, 103, 183—186, 187—189).—XIII. (cf. A., 1926, 1232). *Betaine-amides*, $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$, where R is *Me* (I), m.p. 171—172° (all m.p. are corr.); *Et*, m.p. 203—204°; *Pr*, m.p. 165°; *Bu*, m.p. 177°; *Ph* (II), m.p. 223° (corresponding bromide, m.p. 215°); *p*-tolyl, m.p. 235° (decomp.); *p*-hydroxyphenyl, m.p. 198°; *o*-, m.p. 195°, and *p*-, m.p. 218°, -anisyl; *o*-, m.p. 160°, and *p*-, m.p. 215°, -phenetyl; *p*-nitrophenyl, m.p. 143—144°

(corresponding bromide, m.p. 235—236°); $-\text{C}_{10}\text{H}_7$, m.p. 165.5°; β - C_{10}H_7 , m.p. 188°, and $\text{NHR} = 1$ -piperidyl, m.p. 129°, are prepared from NMe_3 and $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NHR}$ usually in PhMe . Of the alkyl-amides, (I) possesses the max. muscarine-like action (III). With the arylamides, no (III) is observed; (I) gives a strong stimulating nicotine action.

XIV (cf. A., 1932, 622). β -Phenoxyethyl- (IV), m.p. 167°, and γ -phenoxypropyl-, m.p. 156°, -trimethylammonium bromides are described. (IV) produces a marked stimulation of blood pressure and respiration. H. B.

Ethylenic nitriles. α -Methyl- Δ^2 -hexenonitriles and α -butylacrylonitrile. A. CRAEN (Bull. Soc. chim. Belg., 1933, 42, 410—418).—Successive treatment of α -hydroxy- α -methylhexonitrile with SOCl_2 and dry HCl gives α -chloro- α -methyl- (I), b.p. 62—63°/10 mm., β -chloro- α -methyl- (II), b.p. 84—84.2°/10 mm., and α -chloromethyl- (III), b.p. 94—94.6°/10 mm., -hexonitriles. (II) and $\text{C}_5\text{H}_5\text{N}$ at 150° afford *cis*- (IV), b.p. 46—47°/10 mm., and *trans*-, b.p. 59.4—59.6°/10 mm., α -methyl- Δ^2 -hexenonitriles, whilst (III) similarly gives α -butylacrylonitrile (V), b.p. 45.8—46°/10 mm. (I) similarly yields a mixture of (IV) and (V). The above unsaturated nitriles are hydrolysed to the unsaturated amides, m.p. 74—74.2°, 54.8—55.7°, and 75—76°, respectively. H. B.

Effect of ethyl radicals on the thermal decomposition of azomethane. Kinetics of thermal decomposition of lead tetraethyl. Ethyl radicals and hydrogen.—See this vol., 34.

Esters of tetrathio-orthogermanic acid. H. J. BACKER and F. STIENSTRA (Rec. trav. chim., 1933, 52, 1033—1038).—The following are prepared by interaction of the appropriate Na mercaptide with GeCl_4 in C_6H_6 or (better) from the thiol, NaOEt , and GeCl_4 in EtOH : *Me*, m.p. -3°, b.p. 138—140°/4 mm.; *Et*, b.p. 164.5—165.5°/5 mm.; *Pr*, b.p. 191—192°/4—5 mm.; *Pr*, m.p. 15°, b.p. 162—164°/4 mm.; *Bu*, b.p. 222—223°/4—5 mm.; *sec*-, b.p. 200—201°/5 mm., *iso*-, b.p. 199—200°/4—5 mm., and *tert*-.butyl, m.p. 172—173°; *Ph*, m.p. 101.5°; *p*-tolyl, m.p. 110—111° [with Br in CHCl_3 gives $(\text{C}_6\text{H}_4\text{Me})_2\text{S}_2$], and (*p*- C_6H_4)₂ tetrathio-orthogermanate, b.p. 196—196.5°. Interaction of $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$ with $\text{CS}(\text{NH}_2)_2$ gives the corresponding isothiocarbamide derivative, converted by warm NaOH into $\beta\beta'$ -dithioldiethyl ether, b.p. 217°; this with GeCl_4 and NaOEt gives the corresponding spiro-ester, $\text{Ge} \left[\begin{array}{c} \text{S}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{S}\cdot\text{CH}_2\cdot\text{CH}_2 \end{array} \right] \text{O}$, m.p. 159—159.5° H. A. P.

Organo-metallic compounds. II. Reaction between aliphatic organic compounds of tin and tin tetrahalides. K. A. KOZESCHKOV (Ber., 1933, 66, [B], 1661—1665; cf. A., 1929, 712).—The reactions $3\text{SnR}_4 + \text{SnX}_4 = 4\text{SnR}_3\text{X}$; $2\text{SnR}_4 + \text{SnRX}_3 = 3\text{SnR}_2\text{X}$; $\text{SnR}_4 + \text{SnR}_2\text{X}_2 = 2\text{SnR}_3\text{X}$; $\text{SnR}_4 + \text{SnX}_4 = 2\text{SnR}_2\text{X}_2$; $\text{SnR}_4 + 2\text{SnRX}_3 = 3\text{SnR}_2\text{X}_2$; $2\text{SnR}_3\text{X} + \text{SnX}_4 = 3\text{SnR}_2\text{X}_2$, and $\text{SnR}_3\text{X} + \text{SnRX}_3 = 2\text{SnR}_2\text{X}_2$ ($\text{R} = \text{Me}$, *Et*, or *Pr*; $\text{X} = \text{Cl}$, *Br*) occur readily and with good yields, so that they can be used for the prep. of SnR_2X_2 and SnR_3X without useless elimination of alkyl halide. The use of sealed tubes is unnecessary. The possible reaction $\text{SnR}_4 + 3\text{SnX}_4 = 4\text{SnRX}_3$ leads

only to production of SnR_2X_2 . Aryl groups are less firmly bound than alkyl radicals to Sn and the first two alkyl groups are more readily lost than the remaining pair. *Sn Me₂ sulphide*, m.p. 148°, appears new. H. W.

Nitrosites and nitrosates. III. (SIGNA.) L. MONTI and F. BUCCI (*Gazzetta*, 1933, 63, 708—712; cf. A., 1931, 194; 1932, 943).—Methylcyclohexene nitrosate when heated in an inert gas evolves N_2 , NO, and CO_2 ; stilbene ψ -nitrosite gives N_2 and NO, with traces only of CO_2 . $(\text{NO}_2 \cdot \text{CHPh})_2$ sublimes unchanged at 150°; when heated quickly at 240° it partly sublimes and partly decomposes, evolving mainly NO. E. W.

[Photo-]chlorination of benzene.—See this vol., 40.

Catalytic oxidation of ethylbenzene in the liquid phase. C. E. SENSEMAN and J. J. STUBBS (*Ind. Eng. Chem.*, 1933, 25, 1286—1287).—Oxidation of PhEt containing MnO_2 by air at 120° yields CHPhMe·OH (I) (12.8% of the unrecovered PhEt), COPhMe (II) (26%), BzOH (III) (36.5%), and CH_2O , CO_2 , and H_2O . The yields vary considerably with variation of temp. between 110° and 130°. Traces only of (III) are formed at temp. <115°. The yield of (I) tends to an approx. const. val. after 6 hr., whilst that of (II) tends to fall. H. F. G.

Action of fluorine on aromatic compounds under various conditions. I. L. A. BIGELOW, J. H. PEARSON, L. B. COOK, and W. T. MILLER, jun. (*J. Amer. Chem. Soc.*, 1933, 55, 4614—4620).—When F_2 (prep. by electrolysis of KHF_2 described) is passed into a solution of C_{10}H_8 in CCl_4 at 0° [contrary to Ruff and Keim (A., 1932, 142), Cl_2 is liberated from the CCl_4], a product (I), decomp. 148—155°, containing 52.4% F is ultimately obtained. (I) is decomposed by aq. Na_2CO_3 in Et_2O , is converted by fuming HNO_3 into a similar product (57.4% F), is not oxidised by CrO_3 -AcOH at 70°, and is not reduced (H_2 , Pt); oxidation (KMnO_4) results in almost complete destruction. Similar products (% F quoted after substance used), all decomp. 90—110°, are obtained from 1- $\text{C}_{10}\text{H}_7\text{Me}$ 30.7, 2- $\text{C}_{10}\text{H}_7\text{Me}$ 27.2, α - $\text{C}_{10}\text{H}_7\text{OMe}$ 33.3, β - $\text{C}_{10}\text{H}_7\text{OMe}$ 30.4, α - $\text{C}_{10}\text{H}_7\text{OH}$ 30.4, β - $\text{C}_{10}\text{H}_7\text{OH}$ 29.8, 1- $\text{C}_{10}\text{H}_7\text{NO}_2$ 34.4, 1- $\text{C}_{10}\text{H}_7\text{Br}$ 35.9, and tetrahydronaphthalene 26.4; decahydronaphthalene does not give a derivative of this type. Under comparable conditions, the α - gives a higher yield than the β -isomeride. Similar compounds, decomp. 115—150° containing 25.6—31.2% F and 1.3—8.6% Cl are formed similarly from benzoin, deoxybenzoin, CH_2Bz , and Bz_2 ; the Cl content increases with the power of enolisation of the original compound. PhMe and F, in CCl_4 containing a little I at 0° react more slowly; C_6Cl_6 , p - $\text{C}_6\text{H}_4\text{MeCl}$, and fractions containing 38.5—52.7% Cl and 7.8—14% F are isolable. Explosions do not occur when the reactions are carried out in absence of any significant vapour phase. A Cu reaction vessel is described. H. B.

Decomposition of iodobenzene dichloride. IX. Mol. wt. and electrical conductivity of solutions. X. Discussion of salt structure proposed for iododichlorides, iodine trichloride, and phos-

phorus pentachloride. E. V. ZAPPI and J. CORTELEZZI (*Anal. Asoc. Quím. Argentina*, 1933, 21, 71—99; cf. A., 1933, 385, 942).—Stable PhICl_2 is prepared in purified CHCl_3 , and with precautions against formation of HCl. The mol. wt. in PhNO_2 or POCl_3 indicates dissociation, but vals. of λ_∞ in $\text{C}_5\text{H}_5\text{N}$ or PhNO_2 are low, and solutions in POCl_3 , AsCl_3 , or CHCl_3 are non-conducting. It is concluded that such dissociation as occurs is mol., viz., $\text{PhICl}_2 \rightleftharpoons \text{PhI} + \text{Cl}_2$. The dissociation of ICl_3 , $\text{C}_5\text{H}_5\text{NCl}$, and PCl_5 is probably analogous. Conductivity in PhNO_2 or POCl_3 is due to formation of complexes. Ionic formulæ, e.g., $[\text{PhICl}]\text{Cl}$, are to be discarded. R. K. C.

Styrene and metastyrene. S. NATELSON (*Ind. Eng. Chem.*, 1933, 25, 1391—1394).—The combination of C_2H_4 with C_6H_6 to PhEt in presence of AlCl_3 is accelerated by relatively small increases in pressure (about 6 cm.), and by initial addition of HCl with the C_2H_4 , which leads to formation of an additive compound of AlCl_3 with EtCl which appears to be the active catalyst. Vigorous agitation suppresses the formation of $\text{C}_6\text{H}_4\text{Et}_2$, $\text{C}_6\text{H}_3\text{Et}_3$, etc. The best procedure for conversion into CHPh·CH₂ is to chlorinate until 60% of the calc. quantity for CHClPhMe is absorbed (variation in temp. is without marked effect on the final result) and heat the product with Ag-Hg. Metastyrene is conveniently formed by polymerisation with 2% PhCHO and 0.6% O_2 in an autoclave at 150°/10—15 lb. per sq. in. H. A. P.

Highly arylated derivatives of benzene. I. W. DILTHEY, W. SCHOMMER, and O. TRÖSKEN (*Ber.*, 1933, 66, [B], 1627—1628).—Tetraphenylcyclopentadienone (I) and maleic anhydride afford endocarbonyltetraphenylidihydrophthalic anhydride, m.p. 223° (decomp.) [corresponding acid], which passes when heated into CO and tetraphenylidihydrophthalic anhydride, m.p. 243° (varying with rate of heating), converted at about 200° in presence or absence of dehydrogenating agents into tetraphenylphthalic anhydride (II), m.p. 286°. (I) affords the following compounds: from C_2H_2 , 1:2:3:4-tetraphenylbenzene, m.p. 190—191°, obtained also by decarboxylation of (II); from CPh:CH, pentaphenylbenzene, m.p. 246—247°; from toluene or stilbene, C_6Ph_6 , m.p. 421—422° [Durand et al. (A., 1931, 207) give m.p. 266°]; from phenylpropionic acid, pentaphenylbenzoic acid, m.p. 345°; from phenylpropionitrile, pentaphenylbenzonitrile, m.p. 271—272°; from phenylpropionaldehyde, pentaphenylbenzaldehyde. H. W.

Diphenyls. XII. Nitration of halogenated diphenyls. XIII. Attempts to obtain σ -diphenylene. L. MASCARELLI and D. GATTI (*Gazzetta*, 1933, 63, 654—660, 661—665).—XII. 2-Chlorodiphenyl with HNO_3 - H_2SO_4 yields 2-chloro-4'-nitro- (I), m.p. 73—74°, and 2-chloro-3':4'-dinitro-diphenyl (II), m.p. 158—159°, identified by conversion into p -nitro- and 3:4-dinitro-benzoic acids. (II) is reduced to 2-chloro-3':4'-diaminodiphenyl (dihydrochloride, decomp. 233—300°), from which 2:3':4'-trichlorodiphenyl, m.p. 65—66°, is prepared. Nitration of 2:2'-dichlorodiphenyl (cf. A., 1932, 729) gives a $(\text{NO}_2)_2$ -compound, m.p. 205°. 4-Bromodiphenyl yields two isomeric $(\text{NO}_2)_2$ -compounds, m.p. 205—206° and

147—148°. The results of Shaw and Turner with 4:4'-dibromodiphenyl (*ibid.*, 259) are confirmed. 3-Chlorodiphenyl forms a $(NO_2)_2$ -derivative, m.p. 202—203°.

XIII. 2:2'-Dibromodiphenyl is unaffected by Na in Et_2O ; the prep. of *o*-diphenylene by Dobbie *et al.* (J.C.S., 1911, 99, 683) may have been due to catalysis by impurities. 2:2'-Diiododiphenyl is also recovered, with a halogen compound, m.p. 54°. 2:2'-Dichlorodiphenyl gives Ph_2 , *o*- C_6H_4BrI and Cu (+CuO) at 230—240° yield diphenylene oxide.

E. W. W.

Analogues of resolvable diphenyls. M. E. MACLEAN and R. ADAMS (J. Amer. Chem. Soc., 1933, 55, 4683—4688).—Di-2:4:6-trimethylphenyl sulphone, m.p. 202—204° (all m.p. are corr.) (lit. 195°) (from 2:4:6- $C_6H_2Me_3SO_2Cl$, *s*- $C_6H_3Me_3$, and $AlCl_3$ in CS_2), and HNO_3 (*d* 1.42) at 100° (bath) give the 3:3'-(NO_2)₂-derivative, m.p. 172—174°, reduced (Zn, dil. HCl, AcOH) to *di*-3-amino-2:4:6-trimethylphenyl sulphone (I), m.p. 217.5—218.5° (*camphor*- and *bromocamphor*-sulphonates). The 3:3'-(NO_2)₂-derivative, m.p. 171.5—172.5°, of 2:4:6:2':4':6'-hexamethylbenzophenone is similarly reduced to 3:3'-diamino-2:4:6:2':4':6'-hexamethylbenzophenone (II), m.p. 163—164.5° [*camphor*- (+2H₂O) and *bromocamphor*- (+2H₂O)-sulphonates], which is reduced (Clemmensen) to 3:3'-diamino-2:4:6:2':4':6'-hexamethyldiphenylmethane (III), m.p. 160—160.5° (*dihydrochloride*, decomp. 220—290°; *camphor*- and *bromocamphor*-sulphonates). (I), (II), and (III) could not be resolved; their salts do not exhibit mutarotation at 0°. The possibility of stereoisomerism in such compounds is discussed. 3:5-Dinitro-2:4:6:2':4':6'-hexamethylbenzophenone, m.p. 199—200°, is prepared from 3:5-dinitro-2:4:6-trimethylbenzoyl chloride, *s*- $C_6H_3Me_3$, and $AlCl_3$.

Stereochemistry of diphenyls. XXXIV. Preparation and properties of 2:4:5:6:2':4':5':6'-octamethyldiphenyl- and diphenyl-3:3'-disulphonic acids. A. E. KNAUF and R. ADAMS (J. Amer. Chem. Soc., 1933, 55, 4704—4709).—2:3:4:6- C_6HMe_4MgBr and anhyd. $CuCl_2$ in Et_2O give 2:4:5:6:2':4':5':6'-octamethyldiphenyl (*disoduryl*), m.p. 121—122° [3:3'-*Ac*, m.p. 184°, and 3:3'-*di(chloroacetyl)*, m.p. 183—184°, derivatives], which with $ClSO_3H$ at 0° affords *disoduryl*-3:3'-disulphonyl chloride, m.p. 159—160°. Na *disoduryl*-3:3'-disulphonate and strychnine hydrochloride in H_2O give a *distrychnine* salt, m.p. 252—255° (decomp.), $[\alpha]_D^{20}$ -14° in 80% MeOH, separable by EtOH into more sol., m.p. 248—251° (decomp.), $[\alpha]_D^{20}$ -10.3° in 80% MeOH, and less sol., m.p. 252—255° (decomp.), $[\alpha]_D^{20}$ -21.6° in 80% MeOH, salts. These are decomposed by aq. NH_3 to *d*-, $[\alpha]_D^{20}$ +11.2° in H_2O , and *l*-, $[\alpha]_D^{20}$ -11.4° in H_2O , $-NH_4$ *disoduryl*-3:3'-disulphonate, respectively. Diphenyl-3:3'-disulphonic acid [*brucine*, m.p. 268—270° (softens at 244°), and *strychnine* salts], prepared from benzidine-3:3'-disulphonic acid, could not be resolved. H. B.

Di-*p*-substituted derivatives of diphenylmethane and diphenylethane. T. REICHSTEIN and R. OPPENAUER (Helv. Chim. Acta, 1933, 16, 1373—

1380; cf. Connerade, A., 1932, 1122).— CH_2PhCl , polyoxymethylene, and 84% H_2SO_4 at $\geq 20^\circ$ yield 4:4'-di(chloromethyl)diphenylmethane (I), m.p. 110° (corr.), b.p. 180°/0.2 mm. (slight decomp.), the constitution of which is established by its conversion into *pp'*-ditolylmethane. (I) is transformed by KOAc in AcOH into 4:4'-di(acetoxymethyl)diphenylmethane, m.p. 50°, whence 4:4'-di(hydroxymethyl)diphenylmethane, m.p. 123° (corr.), oxidised (N_2O_4 in $CHCl_3$) to diphenylmethane-4:4'-dialdehyde, m.p. 85.5—86° (corr.) [*dioxime*, m.p. 184° (corr.), dehydrated to 4:4'-di(cyanomethyl)diphenylmethane, m.p. 167° (corr.)]. Dibenzyol (improved prep. from CH_2PhCl and Mg activated by I in Et_2O) is converted by polyoxymethylene, anhyd. $ZnCl_2$, and HCl at $\geq 50^\circ$ into 4:4'-di(chloromethyl)diphenylethane (II), m.p. 97°, b.p. 190°/0.2 mm., also obtained by aid of "dichloro-ether" (from 40% CH_2O and HCl) and transformed by Zn dust and AcOH into α -*di*-*p*-tolylethane (III), m.p. 82°. 4:4'-Di(acetoxymethyl)-, m.p. 123° (corr.), and 4:4'-di(hydroxymethyl)-, m.p. 161° (corr.), b.p. about 195°/0.2 mm., -diphenylethane are described. Diphenylethane-4:4'-dialdehyde, has m.p. 126° (vac.). 4:4'-Di(cyanomethyl)diphenylethane, m.p. 130° (corr.), is obtained from (II) and NaCN in H_2O ; it is hydrolysed to the corresponding acid, the *Ce* salt of which when heated at 450°/vac. is transformed mainly into (III) with a little 4:4'-dimethylstilbene unaccompanied by cyclic ketone.

H. W.

Electrolytic oxidation of anthracene to anthraquinone.—See this vol., 38.

Rearrangements of polyinenes. VI. Tetradiphenylditert.-butylethynylethane. J. C. Y. TSAO and C. S. MARVEL (J. Amer. Chem. Soc., 1933, 55, 4709—4713).—Di-*p*-diphenyl ketone (I) and $CBu^tC:MgBr$ give *di*-*p*-diphenylditert.-butylethynylcarb-inol (II), m.p. 172—173° (tube), 180—181° (Maquenne block), converted by conc. H_2SO_4 -AcOH into *Bu^t* β -*di*-*p*-diphenyldivinyl ketone, m.p. 144—145°, and by PBr_3 in Et_2O at 0° into the corresponding bromide (III), m.p. 135—136°. (III) and "mol." Ag in Et_2O give a hydrocarbon (IV), $C_{22}H_{24}$, m.p. (block) 166°, also formed from (II) and $TiCl_3$ in EtOH. (III) and 40% Na-Hg in Et_2O and N_2 afford Na *di*-*p*-diphenylditert.-butylethynylmethyl, converted by *s*- $C_2Me_4Br_2$ at 0° into (IV) and at -80° into the very unstable *s*-tetra-*p*-diphenylditert.-butylethynylethane (V). A solution of (V) in PhMe absorbs O_2 readily at -80° and gives (I); when kept at 0°, (IV) is produced. (IV) is oxidised (O_2) in boiling xylene to about 50% of (I); absorption of O_2 does not occur at room temp.

H. B.

Sensitiveness to light of aromatic nitro-compounds. II. *peri*-Derivatives of 1-nitronaphthalene. R. E. STEIGER (Helv. Chim. Acta, 1933, 16, 1315—1323).—Nitronaphthalenesulphonyl chlorides are hydrolysed with unexpected ease by moist C_5H_5N . 1-Nitronaphthalene-5-sulphonyl chloride and technical C_5H_5N give pyridinium 1-nitronaphthalene-5-sulphonate, m.p. 194—195° (corr.); the prep. of the corresponding K salt is described. Pyridinium 1-nitronaphthalene-8-sulphonate, m.p. 165—167° (corr.), is obtained by heating the sulphonyl chloride

with NaOH followed by HCl and C_5H_5N . *Methylpyridinium 1-nitronaphthalene-8-sulphonate*, m.p. 162—164° (corr.), after softening, is derived from the Me ester and C_5H_5N in C_6H_6 . *K 1-nitronaphthalene-8-sulphonate* is described. H. W.

Dissociable organic oxides : second isomeride of oxytetraphenylrubene (rubrene oxide). L. ENDERLIN (Compt. rend., 1933, 197, 691—693).—Conc. acids convert rubrene oxide (I), in C_6H_6 , into an isomeride (II), $C_{42}H_{28}O_2(+C_6H_6)$, m.p. 205° (decomp.), containing one reactive H. Like (I), (II) is unstable to light and heat, but its thermal decomp. does not yield O. Unlike the isomeride previously described (A., 1930, 1173), it does not regenerate the rubrene on reduction, but with Zn in boiling AcOH yields, almost quantitatively, the hydrocarbon $C_{42}H_{26}$ (A., 1932, 261). A. C.

Compounds related to rubenes. C. DUFRASSE and P. CHOVIN (Compt. rend., 1933, 197, 1127—1129).—Treatment of $CH_2Bz \cdot CO \cdot CO_2Et$ with PCl_5 , decomp. of the excess of PCl_5 with a ketone, and careful thermal decomp. gives a red compound, probably $C_{20}H_{12}O_4$, m.p. 317° (yield about 3%), the absorption spectrum of which is analogous to that of tetraphenylrubene. It does not form a dissociable oxide when irradiated in solution in presence of air. H. B.

Carbon rings. XXVI. Poly-membered cycloalkylamines. L. RUZICKA, M. W. GOLDBERG, and M. HURBIN (Helv. Chim. Acta, 1933, 16, 1339—1342; cf. A., 1933, 599).—*cycloOctanoneoxime*, b.p. 128—129°/14 mm., m.p. about 33°, is reduced by Na and boiling EtOH to *cyclooctylamine* (I), b.p. about 80°/10 mm. [hydrochloride, m.p. 244—245° (decomp.)]; *cyclooctylcarbamide*, m.p. 179—180° (corr.). Similarly, *cyclopentadecanoneoxime*, m.p. 75—76°, affords *cyclopentadecylamine* (II) [hydrochloride, partial decomp. about 300°; sulphate; phosphate; nitrate; tartrate; acetate, m.p. 137·5—138° after softening at 135°; citrate; cyclopentadecylcarbamide, m.p. 165°]. *cycloTriacontane-1:16-dione* affords (Na and boiling amyl alcohol) 1:16-*diaminocyclotriacontane* (III),

$NH_2 \cdot CH < \begin{smallmatrix} CH_2 \\ CH \end{smallmatrix} >^{14} CH \cdot NH_2$ (dihydrochloride, decomp. about 240°; diacetate, m.p. 178—179° after marked softening). The physiological action of (I), (II), and (III) is described. H. W.

Transpositions of anilides. II. A. GIACALONE (Gazzetta, 1933, 63, 761—763; cf. A., 1932, 1024).— $NHPh \cdot CHO$, NH_2Ph , and $NH_2Ph \cdot HCl$ with $ZnCl_2$ at 170° yield *p*-leucaniline and a substance, m.p. 261°. $NHPhAc$ and $NHPhBz$ give only the acet- and benzamides. E. W. W.

Reductive fission of phenyl-R-anilinomethane. I. GASPOULOS (Praktika, 1932, 7, 47—50; Chem. Zentr., 1933, ii, 43).—Reductive fission of $NHPh \cdot CHRPh$ (from $NPh \cdot CHPh + XMeR \rightarrow MgX \cdot NPh \cdot CHRPh \rightarrow NHPh \cdot CHRPh$) with $Zn-Hg$ in hot HCl solution gives NH_2Ph and CH_2RPh . CH_2Ph_2 and $CHPh \cdot C_{10}H_7$ - α were prepared. A. A. E.

Optical activity in relation to tautomeric change. I. Conditions underlying the transport of the centre of asymmetry in tautomeric systems. C. K. INGOLD and C. L. WILSON (J.C.S., 1933, 1493—1505).—Consideration is given to the conditions necessary for the retention or loss of enantiomeric identity during the transformation of a prototropic (or anionotropic) system

$(X \cdot AR^1R^2 \cdot B \cdot CR^3R^4 \rightleftharpoons AR^1R^2 \cdot B \cdot CR^3R^4 \cdot X)$ such that the single asymmetric centre (*) is transported, during conversion, from the point of detachment of the mobile group (X) to the point of its reunion. For a large retention of enantiomeric identity, a mechanism inhibiting intramol. rotation during interconversion is necessary; this is illustrated by the conversion of linalyl acetate or formate into the corresponding optically active α -terpinyl ester, which is a ring-chain, pentad, anionotropic change. The behaviour of a triad, prototropic system (in which there is no such mechanism) is also illustrated; propagation of asymmetry is shown, by examination of (optically active) *p*-chlorobenzhydrylidene- α -phenylethylamine and α -phenylethylidene-*p*-chlorobenzhydrylamine, to be very small. Exploratory experiments with anionotropic and prototropic systems are first described.

Mesityl oxide and $MgPhBr$ in Et_2O at 0° give (probably) α -phenyl- $\alpha\gamma$ -dimethylcrotyl alcohol (attempted acylation results in loss of H_2O), which when distilled affords γ -phenyl- α -methylbutadiene, b.p. 94—96°/16 mm. (ozonolysis products, CH_2O , $BzOH$, and a neutral substance which gives the CHI_3 reaction); this is probably identical with the α -phenyl- $\alpha\gamma\gamma$ -trimethylallene of Klages (A., 1904, i, 567). α -Phenylcrotyl alcohol (I), b.p. 88—90°/1 mm. (Burton, A., 1929, 554), is dehydrated by heating with $o-C_6H_4(CO)_2O$ alone or in C_5H_5N to α -phenylbutadiene and its dimeride. (I) and $(CH_2 \cdot CO)_2O$ at 100° give α -phenylcrotyl succinate, m.p. 72—80° (II) (ozonolysis products, $BzOH$ and $MeCHO$); in C_5H_5N , 20% of (II) and 80% of α -phenylcrotyl *H* succinate, m.p. 76—78°, result. Crotonaldehyde and $MgMeI$ afford α -ethylcrotyl alcohol, b.p. 135—142°/770 mm., which, like (I), is probably a mixture of *cis*- and *trans*-forms; α -ethylcrotyl *p*-nitrobenzoate, m.p. 42—43·5°, and 3:5-dinitrobenzoate, m.p. 47—48°, are prepared from the fraction, b.p. 137·1°/764·8 mm.

$Et \beta$ -hydroxy- $\beta\beta$ -diphenyl- α -methylpropionate and cold conc. H_2SO_4 give 3-phenyl-2-methylindenone (III), m.p. 85° [2:4-dinitrophenylhydrazones, m.p. 259° (decomp.)], reduced (H_2 , PtO_2) to 3-phenyl-2-methylindanone (2:4-dinitrophenylhydrazones, m.p. 176—177°). (III) and $MgPhBr$ (2·5 mols.) afford 1-hydroxy-1:3-diphenyl-2-methylindene, m.p. 92°; reduction (H_2 , PtO_2) of this and subsequent distillation gives 1:3-diphenyl-2-methylindene, m.p. 108°. Attempts to obtain alcohols from (III) and Grignard reagents containing basic groups in C_5H_5N were unsuccessful; in one experiment using *p*- $C_6H_4Br \cdot NMe_2$, a *p*-dimethylaminophenylpyridine, m.p. 228—229°, was obtained.

9-Fluorenylamine (IV) [prepared by reduction (Zn dust, AcOH) of fluorenoneoxime], $COPhMe$, and a little EtOH at 100° give an α -phenylethylidene-9-fluorenylamine (V), m.p. 156·5—157·5°, fluorenylidene-9-fluorenylamine, m.p. 175° (decomp.) [also prepared

from (IV) and fluorenone (VI) at 100°], and unidentified material, m.p. 230—250°. (IV) and CPhMe at 140—145° afford difluorenyl, m.p. 239—240°, also formed when (IV) is heated at 180°. Isomerisation of (V) with 1.33*N*-EtOH-NaOEt at 85° and subsequent hydrolysis (20% HCl) gives (IV), (VI), CPhMe, α -phenylethylamine (VII) (*benzoate*, m.p. 141°), and a red substance (the amount of which increases with time of heating). Fluorenylidene- α -phenylethylamine could not be prepared from (VII) and (VI) or 9 : 9-dichlorofluorene.

Benzhydrylamine (VIII) is prepared by reduction (Na, EtOH) of CPh₂N·OH or by hydrolysis (N₂H₄, H₂O method) of *phthalbenzhydrylimide*, m.p. 149—150° [from CHPh₂Br and *o*-C₆H₄(CO)₂NK or *o*-C₆H₄(CO)₂NH·K₂CO₃ in xylene]. PhCHO and (VIII) give benzylidenbenzhydrylamine (IX), m.p. 101—102° (lit. 98—99°). CPh₂Cl₂ and CH₂Ph·NH₂ at 100° afford benzhydrylidenebenzylamine (X), m.p. 60—61°. The mobility and equilibrium of the system (IX) \rightleftharpoons (X) are measured; at equilibrium, the respective % are 43 and 57. *Benzhydrylidenebenzhydrylamine*, m.p. 152° [from (VIII) (3.5 mols.) and CPh₂Cl₂ (1 mol.) at 100° and from (VIII) and CPhMe at 180°], and *benzhydrylidene- α -phenylethylamine*, m.p. 52° [from (VII) and CPh₂Cl₂ at 100° or 140°], are described. *p*-Methylbenzhydrylidene- α -phenylethylamine, b.p. 198—201°/0.1 mm., is similarly prepared; this appears to be isomerised slowly by EtOH-NaOEt. *p*-Chlorobenzhydrylidene- α -phenylethylamine, b.p. 195—198°/0.05 mm. [from (VII) and *p*-chlorobenzophenone dichloride (XI), b.p. 160°/1 mm., 207—209°/22 mm., at 100°], undergoes half-conversion to equilibrium with 1.33*N*-EtOH-NaOEt at 85° in about 2 days; the equilibrium mixture contains approx. equal amounts of the two isomerides.

Hydrolysis of the azomethines obtained from (XI) and optically impure *d*- α -phenylethylamine (XII) with 20% HCl gives (XII) of a higher rotatory power than the original base; this is ascribed to the asymmetric influence of an optically active solvent [*i.e.*, excess of (XII) used in the prep.]. The (XII) recovered (as hydrochloride) from the original condensation with (XI) has a corresponding lower rotatory power. The phenomenon is not observed with optically pure *d*-, $\alpha_{D}^{17.5} + 22.22^\circ$ (*l*=50 mm.), and *l*- α -phenylethylamine, $\alpha_{D}^{16.5} - 22.92^\circ$ (*l*=50 mm.) (*benzoate*, m.p. 163—163.5°). Equilibration of the *p*-chlorobenzhydrylidene- α -phenylethylamines prepared from the pure bases with 1.33*N*-EtOH-NaOEt at 85° and subsequent hydrolysis gives some (XIII) (below) of very small rotatory power.

p-Chlorobenzhydrylamine (XIII), b.p. 161°/0.9 mm., 188—189°/13 mm. [*hydrochloride*, m.p. 304—305° (decomp.); *d*- α -bromocamphor- π -sulphonate, m.p. 251°; *Ac* derivative, m.p. 132°], is prepared by reduction (Zn dust, AcOH) of *p*-chlorobenzophenoneoxime and is resolved by *d*-camphor-10-sulphonic acid into the *l*-form, $\alpha_{D}^{20.1} - 2.06^\circ$ (*l*=50 mm.) (*d*-bromocamphor-10-sulphonate, m.p. 218°), and by *l*-malic acid into *d*-, $\alpha_{D}^{3.481} + 0.43^\circ$ (*l*=50 mm.) (*l*-malate, m.p. 171°), and *l*-forms, -0.2° (*l*=50 mm.) [*H* *l*-malate, m.p. 160° (decomp.)]. Impure α -phenylethylidene-*p*-chlorobenzhydrylamine is obtained from (XIII) and CPhMe at 140°; considerable racemisation occurs when optically active (XIII) is used. H. B.

Rearrangement of *o*-acetamido-sulphoxides.

A. LEVI, L. A. WARREN, and S. SMILES (J.C.S., 1933, 1490—1493; cf. A., 1933, 58).—2-Nitro-2'-aminodiphenyl sulphide, m.p. 85° (prep. described), and 4-chloro-2-nitro-2'-aminodiphenyl sulphide, m.p. 130° (*Ac* derivative, m.p. 150°), similarly prepared, when acetylated and treated with H₂O₂ in AcOH at 100° during 2 hr. afford 2-nitro-2'-acetamidodiphenyl sulphoxide (I), m.p. 160° (oxidised further to the sulphone), and 4-chloro-2-nitro-2'-acetamidodiphenyl sulphoxide (II), m.p. 179—180°, which with 10% H₂SO₄-EtOH at 70—80° in 2 hr. affords 4-chloro-2-nitro-2'-aminodiphenyl sulphoxide, m.p. 162°, re-acetylated to (II). (I) in EtOH at 50° with 2 mols. *N*-NaOH and excess of MeI undergoes rearrangement to 2-*o*-nitrophenylaminophenyl Me sulphoxide (III), m.p. 149—151°, but with 1 mol. *N*-NaOH gives 2-*o*-nitrophenylacetamidophenyl Me sulphoxide (IV), m.p. 160—161°, converted by NaOH into (III), thereby showing that rearrangement precedes deacetylation, so that the process must be regarded as the displacement of thionyl by ·NHAc. (III) and (IV) liberate SHMe with warm HI. (III) is oxidised by H₂O₂ in AcOH at 100° to 2-*o*-nitrophenylaminophenyl Me sulphone, m.p. 130—131°, identical with the methylation product of the corresponding sulphinic acid. (I) readily dissolves in hot *N*-NaOH (3 mols.) to give an impure product containing sulphinic acid which, when reduced with dil. HI and SO₂, affords bis-2-*o*-nitrophenylaminophenyl disulphide, m.p. 149—151°. (II) with *N*-NaOH (2 mols.) and MeI affords 2-*p*-chloro-*o*-nitrophenylaminophenyl Me sulphoxide, m.p. 152°, oxidised to 2-*p*-chloro-*o*-nitrophenylaminophenyl Me sulphone, m.p. 187°, identical with a sample prepared from the sulphinic acid. The amine from (II) was partly recovered after treatment with 2*N*-NaOH at 90—100° during 2 hr., which indicates that ·NHAc is more active in these rearrangements than ·NH₂. Interaction of 2-nitrophenyl 4-hydroxy-*m*-tolyl sulphide with H₂O₂ in AcOH at 100° during 3 hr. affords 2-nitrophenyl 4-hydroxy-*m*-tolyl sulphoxide, m.p. 206—207°, which is recovered (together with some *o*-NO₂·C₆H₄·OH) after treatment with 2*N*-NaOH at 100° during 15 min. 2-Nitrophenyl 2-acetoxy-1-naphthyl sulphoxide, m.p. 169°, is obtained from the sulphide and H₂O₂ in AcOH, and is hydrolysed (boiling 2*N*-NaOH) to the hydroxy-sulphoxide, m.p. 144° (decomp.), which undergoes no rearrangement with alkali, indicating that aromatic ·OH is less active in these displacements than ·NHAc or ·NH₂. J. L. D.

Reactions of diphenyl-4-carbimide [*p*-xenylcarbimide] with alcohols and amino-compounds.

I. Alcohols and phenols. II. Amines. III. Hydrazines. M. J. VAN GELDEREN (Rec. trav. chim., 1933, 52, 969—975, 976—978, 979—981).—I. 4-C₆H₄Ph·NCO (I) is proposed as a reagent for identifying OH-compounds; it is conveniently used in C₆H₆+light petroleum. The following are described (in addition to many in A., 1931, 834): *n*-hexyl, m.p. 98°; *n*-heptyl, m.p. 103°; *n*-octyl, m.p. 110°; *n*-nonyl, m.p. 115°; *n*-decyl, m.p. 111°; *n*-undecyl, m.p. 106°; *n*-dodecyl, m.p. 113°; CH₂Ph·CH₂, m.p. 151°; CHPh₂, m.p. 197°; and *l*-menthyl, m.p. 157°, *p*-xenylcarbimides. cycloHexyl *p*-xenylcarbimide.

ate has m.p. 140° (lit. 166°). No reaction was observed with $\text{C}_6\text{H}_5\text{OH}$.

II. The following are described: *p*-xenylocarbamide, decomp. 210°; *N*-*p*-xenyl-*N'*-methyl decomp. 186°, *N'*-ethyl, decomp. 210°, *N'*-*n*-propyl, m.p. 195°, *N'*-*n*-amyl, m.p. 152°, *N'*-*n*-butyl, m.p. 153°, *N'*-*n*-heptyl, m.p. 146°, *N'*- α -naphthyl, decomp. 238°, β -naphthyl, decomp. 255°, *p*-piperidyl, m.p. 185°, *N*-*N'*-dimethyl, m.p. 175°, *diethyl*, m.p. 136°, *di-n*-propyl, m.p. 124°, *phenylmethyl*, m.p. 136°, and *diphenyl*-carbamide, decomp. 174°; *N*-phenyl, decomp. 240°, *-o-*, decomp. 225°, *-m-*, decomp. 212°, and *-p*-tolyl, decomp. 246°, *-p*-anisyl, decomp. 232°, and *-m*-nitrophenyl-*N'*-*p*-xenylocarbamide, decomp. 227°; and *s*-di-*p*-xenylocarbamide, decomp. 312°.

III. Interaction of $\text{NHPh}\cdot\text{NH}_2$ and its derivatives containing a primary NH_2 with (I) in C_6H_6 , PhMe, or light petroleum gives 1:4-disubstituted semicarbazides; the products do not interact with PhCHO. Of these 1-phenyl-, decomp. 218° (*p*-Br-, decomp. 225°, and *p*-NO₂-compound, decomp. 235°); 1-*o*-, m.p. 186°, *-m*-, m.p. 178°, and *-p*-tolyl-, m.p. 178°; 1-phenyl-1-methyl-, m.p. 184°, and 1:1-diphenyl-4-*p*-xenyl-semicarbazide, decomp. 236°, are described. By gradual addition of (I) to $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ cooled in ice and salt 4-*p*-xenylocarbamide, decomp. 250—260° [CHPh], decomp. 234°, CMe_2 -, decomp. 225°, and 1-Ac derivative, decomp. 218—220° (no CHPh derivative)], is formed in a yield of 70% of theory; *s*-di-*p*-xenylocarbamylhydrazine is also prepared. H. A. P.

[Complex] ammines from cadmium salts and cyclic diamines. R. CERNATESCU and M. PONI (Ann. Sci. Univ. Jassy, 1933, 18, 385—403).—Vals. of the dissociation const. of the phenylenediamines, determined by electrometric titration with HCl, are in the order $o < m < p$, and bear no apparent relation to the composition of the complex salts with Ni, Cu, and Co. The following compounds are described [*Bo*, *Bm*, *Bp* are *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$]: [CdBo_2](NO₃)₂; [CdBm_2](NO₃)₂; [CdBp_2](NO₃)₂; [CdBo]Cl₂; [CdBm]Cl₂; [CdBp]Cl₂; [CdBo]Br₂; [CdBm]Br₂; [CdBp]Br₂; [CdBo]I₂; [CdBm]I₂; [CdBp]I₂; [CdBo_2]SO₄; [CdBp]SO₄; [$\text{Cd}\{1:8\text{-C}_{10}\text{H}_6(\text{NH}_2)_{2.7}\}$]Cl₂; [$\text{Cd}\{1:8\text{-C}_{10}\text{H}_6(\text{NH}_2)_2\}$]Br₂; [$\text{Cd}\{1:8\text{-C}_{10}\text{H}_6(\text{NH}_2)_2\}$]I₂; [$\text{Cd}\{1:5\text{-C}_{10}\text{H}_6(\text{NH}_2)_5\}$]Br₂; and [$\text{Cd}\{1:5\text{-C}_{10}\text{H}_6(\text{NH}_2)_5\}$]I₂. H. A. P.

Ammines from phenylenediamines and metallic salts. R. CERNATESCU and M. PAPAFIL (Ann. Sci. Univ. Jassy, 1933, 18, 404—414; cf. preceding abstract).—The following compounds are described [*Bo*, *Bm*, *Bp* represent *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$]: [CuBo_2]SO₄·H₂O; [CuBo_2](NO₃)₂; [CuBp]SO₄·H₂O; [CoBp]Cl₂; [CoBo_2]SO₄; [CoBm]SO₄; [CoBp]SO₄; [CoBp_2]Br₂; [NiBo_2]SO₄; [NiBp_2]SO₄; and [NiBp_2]Br₂. H. A. P.

p-Azoxydiphenyl and *p*-azodiphenyl. D. VORLANDER (Ber., 1933, 66, [B], 1666—1667).—*p*-Azoxydiphenyl is an enantiotropic cryst. liquid, the region of existence of the cryst. liquid being about 49° (260—211°), whereas *p*-azodiphenyl is a monotropic cryst. liquid or enantiotropic cryst. liquid with a region of about 1°.

Azo-dyes and intermediates. XII. Preparation of "homologous" azo-dyes with higher mol. wt. XIII. Influence of molecular size on properties of azo-dyes. P. RUGGLI and O. BRAUN (Helv. Chim. Acta, 1933, 16, 858—873, 873—884; cf. A., 1933, 59).—XII. Series of azo-dyes of regularly increasing mol. wt. are prepared by using J-acid (6-amino- α -naphthol-3-sulphonic acid) (I) both as a diazo- and coupling component, halogenated middle or end components being used in order to obtain by elementary analysis an exact measure of mol. size. Gradual addition of Br to an aq. solution of Na naphthionate (II) [$1:4\text{-C}_{10}\text{H}_6(\text{NH}_2)\cdot\text{SO}_3\text{Na}$] gives a ppt. of 2-bromonaphthionic acid (III); at higher temp. 2:4-dibromo- α -naphthylamine, m.p. 115° (Ac derivative, m.p. 226°), is formed. Similarly bromination of the Ac derivative of (II) gives 1:4- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NHAc}$. Bromination of a cold aq. suspension of 1:7- $\text{C}_{10}\text{H}_6(\text{NH}_2)\cdot\text{SO}_3\text{H}$ gives the 2:4-Br₂-derivative (IV) (*K* salt). Diazotised (IV) coupled (alkaline) with (I) gives the monoazo-dye (brownish-red), which after re-diazotisation couples with (I) to the disazo-dye, (IV) \rightarrow (I) \rightarrow (I); repetition of the process gives the trisazo-dye, (IV) \rightarrow (I) \rightarrow (I) \rightarrow (I), and finally the tetrakisazo-dye, (IV) \rightarrow (I) \rightarrow (I) \rightarrow (I) \rightarrow (I), the shades of which deepen through reddish-violet to deep violet. All are isolated as their cryst. Na salts. For comparison the monoazo-dyes, (III) \rightarrow (I), Cleve's acid [$1:6\text{-}$ and $1:7\text{-C}_{10}\text{H}_6(\text{NH}_2)\cdot\text{SO}_3\text{H}$] \rightarrow (I), and (IV) \rightarrow $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, are prepared. Similar series of dyes are prepared from tetrazotised 3:3'-dichloro- (V) and 2:2'-dichloro-4:4'-diaminodiphenyl (VI), and 2, 4, and 6 equivs. of (I), but the tetrakisazo-dye from (VI) and the hexakisazo-dye from both (V) and (VI) were made from the dyes, (I) \rightarrow (I) and (I) \rightarrow (I) \rightarrow (I) and the tetrazotised diamines. In the former series all the dyes were violet, but increasing in blueness with increasing mol. wt., and in the latter the first was a clear brownish-red, and the remainder violet. They were isolated by salting out with NH₄ carbonate or NaOAc (the former causes partial conversion into NH₄ salt) and removal of the precipitant by heat or with EtOH.

XIII. Determinations of solubility, shade, rate of diffusion, dyeing properties, and behaviour towards electrolytes (and acids) are made in the above series of dyes. In all cases the effect of increasing mol. wt. is bathochromic, but is less marked in the higher members and quantitatively is dependent on constitution. Increase in mol. wt. in the series from (IV) causes decreased affinity for wool both in neutral and acid baths, but leads to a regular increase in affinity for cuprammonium silk, so that the dyes containing 3 or 4 equivs. of (I) form a characteristic test for this fabric. The dyes from (V) decrease in substantivity as the series is ascended, whereas those from (VI) behave in exactly the reverse manner. Substantivity is therefore purely a constitutional function, and is not necessarily conferred by mol. complexity. Adsorption by the fibre if the result of poor H₂O-solubility is reversible, but if due to constitutional substantivity is no longer truly reversible.

H. A. P.

Interactions of chloro-substituted aldehydes with chloro-substituted arylhydrazines. F. D.

CHATTAWAY and A. ADAIR (J.C.S., 1933, 1488—1490).—Interaction of 2 : 5- $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ (I) and butylchloral hydrate (II) in EtOH at room temp. during 0.5 hr. affords 2 : 5-dichlorobenzeneazo- β - γ -dichloro- Δ^{α} -butylene (crimson) (III), m.p. 101°, converted by HCl in dry C_6H_6 into a solution (pale yellow) of butylchloral-2 : 5-dichlorophenylhydrazone which easily loses HCl to give (III). (III) in boiling C_6H_6 slowly affords $\alpha\beta$ -dichlorocrotonaldehyde-2 : 5-dichlorophenylhydrazone (IV), m.p. 90° (Ac derivative, m.p. 150°), another isomeride (V), m.p. 116° (Ac derivative, m.p. 139°), being obtained when the hydrazone is formed in cold AcOH. Either Ac derivative with Cl_2 in hot CHCl_3 affords $\alpha\alpha\beta\beta$ -tetrachlorobutaldehyde-2 : 5-dichloro-N-acetylphenylhydrazone, m.p. 154°, which indicates that (IV) and (V) are *cis-trans* forms. 2 : 4 : 5-Trichlorophenylhydrazine hydrochloride and (II) in H_2O at 40—50° afford $\alpha\beta$ -dichlorocrotonaldehyde-2 : 4 : 5-trichlorophenylhydrazone (VI), m.p. 86° (Ac derivative, m.p. 123°), the intermediate azo-butylene being too unstable to isolate. No second form of (VI) [cf. (IV)] is obtained. When the reaction occurs in boiling EtOH, β -chloro- α -ketobutaldehyde-2 : 4 : 5-trichlorophenylhydrazone (VII), m.p. 162°, is obtained, which when boiled with (I) in EtOH affords the 2 : 4 : 5 : 2' : 5'-pentachlorodiphenylosazone of α -keto- β -methoxybutaldehyde, m.p. 212°. (VII) is cyclised by 1 mol. of hot $\text{NaOEt}\cdot\text{EtOH}$ to 4-hydroxy-1-(2' : 4' : 5'-trichlorophenyl)-5-methylpyrazole. (I) and $\text{CCl}_3\cdot\text{CHO}$ in H_2O afford 2 : 5-dichlorobenzeneazo- $\beta\beta$ -dichloroethylene, m.p. 93°, unaffected by boiling EtOH in the absence of HCl. When the reaction is carried out in boiling EtOH, *Et glyoxylate*-2 : 5-dichlorophenylhydrazone (VIII), m.p. 90°, is obtained. *Et glyoxylate*-2 : 4 : 5-trichlorophenylhydrazone (IX), similarly prepared, has m.p. 102°. (VIII) or (IX) in warm CHCl_3 with Cl_2 affords *Et* ω -chloroglyoxylate-2 : 4 : 5-trichlorophenylhydrazone, m.p. 115°, converted into the ω - NH_2 -compound, m.p. 140°, with NH_3 in EtOH- H_2O . J. L. D.

Behaviour of phenylhydrazones with condensing agents. III. A. GIACALONE (Gazzetta, 1933, 63, 757—760; cf. A., 1932, 1026).— $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$ and aromatic aldehydes in hot EtOH form, through the phenylhydrazones, derivatives of CHPh_3 , e.g., 4'-hydroxy-4 : 4'-bis-(*p*-hydroxybenzylidenehydrazino)-triphenylmethane, m.p. 192—193°. 4 : 4'-Bis(benzylidenehydrazino)-3 : 3'- and -2 : 2'-dimethyltriphenylmethanes, m.p. 200° and about 180°, are similarly obtained; *p*-tolylhydrazine does not yield such derivatives. E. W. W.

Preparation of *p*-phenylenedihydrazine hydrochloride. H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4545—4546).— $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ is tetrazotised with nitrosylsulphuric acid in H_3PO_4 at -5° and the solution added to SnCl_2 in conc. HCl at -10°; addition of conc. HCl ppts. *p*-phenylenedihydrazine dihydrochloride (I), decomp. when heated. The free base could not be isolated; aq. solutions are unstable. (I) and aq. CuSO_4 give $p\text{-C}_6\text{H}_4\text{Cl}_2$; $p\text{-C}_6\text{H}_4\text{I}_2$ is formed using I in aq. KI. (I) and aq. KNCO afford *p*-phenylenedisemicarbazide, chars when heated. H. B.

Diazotisation of weakly basic amines. H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4531—

4534).—Successive treatment of NH_2Ph in conc. H_2SO_4 with nitrosylsulphuric acid (I) (theoretical quantity) and HNO_3 (*d* 1.51) (excess) at 0°, addition of the reaction mixture to aq. KOH, and coupling with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ gives (mainly) *m*-nitrobenzeneazo- β -naphthol, indicating that diazotisation with (I) occurs slowly or not at all, since the primarily formed diazonium compound will resist nitration (cf. A., 1922, i, 181). $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is not diazotised by (I) in conc. H_2SO_4 at 0°; it is recovered by addition of PhNO_2 after 2 hr. The following weakly basic amines are diazotised by treatment with (I) in an excess of conc. H_2SO_4 at 0° and subsequent addition of H_3PO_4 (*d* 1.7) [which releases HNO_2 from (I)], also at 0°: 2 : 4-dinitro-, 2 : 6-dichloro- and -dibromo-4-nitro-, 2 : 4 : 6-trinitro-, and 2 : 4 : 6-trinitro-3-methoxy- and -ethoxyanilines. 3 : 5-Dichloro-, m.p. 153°, and 3 : 5-dibromo-, m.p. 153.5°, -4-iodonitrobenzenes; 2 : 6-dichloro-, m.p. > 270°, and 2 : 6-dibromo-, m.p. 221—222°, -4-nitrobenzeneazo- β -naphthols; 2 : 4 : 6-trinitrobenzeneazophenol, m.p. 194°, -anisole, m.p. 148°, and -phenetole, m.p. 171—172°; 2 : 4 : 6-trinitro-3-methoxybenzeneazophenol, m.p. 165°, and -anisole, m.p. 118°, and 2 : 4 : 6-trinitro-3-ethoxybenzeneazophenol, m.p. 149°, are thus prepared. H. B.

Character of the diazonium group. Tetrazotisation of *p*-phenylenediamines. H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4535—4541).—Diazotisation normally occurs when various *p*-phenylenediamines are treated with HNO_2 ; the $\cdot\text{N}_2\text{X}$ group so formed is strongly negative and thus inhibits salt formation of the second NH_2 group. The theories of Cain (J.C.S., 1907, 91, 1049) and Morgan (*ibid.*, 1910, 97, 2561) are rejected. $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ is tetrazotised quantitatively when a solution of its hydrochloride in H_3PO_4 (*d* 1.7) is treated with a solution of NaNO_2 in conc. H_2SO_4 at -5°; excess of HNO_2 is removed with $\text{CO}(\text{NH}_2)_2$. Nitro- (I), 2 : 5- and 2 : 6- (II) -dichloro-, 2 : 6-dibromo-, and trichloro-*p*-phenylenediamine [the Ac_2 derivative of which is prepared from the Ac_2 derivative of (II) and $\text{Ca}(\text{OCl})_2$ in AcOH], and *p*-phenylenediaminesulphonic are similarly tetrazotised. $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ is similarly tetrazotised; treatment with aq. KI gives a poor yield of $o\text{-C}_6\text{H}_4\text{I}_2$. 2 : 5-Diodonitrobenzene, m.p. 109—110°, and 4-iodo-2-nitrophenol, m.p. 81°, are obtained from tetrazotised (I) and aq. KI. 1 : 3-Dibromo-2 : 5-di-iodobenzene has m.p. 115°. H. B.

Character of the diazonium group. Preparation of mixed disazo-dyes. H. A. J. SCHOUTISSEN (J. Amer. Chem. Soc., 1933, 55, 4541—4545).—Coupling of ArN_2X with PhOMe in a medium of conc. H_2SO_4 (1 vol.) + H_3PO_4 (*d* 1.7) (2 vols.) (diazotisation is effected in this medium) occurs rapidly only when NO_2 -groups are *o*- and *p*- to $\cdot\text{N}_2\text{X}$; with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, rapid coupling occurs with *p*- NO_2 -derivatives. Tetrazotised $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ couples with PhOMe and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ as rapidly as 2 : 4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{N}_2\text{X}$, indicating that the $\cdot\text{N}_2\text{X}$ group has the "negative" character of two (*o*- and *p*-) NO_2 -groups. Such coupling occurs with 1 mol. only of ArOH or ArOMe ; the resulting azo-diazonium compound is isolated by dilution of the reaction mixture with H_2O and can then be coupled with a second mol. of ArOH (not ArOMe) in alkaline

solution. Disazo-dyes (m.p. given after the second component) are thus prepared from p - $C_6H_4(NH_2)_2$ and β - $C_{10}H_7\cdot OH + \beta$ - $C_{10}H_7\cdot OH$, β - $C_{10}H_7\cdot OH + PhOH$ (m.p. 231—232°) (the same dye is formed from β - $C_{10}H_7\cdot OMe + PhOH$; hydrolysis of the ether occurs during the first coupling), α - $C_{10}H_7\cdot OH + PhOH$, $PhOH + PhOH$ [m.p. 270° (decomp.)], $PhOMe + PhOH$ (m.p. 206—207°), and $PhOEt + PhOH$ (m.p. 179°). H. B.

Velocity of diazotisation of aromatic amines.—Sec this vol., 36.

[Metallic salts of] diazoamino-compounds. A. MANGINI and I. DEJUDICIBUS (Gazzetta, 1933, 63, 601—612).—These salts are either (I) yellow, non-explosive, regarded as *anti*, e.g., $\begin{array}{c} Ph-N \\ | \\ N-NM-Ph \end{array}$, or (II) deeply coloured, explosive, regarded as *syn* and co-ordinated, e.g., $\begin{array}{c} N-N-Ph \\ || \\ N-NM-Ph \end{array}$, or they are chromo-

isomeric (I and II) in both forms. The following are prepared: from diazoaminobenzene, in Et_2O with $KOMe$, the *K* salt (II); in $MeOH$ with $Hg(OAc)_2$, the Hg^{II} salt (I and II), and similarly the *Cu* salt (+ $MeOH$) (II). From *m*-nitrodiazoaminobenzene, *Cu* (II), Hg^{II} (I and II), and *Ag* (I and II) salts. From *p*-nitrodiazoaminobenzene, *K* and *Na* (nitronic?), *Ag* (I and II), Hg^{II} (I and II), and *Cu* (II) salts. The colours of these and analogous salts are tabulated. E. W. W.

Reactions of diphenyl thiocarbonate with salts of heavy metals. G. A. GARKUSCHA (J. Gen. Chem. Russ., 1933, 3, 596—602).—The reaction of Ph_2 thiocarbonate with salts of heavy metals was investigated to ascertain whether, by analogy with the esters of thiophosphoric acid, derivatives were obtained in which S displaced O attached to the org. radical: $PS(OR)_3 \rightarrow PO(OR)_2SR$. The expected reaction, however, did not take place, but the S was removed as the metal sulphide, being replaced by O with the formation of Ph_2CO_3 , m.p. 78°. H_2O takes part in the reaction, since the perfectly dry reagents do not react. The metal salts were $AgCl$, AgI , $HgCl_2$, HgI_2 , $AgOAc$, o - $C_6H_4(CO_2Ag)_2$, o - $OH\cdot C_6H_4\cdot CO_2Ag$, $Cu(OBz)_2$, $Ag_2C_2O_4$, $Hg(NHBz)_2$, and $Hg(NHAc)_2$. M. Z.

Esters of tetrathio-orthocarbonic acid. H. J. BACKER and P. L. STEDEROUDE (Rec. trav. chim., 1933, 52, 1039—1045).— $C(SPh)_4$ (I) (A., 1913, i, 396) is converted by Br in $CHCl_3$ into the unstable octa- (II), which on keeping in air gives the tetra-bromide, m.p. 179°; this with boiling $EtOH$ gives Ph_2S_2 , and with $2N$ - $NaOH$ the disulphoxide, $C(SPh)_2(SOPh)_2$, m.p. 41—42°, also obtained from (II) and $NaOH$ and by oxidation [of (I)?] with conc. HNO_3 . With $HgCl_2$ in $COMe$, (I) gives the compound $C(SPh)_4\cdot 6HgCl_2$ decomp. 200°. The "salt" of $NH_2\cdot C(NH)\cdot SPh$ with its $(NO)_2$ -derivative gives (I) with $PhSH$ and also with $CMe_3\cdot SH$ in $MeOH$ (instead of the expected mixed ester); with $MeOH$ alone at its b.p. Ph_2S_2 and a little (I) are formed. cyclohexylisothiocarbamide hydrobromide, m.p. 207° [from $C_6H_{11}Br$ and $CS(NH_2)_2$], gives with aq. HNO_3 the "salt", $C_6H_{11}\cdot S\cdot C(N\cdot NO)\cdot N\cdot NOH\cdot NH_2\cdot C(NH)\cdot S\cdot C_6H_{11}$, which explodes at 100—105°, and with N - $NaOH$ at 70—75° gives cyclohexyl tetrathio-orthocarbonate, m.p. 169° (III).

This forms viscous oils with Br and $HgCl_2$, and on oxidation with H_2O_2 in $AcOH$ gives cyclohexylsulphonic acid (*Ba* salt). Crystallographic data of (I) and (III) are given. β -Naphthyl tetrathio-orthocarbonate has m.p. 134—136° (tetrabromide, m.p. 120—130°). H. A. P.

Alkyl derivatives of halogenophenols and their bactericidal action. II. Bromophenols. E. KLARMANN, L. W. GATES, V. A. SHTERNOV, and P. H. COX, jun. (J. Amer. Chem. Soc., 1933, 55, 4657—4662).—*p*-Bromo-*o*-alkylphenols are prepared generally by rearrangement of *p*-bromophenyl esters with $AlCl_3$ and subsequent Clemmensen reduction; *o*-bromo-*p*-alkylphenols are obtained from p - $C_6H_4Alk\cdot OH$ and Br. The following are described: *p*-bromophenyl acetate, b.p. 100°/2 mm., propionate, b.p. 113°/3 mm., butyrate, b.p. 112°/2 mm., valerate, b.p. 134—138°/4 mm., and hexoate, b.p. 139—140°/2 mm.; 5-bromo-2-hydroxyphenyl Me, m.p. 57.3°, Et, m.p. 76°, Pr, b.p. 127—132°/3 mm., m.p. 53.6°, Bu, b.p. 127—136°/2 mm., and *n*-amyl, m.p. 60.5°, ketones; 2-methyl-, b.p. 118—123°/7 mm., m.p. 63.5° (from o - $C_6H_4Me\cdot OH$ and Br), 2-ethyl-, b.p. 110°/3 mm., 2-n-propyl-, b.p. 113—117°/3 mm., m.p. 42°, 2-n-butyl-, b.p. 125—127°/2 mm., m.p. 43.5°, 2-n-amyl-, b.p. 143—145°/3 mm., m.p. 36°, 2-sec.-amyl-, b.p. 134—138°/4 mm. (from p - $C_6H_4Br\cdot OH$, *n*-amyl alcohol, conc. HCl , and $ZnCl_2$), 2-n-hexyl-, b.p. 150—152°/4 mm., m.p. 53.6°, and 2-cyclohexyl-, b.p. 167°/5 mm., m.p. 43.8° (from *o*-cyclohexylphenol and Br), 4-bromophenols; 4-tert.-amyl-, b.p. 122°/4 mm., 4-n-hexyl-, b.p. 148°/7 mm., and 3 : 5-dimethyl-4-n-propyl-, m.p. 91.3°, 2-bromophenols. The above phenols are strongly germicidal towards *Eberthella typhi*, *Staph. pyogenes aureus*, *Mycobacterium tuberculosis (hominis)*, and *Monilia albicans*; they compare favourably with the Cl-analogues (A., 1933, 817). H. B.

Chloro-derivatives of benzylphenols. II. Mono-, di-, and tri-chloro-derivatives of *o*- and *p*-benzylphenols. R. C. HUSTON, R. L. GUILLE, P. S. CHEN, W. N. HEADLEY, G. W. WARREN, L. S. BAUR, and B. O. MATE (J. Amer. Chem. Soc., 1933, 55, 4639—4643).—Cl-derivatives of 2- and 4-hydroxydiphenylmethanes are prepared from chlorobenzyl (and benzyl) chlorides and $PhOH$ (and chlorophenols) by the Claisen method (A., 1925, i, 656) or by condensation with $AlCl_3$; in the former method, the yields (from the *m*-substituted CH_2PhCl) are increased by addition of the corresponding Ph benzyl ether. The presence of Cl in the ring of CH_2PhCl exerts a retarding influence ($m > o > p$) on the yield of hydroxydiphenylmethane and phenol ether in the Claisen reaction, and prevents ether formation with $AlCl_3$. The following derivatives are described: (a) of 2-hydroxydiphenylmethane: 2', b.p. 146—151°/3 mm. (benzoate, b.p. 173—176°/2.5 mm.), 3-, m.p. 40.5—41.5° (benzoate, m.p. 69—71°; benzenesulphonate, m.p. 62—64°; p-toluenesulphonate, m.p. 81.5—83.5°), 3', b.p. 192—194°/14 mm. (benzoate, m.p. 67—67.4°), 5-, m.p. 48—49° (benzoate, m.p. 54—55°; benzenesulphonate, m.p. 68—69°; p-toluenesulphonate, m.p. 75—75.5°), and 4 m.p. 60—61°, Cl-derivatives; 5 : 4'-Cl₂-derivative, m.p. 44.5—45.5° (benzoate, m.p. 84.5—85.5°); 3 : 5 : 2', m.p. 59.5—60.5° (benzoate, m.p. 81—82°),

3 : 5 : 3' -, m.p. 59.4—60° (benzoate, m.p. 63.5—64°; benzenesulphonate, m.p. 114.5—115°; p-toluenesulphonate, m.p. 125.4—126°), and 3 : 5 : 4' -, m.p. 69.5—70.5°, -Cl₃-derivatives; (b) of 4-hydroxydiphenylmethane : 2' -, m.p. 68—69° (benzoate, m.p. 64.5—65.5°), 3 -, b.p. 145—148°/3 mm. (benzoate, m.p. 71—73°; benzenesulphonate, m.p. 65—68°; p-toluenesulphonate, m.p. 51—53°), 3' -, b.p. 200—202°/14 mm. (benzoate, m.p. 57.5—58°), and 4' -, m.p. 87—87.5° (benzoate, m.p. 115—116°), -Cl-derivatives; 3 : 5 : 2' -, m.p. 86.5—87.5° (benzoate, m.p. 86—87°), 3 : 5 : 3' -, m.p. 79—80° (benzoate, m.p. 130—130.4°; p-toluenesulphonate, m.p. 104.5—105°), and 3 : 5 : 4' -, m.p. 61.5—62.5° (benzoate, m.p. 116—117°), -Cl₃-derivatives. The following ethers are obtained in the Claisen method and are synthesised from the requisite phenol, benzyl chloride, and MeOH-NaOMe : Ph o-, b.p. 140—145°/2.5 mm., m., m.p. 36—36.4°, and p-, m.p. 85.5—86.5°, -chlorobenzyl; p-chlorophenyl p-chlorobenzyl, m.p. 80—81°; o-, b.p. 138—140°/3 mm., and p-, m.p. 70—71°, -chlorophenyl benzyl; 2 : 4-dichlorophenyl o-, m.p. 61—62°, m., m.p. 42.5°, and p-, m.p. 64.5—65.5°, -chlorobenzyl; 4-chloro-2-benzylphenyl benzyl, m.p. 53—54°. H. B.

Formaldehyde condensations with phenol and its homologues. II. G. T. MORGAN and N. J. L. MORGAN (J.S.C.I., 1933, 52, 418—420r).—Acidic condensations of m-5- (I) and o-4-xenol (II) with CH₂O, followed in each case by extraction with hot H₂O, yielded small amounts of the six theoretically possible dihydroxytetramethyldiphenylmethanes. The isomerides from (I), of undetermined orientation, were : (III) prisms from MeOH, m.p. 274—276° (dibenzoate, m.p. 148°; Br₄-derivative, m.p. 264°; another Br-derivative, m.p. 164°), (IV) needles from dil. EtOH, m.p. 169.5° (Br-derivative, m.p. 230°), (V) plates from dil. EtOH, m.p. 168° (dibenzoate, m.p. 130°). They were separated through the insolubility of (III) in cold C₆H₆, and the greater solubility of (IV) in light petroleum over (V). (III) was synthesised from 4-hydroxy-2 : 6-dimethylbenzyl alcohol and (I) under acid conditions. Distillation of the resin in vac. gave 25% of volatile material, mainly (I) together with unidentified needles, and left an insol. residue. The isomerides extracted from (II) condensations were : (VI) needle-plates from dil. EtOH, m.p. 163°, (VII) needles from dil. EtOH, m.p. 164.5—166°. Their separation depended on the lower solubility in H₂O, and greater solubility in petroleum, of (VI) over (VII). The third isomeride (VIII) crystallised from a conc. C₆H₆ solution of the resin, and gave minute matted needles from C₆H₆-petrol, m.p. 212—213°. (VI) and (VIII) were synthesised by acidic condensation of o-4-xenol alcohol and (II). If the constitution of the alcohol be assumed as 2-hydroxy-4 : 5-dimethylbenzyl alcohol, (VII) is probably 2 : 2'-dihydroxy-5 : 6 : 5' : 6'-tetramethyldiphenylmethane.

Thiophenol. I. Condensation reaction between thiophenols and condensed aldehyde-ammonias. G. DOUGHERTY and W. H. TAYLOR (J. Amer. Chem. Soc., 1933, 55, 4588—4593; cf. A., 1933, 499).—PhSH, p-C₆H₄Br·SH, p-NO₂·C₆H₄·SH, p-C₆H₄Me·SH, and CH₂Ph·SH react with hexamethylenetetramine (I) in boiling dioxan to give tri(phenyl-, decomp. on attempted distillation [hydrolysed (AcOH-

HCl) to NH₃, PhSH, and CH₂O], tri-(p-bromophenyl-, m.p. 135°, tri-(p-nitrophenyl-, m.p. 146°, tri-(p-tolyl-, m.p. 52°, and tri(benzyl-, m.p. 46°, -thiolmethyl)amines, respectively; 3RSH + (CH₂)₆N₄ → 2N(CH₂SR)₃ + 2NH₃. With hydrobenzamide (II), the following reaction occurs : 2(CHPh·N)₂CHPh + 3RSH → 3CHPh·N·CHPh·SR + NH₃; benzylidene-α-phenylthiolbenzylamine, m.p. 79.5° [hydrolysed (AcOH-HCl) to PhSH, PhCHO, and NH₃], -α-p-tolylthiolbenzylamine, m.p. 74°, and -α-benzylthiolbenzylamine, m.p. 67°, are prepared. 3 : 3' : 3''-Trinitrohydrobenzamide and PhSH similarly give m-nitrobenzylidene-m-nitro-α-phenylthiolbenzylamine, m.p. 122°; hydro-p-toluamide and hydrofurfuramide afford p-methylbenzylidene-α-phenylthiol-p-methylbenzylamine, m.p. 71°, and furfurylidene-α-phenylthiolfurfurylamine, m.p. 49°, respectively. n-Amyl mercaptan reacts slowly with (I) and (II); cryst. products have not been obtained.

H. B.

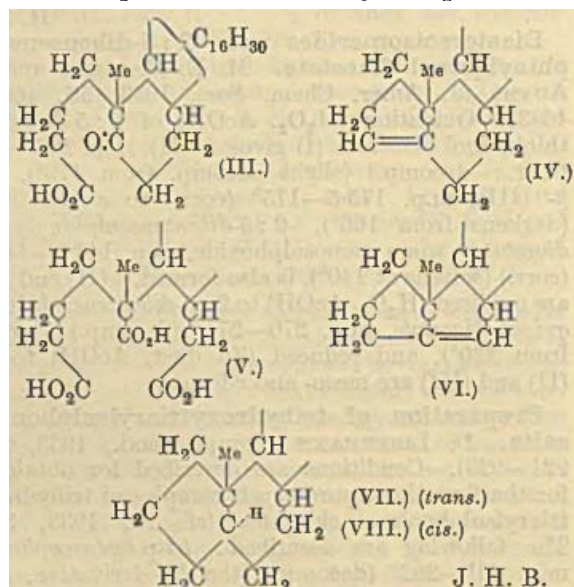
Diastereoisomerides of 2 : 5-dibenzenesulphinyloquinol diacetate. M. E. MACLEAN and R. ADAMS (J. Amer. Chem. Soc., 1933, 55, 4681—4683).—Oxidation (H₂O₂, AcOH) of 2 : 5-diphenylthiolquinol diacetate (I) gives α- (II), m.p. 207—208° (corr.; decomp.) (slight decomp. from 179°), and β- (III), m.p. 173.5—175° (corr.) to a red liquid (darkens from 166°), -2 : 5-dibenzenesulphinyloquinol diacetate; some monosulphoxide, m.p. 142.5—145.5° (corr.) (softens at 140°), is also formed. (II) and (III) are oxidised (H₂O₂, AcOH) to 2 : 5-dibenzenesulphonyloquinol diacetate, m.p. 270—271° (decomp.) (darkens from 220°), and reduced (Zn dust, AcOH) to (I). (II) and (III) are meso- and r-forms. H. B.

Preparation of trihydroxytriarylsulphonium salts. D. LIBERMANN (Compt. rend., 1933, 197, 921—923).—Conditions are described for obtaining, for the first time, pure cryst. samples of trihydroxytriarylsulphonium chlorides (cf. A., 1933, 389). The following are described : tri-p-hydroxyphenyl-, m.p. 261—262° (decomp.) [the Bz derivative, m.p. 35° (+H₂O), is the Bz₄, not Bz₃ derivative as stated in loc. cit.]; trihydroxytritolyl- (1), from o-cresol, m.p. 190° (Bz₄ derivative, m.p. 39°); (2) from m-cresol, m.p. 273—274° (decomp.) (Bz₄ derivative, m.p. 42°); tri-α-hydroxynaphthyl-, m.p. > 350°, and two isomeric tri-β-hydroxynaphthyl-, m.p. 227° and 273—274°, -sulphonium chlorides. A. C.

Preparation of homopiperonal. H. ERDTMAN and R. ROBINSON (J.C.S., 1933, 1530—1531).—Safrole glycol, 3 : 4-CH₂O₂·C₆H₃·CH₂·CH(OH)·CH₂·OH, b.p. 233—236°/20 mm. (from safrole and aq. KMnO₄ at 0°), is oxidised [Pb(OAc)₄ in boiling C₆H₆] to homopiperonal, b.p. 123—125°/1 mm. [oxime, m.p. 121° (lit. 115°, 119—120°, 124—125°); 2 : 4-dinitrophenylhydrazones, m.p. 140—141°], which is converted by conc. HCl in AcOH into 6 : 7 : 3' : 4'-bismethylene-dioxy-2-phenylnaphthalene, m.p. 200—201° [Br₃, m.p. 165—167°, and (probably) 6'-NO₂, m.p. 225—228° (decomp.), -derivatives], and a compound, m.p. 206—208°. H. B.

Cholesterol. H. LETTRÉ (Z. physiol. Chem., 1933, 221, 73—89).—Wolff-Kishner reduction of cholestone (I) semicarbazone gives ψ-cholestene (II). CrO₃ oxidation of (II) affords a ketocarboxylic acid (III),

$C_{27}H_{46}O_3$ [semicarbazone, m.p. 240° (decomp.); *oxime*, m.p. 165 – 166°]. Distillation of (III) yields a hydrocarbon (IV), $C_{26}H_{44}$, m.p. 80° , $[\alpha]_D^{25} +55.8^\circ$ in $CHCl_3$, which with O_3 gives the keto-acid, $C_{26}H_{44}O_3$. Oxidation of (III) with Br yields a tricarboxylic acid (V), $C_{27}H_{46}O_6$, m.p. 146° , then 202 – 203° . These reactions indicate that the double linkings in (I) and (II) correspond. Distillation of (V) at 240 – $260^\circ/14$ mm. gives a hydrocarbon (VI), $C_{25}H_{42}$, m.p. 38 – 39° , $[\alpha]_D^{25} -40.5^\circ$ in $CHCl_3$. Reduction of the pyroketone of the dicarboxylic acid from cholesterol with Zn–Hg in AcOH affords a hydrocarbon (cis) (VII), $C_{26}H_{46}$, m.p. 78° , $[\alpha]_D +25.1^\circ$ in $CHCl_3$. Wolff–Kishner reduction of the semicarbazone of the ketone $C_{26}H_{44}O$ yields the trans-hydrocarbon (VIII), $C_{26}H_{46}$, m.p. 46° , $[\alpha]_D^{25} +33.2^\circ$ in $CHCl_3$. Hydrogenation of (IV) gives (VIII). Thus cholesterol is a derivative of trans- and coprostan of cis-decahydronaphthalene.



isoCholesterol. II. Lanosterol. C. DORÉE and D. C. GARRATT (J.S.C.I., 1933, 52, 355–361T; cf. A., 1933, 710).—Lanosterol (I), $C_{30}H_{50}O_3$, obtained from a neutral wool grease from which agnosterol (Windaus and Tschesche, A., 1930, 1179) was absent, had m.p. 140.5 – 141° , $[\alpha]_D +57.9^\circ$ (acetate, m.p. 113.5° , $[\alpha]_D +57.2^\circ$; benzoate, m.p. 191.5° $[\alpha]_D +74.2^\circ$). CrO_3 under restrained conditions acts on (I) giving lanostenone (II), $C_{30}H_{48}O$, m.p. 116° , $[\alpha]_D +71.9^\circ$ (semicarbazone, m.p. 242° ; phenylhydrazone, m.p. 137° ; 2:4-dinitrophenylhydrazone, m.p. 207°), a ketone, m.p. 89° , $[\alpha]_D +54.4^\circ$ (2:4-dinitrophenylhydrazone, m.p. 118°), and a ketonic acid, $[\alpha]_D +64.2^\circ$ (2:4-dinitrophenylhydrazone, m.p. 133°). Further oxidation gives $COMe_2$ and a volatile aldehyde (traces). On reduction with Na in amyl alcohol (I) is reduced partly to α -dihydrolanosterol (Windaus and Tschesche, loc. cit.); the greater portion is recovered as (?) an isomeride of (I), m.p. 135° , $[\alpha]_D^{25} +58.3^\circ$, the acetate of which is identical with that of (I). Reduction of (I) with Na in EtOH gives lanosterol A, m.p. 143° , $[\alpha]_D^{25} +58.7^\circ$ (acetate, m.p. 127° , $[\alpha]_D^{25} +59.4^\circ$). With Br (I) gives a cryst. Br-derivative (III), m.p. 177° , $[\alpha]_D^{25} +50.0^\circ$, probably a mixture of

substituted derivatives. Reduction of (III) with Zn–AcOH gives (I), and with Na in EtOH lanosterol B (IV), m.p. 150° , $[\alpha]_D +58.9^\circ$ (acetate, m.p. 118° , $[\alpha]_D +55.0^\circ$; benzoate, m.p. 193° , $[\alpha]_D +78.7^\circ$), which with CrO_3 gives (II). (IV) is also formed by the action of Na in EtOH on lanosteryl acetate dibromide. (III) with CrO_3 gives dibromolanostenone, m.p. 188° , $[\alpha]_D -10.5^\circ$ (2:4-dinitrophenylhydrazone, m.p. 199°). A $CHCl_3$ solution of (I) with O_3 yields a mono-ozonide, $C_{30}H_{50}O_3 \cdot O_3$, m.p. 150° , which with H_2O gives an acid, $C_{30}H_{48}O_4$, m.p. 225° , $[\alpha]_D^{25} +43.4^\circ$, and a volatile aldehyde (?) of floral odour. Further attempts to isolate isocholesterol from samples of South African rubber latex gave negative results.

Cinchol. A. WINDAUS and M. DEPPE (Ber., 1933, 66, [B], 1689–1690).—Cinchol belongs to the sitosterol group and has the formula $C_{29}H_{50}O$, since it yields a m-dinitrobenzoate, m.p. 200 – 202° , $[\alpha]_D -10.9^\circ$ in $CHCl_3$ (identical in m.p. and $[\alpha]_D$ with the corresponding ester of rhamnol), and an acetate $C_{31}H_{50}O_2$, m.p. 123° , $[\alpha]_D^{25} -38.3^\circ$ in $CHCl_3$. Cinchol, m.p. 136 – 137° , $[\alpha]_D -33.5^\circ$ in $CHCl_3$, retains H_2O firmly. H. W.

Vitamin of growth. V. Cryptoxanthine, a xanthophyll, $C_{40}H_{56}O$. R. KUHN and C. GRUND-MANN (Ber., 1933, 66, [B], 1746–1750; cf. A., 1933, 431).—Physalis is accompanied in the berry and calyx of *Physalis franchetti* and *alkekengi* by cryptoxanthine (I), $C_{40}H_{56}O$, m.p. 169° (corr.; vac.; Berl) (isolation described). (I) cannot be distinguished spectroscopically from β -carotene (II) and zeaxanthine (III). It contains 1 OH (Zerevitinov) and gives a monoacetate, m.p. 117 – 118° . It absorbs 11 H_2 , thus containing 2 carbon rings. (I) is probably a hydroxy- β -carotene in which the two halves of the mol. correspond, respectively, with (II) and (III). The intermediate position finds its expression in the behaviour towards $CaCO_3$ and Al_2O_3 , respectively. (I), (II), and (III) when oxidised with CrO_3 give 4.85, 5.4, and 4.1 mols. of AcOH, respectively. (I) has $[\alpha]_{D^{25}} \pm 6^\circ$ in C_6H_6 . (I) shows pronounced vitamin-action. H. W.

Influence of p_H on aminated triphenylmethane dyes, and their decomposition by light. P. C. HENRIQUEZ (Rec. trav. chim., 1933, 52, 991–1000).—The tautomerism of malachite-green (I) is followed photometrically for p_H 1.0–8.0, and in ultra-violet light (II) up to p_H 13, the equilibrium being displaced in the latter case to an extent proportional to the intensity of the light. The val. of the dissociation const. of the carbinol base is thus found to be 1.29×10^5 . Exposure of aq. crystal-violet to light gives a red dye of intensity comparable with the original, and formed from it by demethylation; the presence of free NH_2 is proved by diazotisation and coupling with 1:3:6- $NH_2 \cdot C_{10}H_5(SO_3H)_2$. Under similar conditions (I) is converted into a violet dye (? Doebner's violet). Destruction of colour by light is more rapid the more basic is the solution. Exposure to (II) brings about oxidation of fuchsin by H_2O_2 at room temp., the NH_2 groups being unaffected. H. A. P.

Changes in acid solutions of adrenaline.—See A., 1933, 1256.

Diazo-reaction of adrenaline. G. NAKAYAMA (Japan J. Med. Sci., 1933, 2, 285—290).—When KOH is substituted for aq. NH_3 in the Ehrlich diazo-reaction, adrenaline (I) gives a coloration with concns. $> 1:25 \times 10^4$. Pyrocatechol and 3:4-dihydroxy-adrenaline behave similarly to (I), whilst adrenalone yields a non-sp. yellowish-brown coloration. 2:4-Dihydroxyphenylalanine gives a stable orange-red and the 2:5-isomeride a transient reddish-yellow colour. F. O. H.

Addition of hydrogen to acetylene derivatives.
XXI. Synthesis of *s*-diphenyldi- α -naphthylbutenediol and its hydrogenation. J. S. SALKIND and S. V. NEDZVETZKII (J. Gen. Chem. Russ., 1933, 3, 573—577).—The acetylenic glycol, *s*-diphenyldi- α -naphthylbutenediol, was synthesised and hydrogenated to ascertain whether stereoisomerides would be obtained. Interaction of $\text{COPh} \cdot \text{C}_{10}\text{H}_7 \cdot \alpha$ with the Grignard compound from dibromoacetylene, followed by hydrolysis in iced dil. AcOH, yields 42% of the glycol, m.p. 182—183°, but in only one stereoisomeric form. Hydrogenation (colloidal Pd), which was very slow, gave two stereoisomerides, α and β , of $\alpha\delta$ -diphenyl- $\alpha\delta$ -di- α -naphthyl- Δ^8 -butene- $\alpha\delta$ -diol in the proportion 96:4. The α -compound, m.p. 167°, gives a cryst. compound, m.p. 132—134°, with 1EtOH. When heated with Ac_2O and NaOAc the γ -oxide, 2:5-diphenyl-2:5-di- α -naphthyl-2:5-dihydrofuran, m.p. 221—222°, is formed, thus indicating that this glycol is the *cis*-isomeride. Further hydrogenation (very slow) with Pt-black gave $\alpha\delta$ -diphenyl- $\alpha\delta$ -di- α -naphthylbutane- $\alpha\delta$ -diol (I), m.p. 220°. The β -isomeride, m.p. 231—232°, does not form a compound with EtOH. Further hydrogenation with Pt-black gave (I), thus proving that the β -isomeride is the *trans*-form. M. Z.

Attempted resolution of substituted disulphonylmethanes and resolution of α -*p*-carboxybenzenesulphonyl- α -*p*-tolylthiolethane. F. B. KIPPING (J.C.S., 1933, 1506—1510).—*p*-thiolbenzoate (I), b.p. 275° (slight decomp.), 162—164°/22 mm., from *p*- $\text{SH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ and EtOH-HCl [in some preps, *bis-p*-carbethoxyphenyl disulphide, m.p. 65—66°, is obtained; this is also prepared by oxidation (I-EtOH) of (I)], reacts (as Na salt) with CH_2AcCl in EtOH to give *p*-carbethoxyphenylthiolacetone, m.p. 53—54°, oxidised (KMnO_4 , dil. H_2SO_4 , CCl_4) to *p*-carbethoxybenzenesulphonylacetone (II), m.p. 88°. The Na salt of (II) and CH_2PhI in EtOH give α -*p*-carbethoxybenzenesulphonyl- α -benzylacetone, m.p. 104°, hydrolysed (NaOH) to α -*p*-carboxybenzenesulphonyl- β -phenylethane, m.p. 232—233° (*Et* ester, m.p. 77—78°). Di-*p*-tolyl disulphoxide (III) (1 mol.), (II) (1 mol.), and NaOEt (1 mol.) in EtOH afford *p*-carbethoxybenzenesulphonyl-*p*-tolylthiolmethane (IV), m.p. 121°, and some α -*p*-carbethoxybenzenesulphonyl- α -*p*-tolylthiolacetone, m.p. 86—87°; these are difficult to separate and are both hydrolysed (alkali) to *p*-carboxybenzenesulphonyl-*p*-tolylthiolmethane, m.p. 205—206° (*Na* salt), which is oxidised (KMnO_4 , AcOH) to *p*-carboxybenzenesulphonyl-*p*-toluenesulphonylthiolmethane (V), m.p. 240—242°. The *Et* ester, m.p. 147.5°, of (V), also prepared by similar oxidation of (IV), with CH_2PhI and EtOH-NaOEt gives the *Et* ester, m.p.

118—119°, of α -*p*-carboxybenzenesulphonyl- α -*p*-toluenesulphonyl- β -phenylethane (VI), m.p. 185—186° (*l*-menthylamine, m.p. 214—215°, nor-*d*- ψ -ephedrine, m.p. 115—118°, *d*-*sec*-butylamine, m.p. 205—207°, *l*-phenylethylamine, m.p. 186°, quinine, m.p. 215°, and cinchonidine salts). (VI) could not be resolved. Ph_2 disulphoxide, (V), and EtOH-NaOEt afford *p*-carboxybenzenesulphonyl-*p*-toluenesulphonylphenylthiolmethane, m.p. 212° (quinine, m.p. 209—210°, and *l*-menthylamine, m.p. 184—185°, salts), which could not be resolved. Oxidation (KMnO_4 , dil. H_2SO_4 , CCl_4) of the product from (I), CHBrMeAc , and EtOH-NaOEt gives α -*p*-carbethoxybenzenesulphonylthiol *Me ketone* (VII), m.p. 66—67°, the Na salt of which with (III) affords [after hydrolysis (aq. EtOH-NaOH)] di- α -*p*-carboxybenzenesulphonyl- α -*p*-tolylthiolethane (VIII), m.p. 168—169° (*Me*, m.p. 112—113°, and *Et*, m.p. 72°, esters; acid chloride, m.p. 83—84°). This is resolved by *l*-menthylamine into *d*- (IX), m.p. 160°, [α]_D²⁰ +130° in CHCl_3 [*l*-menthylamine salt, m.p. 199—202°; *Me*, m.p. 131—132°, and *Et* (X), m.p. 44—45°, esters; acid chloride, m.p. 101—102°], and *l*-forms, [α]_D²⁰ -126° in CHCl_3 (*Me* ester, m.p. 131—132°). (VIII) can also be resolved with quinine. (IX) racemises fairly rapidly in dil. aq. NaOH or NH_3 at room temp. Oxidation (H_2O_2 , AcOH) of (VIII) or (IX) gives the optically inactive α -*p*-carboxybenzenesulphonyl- α -*p*-toluenesulphonylethane, m.p. 233—234° [*Et* ester, m.p. 120—121°, also prepared by similar oxidation of (X); *Me* ester, m.p. 141°; *l*-menthylamine, m.p. 187—191°, *l*-hydroxyhydrindamine, m.p. 208—210°, *l*-phenylethylamine, m.p. 214—215°, quinine, m.p. 211—212°, and cinchonidine, m.p. 177—178°, salts], which could not be resolved.

The Na salt of (VII) and *Me p*-toluenethiosulphonate in EtOH give (after hydrolysis) α -*p*-carboxybenzenesulphonyl- α -methylthiolethane, m.p. 185° (decomp.) [*l*-hydroxyhydrindamine, m.p. 194° (decomp.), *l*-menthylamine, m.p. 174—177°, strychnine, m.p. 234° (decomp.), and quinine, m.p. 217°, salts], oxidised (KMnO_4 , AcOH) to α -*p*-carboxybenzenesulphonyl- α -methanesulphonylethane, m.p. 273° (*d*-hydroxyhydrindamine, m.p. 186—187°, *l*-phenylethylamine, m.p. 195—198°, *l*-menthylamine, m.p. 189—190°, quinine, m.p. 165—167°, and cinchonidine, m.p. 183—184°, salts). Neither of these acids could be resolved.

H. B.

Relationship between the three forms of *cis*-cinnamic acid. H. V. W. ROBINSON and T. C. JAMES (J.C.S., 1933, 1453—1454).—Rates of addition of Br to the three forms of *cis*-cinnamic acid in CCl_4 with HBr as catalyst have been determined and indicate that the forms are identical in solution.

F. R. S.

α -Methyl-*trans*-hexahydroindene-2-acetic acid and the reduction of Δ^8 - and Δ^9 -unsaturated *trans*-hexahydrohydrindene (2) compounds. R. S. THAKUR (J.C.S., 1933, 1485—1488; cf. A., 1932, 1033).—*Me* (or *Et*) 2-hydroxy- α -methyl-*trans*-hexahydrohydrindene-2-acetate when dehydrated (I) with SOCl_2 (cf. A., 1911, i, 517) affords *Et* α -methyl-*trans*-hexahydroindene-2-acetate (II), b.p. 150—151°/22 mm., unaccompanied by the Δ^8 (or Δ^9)-isomeride (III), m.p. 81—83° (lit. 89—90°). (II) affords no (III)

with P_2O_5 , and is hydrolysed by cold $NaOH-H_2O$ to the acid (IV) (*amide*, m.p. 131—132°, from the undistilled acid chloride), which when oxidised by 3% $KMnO_4$ in $NaHCO_3$ followed by hot dil. HNO_3 affords *trans*-hexahydrophthalic acid, m.p. 226—227° (lit., 222°), *trans*-hexahydrohomophthalic acid, and $H_2C_2O_4$. (IV) is reduced catalytically (H_2 -Adams' catalyst) to α -methyl-*trans*-hexahydrohydrindene-2-acetic acid (V), m.p. 104—105° (*amide*, m.p. 196°; *anilide*, m.p. 176—177°). Equilibration of (IV) with 25% $KOH-H_2O$ in 3—4 days affords the Δ^a -acid, m.p. 196—197°. (I) also gives some α -methyl-*trans*-hexahydrohydrindylidene-2-acetic acid, which is reduced to (V), as is also the Δ^a -acid, with Na-amyl alcohol or Na-Hg in $Na_2CO_3-H_2O$. The semicarbazone, m.p. 179—180°, of α -methyl-*trans*-hexahydrohydrindyl-2-acetone (VI) regenerates with dil. H_2SO_4 a ketone, b.p. 149°/23 mm. (*oxime*, m.p. 85—86° after shrinking). *trans*-Hexahydrohydrindylidene-2-acetic acid is reduced catalytically to *trans*-hexahydrohydrindene-2-acetic acid (VII), m.p. 102—103° after sintering (lit., 120°) [*amide*, m.p. 180° after shrinking; *anilide*, m.p. 132° (lit., 135°)], also obtained by reducing *trans*-hexahydroindene-2-acetic acid. Reduction of *trans*-hexahydrohydrindylidene-2-acetone affords *trans*-hexahydrohydrindyl-2-acetone, b.p. 130—134°/16 mm. [*semicarbazone* (VIII), m.p. 202—203° (decomp.)]. (VIII) affords a ketone, b.p. 141°/25 mm. (*oxime*, m.p. 68—70° after sintering). *trans*-Hexahydro-2-hydrindone and boiling HNO_3 (d 1.42) afford *trans*-, m.p. 160—162°, in good yield and *cis*(?)-hexahydrohomophthalic acid (cf. A., 1923, i, 220).

J. L. D.

Decomposition of acetylsalicylic acid in aqueous solution.—See A., 1933, 1250.

Synthesis of γ -tolyl- γ -butyrolactone. H. WACHS (Riechstoffind., 1932, 7, 196—197; Chem. Zentr., 1933, i, 4056).— γ -Tolyl- γ -butyrolactone (I), m.p. 73°, b.p. 156°/7 mm., having a coconut-like odour, was obtained as follows: $CO_2Et \cdot [CH_2]_2 \cdot CO_2Et \rightarrow CO_2H \cdot [CH_2]_2 \cdot CO_2Et \rightarrow COCl \cdot [CH_2]_2 \cdot CO_2Et \rightarrow C_6H_4Me \cdot CO \cdot [CH_2]_2 \cdot CO_2Et \rightarrow C_6H_4Me \cdot CO \cdot [CH_2]_2 \cdot CO_2H \rightarrow C_6H_4Me \cdot CH(OH) \cdot [CH_2]_2 \cdot CO_2Et \rightarrow$ (I). A. A. E.

Action of potassium cyanide on meconine. V. M. RODIONOV, S. J. KANEVSKAJA, and A. B. DAVANKOV (Ber., 1933, 66, [B], 1623—1627).—Meconine (I) is demethylated by KCN at 180—185° giving MeCN and 3-hydroxy-4-methoxyphthalide (II), m.p. 124—125°, with a small proportion of 4-hydroxy-3-methoxyphthalide (III), m.p. 87—88°. (II) and (III) are converted by p - $C_6H_4Me \cdot SO_3Me$ into (I). The *K* salt of (II) is transformed by p - $C_6H_4Me \cdot SO_3Et$ into 4-methoxy-3-ethoxyphthalide, m.p. 68—69°, oxidised by $KMnO_4$ in alkaline solution to 4-methoxy-3-ethoxyphthalic acid (IV), m.p. 174—175° (anhydride, m.p. 105°). 4-Methoxy-3-ethoxyphthalylethylimide, m.p. 83—84°, is obtained from (IV) and 33% NH_4Et .

H. W.

Reaction between acid chlorides and esters. L. P. KYRIDES and M. N. DVORNIKOFF (J. Amer. Chem. Soc., 1933, 55, 4630—4632).—Slow addition of o - $C_6H_4(COCl)_2$ (I) (0.75 g.-mol.) to o - $C_6H_4(CO_2Et)_2$ (II) (0.75 g.-mol.) and $ZnCl_2$ (0.2 g.) at 120° (and

finally up to 180°) gives $EtCl$ (91%) and o - $C_6H_4(CO)_2O$ (nearly quant.). (I) and o - $C_6H_4(CO_2Bu)_2$ similarly afford $BuCl$ (80%) and some butene (III); o - $C_6H_4(CO_2Bu \cdot sec.)_2$ yields *sec*-. $BuCl$ (50%) and much (III); $(CH_2 \cdot COCl)_2$ and $(CH_2 \cdot CO_2Bu \cdot sec.)_2$ give *sec*-. $BuCl$ (58%) and (III). Equiv. amounts of $BzCl$ and $EtOBz$ with 1% of $ZnCl_2$ at 180—290° afford $EtCl$ (77%), Bz_2O (77%), and a trace of anthraquinone. $BzCl$ (2 mols.) and (II) (1 mol.) at 120—200° give $EtCl$ (63%); reaction probably proceeds in two stages: o - $C_6H_4(CO_2Et)_2 + BzCl \rightarrow o$ - $C_6H_4(CO)_2O + EtCl + EtOBz$; $EtOBz + BzCl \rightarrow Bz_2O + EtCl$. (I) and $EtOBz$ react similarly. Similar reactions with CH_2Ph esters did not give CH_2PhCl . Acyl chlorides and (II) afford large amounts of C_2H_4 and HCl but no $EtCl$.

H. B.

Michael condensation. I. Behaviour of ethyl phenylmalonate in the Michael condensation. R. CONNOR (J. Amer. Chem. Soc., 1933, 55, 4597—4601).— $CHPh(CO_2Et)_2$ (I) does not undergo the Michael condensation. In $EtOH-NaOEt$, Et_2CO_3 and $CH_2Ph \cdot CO_2Et$ are formed; the latter then reacts with the unsaturated ester or ketone. Thus, (I), Et crotonate, and $EtOH-NaOEt$ give 80% of *Et* α -phenyl- β -methylglutarate, b.p. 156—158°/6 mm.; Et tiglate affords 70% of *Et* α -phenyl- β - γ -dimethylglutarate, b.p. 157.5—159.5°/5 mm.; Et cinnamate yields 35% of Et α - β -diphenylglutarate; Ph styryl ketone (II) furnishes 94% of Et γ -benzoyl- α - β -diphenylbutyrate (III). $CNaPh(CO_2Et)_2$ and (II) in C_6H_6 give 9% of *Et* 3-benzoyl-1:2:4:6-tetraphenyl- Δ^3 -cyclohexene-1-carboxylate, m.p. 258°, also prepared from (II), (III), and $NaOEt$ in C_6H_6 .

H. B.

Addition reactions of unsaturated α -ketonic acids. III. M. REIMER and H. H. KAMERLING (J. Amer. Chem. Soc., 1933, 55, 4643—4648).—*m*-Methoxybenzylidenepyruvic acid (I), m.p. 116—117° [*K* salt; *Me* ester, m.p. 57° (Me_2 acetal, m.p. 72°, obtained using warm $MeOH-HCl$); *Et* ester], from m - $OMe \cdot C_6H_4 \cdot CHO$ and $AcCO_2H$ (cf. A., 1931, 1155), and Br (1 mol.) in cold $CHCl_3$ give a dibromide (not isolable), which loses HBr very readily and affords β -bromo-*m*-methoxybenzylidenepyruvic acid (II), m.p. 166—167° (*Me* ester, m.p. 95°). (II) is oxidised (alkaline H_2O_2) to α -bromo-*m*-methoxycinnamic acid, m.p. 122° (*Me* ester), which with Br (1 mol.) in $CHCl_3$ gives α :6-dibromo-3-methoxycinnamic acid (III), m.p. 167—169° (softens at 163°) (*Me* ester, m.p. 79°). (I) and Br (2 mols.) in $CHCl_3$ afford ω :6-dibromo-3-methoxystyrene, m.p. 99°. (II) is brominated to β :6-dibromo-3-methoxybenzylidenepyruvic acid, m.p. 137—139° (*Me* ester, m.p. 143°), oxidised (H_2O_2) to (III). The results of Davies and Davies (A., 1928, 519) on the bromination of *m*-methoxycinnamic acid are confirmed.

H. B.

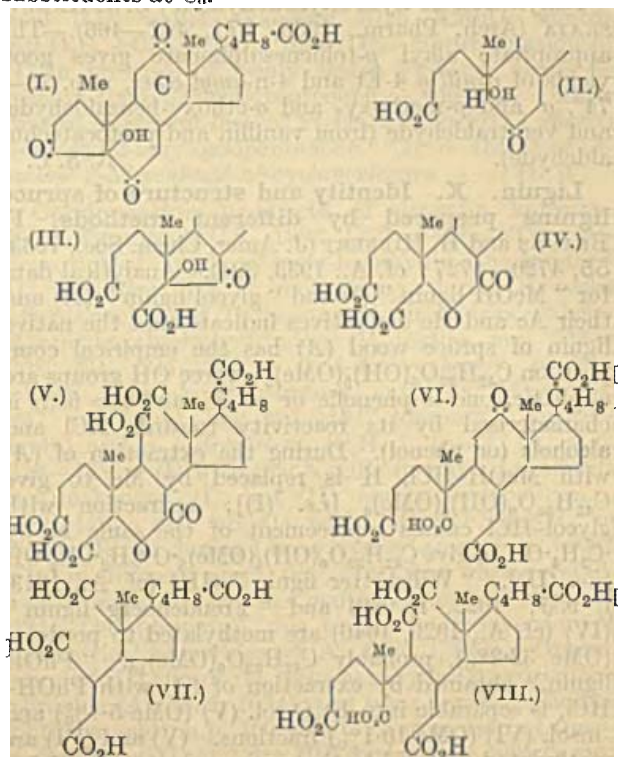
Hydroxy-derivatives of α - γ -diphenylbutyric acid. E. P. KOHLER and R. H. KIMBALL (J. Amer. Chem. Soc., 1933, 55, 4632—4639).—The diphenylcrotonolactone of Anschütz and Montfort (A., 1895, i, 179) is oxidised ($KMnO_4$, $MgSO_4$, aq. $COMe_2$) to α - β -dihydroxy- α - γ -diphenyl- γ -butyrolactone (I), m.p. 149° (cf. A., 1927, 262) [acetate, m.p. 138°; diacetate, m.p. 135°; dibenzoate (II), m.p. 144°; Me_2 ether (III), m.p. 118°; *Me* ether (IV), m.p. 143°, and *Me* ether, m.p. 77°

and 112° (dimorphous)]. $\alpha\beta\gamma$ -Trihydroxy- $\alpha\gamma$ -diphenylbutyric acid (V), m.p. 151° (with loss of H₂O) {Na(+EtOH) and Ag salts; Me ester, decomp. 125° (softens at 115°) [$\alpha\beta$ -dibenzoate, m.p. 178°; also prepared from (II) and MeOH-HCl; $\alpha\beta$ -dibenzoate- γ -acetate, m.p. 157°; $\alpha\beta\gamma$ -triacetate, m.p. 153°]}, is obtained from (I) by the usual procedure. (I) and MeOH-HCl give Me γ -chloro- $\alpha\beta$ -dihydroxy- $\alpha\gamma$ -diphenylbutyrate, m.p. 124°. (I) could not be reduced with Na-Hg; with red P, HI (45%), and AcOH, β -benzoyl- α -phenylpropionic acid (VI) and some $\alpha\gamma$ -diphenyl- γ -butyrolactone result. Similar reduction of (II) gives $\alpha\gamma$ -diphenylbutyric acid, m.p. 75°, also obtained by Clemmensen reduction of (VI). (III) is hydrolysed (EtOH-KOH) to γ -hydroxy- $\alpha\beta$ -dimethoxy- $\alpha\beta$ -diphenylbutyric acid (VII), m.p. 129° (decomp.) [K salt (+1.5H₂O)], whilst methylation (Me₂SO₄, aq. NaOH) of (V) gives $\alpha\beta$ -dihydroxy- γ -methoxy-, m.p. 201°, a hydroxydimethoxy-, m.p. 148—149°, - $\alpha\gamma$ -diphenylbutyric acid, (III), and (IV). (VII) is readily convertible (by crystallisation) into (III). H. B.

Cholatrienic acid. II. Photochemical change of cholatrienic acid and of choladienic acid. Z. URAKI (Z. physiol. Chem., 1933, 221, 40—44; cf. A., 1932, 615).—Ultra-violet irradiation of α -cholatrienic acid I, [α]_D²⁵ -22.63° (which is a mixture of α -cholatrienic acids III and IV), gives amorphous cholatrienic acid VI, [α]_D²⁵ +2.4°, which, like acid III, affords cholanolic acid on hydrogenation (PtO₂). β -Choladienic acid is unchanged on irradiation, indicating that the ultra-violet rays affect the β -ring of the acid I, changing the position of the double linking. J. H. B.

Constitution of bile acids. LIII. Degradation of bromopyrodoxybilianic acid. E. DANE and J. KLEE (Z. physiol. Chem., 1933, 221, 55—66; cf. A., 1932, 274).—Oxidation of pyrodoxybilianic acid with KMnO₄ gives a hydroxytriketocarboxylic acid (I), C₂₃H₃₂O₆, which on hydrolysis affords a hydroxydiketodicarboxylic acid (II). Oxidation of (II) with fuming HNO₃ with heating gives biloidanic acid. With fuming HNO₃ in the cold, (II) yields a (?) nitrohydroxydiketodicarboxylic acid nitrate, decomp. 202°. KMnO₄ in AcOH oxidises (II) to the hydroxydiketotricarboxylic acid (III), C₂₃H₃₂O₉, m.p. 227—228° (decomp.), already described, with probable formation of a 1 : 5-ketoaldehyde as intermediate product. (III) is probably a β -keto-acid. Oxidation of (II) with alkaline KMnO₄ or hydrolysis of (III) affords a ketotetranetricarboxylic acid (IV), C₂₃H₃₂O₉, m.p. 206°, (+H₂O) sinters 150—160°, [α]_D²⁵ +51.3° in EtOH (Me₃ ester m.p. 138—140°), and an isomeride, m.p. 243° (decomp.). With fuming HNO₃, (IV) yields a β -lactonepentacarboxylic acid (V), C₂₃H₃₂O₁₂·H₂O, m.p. 245—250° (decomp.), [α]_D²⁵ +40.8° in EtOH (Me₃ ester, m.p. 165°). The acid (V), now called the β -form, is not identical with the α -form previously described (A., 1932, 615), but is converted into it by conc. HCl. Oxidation of (I) with CrO₃ gives a ketotetracarboxylic acid (VI), C₂₃H₃₄O₉, m.p. 160—163°, [α]_D²⁵ +71.8° in EtOH, and further oxidation with HNO₃ a tetracarboxylic acid (VII), C₁₆H₂₄O₈, m.p. 218—220°, already obtained by oxidation of the diketodicarboxylic acid (Wieland and Schlichting,

A., 1924, i, 857). Oxidation of (I) with CrO₃ opens ring C, affording a β -solanellic acid (VIII), m.p. 217—218°, [α]_D²⁵ -11.4° in EtOH, which is converted by conc. H₂SO₄ at 100° into α -solanellic acid. The solanellic acids must differ in the arrangement of the substituents at C₉.



J. H. B.

Autoxidation of aldehydes.—See A., 1933, 1249.

Catalytic oxidations. II. Benzaldehyde. III. Pyruvic acid.—See this vol., 37.

Chloroimines. IV. Reactions of N-chloroaldehydes with bases. C. R. HAUSER and E. MOORE (J. Amer. Chem. Soc., 1933, 55, 4526—4530).—The relative ease of removal of HCl from

C₆H₄R·CH·NCl (R = *o*- and *m*-NO₂, *p*-Cl, and *p*-OMe) with NaOH (2 mols.) in 95.6% EtOH at 0° or iso-amylamine (I) (2 mols.) in C₆H₆ at 30°, is in the same order as the ionisation consts. of C₆H₄R·OH and C₆H₄R·CO₂H and in the inverse order to those of C₆H₄R·NH₂. (*p*-C₆H₄Cl)₂C·NCl is decomposed only to a slight extent under the same conditions. The relative rates of reaction of *m*-NO₂·C₆H₄·CH·NCl with (I), piperidine, CH₂Ph·NH₂, NH₂Ac, and NPh₃ in C₆H₆ at 30° are in the same order as the ionisation consts. of the bases. The first stage of the reaction is considered to be the withdrawal of a proton* from H; this is followed by removal of Cl-. H. B.

Reactions of aldoxime derivatives with bases.

I. Reactions of acetyl- β -aldoximes with alkali. C. R. HAUSER and C. T. SULLIVAN (J. Amer. Chem. Soc., 1933, 55, 4611—4613).—Acetyl- β -*p*-methoxy-, -*m*-nitro-, -*p*-chloro-, and -3 : 4-methylenedioxy-benzaldoximes, prepared by a modification of Brady and McHugh's method (A., 1926, 69), are converted into

mixtures of the corresponding benzonitrile (I) and β -oxime (II) by aq. or EtOH-NaOH at 0° [(II) predominates] and 30° [(I) predominates]. The first two Ac derivatives and aq. Na₂CO₃ at 0° or 30° give entirely (I). H. B.

Alkylation of hydroxyaldehydes. S. J. KANEV-SKAJA (Arch. Pharm., 1933, 271, 462—466).—The appropriate alkyl *p*-toluenesulphonate gives good yields of *vanillin* 4-Et and 4-*n*-amyl ether, m.p. 73—74°, *o*- and *p*-methoxy- and *o*-ethoxy-benzaldehyde, and veratraldehyde (from vanillin and protocatechu-aldehyde). R. S. C.

Lignin. X. Identity and structure of spruce lignins prepared by different methods. F. BRAUNS and H. HIBBERT (J. Amer. Chem. Soc., 1933, 55, 4720—4727; cf. A., 1933, 394).—Analytical data for "MeOH lignin" (I) and "glycol lignin" (II) and their Ac and Me derivatives indicate that the native lignin of spruce wood (A) has the empirical composition C₄₂H₃₂O₆(OH)₅(OMe)₅; three OH groups are aliphatic, one is phenolic or enolic, and the fifth is characterised by its reactivity towards HCl and alcohols (or phenol). During the extraction of (A) with MeOH-HCl, H is replaced by Me to give C₄₂H₂₂O₆(OH)₄(OMe)₆ [i.e. (I)]; extraction with glycol-HCl causes replacement of the same H by C₂H₄·OH to give C₄₂H₃₂O₆(OH)₄(OMe)₅·O·CH₂·CH₂·OH [i.e. (II)]. Willstätter lignin (III) (cf. A., 1913, i, 955; 1922, i, 989) and "Freudenberg lignin" (IV) (cf. A., 1929, 1046) are methylated to products (OMe 32.2%), probably C₄₂H₃₂O₆(OMe)₁₀. "PhOH lignin" obtained by extraction of (A) with PhOH-HCl, is separable into Et₂O-sol. (V) (OMe 5.4%) and -insol. (VI) (OMe 10.1%) fractions. (V) and (VI) are methylated (CH₃N₂) to the same product (OMe 21.5—21.6%), indicating that they contain the same fundamental unit; further methylation (Me₂SO₄, NaOH) gives a product with OMe 28.2%. Acetylation of (VI) gives a compound (OMe:Ac=1:2), whilst methylation (CH₃N₂) and subsequent acetylation affords a compound (OMe:Ac=3:1); the change in the ratio OMe:Ac indicates that (VI) contains new free phenolic OH groups (arising from condensation of the lignin with PhOH). Condensation of (II) and its Me derivatives (CH₃N₂; Me₂SO₄) with PhOH followed by (a) methylation (CH₃N₂), (b) complete methylation, and (c) benzoylation, and determinations of OMe and the ratios OMe:Bz indicate that three phenolic OH groups are introduced. "PhOH lignin" is C₄₂H₃₂O₆(OH)₄(OPh)(OMe)₅(C₆H₄·OH)₃; this is obtained by condensation of PhOH with (IV) and (III) (in the last case, 8—10% of an almost OMe-free insol. residue is produced also). H. B.

Reactions of substituted cyclohexanones. R. E. MAYER (Helv. Chim. Acta, 1933, 16, 1291—1295).—Chlorination of cyclohexanol (I) suspended in H₂O containing CaCO₃ at 20—25° yields small amounts of unchanged (I), cyclohexanone, 2-chlorocyclohexanone (II), b.p. 79°/7 mm., m.p. 22—23° (yield 56.6%), and more highly chlorinated products containing 2:6-dichlorocyclohexanone, b.p. 106°/7 mm., m.p. 72—73°. (II) is converted by excess of KCN in H₂O into the readily oxidised 2-cyanocyclohexanone (III), b.p. 140—141°/15 mm., smoothly transformed by

10% NaOH into pimelic acid (best obtained from the crude nitrile). (III) is oxidised when exposed to air to adipic acid, the intermediate formation of ϵ -hydroxy- ϵ -cyano-*n*-hexoic acid and δ -aldehydo-*n*-valeric acid being postulated. H. W.

Synthesis of some cyclic Δ^{α} -unsaturated ketones. R. S. THAKUR (J.C.S., 1933, 1481—1485).— α -cyclohexylidenepropionyl chloride (I) [acid, m.p. 81—82° (lit., 79°)] when distilled and hydrolysed by 10% Na₂CO₃-H₂O affords 45% of Δ^{β} -acid, whereas cyclohexylideneacetyl chloride similarly treated exhibits no tautomerism (cf. A., 1932, 1033, 1111). Interaction of (I) (undistilled) and ZnMeI according to the Blaise-Maire reaction and treatment of the product with NH₂·CO·NH·NH₂ affords, in different experiments, a semicarbazone of variable m.p. which depresses the m.p. of the Δ^{β} -semicarbazone (II). Crystallisation gives α -methylcyclohexylideneacetone-semicarbazone (III), m.p. 192—193° (rapid heating), different from (II), and a semicarbazone (IV), m.p. 155—160°, derived from the Δ^{α} -ketone. (III) with H₂C₂O₄ affords α -methylcyclohexylideneacetone (V), b.p. 97—98°/14 mm. (100% Δ^{α} -ketone), which is oxidised by KMnO₄ to cyclohexanone, whereas (IV) with H₂C₂O₄ affords a ketone (VI), b.p. 100—101°/16—17 mm. (92.5% Δ^{α} -ketone). (VI) with NH₂·CO·NH·NH₂ yields (III) and (IV). Catalytic reduction of (V) with Adams' catalyst followed by NH₂·CO·NH·NH₂ gives a semicarbazone, m.p. 112—125°, from which α -methylcyclohexenylacetone (100% Δ^{β} -ketone) (cf. A., 1926, 952) is regenerated. Equilibration of (V) (cf. A., 1929, 927) leads finally to a ketone (10% Δ^{α} -isomeride) which gives a semicarbazone, m.p. 170°, identical with the Δ^{β} -semicarbazone. α -cyclohexylidenepropionic acid when catalytically reduced (Pt-H₂) affords α -cyclohexylpropionic acid (VII), m.p. 62° (amide, m.p. 156—157°; anilide, m.p. 135—136°; *p*-toluidide, m.p. 155—156°), whilst α -cyclohexenylpropionic acid is only partly reduced under these conditions. Catalytic hydrogenation of α -methyl- α -cyclohexenylacetone followed by the action of NH₂·CO·NH·NH₂ on the product gives the semicarbazone (VIII), m.p. 84—106°, of α -methyl- α -cyclohexylacetone (IX) together with γ -cyclohexylsec-butyl alcohol, b.p. 109—110°/15 mm., which is oxidised by CrO₃ to a ketone convertible into (VIII). α -cyclohexylpropionyl chloride and ZnMeI according to the Blaise-Maire reaction give a ketone which affords (VIII), fractional crystallisation of which gives semicarbazones, m.p. 153—157° (X) and 130—131° (XI). (XI) is hydrolysed to (IX), b.p. 89—90°/13 mm., which gives a semicarbazone from which (X), the Δ^{β} -semicarbazone, and impure (XI) are isolable. 2-Methylcyclohexylideneacetyl chloride and MgMeI in Et₂O afford a crude product (XII) which gives 2-methylcyclohexylideneacetone-semicarbazone (XIII), m.p. 194° (Δ^{α} -isomeride) [the Δ^{β} -isomeride is obtained from redistilled (XII)], which regenerates the pure Δ^{α} -ketone, b.p. 99—101°/12 mm. (cf. A., 1930, 1582). The regenerated Δ^{β} -ketone has b.p. 102°/15 mm. Equilibration of the Δ^{α} - or Δ^{β} -ketone affords a product (90% Δ^{β} -) from which only the Δ^{β} -semicarbazone can be isolated. Prepared similarly to (XII), α -methyl-*trans*-decahydronaphthylidene-2-

acetone affords a semicarbazone, m.p. 214—215° (decomp.) (lit., 209—210°), which regenerates a mixture of Δ^{α} - and Δ^{β} -ketones. Prolonged action of 2*N*-NaOEt on this mixture affords the Δ^{β} -semicarbazone, m.p. 195—196°. An α -Me group considerably retards the mobility of the cyclohexane (as does a 2-Me group) and *trans*- β -decalin compounds.

J. L. D.

Octahydrophenanthrene derivatives. J. D. FULTON and R. ROBINSON (J.C.S., 1933, 1463—1466).—Interaction of cyclohexene (I) with $\text{CH}_2\text{Ph}\cdot\text{COCl}$ in CS_2 containing SnCl_4 at -15° during 2.5 hr. followed by NPhEt_2 at 180° during 2 hr. affords Δ^1 -cyclohexenyl benzyl ketone, m.p. 44.5° (semicarbazone, m.p. 171—172°). Ethyl- Δ^1 -cyclohexene gives no satisfactory product. cyclohexanone and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgBr}$ (II) in Et_2O at -15° afford 1- β -phenylethyl-cyclohexanol (III), m.p. 56.5° and -cyclohexene, b.p. 112—113°/2 mm. (nitroschloride, m.p. 118—119°; nitropiperidine, m.p. 117—118°), also obtained from (III) with ZnCl_2 , Ac_2O , or PhNCO . (I) reacts with (II) in Et_2O to give 2- β -phenylethylcyclohexanol (IV), m.p. 17—18° (p-nitrobenzoate, m.p. 73.5°), a homogeneous product, apparently different from that of Bardhan and Sengupta (A., 1932, 1241). (IV) is oxidised by CrO_3 in 0.5 hr. at 55° to 2- β -phenylethylcyclohexanone (V), b.p. 135—136°/2 mm. {oxime, m.p. 74—75°; semicarbazone, m.p. 157° [lit., 179—180° (decomp.)]}. Dehydration of (IV) with ZnCl_2 affords mainly an unsaturated compound (cf. Bardhan and Sengupta), but interaction of (IV) with SOCl_2 in cold $\text{C}_5\text{H}_5\text{N}$ during 1 hr. affords a sulphonyl chloride which decomposes when heated to give 2-chloro- β -phenylethylcyclohexane, b.p. 130—134°/5 mm. (admixed with a hydrocarbon), cyclised by AlCl_3 in warm light petroleum to 1:2:3:4:9:10:11:12-octahydrophenanthrene (VI), b.p. 135—137°/6.5 mm., which crystallises when cooled to -12° and therefore differs stereochemically from Bardhan and Sengupta's product. (VI) is dehydrogenated by S to give phenanthrene (VII). (V) with MgEtBr in boiling Et_2O during 1 hr. affords 2- β -phenylethyl-1-ethylcyclohexanol, b.p. 147—148°/3 mm. (easily dehydrated by ZnCl_2 to 2- β -phenylethyl-1-ethyl- Δ^1 -cyclohexene, b.p. 113—114°), converted by SOCl_2 into the chloride, which is cyclised (AlCl_3) to a saturated hydrocarbon, $\text{C}_{16}\text{H}_{22}$, 12-ethyl-1:2:3:4:9:10:11:12-octahydrophenanthrene (?), b.p. 113—116°/<1 mm., dehydrogenated by S at 170 — 180° in 40 hr. to (VII) and anthracene. Et 3:4-dimethoxycinnamate, m.p. 56°, gives with Br in artificial light, a dibromide, m.p. 107—108°, which when boiled with $\text{EtOH}\cdot\text{KOH}$ (3 mols.) for 7 hr. affords 3:4-dimethoxyphenylpropionic acid, m.p. 154°, decarboxylated by NPhEt_2 at 150 — 160° to 3:4-dimethoxyphenylacetylene, m.p. 73—74° (VIII). (VIII) gives with MgEtBr a compound which does not react with (I). When similarly treated, $\text{CPh}\cdot\text{CH}$ affords a hydrocarbon, m.p. 48—49°. Et homoveratrate, b.p. 159—160°/4 mm. (amide, m.p. 139°), is reduced with Na by the Bouveault reaction to give β -3:4-dimethoxyphenylethyl alcohol, m.p. 47—48° (phenylurethane, m.p. 99°; p-nitrobenzoate, m.p. 85° after softening). 3:4-Dimethoxymandelonitrile, m.p. 104—105°, is converted into the hydrochloride, m.p. 139—140°, of the related iminoethyl ester.

J. L. D.

Jasmine perfumes. I. Constitution of jasmine. L. RUZICKA and M. PFEIFFER (Helv. Chim. Acta, 1933, 16, 1208—1214).—Jasmone (I), regenerated from the semicarbazone, m.p. 209.5—210°, has b.p. 134—135°/12 mm., $\alpha_D^{20} +0^\circ$. Ozonisation of (I) in CCl_4 leads to EtCHO , $\text{CH}_2(\text{CO}_2\text{H})_2$, and lævulic acid (II), whilst oxidation with KMnO_4 affords EtCO_2H , $(\cdot\text{CH}_2\text{CO}_2\text{H})_2$, and (II). Hydrogenation of (I) in presence of feebly active Pt-black yields 3-methyl-2-amyl- Δ^2 -cyclopentenone, whereas more drastic treatment (active Pt-black from PtO_2) affords 3-methyl-2-amylcyclopentanone. (I) is therefore 3-methyl-2- Δ^{β} -pentenyl- Δ^2 -cyclopentenone.

H. W.

Condensation products of dicyclic ketones. R. S. THAKUR (J.C.S., 1933, 1477—1481).—The condensation of 2 mols. of *trans*-hexahydro-2-hydrindone (I) with dry HCl at room temp. during 8 weeks affords unchanged (I), *trans*-hexahydrohydrindylidene-2-*trans*-hexahydrohydrindone (II) [oxime, m.p. 206—208° (lit., 211—212°); 2:4-dinitrophenyl-, p-nitrophenyl-, and phenyl-hydrazone, m.p. 248° (decomp.), 267° (decomp.), and 193—194° (decomp.), respectively] and a hydrocarbon, $(\text{C}_9\text{H}_{12})_n$ [$n=3$ (?)], m.p. 116—118°. (I) with dry NaOEt in a few hr. affords no unchanged (I), but (II) and a substance, m.p. 109—110°. (II) affords with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ in boiling EtOH during 1 hr. a semicarbazone, m.p. 180—210° in different preps. (lit., 140°), but when crystallised from EtOH or when gently warmed, it has m.p. 234—235° (decomp.), due to the interconversion of geometrical isomerides (cf. A., 1924, i, 652). Ozonisation of (II) affords (I), *trans*-hexahydro-2-hydrindone peroxide (A., 1932, 1034), and *trans*-hexahydrohomophthalic acid, m.p. 160—161°. Interaction of *trans*- β -decalone (III) and dry HCl during 1 hr. affords two isomeric Cl-compounds, $\text{C}_{20}\text{H}_{31}\text{OCl}$, m.p. 130—131° (IV) and 118—119° (V), respectively. The crude mixture of (IV) and (V) with boiling $\text{C}_5\text{H}_5\text{N}$ during 1.5 hr. [or by distillation of (IV)] affords a ketone, $\text{C}_{20}\text{H}_{30}\text{O}$, b.p. 228—230°/7 mm. (semicarbazone, m.p. 207°). (III) affords with dry NaOEt at room temp. during 8 days *trans*- β -decalol, no unchanged (III) even after 1 day, and no identifiable condensation product (cf. A., 1925, i, 258), but a rosin-like substance which does not yield a semicarbazone, but with $\text{NH}_2\text{OH}\cdot\text{HCl}$ gives a product, m.p. 255—256° (decomp.). The unhydrolysed residue (VI) obtained by interaction of (III) with $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Et}$ or $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ and Zn (cf. A., 1932, 1032, 1033) affords Δ^2 (or Δ^1)-*trans*-octahydronaphthyl-2-*trans*- β -decalone (VII), m.p. 125—126° [semicarbazone, m.p. 212° (decomp.)], and a product (VIII), m.p. 75—80° [semicarbazone, m.p. 224—225° (decomp.)], different from *trans*- β -decalol. (VII) and (VIII) afford the same phenyl-, m.p. 153—154°, and p-nitrophenyl-hydrazone, m.p. 208° (decomp.). (VII) gives a 2:4-dinitrophenylhydrazone, m.p. 175—176°, whilst (VIII) gives one of m.p. 194—195° (decomp.), although the latter does not depress the m.p. of the former. Ozonisation of (VI) affords (III) and *trans*-cyclohexane-1:2-diacetic acid, but no 1-carboxy-*trans*-cyclohexane-2-propionic acid.

J. L. D.

Polyhalogeno-derivatives of acetomesitylene. II. Bromination of 3:5-dichloroacetomesityl-

ene. C. H. FISHER (J. Amer. Chem. Soc., 1933, 55, 4594—4597; cf. A., 1933, 1296).— p - C_6H_4Cl -COME and excess of Br in absence or presence of solvent give the $\omega\omega$ -Br₂-derivative, m.p. 93.5—94.5° (lit. 92.5°); failure to obtain the $\omega\omega\omega$ -Br₃-derivative is probably due to the reducing action of the HBr formed (thus, $\omega\omega\omega$:3:5-pentabromo-2:4:6-trimethylacetophenone is reduced by 48% HBr in AcOH to the $\omega\omega$:3:5-Br₂-derivative). $\omega\omega$:3:5-Tetrachloro-2:4:6-trimethylacetophenone (I), m.p. 106.5—107.5°, from acetomesitylene and Cl₂ in AcOH, is reduced (Zn dust, AcOH) to 3:5-dichloro-2:4:6-trimethylacetophenone (II), m.p. 107.5—109°, converted [as is (I)] by aq. NaOCl in C₅H₅N into $\omega\omega\omega$:3:5-pentachloro-2:4:6-trimethylacetophenone, m.p. 90—91°. (II) and excess of Br in AcOH give a 1:1 mixture (III), m.p. 103.5—104.5°, of 3:5-dichloro- $\omega\omega$ -dibromo- (IV), m.p. 121—122°, and 3:5-dichloro- $\omega\omega\omega$ -tribromo- (V), m.p. 84—85°, -2:4:6-trimethylacetophenones. (III) could not be separated by fractional crystallisation and is prepared from equimol. amounts of (IV) and (V). (V) is obtained from (II) or (III) and aq. NaOBr in C₅H₅N, whilst (IV) is prepared from (II) and Br (2 mols.) in AcOH.

H. B.

Asymmetric syntheses. III. Action of optically active nitrates on 1-keto-1:2:3:4-tetrahydronaphthalene. W. H. HORNE and R. L. SHRINER (J. Amer. Chem. Soc., 1933, 55, 4652—4654).—An optically inactive *K* salt of 2-nitro-1-keto-1:2:3:4-tetrahydronaphthalene, m.p. 67°, is obtained when 1-keto-1:2:3:4-tetrahydronaphthalene is treated with *d*-, *l*-, or *dl*- β -octyl nitrate in EtOH-KOEt and Et₂O, indicating the structure $\cdot C(OK):C(NO_2)\cdot$ for the salt.

H. B.

Catalytic dehydration of ionone and constitution of ionene. M. T. BOGERT and V. G. FOURMAN (J. Amer. Chem. Soc., 1933, 55, 4670—4680).—Ionene (I), b.p. 114°/14 mm., 240—242°/752 mm., is best prepared by distillation of α - or β -ionone with a little I. The work now and previously (A., 1933, 153) described establishes (I) as 1:1:6-trimethyl-1:2:3:4-tetrahydronaphthalene (cf. Barbier and Bouveault, A., 1897, i, 537). (I) is dehydrogenated (S) to 1:6- $C_{10}H_6Me_3$ and is oxidised (aq. KMnO₄) to β -2:4-dicarboxyphenylisovaleric acid (+H₂O), m.p. 220°, or α -2:4-dicarboxyphenylisobutyric acid (II), m.p. 217° (*Me*₃ ester, m.p. 91°), and α -keto- β -2:4-dicarboxyphenylisovaleric acid (III), m.p. 140—145°, re-solidifying at 150° with m.p. about 206°, according to the conditions used; (II) and (III) are, respectively, the ioneregene- and ionegenone-tricarboxylic acid of Tiemann and Kruger (A., 1894, i, 80). Distillation of the *K* salt of (II) with soda-lime gives PhPr^s. (I) and conc. H₂SO₄ at 90° afford an ionenesulphonic acid [Na (+5H₂O) and Ba (+3H₂O) salts: chloride, m.p. 89°; amide, m.p. 157—158°], whilst (I), HNO₃ (*d* 1.5), and P₂O₅ (or conc. H₂SO₄) in the cold give dinitroionene (IV), m.p. 103°. This is reduced (H₂, PtO₂, EtOH) to a nitroaminoionene, m.p. 171° (hydrochloride, decomp. 237—239°; Ac derivative, m.p. 158°), and oxidised (CrO₃, AcOH, conc. H₂SO₄) to α -dinitroionene (V), m.p. 157° (*oxime*, m.p. 188.5°). (V) is isomerised by a little conc. H₂SO₄ in Ac₂O to

β -dinitroionene (VI), m.p. 99°, which is reconverted into (V) by dissolution in conc. H₂SO₄ or EtOH-NaOH. (IV), (V), and (VI) are oxidised (Na₂Cr₂O₇, AcOH, conc. H₂SO₄) to β -dinitro-2-carboxyphenylisovaleric acid (+H₂O), m.p. 150° (loss of H₂O), re-solidifying with m.p. 177°, which when heated above its m.p. gives β -dinitrophenylisovaleric acid, m.p. 166.5—168.5°, and is oxidised (KMnO₄, dil. H₂SO₄) to α -dinitrophenylisobutyric acid, m.p. 170.5°. The irene of Tiemann and Krüger (*loc. cit.*) is probably (I).

H. B.

7-Phenylthiol derivatives of deoxybenzoin. W. A. MITCHELL and S. SMILES (J.C.S., 1933, 1529).—COPh·CPh(SPh)₂, Zn, and AcCl in Et₂O give 7'-acetoxy-7-phenylthiolstilbene, m.p. 141°, hydrolysed (EtOH-NaOEt) to 7-phenylthioldeoxybenzoin [Ph α -phenylthiolbenzyl ketone], m.p. 81°. 7'-Acetoxy-7-(5-chloro-2-methoxyphenylthiol)stilbene, m.p. 114°, from COPh·CPh(S·C₆H₃Cl·OMe)₂, is similarly hydrolysed to 7-(5-chloro-2-methoxyphenylthiol)deoxybenzoin, m.p. 102°, also prepared from 5-chloro-2-methoxythiophenol (I), benzoin, and EtOH-HCl [use of an excess of (I) in this condensation gives 7:7'-bis-(5-chloro-2-methoxyphenylthiol)stilbene, m.p. 208°]. The production of Ph $\beta\beta$ -diphenylthiol- β -phenylethyl sulphide (II), m.p. 82°, from PhSH (3 mols.), CH₂Bz·OAc (1 mol.), and EtOH-HCl, together with the above change COPh·CPh(SAr)₂ → OAc·CPh·CPh·SAr, support Posner's assumption (A., 1902, i, 220) that the production of (CPh·SAr)₂ from ArSH and benzoin is preceded by the formation of (ArS)₂CPh·CHPh·SAr. Attempts to remove a mol. of PhSH from (II) were, however, unsuccessful.

H. B.

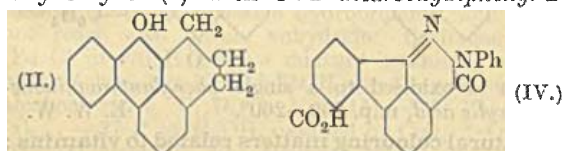
Halogenated benzophenones. J. GANZMULLER (J. pr. Chem., 1933, [ii], 138, 311—312).—Prolonged heating of p -C₆H₄Cl₂, BzCl, and AlCl₃ gives 2:5-dichlorobenzophenone, m.p. 85—86°. 2:5:2'-Tri-, m.p. 145—147°, and 2:5:2':4'-tetra-, m.p. 176°, -chlorobenzophenones are similarly prepared using o -C₆H₄Cl·COCl and 2:4-C₆H₃Cl₂·COCl, respectively.

H. B.

Isomerism of halochromic compounds. II. P. PFEIFFER and H. KLEU (Ber., 1933, 66, [B], 1704—1711; cf. A., 1933, 1052).—Further examples are given of colourless ammonium salts (I), COR·CH:CH·C₆H₄·NMe₂·HClO₄, and coloured oxonium salts (II), NMe₂·C₆H₄·CH:CH·CR'·O·HClO₄ of unsaturated basic ketones (III). (I) are best prepared by dissolution of (III) in an excess of dil. aq. HClO₄ and crystallisation whereas (II) are obtained by partial hydrolysis of the diperchlorates or by dissolution of (III) in 70% HClO₄ which is slowly diluted. In cases of unusual difficulty (I) can be isomerised to (II) by crystallisation from CH₂Cl·CO₂H. The following compounds are described: *p*-chlorophenyl *p*-dimethylaminostyryl ketone, m.p. 140—140.5°, from *p*-NMe₂·C₆H₄·CHO and C₆H₄Cl·COME in NaOH-EtOH, its colourless and violet perchlorate; *p*-tolyl *p*-dimethylaminostyryl ketone, m.p. 122—123°, colourless and blue mono- and yellow di-perchlorate; *p*-anisyl *p*-dimethylaminostyryl ketone, m.p. 127°, colourless and coloured perchlorates; styryl *p*-dimethylaminostyryl ketone, m.p. 158°, its brownish-yellow and bluish-green monopерchlorate and orange-brown dipерchlorate;

Ph *p*-aminostyryl ketone, m.p. 152°, its yellow and pink perchlorate. H. W.

Degradation of 1 : 9-benzanthrone-10 by oxidation. G. CHARRIER and (SIGNA.) E. GHIGI (Gazzetta, 1933, 63, 685—697).—Oxidation of Bz-1-amino-benzanthrone (A., 1929, 1305) by KMnO_4 -NaOH was unsuccessful as a method of degradation, yielding mainly anthraquinone-1-carboxylic acid (I), with a product, m.p. 180—185°. Hydroxytrimethylenephenthrene (II) was, however, thus oxidised to a small quantity only of (I) with 3 : 2'-dicarboxydiphenyl-2-



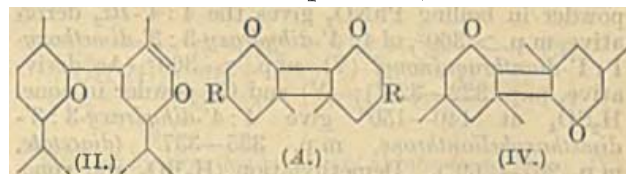
glyoxylic acid (III), m.p. 230° (decomp.) (Na_3 , $\text{Ba}_{3/2}$ salts), also obtained by similar oxidation of benzanthrone. (III) forms a *phenylhydrazone*, m.p. 160° (decomp.), an *oxime anhydride*, $\text{C}_{16}\text{H}_9\text{O}_5\text{N}$, m.p. 250° (decomp.), and Na salt, $\text{C}_{16}\text{H}_{10}\text{O}_7\text{NNa}$, m.p. 270° (decomp.), and a *semicarbazone*, m.p. 220° (decomp.). When distilled from $\text{Ca}(\text{OH})_2$ it gives Ph_2 , and from Zn, fluorene. With dil. H_2SO_4 and MnO_2 , *diphenyl-2 : 3 : 2'-tricarboxylic acid*, m.p. 195—196° (decomp.), is formed; with conc. H_2SO_4 the product is *fluorenone-1 : 5-dicarboxylic acid*, m.p. 295—299° (decomp.), which when distilled alone yields fluorenone, or with Zn, fluorene, and forms an *oxime*, m.p. 295—300° (decomp.), and a *phenylhydrazone*, m.p. about 290°. The last is converted below its m.p., or when heated in AcOH - Ac_2O , into the *phthalazone* derivative (IV), m.p. 294—295°. E. W. W.

Homogeneous catalysis of stereoisomeric change in oximes.—See this vol., 36.

Nitro-derivatives of β -diketones. N. J. TOIVONEN, E. OSARA, and O. OLLILA (Suomen Kem., 1933, 6B, 67—68).—Nitration of 2 : 5 : 5-trimethylcyclohexane-1 : 3-dione (I) in conc. HNO_3 affords 2-nitro-2 : 5 : 5-trimethylcyclohexane-1 : 3-dione (II), m.p. 145—147°, hydrolysed by conc. NaOH to ϵ -nitro- δ -keto- $\beta\beta$ -dimethylheptonic acid, m.p. 60—62° [Na_2 (III) and Ag_2 salts]. (III) with H_2O -NaOBr affords $\text{CMeBr}_2\cdot\text{NO}_2$ and $\beta\beta$ -dimethylglutaric acid. Reduction of (II) affords (I). J. L. D.

Polymerisation of $\alpha\beta$ -unsaturated ketones by alkali and by light. W. TREIBS (J. pr. Chem., 1933, [ii], 138, 299—305).—Polycarvone (I) (A., 1932, 1139) (structure suggested) is depolymerised by heat; it absorbs (Skita reduction) 1H per carvone unit (the resultant hydro-derivative is decomposed but not depolymerised by heat). Prolonged treatment of carvone or (I) with boiling MeOH -KOH gives a *dicarvone*, $\text{C}_{20}\text{H}_{28}\text{O}_2$, m.p. 115—116°, b.p. 230°/15 mm., in addition to that prepared by Ruzicka (A., 1921, i, 34); these are not depolymerised by heat. Piperitone is similarly converted into a *dipiperitone* (II), m.p. 105°. Irradiation (method; A., 1931, 95) of 3-methyl- Δ^2 -cyclohexenone in aq. MeOH gives a saturated (Br; KMnO_4) *dimeride* (A, R=H), m.p. 144—145° (impure *disemicarbazone*, m.p. >250°), and an unsaturated *dimeride*, an oil. 3 : 5-Dimethyl- Δ^2 -cyclohexenone simi-

larly affords a *dimeride* (III) (A, R=Me), m.p. 161—162° (*disemicarbazone*, m.p. >250°), a little of the

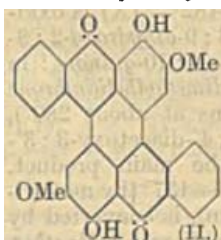


dimeride (IV) (*disemicarbazone*), and an unsaturated *dimeride*, b.p. 203—205°/17 mm. (III) is oxidised (CrO_3 , = 40 per mol., AcOH) to 1 : 2-dimethyl-1 : 2-di- β -carboxypropylcyclobutane-3 : 4-dicarboxylic acid, m.p. 261° (decomp.). H. B.

Course of alkylation of enolates. G. WANAG (Ber., 1933, 66, [B], 1678—1681).—Bindone (I) usually contains *isobindone* (II) from which it can be freed by K_2CO_3 in EtOH , leaving a product, m.p. 209° (slight decomp.). Treatment of (I) with excess of K_2CO_3 and MeI in EtOH leads to bindone *O*-Me ether, m.p. 174°, and (II). The formation of (II) is explained by the supposition that the primary product is bindone *O*-Me ether, which adds H_2O at the double linking and then loses EtOH with production of the K salt of (II). This is supported by the observation that the pure Me or Et ether of (I) freely yields (II) when treated with K_2CO_3 . (I) does not give (II) when heated with K_2CO_3 and EtOH . Homogeneous bindone *O*-Me ether, m.p. 217°, is obtained by treating (I) in MeOH with HCl ; hydrolysis with K_2CO_3 in MeOH results in partial formation of (II), but this is not the case when AcOH - HCl is used. H. W.

Lipins of tubercle bacilli. XXXV. Constitution of phthiocol, the pigment isolated from human tubercle bacillus. R. J. ANDERSON and M. S. NEWMAN (J. Biol. Chem., 1933, 103, 197—201).—The compound $\text{C}_{11}\text{H}_{18}\text{O}_3$ (A., 1933, 1083), now termed *phthiocol* (I), gives (Ac_2O , $\text{C}_5\text{H}_5\text{N}$) a *monoacetate*, m.p. 101—102°, which on reductive acetylation affords a *triacetate*, m.p. 148° to an opaque melt which clears at 158—159°. (I) is oxidised (alkaline H_2O_2) to *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. (I) is 3-hydroxy-2-methyl-1 : 4-naphthaquinone (synthesis to be reported later).

Reduction products of hydroxyanthraquinones, XIV. A. G. PERKIN and (in part) N. H. HADDOCK (J.C.S., 1933, 1512—1520).—The previously described (A., 1931, 355) 4 : 4'-dihydroxy-3 : 3'-dimethoxyhelianthrene (I) is now shown to be a mixture of (I) and 3 : 9-dihydroxy-2 : 8-dimethoxy-5 : 6 : 11 : 12-dibenzperylene-4 : 10-quinone (II). (I) is the main product when 1-hydroxy-2-methoxyanthrone (III) is oxidised



with I in cold $\text{C}_5\text{H}_5\text{N}$; in the hot, (II) predominates. Air oxidation of (III) or 1 : 1'-dihydroxy-2 : 2'-dimethoxydianthrene (*loc. cit.*) in boiling $\text{C}_5\text{H}_5\text{N}$ gives mainly (II). The production of (II) from (III)

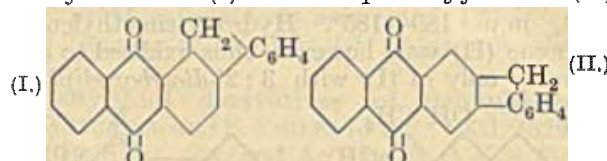
$\text{I}-\text{C}_5\text{H}_5\text{N}$ probably occurs by loss of 2HI from 10-iodo-1-hydroxy-2-methoxy-9-anthranol and subsequent oxidation of the so formed dihydro-derivative of (II). (I) is now syn-

thesised as follows: the *Bz* derivative, m.p. 207—208°, of 4-bromoalizarin 2-Me ether (IV) with Cu powder in boiling PhNO_2 gives the 4:4'-*Bz*₂ derivative, m.p. > 360°, of 4:4'-dihydroxy-3:3'-dimethoxy-1:1'-dianthraquinonyl (V), m.p. > 360° (Ac derivative, m.p. 322—326°); (V) and Cu powder in conc. H_2SO_4 at 140—150° give 4:4'-dihydroxy-3:3'-dimethoxyhelianthrone, m.p. 335—337° (diacetate, m.p. 267—269°). Demethylation (H_3BO_3 , and conc. H_2SO_4 at 140°) of (V) affords 3:4:3':4'-tetrahydroxy-1:1'-dianthraquinonyl (Eckert and Hampel, A., 1927, 881). 3:4:3':4'-Tetrahydroxyhelianthrone (VI) [from (I) and HBr (*d* 1.7) at 180—210°] is acetylated (Ac_2O , $\text{C}_6\text{H}_5\text{N}$) to its tetra-acetate (VII), m.p. 282—286°, and 3:4:3':4'-tetra-acetoxynaphthadanthrone (VIII), m.p. about 360°. Crystallisation of (VII) from COMe , in daylight causes considerable conversion into (VIII). Reduction (SnCl_2 , HCl , AcOH) of the Ac derivative of (IV) gives 4-bromo-1-hydroxy-2-methoxyanthrone (IX) and 4-hydroxy-3-methoxyanthranol, m.p. 198—200°. (IX), Ac_2O , and $\text{C}_6\text{H}_5\text{N}$ afford 4-bromo-1-acetoxy-2-methoxy-9-anthranyl acetate, m.p. 185—188°. When (IX) is heated, it passes gradually into (II). (II) is also formed when (IX) is shaken with cold $\text{C}_6\text{H}_5\text{N}$ or heated with $\text{C}_6\text{H}_5\text{N}$, PhNO_2 , or conc. H_2SO_4 ; loss of 2HBr from 2 mols. of (IX) (anthranol form) and subsequent oxidation (O_2) occur. (II) is not produced from (IX) and I in boiling $\text{C}_6\text{H}_5\text{N}$; a dark brown powder results. 2:3:8:9-Tetrahydroxy-5:6:11:12-dibenzperylene-4:10-quinone [obtained by demethylation of (II) or oxidation ($\text{I}-\text{C}_6\text{H}_5\text{N}$) of 1:2-dihydroxyanthrone (cf. *loc. cit.*)] and (VI) possess very similar dyeing properties (mordanted wool) (as do their SO_3Na derivatives). Digestion of (I) with 20% $\text{EtOH}-\text{KOH}$, evaporation to dryness, and treatment of the residue with Me_2SO_4 and anhyd. Na_2CO_3 at 90—140° gives 3:4:3':4'-tetramethoxyhelianthrone, m.p. 263—265° [oxidised (CrO_3 , AcOH) to 3:4:3':4'-tetramethoxy-1:1'-dianthraquinonyl, m.p. 335—336°], and a compound, $\text{C}_{30}\text{H}_{18}\text{O}_6$ (?), m.p. 285—287°; these are both converted by HBr (*d* 1.7) in cold AcOH into (I). (II) is similarly methylated to a Me_4 ether (+ AcOH), m.p. 317—319°, and a Me_3 ether, $\text{C}_{31}\text{H}_{20}\text{O}_6$, m.p. 289—290°, both of which are converted by cold $\text{HBr}-\text{AcOH}$ into (II); the former may be the 2:3:8:9- Me_4 ether, but since it gives a ppt. with $\text{EtOH}-\text{KOH}$ in C_6H_6 , it may contain free OH groups (formed by reduction during the original treatment with $\text{EtOH}-\text{KOH}$).

Reduction (SnCl_2 , HCl , AcOH) of 1-hydroxy-2-methylanthraquinone gives 1-hydroxy-2-methylanthrone (X), m.p. 136—138°, and 4-hydroxy-3-methylanthranol, m.p. 197°. 1-Acetoxy-2-methyl-9-anthranyl acetate has m.p. 180—182°. (X) is oxidised by I in boiling $\text{C}_6\text{H}_5\text{N}$ to 3:9-dihydroxy-2:8-dimethyl-5:6:11:12-dibenzperylene-4:10-quinone; in cold $\text{C}_6\text{H}_5\text{N}$, 4:4'-dihydroxy-3:3'-dimethylhelianthrone [diacetate, m.p. 297—300° (darkens at about 280°), readily converted (light) into 4:4'-diacetoxy-3:3'-dimethylnaphthadanthrone] is the main product. 3-Bromoalizarin Me_2 ether, m.p. 136—137° [by methylation (as above) of 3-bromoalizarin], is converted by conc. HCl at 135—140° into 3-bromoalizarin 2-Me ether, m.p. 186—187° (acetate, m.p. 150—151°). H. B.

Occurrence of anthraquinone dyes in mineral kingdom (graebeite).—See A., 1933, 1268.

Condensation of *o*-2-fluorenylbenzoic acid. A. DASI and A. SEMPRONJ (Gazzetta, 1933, 63, 681—684).—When this acid, prepared from fluorene and $\text{o}-\text{C}_6\text{H}_4(\text{CO})_2\text{O}$, best in CS_2 , as medium (cf. A., 1904, i, 168), is heated at 300—320° it condenses quantitatively to 1:2- (I) or 2:3-phthaloylfluorene (II),



which is oxidised to a single phenylanthraquinone-carboxylic acid, m.p. 259—260°. E. W. W.

Natural colouring matters related to vitamins: carotenes and flavins. R. KUHN (Chem. and Ind., 1933, 981—986).—British Association lecture.

Cerebronic acid fraction. II. F. A. TAYLOR and P. A. LEVENE (J. Biol. Chem., 1933, 102, 535—540).—The higher fatty acids from the oxidation of cerebronic acid (cf. A., 1929, 1479) contain lignoceric acid (mixed m.p.). Evidence is offered that this is not present in the unoxidised acid. H. A. P.

Cerebronic acid. IX. P. A. LEVENE and P. S. YANG (J. Biol. Chem., 1933, 102, 541—556; cf. Klenk, A., 1928, 868, and preceding abstract).—Repeated fractional hydrolysis of the *Me* ester, m.p. 64°, of cerebronic acid (I) (*Et* ester, m.p. 64—65°) with cold NaOH in MeOH and re-esterification indicates that it is not homogeneous, but is free from lignoceric acid (II); the product finally obtained in this way is the acid $\text{C}_{25}\text{H}_{50}\text{O}_3$ (titration). Confirmation that (I) contains near homologues is afforded by the behaviour on distillation of the Me_2 derivative (ether-ester), m.p. 59°, obtained by action of MeI and Ag_2O in excess of COMe_2 ; this is hydrolysed to the *OMe*-acid, $\text{C}_{26}\text{H}_{52}\text{O}_3$, m.p. 74—76°, thus disproving the presence of the lactide in (I). Oxidation of (I) with KMnO_4 gives a mixture of acids of mol. wt. 340—380 consisting mainly of (II). H. A. P.

Plant colouring matters. LIV. Products of the methylation of zeaxanthine. P. KARRER and T. TAKAHASHI (Helv. Chim. Acta, 1933, 16, 1163—1165; cf. A., 1930, 1440).—Zeaxanthine (I) is converted by *K tert.*-amyl oxide in boiling PhMe followed by MeI at 50° into a mixture of the *Me* (II), m.p. 153°, and *Me*₂ (III), m.p. 176°, ethers in small yield. (II) and (III) are scarcely distinguishable from (I) by absorption spectrum, but differ considerably in their solubility and distribution between MeOH and light petroleum. H. W.

Modifications of gutta-percha hydrocarbon. III. A. W. K. DE JONG (Rec. trav. chim., 1933, 52, 1028—1032; cf. A., 1932, 1036).—By cooling a solution of the spongy form of gutta-percha in 25—30 vols. of light petroleum with ice two modifications are obtained, viz., *a*, which shrinks to a solid cylinder on drying, and *b*, a spongy form which may have closed or open pores. *a* is formed by rapid cooling of solutions prepared at relatively low temp. (40°), and therefore containing crystal nuclei, and is regarded

as composed of particles of colloidal size; *b* is deposited more slowly by solutions prepared at higher temp., and consists of longer and thicker crystals, the product with closed pores probably containing the *a*-form in its interstices.

H. A. P.

Zierone. A. E. BRADFELD, A. R. PENFOLD, and J. L. SIMONSEN (J. Proc. Roy. Soc. New South Wales, 1933, 67, 200—205).—Zierone (I), $C_{15}H_{22}O$ (cf. B., 1927, 28), b.p. 147—149°/18 mm. (2:4-dinitrophenylhydrazone, m.p. 95—97°; semicarbazone, m.p. 182°), is stable to H_2O_2 -NaOH and $KMnO_4$ in hot $COMe_2$, gives an unstable hydrobromide, and does not react with maleic anhydride. Hydrogenation (Pd-C) in EtOH gives a mixture containing much hydrocarbon, but Na and EtOH give the unsaturated alcohol, *zierol*, $C_{15}H_{22}O$, b.p. 151—152°/17 mm., $[\alpha]_{5461}^{20} +37.4^\circ$ in MeOH, oxidised by CrO_3 -AcOH to (I). (I) gives an oily hydroxymethylene derivative (2:4-dinitrophenylhydrazone, m.p. 155—157°), and with Se at 250—280° gives probably Se-guaiazulene (picrate, m.p. 110—111°; cf. A., 1931, 1301). (I) is oxidised by O_3 , giving traces of CH_2O and no $COMe_2$. (I) is thus probably a tricyclic, mono-unsaturated compound, having a $CH_2 \cdot CO$ group; the ethylenic linking is probably not $\alpha\beta$ to the CO group and forms part of a ring. $[R_L]_D^{20}$ (66-93) suggests conjugation of a cyclopropane ring with both the ethylenic linking and the CO group.

R. S. C.

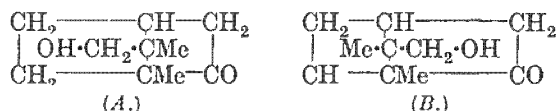
Organic compounds with large molar depression of m.p. J. FIRSCH (Ber., 1933, 66, [B], 1694—1697; cf. A., 1933, 770).—Compounds with high mol. m.p. depression belonging to the tricyclo-hydro-aromatic group have their mol. structure almost equally strongly developed in all three spatial directions. Further examples are: camphenilone, m.p. 38°, $E=64.0$, best obtained by alkaline hydrolysis of nitrocamphene and important because of its low m.p.; isocamphane, m.p. 65°, $E=44.5$, prepared by hydrogenation of camphene (Pd-BaSO₄ in EtOH); tricyclene, m.p. 66°, $E=35.9$, from camphorhydrazone and yellow HgO; bornylene, $E=33.5$; camphane, m.p. 154°, $E=29.5$.

H. W.

Occurrence of π -hydroxy-derivatives in campherol. Y. ASAHINA and M. ISHIDATE (Ber., 1933, 66, [B], 1673—1677; cf. A., 1931, 358).—Further examination shows that "labile 5-ketocamphor" is a somewhat complicated mixture of structural isomerides and that the "1:5:5-trimethylcyclopentane-2:4-dione-1-acetic acid" should be deleted from the lit. Autoxidation of the mixture affords isoketopinac acid (I), m.p. 249—250°, $[\alpha]_D^{20} +3.17^\circ$ in EtOH (cf. Wedekind, A., 1923, i, 808) [semicarbazone, (II) m.p. 255° (decomp.); phenylhydrazone, m.p. 205° (decomp.)], and 2-keto- π -apocamphane-7-carboxylic acid (III), m.p. 272°, $[\alpha]_D^{20} +67.2^\circ$ in EtOH [semicarbazone (IV), m.p. 215—216°] (cf. Hasselström, A., 1931, 626). Treatment of (II) with NaOEt-EtOH at 170—180° yields *l*- π -apocamphane-7-carboxylic acid, m.p. 231°, $[\alpha]_D^{20} -18.16^\circ$ in EtOH, whilst similar treatment of (IV) gives *d*-apocamphane-7-carboxylic acid, m.p. 231°, $[\alpha]_D^{20} +18.0^\circ$ in EtOH. Oxidation of (I) with $KMnO_4$ leads to *trans*-*d*-camphortricarboxylic acid, m.p. (anhyd.) 197°, $[\alpha]_D^{20} +36.8^\circ$ in EtOH (*Ag* salt; anhydride, m.p. 254°).

G

In addition to 3- and 5-hydroxycamphor, campherol therefore contains the two π -hydroxycamphors *A* and *B*.



(A.)

(B.)

Mild oxidation leads to an aldehyde mixture (V) rapidly autoxidised to the 2-keto- π -apocamphane-7-carboxylic acids. Treatment of (V) with $NH_2 \cdot CO \cdot NH \cdot NH_2$ gives a *mono*-, m.p. 202° (decomp.), and a *di*-, m.p. about 360° (decomp.) after becoming discoloured at 300°, -semicarbazone which could not be hydrolysed to their components.

H. W.

Isomeric myrtenols. V. PAOLINI (Gazzetta, 1933, 63, 666—669).—The dextrorotatory myrtenol (A., 1905, i, 801) isolated through the H phthalate (*Ag* salt, m.p. 102°) from the saponified fraction of Calabrian myrtle essence, in which a levorotatory form appears also to be present, is named α -myrtenol.

E. W. W.

Preparation of halogeno- and other 2-phenyl-benzopyrylium salts. (MRS.) C. G. LE FEVRE and R. J. W. LE FEVRE (J.C.S., 1933, 1532).—The appropriately substituted salicylaldehyde and CPhMe, $HClO_4$, and HCl give the benzopyrylium perchlorate in one stage (A., 1930, 217; 1932, 949). The following m.p. have been raised: 2-phenyl-, m.p. 180°; 6-bromo-, m.p. 250—251°; 6:8-dichloro-, m.p. 270—271°, and 6:8-dibromo-2-phenyl-benzopyrylium perchlorate, m.p. 273—275°.

F. R. S.

Synthetic experiments in the chromone group. X. Coumarin and chromone formation. T. C. CHADHA, H. B. MAHAL, and K. VENKATARAMAN (J.C.S., 1933, 1459—1462).—A classification of the action of acid anhydrides and Na salts on phenolic ketones of different types. Phloracetophenone, Ac_2O , and $CH_2Ph \cdot CO_2Na$ (I) form 5:7-diacetoxy-3-phenyl-4-methylcoumarin, m.p. 169°, hydrolysed to the (OH)₂-compound, m.p. 282—283°. *o*-Hydroxyacetophenone, $CH_2Ph \cdot COCl$, and (I) form 3-phenyl-4-methylcoumarin, whilst the ketone, $CH_2Ph \cdot CO_2Et$, and Na dust give 2-benzylchromone, m.p. 86°. *Ph* phenylacetate, m.p. 50°, and $AlCl_3$ give *o*-(II), m.p. 60° (2:4-dinitrophenylhydrazone, m.p. 219°), and *p*-hydroxyphenyl benzyl ketone, m.p. 151° (2:4-dinitrophenylhydrazone, m.p. 224°). (II) with NaOAc and Ac_2O affords 2-methylisoflavone, m.p. 140°, and with Bz_2O and NaOBz forms 2:3-diphenylchromone, m.p. 152°. Respropiofenone, (I), and Ac_2O form 7-acetoxy-3-phenyl-4-ethylcoumarin, m.p. 205°, hydrolysed to the 7-OH-compound, m.p. 254°. β - $C_{10}H_7$ phenylacetate, m.p. 87°, and $AlCl_3$ give 1-phenylacetyl- β -naphthol, m.p. 101°, which with Ac_2O and NaOAc affords 3-phenyl-2-methyl-1:4- β -naphthapyrone, m.p. 161°, and with Bz_2O and NaOBz yields 2:3-diphenyl-1:4- β -naphthapyrone, m.p. 188°. 1:2- $C_{10}H_6Bz \cdot OH$, Ac_2O , and (I) form 3:4-diphenyl-1:2- β -naphthapyrone, m.p. 221—222°.

F. R. S.

Coumarin series. II. Synthesis of some coumarinaldehydes. Catalytic hydrogenation of acid chlorides. T. BOEHM [with G. SCHUMANN and H. H. HANSEN] (Arch. Pharm., 1933, 271, 490—514;

cf. A., 1931, 493).—Hydrogenation of coumarin-3-carboxyl chloride (I) in xylene at 100° gives 70–75% yields of coumarin-3-aldehyde (II); at 180°, 20% of (II) and much coumarin are formed. The views of Zetzsche and Arnd (A., 1926, 405) are thus invalid. Similar reductions quoted below were carried out at 100°. (I) (prepared by SOCl_2), m.p. 147–148°, gives (II), m.p. 131–132° [oxidised by CrO_3 -AcOH or 65% HNO_3 to the acid; *p*-nitrophenylhydrazone, m.p. 287–288° (decomp.); semicarbazone, m.p. 265–266° (decomp.); oxime, m.p. 207° (decomp.)], which with $\text{CH}_2(\text{CO}_2\text{H})_2$ and piperidine (III) in EtOH gives β -3-coumarylacrylic acid, m.p. 266° (Et ester, m.p. 122°), the chloride, m.p. 197–198°, of which is reduced to β -3-coumarylacraldehyde, m.p. 155–156° [*p*-nitrophenylhydrazone, m.p. 289–290° (decomp.); oxime, m.p. 206–207°; semicarbazone, m.p. 242° (decomp.)]. (II) with MeNO_2 gives 3- ω -nitrovinyl-coumarin, m.p. 143–144°. (II), $\text{CH}_2(\text{CO}_2\text{Et})_2$, and a little (III) in cold EtOH give Et, hydroxy-3-coumarylmethylmalonate, m.p. 117°, dehydrated by Ac_2O - $\text{C}_5\text{H}_5\text{N}$ to Et, 3-coumarylmethylenemalonate, m.p. 93–95°. (II) with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ and (III) in EtOH gives a substance, $(\text{C}_7\text{H}_5\text{O}_2)_n$, m.p. 81–82°, with $\text{CH}_2(\text{CN})_2$ in EtOH gives 3-coumarylmethylenemalononitrile, m.p. 198° (decomp.), with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ and Na in EtOH α -cyano- β -3-coumarylacrylamide, m.p. 233°, and with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Et}$ Et α -cyano- β -3-coumarylacrylate, m.p. 202°. Tricarbomethoxygalloyl chloride gives 80% of the aldehyde. Resorcyaldehyde, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and (III) give the *O*-piperidine salt of Et umbelliferone-3-carboxylate (Ac derivative, m.p. 153–154°). Acetylumbelliferone-3-carboxylic acid, m.p. 210–211°, gives the chloride, m.p. 189–190°, hydrogenated to acetylumbelliferone-3-aldehyde, m.p. 165–166° [NaHSO_3 compound; *p*-nitrophenylhydrazone, m.p. 280° (decomp.)]. The following are similarly prepared: carbomethoxy-, m.p. 214–215°, and carbethoxy-umbelliferone-3-carboxylic acid, m.p. 167° (chloride, m.p. 144–145°), and -aldehyde, m.p. 134–135° [*p*-nitrophenylhydrazone, m.p. 263–265° (decomp.)], umbelliferone-3-aldehyde, decomp. > 300° [*p*-nitrophenylhydrazone, decomp. > 300°; oxime, m.p. 224–225° (decomp.)]. Et daphnetin-3-carboxylate (from pyrogallolaldehyde), m.p. 231–232° (Ac derivative, m.p. 129–130°), and the corresponding acid, m.p. 263° derivative, m.p. 213–214°).

R. S. C.

Synthesis of alkyl- and ar[alkyl]-coumarans. J. B. NIEDERL and E. A. STOECH (J. Amer. Chem. Soc., 1933, 55, 4549–4555).—Distillation of the polymeric obtained from allyl alcohol (1 mol.) and a phenol (1 mol.) in boiling AcOH-conc. H_2SO_4 gives an alkylcoumaran (50–65%) and a little of the corresponding *o*-isopropenylphenol. Thus, 2-methylcoumaran, b.p. 208–212°, is prepared using PhOH, whilst 2:4-, b.p. 103°/11 mm., 228–232°, 2:5-, b.p. 99–100°/11.5 mm., 250–255°, and 2:6-, b.p. 253–258°. -dimethylcoumarans are obtained from *p*-, *m*-, and *o*-cresol, respectively. 3-isopropenyl-*o*-cresol and Br give a pentabromo-3-isopropyl-*o*-cresol, m.p. 190–191°. Cinnamyl alcohol and PhOH similarly afford (mainly) 2-benzylcoumaran, b.p. 308–311°, and γ -phenyl-3-*o*-hydroxyphenyl- Δ^a -propene, b.p. 193–196°; *o*-cresol gives 2-benzyl-6-methylcoumaran, b.p. 318–322°, and

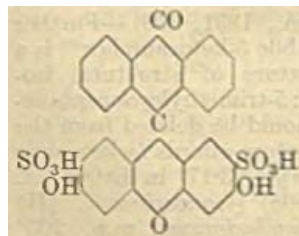
γ -phenyl- β -2-hydroxy-3-methylphenyl- Δ^a -propene, b.p. 212–216°; *m*-cresol yields 2-benzyl-5-methylcoumaran, b.p. 322–327°, and γ -phenyl- β -2-hydroxy-4-methylphenyl- Δ^a -propene, b.p. 207–211°; *p*-cresol furnishes 2-benzyl-4-methylcoumaran, b.p. 320–325°, and γ -phenyl- β -2-hydroxy-5-methylphenyl- Δ^a -propene, b.p. 208–212°. 2-Phenyl-1:4-dimethylcoumaran, b.p. 310–314° (Br_5 -derivative, m.p. 249°), is prepared by Claisen and Tietze's method (A., 1925, i, 389).

H. B.

Colouring matter on the stems of the tomato. B. K. BLOUNT (J.C.S., 1933, 1528–1529).—The colouring matter is rutin. F. R. S.

Synthesis of certain naphtha(1:2:4':3')-coumarin derivatives. R. ROBINSON and J. D. ROSE (J.C.S., 1933, 1469–1472).—Resorcinol, Et benzoylsuccinate, and H_2SO_4 give Et 7-hydroxy-4-phenylcoumarin-3-acetate, m.p. 177°, hydrolysed to the acid (I), m.p. 249–250° [*O*Me-derivative (II), m.p. 209°]. Methylation of (I) affords Me phenyl-2:4-dimethoxyphenylmethylenesuccinate, m.p. 101°, and of the Et ester of (I) yields the 1-Me 2-Et compound, m.p. 93°. (I) and Ac₂O give 4:7'-diacetoxy-naphtha(1:2:4':3')coumarin, m.p. 230°, hydrolysed to the 4:7'-(OH)₂-compound, m.p. >360°. (II) and Ac₂O form 4-acetoxy-7'-methoxynaphtha(1:2:4':3')coumarin, m.p. 184°, hydrolysed to the 4-OH-compound, m.p. 266–267° (decomp.), whilst (II) and P_2O_5 yield 7'-methoxy-4-(7''-methoxy-4''-phenylcoumarin-3''-acetoxy)naphtha(1:2:4':3')-coumarin, m.p. 237°. Veratroyl chloride, EtOH-NaOEt, and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ give Et α -veratroylacetylsuccinate, m.p. 98° (Et veratroylacetate, m.p. 82°), which with resorcinol and H_2SO_4 affords Et 7-hydroxy-4-veratroylcoumarin-3-acetate, m.p. 172°, hydrolysed to 4:7'-diacetoxy-5:6-dimethoxynaphtha(1:2:4':3')-coumarin, m.p. 256–257°. Et *m*-methoxybenzoylacetate, Na, and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ yield Et *m*-methoxybenzoylsuccinate, b.p. 227°/17 mm., which does not condense with resorcinol. F. R. S.

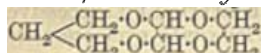
Condensation of *o*-benzoylbenzoic acid with resorcinol. G. CHARRIER and (SIGNA.) E. GHIGI (Gazzetta. 1933, 63, 630–634).—The “rodonine” of Pavolini (A., 1932, 1038) contains S, being the disulphonic acid (probable formula annexed) of the condensation product (A., 1903, i, 640) of resorcinol and anthraquinone, and was patented in 1897 (G.P. 108,536). It may also be obtained by condensation of resorcinol-4:6-disulphonic acid with anthraquinone. E. W. W.



Synthesis of homologues of dioxan. R. CHRIST and R. K. SUMMERBELL (J. Amer. Chem. Soc., 1933, 55, 4547–4548; cf. A., 1932, 1141).—2:3-Dichlorodioxan (I) and MgPhBr give 2:3-diphenyldioxan, m.p. 49°, which when chlorinated at 125° and then hydrolysed (boiling H_2O) affords Bz₂ and (CHO)₂. Chlorination of (I) at 115° gives a (s)-tetrachlorodioxan, m.p. 70° [hydrolysed to (CHO)₂], in addition to those

of m.p. 143—144° and b.p. 93—95°/11—12 mm. (cf. Butler and Cretcher, A., 1932, 949). H. B.

Derivatives of dioxan. IV. J. BOESEKEN, F. TELLEGEN, and P. MALTHA (Rec. trav. chim., 1933, 52, 1067—1072; cf. A., 1933, 511).—Interaction of 2:3-dichlorodioxan with HO·[CH₂]₃·OH in C₆H₆ at the b.p. gives stereoisomeric forms, m.p. 157—158°, and 109.5—111°, of 2:3-dihydroxydioxan trimethylene ether,



The isomeride of higher m.p. appears to be converted by heat into a further modification from which it is regenerated by crystallisation from Et₂O. H. A. P.

Thiophen derivatives. III. I. J. RINKES (Rec. trav. chim., 1933, 52, 1052—1060).—Nitration of 3-methylthiophen (HNO₃-Ac₂O at -10°) gives 2-nitro-3-methylthiophen (I), m.p. 63°, b.p. 124°/20 mm., the orientation of which follows from its formation by the displacement of CO₂H by NO₂ in the nitration of 3-methylthiophen-2-carboxylic acid (II). The constitution of 3-methylthiophen-5-carboxylic acid, obtained by oxidation of methathioxen (cf. A., 1887, 921), is proved by its nitration to the 2-NO₂-compound (III), m.p. 180°, which on decarboxylation gives (I). Further nitration (HNO₃, d 1.51, and conc. H₂SO₄ at -10°) of the Me ester, m.p. 93°, of (III) gives the 2:4-(NO₂)₂-ester, m.p. 64°, the free acid, m.p. 191°, of which is decarboxylated in quinoline to 2:4-dinitro-3-methylthiophen (IV), m.p. 96°, also formed together with (V) (below) by further nitration of (I). Nitration of (II) gives (I), (IV), and 4-, m.p. 208° (Me ester, m.p. 94°), and 5-nitro-3-methylthiophen-2-carboxylic acid, m.p. 182° (Me ester, m.p. 87°), further nitration of which eliminates CO₂H and gives (IV) and 2:5-dinitro-3-methylthiophen (V), m.p. 58°, respectively. H. A. P.

[Indigoid dyes. III.] R. TOBLER (Ber., 1933, 66, [B], 1757; cf. Dutta, A., 1933, 1169).—A question of priority. H. W.

Preparation of glycyl-l-proline by E. Fischer's method. E. ABDERHALDEN and W. NUSSLER (Biochem. Z., 1933, 266, 216—220).—Material previously obtained (A., 1930, 1475) by Fischer's method (I) was impure. In the prep. of alanylproline and in many other cases the method of Bergmann *et al.* (A., 1933, 94) is greatly to be preferred. W. McC.

Piperidine derivatives. XIII. Phenyl- and phenylalkyl-substituted piperidinopropyl benzoates. L. A. WALTERS and S. M. McELVAIN (J. Amer. Chem. Soc., 1933, 55, 4625—4629).—2-Phenyl-, b.p. 270—272°/740 mm. (from C₆H₅N and LiPh in PhMe), 2-γ-phenylpropyl-, b.p. 132—135°/2 mm., and 2-δ-phenylbutyl-, b.p. 142—145°/2 mm., -pyridines, prepared by Ziegler and Zeiser's method (A., 1931, 364), are reduced (H₂, Ni, methylcyclohexane at 150°) to 2-phenyl-, 2-γ-phenylpropyl-, b.p. 161—163°/10 mm. (hydrochloride, m.p. 139—141°), and 2-δ-phenylbutyl-, b.p. 164—166°/9 mm. (hydrochloride, m.p. 129—131°), -piperidines, respectively. α-Phenoxy-α-phenylvaleronitrile, b.p. 190—195°/2 mm. (from CH₃Ph·CN, γ-phenoxypropyl bromide, and NaNH₂ in Et₂O), is reduced (H₂, PtO₂, Ac₂O) to ε-phenoxy-β-phenylamylamine (hydrochloride, m.p. 127—128°),

which when treated with 48% HBr for 36 hr. and then with 10% NaOH in PhMe gives 3-phenylpiperidine, b.p. 255—256°/740 mm. (hydrochloride, m.p. 146—147°). The following benzoate hydrochlorides are prepared from γ-chloropropyl benzoate and the requisite piperidine: γ-2-, m.p. 186—187°, -3-, m.p. 180—181°, and -4-, m.p. 174—175°, -phenylpiperidinopropyl; γ-3-benzylpiperidinopropyl, m.p. 163—164°; γ-2-γ-phenylpropylpiperidinopropyl, m.p. 103—105°, and γ-2-α-phenylbutylpiperidinopropyl, m.p. 179—181°. The pharmacological properties of the esters are discussed (cf. A., 1930, 786). H. B.

Behaviour of the pyridine ring on electrochemical oxidation. IV. Piperidine. M. YOKOYAMA and K. YAMAMOTO (Bull. Chem. Soc. Japan, 1933, 8, 306—312; cf. A., 1932, 758).—Electrolytic oxidation of piperidine produces acids. By oxidation in 2N-H₂SO₄ at 22° α-aminovaleric, glutaric, succinic, and formic acids, CO₂, CO, and NH₃ are obtained; an aldehyde, probably δ-aminovaleraldehyde, is also formed. R. S. C.

Oxidation of pyridine to a 2-pyridylpyridinium salt. P. BAUMGARTEN and E. DASHMAN (Ber., 1933, 66, [B], 1633—1638).—Oxidation of C₅H₅N by K₂S₂O₈ in H₂O at 100° affords 2-pyridylpyridinium sulphate [corresponding acetate, hygroscopic hydrochloride and perchlorate; (C₁₀H₈N₂)₂PtCl₆, m.p. 213—214° (decomp.)], hydrolysed by KOH-EtOH to glutacondialdehydedianil and 2-aminopyridine. Electrochemical oxidation of C₅H₅N in H₂SO₄ appears to follow a similar course. H. W.

Reactions of dinitriles [β-amino-3-arylacrylonitriles] with aromatic hydroxyaldehydes. N. PALIT (J. Indian Chem. Soc., 1933, 10, 529—535).—β-Amino-β-phenyl- (I), -β-p-tolyl- (II), and -β-anisyl- (III), m.p. 117°, -acrylonitriles are best prepared from MeCN, ArCN, and "mol." Na in Et₂O. (II) and o-OH·C₆H₄·CHO (IV) in boiling H₂O give a compound, C₂₄H₁₈O₂N₂, m.p. 217—218° (Ac derivative, m.p. 180—181°), hydrolysed (conc. HCl at 180—185°) to a substance, C₁₄H₂₀O₂N₂, m.p. 198° (shrinking) (Me ether, m.p. 100—110°). 3:5-Dicyano-2:6-di-p-tolyl-4-o-hydroxyphenyl-1:4-dihydropyridine, m.p. 266—267°, is obtained from (II) and (IV) in AcOH at 100° (bath). Compounds, C₂₃H₁₆O₂N₂, m.p. 225—226°, and C₂₃H₁₈O₂N₂, m.p. 247—248°, are similarly obtained (in H₂O or AcOH) from (I) and (III), respectively; in AcOH-HCl, (I) gives a substance, C₂₃H₁₆O₂N₂, m.p. 291—292°. With p-OH·C₆H₄·CHO in AcOH, (I), (II), and (III) afford 3:5-dicyano-2:6-diphenyl-, m.p. 218—219°, -2:6-di-p-tolyl-, m.p. 259—260°, and -2:6-dianisyl-, m.p. 385° (softens at 379°), -4-p-hydroxyphenyl-1:4-dihydropyridine, respectively; these are oxidised (N₂O₃ in EtOH) to the corresponding pyridines, m.p. 265° (shrinks at 255°), 245—246°, and 248—250°, respectively. 3:5-Dicyano-2:6-diphenyl-, m.p. 267—268°, -2:6-di-p-tolyl- (V), m.p. 269—270°, and -2:6-dianisyl- (VI), m.p. 218—220°, -4-m-hydroxyphenyl-1:4-dihydropyridines are similarly prepared using m-OH·C₆H₄·CHO. (V) and (VI) are oxidised (N₂O₃) to the compound, m-OH·C₆H₄·CH(CO·CN)₂, m.p. 256—257°. H. B.

Isatogens and indoles. XII. Oxidative fission of indoxyl derivatives by atmospheric oxygen in

and SOCl_2 in C_6H_6 give *diethyl-γ-chloropropylamine*, b.p. $82^\circ/28$ mm., $169\text{--}171^\circ/760$ mm., the hygroscopic *hydrochloride*, m.p. $62\text{--}64^\circ$, of which with 8-amino-6-methoxyquinoline in dry EtOH at 100° gives 8-*γ*-diethylaminopropylamino-6-methoxyquinoline (I), b.p. $198\text{--}201^\circ/1\text{--}2$ mm. [meconate, m.p. $133\text{--}134^\circ$ (decomp.)]. The 6-*OEt*-analogue, b.p. $214\text{--}218^\circ/2\text{--}3$ mm., similarly prepared, and 40% HBr at 150° give 6:8-diethoxyquinoline, m.p. 230° . $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ and $\text{CHNa}(\text{CO}_2\text{Et})_2$ give $\text{Et}_2\beta$ -diethylaminomalonate, b.p. $136\text{--}142^\circ/12$ mm., which led to *Et* 8-diethylaminobutyrate, b.p. $103\text{--}105^\circ/16\text{--}17^\circ$ mm., 8-diethylaminobutyl alcohol, b.p. $90\text{--}92^\circ/7\text{--}9$ mm., and chloride, cryst., and 8-8-diethylaminobutylamino-6-methoxyquinoline (II), b.p. $200\text{--}210^\circ/3$ mm. (dihydrochloride, cryst., hygroscopic). Similarly were obtained $\text{Et}_2\gamma$ -diethylaminopropylmalonate, b.p. $149\text{--}151^\circ/4$ mm., *Et* 8-diethylaminovalerate, b.p. $130\text{--}131^\circ/25$ mm., ϵ -diethylaminoamyl alcohol, b.p. $131^\circ/23\text{--}24$ mm., and chloride (hydrochloride, m.p. $55\text{--}56^\circ$), ϵ -diethylaminoamylamino-6-methoxyquinoline (III), b.p. $216\text{--}221^\circ/2\text{--}3$ mm. [meconate, m.p. $120\text{--}122^\circ$ (decomp.)], 8- β -hydroxy- γ -diethylamino- (IV), b.p. $240\text{--}245^\circ/2$ mm., and (from γ -piperidinopropyl chloride) 8- γ -piperidino-propylamino-6-methoxyquinoline (V), b.p. $227\text{--}232^\circ/2\text{--}3$ mm. (NO-compound, cryst.). Piperidine and $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ at 100° give $\alpha\beta$ -dihydroxy- γ -piperidinopropane, b.p. $128\text{--}130^\circ/7$ mm., m.p. $67\text{--}68^\circ$. 8-Amino-6-ethoxyquinoline and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ at 50° give 8-ethylamino-6-ethoxyquinoline, b.p. $168\text{--}173^\circ/3$ mm., m.p. 53° (*p*-toluenesulphonate, m.p. 68° ; hydrochloride, m.p. $200\text{--}201^\circ$), which led to 8-*N*-ethyl-*N*-(β -diethylaminoethyl)amino-6-ethoxyquinoline (VI), b.p. $192\text{--}193^\circ/1$ mm., and (by γ -diethylaminopropylene glycol and Na in xylene at $120\text{--}150^\circ$) 8-*N*-ethyl-*N*-(β -hydroxy- γ -diethylaminopropyl)amino-6-ethoxyquinoline (VII), b.p. $207\text{--}212^\circ/1$ mm. 8-Nitro-6-hydroxyquinoline and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{NEt}_2$ in hot NaOH-EtOH give 8-nitro-6- β -diethylaminoethoxyquinoline, m.p. $47\text{--}5^\circ$, reduced by $(\text{NH}_4)_2\text{S}$ to the 8- NH_2 -compound (VIII) (hydrochloride, $+2\text{H}_2\text{O}$, m.p. $209\text{--}212^\circ$; Ac derivative, m.p. 141°); the Bz derivative, m.p. 57° (hydrochloride, m.p. $200\text{--}201^\circ$), with KOEt and EtI gives 8-*N*-benzoyl-*N*-ethylamino-6- β -diethylaminoethoxyquinoline (dihydrochloride, m.p. $182\text{--}183^\circ$). 8-*N*-Benzoyl-*N*-(β -diethylaminoethyl)amino-6- β -diethylaminoethoxyquinoline (trihydrochloride, m.p. 83°) was similarly obtained. $D_{\text{tol.}}/D_{\text{air}}$ for 8- β -diethylaminoethylamino-6-methoxyquinoline, (I), (II), (III), (IV), (VI), (VII), (V), and (VIII) against malaria in canaries is 6, 26.5, 10.6, 25, 14, 0, 0, 6, and 0, respectively. In clinical tests (I) effected 90% of cures in tertiary and quaternary, and 50% in tropical, malaria. It is less toxic than plasmoquine and less often causes complications. It acts on the gametes. R. S. C.

Attempts to find new antimalarials. VI. Preparation of β -6:7-dimethoxyquinaldyl(4)-ethylamine dihydrochloride. K. MIKI and R. ROBINSON (J.C.S., 1933, 1467—1469).— β -2-Nitro-4:5-dimethoxybenzoylpropionic acid (cf. Haq *et al.*, A., 1933, 1060) is reduced to the NH_2 -compound, which condenses with COMe, to β -6:7-dimethoxyquinaldyl(4)-propionic acid (I), m.p. 249° [hydrochloride, m.p. 216°

(decomp.)]. The acid is converted successively into the Me ester, m.p. $101\text{--}102^\circ$, hydrazide, m.p. $188\text{--}189^\circ$, azide, decomp. $94\text{--}95^\circ$, and β -6:7-dimethoxyquinaldyl(4)-ethylurethane, m.p. 154° , and -ethylamine, m.p. 249° (dihydrochloride). (I), EtOH, and NaOH give a substance, m.p. $271\text{--}272^\circ$ (decomp.). F. R. S.

Symmetrical sec.-hydrazides of pyridine- and quinoline-monocarboxylic acids. R. GRAF [with H. RUDLER] (J. pr. Chem., 1933, [ii], 138, 289—291).—sec.-Hydrazides, $(\text{NH}\cdot\text{CO}\cdot\text{R})_2$, where R is 2-, m.p. $218\text{--}219^\circ$, 3-, m.p. $227\text{--}228^\circ$, and 4-, m.p. $254\text{--}255^\circ$, -pyridyl, 2-, m.p. $239\text{--}240^\circ$, and 4-, m.p. $254\text{--}256^\circ$, -quinolyl, and 2-phenyl-4-quinolyl, m.p. $328\text{--}329^\circ$ (decomp.) (previous darkening), are prepared from the appropriate R-COCl and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in C_6H_6 . H. B.

N-Methylolamides of pyridine- and quinoline-monocarboxylic acids. R. GRAF [with H. RUDLER] (J. pr. Chem., 1933, [ii], 138, 292—298).—The following are prepared from the appropriate amide, 40% CH_2O , and aq. K_2CO_3 (or KOH): pyridine-2-, m.p. $102\text{--}104^\circ$, and -3-, m.p. $141\text{--}142^\circ$ (decomp.), 6-methylpyridine-2-, m.p. 95° (sinters from 90°), quinoline-2-, m.p. $129\text{--}131^\circ$, and 2-butoxyquinoline-4-, decomp. from 129° (loss of CH_2O) (clear melt at 140°), -carboxy-*N*-methylolamides. Treatment of 2-butoxyquinoline-4-carboxylamide, m.p. $161\text{--}162^\circ$ (from 2-chloroquinoline-4-carboxylamide and BuOH-NaOBu), with 40% CH_2O and NH_4Et in MeOH gives 2-butoxyquinoline-4-carboxydiethylaminomethylamide (I), m.p. $69\text{--}71^\circ$, which possesses anaesthetic properties but is rapidly hydrolysed by dil. acids. Hydrolysis (20% HCl) of (I) gives methylenedi-(2-butoxyquinoline-4-carboxylamide), m.p. $> 290^\circ$; $\text{NHBz}\cdot\text{CH}_2\cdot\text{NEt}_2$ is hydrolysed (10% HCl) to $\text{CH}_2(\text{NHBz})_2$ (Einhorn *et al.*, A., 1906, i, 245). 3-Cyanopyridine is a by-product in the prep. of pyridine-3-carboxylamide from the chloride and dry NH_3 in C_6H_6 . H. B.

Complex bromo-compounds of antimony.—See this vol., 43.

Acridine derivatives. (SIGNA.) L. MONTI (Gazzetta, 1933, 63, 724—730).—*N*-Hydroxymethylchloroacetamide and -benzamide with acridine and H_2SO_4 give, respectively, *N*-acridylmethylchloroacetamide and -benzamide, m.p. $172\text{--}174^\circ$ and $162\text{--}164^\circ$, either of which can be hydrolysed to acridylmethylamine [picrate, m.p. $202\text{--}204^\circ$ (decomp.)] by acid, but is decomposed by alkali. 9-Methylacridine in HCl with CH_2O and NHMe_2 or piperidine yields, respectively, β -9-acridylethylidimethylamine dihydrochloride, m.p. $185\text{--}190^\circ$ (decomp.) (corresponding picrate, decomp. $130\text{--}135^\circ$), or 9- β -piperidinoethylacridine dihydrochloride, m.p. $169\text{--}170^\circ$ (corresponding picrate, m.p. $138\text{--}140^\circ$). E. W. W.

Effect of unsaturated aliphatic groups in barbituric acids. H. A. SHONLE and J. H. WALDO (J. Amer. Chem. Soc., 1933, 55, 4649—4652).— δ -Chloro- Δ^8 -pentene, b.p. $58^\circ/155$ mm., δ -chloro- Δ^8 -hexene, b.p. $73\text{--}76^\circ/136$ mm., and γ -bromohexane, b.p. $65\text{--}67^\circ/49$ mm., are prepared from the corresponding alcohols and HHal in the cold. *Et* isoamylpropargyl-, b.p. $142^\circ/11$ mm.— $151^\circ/14$ mm., ethyl-(α -methyl- Δ^8 -butenyl)-, b.p. $135\text{--}138^\circ/15$ mm., ethyl-(α -ethylbutenyl)-, b.p. $143\text{--}144\text{--}6^\circ/15$ mm., ethyl-(α -ethyl-

butyl-, b.p. 132.8°/8.5 mm.—135°/9 mm., and *propyl*-*sec*-.*butyl*-, b.p. 112°/6 mm.—114°/5 mm., -malonates are prepared and purified by the method previously described (A., 1930, 1047). 5-*sec*-.*Butyl*-5-*propargyl*-, m.p. 167—168°, 5-*isoamyl*-5-*propargyl*-, m.p. 163—164°, 5-*ethyl*-5- α -*methyl*- Δ^{β} -*butenyl*- (I), m.p. 114.5—116°, 5-*ethyl*-5- α -*ethyl*- Δ^{β} -*butenyl*- (II), m.p. 93—94°, 5-*ethyl*-5- α -*ethylbutyl*-, m.p. 112—115°, and 5-*propyl*-5-*sec*-.*butyl*-, m.p. 136—138°, -barbituric acids are prepared by the usual method. (I) and (II) have smaller hypnotic actions than the corresponding saturated compounds; they cause convulsions even in small doses.

H. B.

Microscopic determination of barbital and dial by ammoniacal silver nitrate; crystallographic study. C. STRYZOWSKI and L. DEVERIN (Helv. Chim. Acta, 1933, 16, 1288—1291).—Detailed description is given of the microscopic characters of the crystals obtained by the interaction of diethyl- and diallyl-barbituric acid with $\text{NH}_3\text{-AgNO}_3$ under varied conditions.

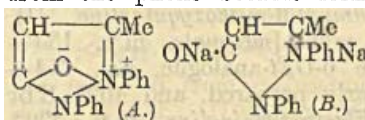
H. W.

Microchemical behaviour of antipyrine. C. VAN ZIJP (Pharm. Weekblad, 1933, 70, 1243—1248).—Antipyrine (I) with $\text{KNO}_3\text{-HNO}_3$ (dil.) gives blue-green dichroic crystals of the oximino-compound, which is converted by 50% HNO_3 at 90—100° into a reddish-violet compound, of characteristic appearance under crossed nicols. (I) sublimes at 90° and crystallises from H_2O in rectangular, hexagonal (angles 116°, 128°) and rhombic (angles 114°, 66°) plates. Salipyrine gives the HNO_3 reaction but does not crystallise like (I). Pyramidone does not give the reddish-violet colour.

S. C.

Constitution of antipyrine. Action of sodium on 1:2-diphenyl-3-methylpyrazolone. A. HEYMANS and W. ROHLAND (Ber., 1933, 66, [B], 1654—1661).—Interaction of hydrazobenzene with $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Et}$ at 130—150° and, after removal of EtOH and H_2O , at 160—180° leads to 1:2-diphenyl-3-methylpyrazole-5-one (I), m.p. 130° (picrate, m.p. 138°), identical with the "phenylhydroxymethylquinizine" of Muller and of Perger. (I) is transformed by Br in CHCl_3 into 4-bromo-1:2-diphenyl-3-methylpyrazol-5-one, m.p. 145°, and by HCl and NaNO_2 into non-cryst. 4-nitroso-1:2-diphenyl-3-methylpyrazol-5-one (II), converted by $\text{NHPH}\cdot\text{NH}_2$ in boiling EtOH into the compound $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}_5$. (II) is reduced by SnCl_2 and HCl to 4-amino-1:2-diphenyl-3-methylpyrazol-5-one, m.p. 165°. Treatment of (I) with Na and CO_2 in xylene leads to NH_2Ph and acetoacetanilide (due to hydrolysis of β -anilinocrotonanilide) and small amounts of 1:2-diphenyl-3-methylpyrazolidone-3-carboxylic acid (II), decomp. 122° (Me ester, m.p. 130°), which readily loses CO_2 with production of 1:2-diphenyl-3-methylpyrazolid-5-one (III), m.p. 126°, very resistant towards dehydrogenation. Evidence of the position of CO_2H in (II) is found in its non-formation from CO , and the Na enolate (IV) of (III). In absence of CO_2 (I) adds 2Na giving a product (V) converted by the successive action of Ac_2O and CO_2 into 4-acetyl-1:2-diphenyl-3-methylpyrazolid-5-one-3-carboxylic acid (VI), m.p. 165° (decomp.), passing by loss of CO_2 into 4-acetyl-1:2-diphenyl-3-methylpyrazolid-5-one, m.p. 135° [also obtained from (IV) and Ac_2O]. Reasons are advanced

for considering the production of (V) and consequently of (II) to occur secondarily from a common intermediate. This can be derived without difficulty only from the phenol-betaine form A of (I) and must



therefore be B. In support, it is found that if addition of the Na occurs under the mildest possible con-

ditions and the product is immediately treated with Ac_2O (VI) is accompanied by β -anilinocrotonanilide $\text{NHPH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NPhAc}$ (VI), m.p. 112°, readily hydrolysed by acid to NH_2Ph , AcOH , and $\text{CH}_3\text{Ac}\cdot\text{CO}\cdot\text{NHPH}$. Under the influence of traces of acid (VI) is isomerised to β -acetanilidocrotonanilide, $\text{NPhAc}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHPH}$, m.p. 164°, hydrogenated ($\text{Pd}\text{-MeOH}$) to β -acetanilidobutyranilide, m.p. 184°, and hydrolysed to NHPHAc , NH_2Ph , and $\text{CH}_3\text{Ac}\cdot\text{CO}\cdot\text{NHPH}$.

H. W.

Complex compounds of nitroso- and bromo-antipyrine. R. RASCANU (Ann. Sci. Univ. Jassy, 1933, 18, 72—97).—The following complex salts are described (N = nitroso-, B = bromo-antipyrine):

$[\text{UO}_2, N_4](\text{NO}_3)_2$; $2N, \text{H}_2\text{PtCl}_6, 2\text{H}_2\text{O}$; $N, \text{HAuCl}_4, 2\text{H}_2\text{O}$; $\text{CdCl}_2, 2(N, \text{HCl}), 2\text{H}_2\text{O}$; $\text{H}_2\text{SnCl}_6, 3(N, \text{HCl}), 4\text{H}_2\text{O}$; $[\text{UO}_2, B_2](\text{NO}_3)_2$; $[\text{UO}_2, B_2]\text{Cl}_2$; $[\text{UO}_2, B_2]\text{Br}_2$; N, HBr (by action of 40% aq. HBr); and antipyrine hydrobromide, m.p. 179—180° (from perbromoantipyrine and boiling COMe_2). All are decomposed by boiling H_2O , the UO_2 compounds being most stable.

H. A. P.

2-Thiol-4(5)-hydroxymethylglyoxaline. A. O. JACKSON and C. S. MARVEL (J. Biol. Chem., 1933, 103, 191—195).— $\text{o-C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ (I) and NaOAc in EtOH give ω -acetoxyacetonylphthalimide, m.p. 141—142° [and not the ω -OH-derivative as stated by Gabriel (A., 1911, i, 644)], hydrolysed (20% HCl at 85—95°) to α -amino- γ -hydroxyacetone hydrochloride, m.p. 136—137°. This and aq. KCNS afford 2-thiol-4(5)-hydroxymethylglyoxaline (II), m.p. 203—204°, converted by aq. FeCl_3 into 4(5)-hydroxymethylglyoxaline. (II) and SOCl_2 (or HCl in CHCl_3 at 20—25° or conc. HCl at 70—75° give the pentahydrochloride, decomp. 265°, of a polymeric base, $\text{C}_{20}\text{H}_{22}\text{ON}_{10}\text{S}_5$, decomp. 300°, which gives the colour reactions of a 2-thiolglyoxaline. (I) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ afford cyanoacet- ω -phthalimidoacetonylamide, m.p. 196—197°, which with Br in AcOH gives Br_1 -, m.p. 299—300° (Maquenne block), and Br_2 -, m.p. 345—346° (Maquenne block), -derivatives.

H. B.

Methylation of pyrazoles with diazomethane. K. VON AUWERS and O. UNGEMACH (Ber., 1933, 66, [B], 1690—1694).—Et 4-phenylpyrazole-5-carboxylate (I) is converted by treatment with Me_2SO_4 and NaOH and subsequently with $\text{EtOH}\text{-HCl}$ into 4-phenyl-1-methylpyrazole-5-carboxylic acid, m.p. 210—211° (decomp.) [transformed with difficulty into the Et, m.p. 52.5—53.5°, and Me (II), m.p. 69°, ester], and Et 4-phenyl-1-methylpyrazole-5-carboxylate [corresponding acid, m.p. (hydrated) about 100°, m.p. (anhyd.) 132°]. Treatment of (I) in Et_2O with CH_2N_2 leads almost exclusively to (II) accompanied by only traces of the 1:3-derivative. Me 3-phenylpyrazole-5-carboxylate and CH_3N_2 yield a product hydrolysed almost

exclusively to 3-phenyl-1-methylpyrazole-5-carboxylic acid. Similar differences in behaviour on treatment with KOH and Me_2SO_4 or MeI or with CH_2N_2 are not observed with 5(3)-chloro-3(5)-methylpyrazole.

H. W.

Piperazine derivatives as local anaesthetics. W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1933, 22, 950—953).—*N*-Carbethoxymethylpiperazine, b.p. 153—159°/9—11 mm., obtained from piperazine and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, gives with γ -chloro-*n*-propyl alcohol *N*-carbethoxymethyl-*N'*- γ -hydroxy-*n*-propylpiperazine (I), an oil. (I) is converted by SOCl_2 into the corresponding chloropropyl derivative, an oil, which, with $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$ in dry EtOH, gives the *O*-*p*-aminobenzoyl derivative of (I), an oil. *NN'*-Bis-(β -hydroxy- β -methylhexyl)piperazine (Fournneau and Samdahl, A., 1930, 1597) forms a bisphenylurethane, m.p. 180—181°. The products are either unsuitable for biological trial, or exhibit little local anaesthetic activity.

W. S.

Bis-2-pyridylaniline and *N*-2-pyridylpiperidine. J. P. WIBAUT and G. TILMAN (Rec. trav. chim., 1933, 52, 987—990).—Interaction of 2-bromopyridine (I) with NH_2Ph at the b.p. gives 2-pyridylaniline (picrate, m.p. 219°), which with (I) and Cu-bronze in $s\text{-C}_6\text{H}_5\text{Me}_2$ at the b.p. gives bis-2-pyridylaniline, m.p. 93° (corr.), which is non-basic. With $\text{C}_5\text{H}_{11}\text{N}$ at 145° (I) gives *N*-2-pyridylpiperidine, b.p. 80°/0.06 mm. (picrate, m.p. 137.5—138.5°; picrolonate, m.p. 168°).

H. A. P.

Pyrimidines. Molecular rearrangement of ethyl 2-ethylthiol-6-thiocyanopyrimidine-5-acetate. Y. F. CHU and C. M. MA (J. Amer. Chem. Soc., 1933, 55, 4655—4657).—Et 6-chloro-2-ethylthiopyrimidine-5-acetate (I), b.p. 174°/4 mm. (from the 6-OH-ester and POCl_3 at 100°), and KCNS in C_6H_6 give (impure) Et 2-ethylthiol-6-thiocyanopyrimidine-5-acetate (II), which with $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ affords Et 2-ethylthiol-6-thiopyrimidine-5-acetate, m.p. 130—131°, also prepared from (I) and NaHS. (I) and KCNS in boiling PhMe give Et 2-ethylthiol-6-thiocarbamidopyrimidine-5-acetate (III), b.p. 190—200°/4 mm., which when distilled repeatedly passes into a polymeric form, b.p. 220°/4 mm., m.p. 140—141°. (II) is isomerised slowly at the b.p. to (III). Et 2-ethylthiol-6-thiocarbamidopyrimidine-5-acetate, m.p. 135—136° (free acid, m.p. 220—221°; acid amide, m.p. 230°), Et 2-ethylthiol-6-phenylthiocarbamidopyrimidine-5-acetate, m.p. 112.5—113°, and 2-ethylthiol-6-thiourethanopyrimidine-5-acetic acid, m.p. 146—148°, are prepared from (III) and the appropriate reagents.

H. B.

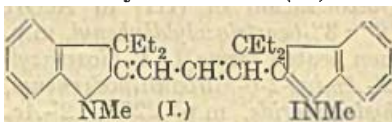
Reactive capacity of the methyl group. I. Synthesis of 6 : 6'-dibenzoylindigotin. L. CHARDONNENS (Helv. Chim. Acta, 1933, 16, 1295—1302).—3-Nitro-4-methylbenzophenone (I) condenses with PhCHO in presence of piperidine at 150—155° to 2-nitro-4-benzoylstilbene, m.p. 120—121°. (I) and $p\text{-NO}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ in boiling EtOH containing anhyd. Na_2CO_3 slowly afford 2-nitro-4-benzoylbenzaldehyde-*p*-dimethylanil (II), m.p. 174—175°; the corresponding Et₂ compound (III), m.p. 146—147°, is similarly prepared. (II) and (III) are hydrolysed by HCl- H_2O in presence of C_6H_6 to 2-nitro-4-benzoylbenzaldehyde (IV), m.p. 102.5—103° (phenylhydrazone, m.p. 206°;

2-nitro-4-benzoylbenzoic acid, m.p. 187—189°); a substance, m.p. 215°, was on one occasion obtained as by-product. (IV) condenses with COMe_2 in presence of NaOH to 6 : 6'-dibenzoylindigotin, m.p. about 355—360° (decomp.). Bz thus appears able to activate the Me.

H. W.

Alkylindoleninium iodide reds. (SIGNA.) E. GHIGI (Gazzetta, 1933, 63, 698—701).—

$\text{CHET}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}_2 + \text{ZnCl}_2$ in MeOH form 2-methyl-3 : 3-diethylindolenine (A., 1899, i, 450) (picrate, m.p. 188—189°), the methiodide of which with



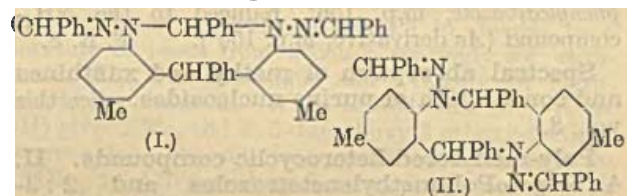
$\text{CH}(\text{OEt})_3$ gives the

indocyanine $\text{C}_{29}\text{H}_{37}\text{N}_2\text{I}$ (I), m.p. 271°. The ethiodide yields the compound " $\text{C}_{31}\text{H}_{42}\text{N}_2\text{I}$ " [$\text{C}_{31}\text{H}_{41}\text{N}_2\text{I}$?], m.p. 293—294°; similar compounds $\text{C}_{27}\text{H}_{33}\text{N}_2\text{I}$ and $\text{C}_{35}\text{H}_{33}\text{N}_2\text{I}$, m.p. 254° and 272°, are derived from 2 : 3-dimethyl-3-ethyl- and -3-phenyl-indolenines. All these indocyanines are intensely coloured.

E. W. W.

Condensation of aldehydes with hydrazones.

VIII. Eight-membered heterocyclic nuclei. A. GIACALONE (Gazzetta, 1933, 63, 764—766).—The substance (I) is prepared by diazotising and reducing 2 : 2'-diamino-5 : 5'-dimethyltriphenylmethane to the 2 : 2'-dihydrazino-compound, of which the hydrochloride, m.p. 190°, gives with PhCHO the 2 : 2'-di-



benzylidenehydrazino-compound, and with further PhCHO and H_2SO_4 the substance (I), m.p. 151—152°. This is not identical with the product from PhCHO and its *p*-tolylhydrazone (A., 1933, 402), which is probably (II). *p*-Benzylidenehydrazinobenzoic acid, m.p. 221°, does not condense further with PhCHO. E. W. W.

Hydrolysis and reduction of hydantoin-oxindoles. H. R. HENZE and C. M. BLAIR (J. Amer. Chem. Soc., 1933, 55, 4621—4625).—Hydrolysis [aq. $\text{Ba}(\text{OH})_2$ at 115—120°] of hydantoin- $\Delta^{5:3}$ -oxindole (I) gives oxindole; hydantoin- $\Delta^{5:3}$ -5'-methyl-oxindole (II), m.p. > 310° (from 5-methylisatin, hydantoin, AcOH , Ac_2O , and NaOAc at 150°), similarly affords 5-methyloxindole (III). Reduction of (I) by the method of Hill *et al.* (A., 1930, 480) gives hydantoin-5 : 3'-oxindole, m.p. 281—282° (corr.; decomp.) (lit. 276°), hydrolysed (as above) to 2-keto-1 : 2-dihydroquinoline-4-carboxylic acid and not the 2 : 3-dihydroxy-3 : 4-dihydro-derivative (cf. Kotake, A., 1927, 1199). 1-Acetylhydantoin- $\Delta^{5:3}$ -1'-acetyl-oxindole has m.p. 258° (corr.; decomp.) (sinters at 240—245°) (cf. *loc. cit.*). Reduction [HI (*d* 1.7), AcOH] of (II) gives hydantoin-5 : 3'-5'-methyloxindole, m.p. 306—307° (corr.; decomp.), hydrolysed (as above) to (III); reduction with red P, HI (*d* 1.7), and AcOH at 150° affords 2-keto-6-methyl-1 : 2 : 3 : 4-tetrahydroquinoline-4-carboxylic acid, m.p. 219—220°

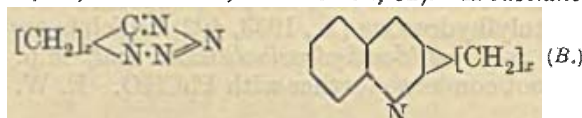
(corr.). 2-Keto-6-methyl-1:2:3:4-tetrahydroquinoline has m.p. 114—115° (corr.) (lit. 106°). H. B.

Dicarbazyls. IV. Synthesis of 1:1'-dicarbazyl. T. F. MACRAE and S. H. TUCKER. V. Synthesis of 3:9'-dicarbazyl. (MISS) M. C. NELMES and S. H. TUCKER (J.C.S., 1933, 1520—1523, 1523—1525).—IV. 2:2'-Diaminodiphenyl (I), $\text{o-C}_6\text{H}_4\text{Cl-NO}_2$ (II), and BaCO_3 give 2:2'-di-o-nitroanilinodiphenyl, m.p. 188.5—189.5° (NN'-Ac₂ derivative, m.p. 246—249°), reduced to the NH_2 -compound (III), m.p. 225—227°. Diazotisation of (III) in AcOH affords 2:2'-di-1'':2'':3'':3'-benztriazolyldiphenyl, m.p. 194—196°, which when heated forms 1:1'-dicarbazyl, m.p. 205—207°. 2'-Amino-2-o-nitroanilinodiphenyl, m.p. 113—114.5° (hydrochloride, m.p. 222°; 2'-Ac₂ compound, m.p. 192—194°), is obtained by heating (I) with (II) and K_2CO_3 at 205—208° for 35 hr. 1:1'-Dicarbazyl is not identical with any of the products of oxidation of carbazole.

V. 9-p-Aminophenylcarbazole, obtained from the NO_2 -derivative (improved prep.), with (II) and Na_2CO_3 gives 9-p-(o-nitroanilino)phenylcarbazole, m.p. 181—185° (Ac derivative, m.p. 205—207°), reduced to the NH_2 -compound (IV), m.p. 115—116° (picrate, m.p. 137°; o-Ac derivative, m.p. 180—181°). (IV) on diazotisation affords 9-p-1'':2'':3'':3'-benztriazolyldiphenylcarbazole, m.p. 163°, converted into 3:9'-dicarbazyl, m.p. 212—214° (9-Ac derivative, m.p. 197°). Carbazole, (II), and K_2CO_3 form 9-o-nitrophenylcarbazole, m.p. 156°, reduced to the NH_2 -compound (Ac derivative, m.p. 150°). F. R. S.

Spectral absorption of methylated xanthenes and constitution of purine nucleosides.—See this vol., 8.

Poly-membered heterocyclic compounds. II. 4:5-cycloPolymethylenetetrazoles and 2:3-cyclopolymethylenequinolines. L. RŮŽICKÁ, M. W. GOLDBERG, and M. HURBIN (Helv. Chim. Acta 1933, 16, 1335—1339; cf. this vol., 82).—A substance



$\text{C}_8\text{H}_{11}\text{N}_5$, m.p. 90—91°, is derived from cyclohexanone, H_2SO_4 , and N_3H . Treatment of cycloheptanone with N_3H and H_2SO_4 in C_6H_6 yields 4:5-cyclohexamethylenetetrazole (A; $x=6$), m.p. 66—68°. 4:5-cycloheptamethylenetetrazole (A; $x=7$), b.p. 145—146°/0.1 mm., and 4:5-cyclotetradecamethylenetetrazole (A; $x=14$), m.p. 97—98°, are similarly obtained. cycloOctanone is converted by $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in EtOH containing a little NaOH into 2:3-cyclohexamethylenequinoline (B; $x=6$), b.p. 130—135°/0.1 mm. (hydrochloride, m.p. 200—202°; picrate, m.p. 212°). Similarly, cyclopentadecanone affords 2:3-cyclotridecamethylenequinoline (B; $x=13$), b.p. 197°/0.1 mm. (picrate, m.p. 169—171°; hydrochloride; sulphate; phosphate). The physiological action of the compounds is described.

H. W.

Chlorophyll-like bacterial pigment.—See this vol., 112.

Dioximes. C. G. PONZIO. CI. M. MILONE. CII. E. DURIO (Gazzetta, 1933, 63, 730—743, 744—

746, 747—751).—C. Mol. wt. determinations show that the Ac derivative (A., 1923, i, 1020) of α -phenylglyoxime peroxide is bimol.; it is renamed as the Ac₂ derivative of dibenzoylfuroxandioxime [3:4-diacetoximinodibenzyl-1:2:5-oxadiazole 2-oxide] (I), new m.p. 117—118°. When heated at 125—130°, (I) is converted into an isomeride (II), m.p. 130°; (I) or (II) in 20% NaOH with EtOH is hydrolysed in the cold to dibenzoylfuroxandioxime (III), m.p. 110° (decomp.), which is converted by HNO_3 (d 1.40) into a compound $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3$, m.p. 122°. At 100° (II), or (I) or (II) with EtOH, is isomerised by 5% NaOH to 3-benzoylformyl-4-phenyl-1:2:5-oxadiazole- α -dioxime (IV) (A., 1933, 726). (IV) can also be obtained from the compound described (A., 1931, 1157) as the dimeride of the Bz derivative of oximino-phenylacetone nitrile oxide, and now renamed as the Bz₂ derivative of dibenzoylfuroxandioxime [3:4-dibenzoximinodibenzoyl-1:2:5-oxadiazole 2-oxide]. Similarly the substance described (A., 1924, i, 294) as the Ac derivative of the oxide of *p*-toluoyl cyanide oxime is renamed as the Ac₂ derivative of di-*p*-toluoylfuroxandioxime; it is converted by 5% NaOH+EtOH into 3-*p*-toluoylformyl-4-*p*-tolyl-1:2:5-oxadiazole- α -dioxime (V) (A., 1933, 726). The corresponding Bz derivative (A., 1931, 1157) is renamed as a Bz₂ derivative; it also yields (V). The Ac₂ derivatives of diaroyloxadiazole dioximes with $\text{NHPh}\cdot\text{NH}_2$ give osazones, not of the diaroyloxadiazoles, but isomeric, and hence probably of the aroylformylaryloxadiazoles, $\text{NHPh}\cdot\text{N}\cdot\text{C}\cdot\text{Ar}\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{C}_2\text{N}_2\text{O}\cdot\text{Ar}$. Benzoylformylphenyloxadiazoleosazone, m.p. 177—178°, like dibenzoyloxadiazoleosazone (new m.p. 175—176°), resists acid or alkaline hydrolysis. *p*-Toluoylformyl-*p*-tolylloxadiazoleosazone has m.p. 179°.

CI. The action of ultra-violet light on the α -phenyl-, *p*-tolyl-, and -phenylmethyl-glyoximes, and on the α - and γ -diphenylglyoximes (benzildioximes of m.p. 211° and 163°), causes isomerisation into the β forms (determined by their complex Ni salts), which are therefore considered the more stable. The change is more rapid in EtOH solution than in the solid.

CII. Glyoxime, and its Me, Me₂, Me Et, and α - and β -Ph, *p*-C₆H₄·Me, and Ph Me derivatives, all fail to react with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, as do the oximino-derivatives of COPhEt and COMe·CH₂Ph. β -Chloroglyoxime, and chloro-oximino-acetone, -acetophenone, and -*p*-methylacetophenone (best prepared by action of Cl_2 on oximino-*p*-methylacetophenone in AcOH) react to form 3-o-phenylenediaminoquinoline, m.p. 160—170°, and its 2-methyl, m.p. 242° (decomp.) (hydrolysable to 3-hydroxy-2-methylquinoxaline), 2-phenyl, decomp. 217—218° [Ac derivative, m.p. 155—156° (decomp.)], and 2-*p*-tolyl, m.p. 217° (decomp.), derivatives; the last are also obtainable from the corresponding substituted chloroglyoximes.

E. W. W.

Directive effect of [nuclear] substituents on cyclisation of *s*-diarylthiocarbamides. II. Effect of the fluorine atom on thiazole cyclisation of *p*-fluoro-*s*-diphenylthiocarbamides by bromine. III. Effect of the carbethoxy-group on formation of anilino benzthiazoles from *p*-carbethoxy-*s*-diphenylthiocarbamides and bromine. M. O. FAROOQ and R. F. HUNTER (J. Indian Chem.

Soc., 1933, 10, 465—470, 563—571; cf. A., 1933, 168).—II. p -C₆H₄F·NCS and the appropriate ArNH₂ give 4-fluoro-4'-methyl-, m.p. 169°, 4-chloro-4'-fluoro-, m.p. 158—159°, 4-bromo-4'-fluoro-, m.p. 164—165°, and 4-fluoro-4'-nitro-, m.p. 170—171°, -s-diphenylthiocarbamides, which are converted by Br in CHCl₃ into 4'-fluoro-5-methyl-, m.p. 183°, 5-chloro-4'-fluoro-, m.p. 222—223°, 5-bromo-4'-fluoro-, m.p. 222—223°, and 5-fluoro-4'-nitro-, m.p. 252—253°, -1-anilinobenzthiazole (intermediate hydroperbromides described), respectively. F thus resembles the other halogens (A., 1929, 582; 1930, 1452). 4'-Fluoro-5-nitro-1-anilinobenzthiazole has m.p. 278—279°. 1-Chloro-5-fluorobenzthiazole, m.p. 97—98°, is prepared from 5-fluoro-1-aminobenzthiazole.

III. p -Carbethoxy-s-diphenylthiocarbamide (I), m.p. 129—130° (from p -CO₂Et·C₆H₄·NCS and NH₂Ph), and Br in CHCl₃ give Et 1-anilinobenzthiazole-4'-carboxylate, m.p. 182—183° (hydroperbromide). 4-Bromo-4'-carbethoxy-, m.p. 158—159°, 4-carbethoxy-4'-methyl-, m.p. 160—161°, 4-chloro-4'-carbethoxy-, m.p. 159—160°, and 4-nitro-4'-carbethoxy-, m.p. 154—155°, -s-diphenylthiocarbamides similarly afford Et 5-bromo-, m.p. 227—228° [also obtained from (I) and an excess of Br], 5-methyl-, m.p. 206—207°, and 5-chloro-, m.p. 226°, -1-anilinobenzthiazole-4'-carboxylate and Et 4'-nitro-1-anilinobenzthiazole-5-carboxylate, m.p. 241—243°, respectively. Et 5-nitro-1-anilinobenzthiazole-4'-carboxylate, m.p. 242—243°, and analogous compounds are synthesised from the 5-substituted-1-chlorobenzthiazoles and the appropriate p -C₆H₄R·NH₂. The esters isolated (by cyclisation) are often impure. 1-Chloro-5-bromo-, m.p. 101—102° (lit. 89°), and 1:5-dichloro-, m.p. 101°, -benzthiazole are prepared from the 5-halogeno-1-aminobenzthiazoles. 1-Chlorobenzthiazole and cold HNO₃ (d 1.5) give the 5-NO₂-derivative.

H. B.

Thiazoles. XIX. Synthesis of "2-(m -nitrophenyl)benzothiazolyl pp' -disulphide" [2:2'-dinitro-4:4'-bisbenzthiazolyldiphenyl disulphide]. M. T. BOGERT and R. B. CONKLIN (Coll. Czech. Chem. Comm., 1933, 5, 443—447).—Interaction of 4-chloro-3-nitrobenzoyl chloride with (σ -NH₂·C₆H₄·S)₂Zn gives 2-(4'-chloro-3'-nitrophenyl)benzthiazole, m.p. 165.5—166.5° (corr.), which with Na₂S and S in boiling EtOH gives 2:2'-dinitro-4:4'-bisbenzthiazolyldiphenyl disulphide, m.p. 292—293° (corr.).

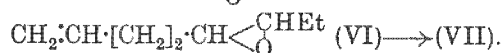
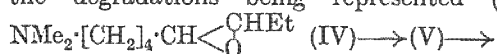
H. A. P.

Volatile alkaloid in *Helvella esculenta*. D. AYE (Arch. Pharm., 1933, 271, 537—539).—Fresh, but not dried, *H. esculenta* contain a small amount of a volatile, liquid alkaloid, C₈H₁₂(or 14)N₂ (impure picrate, m.p. 145—150°).

R. S. C.

Constitution of conhydrine. E. SPATH and E. ADLER (Monatsh., 1933, 63, 127—140).—Dehydration of conhydrine (I) (P₂O₅ in PhMe at 120—140°) and reduction of the mixed coniceines (H₂-Pd in 20% AcOH) gives dihydroconiceine (II), the 2:4-dinitrobenzoyl derivative, m.p. 138—138.5°, of which racemises the corresponding derivative of (+)-coniine, thus confirming Loeffler's conclusion (A., 1909, i, 180) that (II) is identical with (—)-coniine. Hofmann degradation of the base from *N*-methylconhydrine methiodide (III), m.p. 221—223°, affords conhydrine-

methine (IV), b.p. 91°/10 mm., [α]_D²⁰ +30.36° (picrate, m.p. 109—110° in vac.) (no double linking, CO, or OH group), which by long keeping with H₂O and subsequent addition of NaI re-forms (III). With MeI in COMe₂ (IV) gives a methiodide (V), m.p. 134—135°, [α]_D²⁰ +16.6° in H₂O, Hofmann degradation of which gives a compound (VI), b.p. 157—159°/744 mm., [α]_D²⁰ +28.7° [converted by H₂O at 170—180° into (VII)], and $\epsilon\epsilon$ -dihydroxy- Δ^2 -*n*-octene (VII), m.p. 75—76°, reduced by H₂-Pd in H₂O to $\gamma\delta$ -dihydroxy-*n*-octane (VIII), m.p. 94—96°. Low-temp. oxidation of (VII) with H₂SO₄-KMnO₄ gives EtCHO (as its dimedon compound) and (·CH₂·CO₂H)₂, whereas (VIII) similarly treated affords *n*-valeric acid. These results confirm that (I) is 2- α -hydroxypropylpiperidine, the degradations being represented (III)→



J. W. B.

Cactus alkaloids. X. Constitution of pello-tine and anhalonidine. E. SPATH and F. BOSCHAN (Monatsh., 1933, 63, 141—153).—The methiodide of pello-tine (I) is converted by CH₂PhCl and NaOH in EtOH into its O-CH₂Ph ether, m.p. 193—195°, and with EtI similarly into O-ethylpello-tine methiodide, m.p. 185—186°, converted by AgCl into the methochloride, which when heated with 4% Na-Hg in H₂O gives a basic oil, reduced (H₂-Pd in AcOH) to a mixture of bases from which a sparingly sol. methiodide (II), m.p. 238—239°, and a readily sol. methiodide are obtained. When heated with 25% KOH (II) gives NMe₃ and 4:5-dimethoxy-3-ethoxy-2-ethylstyrene (not characterised), oxidised by KMnO₄ in COMe₂ to 4:5-dimethoxy-3-ethoxy-2-ethylbenzoic acid, m.p. 102—103°, which with HNO₃ at -14° affords 5:6-dinitro-3:4-dimethoxy-2-ethoxyethylbenzene (III), reduced by Zn-HCl to the corresponding 5:6-diamine (IV), m.p. 80.5—81° (Bz₂ derivative, m.p. 229—230°), the structure of which is proved by the following synthesis. 2-Hydroxy-3:4-dimethoxyacetophenone (V) (A., 1903, i, 272) is reduced (Clemmensen) to 2-hydroxy-3:4-dimethoxyethylbenzene, b.p. 124°/10 mm., the 2-Et ether, b.p. 122—123°/10 mm., of which is nitrated to (III), reduced to a diamine identical with (IV). The structure of (V) is proved by condensation with PhCHO, oxidation to 2-hydroxy-3:4-dimethoxybenzoic acid (A., 1904, i, 808), the 2-Et ether of which is identical with the acid obtained by ethylation and subsequent oxidation of 2-hydroxy-3:4-dimethoxybenzaldehyde (A., 1931, 1411). The revised structure of (I) (A., 1933, 77) and therefore of anhalonidine is thus confirmed.

J. W. B.

Hedyotine, an alkaloid from the root of *Hedyotis auricularia*. B. B. DEY and S. LAKSHMINARAYANAN (Arch. Pharm., 1933, 271, 485—490).—The roots of *H. auricularia*, Linn., yield to MeOH 0.12—0.28% of hedyotine, C₁₆H₂₂O₆N₂, unstable, not isolated pure (OMe absent) [hydrochloride, m.p. 245° (sinters at 227°; decomp. 250°); nitrate, m.p. 252° (decomp.) after sintering at 238°; picrate, m.p. 265° (decomp.); aurichloride, m.p. 305—310° (decomp.); platini-chloride: tetrachloroiodide, m.p. 167—170° (decomp.)];

(?) *perbromide*, m.p. from 240°; *dichromate*; compounds with metallic salts, amorphous]. R. S. C.

Reactions between amino-acids and nicotine. I. S. JAITSCHEV (Biochem. Z., 1933, 265, 426—428).—Monoamino-diacids (aspartic and glutamic) and hippuric acid react with nicotine, but the monoamino-mono-acids (glycine, leucine) and asparagine do not. P. W. C.

Toddalia aculeata (Pers.). I. Two alkaloids and a neutral, crystalline substance from its root-walls. B. B. DEY and P. P. PILLAY (Arch. Pharm., 1933, 271, 477—485).—The root-walls of *T. aculeata* contain, besides known constituents, a lactone, $C_{16}H_{20}O_6$, m.p. 132—135° (*Ac.* derivative, m.p. 111—112°; gives with very dil. NaOH an acid, m.p. 177—178°), a weak *tert.* base, *toddaline*, $C_{17}H_{12}O_2(OMe)_2(NMe)$, m.p. 269—270° [*hydrochloride*, $+H_2O$, m.p. 205—206°; *platinichloride*, m.p. 254—256°; *aurichloride*, m.p. 201—202°; *nitrate*, m.p. 239° (decomp.) after sintering at 235°; *picrate*, m.p. 237—238°; *sulphate*, m.p. 236—239° (decomp. from 210°)], and a strong base, *toddalinine*, $C_{17}H_9O_3(OMe)(NMe)$, $+0.5H_2O$, m.p. 180—200° (decomp.) [*hydrochloride*, $+2H_2O$, m.p. 283—285°; *platinichloride*, m.p. 231—232° (decomp.); *picrate*, decomp. 230—235°]. Colour reactions differentiate the bases from berberine, which is not present in the root (cf. J.C.S., 1895, 67, 413). R. S. C.

Compounds from sparteine and cyclic substituted barbituric acids. F. MERCIER and L. J. MERCIER (Compt. rend., 1933, 197, 941—943).—The prep. and properties of the neutral (1:2) salts *sparteine* 5-phenyl-5-ethylbarbiturate (I), m.p. 148—150°, and 5-phenyl-5-methylbarbiturate (II), m.p. 154—156°, are described. No definite basic salts were obtained. (I) is more stable than (II). A. C.

Lupin alkaloids. VIII. Synthesis of β -lupinane. K. WINTERFELD and F. W. HOLSCHNEIDER (Ber., 1933, 66, [B], 1751—1756; cf. A., 1933, 78).—The Grignard compound from Et γ -bromopropyl ether transforms 2-acetylpyridine (I) into 2-pyridylmethyl- γ -ethoxypropylcarbinol, b.p. 142—144°/11 mm., the *hydrochloride* of which is hydrogenated (PtO₂-Pt-black-abs. EtOH) to 2-piperidylmethyl- γ -ethoxypropylcarbinol (II), b.p. 152—153°/12 mm. (II) is transformed by boiling HI into β -lupinane (*picrate*, m.p. 163°; *aurichloride*, m.p. 143—144°); further amounts of the base are obtained by treatment of the residues with NaOEt. The intermediate production of 2-8-iodo- α -methylbutylpiperidine is assumed. Analogous attempts to obtain 2-pyridylmethyl- γ -phenoxypropylcarbinol from (I) gave α , α -diphenoxyhexane, m.p. 83°, and unchanged (I). Treatment of (II) with PBr₃ leads to a lupinane-like base. H. W.

Derivatives of 1-methyltropene. B. K. BLOUNT and R. ROBINSON (J.C.S., 1933, 1511—1512).—Lävulaldehyde (improved prep.), $CO(CH_2CO_2)_2Ca$, and NH_2Me yield 1-methyltropinone, b.p. 124°/27 mm. [*picrate*, m.p. 201° (decomp.); *methiodide*, m.p. 273—282° (decomp.)], reduced (Na-BuOH) to 1-methyl- ψ -tropine, m.p. 71° [*picrate*, explodes 280°; *hydrobromide*, m.p. 286°], which with Bz_2O gives benzoyl-1-methyl- ψ -

tropine (methyltropacocaine), b.p. 210°/15 mm. (*picrate*, m.p. 163—164°). F. R. S.

Green coloration of solutions of quinine salts. M. BACHSTETZ and G. CAVALLINI (Annali Chim. Appl., 1933, 23, 490—494).—The green coloration appearing in solutions of quinine salts (with or without urethane) on sterilisation or ageing is dependent on the presence of Cu and on an oxidising reaction catalysed by Cu. The compound $(C_{20}H_{24}O_2N_2.HCl.2H_2O)_3.CuCl_2$ is described. The coloration may be avoided by crystallising the salt repeatedly and excluding O₂ from the bottle containing the solution (cf. Erben, A., 1925, i, 573). T. H. P.

Strychnos alkaloids. LXXVII. Benzylidene and C-benzyl derivatives of brucine and strychnine and their sulphonic acids. H. LEUCHS and H. S. OVERBERG (Ber., 1933, 66, [B], 1711—1718; cf. A., 1933, 1061).—C-Benzylstrychninesulphonic acid I, $[\alpha]_D^{25}$ —159° in 0.1N-NaOH, is obtained by reduction of the C-CHPh derivative by Na-Hg and H₂O. Strychninesulphonic acid II, PhCHO, and NaOH afford C-benzylidene-, $[\alpha]_D^{25}$ —441° in 0.1N-NaOH, whence C-benzyl-, $[\alpha]_D^{25}$ —123.3° in 0.1N-NaOH, -strychninesulphonic acid II. C-Benzylidene- and C-benzyl-, m.p. 205° (decomp.), -strychninesulphonic acid III are analogously prepared. Benzylidene-strychnine is reduced to C-benzylstrychnine (I), m.p. (from EtOH) about 65°, decomp. about 90°, m.p. (from MeOH) 102—105° (decomp.), $[\alpha]_D^{25}$ —76°/d in EtOH (*methiodide*, decomp. about 305°). Oxidation of (I) with $KMnO_4$ in COMe, affords C-benzylstrychninonic acid, m.p. 208—210° (decomp.) after softening at 200°, $[\alpha]_D^{25}$ —19.0° in 0.1N-NaOH, and C-benzylstrychninolic acid, m.p. 220—223°, readily converted into benzylstrychninolone. C-Benzylidihydrostrychnine, m.p. 187—189° (vac.), $[\alpha]_D^{25}$ —13.4°/d in abs. EtOH [*methiodide*, m.p. about 310° (decomp.)], is prepared by reduction (Na-Hg in EtOH) of the corresponding CHPh derivative. Oxidation of benzylidenebrucine (II) (CrO_3 , O=18) leads to the compound $C_{23}H_{24}O_4N_2$ (*perchlorate*, $[\alpha]_D^{25}$ —229°/d in H₂O). Reduction of (II) by Na-Hg in EtOH leads to C-benzylbrucine [*methiodide*, m.p. 255—258° (decomp.)], which is not advantageously oxidised by CrO_3 , whereas hydrogenation (PtO₂) leads to non-cryst. C-benzylidihydrobrucine (non-cryst. *methiodide*). Brucinesulphonic acid I, NaOH, and PhCHO in H₂O-EtOH afford benzylidenebrucinesulphonic acid I, $[\alpha]_D^{25}$ —232° in 0.1N-NaOH, reduced to benzylbrucinesulphonic acid I, $[\alpha]_D^{25}$ —146.3° in 0.1N-NaOH, which yields only BzOH as cryst. product of oxidation by CrO_3 and oxidised by CrO_3 in AcOH-H₂SO₄ to the compound $C_{23}H_{24}O_4N_2S$, plates or prisms, which does not react with $NH_2.CO.NH.NH_2$ or BaO₂. The CHPh derivative of the Hanssen C₁₆-sulphonic acid has $[\alpha]_D^{25}$ —104° in 0.1N-NaOH.

[With DORNOV.] C-Benzylidenebrucinesulphonic acid II, $[\alpha]_D^{25}$ —386.5° in 0.1N-NaOH, is reduced (Na-Hg) to C-benzylbrucinesulphonic acid II, $[\alpha]_D^{25}$ —112° in 0.1N-NaOH. H. W.

Metathebainone. L. F. SMALL and E. MEITZNER (J. Amer. Chem. Soc., 1933, 55, 4602—4610).—Metathebainone (I) is reduced [H_2 , PtO₂, 0.2N-HCl

(sufficient for neutralisation)] to *metathebainol* (II), (+CHCl₃), m.p. 87—88°, (+MeOH), m.p. 92—93°, [α]_D —66.7° in EtOH (using solvent-free base) [*hydrochloride* (+EtOAc), m.p. 162° (decomp.), re-solidifying with decomp. > 220°; *hydriodide* (+H₂O); *methiodide*, m.p. 225°; *Ac* derivative, m.p. 150° (becoming red; turns pink at about 143°); *Ac*₂ derivative, m.p. 140°, hydrolysed (aq. EtOH—KOH) to a new base, m.p. 150°], which could not be reduced (Na; Na—Hg; catalytic). Reduction of (I) by Kondo and Ochiai's method (A., 1929, 1088) gives 65% of (II) and 5% of dihydrometathebainone (III); reduction does not occur in EtOH or dil. AcOH using Pt or Pd. (III) is reduced (H₂, PtO₂, EtOH) to *dihydrometathebainol*, m.p. about 120° (*hydriodide* +2H₂O, [α]_D +16.4° in H₂O). Reduction (Wolff-Kishner) of (I) gives *dihydrodeoxymetatcodeine*, b.p. 130—135°/0.001 mm., [α]_D —93.8° in EtOH; (III) similarly affords *tetrahydrodeoxymetatcodeine* (*hydriodide*, [α]_D —12.5° in H₂O). (II) and EtOH—KOH at 160° give *anhydrometathebainol*, C₁₈H₂₁O₂N, b.p. 130°/0.001 mm., [α]_D —201° in EtOH [(+MeOH), m.p. 107°; *Ac* derivative, m.p. 166°], reduced (H₂, PtO₂, EtOH) to *dihydroanhydrometathebainol*, b.p. 130°/0.001 mm. The so-called β -dihydrothebainone of Kondo and Ochiai (*loc. cit.*) is a mixture of (II) and (III). The existence of a diastereoisomer of (III) has not yet been demonstrated.

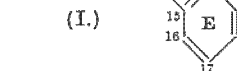
H. B.

Synthesis of physostigmine (eserine). VIII. F. E. KING, R. ROBINSON, and H. SUGINOME. **IX.** Improvement of the synthesis of *dl-eserethole*. F. E. KING, M. LIGUORI, and R. ROBINSON (J.C.S., 1933, 1472—1475, 1475—1477).—VIII. The product, m.p. 170°, obtained by decarboxylation (cf. A., 1932, 287) is 3-keto-4-o-carboxybenzoyl-10-ethoxy-7-methyl-3:4:5:6-tetrahydro-4- ψ -carboline. *l*-Eserethole forms a *H* d-tartrate, m.p. 164—165°, a *H* d-racemate, m.p. 159°, and a *H* l-tartrate, m.p. 172—173°. *dl*-Noreserethole and Me *p*-toluenesulphonate give *dl-eserethole H* l-tartrate, (+H₂O), m.p. 125—140°, and the *methopicate*, m.p. 184—186°. 1-Eserethole *methopicate* has m.p. 190° (decomp.), and *dl-eserethole picrate*, 138—140°. $\alpha\gamma$ -Dibromobutane and PhOH give a phenoxybromide which condenses with Et methylmalonate to Et ϵ -phenoxy- γ -methylpentane- $\beta\beta$ -dicarboxylate, b.p. 211—212°/17 mm. The general correctness of the conclusions of Part II (*loc. cit.*) has been confirmed.

IX. γ -Phenoxy- α -methylbutaldehyde (improved yield; 2:4-dinitrophenylhydrazones, m.p. 109—110°) and *p*-methoxyphenylhydrazine give 5-methoxy-3-methyl-3- β -phenoxyethylindolenine, purified through the *picrate*, m.p. 157° (*methiodide*, m.p. 180—181°). The methochloride could not be heated with aq. HBr without suffering deep-seated change. γ -Phthalimido- α -methylbutyric acid forms successively the *amide*, m.p. 162—163°, the *nitrile*, m.p. 102°, and the *aldehyde* (2:4-dinitrophenylhydrazones, m.p. 191°), which with *p*-ethoxyphenylhydrazine gives 5-ethoxy-3-methyl-3-(β -phthalimidoethyl)indolenine, identical with the substance described in Part II. F. R. S.

Yohimbine. G. BARGER and C. SCHOLZ (Helv. Chim. Acta, 1933, 16, 1343—1354; cf. A., 1933,

840).—Distillation of yohimbine (I) with Se dust yields yobirine (II), which is C₁₉H₁₆N₂ instead of C₁₉H₁₈N₂ advocated by Mendlik *et al.* (A., 1931, 369); their "dihydroyobirine" is consequently *tetrahydroyobirine* (III). The nucleus E, obtained as *o*-C₆H₄(CO₂H)₂ by oxidation of (II), is tetra- and



hexa-hydrogenated in (III) and (I), respectively. The rings A, B, and C are identified in harman (*loc. cit.*) and D is identified by the oxidation of (III) with HNO₃ to berberonic [pyridine-1:4:5-tricarboxylic] acid. The structure explains the production of isoquinoline by distillation of (I) with Zn dust, rupture of ring C taking place. In general, ring D suffers preferential fission, thus explaining the production of 2:3-dimethylbenzoic acid by fusion of keto-yobirine (IV) with KOH (Mendlik *et al.*, *loc. cit.*); moderation of the action by use of KOH in amyl alcohol leads to the identification of norharman as second product of fission and thus renders account of all the atoms of (IV). Degradation can occur so that C-14 remains attached to ring C since *m*-toluic acid results from treatment of (I) or yohimboic acid with superheated steam or molten KOH. The possibility that the same C—N scaffolding is not present in (I) and (II) is discussed. For the primary product (III) conditions appear more favourable; its isolation from (V) by means of molten KOH or steam at 300° is described and it possibly results by distillation of (V) with CaO at 4 mm. pressure. The presence of NMe in (I) could not be detected. Oxidation of (I) gives only (CH₂·CO₂H)₂. H. W.

Arsinic acids of the fluorenone and the fluor-enol series. G. T. MORGAN and (Miss) J. STEWART (J.C.S., 1933, 1454—1457).—Na aminofluorenone-2-arsinate and the appropriate carbamide yield *fluorenone-7-glycine-ureide* (Na salt), *-methylureide* [Na salt (+H₂O)], and *-phenylureide-2-arsinic acid* (Na salt; Na₂ salt). Na 7-carbamylmethoxyfluorenone-2-arsinate, from 7-hydroxyfluorenone-2-arsinic acid, has increased trypanocidal activity. 9-Fluorenone-2-arsinic acid (Na salt) is obtained from 2-amino-9-fluorenone. Na 7-aminofluorenone-2-arsinate (I) (acid), by reduction of the fluorenone, with Ac₂O gives 7-acetamido-9-fluorenone-2-arsinic acid (Na salt) and subsequently the 9-acetoxyfluorenone compound. (I), NH₂·CO·CH₂Cl, and NaI form a mixture of 9-fluorenone-7-glycineamide-2-arsinic acid (Na salt) and 9-O-carbamylmethylfluorenone-7-glycineamide-2-arsinic acid (Na₂ salt). (I) with KCNO in AcOH gives 7-carbamido-9-fluorenone-2-arsinic acid [Na salt (+2H₂O)], with MeNCO forms the 7-Me derivative [Na₂ salt (+0.5H₂O)], and with PhNCO yields the 7-Ph derivative [Na₂ salt (+3H₂O)]. F. R. S.

Preparation of derivatives of germanium tri-phenyl by means of sodium triphenylgermanide. C. A. KRAUS and C. S. SHERMAN (J. Amer. Chem. Soc., 1933, 55, 4694—4697).—GePh₃Prⁿ, m.p. 86—86.5°, GePh₃Buⁿ, m.p. 84.5—85.5°, GePh₃n-amyl, m.p. 42—43°, and GePh₃benzyl, m.p. 82.5—83.5°, are prepared from NaGePh₃ and the requisite halide in liquid NH₃.

NaGePh_3 and GeEt_3Br in C_6H_6 give *triphenyltriethyl-digermane*, $\text{GePh}_3\cdot\text{GeEt}_3$, m.p. 89.5—90.5°. H. B.

Action of molybdenum pentachloride on organomagnesium compounds. I. GASOPOULOS (Praktika, 1932, 7, 180—183; Chem. Zentr., 1933, ii, 534; cf. Bennett and Turner, A., 1921, i, 472).—The reaction, $6\text{MgRCl} + 2\text{MoCl}_5 = 2\text{MoCl}_2 + 3\text{R}\cdot\text{R} + 6\text{MgCl}_2$, is energetic; the MoCl_5 must be added in small portions to an Et_2O solution of excess of the Mg compound. Ph_2 , $(\text{CH}_2\text{Ph})_2$, 4:4'-ditolyl, $(\cdot\text{CH}_2\text{Pr}^i)_2$, and $[\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^i]_2$ have been prepared. A. A. E.

New complex organomagnesium compound: β -magnesyphenylacetoneitrile. D. IVANOFF and I. PAOUNOFF (Compt. rend., 1933, 197, 923—925).— $\text{CH}_2\text{Ph}\cdot\text{CN}$ and RMgX ($\text{R}=\text{Ph}$, Et , and Pr^i) yield RH and the Mg derivative $\text{CN}\cdot\text{CHPh}\cdot\text{MgX}$ (I), converted by CO_2 into $\text{CN}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ (II). The best yield (40%) of (II) is obtained when $\text{R}=\text{Pr}^i$. (I) reacts with COPh_2 yielding, in addition to polymerides, β -hydroxy- $\alpha\beta$ -triphenylpropionitrile, m.p. 140—141°, and $\alpha\beta$ -triphenylacrylonitrile. A. C.

Labilities or electronegativities of unsaturated alkyl radicals as determined by hydrogen chloride scission of organo-lead compounds. H. GILMAN, E. B. TOWNE, and H. L. JONES (J. Amer. Chem. Soc., 1933, 55, 4689—4693).—Mg Δ^r -butenyl bromide and PbPh_3Cl give $\text{Pb Ph}_3 \Delta^r$ -butenyl, m.p. 84—86°, which with HCl in CHCl_3 at 40—45° affords $\text{Pb Ph}_3 \Delta^r$ -butenyl chloride, m.p. 134—135° (decomp.), and C_6H_6 . The following are prepared similarly, the fission products with HCl being given in parentheses: $\text{Pb Et}_3 \Delta^r$ -butenyl, b.p. 78°/3 mm. ($\text{Pb Et} \Delta^r$ -butenyl dichloride and C_6H_6); $\text{Pb Ph}_3 \beta$ -styryl, m.p. 107—109° (PbPh_3Cl and styrene); $\text{Pb Ph}_3 \alpha$ -naphthyl (62.5% of C_{10}H_8); Pb Ph_3 di- α -naphthyl (PbPh_3Cl_2 and C_{10}H_8); Pb Ph_3 benzyl, m.p. 91° (C_6H_6 and Pb Ph_3 benzyl chloride, sinters at 157°); Pb Ph_3 allyl (PbPh_3Cl and C_3H_6) (cf. Austin, A., 1931, 1317). From the above and previous work (A., 1933, 71), the relative order of labilities is α -thienyl, α - C_{10}H_7 > Ph > Et , CH_2Ph (as found for other organo-metallic compounds) and allyl, β -styryl > Ph > Δ^r -butenyl. H. B.

1:4-Selenothian. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1933, 1529—1530).—1:4-Selenothian, $\text{S} \langle \text{CH}\cdot\text{CH} \rangle \text{Se}$, m.p. 107°, is prepared from $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}$ (I) and aq. Na_2Se . (I) and Al_2Se_3 at 150—170° give (after decomp. with H_2O and steam distillation) dithian and much H_2Se . $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{Se}$ and aq. Na_2S afford C_2H_4 (?) and Se . H. B.

Vegetable proteins. II. Purified edestin and edestan. G. FLORENCE, J. ENSELME, and M. POZZI (Bull. Soc. Chim. biol., 1933, 15, 1113—1116; cf. A., 1932, 1262).—In alkaline solution the ultra-violet absorption band of edestin (I) at 280 m μ tends to disappear. Edestan (II) shows an increased absorption in alkaline solution. (I) and (II) contain the same quantity of phenolic NH_2 -acids but differ in ultra-microscopic appearance. H. D.

Protein salts of organic bases. M. A. LISSETZIN (Biochem. Z., 1933, 266, 25—28).—Caseinogen and similar proteins react with equiv. amounts of org.

bases (including alkaloids) to give compounds (I) many of which are H_2O -sol. (I) are not coagulated by heat unless a salt (e.g., of Ca) is present but are pptd. unchanged by $(\text{NH}_4)_2\text{SO}_4$. W. McC.

Validity of the mass action law in the reaction of proteins with acids and bases.—See this vol., 36.

Optical rotatory power of heat-denatured ovalbumin. H. A. BARKER (J. Biol. Chem., 1933, 103, 1—12).—The $[\alpha]$ of alkali-denatured ovalbumin increases with time of heating to a limiting val. (independent of temp.) which is reached the more quickly the higher is the temp. This val. is a function of the p_{H} and protein concn. of the solution. Any change of these factors after heating has little influence on $[\alpha]$. The p_{H} of an ovalbumin solution decreases in acid and increases in alkaline solution when heated. $[\alpha]$ is the only property suitable for the quant. characterisation of a denatured protein. M. S. B.

Secondary reaction between ovalbumin and acid. G. ETTISCH and G. V. SCHULZ (Biochem. Z., 1933, 265, 370—374).—The secondary reaction (see A., 1933, 788) of ovalbumin with acid increases with rise of temp. and is associated with acid hydrolysis. P. W. C.

Protamines of some species of fish.—See this vol., 96.

Action of heavy metals on cysteine and on thiol groups of proteins. S. M. ROSENTHAL and C. VOEGTLIN (U.S. Pub. Health Rep., 1933, 48, 347—364).—Conditions for oxidative degradation of cystine and coagulated ovalbumin (I) in presence of Cu are given. Fe and Mn cause cysteine \rightarrow cystine. With (I) Mn causes half the O_2 absorption given with Cu , where oxidation of $\cdot\text{SH}$ is suggested. The effects of Fe and Cu on dialysed tissues are described. NUTR. ABS. (m).

Effect of ultra-violet, radium, and X-ray radiation on glutathione in pure solution. G. E. WOODWARD (Biochem. J., 1933, 27, 1411—1414).—The concn. of total and reduced glutathione (I) after ultra-violet irradiation varied with the time of exposure and p_{H} of the solution. For p_{H} 6.8 and $t=4$ hr. the total (I) recovered was 62%, and the $\text{SO}_4^{''}$ formed was 12.6%, the rest being sulphones and org. sulphides. β - and γ -rays exert a slight oxidative and destructive effect on (I); X-rays do not. H. D.

Cystine from deaminised casein. A. WHITE (J. Biol. Chem., 1933, 103, 295—297).—The proportion of cystine yielded by casein (I) on hydrolysis is uninfluenced by preliminary deamination of (I). H. D.

Ter Meulen method for direct determination of oxygen in organic compounds. W. W. RUSSELL and J. W. FULTON (Ind. Eng. Chem. [Anal.], 1933, 5, 384—386).—The method is improved by vaporising the substance in an electric furnace and using a Pt-coated SiO_2 cracking surface and ThO_2 -Ni as hydrogenation catalyst. R. S. C.

Semimicro-determination of nitrogen by the Dumas method. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1933, 16, 575—580).—An improved apparatus and technique are described to deal with 15—25 mg.

of sample, a special feature being a cartridge composed of a mixture of sample and CuO powder between layers of fine CuO powder, the whole being held in position in the combustion tube by coils at each end produced by heating Cu and immersing while hot in MeOH (which ignites) and cooling in vac. Errors due to contaminated CO₂, the v.p. of the KOH, and drainage in the azotometer are negligible, but allowance must be made for air occluded in the filling; the max. error was $\pm 0.17\%$ for org. compounds containing 4–15% N. J. G.

Determination of picric acid, and its separation from aqueous solution. A. ZACHAROV (J. Appl. Chem. Russ., 1933, 6, 998–1001).—Picric acid (I) is quantitatively pptd. as

[C₆H₂(NO₂)₃O]₂.Cu(NH₃)₄.3H₂O (II) by aq.-ammoniacal CuSO₄ (III). (I) can be determined gravimetrically as (II), or volumetrically by adding standard (III) until the colour changes from orange to green. Pure (I) can be recovered from factory waste H₂O as (II), from which (I) is regenerated by aq. H₂SO₄. R. T.

Fractionation and purification of organic substances by chromatographic adsorption. I. Application. II. Chlorophylls. A. WINTERSTEIN and G. STEIN (Z. physiol. Chem., 1933, 220, 247–263, 263–277).—I. Chromatographic analysis is useful for separating ergosterol-cholesterol, oleanol-oleanylene, dipalmityl ketone-hentriacontane, and similar mixtures. Activated Al₂O₃ is a useful adsorbent.

II. Using sucrose as adsorbent, chlorophylls *a* and *b* may be separated; the extinction coeffs. offer a criterion of purity. The absorption bands of the pure preps. are given. J. H. B.

Hammarsten reaction of cholic acid. K. YAMASAKI (J. Biochem. Japan, 1933, 18, 311–322).—The visual and spectroscopic appearances of the bile acids, their derivatives, and similar compounds on treatment with 25% (A., 1909, ii, 836) or 37% HCl are described. F. O. H.

Detection of local anaesthetics. R. FISCHER (Arch. Pharm., 1933, 271, 466–470).—By m.p. determinations of the ppts. with trinitroresorcinol

(I), C₆H₂(NO₂)₃.CO₂H, PtCl₄, and picric acid, 13 common local anaesthetics (0.3 mg.; micro-technique) can be identified. The crystal forms are variable. An unstable modification of (I) has m.p. 165–166°. R. S. C.

Reactions for differentiating novocaine and panthesin. P. DUQUENOIS (Bull. Sci. pharmacol., 1933, 40, 287–289; Chem. Zentr., 1933, ii, 583).—2% aq. AgNO₃ gives with novocaine (I) a white ppt., but no reaction with panthesin (II). The following give no ppt. with (I), but with (II) form ppts.: saturated aq. NaHCO₃ or Na₂B₄O₇ white, Na₂Fe(NO)(CN)₅ dirty white, Na nitrophenoxide (1%) or PtCl₄ (2.5%) + HgCl₂ (5%) yellow. A. A. E.

Gravimetric and volumetric determination of antipyrine as hydroferrocyanide in presence of amidopyrine. I. M. KOLTHOFF (J. Amer. Pharm. Assoc., 1933, 22, 947–950).—The iodometric determination of antipyrine (I) is inapplicable in presence of amidopyrine, which, however, has little influence on the pptn. of the former as cryst. (C₁₁H₁₂N₂O)₂.H₄Fe(CN)₆ in acid solution (0.5N-HCl). The ppt., which is appreciably sol. in several aq. solutions, should be washed with its own saturated aq. solution and either dried and weighed, or dissolved in standard alkali and determined acidimetrically. The qual. sensitivity is 400 p.p.m. of (I), but ≥ 0.1 g. should be used for a determination. W. S.

Micro-chemistry of the opium alkaloids. L. KOFLER (Oesterr. Chem.-Ztg., 1933, 36, 174–176).—A lecture. These alkaloids cannot be distinguished by crystal forms, which are variable. Anhyd. morphine (I) sublimes in two forms, m.p. 197° (metastable) and 240° (decomp.) (stable), respectively. Crystallographic data are given for (I) and its hydrate [m.p. 300° (decomp. from 200°)] and for its anhyd. and hydrated (m.p. about 140°) hydrochloride. R. S. C.

Spectroscopic characterisation of organic dyes and other coloured substances. J. FORMANEK (Coll. Czech. Chem. Comm., 1933, 5, 411–414).—Polemical against Chloupek (A., 1933, 844).

D. R. D.

Analysis of protein solutions.—See this vol., 121.

Biochemistry.

Apparatus for automatically measuring respiratory exchange of small animals. H. H. LEWIS and J. M. LUCK (J. Biol. Chem., 1933, 103, 209–226).—Air is pumped through the animal chamber, fitted with a device for recording the muscular activity of the rat during the experiment, into a CO₂-absorption unit; during its return to the pump O₂ is automatically added and the cycle begins again. The CO₂ absorbed is measured by the decrease in conductivity of a dil. Ba(OH)₂ solution. The O₂ consumption is measured by recording the compensating flow of H₂O into the O₂ reservoir on a kymograph and subsequent determination of the total vol. of H₂O entering. The animal chamber, absorption cell, and O₂ reservoir are immersed in a

H₂O thermostat, and the entire apparatus in an air thermostat. The average fasting metabolic rate of eighteen white rats at 28° was 744 g.-cal. per day per sq. m. body-surface. H. D.

Spectroscopic detection of carbon monoxide in blood. J. KOLLER (Deut. Z. ges. gerichtl. Med., 1933, 21, 275–277; Chem. Zentr., 1933, ii, 915–916).—For blood containing $> 20\%$ CO the use of Na₂SnO₂ is preferred to that of (NH₄)₂S; for $< 20\%$ neither reagent is satisfactory. A. A. E.

Detection and determination of carbon monoxide in blood. A. A. CHRISTMAN and E. L. RANDALL (J. Biol. Chem., 1933, 102, 595–609).—The method depends on the colorimetric determination

of excess PdCl_2 with KI after reduction with the CO liberated by $\text{K}_3\text{Fe}(\text{CN})_6$. NO and CN' interfere; H_2S is without effect on the determination. A. L.

Gas and electrolyte equilibria in blood. XVII. Effect of oxygenation and reduction on the carbon dioxide absorption curve and $p_{K'}$ of whole blood. D. D. VAN SLYKE and J. SENDROY, jun. (J. Biol. Chem., 1933, 102, 505—519).—The effect of oxygenation and reduction on the HCO_3' content and buffer val. of dog blood is studied and previous data on horse blood are recalcd. with the more accurate const. available. At p_{H} 7.4 the increase in combined CO_2 caused by removing 1 millimol. of O_2 averages 0.52 millimol. for horse blood and 0.45 millimol. for dog blood, these vals. differing to almost the same extent as the vals. 0.66 and 0.60 previously found for solutions of the cryst. hæmoglobin (I) from the two species at the same p_{H} . The buffer val. (II) of dog blood per unit of (I) content is also slightly < the (II) of horse blood, this difference again being similar to that between solutions of the cryst. (I). The Hasselbalch $p_{K'}$ vals. for whole blood of varying (I) content and oxygenation are recalcd. and expressed in a line chart. A. L.

First dissociation constant $p_{K'}$ of carbonic acid in hæmoglobin solutions and its relation to the existence of a combination of hæmoglobin with carbon dioxide. R. MARGARIA and A. A. GREEN (J. Biol. Chem., 1933, 102, 611—634).—The apparent first dissociation const. $p_{K_1'}$ of H_2CO_3 is determined in the presence of varying concn. of hæmoglobin (I), H_2CO_3 , and CO_2 , the p_{H} of the mixtures being determined with a glass electrode. At const. ionic strength (II) and (I) concn. $p_{K_1'}$ varies approx. linearly with the p_{H} , and the difference between $p_{K_1'}$ in the presence of, and $p_{K_1'}$ in the absence of, (I) at const. (II) is the greater the higher is the (I) concn. At very low (II), $p_{K_1'}$ at const. p_{H} increases with increasing (II), and at high (II) $p_{K_1'}$ is lower the lower is the proportion of NaHCO_3 making up the total electrolyte concn. If the deviation of $p_{K_1'}$ from $p_{K_1'}$ be assumed to be entirely due to the combination of CO_2 with (I), and this quantity is calc., the amount found for low (II) increases with increase in the calc. $[\text{HCO}_3']$. The difference between p and $p_{K_1'}$ is greater in reduced than in oxy-(I) solutions, so that combination of CO_2 with (I) may take place more easily in the first case. O_2 dissociation curves at const. p_{H} and (II) in NaHCO_3 - CO_2 solution are moved to the right of those in the absence of CO_2 under identical conditions of (II), p_{H} , and (I) concn. $p_{K_1'}$ in a 1% hæmatin solution of 0.04N-Na⁺ is the same as in the absence of hæmatin in a solution of the same (II). These results are believed to indicate the real existence of a CO_2 or HCO_3 -(I) compound. A. L.

Existence of a carbhæmoglobin. R. JANZEN and H. NERTER (Pflüger's Archiv, 1933, 232, 349—356; Chem. Zentr., 1933, ii, 239).—The existence of a CO_2 -hæmoglobin complex has not been confirmed. A. A. E.

Preparation of pure hæmoglobin solutions by electrodialysis. G. ETTISCH and G. GROSCURTH (Biochem. Z., 1933, 266, 441—447).—A method is described for the prep. of pure hæmoglobin solutions

by electrodialysis for 2½ hr. of hæmolysed red corpuscles using glycine-collodion anodic and parchment cathodic membranes. P. W. C.

Sedimentation constants, mol. wts., and isoelectric points of respiratory proteins. T. SVEDBERG (J. Biol. Chem., 1933, 103, 311—325).—The sedimentation consts. (I) of the respiratory proteins (II) of the blood from many different species were determined by the ultra-centrifuge, use being made of their sp. absorption in the long ultra-violet to measure the migration. The (I) of the (II) in corpuscles are generally < of those contained in plasma; biological kinship is usually accompanied by identity in the (I) of (II). Comparison of the mol. wts. of (II) as calc. from (I) shows them to be multiples of 34,500. The isoelectric points (III) of the (II) vary from species to species and are lower in invertebrates than in vertebrates. The (I) and mol. wts. can be used as group characteristics, whilst (III) are species characteristics. H. D.

Availability of iron from different sources for hæmoglobin formation. C. A. ELVEHJEM, E. B. HART, and W. C. SHERMAN (J. Biol. Chem., 1933, 103, 61—70).—The dipyriddy reagent indicates that FeCl_3 , Fe glutamate, $\text{Fe}_4(\text{P}_2\text{O}_7)_3$, FePO_4 , 47% of total Fe in wheat and yeast, and 57% of Fe in oats are available for hæmoglobin production. H. G. R.

Iron. VIII. Differentiation of the "readily eliminated" blood-iron from the hæmoglobin-iron and from the inorganic iron. G. BARKAN (Z. physiol. Chem., 1933, 221, 241—251; cf. A., 1933, 623).—The "readily eliminated" blood-Fe may be separated from other compounds containing Fe, since it is not taken up by $\text{Al}(\text{OH})_3$ under conditions in which hæmoglobin and inorg. Fe added to blood are strongly adsorbed. J. H. B.

Blood-iron in animals with hæmocyanin and the dissociation of copper from hæmocyanin. G. BARKAN (Klin. Woch., 1933, 12, 546—547).—The blood of the crab (*Ashtacus fluviatilis*) incubated for 24 hr. with 0.4% HCl gives an ultrafiltrate containing per c.c. of blood approx. 9×10^{-7} mol. of Cu but practically no Fe. NUTR. ABS. (m).

Detection of bloodstains on green leaves. R. M. MAYER (Deut. Z. ges. gerichtl. Med., 1933, 20, 577—582; Chem. Zentr., 1933, i, 3994).—For the detection of old bloodstains on green leaves isolation as protoporphyrin in 3% HCl is recommended. Spectroscopic confirmation is necessary. A. A. E.

"Fluorinated" methæmoglobin. Spectrophotometric study and its application to the determination of methæmoglobin and fluorides. R. FABRE and S. BAZILLE (J. Pharm. Chim., 1933, [viii], 18, 465—470).—The presence of 10% of methæmoglobin (I) in oxyhæmoglobin can be determined by addition of NaF and subsequent spectroscopic examination; the band at λ 6320 Å. [for (I)] is displaced at λ 6100. Determination of the optical density of the max. (for λ 6100—6200) of solutions of (I) containing various amounts of NaF can be used to detect 0.1—2 mg. of NaF. H. B.

Role of proteins in regulating the resistance of red blood-cells. G. PETRANYI and S. BLAZSÓ (Z.

ges. exp. Med., 1933, 88, 610—615).—Administration of peptone and milk to rabbits leads to an increase of the protein of the red cells. There is no correlation between corpuscular resistance and plasma-protein or non-protein-N of plasma or corpuscles.

NUTR. ABS. (m)

Enzymes of leucocytes. IX. Amylases. II. R. WILLSTATTER and M. ROHDENWALD (Z. physiol. Chem., 1933, 221, 13—32; cf. A., 1932, 292).—There are eight amylases now classified on the basis of solubility in glycerol (*G*), inhibition by *G* (*a*), and dependence on added $\text{PO}_4^{'''}$ (*b*) as follows: I lyo- and desmo-amylase, $+a+b$, inhibited by *G* and independent of added $\text{PO}_4^{'''}$; II lyo- and desmo-amylase, $+a-b$, inhibited by *G* and needing addition of $\text{PO}_4^{'''}$; III lyo- and desmo-amylase, $-a+b$, not inhibited by *G* and independent of $\text{PO}_4^{'''}$; IV lyo- and desmo-amylase, $-a-b$, not inhibited by *G*, inactive without added $\text{PO}_4^{'''}$. α -Lyo-amylase becomes IV lyo-amylase. *G* extracts from dry leucocytes I lyo-amylase, which becomes active on dialysis of the *G* and undergoes conversion into III. This enzyme and probably IV lyo-amylase is present in the living leucocytes. Three at. groups in the mol. are held responsible for the behaviour of these amylases, the specifically active group and those influencing *a* and *b*, respectively. The leucocyte amylases belong to the α - or dextrinogen type. J. H. B.

Blood picture of the turtle after complete anoxia. J. M. JOHLIN and F. B. MORELAND (J. Biol. Chem., 1933, 103, 107—114).—After complete absence of O_2 for 28 hr., blood-sugar rises from 50 to 1200 and lactic acid to 1000 mg. per 100 c.c., and blood- p_{H} is decreased from 7.9 to 6.8. CO_2 expired is $>$ the total HCO_3 of the blood. H. G. R.

Diurnal variations in the blood of fish. L. BAUDIN (Compt. rend., 1933, 197, 1353—1354).—In various fish (*Blennius gattorugine*, *Crenilabrus melops*, and *Perca fluviatilis*) the no. of cells and the O_2 capacity of the blood increase to a max. in early afternoon and then diminish towards evening. The degree of O_2 saturation shows a large decrease in the afternoon, but the (more nearly const.) CO_2 content passes through a min. about noon. J. W. B.

Electrodialysis of serum with the glycine-collodion membrane. G. ETTISCH and J. A. DE LOUREIRO (Biochem. Z., 1933, 266, 422—435).—Using as anodic diaphragm a membrane prepared from a collodion solution shaken with solid glycine, electrodialysis of 50 c.c. of serum is complete in 35 min., the reaction remaining unchanged for the first 30 min. and no protein being pptd., the final reaction with almost complete elimination of electrolytes being attained in the subsequent 5 min. P. W. C.

Fractionation of serum by electrodialysis. G. ETTISCH (Biochem. Z., 1933, 266, 436—440).—The use of the ultracentrifuge is discussed. P. W. C.

Analysis of serum with the ultracentrifuge. P. VON MUTZENBECHER (Biochem. Z., 1933, 266, 226—249).—Serum-albumin and -globulin can be separated in the ultracentrifuge using the refraction method, and the relative amounts determined from the curves obtained. Normal horse and human sera examined in

this way show the presence of four different mols., the sedimentation consts. for which in very dil. solution are 4.5, 6.8, 9, and 17. The first two are identical with those for pure albumin and globulin, and form the chief part of the serum-protein. The sedimentation consts. of human sera decrease more slowly with increasing concn. of the serum than those of horse serum. With two pathological sera considerable deviations occur, in one case a mol. which normally was present only in small amount being increased to 50% of the total protein. P. W. C.

Fractions of serum. P. VON MUTZENBECHER (Biochem. Z., 1933, 266, 250—258).—The sedimentation consts. (I) of globulin are redetermined. Serum-globulin pptd. with $(\text{NH}_4)_2\text{SO}_4$ contains chiefly a mol. of mol. wt. 138,000 and (I) of 7.1×10^{-13} , together with smaller amounts of mols. having (I) of 9.0×10^{-13} and 19×10^{-13} . In all albumin preps. the chief fraction has (I) of 4.5×10^{-13} . Albumin purified by dialysis contains in addition small amounts of smaller mols., but after pptn. by full saturation with $(\text{NH}_4)_2\text{SO}_4$ it contains also mol. aggregates of albumin. P. W. C.

Dissociation and association of serum molecules. P. VON MUTZENBECHER (Biochem. Z., 1933, 266, 259—265).—When increasing amounts of $(\text{NH}_4)_2\text{SO}_4$ are added to serum (I) the no. of small mols. increases, and these are difficultly sedimented. The sedimentation const. (II) of the albumin fraction also decreases. Electrodialysis of (I) causes a partial association of the protein remaining in solution. Proteins of (I) in 0.1*N*-salt solution are stable between p_{H} 3.5 and 11.5, but (II) begins to diminish above p_{H} 10 and below p_{H} 5. P. W. C.

Precipitation of proteins by neutral salts. G. SANDOR, A. BONNEFOI, and J. J. PEREZ (Compt. rend., 1933, 197, 1254—1256).—Pptn. of the globulins and albumins of horse serum by $(\text{NH}_4)_2\text{SO}_4$ is studied and discussed. J. L. D.

Basic amino-acids of serum-proteins. R. J. BLOCK (J. Biol. Chem., 1933, 103, 261—267).—Serum-albumin and -globulin prepared by pptn. with different concns. of MgSO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and NaCl contained varying quantities of total N, histidine, arginine, and lysine. H. D.

Determination of blood-cholesterol. H. BANERJI (J. Indian Chem. Soc., 1933, 10, 573—576).—Oxalated blood (0.25 c.c.) is dried on fat-free filter-paper at 37°, the cholesterol extracted with CHCl_3 , and determined colorimetrically (Ac_2O , conc. H_2SO_4). The method gives more accurate results than that of Myers *et al.* (A., 1918, ii, 461). H. B.

Determination of blood-cholesterol. I. Extraction and gravimetric methods. II. Combination of colorimetric and digitonin methods. K. KUSUI (J. Biochem. Japan, 1933, 18, 227—236, 237—241).—I. For the determination of cholesterol (I) in blood or serum, the method of Onizawa (A., 1929, 952) or of Mühlbock and Kaufmann (A., 1931, 755) achieves complete extraction whilst that of Fex (A., 1920, i, 697) does not. A simplified gravimetric method for the determination of (I) and its esters is described.

II. Free (I) in blood or serum (2.5 c.c.) is determined gravimetrically by digitonin pptn., and esters of (I) colorimetrically by treatment with Ac_2O and H_2SO_4 . F. Ö. H.

Glycogen content of blood. Its significance for metabolic processes. E. BONG (Pflüger's Archiv, 1933, 232, 482—499).—In adult dogs the glycogen content (I) of the blood varies from 13 to 30 mg. per 100 c.c. (average 21); in puppies (II) it averages 18 mg. In fasting dogs (I) varies directly with the liver-glycogen (III). After carbohydrate-rich diet there is a rapid rise in (I) to supernormal vals. (63 mg.) and after the third day a gradual fall to normal or subnormal: in (II) the rise is more marked and rapid. High (I) is accompanied by low blood-sugar (IV); while (I) and (III) fall the blood- and liver-fat increase. Support is given to Junkersdorf's theory that overloading of the liver with glycogen leads to functional inefficiency of the liver, and therefore to defective regulation of (IV). High-carbohydrate diet with insulin leads to a very marked lowering of (I) (average 9 mg.): there is a rise in the glycogen and fat of muscle, but (III) is < without insulin. Dogs treated with phloridzin show an increase of (I). After injection of thyroxine there is a rise of (IV) and (I) and fall of muscle-glycogen and (III). In dogs with an Eck fistula the lowest vals. for (I) are found, supporting the view that (I) and (III) are correlated.

NUTR. ABS. (m)

Distribution of blood-sugar. F. KERTI and F. STENGEL (Z. ges. exp. Med., 1933, 88, 78—91).—The relative sugar concn. of whole blood (I), plasma, and serum differs by as much as 20% in healthy individuals and 30% in diabetics (II), in whom the sugar of (I) is more frequently lower than that of plasma or serum. The relative concns. vary in the same person from day to day; sex, age, ingestion of food, or the presence of hyperpica has no const. effect in (II) or non-diabetics (III). In the blood of (II) and (III) kept at 18—25° in sterile tubes for 14 days various changes in the distribution of the sugar occur.

NUTR. ABS. (m)

Micro-analysis of urine and blood by the step photometer. X. Determination of blood-sugar. C. URBACH (Biochem. Z., 1933, 265, 390—400).—The method is described and a table gives comparative vals. by this and the usual analytical methods for samples of blood of rat, cat, rabbit, and man. P. W. C.

Normal urea level in human blood. H. GEMEINHARDT (Z. ges. exp. Med., 1933, 88, 622—629).—The NaOBr method for blood-urea (I) gives results averaging 1.1 mg. per 100 c.c. > the urease method. The average (I) of patients without renal disease is 36.05 mg. per 100 c.c. In women (I) is 3 mg. per 100 c.c. lower and tends to increase with age: there is no correlation between (I) and either wt. or height, although there is a slight correlation with Rohrer's index ($100P/L^3$, where P =wt. in g. and L =height in cm.). In non-renal diseases lack of salts, tissue- H_2O , and secretions, and toxic effects on the kidneys play a part in the rise in (I).

NUTR. ABS. (m)

Manometric micro-Kjeldahl and blood-urea determinations. D. D. VAN SLYKE and V. H.

KUGEL (J. Biol. Chem., 1933, 102, 489—497).—The determination of blood-urea and -NH_3 using separate solutions of NaOH and Br in aq. KBr has advantages over that using alkaline NaOBr. The procedure is described. Somogyi's method (A., 1930, 1055) of pptg. blood-proteins with Zn(OH)_2 removes most of the non-urea substances present in tungstic acid filtrates, and using this in conjunction with the above on bloods with < 50 mg. urea-N per 100 c.c., the average error is ± 0.02 mg. A. L.

Determination of ammonia in blood. D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1933, 102, 499—504).—The procedure for the removal of NH_3 from blood by the Nash-Benedict aeration method (A., 1922, i, 191) and its colorimetric determination with HOCl and PhOH (I) (cf. Thomas, A., 1912, ii, 991) is described. (I) is more sensitive than Nessler's reaction and the product does not flocculate. A. L.

Conditions for the formation in serum of colloid-calcium-phosphorus complexes. M. LASKOVSKI (Biochem. Z., 1933, 265, 401—412).—Increase of serum-Ca (I) causes decrease of PO_4 in the ultrafiltrate (II), the product of the Ca and P contents of (II) remaining const. Increase of serum- PO_4 (III) decreases the Ca content of (II), but to only a certain limiting val. (3.5—4.0 mg. per 100 c.c.) and thereafter the $\text{Ca} \times \text{P}$ product in (II) increases with the increase of PO_4 . With simultaneous increase of (I) and (III), providing the Ca/P ratio does not exceed 1, the Ca of (II) is often unchanged. P. W. C.

Spectrophotometric detection of bile acids in blood. N. SCHEINFINKEL (Biochem. Z., 1933, 265, 380—385).—A modification of the Aldrich and Bledsoe method (A., 1928, 788) and its adaptation for use with the spectrophotometer are described. The bile acid content of dog's blood is 0.8 mg. per 100 c.c.

P. W. C.

Biochemical properties of bile-pigments. II. Influence of calcium cations on agglutinating and hæmolytic power of bilirubin. A. CLEMENTI and F. CONDORELLI (Biochem. Z., 1933, 266, 221—225).—The characteristic agglutinating action of bilirubin previously obtained with red cells suspended in Ringer's solution (A., 1931, 1179) proceeds only slowly when the cells are suspended in 0.9% NaCl, the Ca^{++} of the Ringer's solution (also Ba^{++} and Sr^{++}) accelerating the process considerably. P. W. C.

Photobiological sensitisation and desensitisation in the ultra-violet. W. HAUSMANN and F. M. KUEN (Klin. Woch., 1933, 12, 711—712; Chem. Zentr., 1933, ii, 405).—Serum, pinakryptol, glucose, and fructose arrest, whilst resorcinol and Na_2SO_3 increase, hæmolysis following irradiation of erythrocytes in presence of hæmatoporphyrin. A. A. E.

Coagulation. V. Isoelectric point of fibrin. K. KLINKE and K. BALLOWITZ (Z. ges. exp. Med., 1932, 84, 224—229; Chem. Zentr., 1933, ii, 899).—The isoelectric point of fibrinogen is p_H 4.4 (4.29—4.54), and of fibrin 5.23—5.66; hence the substances are colloid-chemically distinct. Thrombin-fibrin and fibrin formed by heat-coagulation have practically the same isoelectric point. A. A. E.

Chemical nature of thrombin. F. KRAUS and H. J. FUCHS (Biochem. Z., 1933, 266, 458).—Fischer's work (A., 1933, 1065) is criticised. P. W. C.

Potentiometric determination of antibody-haptene equilibrium. H. ERLÉNMEYER, E. BERGER, and M. LEO (Biochem. Z., 1933, 266, 355—359).—Preliminary work for determination of the concn. of atoxyl-antibody in atoxyl-antiserum, depending on potential changes in the reduction-oxidation system $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}^{\text{V}}\text{O}_3\text{H}_2|\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}^{\text{III}}\text{O}_2\text{H}_2$, is described. P. W. C.

Specificity of brominated and iodinated proteins. M. H. FINKELSTEIN (J. Immunol., 1933, 25, 179—182).—Iodinated and brominated (I) proteins (Wormall) showed close antigenic relationship. (I) (Wormall) showed only slight immunological relationship with (I) (Bruynoghe), which probably suffered oxidation. CH. ABS.

Electric charge of antibodies. L. OLITZKI (J. Immunol., 1933, 24, 505—512).—Experiments on protein-free solutions show that agglutinins (H- and O-type) carry a negative charge over the range p_{H} 10.0—3.4; below this point they are too sensitive to acid reactions to make measurement possible. CH. ABS.

Specific precipitation test for the standardisation of type I antipneumococcus serum. R. BROWN (J. Immunol., 1933, 25, 149—154).—Pptn. tests agreed (92.3%) with mouse protection tests. CH. ABS.

Lipoidal content of antipneumococcic horse serum. L. D. FELTON and G. KAUFFMANN (J. Immunol., 1933, 24, 543—548).—Immune sera (types I and II) contain, per 100 c.c., 1.34 g. (normal 1.05 g.) of material sol. in $\text{EtOH}-\text{Et}_2\text{O}$; this has not been correlated with the lipin and total N content or with protection. CH. ABS.

"Super-contraction" and "set" in animal hairs. H. J. WOODS (Nature, 1933, 132, 709—710).—The mechanism of the behaviour of animal hairs under various conditions of stress or relaxation is discussed in terms of mol. structure. L. S. T.

Spectral absorption of visual purple before and after illumination. Y. HOSOYA and V. BAYERL (Pflüger's Archiv, 1933, 231, 563—570; Chem. Zentr., 1933, i, 3959).—2% aq. panatoxin (from *Panax ginseng*) is recommended for the extraction of visual purple from the frog's retina. Max. absorption is at 520 m μ . A. A. E.

Calcium salts of bone. C. M. BURNS (J. Physiol., 1933, 78, 1—2r).—The Ca:P ratio in old bones (rat, cat) is 2.0 to 2.2 and in young bones (I) 1.85 to 2.0. Allowing for the Ca present as CaCO_3 these ratios suggest that (I) contain not only $\text{Ca}_3(\text{PO}_4)_2$ but also compounds (II) of the type CaRPO_4 , where R is org. or inorg. Such (II) may explain the reactions of growing (I) to madder. NUTR. ABS. (m)

Sulphur in the animal organism. L. SILBERSTEIN (Compt. rend., 1933, 197, 1068—1069).—The S content of animals and animal organs has been determined. W. O. K.

Total phosphorus in the young rat. A. LEULLIER and G. BÉRUARD (Compt. rend. Soc. Biol., 1933, 112, 483).—The total P increases from 12.50—13.04 mg. at the age of 1 day to 218.7 mg. at 30 days and 500 mg. at 70 days. After weaning the rat grows more quickly and retains more P. The % of P is doubled between birth and the eighth day, after which it remains steady. NUTR. ABS. (b)

Mineral content of the muscles of fish in water containing increased concentration of mineral salts. S. KAPLANSKI and N. BOLDIREVA (Biochem. Z., 1933, 265, 422—425).—With increase of NaCl and CaCl_2 content of H_2O to 1.5—2%, the corresponding cation contents of the musculature of fish greatly increase, but of the blood remain unchanged. On the other hand, the Cl' content of the muscle is unchanged, but of the blood is greatly increased. P. W. C.

Iron in the liver of the foetal calf. G. ROUSSEL and Z. GRUZEWSKA (Compt. rend., 1933, 197, 943—944).—A min. val. of 0.007—0.01% Fe (fresh organ) was observed at 6—7 months, and a max. of 0.179% at 8.5—9 months. A. C.

Histospectrographic detection of copper in the normal and pathological liver. A. POLICARD (Bull. d'Histol. appl., 1933, 10, 94—103).—By the method described the presence of Cu in various types of normal and pathological (I) livers is confirmed. Such (I) include those of rabbits treated with powdered Cu suspended in lard. Human livers normally contain Cu; those of normal rats, in two cases out of three, contained none. NUTR. ABS. (m)

Physiological products of the lac insect. I. N. K. R. RAO and M. SREENIVASAYA (J. Indian Inst. Sci., 1933, 16A, 76—83).—Extraction of the incrustation deposited by lac insects with 0.9% aq. NaCl yields a globulin-like protein, polypeptides resembling protamines, and a fat (I val. 30.4, sap. val. 182, acid val. 5.0). F. O. H.

Physiological products of the lac insect. II. Water-soluble nitrogenous constituents. N. K. R. RAO (J. Indian Inst. Sci., 1933, 16A, 97—102).—From the aq. extract of the lac insect, various fractions isolated include four containing N, two of which are pptd. by phosphotungstic acid (I), and the other two are not pptd. by (I). These account respectively for about 40% and 25% of the total N, whilst tyrosine accounts for 2.5%. W. O. K.

Nitrogen content of organisms and its significance. A. ROCHE (Compt. rend. Soc. Biol., 1933, 113, 105—107).—The N content of rats of various ages and nutritional levels varies between 1.5 and 4.6% of the fresh wt. (I) (average of 3.1% for the well-nourished adult rat). In complete inanition or after N starvation the vals. range from 3.6 to 4.6%. As the fat and H_2O content of the animals calc. on (I) vary greatly the N vals. are of doubtful significance. NUTR. ABS. (m)

Determination of residual nitrogen in organs. I. Liver. H. ELIAS and H. KAUNITZ (Biochem. Z., 1933, 266, 323—328).—A method is described for the prep. of aq. liver suspensions (depending on the use of

rapid freezing and trituration with sand) in which the residual N and its fractions can be determined.

P. W. C.

Protamines of some species of fish. M. A. LISSITZIN and N. S. ALEXANDROVSKAYA (Z. physiol. Chem., 1933, 221, 156—164).—Protamines were isolated as sulphates: from *Luciperca sandra*, *percin* (I), $[\alpha]_D^{20}$ —55° in H₂O (sulphate, $[\alpha]_D^{20}$ —67·4° in H₂O); from *Huso huso* or *Acipenser huso*, *acipenserin* (II) (sulphate, $[\alpha]_D^{20}$ —45° in H₂O). (I) and (II) contain, respectively, 76·7, 78·6% of arginine-N, 7·6, 11·2% of histidine-N, 0·0, 7·2% of lysine-N, 9·5, 0·0% of mono-NH₂-acid-N. (I) (equiv. wt. 244) combines with caseinogen (III) (equiv. wt. 1227) in the wt. ratio 1:5. The compound (IV) is insol. in H₂O, but sol. in 10% aq. NaCl from which it is pptd. on dilution. (IV) is decomposed into its constituents by alkali and acid; the dissolution and pptn. effects obtained are those of (III). (IV) is salted out by (NH₄)₂SO₄ and the solution in 10% NaCl is coagulated by heat in presence of a trace of Ca. (II) forms a (IV) with similar properties.

J. H. B.

Analysis of muscles of marine invertebrates. D. M. NEEDHAM, J. NEEDHAM, E. BALDWIN, and J. YUDKIN (Z. physiol. Chem., 1933, 222, 63—64).—The detection of creatinephosphoric acid in various genera by Riesser and Hansen (A., 1933, 1094), which is contrary to the authors' observations (A., 1932, 532), is probably due to their having used the method of Lohmann and Jendrassik, which is untrustworthy.

J. H. B.

Determination of protein-nitrogen. Nitrogenous non-protein substances in spermine preparations. I. S. JAITSCHNIKOV (J. Gen. Chem. Russ., 1933, 3, 434—436).—Fassbender's Cu(OH)₂ reagent, Pb(OAc)₂, and phosphotungstic acid ppt. not only proteins, but also purine and hexone bases. Pharmaceutical preps. of spermine contain xanthine and arginine, with traces of guanine, hypoxanthine, adenine, and lysine.

R. T.

Occurrence of betaines in *Arca Noæ*. F. KUTSCHER and D. ACKERMANN (Z. physiol. Chem., 1933, 221, 33—39).—The so-called lysine fraction of *A. Noæ* contains glycinebetaine and, in smaller amounts, γ -butyrobetaine, carnitine, stachydrine, and a substance C₇H₁₀O₂N₂ (*aurichloride*; *hydrochloride*, m.p. 168—172°), an isomeride of trigonelline.

J. H. B.

Trimethylamine oxide and other nitrogenous bases in crab's muscle. F. A. HOPPE-SEYLER (Z. physiol. Chem., 1933, 221, 45—50).—NMe₃O was isolated from the lobster (*Homarus vulgaris*) and shown indirectly to be present in the river-crab (*Astacus fluviatilis*). Lobster muscle also contains NMe₃, *d*-arginine, betaine, probably choline, and a base (I), C₇H₇O₂N, similar to but not identical with trigonelline. In presence of conc. HCl it gives a regular, m.p. 185—190°, decomp. 191°, and with dil. HCl an irregular, *aurichloride* (C₇H₇O₂N)₄·3HAuCl₄, m.p. 139—143°. (I) was also obtained from *Arca Noæ*.

J. H. B.

Preparation of glutathione. M. T. RÉGNIER (J. Pharm. Chim., 1933, [viii], 18, 369—376).—Brewer's yeast is extracted with aq. EtOH (45—70%

according to the H₂O content of the yeast), Pb(OAc)₂ added, the ppt. washed with 45% EtOH and H₂O, dissolved in 0·5N-H₂SO₄, the solution filtered and pptd. with Cu₂O at 40°, the ppt. washed free from sulphate, decomposed in aq. suspension by H₂S, and the filtered solution evaporated at < 30°/vac. Glutathione is crystallised from the resulting syrup by adding EtOH; yield approx. 1 g. per 1000 g. of fresh yeast.

H. A. P.

Glutathione content of the suprarenal glands.

A. D. MARENZI and B. BRAIER (Anal. Farm. Biochim., 1933, 4, 50—54).—The apparent high content of glutathione (I) in the suprarenals is in part due to the simultaneous determination of ascorbic acid (II) and adrenaline (III) (cf. Birch and Dann, A., 1933, 541). Approx. determinations may be made by destroying successively (II) by heating the alkaline extract to 40° for 2 hr., and (III) by autoclaving for 30 min. at 0·5 atm.

R. K. C.

Thiol and ascorbic acid content of the lens of the eye. H. VON EULER and C. MARTIUS (Z. physiol. Chem., 1933, 222, 65—69).—In the ox-lens about $\frac{1}{2}$ of the total reduction (I titration) is due to ascorbic acid (I) (indophenol titration). The (I) normally present in the human lens cannot be detected in cataract, and the glutathione is much diminished.

J. H. B.

Fermentable sugar in heart and skeletal muscle. G. T. CORI, J. O. CROSS, and C. F. CORI (J. Biol. Chem., 1933, 103, 13—24).—Fermentable sugar (I) in skeletal muscle of rats is 10—12 and 13—53 mg. per 100 g. at plasma-sugar (II) levels of 80—120 and 140—380 mg. per 100 c.c. Adrenaline causes a larger rise in (I) than can be accounted for by the rise in (II), which is probably due to breakdown of muscle-glycogen, whereas moderate insulin hypoglycemia (III) causes a decrease in (I). Heart muscle at (II) levels of 130—180 contains 46—59 mg. per 100 g. of (I), and during (III) is reduced to 14—24. Tetanic stimulation of muscle is accompanied by an increase in (I).

H. G. R.

Extraction from heart-muscle of a hæmin differing from blood-hæmin. E. NEGELEIN (Biochem. Z., 1933, 266, 412—416).—A hæmin is extracted from horse heart-muscle with HCl-COMe₂ which on dissolving in aq. C₅H₅N gives a hæmochromogen absorption band at 587 m μ . The corresponding bands of phæohæmin-*b* from chlorophyll and *Spirographis* hæmin are at 584 m μ , whilst for blood-hæmin the band is at 557 m μ . The hæmin was obtained cryst. as the C₅H₅N-hæmochromogen, but the free hæmin (as the FeCl₃ compound) was not obtained cryst. The amorphous ferrichlorohæmin contained 6·5% Fe and contained 1 atom Fe for 4 atoms of N. P. W. C.

Isolation of hepatoflavin. K. G. STERN (Nature, 1933, 132, 784—785).—The isolation of cryst. "hepatoflavin" (I), from horse liver is described. Aq. solutions of (I) are lemon yellow in colour, and exhibit a strong green fluorescence in filtered ultra-violet light. All fractions containing (I), with or without protein, show a strong absorption band near 2600 Å. Absorption at longer λ is less uniform and depends on p_H and other factors. Intensive irradiation of

flavin preps. in alkaline solution gives a greenish-coloured photo-decomp. product (II) which displays absorption bands at 2630, 3650, and 4420 Å. The absorption of (II) is identical with that of the corresponding photo-decomp. products obtained by Warburg and Christian (A., 1932, 1285) from yeast, and by other workers (A., 1933, 847) from various mammalian tissues.

L. S. T.

A. Unsaturated fatty acids of the oleic series in Japanese sardine oil. B. Unsaturated fatty acid, $C_{20}H_{38}O_2$, in Japanese sardine oil. M. TAKANO (J. Soc. Chem. Ind. Japan, 1933, 36, 549—550B, 550—551B; cf. B., 1926, 758; A., 1930, 451).—A. Zoomaric and oleic acid (mainly), also gadoleic (?) and eicetoleic acid, are isolated.

B. Fatty acids, b.p. 220—225°/6 mm., are isolated; fractional crystallisation of the Li salts affords eicosenoic acid (I), m.p. 22—23°, hydrogenated to arachidic acid. Decomp. of the ozonide of (I) affords undecolic and azelaic acid.

J. L. D.

Fat of *Rana temporaria*. E. KLENK (Z. physiol. Chem., 1933, 221, 264—270).—The fatty acids of the fat consist of saturated acids, C_{14} , 4%, C_{16} , 11%, C_{18} , 3%; singly unsaturated C_{16} , 15%; one to two double linkings, C_{18} , 52%; about three double linkings, C_{20} , C_{22} , 15%. Myristic, palmitic, stearic, linolenic, linoleic, oleic (?), arachidonic, and clupanodonic acids were detected. The composition is intermediate between those of the fats of mammals and fishes.

J. H. B.

Phosphatides. VII. Sphingomyelins of heart-muscle. VIII. Fatty acids of the liver-phosphatides and liver-oils of *Rana temporaria*. E. KLENK (Z. physiol. Chem., 1933, 221, 67—72, 259—264; cf. A., 1933, 846).—VII. A phosphatide obtained from ox-heart is a mixture of lignoceryl- and stearyl-sphingomyelin.

VIII. The phosphatide-fatty acids consist of saturated, mainly of chain-length C_{16} , 25%; one to two double linkings, mainly C_{18} , 42%, and about three double linkings, C_{20} and C_{22} , 33%. The liver-oils contain saturated acids, C_{16} , 19—23%, one to two double linkings, C_{16} and C_{18} , 61%, about three double linkings, C_{20} and C_{22} , 16—20%.

J. H. B.

Lipins of animal organs. VIII. Occurrence of lignocerylsphingosine in ox-spleen. C. TRÖPP and V. WIEDERSHEIM (Z. physiol. Chem., 1933, 222, 39—43; cf. A., 1933, 967).—Lignocerylsphingosine was isolated from ox-spleen in yields of 0.06—0.16%. No cerebrosides were detected.

J. H. B.

Pigments of silk. G. BARBERA (Annali Chim. Appl., 1933, 23, 501—508).—The pigments of silk consist, for the native (Italian) yellow races of silkworm, of mixtures of carotenoids, and for the Japanese green race, of substances of flavone character.

T. H. P.

Determination of bile salts in bile. S. A. PEOPLES (Proc. Soc. Exp. Biol. Med., 1933, 30, 1117—1120).—The bile salts are flocculated with 1% aq. $FeCl_3$ and the Fe in the ppt. is determined colorimetrically (Lyons). Each 0.1 mg. of Fe is associated with 2.5 mg. of glycocholic or with 2.98 mg. of taurocholic acid.

NUTR. ABS. (m)

Occurrence of taurocholic acid in hen's bile. K. YAMASAKI (J. Biochem. Japan, 1933, 18, 323—324).—Treatment of the bile with aq. $FeCl_3$ and extraction with EtOH etc. yields a product which on hydrolysis affords cholic acid, m.p. 195—196°, $[\alpha]_D^{20} +30.05^\circ$ in EtOH, and taurine. The yields indicate that the bile has a very low content of taurocholic acid.

F. O. H.

Gastric secretion in dogs with Eck's fistula. S. I. LEBEDINSKAJA (Z. ges. exp. Med., 1933, 88, 264—270).—In dogs with Pavlov pouches the gastric secretion is greatly increased in vol. and duration after the formation of Eck's fistula, whilst acidity increases and digestive activity diminishes. The changes in gastric secretion become more marked with time. Normal hepatic function is necessary for a physiological gastric secretion. NUTR. ABS. (m)

p_H of stomach contents and its electrometric titration. L. KISS (Magyar orvosi Arch., 1933, 34, 145—151; Chem. Zentr., 1933, ii, 571).—The p_H is not characterised by the usual determination of free HCl; the latent acidity is linearly proportional to the protein content.

A. A. E.

Determination of protein- and non-protein-nitrogen in gastric juice. L. MARTIN (J. Amer. Med. Assoc., 1933, 100, 1475—1478).—Normal gastric juice contains N in the following fractions in mg. per 100 c.c.: 48 total (I), 22.6 as protein, 25.5 non-protein (II), of which 7.2 as NH_2 -acid, 2.6 as urea, and 5.2 as NH_3 . In peptic ulcer the (I) and (II) are slightly increased. In benign achlorhydria and pernicious anaemia, vals. up to 109 mg. per 100 c.c. for (I) occur. In gastric carcinoma (I) and (II) show average vals. of 200 and 105, respectively.

NUTR. ABS. (m)

Enzymes in human colostrum. II. Oxidoreductase, catalase. III. Carbohydrase, diastase, and invertase. IV. Esterase, monobutyrase, tributyrase, castor-oil- and olive-oil-decomposing enzymes. Y. KATSU (Japan. J. Obstet. Gynecol., 1933, 16, 2—8, 10—20, 21—44).—II. Catalase was present in human colostrum and milk during the first week after parturition (I), particularly in the milk of primipara. Much catalase was present in the serum of the puerperal woman; the quantity decreased gradually after (I).

III. Human colostrum or milk contains much diastase during the first week after (I). Colostrum contains a little invertase (optimum p_H 6.24—6.42).

IV. Monobutyrase and tributyrase are present in the colostrum of the healthy puerperal woman. Enzymes decomposing castor oil or olive oil were not found.

CH. ABS.

Human milk. XIV. Determination of nitrogenous constituents. B. N. ERICKSON, N. STONER, and I. G. MACY (J. Biol. Chem., 1933, 103, 235—248).—By analysis of the N constituents of human milk filtrates after pptn. with H_2WO_4 under different conditions an optimal pptn. was obtained by addition of 0.1 c.c. of 10% Na_2WO_4 and 0.2 c.c. of H_2SO_4 per c.c. of milk. Considerable differences in non-protein-N were found in the filtrates according as H_2WO_4 or CCl_3CO_2H was used for pptn.; the discrepancy

increases with the time of keeping of the milk before pptn., indicating the presence of proteolytic decomp. products. An increased NH_2 -acid-N in both filtrates after hydrolysis demonstrates the presence of simple peptides in fresh milk. H. D.

Carbohydrate and caseinogen variations during milking in women. C. VINCENT and J. VIAL (Compt. rend. Soc. Biol., 1933, 113, 113—114).—During a milking the carbohydrate content (I) of the milk at various stages is almost const., with a slight fall about the middle. The % of caseinogen varies considerably with a marked max. generally when (I) shows its min. NUTR. ABS. (m)

Quantity and fat content of milk from the two human breasts. C. VINCENT and J. VIAL (Compt. rend. Soc. Biol., 1933, 113, 111—113).—During simultaneous manual expression of milk from the two human breasts (period of several weeks) a larger quantity of milk is obtained from one breast, and this breast always gives the higher yield at all milkings. The side differs in different subjects. There is no marked difference in the % of fat in the milk of the two breasts. NUTR. ABS. (m)

Unreported fatty acids in butter-fat. A. W. BOSWORTH and J. B. BROWN (J. Biol. Chem., 1933, 103, 115—134).—The following acids have been identified in butter: decenoic and tetradecenoic, hexadecenoic and eicosenoic (doubtful). There is evidence for a C_{20} , a C_{22} , or a C_{24} acid with two double linkings, highly unsaturated acids of the arachidonic type, probably C_{22} series, and tetracosic with small amounts of behenic and cerotic acids. Linoleic acid was not found. H. G. R.

Linoleic and linolenic acid content of butter-fat. H. C. ECKSTEIN (J. Biol. Chem., 1933, 103, 135—140).—Butter-fat contains 0.17—0.25% of linoleic acid and 0.07—0.17% of linolenic acid (II). (II) can be increased by adding linseed meal to the feed. H. G. R.

Alteration of the titratable acidity of milk by addition of calcium chloride. A. KERN (Milch. Forsch., 1933, 15, 501—506).—The titratable acidity of milk increases on the addition of a small quantity of aq. CaCl_2 . The increase in titration is const. for the same milk even when it has turned sour. There is a difference in the apparent increase of acidity in diseased or colostrual milk. E. B. H.

Correlation between properties of milk and type of inflammation in acute mastitis. R. B. LITTLE and F. S. JONES (J. Amer. Vet. Med. Assoc., 1933, 82, 818—825).—In cows suffering from udder disease there is incomplete correlation between increase in leucocyte content and in whey proteins and change in p_{H} of the milk. In acute attacks all properties considered, in less severe cases only one or two, may change. The changes in the milk are indicative of the severity and character of the inflammation. NUTR. ABS. (m)

Ethyl sulphide formation in the animal organism. J. WOHLGEMUTH (Z. physiol. Chem., 1933, 221, 207—208).— Et_2S excreted by the dog is probably formed by intestinal bacteria, and is not an endo-

genous metabolic product (cf. Christomanos, A., 1931, 976). J. H. B.

Identification of catatonin. E. DINGEMANSE and J. FREUD (Acta Brev. néerl. Physiol., 1933, 3, 59—51; Chem. Zentr., 1933, ii, 568).—Urine (1 litre) affords: men 4—12, women 0.5—2, children and diseased persons 0.25—0.5, mental patients 0.125—0.25 units. There are probably considerable losses during isolation. Catatonin is possibly identical with nicotine. A. A. E.

Crystalline urine-urobilin. Stercobilin and copromesobiliviolin. C. J. WATSON (Z. physiol. Chem., 1933, 221, 145—155).—Cryst. urobilin (I) was isolated from urine; it is probably identical with stercobilin (II) (*Cu* salt). An improved separation of copromesobiliviolin (III), m.p. 170—180°, decomp. 240—250° (*Cu* salt), is described. (III) is spectroscopically identical with mesobiliviolin (IV) from mesobilirubinogen (V). The blue pigments accompanying (III) and (IV) are similarly identical. (I) was obtained by oxidation of (V) *in vitro*. The blue and violet oxidation products of bilirubin are spectroscopically similar to, but not identical with, (IV). J. H. B.

Renal threshold of bilirubin. II. E. H. BENSLEY (J. Biol. Chem., 1933, 103, 71—79).—The direct type of bilirubin only is excreted in urine, and there is no evidence of any threshold in the kidney. H. G. R.

Determination of urinary protein by polarisation. SEILER (Schweiz. Apoth.-Ztg., 1933, 71, 264—265; Chem. Zentr., 1933, ii, 582).—Readings obtained on ordinary apparatus are within the error of observation. A. A. E.

Filtration and secretion of exogenous creatinine in man. N. JOLLIFFE and H. CHASIS (Amer. J. Physiol., 1933, 104, 677—680).—In man the average clearance vals. (I) (c.c. plasma cleared per min. per sq. m. body-surface) for xylose (II), urea, and creatinine (III) are respectively 52.9, 36.6, 91.4. The val. for (III) is > that for (II), and as (II) is excreted solely by filtration it follows that (III) is excreted partly by secretion in the tubules. The (I) vary for different subjects, but the ratios of one to another are fairly const. for all. NUTR. ABS. (m)

Urea clearance in dogs. R. L. HOLMAN (Amer. J. Physiol., 1933, 104, 615—623).—The clearance vals. (I) are not const. for each animal. A rise in blood-urea due to fasting reduces (I) whilst a fall due to injury to the liver raises it. NUTR. ABS. (m)

Reaction of kidneys to different water-salt loads. I. In resting condition. II. During muscular activity. A. M. SIMKINA and A. A. MICHELSON (J. Physiol. U.S.S.R., 1932, 15, 353—365, 366—369).—I. In the dog the optimal solution for max. H_2O -retention (I) is 1% aq. NaCl . Other concns. give a smaller (I), whilst 2.5% NaCl produces a diuresis (II). At the height of (II) the concn. index falls continuously. The (II) produced by H_2O and 0.5% NaCl during an ordinary diet occurs at the expense of normal reabsorption; in many cases using higher concns. of NaCl (II) was due to increased

filtration; in the case of a Cl-deficient diet both factors operate.

II. During muscular activity (II) is much less, and the solution for max. (I) is 1% NaCl. Directly after activity an anuresis is observed, dependent on the quantity and quality of the ingested solution, and due to the increased reabsorption. It is followed by an increase in (II). H. D.

Prevention of anæmia in suckling pigs, with observations on the blood picture. T. S. HAMILLTON, G. E. HUNT, and W. E. CARROLL (J. Agric. Res., 1933, 47, 543—563).—Conditions leading to anæmia are examined. Preventive treatment consisting of wetting the sow's udder with solutions of Fe or Fe and Cu salts is described. Relationships between the hæmoglobin content and cell vol. of the blood are traced. A. G. P.

Rôle of iron in anæmias. I. Iron content of liver, liver extracts and preparations. II. Iron content of normal and pathological blood, its relation to hæmoglobin content and factors affecting it. A. H. MULLER (Z. ges. exp. Med., 1933, 88, 776—781, 782—792).—I. The Fe of liver is not an important factor in the therapeutic results obtained by liver administration. Fe is present in traces only in liver preps.

II. The blood-Fe (I) varies greatly in health and in anæmia. There is no const. relationship between (I) and hæmoglobin (II). Administration of ferrum reductum leads to an increase of (I) which occurs before the final rise of (II). The increase in (I) appears to be independent of its original level and is not closely related to the amount of Fe administered. There is no increase of (I) in pernicious anæmia after the administration of Fe, but this occurs after combined liver-Fe therapy. NUTR. ABS. (m)

Filterable agent of Rous chicken sarcoma. W. NAKAHARA and H. NAKAJIMA (Gann, 1933, 27, 202—214).—The substance is poorly adsorbed on kaolin, but well on $\text{Al}(\text{OH})_3$, at p_{H} 7—10. Adsorption on $\text{Al}(\text{OH})_3$ is slight at p_{H} 4—6. After removal from $\text{Al}(\text{OH})_3$ (with $M/7\text{-NaH}_2\text{PO}_4$ or $N/25\text{-NH}_3$, but not by buffer solutions at p_{H} 4—6 or by glycine or $\text{NH}_4\text{H}_2\text{PO}_4$) the substance was much less active. CH. ABS.

Metabolism of heterotransplanted tumours. O. ROSENTHAL (Biochem. Z., 1933, 265, 413—421).—The carbohydrate metabolism of tumours arising in rats by transplantation of mouse sarcoma S 37 resembles that of the Jensen sarcoma in rats and differs from the original metabolism. The change in biochemical behaviour is discussed. P. W. C.

Relationship between tumour growth and blood-amino-acid content. S. L. MALOWAN (Arch. wiss. prakt. Tierheilk., 1932, 65, 279—284).—The presence of tumours produced no change in protein-N in men, but gave a lower val. in rats and mice; $\text{NH}_2\text{-N}$ was slightly raised in men and unchanged in rats and mice. In rats and mice there is no increased activity of the proteases in cancer. NUTR. ABS. (b)

Effect of X-rays on blood-gases and alkali reserve in cancer. A. GREMME (Arch. Gynakol., 1933, 152, 667—678).—In women, after irradiation

of carcinoma the alkali reserve of the blood falls concomitantly with the CO_2 tension, but the vals. generally rise to normal again. Sometimes the O_2 saturation of the blood falls, but not the CO_2 tension. NUTR. ABS. (m)

Cancer chemotherapy. XI. Effect of CO , HCN , and pituitrin on tumour growth. L. C. MAXWELL and F. BISCHOFF (J. Pharm. Exp. Ther., 1933, 49, 270—282).—Exposure of mice bearing transplantable tumours (I) to CO or HCN reduced the rate of increase of body-wt. (II) and of tumour growth (III), whilst treatment with sublethal doses of pituitrin reduced (II) but did not affect (III). Changes in the lipin (IV) and cholesterol of (I), and in the (IV) and glycogen of the body tissues, were not found. W. O. K.

Recent developments in the study of dental caries. R. W. BUNTING (Science, 1933, 78, 419—424). L. S. T.

Periodicity of carbohydrate metabolism and rhythmic functioning of the liver. Significance in insulin treatment of diabetes. J. MOLLERSTROM (Arch. Int. Med., 1933, 52, 649—663; cf. A., 1933, 302).—The periodicity of liver function is independent of meal times, and insulin therapy should be conducted in relation to the former rather than the latter. P. G. M.

Histochemical study of diabetic arteritis. F. RATHERY and S. DOUBROW (Compt. rend. Soc. Biol., 1933, 113, 56—57).—The fat in the intimal coat of the vessel in diabetic arteritis consists mostly of palmitates and stearates. Oleic fats would be most suitable in the diet for prophylaxis. NUTR. ABS. (m)

Hypercholesterolaemia. Disturbance of cholesterol excretion. R. SCHONHEIMER (Z. klin. Med., 1933, 123, 749—763; Chem. Zentr., 1933, ii, 1050).—The blood contained excess of cholesteryl ester. On ingestion of cholesterol (I), no (I) or dihydro-(I) was found in the faeces, but the latter was isolated from the blood. The condition was ameliorated by a vegetable diet. A. A. E.

Effect of organ extracts on blood-pressure of hypertonics and the blood-adenylic acid in pathological blood-pressure. K. A. BOCK (Z. ges. exp. Med., 1933, 87, 799—805; Chem. Zentr., 1933, ii, 567).—In hypertension of various origins there is no lack of blood-adenylic acid. A. A. E.

Glucose metabolism in hyperthyroidism. H. GOTTA and M. YRIART (Compt. rend. Soc. Biol., 1933, 113, 454—456).—In patients suffering from hyperthyroidism ingestion of glucose results in a rise of blood-sugar which is > that obtained with normal persons; nevertheless in the former more of the ingested glucose is oxidised than in the latter, as judged by the R.Q. The abnormal blood-sugar curves are therefore to be attributed rather to inadequate formation of glycogen in the liver than to deficiency of insulin secretion. NUTR. ABS. (m)

Inter-relations of liver functions. Rôle of glycogen in the physiology of the liver. F. K. GASSMANN (Z. ges. exp. Med., 1933, 88, 593—598).—The percentage output of bilirubin in patients with

hepatic inefficiency is increased by administration of sugar and diminished in hepatic disease and health by withdrawal of sugar by means of insulin injection. The improvement in hepatic function is attributed to increased formation of new liver-cells. Owing to the dependence of cell growth on glycolysis (I) and better (I) from fructose (II) than from glucose, (II) is said to be more efficient. NUTR. ABS. (m)

Storage of glycogen in the diseased liver after administration of different sugars. F. K. GASSMANN (Z. ges. exp. Med., 1933, 88, 599—604).—In the livers of dogs administration of fructose (I) leads to a much greater glycogenogenesis than does that of glucose (II); intravenous administration (III) gives the best results. Simultaneous injection of insulin increases glycogenogenesis with (II), but decreases it slightly with (I). In the treatment of hepatic disease in man (III) of 20—40 c.c. of 20% (I) or 10% (I) at the rate of 100 c.c. per hr. is recommended.

NUTR. ABS. (m)

Glycogen-storing disease. P. KIMMELSTIEL (Beitr. pathol. Anat., 1933, 91, 1—18).—Excessive deposits of glycogen (I) were found in the liver, brain, muscles, and heart of an infant which died of the disease; the kidneys contained little (I) and all other organs were free, whilst the deposits in the brain were localised. Diastatic fermentation of the child's liver-(I) was slower than that of (I) from dog's liver and commercial preps. An abnormal type of (I), resistant to diastase, is laid down in (I)-storing disease.

NUTR. ABS. (m)

Use of 3:5-di-iodothyronine in the treatment of myxœdema. A. B. ANDERSON, C. R. HARRINGTON, and D. M. LYON (Lancet, 1933, 125, 1081—1084).—3:5-Di-iodothyronine relieves symptoms of myxœdema, and restores and maintains the basal metabolic rate at an approx. normal level. L. S. T.

Clinical applications of dinitro-*o*-cresol. E. C. DODDS and J. D. ROBERTSON (Lancet, 1933, 125, 1137—1139, 1197—1198).—Dinitro-*o*-cresol (I) has a powerful action in increasing the metabolic rate in normal adults, but is of no use in alleviating symptoms of myxœdema. This indicates that the increase in metabolism induced by (I) may be different from the normal metabolic process. L. S. T.

Water excretion as a measure of equilibrium with environment. D. N. PARFITT (Brit. Med. J., 1933, i, 1102—1103).—In states of emotional tension there is a delay in H₂O secretion. A simple H₂O excretion test is described. The results show general agreement with those obtained by the hyperglycœmic index test on the same patients. Such tests give increased accuracy of prognosis in certain mental diseases. NUTR. ABS. (m)

Muscle-potassium in some neurological conditions. A. LEULIER, B. POMMÉ, and A. BERNARD (Compt. rend. Soc. Biol., 1933, 112, 1413—1414).—In cases of lower motor neurone lesions but not in parkinsonian post-encephalitis there is reduction in the K content of the affected muscles. In diphtheritic peripheral neuritis the affected quadriceps contains 3.11 mg. of K per 100 g., whilst the normal muscle contains 4.21. NUTR. ABS. (m)

Acid-base equilibrium in relation to œdema. O. L. E. DE RAADT (Klin. Woch., 1933, 12, 224—225).—Nephritic, nephrotic, and cardiac œdema are all due to acidosis due to insufficiency of the kidney or of the circulation. The formation of NH₄HCO₃ in acidotic tissues leads to retention of H₂O and NaCl for further neutralisation, through the reaction: NaCl + (NH₄)HCO₃ = NaHCO₃ + NH₄Cl. Hunger-œdema is due to the same mechanism.

NUTR. ABS. (b)

Behaviour of atoxyl-resistant lipase after gastric operations. H. DIBOLD and M. TAUBENHAUS (Klin. Woch., 1933, 12, 857—860).—After resection of the stomach an increased atoxyl-resistant lipase content of the blood is observed (12 out of 27 cases). Similar results are obtained in evident pancreatic disease (9 out of 11), but seldom in other cases (6 out of 39).

NUTR. ABS. (m)

Colloid-chemical investigations on the swelling of gelatin jellies in the serum of gynæcological patients. N. M. MOGILEVSKAJA (Kolloid-Z., 1933, 65, 234—236).—The effect of the blood-serum on the elasticity of a gelatin jelly gives an indication of disease. E. S. H.

Serum-calcium and -phosphorus during pregnancy. J. W. MULL and A. H. BILL (Proc. Soc. Exp. Biol. Med., 1933, 30, 854—856).—Serum-Ca shows a decline until about a week before delivery, when a rise begins and continues until the second week *post partum*. The vals. in the period Jan. to Apr. are generally < those in May to Dec. Serum-P decreases very slightly *ante partum* with a sharp rise just prior to and after delivery: it exhibits no seasonal variation. NUTR. ABS. (m)

Calcium content of the cerebrospinal fluid in normal pregnancy and in eclampsia. Cerebrospinal fluid-calcium in infants. D. F. ANDERSON (Brit. J. Exp. Path., 1933, 14, 155—159).—In eclampsia (16 cases) the Ca of the fluid ranges from 4.1 to 5.9 mg. (average 5.3) and in normal pregnancy (27 cases) from 4.3 to 6.2 mg. per 100 c.c. (average 5.2). These figures and others from cases taken at random are within physiological limits; abnormal variations which could be connected with the occurrence of convulsions are not found. In infants a few days old having convulsions the vals. range from 6.1 to 6.9 mg. per 100 c.c. (average 6.5).

NUTR. ABS. (m)

Carbohydrate metabolism in cases of unexplained miscarriages. E. C. P. WILLIAMS (Lancet, 1933, 225, 858—861).—A lowered tolerance for glucose has been observed in 90% of cases of unexplained repeated miscarriage. L. S. T.

Carbohydrate metabolism in pregnancy and after. I, II. Sugar and diastase in blood. P. GOLDSCHMIDT-FURSTNER (Arch. Gynakol., 1933, 153, 417—426, 427—433).—During pregnancy the diastatic activity of the blood falls progressively from the normal val., but rises again after parturition (I); the blood-sugar (II) rises during (I) and then falls. Injection of extracts of pituitary results in a rise of (II) and diastase (III), whilst injection of glucose or adrenaline results in a fall of blood-(III), which later

risers as (II) falls. The changes following the injection of insulin are irregular, but in general (III) falls and later rises. NUTR. ABS. (m)

Absorption and assimilation of protein in pregnancy. O. BOKELMANN and W. SCHERINGER (Arch. Gynakol., 1933, 153, 201—212).—The absorption of protein is the same in pregnant and non-pregnant women. During pregnancy there is no retention of NH_2 -acids, non-protein-N, or coagulable N in the blood; N is not retained in the tissue fluids. Hence the N is retained as protein in the tissues (probably in the liver). NUTR. ABS. (m)

Protein metabolism and renal function during pregnancy and the early puerperium. O. BOKELMANN and W. SCHERINGER (Arch. Gynakol., 1933, 153, 447—467).—In early pregnancy the metabolic effect of a large meal (650 g.) of meat is as in non-pregnant women. During the early puerperium the condition of N-sparing and reduced protein catabolism characteristic of pregnancy is reversed. A condition of functional renal insufficiency after parturition, distinct from true "pregnancy kidney," is evidenced by disturbances of acid-base equilibrium and NH_3 production after a protein meal: simultaneous administration of acid emphasises this condition. NUTR. ABS. (m)

Thyroid hormone and the blood of menstruating and pregnant women. C. MÜLLER (Arch. Gynakol., 1933, 153, 244—251; Chem. Zentr., 1933, ii, 404).—The hormone was not detected. A. A. E.

Parathyroid hormone in the blood in pregnancy. F. HOFFMANN (Arch. Gynakol., 1933, 153, 181—200; Chem. Zentr., 1933, ii, 404—405).—Blood-plasma of pregnancy affords a prep. which raises dogs' blood-Ca and has other properties of parathyroid hormone. A. A. E.

Potassium and sodium in regulation of mineral metabolism by the kidneys in renal disease. H. GLATZEL (Klin. Woch., 1933, 12, 853—855).—In nephritis (I) there is delayed excretion and lower concn. of Na and K in the urine. The total eliminated $\text{Na} + \text{K}$ in the same subject is the same whether the diet fed is rich in either. In (I) therefore a max. alkali concn. exists in the urine, in which Na and K can replace each other to a certain extent. In normal subjects on acid or alkaline diet the acid-base equilibrium (III) of the blood and tissues is maintained mainly by the excretion of NH_3 or org. acids, and Na, Ca, and Cl, K taking no part in this regulating mechanism (II). In kidney diseases (II) is upset and (III) can be maintained only by the help of the fixed ions. The excretion of K then plays an important part in the regulation of p_{H} , so that a significant loss of K may result. NUTR. ABS. (m)

Calcium content of muscles and liver of normal and starved guinea-pigs, or afflicted with acute or chronic scurvy. A. MICHAUX (Compt. rend., 1933, 197, 1453—1455).—The muscle-Ca of guinea-pigs fed on a scorbutic diet is the greater the larger is the dose (4—5%) of Ca lactate added to the normal diet, and is very high in severe cases of acute or chronic scurvy, but the liver-Ca is < in animals fed

on a normal diet, and is approx. the same as in those given distilled H_2O only. All animals received only H_2O for the 15 hr. preceding death. J. W. B.

Silicosis. W. R. JONES (J. Chem. Met. Soc. S. Africa, 1933, 34, 99—123).—The mineral in silicotic lungs responsible for the disease consists of minute acicular fibres, usually sericite and not quartz (cf. A., 1933, 1192). Preventive methods are discussed. W. O. K.

Variations in blood-sugar after splenectomy. F. RATHERY and I. COSMULESCO (Compt. rend. Soc. Biol., 1933, 113, 548—551).—The changes in the sugar content of the blood of dogs, produced by splenectomy, are variable. NUTR. ABS. (m)

Effect of work on gas exchange in pulmonary tuberculosis. T. EBINA and I. SATO (Tôhoku J. Exp. Med., 1933, 21, 125—136).—As regards O_2 consumption (I) tuberculous subjects are divided into: (a) those with markedly increased (I) during work and a quick return to the resting val.; (b) those with a smaller increase during work and a prolonged recovery period; and (c) those who behave like controls. NUTR. ABS. (m)

Plasma-phosphatase in pulmonary tuberculosis. L. BINET and J. PAUTRAT (Compt. rend., 1933, 197, 945—946).—The phosphatase content of venous plasma increases in fibrous pulmonary tuberculosis. A. C.

Lipolytic power of the liver of the normal and the tuberculous pig. M. GHIRON (Annali Chim. Appl., 1933, 23, 495—501).—A glycerol extract of pig's liver (previously extracted with COME_2 and Et_2O) shows marked lipolytic action on tributyrin, PrCO_2Me , neutral olive oil, and fats extracted from dried tubercle bacilli by COME_2 , the last being emulsified in a system of activators formed from CaCl_2 and ovalbumin. The results obtained similarly with an extract of tuberculous pig's liver indicate that the disease stimulates the production of lipolytic enzymes of the liver (cf. B., 1932, 622). T. H. P.

Micro-incineration of tubercles. E. R. LONG (Proc. Soc. Exp. Biol. Med., 1933, 30, 1090—1092).—The nuclei of the cells (man, guinea-pig) ignited at 540° for 4 hr. are richest in ash (I), and the cytoplasm is generally low in mineral content. The (I) from regions of degeneration and necrosis is < that of corresponding undegenerated tissue because sol. mineral material diffuses away. In late stages of human tuberculosis there is increase of (I) in the necrotic tissue. In tuberculous rabbits treated with viosterol remineralisation seems to increase. NUTR. ABS. (m)

Gastric pepsin. II. Secretion of pepsin in cases of duodenal ulcer and pseudo-ulcer. F. R. VANZANT, A. E. OSTERBERG, W. C. ALVAREZ, and A. B. RIVERS (J. Clin. Invest., 1933, 12, 557—565).—In cases of healed duodenal ulcer peptic activity (I) generally fell within normal limits, although the average was above normal. In cases with definite symptoms of duodenal ulcer the average (I) was 2.5 times the normal mean, with gastric ulcer it was only slightly > normal, and with duodenal or jejunal ulcer after gastro-enterostomy (I) was high.

In patients with symptoms of duodenal ulcer but in whom this was not present it was as high as in the ulcer patients. This test is a more sensitive index than the determination of free HCl.

NUTR. ABS. (b)

Physiology of bone-marrow. K. FELIX, A. GRASSMUCK, K. HUCK, and K. MATZEN (Z. physiol. Chem., 1933, 221, 137—144).—The O_2 uptake of red marrow (I) of calves is 0.28—0.32 c.c. per g., of fatty marrow (II), 0.09—0.15 c.c. in 5 hr. The optimum p_H is 8.3. The purine-N of (I) is 0.18—0.24%, of (II) 0.06—0.08%. The O_2 uptake increases with the purine-N content. It is also increased by alanine, the anti-anæmic and other substances in preps. from liver and gastric mucosa, probably by proline and tryptophan, but not by aspartic or glutamic acid, glycine, or glycylglycine. J. H. B.

Effect of restricted diet on oxidative processes. I. KANAI (Z. ges. exp. Med., 1933, 88, 725—732).—In rats fed on diets consisting chiefly of protein (I), fat, or carbohydrate (II), respectively, the C:N and "Vacat"-O (III):N ratios are low with (I) and high with fat and (II). (III):C is lowest with (I) and highest with (II). The total amount of (III) is greatest with (I). Although the total amount of incompletely oxidised material in the urine is greatest with (I), oxidation during intermediate metabolism is then relatively much better.

NUTR. ABS. (m)

Respiration of *Diphyllobothrium latum* (L.). Respiration enzymes. E. A. H. FRIEDHEIM and J. G. BAER (Biochem. Z., 1933, 265, 329—337).—The respirations of *D. latum* (egg, larva, and adult) and of *Tricnophorus lucii* (adult) are not inhibited by CO in presence of only 5% O_2 , the effects being the same for anaerobically living worms and aerobically developing eggs. The KCN inhibition, however, is incomplete with the worm, but complete with the egg. The presence of cytochrome c is indicated.

P. W. C.

Eosin and tissue respiration. R. DEL ZOPPO (Arch. Farm. speriment., 1933, 56, 536—542).—Intravenous injection of 20—30 c.c. of 1% eosin into rabbits causes a diminution of respiratory activity of the liver, kidney, spleen, and testicle, and an increase in O_2 content of the blood, particularly venous blood.

R. K. C.

Intermediate metabolism of the endocrine glands. A. UTEVSKI, S. EPSTEIN, V. OSSINSKAJA, and E. MIMA (Biochem. Z., 1933, 265, 320—328).—The thymus (I) and thyroid (II) glands contain small amounts of glycogen. In the ox, the lactic acid (III) content of (I) is much > that of (II). The (III) content of the glands in exophthalmic goitre (IV) and strumatic diseases is much > in the glands of normal animals. Alanine increases the formation of (III) in (I), but not in (II). In (IV) the formation of (III) is slightly increased in presence of alanine. MeCHO is formed only in small amounts in both (I) and (II), which are poor in carboxylase. The amount of MeCHO is increased on adding glycogen or glucose.

P. W. C.

Fate in the animal body of anthocyanins from Concord grapes. M. K. HORWITT (Proc. Soc. Exp.

Biol. Med., 1933, 30, 949—951).—Anthocyanins are not easily absorbed from the intestine. The small quantity which passes through is apparently excreted unchanged by the kidney.

NUTR. ABS. (m)

Changes in blood-constituents produced by partial inanition and muscular fatigue. F. W. SCHLUTZ, A. B. HASTINGS, and M. MORSE (Amer. J. Physiol., 1933, 104, 669—676).—In dogs, blood analysis shows that swimming is much more fatiguing than treadmill exercise. Exercise accompanied by under-nutrition produces changes in the same direction, but of greater magnitude than in the normal animal. Return to the normal level is delayed in malnutrition.

NUTR. ABS. (m)

Rigor of muscle and changes induced by various physiological factors. I. Calf muscle of guinea-pigs and rats. W. LENKEIT (Arch. Tierernähr. Tierzucht, 1933, 9, 266—349).—Relationships are examined between the post-mortal rigor of muscles and their colloidal condition as shown by H_2O -absorbing properties when placed in contact with hyper-, iso-, and hypo-tonic solutions of alkali chlorides.

A. G. P.

Effect of p_H on carbohydrate changes in isolated anaerobic frog muscle. M. KERLY and E. RONZONI (J. Biol. Chem., 1933, 103, 161—173).—During anaerobic breakdown of muscle-carbohydrate at an alkaline reaction the lactic acid (I) increase balances the carbohydrate (II) decrease, there is a small increase in hexose monophosphate (III), and the formation of lower (II) from glycogen (IV) is small. As the reaction becomes more acid, (I) decreases while (III) increases to balance (II). At p_H 6 considerable quantities of glucose and an intermediary (II) are formed from (IV).

H. G. R.

Disappearance of hexose phosphate from intact frog muscle. E. RONZONI and M. KERLY (J. Biol. Chem., 1933, 103, 175—181).—Under anaerobic conditions at p_H 6, 70—80 mg. of hexose phosphate (I) are formed per 100 g., the phosphocreatine (II) almost completely hydrolysed, and 50% adenosine triphosphate (III) is dephosphorylated in 2½ hr., but no lactic acid (IV) is formed. On treatment with O_2 the normal level for these substances is again reached, with increased consumption of O_2 which becomes normal when (II) is reconstituted. In N_2 at p_H 9, the breakdown of (II) is slower with little change in (I) and a normal production of (IV). There is no reconstitution of (II) and (III).

H. G. R.

Chemical processes accompanying the activity of muscle. E. M. KREPS (J. Physiol. U.S.S.R., 1932, 15, 258—275).—A summary.

T. H. P.

[Carbohydrate metabolism in muscle.] A. HAHN (Z. Biol., 1933, 94, 97—98).—Meyerhof's views (A., 1933, 742) of the source of $AcCO_2H$ in muscle extracts and of the presence of natural H acceptors are discussed.

A. G. P.

Lactic acid metabolism of the dog's isolated heart. A. RUHL and H. ROLSHOVEN (Klin. Woch., 1933, 12, 776—777).—The amount of lactic acid (I) removed from the blood by the heart is not increased when the work of the heart-muscle is increased. Poisoning of the heart with histamine, somnifen, and

avertin does not decrease removal of (I) nor does treatment with strophanthin, caffeine, or adrenaline. The amount removed is greater when the blood-(I) is high. Synthesis of carbohydrate from the lactate (II) is assumed, although there is no connexion between the O_2 uptake and the amount of (II) absorbed. After poisoning with cyanide, the heart loses (II).

NUTR. ABS. (m)

Bile acids and carbohydrate metabolism. XXIX. Influence of bile acids on tissue oxidation and carbohydrate utilisation. Z. URAKI (J. Biochem. Japan, 1933, 18, 207—225).—Dehydrogenation and the oxidation of glucose, fructose, glycogen, and glycerophosphoric, lactic, and succinic acids by muscle- and liver-tissues are inhibited by cholic acid; the oxidation of hexose mono- and di-phosphate is, however, not influenced. The mechanism of the inhibition is discussed.

F. O. H.

Is d-glucose absorbed from the dog's stomach? S. J. MADDOCK, H. C. TRIMBLE, and B. W. CAREY, jun. (J. Biol. Chem., 1933, 103, 285—294).—Determination of the glucose in the blood from the peripheral and intra-abdominal vessels of dogs with ligatured pylori before and after ingestion of glucose in quantities of from 5 to 27 g. shows practically no gastric absorption; a similar result was obtained by a method dispensing with the use of anaesthetics and fistulae.

H. D.

Citric acid metabolism. A. C. KUYPER and H. A. MATTILL (J. Biol. Chem., 1933, 103, 51—60).—Serum-citrate is decreased by alkalosis (I) and inanition and increased by acidosis (II). Citric acid (III) in urine is increased after meals and by (I) and decreased by (II) and exercise. (III) is not completely oxidised by the human organism, and no correlation was observed between the oxidation and any particular tissue.

H. G. R.

[Glycuronic acid.] I. Origin in the urine of rabbits. C. O. MILLER and J. CONNOR. II. Metabolism in the dog. C. O. MILLER, F. G. BRAZDA, and E. C. ELLIOT. III. Glycuronic acid as a growth factor in guinea-pigs. C. O. MILLER, A. E. SIEHRS, and F. G. BRAZDA (Proc. Soc. Exp. Biol. Med., 1933, 30, 630—633, 633—636, 636—638).—I. The rabbit is apparently unable to synthesise glycuronic acid (I) from carbohydrates (II) or NH_2 -acids (III), or only very slowly. The acid, which is produced by the digestion of mucin, was readily available when required by the body for combination with certain toxic substances.

II. The dog is probably provided with a store of (I) or may be able to synthesise it from (II) or (III). When stores of (I) were depleted, borneol given by stomach tube rapidly exerted a toxic effect. Mucin, included in the diet, protected against comparatively large doses of borneol, presumably because of (I) provided by its digestion.

III. (I) did not protect guinea-pigs on a scorbutic diet from developing scurvy nor reduce the severity of the disease. It did, however, postpone the period of loss of wt., and facilitated wt. recovery when orange juice was added to the diet. Like the rabbit, the guinea-pig either cannot synthesise (I), or only slowly.

NUTR. ABS. (b)

Nutritive value of calcium gluconate. T. TAKAHASHI, T. ASAI, and M. KANEKO (J. Agric. Chem. Soc. Japan, 1933, 9, 567—572).—Ca as $CaCl_2$, $CaCO_3$, lactate, and gluconate (I) was given to rats (0.6% of standard feed); (I) was the best source of Ca.

CII. ABS.

Complete utilisation of heat of combustion of ethyl alcohol by homeotherms in thermoneutrality. E. LE BRETON and G. SCHAEFFER (Compt. rend., 1933, 197, 1066—1068).—In warm-blooded animals in a temp. thermally neutral, the ingestion and combustion of EtOH does not result in the liberation of extra heat.

W. O. K.

Glycogen formation in the white rat after oral administration of propionic, butyric, valeric, and hexoic acids. H. C. ECKSTEIN (J. Biol. Chem., 1933, 102, 591—594).—Using the Cori technique, increases in liver-glycogen (I) are shown to result from the administration of $EtCO_2H$. With butyric, valeric, and hexoic acids, no increase in (I) was apparent, although absorption had taken place. Mobilisation of body-glycogen did not occur throughout the experiments.

A. L.

Dietary production of fatty livers in rats. N. R. BLATHERWICK, E. M. MEDLAR, P. J. BRADSHAW, A. L. POST, and S. D. SAWYER (J. Biol. Chem., 1933, 103, 93—106).—Fatty livers are produced by feeding whole liver or eggs, whereas lecithin tends to decrease the fat, which appears to be that normally present. Lipins of blood and kidneys are not materially altered.

H. G. R.

Physiology of intermediate metabolism after Claude Bernard's piqure. IV. Alkali reserve and blood-chloride. V. Residual nitrogen and certain other blood-components. G. D. OBRATZOV, E. T. MINKER-BOGDANOVA, and M. N. KALLINKOVA (J. Physiol. U.S.S.R., 1932, 15, 206—211, 212—217).—With the rabbit, piqure causes alteration of the acid-base equilibrium, the alkali reserve falling and the blood-Cl' rising at once, but gradually becoming normal later. The residual N undergoes no sp. change, inorg. PO_4''' increases, org. PO_4''' and Ca decrease, and K shows no clear change. From these and earlier results it appears that piqure causes, besides hyperglycaemia, other changes in the blood-components similar to those produced by adrenaline.

T. H. P.

Calorigenic action of glycine. H. G. LEWIS and J. M. LUCK (J. Biol. Chem., 1933, 103, 227—233).—In doses above 0.6 g. per kg. body-wt. glycine (I) administered subcutaneously to fasting rats produces an excess metabolism < that produced by (I) administered orally. Above 2.2 g. (I) is toxic, and often produces a lowered metabolic rate. The increased metabolism induced by moderate doses occurs soon after dosage and lasts > 1 hr.

H. D.

Specific dynamic action of protein and its relation to post-prandial excretion of urea. E. MAY and A. MEYER-HEINE (Compt. rend. Soc. Biol., 1933, 112, 1311—1313).—In normal subjects 1½ hr. after a test meal of 200 g. veal, 100 g. bread, and 100 c.c. H_2O there is an average increase of 20% in the metabolic rate (min. increase 10%). Urea excre-

tion during the same period runs parallel to the sp. dynamic action. NUTR. ABS. (m)

Blood-urea and nutrition. G. V. DERVIS and A. V. LYSLOVA (J. Physiol. U.S.S.R., 1932, 15, 439—445).—On a meat diet the blood-urea (I) is 2—3 times that on a carbohydrate (II) diet and even greater when meat is taken without drinking. A single meal of meat produces a considerable rise in (I), which reaches a max. in 8 hr. A single meal of (II) produces a small decrease in (I). H. D.

Residual nitrogen and creatinine on different diets. E. A. KAFIYEVA (J. Physiol. U.S.S.R., 1932, 15, 446—450).—On a meat diet (I) the residual N (II) is twice as great as on a carbohydrate diet. The increase of creatine-creatinine (III) on (I) runs parallel with that of (II), the increase of N corresponding with the increase in (III) being 5% of the increase in (II). H. D.

Effect of restriction of protein intake on the serum-protein concentration of the rat. A. L. BLOOMFIELD (J. Exp. Med., 1933, 57, 705—720).—Rats receiving for 21 weeks a diet low in protein (2.6% from yeast and 0.3% from lucerne), but otherwise adequate, show no significant decrease in the serum-protein except for an initial fall of about 10%. NUTR. ABS. (m)

Nutritive protein value of five varieties of rice. A. J. HERMANO (Philippine J. Sci., 1933, 51, 567—572).—Young rats fed on a diet containing approx. 5—10% of protein never attained normal maturity. Mancasar rice, although containing less protein than three other varieties, appears to have the highest nutritive val. No relation exists between ash, carbohydrate, and fat contents, and nutritive val. P. G. M.

Comparative study of the paired and *ad libitum* feeding methods for determining amino-acid deficiencies of foods. C. L. SHREWSBURY and J. W. BRATZLER (J. Assoc. Off. Agric. Chem., 1933, 16, 582—584).—Statistical analysis of the results obtained with rats using 10 and 15% of soya-bean protein in a purified diet and 6% as a supplement to maize showed that paired feeding (with equalised consumption) gave the more trustworthy results. J. G.

Outlook in the science of nutrition. L. B. MENDEL (Science, 1933, 78, 317—322).—A survey. L. S. T.

Metabolism in high external temperatures on different diets. A. A. MITTELSTEDT (J. Physiol. U.S.S.R., 1932, 15, 424—438).—Men were maintained in a room at 50° and 29 mm. aq. v.p. on a diet (I) containing sufficient protein and on one (II) deficient in protein. On (I) retention of N and no increased intensity of oxidation (III) were observed, whilst on (II) increased N excretion and increased (III) occurred. Cl⁻ excretion on (I) was > that on (II). The excretion of salts showed no regularities. H. D.

Chemistry of embryonic growth. III. Embryonic growth of the pig in relation to nitrogen compounds. V. A. WILKERSON and R. A. GORTNER (Amer. J. Physiol., 1932, 102, 153—166).—Total N remains const. after the embryo has reached 50 mm., following an early fall. Glutathione and S increase

rapidly up to 30—50 mm. and then gradually decrease. H₂O content is const. from 15 to 160 mm. after an initial rapid decline, and then decreases gradually until after birth. The arginine content is highest in young embryos; histidine and tyrosine also decrease during development. There is a continuous rise in ash content up to 240 mm. P. G. M.

Influence of varied nutrition of pregnant sows on the development of the piglings. D. DJAPARIDSE (J. Landw., 1933, 81, 249—280). A. G. P.

Uric acid synthesis in the bird. I. Pigeon. II. Hen and goose. W. SCHULER and W. REINDEL (Z. physiol. Chem., 1933, 221, 209—231, 232—240; Klin. Woch., 1933, 12, 736—738).—I. Both liver and kidneys are concerned in uric acid synthesis in the pigeon. An unknown precursor (not a purine) is produced in both organs by an enzymic reaction with p_H and temp. optima of 7.6—7.7 and 40°, respectively. The same precursor is present in muscle and other organs, but is not there produced by enzymic synthesis. The actual synthesis of uric acid from the precursor takes place only in the kidney. This reaction has an optimum p_H of 7.1 and is a function of living tissue. The N sources for the synthesis are NH₂-acids (degraded by way of NH₃) but not urea. The sources of C are not glycerol, or lactic or tartronic acid.

II. In the hen and goose the synthesis of uric acid follows the same course as in the pigeon, but here the surviving liver as well as kidney tissue is able to transform the precursor into uric acid. The precursor is identical in all three species. J. H. B.

Purine metabolism in fish and amphibia. E. STRANSKY (Biochem. Z., 1933, 266, 287—300).—Fish and amphibia excrete urea (I). Uric acid (II) and allantoin (III) cannot be detected with certainty in frog's urine. The livers of these animals convert (III) and (II) by way of (III) into (I). (III) and allantoinic acid (IV) give a positive Ehrlich aldehyde reaction. (III) and (IV) may be differentiated by xanthohydrol. The glyoxylic acid reaction is not characteristic for (III) and is given strongly by (IV). Vertebrates are classified according to the end-products of their purine and protein metabolism. P. W. C.

Rate of change of alkali reserve after ingestion of organic salts. I. Normal variations in acid-base balance under basal conditions. J. CAPE and E. L. SEVRINGHAUS (J. Biol. Chem., 1933, 103, 257—260).—The p_H , CO₂ content, and total base in the sera of normal individuals under basal conditions showed no significant variations over a morning period of 5 hr. H. D.

Calcium and phosphorus metabolism of normal young children. II. Variation in calcium and phosphorus storage. T. PORTER-LEVIN (J. Amer. Dietetic Assoc., 1933, 9, 22—35).—The mineral intake of children is remarkably const. (average Ca intake 1.010±0.004 g. per day; average P intake 1.050±0.004 g.). The average excretion of Ca is 87 and of P 83%. The average "per kg." retentions (I) are 0.007 g. Ca and 0.008 g. P per day, but the retentions vary greatly from period to period, P retention being slightly less variable than that of Ca.

15 to 21 consecutive days are required to cover the entire range of variation in these (I).

NUTR. ABS. (m)

Relation of milk ingestion to calcium metabolism in children. A. L. DANIELS, M. K. HUTTON, E. KNOTT, G. EVERSON, and O. WRIGHT (Proc. Soc. Exp. Biol. Med., 1933, 30, 1062—1063).—The amount of Ca, P, and N retained by a child on an adequate or abundant consumption of milk depends primarily on physiological condition. When the previous diet has been below requirements, more of these factors is retained, at least in earlier stages, than if the previous diet had been adequate. Well-nourished children retain approx. the same quantity of Ca whether receiving a pint or a quart of milk per day.

NUTR. ABS. (m)

Effect of calcium-deficient roughages on milk-production and welfare of dairy cows. R. B. BECKER, W. M. NEAL, and A. L. SHEALY (Florida Agric. Exp. Sta. Bull., 1933, No. 262, 28 pp.).—Cows on low-Ca pasture from acid sandy soils showed lowered bone strength, and milk yields were subnormal even when high-protein supplements were used. Addition of 2% bone meal and 5% lucerne hay increased bone strength to > normal and increased milk yields without additional storage of fat. The Ca and P required for reproduction was much < that for lactation.

A. G. P.

Iron in the nutrition of infants. III. Metabolism of iron in infants breast-fed for the first year. A. WALLGREN (Rev. franc. Pediat., 1933, 9, 196—235).—The daily Fe balance varied from -0.274 to +1.054 mg., but was usually positive. The retention of Fe was less in the first 5 months, but there was no fall in blood-haemoglobin even when the Fe balance was negative. The amount of Fe contained in breast-milk (average 0.642 mg. per 1000 g.) was sufficient for the requirements of the infants. The Fe contained in the tissues of the normal, new-born infant together with that liberated from dead red cells may amplify the small intake. The relatively large amounts of Fe found in the faeces in the early months indicate that some of the endogenous Fe is excreted.

NUTR. ABS. (b)

Copper and iron as dietary factors. H. L. KEIL, H. H. KEIL, and V. E. NELSON (Proc. Soc. Exp. Biol. Med., 1933, 30, 1153—1155).—Normal haemoglobin regeneration in milk-fed anæmic rats occurs with 0.15 mg. colloidal Fe and 0.002 mg. CuSO_4 injected intraperitoneally, daily, in addition to a daily oral dose of 0.5 mg. Fe as FeCl_3 . Rats on milk, Cu, and Fe in the first generation reproduce as well as do rats on a mixture of NaI, NaF, K_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, MnSO_4 , and Na_2SiO_3 , but in the former case, the mortality of the young is considerably greater and their wt. at birth is less.

NUTR. ABS. (m)

Action of copper and other elements in iron metabolism. E. MUNTWYLER and R. F. HANZAL (Proc. Soc. Exp. Biol. Med., 1933, 30, 845—846).—Administration of Fe for 14 days to rats rendered anæmic by a milk diet results in increase in the Fe content (I) of the liver and improvement in the blood count (II). Succeeding administration of milk diet only causes decrease in (I) and (II). Addition of Cu

only, as a dietary supplement at the end of this period, produces a rise in (II), but a fall in (I). The Cu mobilises the Fe stores of the liver to produce haemoglobin and erythrocytes.

NUTR. ABS. (m)

Chlorine metabolism. II. Blood-chlorine and -nitrogen after chlorine-free and low-chlorine diets. III. Blood-chlorine and -nitrogen after administration of sodium chloride. G. FERRO-LUZZI (Arch. Farm. speriment., 1933, 56, 477—486, 502—511; cf. A., 1933, 531).—II. With a Cl-free diet patients suffer general discomfort after 8—10 days, and the urinary Cl falls, but neither Cl nor N in the blood changes significantly. The diet is better tolerated after addition of milk.

III. After ingestion of 10 g. of NaCl by human patients the blood-Cl rises markedly and the blood-N slightly, whilst the no. of red corpuscles falls. The rise in blood-N is regarded as an effect of functional interference with the kidney as a result of varying the mol. concn. of the blood.

R. K. C.

Action of the brain cortex on respiration. R. P. OLNJANSKAYA (J. Physiol. U.S.S.R., 1933, 15, 314—329).—Mental stimuli and irritants acting on persons doing work cause changes in the rate of respiration.

A. L.

Widmark's method for determining blood-alcohol and its forensic significance. J. KOLLER (Deut. Z. ges. gerichtl. Med., 1933, 21, 269—274; Chem. Zentr., 1933, ii, 915).—The method is satisfactory; the significance of the results is discussed.

A. A. E.

Action of amino-acids on the alcohol content of blood. E. M. P. WIDMARK (Biochem. Z., 1933, 265, 237—240).—Addition of glycine or alanine to an alcoholic drink administered to fasting dogs leads to a decreased blood-EtOH during the post-absorptive period.

P. W. C.

Anæsthetic action of a series of naphthalene derivatives. M. E. FISK and F. P. UNDERHILL (J. Pharm. Exp. Ther., 1933, 49, 329—336).—Of seven compounds tested of the general formula

$\text{R}\cdot\text{CO}_2\cdot[\text{CH}_2]_n\cdot\text{NAlk}_2$ ($n=2$ or 3 and $\text{R}=\text{C}_{10}\text{H}_7$, $\text{OH}\cdot\text{C}_{10}\text{H}_6$, or $\text{OEt}\cdot\text{C}_{10}\text{H}_5$), all possess local anæsthetic action, but most produce considerable local irritation. $\text{NEt}_2\cdot[\text{CH}_2]_3$ 2-ethoxy-3-naphthoate was superior to the others.

W. O. K.

Effect of calcium administration on the toxicity of carbon tetrachloride in mice. F. WOKES (Quart. J. Pharm., 1933, 6, 413—417).—Addition of CaCO_3 (0.2—3%) or Ca lactate (0.15—0.3 g. per kg.) to the diet produced no and a slight protection again the poison, respectively.

R. S. C.

Variation in the susceptibility of mice to certain anæsthetics. J. C. GAGE (Quart. J. Pharm., 1933, 6, 418—426).—The ratio anæsthetic dose/toxic dose for mice for paraldehyde and avertin *per rectum*, nembutal and pernocton intravenously, is about 1 : 2, the doses causing anæsthesia for 1 hr. being about 0.1 c.c., 0.03 c.c., 6 mg., and 0.06 c.c. per 100 g. body-wt., respectively. A small proportion of mice is abnormally susceptible.

R. S. C.

Permeability of the placenta to barbituric acid derivatives. R. FABRE (J. Pharm. Chim., 1933,

[viii], 18, 417—418).—Veronal passes unchanged through the placenta, and may be detected in foetal blood and organs. S. C.

Copper metabolism. II. Copper content of liver. S. SUMEGI (Frankfurter Z. Path., 1933, 44, 490—507).—In the livers of rabbits poisoned with CHCl_3 a severe necrosis of the central zone of the lobuli is of fibrinous character at first, but after some weeks regeneration takes place. The Cu content of the CHCl_3 -livers is increased above the max. normal val. in 58% of the cases and is independent of the amount of CHCl_3 given. After some weeks the difference decreases, but persists even if large amounts of Cu be given. A pigment containing a varying amount of Cu appears mostly in the healthy liver cells and represents a definite stage in excretion. The necrotic cells do not contain it; the regenerated cells only slowly acquire the power of excreting it. Hæmosiderosis was observed especially at the beginning of the Cu injections as a result of the hæmotoxic action of Cu. The increase of Cu found in human cirrhotic livers is the result of acute parenchymatous lesions. NUTR. ABS. (b)

Effect of anaesthetics on blood-sugar before and after bulbar puncture. J. VIDAL (Compt. rend. Soc. Biol., 1933, 112, 760—762).—With the rabbit, neither somnifen nor chloralose has any appreciable effect on the blood-sugar level, but they inhibit piqure hyperglycæmia (I). Urethane causes slight (I), but does not prevent piqure-(I).

NUTR. ABS. (b)
Disturbances of carbohydrate metabolism in narcosis. Effect of pernocton on carbohydrate metabolism. H. HELLER and P. NATHAN (Deut. med. Woch., 1933, 59, 956—958).—Changes (hyperglycæmia, loss of liver-glycogen) in carbohydrate metabolism during general anaesthesia may be dangerous. Since pernocton (I) anaesthesia has no effect on blood-sugar or blood-lactic acid, (I) is recommended for diabetics and in liver disease. NUTR. ABS. (m)

Nervous regulation of blood-sugar. Decerebration hyperglycæmia. J. J. R. MACLEOD and S. DONHOFFER (Klin. Woch., 1933, 12, 778—781).—Puncture of the floor of the fourth ventricle of the brain of starved, deeply anaesthetised (barbituric derivatives) rabbits does not produce hyperglycæmia (I). In rabbits, similarly starved and under intravenous amytal or local anaesthesia, decerebration (II) at the pons, but not at other levels, produces a considerable (I). (I) is not necessarily accompanied by a diminution of liver-glycogen, but practically always by a fall of muscle-glycogen (III); the total glycogen which disappears is insufficient to account for (I). Blood-lactic acid is increased, probably from (III). The respiratory exchange is unaffected. In normally fed animals (I) is prevented by double adrenalectomy, vagotomy, and atropine or atropine and ergotamine; when the liver contains much glycogen (> 5%) (II) leads to (I) under these conditions. Two physiological types of glycogen are postulated: (a) a storage form which is readily released by a stimulus unaffected by atropine etc.; (b) a gluconeogenic form, a new product from protein and fat, the release of which requires other conditions. Amytal and luminal arrest

the decerebration (I), an effect connected with the absence of rise of blood-sugar with these anaesthetics.

NUTR. ABS. (m)

Operative interference with carbohydrate metabolism. Y. KOMATSU (Arch. klin. Chirurg., 1933, 174, 65—97).—Postprandial hyperglycæmia (I) of the dog is less pronounced after denervation (II) of the liver; adrenaline hyperglycæmia (III) is usually affected in a similar way. These changes occur a few days after operation and remain fairly const. (I) and (III) increase after partial removal of the pancreas (IV). This effect may diminish in a few months, but never disappears completely. 3—4 months after (IV). (II) reduces (I) to a normal level, provided no severe diabetes has meanwhile developed. Simultaneous (II) may suppress completely the effect of (IV). (II) has no effect on (III) after (IV).

NUTR. ABS. (b)

Blood-sugar-depressant principle of onions (*Allium sativum*) active per os. I. P. LALAND and O. W. HAVREVOLD (Z. physiol. Chem., 1933, 221, 180—196).—Onion extract administered per os depresses the blood-sugar (I) of rabbits and depancreatized dogs. The active principle is volatile in steam and sol. in Et_2O . A substance is also present which increases (I). The depressant fractions lost their activity in 1—10 days at 0°. By fractionation in high vac. and recrystallisation, an *alkaloid* (?), m.p. 174°, was isolated. The presence of S, which occurs in the active fractions as allyl and diallyl sulphides, together with the alkaloid, appears necessary for the production of the effect. A "picrate fraction" obtained from potatoes had a similar depressant effect on (I). J. H. B.

Substances decreasing blood-pressure. I. M. TOKI, Z. MIYOSHI, and N. UYEDA (J. Agric. Chem. Soc. Japan, 1933, 9, 625—631).—The depressor substance in yeast is insol. in org. solvents and stable towards enzyme action. When yeast is autolysed the pressor substance, unstable and sol. in EtOH , is produced and then disappears; finally only the depressor action is retained. CH. ABS.

Effect of cocaineisation on the depressor action of limiting doses of β -methyladrenaline. RAYMOND-HAMET (Compt. rend. Soc. Biol., 1933, 112, 452—453; Chem. Zentr., 1933, ii, 897).

Detoxication of veronal with ephedrine. L. NIERHOFF (Z. ges. exp. Med., 1933, 88, 430—436; Chem. Zentr., 1933, ii, 740).—In rats and cats the abs. mortality after veronal poisoning is not diminished by ephedrine, although in 50% of the cases it produced a favourable symptomatic-therapeutic effect.

A. A. E.

[Pharmacology of] morphine, codeine, and their derivatives. III. Morphine methochloride and codeine methochloride. N. B. EDDY (J. Pharm. Exp. Ther., 1933, 49, 319—328).—The methochlorides (I) of morphine (II) and codeine (III) exhibit many of the pharmacological actions of (II) and (III), but usually in diminished strength, and the differences between the two quaternary salts are generally similar to those between (II) and (III). Both (I) have a curare-like action on frogs. W. O. K.

Relative activity of ergotamine and ergotamine. Assay of ergot preparations. E. LOZINSKI, G. W. HOLDEN, and G. R. DIVER (Quart. J. Pharm., 1933, 6, 395—398).—Ergot alkaloids contain about 60% of ergotamine (I). Ergotamine (II) has about 60% of the biological activity of (I). Agreement between the colorimetric determination and biological assay using (II) as standard is a result of these relations.

R. S. C.

Pharmacology of acetyl- β -methylcholine and the ethyl ether of β -methylcholine. J. H. COMROE, jun., and I. STARR, jun. (J. Pharm. Exp. Ther., 1933, 49, 283—299).—The actions of acetyl- β -methylcholine (I) and of β -methylcholine Et ether (II) on animals closely resemble that of muscarine and are similar to the effect of stimulation of the parasympathetic together with peripheral vasodilation. (I) is more active than (II).

W. O. K.

Hippuric acid in the animal organism. VII. Hydrazine intoxication and hippuric acid synthesis in the rabbit. V. T. TULANE, A. A. CHRISTMAN, and H. B. LEWIS. IX. Rate of synthesis and excretion of hippuric and phenacetic acids by the rabbit. V. T. TULANE and H. B. LEWIS (J. Biol. Chem., 1933, 103, 141—150, 151—160).—VII. Synthesis and excretion of hippuric acid (I) are delayed by N_2H_4 intoxication. The decreased excretion of (I) in the early stages is not accompanied by increased excretion of $BzOH$ (II) in any other form.

IX. When $CH_3Ph\cdot CO_2Na$ (III) is fed, the excretion of phenacetic acid (IV) is small, but increases to 6% when (II) is added and to 21% with glycine. The time for excretion of "extra" (IV) when (III) is fed is considerably > for (I) when (II) is fed.

H. G. R.

Excretion of foreign protein. Prolonged albuminuria due to injection of egg-white. L. BRULL (Compt. rend. Soc. Biol., 1933, 113, 67—69).—In dogs receiving subcutaneous injections of ovalbumin containing up to 2 g. of N for periods up to 1 month, 4—68% of the protein is excreted. Renal elements are absent from the urine and there is no evidence of subsequent renal disturbance. The non-protein-N of the blood does not increase.

NUTR. ABS. (m)

Glutathione in tissues following administration of "Tiargirio." G. PARADISO (Arch. Farm. sperim., 1933, 56, 487—501).—Reduced glutathione (I) has been determined in the blood, liver, and heart of rabbits and dogs by Tunnicliffe's method (A., 1925, i, 752), which is recommended. No change in (I) is produced by injection of "Tiargirio," a prep. of Hg thiosalicylate.

R. K. C.

Poisonous principles of *Dimorphotheca spectabilis*, Schltr., and *Dimorphotheca Zeyheri*, Sond. C. RIMINGTON (18th Rep. Director Vet. Services, Union S. Africa, 1932, 955—972).—The toxic substance in the two plants is linamarin or phaseolutin (cryst. form). It is hydrolysed by an enzyme present in the plants, but not appreciably by emulsin or maltase. *D. spectabilis* yielded about 1.7 g. of HCN by enzymic hydrolysis in the fresh state and *D. Zeyheri* about 1.1 g. per 100 g. (dry wt. basis). Dried plant powder produced typical HCN poisoning in rabbits. The unhydrolysed glucoside

in doses equiv. to 1 min. lethal dose in terms of HCN was not toxic, but was so when previously hydrolysed with plant powder.

NUTR. ABS. (b)

Constituents of leaves of *Solanum tuberosum* determining alimentation of the larvæ of *Leptinotarsa decemlineata*. M. RAUCOURT and B. TROUVELOT (Compt. rend., 1933, 197, 1153—1154).—The substance(s) is contained in the green solid part of the expressed juice and is also obtained by extraction of the leaves with EtOH. It is only slightly sol. in C_6H_6 , light petroleum, Et_2O , $COMe_2$, and $CHCl_3$, it is non-volatile, is not decomposed at 105°, but is destroyed by fermentation.

H. B.

Physico-chemical factors in the oecology of anopheline larvæ at Tongking. H. G. S. MORIN and H. BADER (Ann. Inst. Pasteur, 1933, 51, 656—668).—An investigation of the "carbonic index" (I) (a measurement of the excess of free and half-combined over the potential CO_2) of the H_2O of the rivers of Tongking at various points and at different seasons. A parallelism exists between (I) and the anopheline population of the various waters.

A. W.

Theory of diffusion in cell models. L. G. LONGSWORTH (J. Gen. Physiol., 1933, 17, 211—235).—The differential equations for the simultaneous diffusion of H_2O and salt in a cell model have been solved. The theoretical time curves for the diffusing substances accurately reproduce the characteristics of the experiment.

H. G. R.

Potassium as an adrenaline-producing element. R. HAZARD (Compt. rend., 1933, 197, 1455—1458).—Intravenous injection of KCl into chloralosed dogs produces hypertension (I) and hyperglycæmia (II), and other effects like those of adrenaline (III). The excitation causing (III) secretion is peripheral, since paralysis of the ganglia by a previous injection of sparteine increases and prolongs (I) without modifying (II). (I) is replaced by hypotension in animals previously submitted to the action of vohimbine.

J. W. B.

Excretion of calcium after injection of barium. Y. POURBAIX (Compt. rend. Soc. Biol., 1933, 112, 1556—1559).—Subcutaneous or intraperitoneal injection of Ba gluconate or chloride into guinea-pigs on a neutral diet causes increase of Ca in the urine. The excess Ca eliminated is much > equiv. to the Ba injected.

NUTR. ABS. (m)

Calcium and the resistance of *Nereis* to brackish water. W. G. ELLIS (Nature, 1933, 132, 748).—Wt. curves show that the resistance of *N. diversicolor* to immersion in brackish H_2O depends on the presence of Ca in the environment.

L. S. T.

So-called normal lead in the human body. F. WEYRAUCH and H. MÜLLER (Z. Hyg., 1933, 115, 216—220; Chem. Zentr., 1933, ii, 1047).—The organs of men not brought into contact with Pb in their work are free from Pb, but the bones contain > 0.25 mg. Pb in 3 g. of ash.

A. A. E.

Sodium iodobismuthite (iodobismutol). Muscular absorption of bismuth. P. J. HANZLIK and J. B. SPAULDING (J. Pharm. Exp. Ther., 1933, 49, 257—269).—Intramuscular injection of therapeutic

doses of iodobismutol [6% Na iodobismuthite and 12% NaI in $(\text{CH}_2\text{OH})_2$] into animals is followed by prompt absorption of the Bi, frequently almost complete after 24 hr. W. O. K.

Irritation and toxicity of sodium iodobismuthite (iodobismutol) prepared with propylene glycol and diethylene glycol. P. J. HANZLIK, H. G. MEHRTESS, and J. B. SPAULDING (J. Pharm. Exp. Ther., 1933, 49, 300—305).—The replacement of $(\text{CH}_2\text{OH})_2$ (I) in iodobismutol by propylene glycol does not alter or only slightly increases its local irritant action in man when injected intramuscularly, whilst it decreases its general toxicity, whereas replacement of (I) by diethylene glycol increases its toxicity. W. O. K.

Effect of water containing the isotope of hydrogen on fresh-water organisms. H. S. TAYLOR, W. W. SWINGLE, H. EYRING, and A. H. FROST (J. Chem. Physics, 1933, 1, 751).—Water containing 92% of H^2 killed tadpoles of *Rana clamitans* (I), the fish *Lebistes reticulatus* (II), the flatworm *Planaria maculata* (III), and the protozoan *Paramecium caudatum* (IV). 30% heavy H_2O did not affect (I), (II), and (III), and 15—20% did not affect (IV). H. S. P.

Effect of preservatives on enzyme action. H. KLUGE (Z. Unters. Lebensm., 1933, 66, 412—435).—BzOH (I) does not interfere with the action of amylase and lipase. Pancreatin is inhibited by (I), CH_2O , salicylic acid, Na_2SO_3 , and NaF. (I) and NaOBF have no effect on normal, but have a harmful effect on scorbutic, guinea-pigs. E. C. S.

Cryolysis and the mechanism of enzyme action. F. F. NORD [with G. WEISS] (Ergebn. Enzymforsch., 1933, 2, 23—49; Chem. Zentr., 1933, ii, 72).—Ovalbumin, gelatin, gum arabic, saponin, and Na oleate in solution or emulsion suffer irreversible physical change at low temp., as indicated by surface tension, viscosity, conductivity, gas absorption, etc. Emulsions made with frozen material have a somewhat increased stability. Surface tension measurements with ovalbumin and Na oleate solutions charged with C_2H_4 have also been made. After 2 hr. at -18° the colloids exhibit increased gas absorption, attributed to diminution of particle size. A. A. E.

Influence of mitogenetic radiation on enzymic processes. S. MARDASHEV and M. MOGILEVSKI (Biochem. Z., 1933, 265, 429—436).—The systems arginine+arginase or sucrose+invertase can be used in place of yeast as detector of mitogenetic radiation, the action of the enzyme being usually depressed by the radiation. P. W. C.

Mitogenetic spectral analysis of polysaccharide degradation. J. S. KLENITZKI and E. G. PROKOFIEVA (Biochem. Z., 1933, 265, 375—379).—The mitogenetic spectrum is sp. for the degradation of a particular mol. structure. Thus, the same mitogenetic spectrum is obtained for the hydrolysis of starch by salivary or pancreatic amylase, of maltose, and of salicin. The spectrum for hydrolysis of sucrose, on the other hand, is the same whether hydrolysis is by invertase or acid, but is different from that of the above reactions. P. W. C.

Intracellular enzymes of tissues and glands. III. Pancreatic amylase. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1933, 221, 202—206; cf. A., 1933, 864).—In pig's pancreas $\approx 0.2\%$ of the amylase (I) present is desmo-amylase. In 100% glycerol pancreatic (I) rapidly becomes irreversibly inactivated, although stable in 87%. Pancreatic (I) is only slightly inhibited by glycerol. J. H. B.

Combined role of H and Cl ions in the activation of amylase. L. AMBARD and S. TRAUTMANN (Compt. rend. Soc. Biol., 1933, 112, 1532—1534).—Possibly nascent HCl (not Cl') is the co-enzyme which promotes the action of amylase on starch.

NUTR. ABS. (m)
Adsorption of amylases by starch grains. P. T. BOEKESTEIN (Acta Brev. néerl. Physiol., 1932, 2, 132—134; Chem. Zentr., 1933, ii, 397—398).—Pancreatic (I), but not malt, amylase is adsorbed on rice, wheat, and potato starches; on rise of temp. the adsorption of purified (Willstatter) (I) diminished considerably. The starch grains were not attacked by the enzyme. The relation of p_H to absorption has been studied. Starch treated with *N*-HCl absorbs less enzyme. The effect of glycogen, starch solution, maltose, fructose, glucose, and sucrose on the absorption has been examined. In this way (I) containing only traces of lipase and trypsin, and giving greatly weakened protein reactions, has been prepared. A. A. E.

Limited saccharification of starch and amylase "complement." K. MYRBACK and S. MYRBACK (Svensk Kem. Tidskr., 1933, 45, 230—236).—Peptic hydrolysates of bottom yeast do not accelerate the maltose formation (I) from starch by malt-amylase (II). The hydrolysis by pancreatic (II) is also not affected by yeast "complement" or glutathione. The extent of (I) by green malt extract is $>$ that by α - or β -(II) prepared from it, the two isolated forms having the same activity. (I) is also not appreciably influenced by the proportion of α - and β -(II) nor by the abs. amount of (II). Amylose (J.C.S., 1923, 123, 2666), however, exhibits a 70% (I) with β -(II), but is completely hydrolysed by a mixture of α - and β -(II). The results of Pringsheim (A., 1932, 100) are probably due to the character of the substrate employed. F. O. H.

Amylosynthase. XII. Regeneration. XIII. Amylosynthase of glutinous rice. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 547—549, 549—552). XII. Amylosynthase (I) is inactivated by acids, alkalis, HgCl_2 , and heat; it is not reactivated by neutralisation, H_2S , and cooling. When (I) pptd. by CdCl_2 is treated with $(\text{NH}_4)_2\text{SO}_4$, enzymic activity is restored.

XIII. The optimum p_H of (I) from glutinous rice (prep. described) is 6.7—6.8. It differs from (I) of yeasts; sol. glycogen and hexahexosan are not polymerised. CH. ABS.

Determination of diastase. O. FISCHER (Z. ges. exp. Med., 1933, 86, 258—268; Chem. Zentr., 1933, ii, 232).—The dextrin (I)- and starch-decomposing powers of diastase are parallel. For the determination of diastase in urine, (I) is added and the amount of

(I) undecomposed is determined colorimetrically after addition of a solution of I in aq. KI.

A. A. E.

Emulsin. XII. I. Fission of phenyl- β -*D*-isorhamnoside by emulsin. B. HELFERICH, H. ROHR, and E. GUNTHER. II. Fission of β -*D*-glycuronides (paired glycuronic acids) by emulsin. B. HELFERICH and G. SPARNBERG. III. Deterioration of emulsin produced by ultra-violet rays. B. HELFERICH and G. BRIEGER. IV. Influence of formaldehyde on the fission of β -glucosides and β -galactosides by emulsin. B. HELFERICH and S. WINKLER (Z. physiol. Chem., 1933, 221, 90—92, 92—94, 94—98, 98—100; cf. A., 1933, 635).—I. Phenyl- β -*D*-isorhamnoside, m.p. 161—162° (corr.), $[\alpha]_D^{25}$ —80.8° in CHCl_3 [Ac_3 derivative, m.p. 134—135° (corr.), $[\alpha]_D^{25}$ —7.3° in CHCl_3], is hydrolysed by different preps. of emulsin at rates bearing a const. ratio to the rates of hydrolysis of the corresponding glucoside.

II. The fission of Na 1-menthyl- β -*D*-glycuronate (+1.5 H₂O), $[\alpha]_D^{25}$ —98.4° in H₂O, does not run parallel with the fission of *l*-menthyl- and phenyl- β -*D*-glucosides.

III. Only ultra-violet rays of λ 254 m μ are harmful to emulsin. Purified enzyme is more affected than the crude product. The destruction of activities towards phenyl- β -*D*-glucoside and -galactoside run parallel, indicating that the same enzyme is responsible for both hydrolyses. The difference in loss of activity towards β -*D*-glucoside and α -*D*-mannoside indicates that the enzymes here are different.

IV. Destruction by CH_2O indicates that β -*D*-galactoside and β -*D*-glucoside differ, which is contrary to previous results.

J. H. B.

Glucosides acting on the heart. III. Scillarenase. A. STOLL, W. KREIS, and A. HOFMANN (Z. physiol. Chem., 1933, 222, 24—38; cf. A., 1933, 1146).—Scillarenase (I) hydrolyses scillarene A to proscillaridin A with elimination of 1 mol. of glucose. (I) is a desmo-enzyme and is obtained as an autolysate, talc-prep., or cell-residue prep., from the sea-onion. EtOAc partly, MeOH completely, destroys the activity. EtOH and COMe_2 do not permanently affect activity, although EtOH shows inhibition. The p_H and temp. optima are 5—6 and 37°, respectively. (I) is inactivated in 1 hr. at 98°. It is not liberated from the cell by papain or diastase. (I) does not hydrolyse digilanic acid, deacetyldigilanic acid, or scillabiose.

J. H. B.

Dilatometric studies in enzyme action. III. Contraction constants of enzyme-substrate reactions. H. B. SREERANGACHAR and M. SREENIVASAYA (J. Indian Inst. Sci., 1933, 16A, 69—75).—The system emulsin (I)—salicin, but not (I)—amygdalin, (I)—arbutin, or (I)—asculin, gives a depression in the dilatometer (A., 1932, 880) during hydrolysis. "Contraction consts." were determined for the hydrolysis of starch and glycogen by ptyalin and taka-, malt-, and pancreatic diastase.

F. O. H.

Cytochrome c. K. ZEILE and F. REUTER (Z. physiol. Chem., 1933, 221, 101—116).—The mesoporphyrin was obtained by way of the hæmatoporphyrin from cytochrome c (I); the ester proved

identical with mesoporphyrin ester IX from blood-hæmin. Thus (I) contains a porphyrin nucleus as derivative of ætioporphyrin III with the same arrangement of side-chains as in the natural blood-pigment. The mol. wt. of the smallest unit of (I), based on the hæmin content, is 18,700. Determination of (I) makes use of the fact that oxidised (I) is, and reduced (I) is not, adsorbed by kaolin. (I) of 92% purity was obtained by fractional pptn. at varying p_H . The diffusion coeff. of (I) gives a mol. wt. up to 10 times the min. unit based on hæmin content.

J. H. B.

Supposed direct spectroscopic observation of the "oxygen-transporting ferment." D. KEILIN (Nature, 1933, 132, 783).—Warburg and Negelein's observations on *B. pasteurianum* (I) (A., 1933, 862) are in the main confirmed, but their interpretation is criticised. The absorption spectrum (II) of the cytochrome of (I) varies with the strain of the organism, the culture medium, and the age of the culture. The effect of CO on (II) also varies with the culture. These results, together with spectroscopic investigations of other bacteria, show that the shading in the yellow (590 m μ) and the band in the red (630 or 636 m μ) are not the absorption bands of the O-transporting enzyme, but are those of derivatives of cytochrome and probably of its component α .

L. S. T.

Reactions of the yellow [oxidation] enzyme. O. WARBURG and W. CHRISTIAN (Biochem. Z., 1933, 266, 377—411).—The yellow enzyme (I) consists of a colloidal carrier and a pigment (II) which can be eluted slowly by MeOH. (II) on irradiation in alkaline solution gave a substance $\text{C}_{13}\text{H}_{12}\text{O}_2\text{N}_4$, m.p. 320° (decomp.), the spectrum of which showed its close relationship with (II); on treatment with BaO it gave urea and a substance $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$, m.p. 213° (decomp.). The leuco-form of (I) with atm. O_2 gave (I) + H_2O_2 and with methylene-blue gave (I) + leucomethylene-blue. Since (I) contains no metal, the O transport of (I) is not inhibited by either CO or HCN. (I) is responsible for the O transport in anaerobic lactic acid cultures and is present in all cells, including those of higher animals.

P. W. C.

Inactivation of mussel catalase by oxygen. G. W. MARKS and D. L. FOX (J. Biol. Chem., 1933, 103, 269—283).—Mussel catalase (I) is prepared by keeping the minced tissue over-night at 20° in contact with PO_4^{3-} buffer and filtering. (I) stored under N_2 is inactivated more slowly than when kept under O_2 or air. By plotting the log. activity against t a straight line is obtained between 7 and 19 days; the quantity of H_2O_2 decomposed by a given extract is proportional to the concn. of extract except in high concns. By substituting in the unimol. equation vals. of k are obtained for the inactivation of (I) showing a steady drift. The Arrhenius equation is applicable for the variation of k with temp. The inactivation in air is uninfluenced by the presence of H_2O_2 .

H. D.

Peroxidase reaction. XL. Short-timed peroxidase reaction of blood-leucocytes of mothers secreting, and of sucklings nursed with, "aper-

oxidatic milk." M. CHIBA and J. ABE. **XLI.** Prolongation of short-timed peroxidase reaction of leucocytes as a sign of avitaminosis-*B*, and effect of vitamin-*B* on it. M. CHIBA (Tôhoku J. Exp. Med., 1932, 19, 479—485, 486—512).

CH. ABS.

Membrane potential of peroxidases and oxidases in equilibrium with metallic ions. M. PADOA and G. TEDESCHI (Biochem. Z., 1933, 266, 452—457).—The membrane potential of oxidase in equilibrium with Mn^{++} is nil up to p_H 6.2, then increases up to 40 mv. at p_H 7, and above this decreases due to coagulation of enzyme. Mn^{++} also increased the activity of the oxidase, the increase varying with p_H and disappearing below 6.2.

P. W. C.

Micro-method for determination of phenolase. S. BLAZSÓ (Biochem. Z., 1933, 266, 281—286).—The oxidation of pyrocatechol is studied using the $H_3Fe(CN)_6$ technique of Hagedorn and Jensen and a table constructed which permits the reading of the amount of phenol in terms of the $Na_2S_2O_3$ used in back-titration. The method is employed in determinations of the phenolase contents of rabbit's skin and blood.

P. W. C.

Alcohol-oxidase. H. MIZUSAWA (J. Biochem. Japan, 1933, 18, 243—258).—EtOH is rapidly dehydrogenated by alcohol-oxidase (I), a max. action occurring in 0.04*M*-EtOH. The main source of (I) is the liver, from which it can be prepared by pptn. of aq. extracts by $COMe_2$. MeOH, PrOH, glycol, glycerol, erythritol, and sorbitol are also dehydrogenated by (I). Ultra-violet and X-rays, KCN, C_4H_4N , and adrenaline inhibit, whilst extracts of adrenal cortex accelerate, (I). (I), which, unlike methylene-blue, has a significant reduction potential, has a stronger action in alcoholised than in normal animals.

F. O. H.

Decomposition of lactic acid by yeast enzymes. A. HAHN, E. FISCHBACK, and H. NIEMER (Z. Biol., 1933, 94, 58—66).—The isolation from yeast of a lactic acid dehydrase is described. In the presence of a H acceptor [methylene-blue, $C_6H_5(NO_2)_2$] lactic acid is converted into $AcCO_2H$ and $MeCHO$. The action is unaffected by the presence of O_2 .

A. G. P.

Mechanism of oxidation processes. **XXXVI.** Enzymic dehydrogenation of lactic acid, pyruvic acid, and methylglyoxal by yeast. H. WIELAND, O. B. CLAREN, and B. N. PRAMANIK (Annalen, 1933, 507, 203—212).—Aerobic dehydrogenation of lactic acid (I) proceeds similarly to that of EtOH (A., 1933, 865) when "impoverished" yeast (II) (A., 1932, 303) is used; $AcOH$, EtOH, and (mainly) CO_2 are produced. The following reactions probably occur: (i) $OH\cdot CHMe\cdot CO_2H \rightarrow AcCO_2H$; (ii) $AcCO_2H \rightarrow MeCHO + CO_2$; (iii) $2MeCHO + H_2O \rightarrow AcOH + EtOH$; (iv) $MeCHO + O \rightarrow AcOH$. In two cases, small amounts of succinic acid were isolated. The carbohydrate content and wt. of (II) do not increase during these experiments (cf. Hoffert, A., 1926, 642). Dehydrogenation of (I) is more dependent on the substrate concn. than in the cases of EtOH and $AcOH$; O_2 consumption occurs much more rapidly

at the higher concns. studied ($M/32-M/4$). $AcCO_2H$ (III) (as Na salt) is first decarboxylated to $MeCHO$ (which then reacts as above). A smaller amount of (III) [compared with (I)] is oxidised completely; reaction (iii) (above) appears to be inhibited by (III). The O_2 -consumption is much greater at the higher concns. $AcCHO$ (IV) is also dehydrogenated to (mainly) $MeCHO$; in some cases, (III) is isolated and probably results thus: $AcCH(OH)_2 - 2H \rightarrow (III)$. Re-synthesis of (IV) to carbohydrate does not occur. The course of the dehydrogenation of (IV) appears to differ from that of EtOH, $AcOH$, or (I). (IV) exhibits a retarding action on the oxidation.

H. B.

Indoxyluria. G. LAROCHE and J. DESBORDES (Ann. Méd., 1932, 32, 221—224; Chem. Zentr., 1933, ii, 738).—Experiments on surviving liver of guinea-pigs and rabbits disclosed considerable accumulation and rapid oxidation of indole to indoxyl. Conversion in other tissues is slower.

A. A. E.

Reducing power of liver tissue in presence of alkaloids, bases, salts, and mineral waters. A. BOUTARIC and T. JACQUINOT (Bull. Acad. Med., 1932, 107, 1054—1057; Chem. Zentr., 1933, ii, 233).—Theobromine, pilocarpine, strychnine, aconitine, emetine, sparteine, morphine, and cocaine, HCl , H_2SO_4 , and $HClN$ retard, whilst mineral H_2O , NH_3 , $NaOH$, and KOH accelerate, the decolorisation of methylene-blue by pig's liver. Corresponding behaviour is exhibited by acid- or basic-reacting salts.

A. A. E.

Reductases of liver and milk and the zymosthenic action of mineral waters. M. LOEPER, A. MOUGEOT, and V. AUBERTOT (Bull. Acad. Med., 1933, 109, 179—182; Chem. Zentr., 1933, ii, 233).—The mineral waters examined accelerated the reduction of methylene-blue by the reductase of pig's liver and cow's milk; the "zymosthenic index" is the ratio of the time necessary in distilled to that in mineral H_2O . Vals. are given for various waters.

A. A. E.

Carboxylase. I. W. LANGENBECK, R. JUTTEMANN, O. SCHAEFER and H. WREDE (Z. physiol. Chem., 1933, 221, 1—9).—In the purification of carboxylase, most of the protein is pptd. by $MeOH$ and the remainder by tannin, excess of which is removed by hide powder. After adsorption on $Al(OH)_3$ and elution with KH_2PO_4 solution the product is dialysed. The temp. is maintained at about -20° except during dialysis and the reagents are dissolved or suspended in 30% $MeOH$ which prevents freezing. The final prep. has 1000 times the activity of the original yeast maceration juice.

J. H. B.

Esterase of intestinal secretion. L. REALE (Arch. Farm. speriment., 1933, 56, 512—535).—The secretion of the dog has a ratio of lipase to esterase activity of 0.29. The esterase is not dialysable. On pptn. by $MgSO_4$ or $(NH_4)_2SO_4$ it is found in both albumin and globulin fractions. Electrophoresis causes migration to the anode at p_H 8.3—5.0 and to the cathode at p_H <4.5, the isoelectric point being at p_H 4.7. The secretion has p_H 7.3. The activity is maximal at p_H 7.3 and 37° .

R. K. C.

Physiology of digestion in infants. XVI. Gastric lipase. H. LICHTENBERG (Z. Kinderheilk., 1933, 54, 732—741).—Gastric lipase (I) attacks best short-chain, and pancreatic lipase long-chain, triglycerides, whilst human milk-lipase attacks intermediate fats. For (I) in presence of peptic digestion products the optimal p_H is 5; in the presence of tryptic digestion products (II) it is 7. (II) promote the action of lipase. NUTR. ABS. (m)

[Lipase.] **IV. Inhibitory effect of primary alcohols on the lipase of carp-liver.** J. C. KERNOT and H. W. HILLS (Z. physiol. Chem., 1933, 222, 11—15; cf. A., 1933, 534).—The inhibitory effect of primary alcohols on the hydrolysis of Et butyrate (I) and crotonate (II) by carp- and pig-liver lipase increases with chain length. The rate of hydrolysis of (I) is about 14 times that of (II). J. H. B.

Autolysis of the skin of pigmented and non-pigmented animals. S. BLAŽSÓ (Biochem. Z., 1933, 266, 266—273).—There is little or no difference between the autolytic powers (I) at p_H 3.8, 5.7, and 7.32 of the skins of albino, black, or brown rabbits, so long as the skins themselves are unpigmented. The (I) of pigmented skin, however, may be 300% > that of unpigmented skin. No difference was obtained in (I) of the skins of old and young animals. P. W. C.

Muscle autolysis. II. Changes of the total amount of reducing substances, lactic and phosphoric acids. I. A. SMORODINCEV, N. V. SCHIROKOV, and L. A. PHILTOVA (Biochem. Z., 1933, 266, 274—280).—During the storage of flesh, the amount of reducing substances increases at room temp. by 50% in 24 hr. and by > 100% in 3 days, at 4—8° by 50%, and at 17—25° by 200% in 3 days. The increase of lactic acid reaches max. vals. after 24 hr., when it is three times the amount obtained in the first hr., the increase in the same time at 4—8° being 185% and at 17—25° 283% of that in the first hr. Changes in org. and inorg. P amount to only 20—25% of the vals. for the first hr. P. W. C.

Enzymic ammonia elimination from thymonucleic acid by rabbit-liver. E. BUDING (Z. physiol. Chem., 1933, 222, 6—10).—The enzyme system of rabbit's liver which deaminates thymonucleic acid (I) can be separated into H₂O-sol. and -insol. components. Both are heat-sensitive and inactive alone, but reactivated on mixing. Part of the deamination of nucleoproteins and (I) occurs in the guanine nucleus. J. H. B.

Fermentative uricolysis. H. KLEINMANN (Klin. Woch., 1933, 12, 712; Chem. Zentr., 1933, ii, 726).—Human tissue, unlike pig's tissue, contains no uricase. Uricolysis is optimal at p_H 8.85 and 10.03; it is increased by O₂ and arrested by NaCN and H₂S. The fission products are: allantoin (40—50% of theory), CO₂, urea, and H₂C₂O₄. A. A. E.

Hæmatoporphyrin, an artificial proteolytic enzyme. M. J. BOYD (J. Biol. Chem., 1933, 103, 249—256).—Fibrinogen (I) exposed to light for 5 hr. in presence of hæmatoporphyrin (II) loses its clotting power and heat-coagulability with the formation of an albumose. With shorter exposures a heat-

coagulable protein appears as an intermediate product. A serum-albumin solution containing (II) undergoes hydrolysis on exposure to light, but not so rapidly as (I); serum-globulin and ovalbumin failed to react similarly. In an atm. of H₂ no hydrolysis of (I) and no loss of (II) occur, although the fluorescence of (II) appears to be uninfluenced. The phenomenon is one of photo-sensitisation. H. D.

Proteolytic enzymes in pancreatic and intestinal juice. E. LE BRETON and F. MOCOROA (Ann. Physiol. Physicochim. biol., 1933, 7, 215—219; Chem. Zentr., 1933, ii, 559).—Pure pancreatic juice does not attack ovalbumin or caseinogen unless activated with kinase or CaCl₂; hence it contains a prokinase and an inactive proteinase. It decomposes scombrin, clupein, and chloroacetyltyrosine, and hence contains active carboxypolypeptidase. It does not attack di- and tri-peptides. Dog's intestinal juice contains no tryptic enzyme, but two enzymes of the erepsin class (dipeptidase and aminopolypeptidase) and a very active kinase. A. A. E.

Action of papain on milk. A. UNDERRAIN (Milch. Forsch., 1933, 15, 433—447).—Papain acts on milk even when the latter is at b.p. The optimum temp. for papain is 87°. Albumin and globulin act as protective agents against the action of papain on caseinogen. E. B. H.

Absorption of pepsin by crystalline proteins. J. H. NORTHROP (J. Gen. Physiol., 1933, 17, 165—194).—With a ratio of pepsin (I) to edestin (II) of 2:1 and at p_H 4.0, the formation of the insol. complex (III) is a max. The peptic activity of (III) is equiv. to the amount of (I) present and may be extracted with cold 0.25N-H₂SO₄. On dissolving (III) in acid (p_H 2.0), (II) is rapidly digested and (I) may be isolated. H. G. R.

Action of pepsin on muscle-globulin and collagen. I. A. SMORODINCEV and A. N. ADOVA (J. Biochem. Japan, 1933, 18, 325—332).—Muscle-globulin is more readily hydrolysed by pepsin than is collagen (I). Unlike that of gelatin, the viscosity (II) of (I) increases during digestion. This increase is unaccompanied by combination with alkali, which, however, occurs at a later stage when (II) diminishes. The first phase of protein hydrolysis is a flocculation of the micellæ accompanied by an increase in (II); fission of the peptide linking does not occur. F. O. H.

Determination of trypsin. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1933, 17, 151—157).—After pptn. of the undigested hæmoglobin with CCl₃-CO₂H, the blue colour obtained with the Folin-Ciocalteu reagent (A., 1927, 892) is taken as a measure of the tryptic activity. H. G. R.

Determination of active native trypsin in presence of inactive denatured trypsin. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1933, 17, 159—164).—An alkaline solution of urea prevents the change of inactive denatured trypsin into the active native variety and may be used as a medium for determination of the latter. H. G. R.

Chemistry of alcoholic fermentation. A. HARDEN (J. Inst. Brew., 1933, 39, 644—646).—A review of new theories of fermentation. R. H. H.

Increase of yeast fermentation. IX. By urine of healthy and pathological subjects. X. By animal, plant, and chemical substances. H. ZELLER (Biochem. Z., 1933, 266, 360—366, 367—376).—IX. Tables show the changes of induction time (I) and of fermentation power (II) of yeast on adding normal and pathological urines. Autoclaving the urine increases (I) and decreases (II). (II) is increased by night urine of adults by $> 100\%$, of children by 200% , by urine in fevers of adults by 300% , and of children by 500% . The effect of urines in fever cases is in part dependent on the readily hydrolysable NH_3 of the urine.

X. A table shows the effect on fermentation of many org. and inorg. substances, and the results are discussed in relation to the effect on the early and later part of the fermentation cycle. P. W. C.

Nitrogenous metabolism of yeast. II. Yeast growth and fermentation in synthetic media. III. Ability of certain pure chemical compounds to function as nitrogen sources for yeast. R. S. W. THORNE (J. Inst. Brew., 1933, 39, 597—607, 608—621; cf. B., 1932, 203).—The extent of growth of yeast in artificial media is $15\text{--}20\%$ of that usual in wort. English yeast (I) does not grow or ferment as energetically as Froberg yeast (II), but addition of bios to (I) produced favourable effects. $(\text{NH}_4)_2\text{HPO}_4$ is a very good nutrient for (II) and for (I) in the presence of bios. NH_2 -acids except cystine function as nutrients, but KNO_3 , NH_2Ac , $\text{EtCO}\cdot\text{NH}_2$, alloxan, allantoin, betaine, and choline are useless.

R. H. H.

Kinetics of the accumulation of organic substance in cultures containing two types of yeast. G. F. GAUSE (Biochem. Z., 1933, 266, 352—354).—In an investigation of the accumulation of org. substance (yeast vol.) in a culture composed of two yeasts, *Saccharomyces cerevisiae* and *Schizosaccharomyces kefir*, the coeffs. α and β calc. according to a given equation agree with the corresponding coeffs. for the production of EtOH , and the applicability of the equation for such cultures is regarded as proved.

P. W. C.

Effect of cyanides on the development of yeast. M. N. MEISSEL (Zentr. Bakt. Par., 1933, II, 88, 449—459).—The toxicity of cyanides to yeast was in the order $\text{Hg}(\text{CN})_2 > \text{NaCN} > \text{KCN} > \text{NH}_4\text{CNS}$. Exposure to KCN solution resulted in increased fat production by the yeast. Morphological and physiological effects of cyanides are described. A. G. P.

"Radium yeasts." G. A. NADSON and E. J. ROCHLIN (Arch. Mikrobiol., 1933, 4, 189—208; Chem. Zentr., 1933, ii, 560).—"Radium yeasts-A, -B, and -C," produced by the action of Rn on Berlin press-yeast XII, have sp. morphological and physiological properties; -B is particularly active.

A. A. E.

Formation of gluconic acid by *Aspergillus niger*. E. KARDO-SYSSOJEVA (Biochem. Z., 1933, 266, 337—351).—A strain of *A. niger* is grown at $30\text{--}35^\circ$ on a solution containing 20% sucrose and the usual salts, the substrate removed, and the mycelium (under surface) washed and floated on solutions containing 20% sucrose, or sucrose with

varying amounts of salts with and without addition of CaCO_3 . Decreased concn. of salts or addition of CaCO_3 favours the formation of gluconic acid (I). Increase of N-containing salts stimulates accumulation of (I) in acid medium, but inhibits in presence of CaCO_3 . When an established mycelium is floated on a solution containing $1/25$ the usual salts, the amount of (I) formed is 100% of the sugar utilised or 50% of the sugar present in the medium. P. W. C.

Direct conversion of nitrates into ammonia by the mycelium of the lower fungi. D. BACH and D. DESBORDES (Compt. rend., 1933, 197, 1463—1465).—At p_{H} $1.16\text{--}2.65$ the disappearance of $\text{NO}_3\text{-N}$ (I) from a nitrate-glucose- NaCl medium (Ca citrate buffer) in contact with *Aspergillus repens* is almost exactly accounted for by the amount of $\text{NH}_3\text{-N}$ (II) appearing in the medium, no gain in wt. of the mould being observed. Above p_{H} 4.4 (p_{H} 6.6), however, the very rapid disappearance of (I) is accompanied by the appearance of only traces of (II), loss of NH_3 from the cell by exosmosis being now prevented and resulting in rapid increase in the wt. of the mould. J. W. B.

Evolutionary cycle of *Actinomyces* in cultures after ultrafiltration through collodion. A. SARTORY, R. SARTORY, and J. MEYER (Compt. rend., 1933, 197, 1465—1467).—When incubated under various conditions, the ultrafiltrates of cultures of *A. bovis*, Harz, show both typical and atypical forms ("symplastic," pseudo-diphtheria and -streptococcus, filamentous with arthrospores, etc.) which appear to represent labile and stable evolutionary phases of the morphology of the organism. F. O. H.

A chlorophyll-like bacterial pigment. K. NOACK and E. SCHNEIDER (Naturwiss., 1933, 21, 835).—Bacteriochlorin from the S-free purple bacteria (absorption band in Et_2O at $595\text{--}550\text{ m}\mu$) resembles chlorophyll in basicity and contains Mg which can be removed by acid. Bacteriopheophytin, which remains, closely resembles pheophytin. The application of Stoll's method for the direct prep. of pheophorbide yields (I) a crystallisable compound of relatively slight basicity, $\text{C}_{34}\text{H}_{35}\text{O}_5\text{N}_4\cdot\text{OMe}\cdot 0.5\text{H}_2\text{O}$, corresponding with a semi-hydrated pheophorbide *b* (Me ester, $\text{C}_{36}\text{H}_{40}\text{O}_6\text{N}_4$); (II) a non-cryst. *a* modification. The action of $\text{HI}\text{--AcOH}$ yielded a mixture of porphyrins of which the spectrum resembles that of phylloerythrins. With $\text{Fe}\text{--HCO}_2\text{H}$ two porphyrins are obtained, spectroscopically resembling pheophorphyrin, $\text{C}_{33}\text{H}_{33}\text{O}_6\text{N}_4$ (HCl no.=5), and $\text{C}_{33}\text{H}_{32}\text{O}_5\text{N}_4\cdot\text{OMe}$ (HCl no.=9). It is suggested that the name bacteriochlorin be altered to bacteriochlorophyll.

W. O. K.

Carotenoids of bacteria. E. CHARGAFF (Compt. rend., 1933, 197, 946—948).—The distribution of pigments in *Sarcina lutea* (A., 1933, 97), *S. aurantiaca* (I), *Staph. aureus* (II), and *Mycobacterium phlei* (III) has been determined by the method of Kuhn and Brockmann (A., 1932, 785). (I) contains β -carotene, and its xanthophyll fraction is zeaxanthin, which is the only pigment in (II). Lutein is probably the xanthophyll ester in (III), the hydrocarbons of which are separable by adsorption, and consist mainly of β - with 4% of γ -carotene (A., 1933, 431). A. C.

Bacteria fermenting xylan. R. PATRICK and C. H. WERKMAN (Iowa State Coll. J. Sci., 1933, 7, 407—418).—A medium containing xylan 2.5, NH_4Cl 2, and K_2HPO_4 1 g. in 1 litre of H_2O , at p_{H} 7.0, was fermented by various bacilli with the production of acid but not gas.

CH. ABS.

Gaseous metabolism of *L. pentoaceticus* with reference to the *Lactobacillus* group. G. A. HUNT (J. Bact., 1933, 26, 341—360).—*L. pentoaceticus* (I) differs from other organisms of the group in utilising relatively large proportions of O_2 during the fermentation of carbohydrates and producing an approx. equal vol. of CO_2 . Xylose and lactates are readily utilised by (I) with the same ratio of O_2 intake to CO_2 produced. All members of the group examined are inhibited by 0.1N-NaF and by 0.0001N- $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ but not by KCN solutions of $< 1\%$. Methylene-blue and pyocyanine accelerate O_2 consumption either in the presence or absence of KCN. Acids produced by (I) under aerobic conditions have a higher ratio of volatile to non-volatile constituents than those obtained under anaerobic conditions.

A. G. P.

Action of nitrates on the fermentation of glucose by *B. coli*. J. TIKKA (Suomen Kem., 1933, 6, B, 67).—Glucose (buffered at p_{H} 7) is fermented by *B. coli* in presence of KNO_3 (I) to give much less H_2 and lactic acid, and more AcOH, than without (I).

J. L. D.

Propionic acid bacteria. II. Classification. C. H. WERKMAN and R. W. BROWN (J. Bact., 1933, 26, 393—429).—Chemical and morphological characteristics are recorded and a system of classification is described.

A. G. P.

Propionic acid bacteria. F. DOMKE (Milch. Forsch., 1933, 15, 480—500).—Methods for detecting their presence in dairy products are considered.

E. B. H.

Putrefaction of hydroxyproline. W. KEIL and A. GUNTHER (Z. physiol. Chem., 1933, 221, 10—12).—Putrefactive organisms convert *l*-hydroxyproline into $\text{NH}_2\cdot[\text{CH}_2]\cdot\text{CO}_2\text{H}$. Proline and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ were not detected in the reaction products.

J. H. B.

Effect of light on the carbon monoxide inhibition of butyric acid fermentation. W. KEMPNER and F. KUBOWITZ (Biochem. Z., 1933, 265, 245—252).—The CO inhibition of anaerobic PrCO_2H fermentation with *Clostridium butyricum*, like that of the O_2 respiration of aerobic cells, can be removed by irradiation, but for the former process a lower temp. and light of greater intensity are required. The reaction reverses on darkening.

P. W. C.

Vibrio isolated at Damascus from cases of summer diarrhoea in man. *Vibrio enteriditis* (n. sp.). M. HURI (Ann. Inst. Pasteur, 1933, 51, 640—649).—The organism is strictly aerobic, and grows well with all ordinary media, with optimum p_{H} 8—8.2 and best at 37°. Inoculation experiments with various types of animals, and serological tests, are described. It differs from other known vibrios in complete absence of proteolytic properties, and also in biochemical and serological characteristics.

A. W.

Differentiation between Gram-positive and Gram-negative micro-organisms by the use of enzymes. D. W. BRUNER (J. Bact., 1933, 26, 361—371).—An aged glycerol extract of pancreas added in appropriate amounts to the medium permitted the growth of Gram-positive but prevented that of Gram-negative organisms. Trypsin effects a lysis of the latter organisms.

A. G. P.

Importance of peptone as a nutrient substrate for aerobic bacteria. Utilisation of peptone by *Staphylococcus aureus*. J. HIRSCH and A. W. MULLER (Z. Hyg., 1933, 115, 443—494).—Peptone (I) serves as a source of energy as well as of N for bacteria. The production of NH_3 from (I) by *S. aureus* occurs only in the presence of O_2 . NH_3 is derived directly from the free NH_2 groups of (I), and the amount produced is directly proportional to the concn. of (I) in the substrate. Addition to the medium of energy sources other than (I) retards NH_3 formation. The requisite energy is derived from the oxidative deamination process. (I) also contains substances stimulating the reproduction of bacteria. The val. of meat extracts in culture media depends more on the proportion of stimulating substance than on the nutrient or energy sources which they contain.

A. G. P.

Action of normal blood on the transmissible lysis of *Staphylococcus aureus*. W. MUTSAERS (Ann. Inst. Pasteur, 1933, 51, 605—625).—The strong, temporary inhibitory action of normal sera on the lysis of *S. aureus* (I) by the corresponding bacteriophage (II) is due to a protective action of the serum-albumin; it does not occur with other varieties of staphylococci. An extract of leucocytes (III), made by the method of Gengou, acts like (III) in destroying (II), and this destructive action is lost completely by heating to 100°, and very largely by filtration through an L3 Chamberland candle or after adsorption by emulsions of cholera vibrio. Blood-platelets have no fixing or destructive action on staphylococcal (II).

A. W.

Staphylolysin. J. FORSSMAN (Biochem. Z., 1933, 265, 291—319).—Using a described method of titration, the sensitivity of the blood-cells of various animals, the effect of the lysin at different temp., the influence of dilution (I) and of the no. of cells (II), and the adsorption of the lysin by the various cells are determined. The activity of staphylolysin decreases almost in proportion to (I) and increases almost in proportion to (II), usually displaying its greatest activity at 37°. More resistant cells often adsorb considerable amounts of, and sensitive cells often adsorb no, lysin.

P. W. C.

Immunisation of the rabbit by diphtheria anatoxins of different antigenic values. Y. ASAKAWA (Ann. Inst. Pasteur, 1933, 51, 565—583).—The degree of immunity induced in rabbits by two subcutaneous injections of diphtheria anatoxin (I), with an interval of 3 weeks between the injections, varies considerably from one animal to another. In general, immunity, as measured by intradermal tests, increases rapidly a few days after the second injection, with progressive increase up to or beyond the third month. The average antitoxin titre of the blood of

the immunised rabbits increases during the second and third weeks after the second injection of (I), and then falls to a fairly const. level. A. W.

Merthiolate as a preservative for biological products. II. Diphtheria toxoid. L. C. MORGAN, W. A. JAMIESON, and H. M. POWELL (J. Immunol., 1933, 25, 121—126). CH. ABS.

Substance inhibiting bacterial growth produced by strains of lactic streptococci. H. R. WHITEHEAD (Biochem. J., 1933, 27, 1793—1800).—Two streptococci (I), which inhibited the growth of normal cheese lactic acid cocci, were identified as strains of *S. cremoris* and *S. mastiditis*. The inhibition persists after the destruction of (I). Acid production is similarly inhibited in caseinogen broth. A conc. solution of the inhibiting substance (II) was obtained from milk incubated with (I) by EtOH extraction from the conc. whey. (II) is a protein derivative; it is destroyed by trypsin and resistant to pepsin. H. D.

Hæmolytic action of bacterial cells of streptococci. K. MATSUNAGA (Kitasato Arch. Exp. Med., 1933, 10, 196—206).—The hæmolytic power of the bacterial cells of hæmolytic streptococci is > 10 times that of the corresponding sol. hæmolysin. It is inseparable from the cells and vanishes before their death. The effect is weakened or destroyed by 30 min. at 50—55°, and is unaffected by changes in p_H between 6.0 and 8.0. It is inhibited by PhOH, AgNO₃, and PhMe. CH. ABS.

Influence of salts on the hæmolytic action of the bacterial cells of streptococci and other conditions that determine the hæmolysis. K. MATSUNAGA (Kitasato Arch. Exp. Med., 1933, 10, 207—219).—Mg and Ca are essential for the hæmolysis of erythrocytes by streptococci. The reaction caused in presence of Mg is inhibited by Ca and promoted by K; that in presence of Ca is inhibited by K. Salt-free peptone has little effect. CH. ABS.

Serum-proteins of healthy hill bulls and their variations during rinderpest and after recovery. K. C. SEN and A. C. ROY (Indian J. Vet. Sci., 1933, 3, 39—64).—In fatal rinderpest the serum-total protein (I), -globulin, and -euglobulin were low, but the latter two were normal relatively to (I). Considerable fluctuation occurred after recovery. In rinderpest associated with piroplasmosis and/or coccidiosis the serum underwent gelation when kept. CH. ABS.

Fractional precipitation of the anti-body-containing protein of anti-rinderpest serum. I. J. R. HADDOW, K. C. SEN, and A. C. ROY (Indian J. Vet. Sci., 1933, 3, 149—159).—The total globulin fraction is more potent than the H₂O-insol. protein or the euglobulin. CH. ABS.

Fractionation of antimeningococcus serum. P. P. MURDICK and S. M. COHEN (J. Immunol., 1933, 24, 531—541).—Agglutinative, precipitative, and antitoxic activity is associated with the H₂O-insol. globulin, separation of which is described. CH. ABS.

Syphilis antigens. E. BALBI (Z. Immunität., 1933, 78, 524—539; Chem. Zentr., 1933, ii, 1051—

1052).—Immunisation and complement-formation experiments with EtOH extracts of brain after treatment with COMe₂ and Et₂O are described. Brain-antigen is adsorbed on Al(OH)₃-B but not on Al(OH)₃ (Merck). The antigen is removed from heart extracts by Al(OH)₃. A. A. E.

Bacteriophage and fatigue of soils cultivated with lucerne. A. DEMOLON and A. DUNEZ (Compt. rend., 1933, 197, 1344—1346).—Bacteriophage (I) is detected in the nodules (max.), roots, and stems, but not in the leaves, of lucerne > 1 year old, but not in young plants. (I) passes into the soil and thence into new plants. In agreement with the known period in which soil becomes fatigued, diffusion of (I) to the whole region occupied by the roots occurs in 2 years. J. W. B.

Determination of chemotherapeutical substances fixed by spirochaetes and trypanosomes. E. SINGER and V. FISCHL (Naturwiss., 1933, 21, 787).—Determination of As by a method based on that of Sanger and Black shows that spirochaetes and trypanosomes in the blood of animals treated with arsenicals take up and fix the latter. Similar results have been obtained with metallic compounds other than arsenicals. W. O. K.

[Bacterial growth]-arresting and toxic effect of silver nitrate in nutrients and electrolytes. G. GLUCK (Arch. Hyg. Bact., 1933, 110, 38—60; Chem. Zentr., 1933, ii, 559).—The effect of AgNO₃ on *B. coli* in H₂O and non-interfering electrolytes is slow but considerable. It is diminished by proteins. A. A. E.

Presence of a substance resembling acetylcholine in the venous blood of the tongue of dogs on excitation of the nervus lingualis. W. FELDBERG (Pflüger's Archiv, 1933, 232, 88—104; Chem. Zentr., 1933, ii, 239).—The substance is considered to be acetylcholine. A. A. E.

Adrenal cortex and sex. Effect of cortical extract on normal and castrated rats. S. I. SIMPSON, A. KOHN-SPEYER, and V. KORENCHESKY (Lancet, 1933, 125, 1194—1196).—No effect of a potent cortical extract on the sexual, endocrine, or some other organs of normal or castrated male rats could be obtained. This is apparently not in harmony with clinical evidence of the effect of adrenal tumours on primary and sexual characteristics. L. S. T.

Ergotamine and the effect of adrenaline on blood-lactate. M. W. GOLDBLATT (J. Physiol., 1933, 78, 96—105).—In cats anaesthetised with amytal and urethane the hyperglycaemia and rise in blood-lactate observed after injection of adrenaline is inhibited by previous injection of ergotamine. NUTR. ABS.(m)

Action of organ extracts on adrenaline. F. SCHUTZ (Biochem. Z., 1933, 265, 282—290).—A thermolabile substance is extracted from liver which at p_H 6.1—6.4 accelerates the oxidation of *l*-adrenaline to the red oxidation product and also accelerates the oxidation of *d*-adrenaline and more slowly of *l*-dihydroxyphenylalanine but does not act on *l*-tyrosine. P. W. C.

Effect of active substances of the adrenal cortex and of adrenaline on the behaviour of muscle of normal and adrenalectomised frogs. K. WACHHOLDER and V. MORGENSTERN (Pflüger's Archiv, 1933, 232, 444—453; Chem. Zentr., 1933, ii, 564).—High concns. (5—25 mg. per 100 c.c.) of Schmitz and Kühnau's cortical hormone-B abolish reactivity towards acetylcholine (I) in both cases; 0.01—0.05 mg. per 100 c.c. increases (I) contraction, whilst 0.02—0.2 mg. per 100 c.c. retards fatigue, especially in adrenalectomised animals. Hormone-A has a similar but weaker action. With Swingle and Pfiffer's eucortone increased performance of isolated muscle was observed only with adrenalectomised animals and at high concn. Adrenaline at a concn. 1 in 5×10^5 has a slightly stimulating action, but at other concns. is depressant. A. A. E.

Adrenaline hyperglycæmia. M. ROTHSCILD (Z. ges. Exp. Med., 1933, 88, 33—41).—Adrenaline hyperglycæmia (I) in rabbits increases when sugar is given 3—8 hr. before the injection of adrenaline (II), the blood-sugar (III) being normal before the (II) is injected. (I), which depends on the capacity of the individual to store glycogen, is greater when alimentary hyperglycæmia is lower. Removal of the thyroid causes rise in (I), which is reduced by previous feeding with thyroxine. Injection of 20 units of parathyroid extract reduces (III) by 10—20 mg. per 100 c.c. in 1—2 hr., but has no effect on (I). NUTR. ABS. (m)

Influence of thyroid in tissue oxidation. W. BUNGELE (Klin. Woch., 1933, 12, 933—934; Chem. Zentr., 1933, ii, 236).—Addition of thyroxine to the suspension liquid did not increase the O_2 demand of the tissues examined. Prolonged feeding with thyroid increased that of isolated organs. A. A. E.

Effect of alkali on the absorption of thyroxine from the gastro-intestinal tract. Intravenous injection of thyroxine. W. O. THOMPSON, P. K. THOMPSON, L. F. N. DICKIE, and J. M. ALPER (Arch. Int. Med., 1933, 52, 809—820).—The Na_2 salt (I) is 75 times as effective as pure thyroxine when administered *per os*; the Na salt is only one third as effective as (I). Intravenous injection is somewhat more effective than oral administration. Synthetic and natural thyroxine are equally effective in the treatment of myxœdema. P. G. M.

Water exchange. XVII. **Effect of thyroxine on excretion of urine.** J. HATAFUKU and S. TAKAHASHI (Tôhoku J. Exp. Med., 1933, 21, 102—106).—Perfusion of the toad's kidney through the renal artery with Ringer's solution containing thyroxine (II) usually produces diuresis (I) with low concn. of (II) and oliguria (III) with large concn. (I) results from diminished tubular re-absorption under (II), but this, in excessive amount, so increases the O_2 consumption of the kidney that asphyxia and consequent lowered functional capacity result in oliguria. Perfusion through the renal portal vein produces slight (I) only, and (III) extremely rarely. NUTR. ABS. (m)

Antagonism between di-iodotyrosine and thyroxine and the rôle of diet in hyperthyroidism. I. ABELIN and A. SCHÖNENBERGER (Z. ges. exp. Med.,

1933, 88, 528—542).—Administration of di-iodotyrosine (I) to dogs rendered hyperthyroid by thyroid gland (II) or thyroxine (III) reduces the increased basal metabolic rate (IV), cardiac and respiratory activity, and nervous hyper-excitability and leads to an increase in wt., although feeding of (II) or (III) is continued. Continued administration removes hyperthyroidism (V) and (IV) occasionally becomes subnormal. The dosage depends on the degree of (V), since excess leads to increased secretion of (III). With occasional intermissions, administration of (I) can be continued with efficient results for long periods. NUTR. ABS. (m)

Determination of parathyroid hormone. F. J. DYER (Quart. J. Pharm., 1933, 6, 426—430).—The rise of Ca content in the urine of male rats following injection of parathyroid extract (I) is confirmed, but is too variable to be used as a standard for estimating the activity of (I). R. S. C.

Effect of parathyroid extract on secretion of insulin. E. ZUNZ and J. LA BARRE (Compt. rend Soc. Biol., 1933, 112, 1544—1545).—Crossed circulation experiments on dogs under chloralose show that injection of 5—10 units of parathyroid extract into the donor causes a considerable fall of blood-sugar in the recipient. The suprarenals play no part. NUTR. ABS. (m)

Physiology of the liver. XXIV. **Effect of insulin on blood-sugar following total removal of the pancreas and liver.** F. C. MANN and J. L. BOLLMAN (Amer. J. Physiol., 1933, 103, 45—47).—Using a depancreatized dog, the observation by Mann and Magath that insulin exerts its hypoglycæmic action in absence of the liver was confirmed. NUTR. ABS. (b)

Effect of insulin on the respiratory quotient, oxygen consumption, sugar utilisation, and glycogen synthesis in the normal mammalian heart in hyper- and hypo-glycæmia. E. W. H. CRUICKSHANK and C. W. STARTUP (J. Physiol., 1933, 77, 365—395).—Hyperglycæmia was associated with an increase in O_2 consumption (I), sugar utilisation (II), and glycogen synthesis (III). The reverse occurred in hypoglycæmia (IV), but the R.Q. throughout remained at unity except in progressive and marked insulin-(IV) when it was lowered. Insulin increased slightly the (I) and (II), and largely (III). NUTR. ABS. (b)

Relation of insulin to liver-glycogen. R. C. BODO and I. NEUWIRTH (Amer. J. Physiol., 1933, 103, 5—17).—In dogs fed on high-carbohydrate diet and anaesthetised with morphine and chloralose, there occurred a steady decrease in liver-glycogen (I). With a continuous intravenous infusion of glucose (II), however, (I) increased, whilst its distribution in the liver remained uniform. When, with (II) infusion, relatively large amounts of insulin were administered in single injections, (I) fell. A continuous slow infusion of insulin prevented storage of (I). NUTR. ABS. (b)

Liver-glycogen storage in diabetic animals. R. C. BODO, F. C. TUI, and L. FARBER (Amer. J. Physiol., 1933, 103, 18—24).—In completely depancreatized dogs, after fasting for 48 hr., the liver

is free from glycogen (I). On administering glucose (II), with or without anaesthesia, (I) is restored to a max. val. of 1%. Administration of both (II) and insulin produces in the depancreatized animal a still greater recovery of (I). NUTR. ABS. (b)

Heat-precipitation of insulin. V. DU VIGNEAUD, R. H. SIFFERD, and R. R. SEALOCK (J. Biol. Chem., 1933, 102, 521—533).—The heat-pptn. (I) of insulin by HCl, H₂SO₄, and H₃PO₄ at varying concn. compared with the amount of NH₃ liberated under the same conditions indicates that the NH₃ liberation is merely coincidental with (I). Inactivation of insulin by H₂S or NaCN prevents (I); the isolation, however, of an inactive heat-ppt. from insulin after treatment with 6N-H₂SO₄ indicates that the groups responsible for the activity and (I) are not the same. Regenerated heat-ppt. yields a heat-ppt. again with 0.1N-HCl or -H₂SO₄ more readily than the original insulin. A. L.

Diastase inhibition in the liver in fatal insulin hypoglycaemia. H. POPPER and O. WOZASEK (Virchow's Archiv, 1933, 288, 673—681).—A non-diabetic child, which died in hypoglycaemia after treatment with insulin for malnutrition, had a large amount of liver-glycogen; there was also a powerful inhibition of liver-diastase. NUTR. ABS. (m)

A blood-sugar-increasing substance from the pancreas. H. TANGL and F. THAN (Biochem. Z., 1933, 266, 448—451).—The aq. extract of an acidified CCl₄ extract of pancreas (3 kg.) gave on neutralisation and evaporation 0.1—0.8 g. of a substance which increased the blood-sugar of dogs by 100—200%. P. W. C.

Effect of callicrein on blood-sugar in man. E. ALTENBURGER (Klin. Woch., 1933, 12, 789—791).—Callicrein (I), injected intramuscularly into normal men, produces a fall of blood-sugar from the fasting level, and diminishes the hyperglycaemia and increases the subsequent hypoglycaemia after carbohydrate feeding; sometimes hypoglycaemic symptoms are induced. NUTR. ABS. (m)

Anterior pituitary extract and insulin resistance. E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 112, 499—501; Chem. Zentr., 1933, ii, 896).—Injection into dogs of alkali extracts of the anterior pituitary lobe increases the blood-sugar (I); injection of insulin then diminishes (I), but not to the normal low val. Insulin intoxication is not observed with animals which have received such extracts. After hypophysectomy resistance to insulin is considerably diminished. A. A. E.

Pituitary and glycogen in the toad. B. A. HOUSSAY, E. DI BENEDETTO, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1933, 113, 465—467).—In the toad (I), either total hypophysectomy or removal of the pars glandularis results in a diminution of blood-sugar, a considerable decrease in liver-glycogen (II), and a less marked fall of muscle-glycogen (III); a restoration to normal vals. follows the injection of pituitary extracts. In normal and hypophysectomised (I), (II) and (III) formation from injected glucose is increased if extracts of pituitary are simultaneously administered. NUTR. ABS. (m)

Role of the liver in the diabetes-producing action of the pituitary in the toad. C. A. CAMPOS, J. L. CURUTCHET, and A. LANARI (Compt. rend. Soc. Biol., 1933, 113, 467—469).—The rise of blood-sugar (III), which follows implantation (I) of anterior pituitary gland (II) into a depancreatized hypophysectomised toad, appears after 7 hr., attains a max. in 24—30 hr., and disappears after 70 hr. (I) of (II) into a depancreatized hepatectomised toad does not result in a rise of (III), so that the presence of the liver is necessary for the production of diabetic symptoms by the secretion of the pituitary gland of the toad. NUTR. ABS. (m)

Pituitary and pancreatic diabetes in batrachians and reptiles. B. A. HOUSSAY and A. BIASOTTI (Compt. rend. Soc. Biol., 1933, 113, 469—471).—Extirpation of the pars glandularis of the pituitary gland hinders or prevents the appearance of diabetic symptoms (I) following pancreatectomy in the following batrachians (II): *Leptodactylus ocellatus*, *Ceratophrys ornata*, *Bufo d'Orbigny*, and in the serpent *Ophis merremii*; in (II) implantation (III) of anterior pituitary material causes appearance of the symptoms. The results of either hypophysectomy or (III) are unaffected by the absence of the following organs: lungs, kidneys, adrenal glands, testes or ovaries, thyroid gland, and the alimentary apparatus. Normal and diabetic urines contain an easily adsorbed substance which stimulates the appearance of (I) in the hypophysectomised depancreatized toad. NUTR. ABS. (m)

Action of anterior pituitary extract on phloridzin diabetes. B. A. HOUSSAY, A. BIASOTTI, E. DI BENEDETTO, and C. T. RIETTI (Compt. rend. Soc. Biol., 1933, 112, 497—499).—Removal of the pituitary glands reduces the glycosuria (I), diuresis (II), N excretion, and D/N ratio of the phloridzinised dog, and the animal dies of hypoglycaemia (III). The injection of anterior pituitary extract prevents (III) and increases (I), (II), and ketonuria, especially when accompanied by a diet of meat or sugar. NUTR. ABS. (b)

Is the thyroid-stimulating hormone of the anterior pituitary excreted by the kidney? M. KROGH and H. OKKELS (Compt. rend. Soc. Biol., 1933, 113, 635—641).—When a concentrate of the urines of cases of Graves' disease prepared by a process known to separate the thyrotropic factor from anterior pituitary extracts is injected intraperitoneally into adult male guinea-pigs there is no significant thyroid reaction and the basal metabolic rate is not affected. NUTR. ABS. (m)

Effect of anterior pituitary extract on blood-iodine in dogs after removal of thyroid or pituitary. B. A. HOUSSAY, A. BIASOTTI, and P. MAZZOCCO (Compt. rend. Soc. Biol., 1933, 113, 459—460).—The increase in blood-I in normal or hypophysectomised dogs after injection of anterior pituitary extracts (I) is due to the thyroid gland in the absence of which (I) usually cause a fall in blood-I. NUTR. ABS. (m)

Metabolism and specific dynamic action in fasting and fed dogs after removal of the pituitary or damage of the tuber cinereum. P. MAZZOCCO

(Compt. rend. Soc. Biol., 1933, 113, 456—459).—As regards the sp. dynamic action (I) of meat there is no difference between normal and hypophysectomised dogs, but (I) is slightly higher, especially after a three days' fast, in dogs with the pars tuberalis cauterised.

NUTR. ABS. (m)

Relation between anterior pituitary lobe and thyroid gland. W. HOHLWEG and K. JUNKMANN (Pflüger's Archiv, 1933, 232, 148—158; Chem. Zentr., 1933, ii, 562).—Injection of follicular hormone (progynon) into rats prevents anterior pituitary (I) changes due to castration (II), but not somewhat similar changes due to thyroidectomy (III); the latter are prevented by ingestion of thyroid or injection of thyroxine. In (II) the gonadotropic hormone of (I) is increased, but in (III) the thyreotropic hormone (IV) of (I) is normal. After (III) and injection of thyroxine, (IV) is diminished.

A. A. E.

Anterior pituitary hormone in endocrine deficiency. II. Determination of sexual (anterior pituitary and follicular) hormone in health and in mental and neural disease. W. OESTERREICHER (Klin. Woch., 1933, 12, 896—899; Chem. Zentr., 1933, ii, 234).—In endocrine deficiency the amounts of pituitary sexual hormones in the blood, urine, and pituitary are increased except in cases of pituitary injury.

A. A. E.

Influence of the anterior pituitary hormone on the genital system of male mammals. B. ZAVADOVSKI, M. G. GRIGOREVA, and V. SARAFANOV (J. Physiol. U.S.S.R., 1933, 15, 518—633).—A method based on the measurement of the seminal vesicles is proposed for the standardisation of the anterior pituitary hormone and applied to the diagnosis of pregnancy.

A. L.

Function, assay, and preparation of galactin, a lactation-stimulating hormone of the anterior pituitary. Factors controlling normal lactation. W. V. GARDNER and C. W. TURNER (Missouri Agric. Exp. Sta. Res. Bull., 1933, No. 196, 61 pp.).—The extraction, properties, and biological assay of galactin (I) are described. (I) retains its activity after storage for 6 months. Factors influencing the control of lactation by (I) are examined.

A. G. P.

Separation of the pressor and oxytocic substances from the posterior lobe of the pituitary gland. R. L. STEHLE (J. Biol. Chem., 1933, 102, 573—590).—The material is treated with 0.5% aq. AcOH, and inert substances in the conc. filtrate are removed by pptn. first with EtOH, and then with Ba(OH)₂, Fe₂(SO₄)₃, and colloidal Fe. The concentrate obtained is then dissolved in aq. EtOH and fractionally pptd. with EtOAc, when the pressor fraction is pptd. first. Further purification is obtained by utilising the different distribution of the substances between the two phases of a H₂O—EtOH—EtOAc system, the pressor substance being found in the aq., the oxytocic in the EtOAc, phase. Some chemical properties and pharmacological actions of the fractions are described.

A. L.

Secretion of the posterior lobe of the pituitary after administration of drugs. A. SIMON (J.

Pharm. Exp. Ther., 1933, 49, 375—386).—Administration of insulin to unanæsthetised dogs failed to produce in the cerebrospinal fluid a definite increase of vasopressin, whilst diuretics (urea or novasurol) did not increase the oxytocic potency of the fluid.

W. O. K.

Influence of pituitary gland on parturition. II. Metabolism during injection of posterior pituitary extracts. III. Posterior pituitary and the water balance. S. MORRIS (J. Obstet. Gynaecol., 1933, 40, 580—597, 598—605).—II. Small doses of pituitrin cause antidiuresis (I) and decrease (25%) in urinary N; large doses cause (I) followed by diuresis. Urea-N is decreased; NH₃- and NH₂-acid-N are increased. Anterior pituitary extracts sensitise the body towards pituitrin.

III. Posterior pituitary extracts convert blood-org. Cl into -Cl', increasing the osmotic pressure and causing retention of H₂O.

CH. ABS.

Anterior pituitary sexual hormone from urine of pregnancy. F. HAUROWITZ, M. REISS, and J. BALINT (Z. physiol. Chem., 1933, 222, 44—49).—The activity of the crude urinary hormone (I) is greatly increased (100—300-fold) by adsorption on BzOH, also to some extent on keeping the aq. solution at 38°. Purified (I) is pptd. by EtOH, COMe₂, and phosphotungstic acid and gives an opalescence with Esbach's reagent, sulphosalicylic acid, or tannin, but is not pptd. by CCl₃·CO₂H or on boiling. It is salted out by (NH₄)₂SO₄. It contains about 7% of sugar and gives the biuret, Sakaguchi, Millon, and Pauly reactions. Only a single hormone is postulated, since both follicular ripening and luteinisation are produced together by all preps.

J. H. B.

Excretion of prolan in the urine of aged women. C. HAMBURGER (Klin. Woch., 1933, 12, 934—935; Chem. Zentr., 1933, ii, 233).—In 75% of the cases examined (59—85 years) there was increased excretion of prolan, the quantities (100—300 mouse units per litre) being approx. those observed after castration.

A. A. E.

Relationship of the (œstrus) dose of follicular hormone (menoformone) in rats and mice. S. E. DE JONGH and E. LAQUEUR (Acta Brev. neerl. Physiol., 1933, 3, 33—35; Chem. Zentr., 1933, ii, 561).—A rat unit—9 mouse units (approx.).

A. A. E.

Conjugation in *Rhizopus* inhibited by female sex hormone. G. W. PLUMB and L. W. DURRELL (Science, 1933, 78, 386).—Œstrin inhibits zygospore formation in *R. nigricans*.

L. S. T.

Humoral excitation of the nesting instincts in rabbits. E. B. TIETZ (Science, 1933, 78, 316).—Loosening of hair in the rabbit parallels the involution of the corpus luteum; an additional factor is necessary for excitation of the nesting instinct, which, in absence of pregnancy, can be induced by the injection of the urine of pregnant women.

L. S. T.

Occurrence of male sexual hormone in the urine of newly born infants and in the placenta. Antagonistic action of sexual hormone. H. GOECKE, P. WIRZ, and H. DANERS (Arch. Gynakol., 1933, 153, 233—243; Chem. Zentr., 1933, ii, 233).—

Male sexual hormone is present in the urine of newly born boys and girls, and in the placenta in the latter, but not in the former, case. A. A. E.

Hormone and vitamin actions and their mutual relationships. E. ABDERHALDEN (Med. Klinik, 1933, 29, 523—525; Chem. Zentr., 1933, ii, 893—894).—A discussion. A. A. E.

Vitamins and the prevention of abortion in sheep. H. DRYERRE (Nature, 1933, 132, 751).—Feeding with a concentrate of vitamins-A, -D, and -E appears to reduce abortion in ewes. L. S. T.

Occurrence of vitamin-A in the oil of West Indian sharks. C. F. ASENJO (Science, 1933, 78, 479). L. S. T.

Vitamin-A content of barley. E. H. HUGHES (J. Agric. Res., 1933, 47, 487—494).—Diets containing barley as the sole source of vitamin-A (I) failed to produce normal growth in rats. The (I) of barley was > that of white maize, but approx. one sixth of that of yellow maize. A. G. P.

Carotene and vitamin-A in the human organism. F. KAUFFMANN and W. VON DRIGALSKI (Klin. Woch., 1933, 12, 306—308).—The carotene (I) content of human blood is usually < 0.01 mg. per 100 c.c. (max. 0.27 mg.). When carrot juice, eggs, or (I) are administered to cases previously giving negative tests, a latent period (II) occurs before an increase can be detected, probably due to absorption of (I) by the organs. There is no (II) in cases already showing (I) in the blood. The max. val. obtainable on diets rich in (I) varies from 0.11 to 0.27 mg. per 100 c.c. in different individuals. Slight xanthosis results from feeding (I), the intensity depending on the (I) val. Carotenæmia cannot be prevented by exposure of the subject to insolation. Urine, bile, gallstones, cerebrospinal fluid, non-hæmorrhagic ascitic fluid, and sweat are free from (I) and vitamin-A, which are, however, found in the faeces of rats receiving them in excess. Except during lactation, loss of vitamin-A reserve in man can take place only through normal utilisation or decomp. NUTR. ABS. (m)

Vitamin-A content of rat's liver after feeding with α -, β -, and γ -carotene, and the antimony trichloride reaction of vitamin-A preparations. H. BROCKMANN and M. L. TECKLENBURG (Z. physiol. Chem., 1933, 221, 117—128).—Rats receiving α -, β -, or γ -carotene stored vitamin-A (determined by SbCl_3 reaction) in the liver. β -Carotene gave much the best yield. Lutein, zeaxanthin, and lycopene were inactive. Rat-liver oils before and after saponification show the absorption band 620 μ , unsaponified fish oils, 608—609 μ , shifting to 620 μ on saponification which removes an impurity present. A band at 573 μ is due to oxidation products. J. H. B.

Growth-promoting action of carotenes and xanthophylls. R. KUHN and H. BROCKMANN [with A. SCHEUNERT and M. SCHIEBLICH] (Z. physiol. Chem., 1933, 221, 129—136).— α -, β -, and γ -Carotene restore growth and cure xerophthalmia in rats, the limiting doses being 5, 2.5, and 5×10^{-6} g., respectively. The accepted constitutions by which β -carotene affords 2 mols. and α - and γ -carotene each one mol. of vitamin-

A, respectively, are thus confirmed. Lutein, zeaxanthin, violaxanthin, azafrin Me ester, dihydrocrocin, and chlorophyll were inactive. J. H. B.

Vitamin-A and lipin metabolism. H. J. JUSATZ (Naturwiss., 1933, 21, 800).—The serum-cholesterol of rabbits receiving daily 0.5—1.5 c.c. of a vitamin-A prep. (40,000 units per c.c.) for a period of 1 month is increased by approx. 80% (cf. A., 1933, 645). F. O. H.

Vitamin-A deficiency in normal and depancreatized dogs. E. P. RALLI, A. PARIENTE, G. FLAUM, and A. WATERHOUSE (Amer. J. Physiol., 1933, 103, 458—467).—Depancreatized dogs showed symptoms claimed to resemble those of vitamin-A (I) deficiency, which were not cured by feeding carotene, nor (in one dog) by (I). The (I) content of the livers of depancreatized dogs was low. Failure to utilise (I) may be related to a disturbance in fat metabolism. NUTR. ABS. (b)

Toxicity of vitamin-A. W. VON DRIGALSKI (Klin. Woch., 1933, 12, 308—309).—Large daily doses (20,000—40,000 rat units) of vitamin-A cause loss of wt., disease, and death (in 5—19 days) in rats. NUTR. ABS. (m)

Relationship between the antimony trichloride blue value of cod-liver oils and that of their unsaponifiable fractions. F. J. DYER (Quart. J. Pharm., 1933, 6, 338—346).—The SbCl_3 blue vals. of 39 cod-liver oils and of their unsaponifiable fractions are recorded, the average ratio being 1:1.65. Distribution of the results (1.163—2.055) is statistically normal. R. S. C.

Vitamin-D potency of sun-irradiated, dried yeast. K. H. COWARD (Lancet, 1933, 225, 920).—Dried yeast may be activated antirachitically by exposure to strong sunlight. L. S. T.

Clinical tests of the antirachitic activity of calciferol. J. C. SPENCE (Lancet, 1933, 225, 911—915).—Calciferol (I) acted as effectively as cod-liver oil or irradiated ergosterol in 12 cases of human rickets. 1 c.c. of (I) solution (3000 units) daily produced a max. curative effect. L. S. T.

Substances which affect the residual nitrogen increase in cats brought about by vitamin-D. S. HERMANN and M. ZENTNER (Biochem. Z., 1933, 266, 418—421).—Vigantol is able to increase the blood-residual N (I) in cats by 100%, the effect being completely inhibited if Kombuchal (II) is fed together with vigantol. Gluconic acid, one constituent of (II), inhibits the increase of (I) only in 40% of cases, whilst citric acid is inactive. P. W. C.

Effect of overdoses of irradiated ergosterol, administered for approximately two months, on the composition and structure of the bones of rats. J. H. JONES and G. M. ROBSON (Amer. J. Physiol., 1933, 103, 338—350).—Of three similarly constituted groups of rats, on a diet low in Ca, group *a* was killed after a week, and *b* and *c* after 7—9 weeks; *c* had received in addition large daily doses of irradiated ergosterol (I). The ash content and X-ray density of the bone were the same in groups *a* and *b*, but markedly lowered in *c*. The histology of the bones in *c* also showed marked changes. In another similar

series, on a slightly different diet also low in Ca, the rats receiving no addition of (I) showed a lowering of ash and of serum-Ca, whilst in rats receiving moderate, non-toxic doses of (I), the lowering of ash was less and the serum-Ca was normal. NUTR. ABS. (b)

Avitaminosis. XIV. Effect of vitamin-A deficiency on concentration of blood-lipins of the albino rat. **XV.** Effect of vitamin-D deficiency on concentration of lipins of the blood of the albino rat. B. SURE, M. C. KIR, and A. E. CHURCH (Proc. Soc. Exp. Biol. Med., 1933, 30, 620—621; 621—622).—XIV. The vals. for the content of fatty acids (I), phospholipins (II), and cholesterol (III) in the blood of rats deprived of vitamin-A were normal.

XV. Vitamin-D deficiency did not affect the (I), (II), or (III) content of the blood. NUTR. ABS. (b)

Fresh and dried yeast as sources of vitamin-B₁. R. WALKER and E. M. NELSON (Amer. J. Physiol., 1933, 103, 25—29).—The vitamin-B₁ obtained by rats (growth criterion) from yeast cakes when fed fresh was approx. half that obtained from the same cakes if dried before feeding. This is ascribed to the fact that viable yeast cells pass unaltered through the digestive tract. The dried yeast cakes were found to be half as active as a commercial dried yeast, possibly owing to the freedom of the latter from starch.

NUTR. ABS. (b)

Effects of variations in the amounts of vitamin-B and protein in the ration. A. G. GOGAN and R. W. PILCHER (Missouri Agric. Exp. Sta. Res. Bull., 1933, No. 195, 46 pp.).—Additions of vitamin-B to a basal diet for rats increased the food intake (I) and growth rate. Raising the protein level increased the growth rate without affecting the gross intake of food. When the two changes were made simultaneously (I) was greatly increased and the growth was still further accelerated. No inter-relationships were apparent between the level of protein intake and the vitamin-B requirement. A. G. P.

Dietary requirements for fertility and lactation. XXV. Does the amount of fat in diet influence vitamin-B requirements for lactation? B. SURE (Proc. Soc. Exp. Biol. Med., 1933, 30, 622—623).—Rats deprived of vitamin-B₁ were no more successful in rearing their young when the diet contained 20% or 30% of lard than when it contained 10%. NUTR. ABS. (b)

Quantitative relationships between vitamin or hormone requirement and nutrient substances involved in metabolism. E. ABDERHALDEN [with WERTHEIMER] (Münch. med. Woch., 1933, 80, 722; Chem. Zentr., 1933, ii, 894).—The relation between vitamin-B₁ and carbohydrate metabolism, which has been confirmed, is discussed. A. A. E.

Role of vitamin-B in the utilisation of sugars by the pigeon. Comparative effect of hexoses and disaccharides in diets containing 66% of sugar. R. LECOQ (Compt. rend., 1933, 197, 1155—1157).—The presence in the diet of 66% of galactose or lactose leads to alimentary unbalance; addition of large amounts of vitamin-B (I) (dry brewer's yeast) has no effect on the time of survival. The action of

fructose (and sucrose) is similar but not so marked. Glucose and maltose require the same amount of (I) to prevent death; the min. dose is twice that required for a diet containing 35% of the sugar (A., 1933, 541). H. B.

Hydrogen-ion concentration in the organs of pigeons fed on polyneuritis-producing diets. R. McCARRISON, G. SANKARAN, and K. B. MADHAVA (Indian J. Med. Res., 1933, 20, 739—756).—*p_H* determinations on the organs of pigeons killed at the onset of polyneuritis gave evidence of increased acidity of the pons, optic lobes, cerebellum, and cerebrum, decreased acidity of skeletal muscles and liver, and an increase in the difference in reaction between auricle and ventricle as compared with normal controls. NUTR. ABS. (b)

Ascorbic acid (vitamin-C). M. BACHSTETZ (Giorn. Chim. Ind. Appl., 1933, 15, 510—511).—Ascorbic acid has been isolated from *Capsicum annuum* (Voghara variety). T. H. P.

Vitamin-C in the adrenal gland of the human foetus and the physical state of the vitamin in the gland cell. G. BOURNE (Nature, 1933, 132, 859—860).—The cytological method previously described (A., 1933, 372) has been applied to the adrenal glands of a 55-cm. human foetus. The whole of the gland blackened, the cortex (I) > the medulla. The outer portions of (I) reacted < the deeper, whilst the "fetal cortex" showed a strong reaction. The nuclear aggregation of the stained granules was strong enough to obscure the nuclei in many cases. The physical condition of the vitamin in the gland cell is discussed. L. S. T.

Determination of vitamin-C. L. K. WOLFF, M. VAN EEKELLEN, and A. EMMERIE (Acta Brev. néerl. Physiol., 1933, 3, 44—45; Chem. Zentr., 1933, ii, 571).—After trituration of the tissue with sand and extraction with 5% aq. CCl₃-CO₂H (5—10 c.c. per g.) the following vals. (c.c.) were obtained on titration with 0.02% aq. 2:6-dichlorophenol-indophenol: ascorbic acid (1 mg.) 16.4, lemon juice (1 c.c.) 5.5, rabbit's liver (1 g.) 1.1, rabbit's adrenal (1 g.) 23.9, pig's spleen (1 g.) 2.8, pig's kidney (1 g.) 1.7, pig's adrenal (1 g.) 37.6, pig's pancreas (1 g.) 1.9, tuberculous human liver (1 g.) 0.5, human adrenal (1 g.) 1.2. Adrenaline does not reduce. Small quantities of glutathione and Fe do not interfere. A. A. E.

Influence of temperature and light density on photosynthesis and respiration and an explanation of "solarisation" and "compensation point." N. R. DHAR (J. Indian Chem. Soc., 1933, 10, 541—561).—The non-applicability of the Arrhenius equation to photosynthesis and many other phenomena in plant life are explained by assuming the reversible equilibrium $n\text{CO}_2 + n\text{H}_2\text{O} \rightleftharpoons \text{C}_n\text{H}_{2n}\text{O}_n + n\text{O}_2$, in which the direct action (photosynthesis) is opposed by the reverse action (respiration). E. S. H.

Relationship between physiological phenomena and pigment formation in plants. V. Anthocyanins and transpiration. H. KOSAKA (J. Dept. Agric. Kyushu Imp. Univ., 1933, 4, 95—126).—The total transpiration and the daily variation are increased

in those plants which contain large amounts of anthocyanin pigments (*Oryza sativa*, *Perilla nankinensis*, etc.) in the leaves and stems. Lack of sunlight has an inhibiting effect.
P. G. M.

Changes in composition of Florida avocados in relation to maturity. A. L. STAHL (Florida Agric. Exp. Sta. Bull., 1933, No. 859, 61 pp.).—Chemical and physical changes with advancing growth are recorded. Of these, the increase in oil and fat content (I) in the immature fruit is most marked. An inverse relationship is established between (I) and the *d* of the fruits. Firm fruit, stored until soft, showed an increase in (I) and hydrolysable sugars and a decrease in *d*, H_2O , free reducing and total sugar contents.
A. G. P.

Biochemistry of seed germination, especially of *Zea mays*. R. C. MALHOTRA (J. Biochem. Japan, 1933, 18, 173—197).—During the germination (I) of peas (II), maize (III), and wheat, starches (IV), hemicelluloses (V), and, to a smaller extent, fats are utilised; proteins are catabolised only with (II). Sugars are formed during (I), but the calorific energy of the seeds decreases. The wt. of the seedlings is always < the initial wt. of their seeds. With (III), fats and heat energy diminish more rapidly in the embryo (VI) than in the endosperm (VII) where (IV) and (V) are mostly used. The N content remains approx. const. in both parts of the seed. Isolated (VI) of (III) during (I) show changes similar to those of the intact (VI), whilst isolated (VII) kept under conditions suitable for (I) exhibit changes only in sugars and (IV). The mechanism of these changes is discussed.
F. O. H.

Biochemistry of the wheat plant. R. C. MALHOTRA (J. Biochem. Japan, 1933, 18, 199—205).—During the growth of wheat, the H_2O content attains min. vals. during the early and late stages, whilst the content is highest at maturity (I). Both sugars and hemicelluloses gradually increase until just before (I) when they diminish. The total N content remains const. until three months before (I) when it slowly increases. Starch is completely utilised during the first three months for the development of the grain.
F. O. H.

Cause of the chemical variation of chickpea seeds. N. N. IVANOV (Bull. Appl. Bot., Leningrad, 1933, [iii], No. 1, 3—11).—The protein content (12.3—31.5%) is related to soil and locality. Low vals. are associated with absence of sp. bacteria, and the plant then assimilates combined N from the soil.
CH. ABS.

Carbohydrate metabolism of the soya-bean during germination. S. SASAKI (J. Agric. Chem. Soc. Japan, 1933, 9, 693—696).—Reducing sugar, produced after germination in the dark, decreased after one week; sucrose and stachyose decreased gradually. Dextrin and starch were found in the germinated seeds and increased considerably. During germination araban and cellulose increased, whilst galactan decreased.
CH. ABS.

***Brassica japonica*, Sieb., var. *Sugukina* Makino (*B. hipposinica*, Bailey).** I. Chemical changes during growth. H. KOJIMA (J. Agric.

Chem. Soc. Japan, 1933, 9, 664—671).—The reducing sugar increased, and polysaccharide decreased, with growth.
CH. ABS.

Composition of the seeds of the pine and the acorns of the oak of different geographical origins. V. A. VINOGRADOV (Bull. Appl. Bot., Leningrad, 1933, [iii] No. 1, 183—193).—The total ash of the pine, and the total ash, fat, and H_2O extractives of acorns of *Quercus robur pedunculata* are independent of geographical location, but various parts of the seeds contain different amounts of ash.
CH. ABS.

***Cucurbita*.** V. V. ARASIMOVICH (Bull. Appl. Bot., Leningrad, 1933, [iii], No. 1, 73—99).—In *C. maxima*, *C. pepo*, and *C. mixta* the sugar content does not increase proportionately to the maturation of the fruit. Glucose is > fructose; sucrose is sometimes absent. Invertase is active only during the first two weeks of maturation. The oil and protein of the seeds accumulate at the expense of the sugars. The I val. of the oil increases, whilst the acid val. and enzymic activity of the seeds decrease, with maturation.
CH. ABS.

Physiologically balanced culture solutions with stable hydrogen-ion concentration. S. F. TRELEASE and H. M. TRELEASE (Science, 1933, 78, 438—439).—With a suitable ratio of NO_3/NH_4 wheat cultures could be maintained at a p_H which remained approx. const. during the 8-day period between solution renewals.
L. S. T.

Growth-promotion experiments with living orchid pollen. F. LAIBACH (Ber. Deut. bot. Ges., 1933, 51, 336—340).—Living pollen from tropical orchids when placed on cut surfaces of leaf stems, epicotyls of seedlings, etc. promotes growth activity in neighbouring tissue.
A. G. P.

Occurrence of growth substance in marine algæ. H. G. VAN DER WEIJ (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 759—760).—Of several kinds of marine algæ examined, only young, rapidly growing specimens of *Valonia macrophysa* contained growth substance. Extraction of the cell wall with Et_2O indicated its presence there in a concn. < 20 times that in the sap.
R. K. C.

Growth substance in *Elæagnus angustifolius*. H. G. VAN DER WEIJ (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 760—761).—Growth substance (I) was transmitted to agar by young leaves or the base portions of young stem, but the tops of the latter or vegetation tips (the upper 3—4 mm. of a young shoot), did not yield (I).
R. K. C.

Evaporation, transpiration, and oxygen consumption by roots. W. A. CANNON, D. DEMAREE, and E. A. PURER (Science, 1933, 78, 388—389).—The rate of O_2 consumption (I) by the root of the willow is indirectly affected by light relations of the shoot, and may be directly affected by the temp. of the culture solution. There is no apparent positive relation between transpiration rate and that of O_2 absorption by the root, but there may be a direct relation between the evaporating power of the air and (I).
L. S. T.

Relation of moisture to respiration and heating in stored oats. A. L. BAKKE and N. L. NOECKER (Iowa Agric. Exp. Sta. Res. Bull., 1933, No. 165, 319—336).—The O_2 consumption of stored oats increases with their H_2O content. No relationships between H_2O content and temp. attained are apparent. Mould growth reached a max. at 30—35° and with a H_2O content of 24—40% according to aeration. When the H_2O content was < 15% all heat evolved was radiated. A. G. P.

Iodocolorimetry of cellulose dextrans and determination of cellulose. L. PALOHEIMO and V. VALAVAARA (Biochem. Z., 1933, 266, 301—322).—The cellulose dextrans (I) obtained by the action of 70% H_2SO_4 give a strong colour with I in KI, which can be used for the photometric determination of cellulose. The influence of temp., age of solution, duration of hydrolysis, I and (I) concns. on the light absorption of (I) after adding I are investigated. P. W. C.

Bog moss. II. Composition of *Sphagnum fimbriatum*, Wils. M. WATANABE (J. Agric. Chem. Soc. Japan, 1933, 9, 649—654).—Part of the cellulose, obtained by chlorination, is insol. in cuprammonium solution. On hydrolysis with H_2SO_4 it afforded a low yield of glucose. CH. ABS.

Metabolism of calcareous algæ. I. P. HAAS and T. G. HILL (Biochem. J., 1933, 27, 1801—1804).—Extraction of *Corallina officinalis* with hot H_2O and of the conc. solution with EtOH yielded hexa-acetyl-floridoside, m.p. 100—101°, $[\alpha]_D + 108.5^\circ$, deacetylated to floridoside. A polypeptide of aspartic acid was pptd. from the aq. extract with $Hg(OAc)_2$. H. D.

Floridoside, present in *Florideæ*. H. COLIN and E. GUEGUEN (Compt. rend., 1933, 197, 1688—1690).—The presence of floridoside (I) (A., 1930, 835, 1324) in the EtOH extracts of a large variety of species of *Florideæ* is established by high dextrorotation and non-reducing properties, no sucrose, glucose, or fructose being detected. (I) is isolated from *Furcellaria fastigiata* extract after purification with phosphotungstic acid and removal of mineral matter with a zeolite. J. W. B.

Optical activity of phytol. T. WAGNER-JAUREGG (Z. physiol. Chem., 1933, 222, 21—23).—The optical activity of crude phytol is completely accounted for by that of the residue after distillation. The natural substance is probably inactive. J. H. B.

Fluorescence spectra of hypericin and mycoporphyrin. C. DHÉRE (Compt. rend., 1933, 197, 948—950).—In C_8H_8N , hypericin (I), the pigment of *Hypericum perforatum*, shows fluorescence spectral bands at 657—648, 626—619, and 610—599 m μ , and an absorption band at 606—596 m μ , which coincide with the bands for mycoporphyrin (II) (*Penicillium clavariae formis*). There is similar agreement in EtOH solution. (I) and (II) are probably identical. A. C.

Pigment of *Carica papaya*, L. I. R. YAMAMOTO and S. TIN (J. Agric. Chem. Soc. Japan, 1933, 9, 752—757).—In addition to violaxanthin, caricaxanthin, m.p. 166°, containing two OH groups, is present. CH. ABS.

Mandarin pigment. I. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1933, 221, 278—280).— β -Carotene was isolated from the flesh and rind of the mandarin (*Citrus madurensis*). Violaxanthin and other xanthophylls were also present. J. H. B.

Pinene from the Lauraceæ. *Nectandra olæophora*, Bar. Rod. N. B. GONSALVES (Arch. Pharm., 1933, 271, 461—462).—The oil from this tree contains much α -pinene, some β -pinene and camphene. R. S. C.

Distribution of saponins in plants. T. SOLACOLU and E. WELLES (Arch. Pharm., 1933, 271, 470—477).—The approx. saponin content of different parts of many plants is estimated by the blood-gelatin method. R. S. C.

Toddalia aculeata (Pers.). I. Two alkaloids and a neutral crystalline substance from its root-walls.—See this vol., 88.

Exudation and volatilisation of alkaloids from plants. J. CHAZE (Compt. rend., 1933, 197, 1148—1150).—An alkaloidal exudate is detected histochemically (by KI_3) on the leaves, stems, and flowers of the hemlock. In warm sunlight, exudation is followed by rapid volatilisation. H. B.

Indian medicinal plants. III. Leaves of *Erythrina indica*. S. N. CHAKRAVARTI, M. L. SITARAMAN, and A. VENKATASUBBAN (J. Annamalai Univ., 1933, 2, 238—242).—The leaves contain a N-free substance, m.p. 83°, extractable by boiling Et₂O, EtOH, or light petroleum, which does not give glucoside or phytosterol reactions, and an alkaloid, m.p. 117°, pptd. from the 1% HCl extract by $KBiI_4$. H. A. P.

Proteins and non-protein nitrogenous substances in the juice of "erba medica." G. BARBERA (Annali Chim. Appl., 1933, 23, 462—470).—The apical parts of "erba medica" are very rich in non-proteins, mostly NH_2 -acids and amido-compounds, these containing about 50% of the total N compounds of the fresh juice. The remaining 50% is largely protein precipitable by EtOH and sol. in KOH.

"Manna-grass" (*Glyceria spectabilis*), a species of high hydrocyanic acid content. H. MINNSEN (Landw. Versuchs-Stat., 1933, 117, 279—312).—The relatively large proportion of HCN in manna-grass probably occurs as an easily decomposable compound other than a glucoside. Ensilage of the material reduces the HCN content. The liberation of HCN is accelerated by treatment of leaves with 1% tartaric acid solution. Small amounts of HCN also occur in the female inflorescence of maize. A. G. P.

Comparative zinc content of green and etiolated leaves. G. BERTRAND and M. ANDREITCHIEVA (Compt. rend., 1933, 197, 1374—1376).—Determination of the Zn present in a large variety of green and either artificially etiolated or inner, yellow, leaves (cabbage, lettuce) confirms the previous conclusion (A., 1929, 362) that the Zn content is the greater the greater is the chlorophyll content of the leaf. J. W. B.

Changes in the cell contents of wood (xylem parenchyma) and their relationships to the respiration of wood and its resistance to *Lyctus* attack and to fungal invasion. S. E. WILSON (Ann. Appl. Biol., 1933, 20, 661—690).—Starch present in the xylem parenchyma of the sap wood of trees when felled disappears during delayed drying, e.g., when stored in log form. This is attributable to the continued activity of sapwood cells. Kiln-drying or steaming kills the cells and starch remains, thus rendering wood more liable to infestation by *Lyctus* beetles, of which starch forms the principal food. A. G. P.

Nature of the sheath material in the feeding punctures produced by the potato leaf hopper and the three-cornered lucerne hopper. F. F. SMITH (J. Agric. Res., 1933, 47, 475—485).—The sheathing substance is mainly of insect origin and gives positive tests for pectin, protein, and, probably, chitin. Colour tests differentiating sheath material from plant tissue are given. A. G. P.

Exanthema in pears and its relation to copper deficiency. J. OSERKOWSKY and H. E. THOMAS (Science, 1933, 78, 315—316).—Exanthema in pears appears to be due to a deficiency of Cu. Spraying with Bordeaux mixture or the introduction of sol. Cu salts into the trunks of trees effects a marked improvement in diseased trees (I). The Cu content of leaves of (I) is always < that of leaves from disease-free localities. L. S. T.

Qualitative analysis of protein solutions. A. SCHMUTZ (Z. physiol. Chem., 1933, 221, 197—201).—A nephelometric method employing fractional pptn. with $(\text{NH}_4)_2\text{SO}_4$ is described. When the content of saturated $(\text{NH}_4)_2\text{SO}_4$ solution is plotted against turbidity, various proteins give characteristic curves. J. H. B.

Biuret reaction in medicine and the chemistry of foodstuffs. H. KÜHL (Pharm. Zentr., 1933, 74, 751—754).—A summary of earlier results of the application of the biuret reaction in urine testing and cereal analysis. Physico-chemical differences in composition of flours can be detected by its use. P. G. M.

Deproteinisation with iodine. A. BAUDOUIN and J. LEWIN (Compt. rend. Soc. Biol., 1933, 113, 155—157; Chem. Zentr., 1933, i, 96).—When wet decomp. is effected with H_2SO_4 in presence of oxalate, pptn. with $\text{CCl}_3\text{CO}_2\text{H}$ or I gives concordant vals. for non-protein-N in the filtrate (e.g., from blood). A. A. E.

Determination of ethyl iodide by the katharometer in determinations of cardiac output in man. J. S. DONAL, jun., and C. J. GAMBLE (Amer. J. Med. Sci., 1933, 185, 744).—A sample of respired air is freed from CO_2 and H_2O by exposure to ascarite and P_2O_5 ; the thermal conductivity is determined before and after removal of EtI with liquid air. The average error is 0.00055 vol.-%. CH. ABS.

Determination of ketonic substances by means of the step photometer. W. NEUWEILER (Klin. Woch., 1933, 12, 869—870).—The method is based

on the colour reaction of COMe_2 with salicylaldehyde in presence of KOH. Pulfrich's instrument is used for comparing the absorption with that of a standard solution. 5 c.c. of blood are required.

NUTR. ABS. (m)

Carbohydrates. I. Micro-determination of menthol-, borneol-, and β -naphthol-glycuronic acid in blood. II. Colorimetric micro-determination of free and conjugated menthol in blood and tissue. H. MASAMUNE (J. Biochem. Japan, 1933, 18, 259—276, 277—283).—I. The method of Quick (A., 1924, ii, 876) for urine is applied to blood (1 c.c.). The mol. reducing power of glycuronic acid (I) = that of glucose. The hydrolysis consts. of menthol-, β -naphthol-, Na borneol-, and phenol-glycuronic acid are 0.1495, 0.0288, 0.2154, and 0.0203, respectively. Data for the blood content of (I) (calc. as phenolglycuronic acid) for various animals are given.

II. The tissue (1 g.) or blood (1 c.c.) is deproteinised with EtOH , free menthol distilled with the solvent, the distillate treated with $p\text{-NMe}_2\text{-C}_6\text{H}_4\text{-CHO}$, and the red colour produced compared with suitable standards. The residue is treated with aq. NaOH followed by aq. CdSO_4 and filtered, the filtrate being tested as above. F. O. H.

Micro-determination of glycogen. S. SIMONOVITS (Biochem. Z., 1933, 265, 437—443).—Glycogen (I) determinations by Sahyun's method (A., 1932, 77) gave much lower results than by Pfluger's macro-method, some (I) being lost by adsorption on the charcoal. A method which gives reasonably accurate results with 0.6 mg. of (I) is described. P. W. C.

Micro-determination of cholesterol. G. MONASTERIO (Biochem. Z., 1933, 265, 444—447).—Cholesterol (I) is pptd. with digitonin, the digitonide oxidised with CrO_3 , and the excess of the latter determined by micro-iodometric titration. The method is used for determination of free and combined (I). P. W. C.

Micro-incineration of tissues. R. F. MACLENNAN (Science, 1933, 78, 367).

Determination of iron in biological material. R. F. HANZAL (Proc. Soc. Exp. Biol. Med., 1933, 30, 846—848).—A colorimetric method is based on the reaction between Fe salts and $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ in alkaline solution. NUTR. ABS. (m)

Semi-micro-determination of sulphur in finger nails. R. C. NEALE and W. A. PEABODY (J. Lab. Clin. Med., 1933, 18, 1178—1181).—The material (25 mg.) is fused with Na_2O_2 ; S is pptd. as BaSO_4 with BaCl_2 , excess of which is titrated with $\text{K}_2\text{Cr}_2\text{O}_7$ (phenol-red indicator). CH. ABS.

Separation and determination of bismuth and arsenic in biological material. E. H. MAEHLING (J. Lab. Clin. Med., 1933, 18, 1058—1061).—The sample (5 c.c.) is digested with H_2SO_4 and HNO_3 ; the product is treated with N_2H_4 , H_2SO_4 and distilled. The distillate is oxidised with $\text{Br-H}_2\text{O}$ and As^v determined volumetrically or colorimetrically. Bi in the residue is determined by Leonard's method. CH. ABS.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1934.

General, Physical, and Inorganic Chemistry.

Ground state of the hydrogen molecule. H. M. JAMES and A. S. COOLIDGE (J. Chem. Physics, 1933, 1, 825—835).—Mathematical. The method of Hylleraas for the He atom is extended to the H₂ mol. N. M. B.

Relative intensities of atomic spectral lines from a hydrogen discharge tube. W. W. JACKSON (Phil. Mag., 1934, [vii], 17, 33—53).— H_α varies parabolically and H_β and P_α vary linearly with the discharge current at const. pressure and p.d. across the tube. Relative transition probabilities have been calc. H. J. E.

Negative sections of the cold-cathode glow discharge in helium. K. G. EMELÉUS, W. L. BROWN, and H. McN. COWAN (Phil. Mag., 1934, [vii], 17, 146—160).—Discharge characteristics are described. H. J. E.

Stark effect with the helium 5876 line with high resolution. R. RITSCHL (Physikal. Z., 1934, 35, 53).—The Stark effect with the He 5876 line has been investigated with high resolution to discover the behaviour of each component in the electric field. A. J. M.

Measurement of arc temperature from C₂ bands. Transition probability of vibrational transitions. D. T. J. TER HORST and C. KRYGSMAN (Physica, 1933, 1, 114—118).—From the intensities of the C₂ rotation bands the temp. of an arc is calc. as 6000° abs., in agreement with the val. calc. from CN bands. Assuming the same temp. for the vibrational bands, the ratio of transition probabilities agrees with theory (Wurm, Z. Astrophys., 1932, 5, 260). J. W. S.

New terms in the spectra of N III, N IV, N V, O III, O IV, and O V. W. M. CADY (Physical Rev., 1933, [ii], 44, 821—825; cf. Edlén, A., 1933, 991).—Full data and analyses are given for the extreme ultra-violet spectra due to a new type of violent condensed discharge through air at low pressure in a quartz capillary. N. M. B.

Analysis of the N₂⁺ bands. A. E. PARKER (Physical Rev., 1933, [ii], 44, 914—918).—Rotational analyses for the (4, 7), (5, 8), (6, 9), and (7, 10) bands, perturbation data for the (5, 8) band, and additional lines in the (5, 8) and (13, 15) bands are tabulated. N. M. B.

Combination relations in the absorption spectrum of liquid oxygen. J. W. ELLIS and H. O. KNESER (Z. Physik, 1933, 86, 583—592).—The absorption spectrum was investigated between 340

and 2750 m μ , and a new band at 1261 m μ is recorded. The complete spectrum, including infra-red bands, is represented by a linear formula involving the frequencies 793 and 1307 mm.⁻¹ and the vibrational frequency of O₂. Certain combination bands are ascribed to (O₂)₂. A. B. D. C.

Wave-lengths of the red lines of neon and their use as secondary standards. C. V. JACKSON (Proc. Roy. Soc., 1933, A, 143, 124—135).—Direct comparisons of the wave-lengths of the red lines of Ne with the primary standard show that, for resolving powers > 250,000, the Ne lines have const. wave-lengths. With lower resolving powers, however, the wave-lengths become systematically lower, until a min. is reached at about 100,000. This is caused by blending of the weak satellite (due to Ne²²) with the main line. A table of corrections to be applied to the standard Ne wave-lengths when used with apparatus of low resolving power is given. L. L. B.

Natural width of neon lines in the visible spectrum. I. W. SCHÜTZ. II. H. SCHILLBACH (Ann. Physik, 1933, [v], 18, 705—720, 721—745).—I. An experimental test of the quantum theory applied to the natural width of Ne lines is proposed and the theory of it discussed. The difference between the results obtained by application of the old and new (Dirac-Weisskopf-Wigner) quantum theories is that according to the latter, within a group of Ne lines with a common initial level the width of the lines due to transition to the unstable s_2 level should be > that of lines due to transition to the metastable s_3 and s_5 levels.

II. An account of the experimental work in connexion with the above is given, involving the determination of the intensity distribution in the Ne lines by an interferometric method, and the density of the dispersion electrons. The results agree with the theory of Weisskopf and Wigner. A. J. M.

Dependence of the intensity of the visible Ne lines of the positive column on the current strength. W. SCHÜTZ (Ann. Physik, 1933, [v], 18, 746—754).—Photographs of the Ne spectrum were taken so that the product of time of exposure and current strength was const. The lines of a group (p_k-s_i) with a common initial term were not of const. intensity under these conditions. A. J. M.

Line absorption of sodium vapour for the two D-lines. W. ZEHDEN (Z. Physik, 1933, 86, 555—582).—Line absorption was measured with an accuracy of 4% for the pressure range 1×10^6 to

4×10^{-5} mm., and the results are compared with those of magnetorotation. A. B. D. C.

Energy balance, electron temperature, and voltage gradient in the positive column in mixtures of Na vapour with Ne, He, and A. M. J. DRUYVESTEYN and N. WARMOLTZ (Phil. Mag., 1934, [vii], 17, 1—27; cf. A., 1933, 1).—Either in pure Na vapour, or in Na + a few mm. of Ne, He, or A, the power input in the discharge equals the output (radiation + wall energy). Discrepancies occur at higher pressures of the rare gas. H. J. E.

Nuclear spin and magnetic moment of sodium from hyperfine structure. L. P. GRANATH and C. M. VAN ATTA (Physical Rev., 1933, [ii], 44, 935—942).—The observed hyperfine structure of the Na *D* lines showed component separations: D_2 (λ 5890), 0.0555, D_1 (λ 5896), 0.0612 cm.⁻¹ Relative intensity measurements indicate a nuclear spin of 3/2. The calc. nuclear magnetic moment is 2.7/1840 Bohr magneton. N. M. B.

Transport of matter in arcs and flames. Optical determination of the radii of alkali atoms. L. A. GINSEL (Arch. Neerland., 1933, [iii], 14, 285—333).—The intensity variation of spectral lines due to the metal atom in an arc between the metal and a C electrode was used to examine factors influencing the transport of metal. Line intensity measurements were used to calculate the diffusion consts. of Na, K, Rb, and Cs in a Bunsen flame, and their at. radii. H. J. E.

Remarkable optical properties of the alkali metals. C. ZENER (Nature, 1933, 132, 968).—Treating electrons as moving in no field, Wood's observations (A., 1933, 1096) on the transparency of the alkali metals in ultra-violet light can be qualitatively accounted for; approx. vals. of the crit. wave-length are calc. L. S. T.

Band system of ionised aluminium hydride. W. HOLST (Nature, 1933, 132, 1003).—The new system at 3600 Å. (A., 1933, 991) must be attributed to AlH. New systems at 2700 Å. and 3380 Å. are reported. L. S. T.

Nuclear spin of phosphorus from band spectrum analysis. (Miss) M. F. ASHLEY (Physical Rev., 1933, [ii], 44, 919—926).—Photographs of the emission spectrum of P₂ showed a strong alternation in intensity in successive rotational lines of branches, giving an intensity ratio 3 : 1 from which the nuclear spin of the P atom is 1/2. Fine structure analyses of the (6, 22), (6, 23), (8, 87), (8, 28), and (9, 28) bands are tabulated. N. M. B.

Displacement and unsymmetrical broadening of absorption lines by foreign gases. C. FUCHTBAUER and F. GOSSLER (Z. Physik, 1933, 87, 89—104).—Displacement and broadening have been investigated with H₂ as foreign gas in addition to those already given (A., 1933, 1096), and the spectrum of K has been similarly investigated. A. B. D. C.

Zeeman effect and uncoupling phenomena in the CaH bands. W. P. CUNNINGHAM and W. W. WATSON (Physical Rev., 1933, [ii], 44, 815—817; cf. A., 1930, 1074; 1932, 315).—The effect of the

strong *l*-uncoupling in the ²Π state on the Zeeman patterns of the lines of the ²Π → ²Σ CaH band at 7000 Å. is discussed. N. M. B.

Probe measurements for luminous arcs in air at atmospheric pressure. J. L. MYER (Z. Physik, 1933, 87, 1—18).—Potential drop in different regions of the arc was investigated using Fe, Cu, C, Ni, and Zn as electrodes. The cathode fall corresponds with the second ionisation potential of the cathode and is little affected by the anode material; the anode fall was similarly investigated and gave results agreeing with those of Nottingham (J. Franklin Inst., 1928, 206, 43). A. B. D. C.

Standard copper wave-lengths in the region 100—450 Å. P. G. KRUGER and F. S. COOPER (Physical Rev., 1933, [ii], 44, 826—830).—Intensities and 476 standard wave-lengths are tabulated. Possible errors are discussed. N. M. B.

Zeeman separation of infra-red krypton I lines. B. POGANY (Z. Physik, 1933, 86, 729—737).—*g*-Coupling is worked out (cf. A., 1933, 1219). A. B. D. C.

Absorption spectra due to excitation of inner electrons. II. Mercury spectrum between 1190 and 600 Å. due to excitation of the (5*d*)¹⁰ shell (HgI^b). III. Cadmium spectrum from 1100 to 600 Å. due to excitation of the (4*d*)¹⁰ shell (CdI^b). H. BEUTLER (Z. Physik, 1933, 86, 710—728; 87, 19—27). A. B. D. C.

Line shape as a function of the mode of spectrograph slit irradiation. D. C. STOCKBARGER and L. BURNS (J. Opt. Soc. Amer., 1933, 23, 379—385).—Non-coherent, coherent, lens, and broad source modes of slit irradiation have been studied and the line shape and its effect on resolution have been investigated for each mode. W. R. A.

Limitations of the theory of complex spectra. H. H. MARVIN (Physical Rev., 1933, [ii], 44, 818—820).—The extension of the theory of two-electron systems to include *d*⁹*p* and *d*⁹*d* is discussed. N. M. B.

Measurement of visibility curves for the Michelson interferometer. (Miss) E. J. M. VAN DER SLOOTEN and C. JANSSEN (Z. Physik, 1933, 86, 760—764).—Observed variation of visibility with path difference agrees with the theoretical variation only when polarised light is used. A. B. D. C.

Asymmetries of pressure-broadened spectral lines. H. MARGENAU (Physical Rev., 1933, [ii], 44, 931—934; cf. A., 1933, 879).—Asymmetries in the intensity distribution of pressure-broadened lines are explained by calc. line contours, taking account of repulsive portions of the energy curves. N. M. B.

Determination of spectral intensities applied to problems of atomic and molecular physics. L. S. ORNSTEIN (J. Phys. Radium, 1933, [vii], 4, 613—624).—Methods of determination of spectral intensities are reviewed. The probability of emission, activation, and excitation of atoms by electron collision is discussed. The application of the laws of spectral intensity to the kinetic theory of gases, the theory of the electric arc, and other problems is given. A. J. M.

General conditions for glow discharge without cathode fall and dark space. A. GUNTHER-SCHULZE and H. FRICKE (Z. Physik, 1933, 86, 821—827).—Various substances are given for the cathode required to produce this glow. Among the best are BeCO_3 , MgO , CaCO_3 , ZrO_2 , ThO_2 , SiO_2 , ZnSiO_3 , Al_2O_3 , Sb_2O_3 , Ta_2O_5 , talc, and glass. A. B. D. C.

Emission of light in gaseous discharges. II. W. DE GROOT (Physica, 1933, 1, 28—34).—Methods of calculation are discussed. F. L. U.

Distribution of radiation in the arc. L. S. ORNSTEIN and H. BRINKMAN (Z. wiss. Phot., 1933, 32, 200).—Attention is directed to papers by the authors to which no reference was made by Brückensteinkuhl (A., 1933, 440). J. L.

Discharge produced by superposing a constant on a high-frequency field. (MLLE.) M. CHENOT (Compt. rend., 1933, 197, 1599—1601).—The effect of superposing a.c. and d.c. on the discharge in a vac. tube with electrodes 30 mm. apart is described, and shown to be largely due to foreign matter in the cathode. C. A. S.

Light of the night sky and active nitrogen. J. KAPLAN (Nature, 1933, 132, 1002—1003). L. S. T.

Simultaneous presence of carbon and titanium oxide bands in [spectra of] sun-spots. P. SWINGS (Bull. Acad. roy. Belg., 1933, [v], 19, 1071—1073; cf. A., 1931, 991).—Stars of spectral type K3 contain sensibly equal nos. of C_2 and TiO mols. The C_2 concn. decreases and the TiO concn. increases in the $S-M$ branch, and vice versa in the $R-N$ branch. J. W. S.

Stellar spectra showing both emission lines of H, He I, He II, C III, O III, and nebularium, and absorption bands of TiO . P. SWINGS (Bull. Acad. roy. Belg., 1933, [v], 19, 1074—1077; cf. Astrophys. J., 1933, 77, 44).—The variable stars AX Persei, RW Hydrae, and CI Cygni, the spectra of which show this phenomenon, probably consist of doublets, a hot star giving rise to the emission spectra, and a cooler star of high Ti concn., the two being so close as to be inseparable spectroscopically. J. W. S.

Scandium oxide bands in the spectra of cold stars. P. SWINGS (Bull. Acad. roy. Belg., 1933, [v], 19, 1078—1095).—The results of Bobrovnikoff (Astrophys. J., 1933, 77, 345) are discussed. J. W. S.

X-Ray K- and L-spectra of aluminium. (A) M. SIEGBAHN and T. MAGNUSSEN. (B) M. SIEGBAHN and H. KARLSSON (Nature, 1933, 132, 895, 895—896).—(A) The L-line of Al from Al_2O_3 compared with metallic Al is displaced towards longer wave-lengths and has a different structure without the sharp edge (cf. this vol., 3).

(B) Al metal gives a β -line, corresponding with a transition from the free electron levels to the K-level, with a sharp edge on the short wave-length side, which is not formed by Al_2O_3 , where the corresponding line is more symmetrical. L. S. T.

Dependence of refractive index for X-rays on the angle of incidence. F. JENTZSCH and H. STEPS (Naturwiss., 1933, 21, 883—884).—The dependence of

n of glass for X-rays on the angle of incidence predicted by Orban (A., 1933, 1233) has been verified. A. J. M.

Atomic constants deduced from secondary cathode-ray measurements. H. R. ROBINSON, J. P. ANDREWS, and E. J. IRONS (Proc. Roy. Soc., 1933, A, 143, 48—60).—The results of new measurements of the energies of the groups of homogeneous secondary cathode rays expelled from Au, W, Ag, and Cu by the K series X-rays of Cu are compared with the vals. predicted by X-ray spectroscopic data. The results are consistent with recent work on electron diffraction, rather than with the accepted vals. of h and e . L. L. B.

Photo-electric yields in the extreme ultra-violet. C. KENTY (Physical Rev., 1933, [ii], 44, 891—897).—Yields for Ni, W, Mg, W-O, and constantan surfaces illuminated by short-wave radiation from positive columns in He, Ne, and A down to 584 Å. varied with the surface and gas (except from Mg). N. M. B.

Determination of Planck's constant from velocity measurements of photo-electrons. S. PRILEZAEV (Z. Physik, 1933, 87, 28—31).—A reply to Du Bridge (A., 1933, 657). A. B. D. C.

Thermionic constants of platinum. H. L. VAN VELZER (Physical Rev., 1933, [ii], 44, 831—836).—Supersaturation curves for various ageing temp. using cylindrical Pt filaments are given. Stable states were found at 1650° and 1785° abs.; for the latter $A=60$ amp./cm.² deg.², $\phi=5.29$ volts. N. M. B.

Concentration of excited atoms and positive ions of sodium in a low-voltage sodium arc. M. J. DRUYVESTEYN (Physica, 1933, 1, 14—27).—In a Na-vapour lamp containing a small quantity of Ne the no. of Na atoms in the $2p$ condition is about 12% of the no. (Q) of normal atoms, and the no. of positive Na ions is $2Q-5Q$. F. L. U.

Diffusion of positive ions of salts through copper, silver, and gold at high temperatures. Mass-spectrograph analysis of emitted ions. J. CICHOCKI (Ann. Physique, 1933, [x], 20, 478—517).—Investigations previously reported for Cu films (cf. A., 1933, 3) are continued for Ag and Au. The emitted ions undergo an energy loss, indicated by line displacement towards lower magnetic field vals. An approx. explanation of the mechanism is given on the hypothesis of emission of large unstable ions. N. M. B.

Measurement of ionic mobilities in the positive column. S. HARRIS (Phil. Mag., 1934, [viii], 17, 131—145).—Ionic mobilities in air and H_2 were calc. from measurements on the speed of rotation of the positive column around an annular discharge tube with varying magnetic and electric fields, current, and pressure, and from the Hall effect. H. J. E.

Passage of slow positive ions through highly diluted gases. O. BEECK (Physikal. Z., 1934, 35, 36—52).—A summary of work on the effective cross-section of gas mols. towards slow ions, the charge and ionisation cross-sections, excitation and dissociation by collision with positive ions, and the scattering of slow protons. A. J. M.

Emission of electrons from metals by very slow canal rays. G. VALLE (*Atti R. Accad. Sci. Torino, Cl. Sci. Fis. Mat. Nat.*, 1932, 67, 490—499; *Chem. Zentr.*, 1933, ii, 1309).

Electron-microscopic observations of the movement of emission substances on oxide cathodes. E. F. RICHTER (*Z. Physik*, 1933, 86, 697—709).—Inversion of images on cathode surfaces is due to evaporation and recondensation of the emitting substance.

A. B. D. C.

Electron velocity in insulators under high field intensities and its relation to the theory of electrical breakdown. A. GUNTHER-SCHULZE (*Z. Physik*, 1933, 86, 778—786).

A. B. D. C.

Determination of inner potentials from electron diffraction. V. E. LASCHKAREV (*Z. Physik*, 1933, 86, 797—801).—Theoretical.

A. B. D. C.

Stationary treatment of elastic scattering of very fast electrons. F. SAUTER (*Z. Physik*, 1933, 86, 818—820).—This method gives results very simply using relativistic wave mechanics.

A. B. D. C.

Field electron emission from liquid mercury. J. W. BEAMS (*Physical Rev.*, 1933, [ii], 44, 803—807).

N. M. B.

Reflexion of electrons from liquid mercury. R. B. BRODE and E. B. JORDAN (*Physical Rev.*, 1933, [ii], 44, 872—875).—Curves for elastically scattered electrons as a function of electron velocity and angles of incidence and reflexion show a preference for reflexion backwards to the direction of the incident beam.

N. M. B.

Magnetic deflexion method for angular distribution of electrons scattered by gas molecules. A. P. GAGGE (*Physical Rev.*, 1933, [ii], 44, 808—814).—A method is described, applicable to scattering angles up to 180° and to elastic and inelastic collisions of slow electrons, for evaluating the scattering coeff. for electrons colliding with gas mols., if the electrons before and after collision describe circular paths in a uniform magnetic field. Results for 80- and 30-volt electrons in Hg vapour are given.

N. M. B.

Photo-electric investigation of the temperature variation of electron emission potential from a nickel surface with an atomic barium layer. R. SUHRMANN and R. DEPONTE (*Z. Physik*, 1933, 86, 615—634).—The temp. range was 20—500°.

A. B. D. C.

Measurements of light excitation efficiencies in argon and mercury spectra by electron collision. O. FISCHER (*Z. Physik*, 1933, 86, 646—666).—Excitation functions were obtained for the violet group of the A arc spectrum and for the blue spark lines with a pressure range of 5—25 × 10⁻³ mm.

A. B. D. C.

Electron scattering in methane, acetylene, and ethylene. A. L. HUGHES and J. H. McMILLEN (*Physical Rev.*, 1933, [ii], 44, 876—882).—Scattering coeffs. for elastic collisions are tabulated for various voltage and temp. ranges. Total absorption coeffs. are calc. For energies > 100 volts scattering coeffs. of electrons by mols. with two C atoms were < those by mols. with one C atom; for 10-volt electrons the reverse was the case. Interference effects between

electron waves scattered by individual atoms were found.

N. M. B.

Electron attachment and negative ion formation in oxygen and oxygen mixtures. N. E. BRADBURY (*Physical Rev.*, 1933, [ii], 44, 883—890).—The probability of electron capture for O₂, air, and O₂-rare gas mixtures was measured by the analysis of a mixed current stream at two points by separating ionic fractions between wire grids. In O₂, and its mixtures an increase in attachment probability occurs at 1.6-volt electronic energy, due to low-energy electrons following inelastic impacts with O₂ mols.

N. M. B.

Electronic flux in problems of several electrons. J. WINTER (*J. Phys. Radium*, 1933, [vii], 4, 646—649).—Theoretical.

A. J. M.

Polarisation of electrons. G. P. THOMSON (*Nature*, 1933, 132, 1006).—The asymmetrical scattering of electrons reported by Rupp (*A.*, 1932, 317) could not be confirmed.

L. S. T.

Experimental detection of polarised electrons. E. RUPP (*Conv. Fis. Nucl.*, 1932, 1, 143—151; *Chem. Zentr.*, 1933, i, 1735).

L. S. T.

Complex processes of materialisation. L. GOLDSTEIN (*Compt. rend.*, 1933, 197, 1596—1598).—The probability of the simultaneous creation of pairs of electrons and ionisation by the absorption of a photon by, or the collision of an electron with, an atom, in either case possessed of suitable energy, has a finite val., although < the probability of the creation of pairs of electrons from a heavy nucleus (cf. this vol., 6).

C. A. S.

Annihilation of positrons on contact with matter and the resultant radiation. J. THIBAUD (*Compt. rend.*, 1933, 197, 1629—1632).—Positrons falling on matter are very quickly dematerialised with evolution of photons of energy < 500 kev. Such positrons (average energy 800 kev.) and the photons produced by them give a distinctly different absorption curve from that given by the electrons forming the general radiation, photons X, produced by the positrons among the at. electrons (of average energy 500 kev.). For a thickness of Pt 500 mg. per sq. cm. absorption increases linearly for both positrons and electrons, μ/ρ for electrons being 1.6 times that for positrons; for greater thicknesses the photons due to positrons abandon in the film 1/180 of the intensity of the primary positrons, whilst X yields only 1/7500 of the initial energy of the electrons. Positrons thus produce new radiation 40 times as penetrating as that due to collision of electrons. These results are substantiated by measurement of the energy left in the film. The average quantity of the positrons in Pt is 580 mg. per sq. cm., and average life in ordinary air 1.2 × 10⁻⁸ sec. (cf. *A.*, 1933, 993, 1098; this vol., 4).

C. A. S.

Experimental proof of annihilation of positive electrons. F. JOLIOT (*Compt. rend.*, 1933, 197, 1622—1625).—Positive and negative electrons (from Po) were alternately magnetically directed on a radiator of Pb or Ag, placed above a Geiger-Müller counter, and the results with each compared. Absence of radiation of energies 1 or 0.64 × 10⁶ ev., coupled

with the presence of that of 0.5×10^6 ev. in approx. the required amount, indicates that when the positive electrons are absorbed in matter photons of energy approx. 0.5×10^6 ev., in no. double that of the incident positive electrons, are emitted, as required by Dirac's theory.

C. A. S.

Displacement in an electrostatic field of magneto-electronic cycloids. L. CARTAN (Compt. rend., 1933, 197, 1604—1606; cf. A., 1933, 993; this vol., 4).—The general case (of which Thibaud's method of collecting positrons is a special one) in which the electric field is directed in any direction is dealt with mathematically, and Thibaud's formula deduced.

C. A. S.

Stopping of fast particles with emission of radiation and the birth of positive electrons. W. HEITLER and F. SAUTER (Nature, 1933, 132, 892).—Dirac's theory of the electron has been used to calculate (i) the probability that a fast electron, passing through matter, emits a quantum of radiation (I) with energy comparable with its own, and (ii) the probability that (I), colliding with a nucleus, gives birth to a positive electron.

L. S. T.

Positive electron. P. M. S. BLACKETT (Nature, 1933, 132, 917—919).—A summary.

L. S. T.

Positive electron tracks. D. SKOBELEZYN (Nature, 1934, 133, 23—24).

L. S. T.

At. wt. of molybdenum. R. LAUTHÉ (Compt. rend., 1933, 197, 1730—1732).—Commercial MoO_3 was converted into $\text{MoOCl}_2(\text{OH})_2$, and the redistilled product changed back into MoO_3 , and this sublimed at $> 793^\circ$ and reduced to Mo at 800° by H_2 . The mean of seven experiments Mo/MoO_3 gave 96.01 ± 0.01 . Oxidation of Mo to MoO_3 gave 96.02 , in good agreement with Aston's 95.97 ± 0.05 (cf. A., 1930, 1338) and the accepted val. 96.0 .

C. A. S.

Constitution of neodymium, samarium, europium, gadolinium, and terbium. F. W. ASTON (Nature, 1933, 132, 930—931).—Provisional analyses by accelerated anode rays are Sm, a strong pair 152 and 154, and a triplet 147, 148, and 149; Eu, two odd mass nos. 151 and 153 in approx. equal abundance; Gd, apparently consisting of 155, 156, 157, 158, and 160 with faint effects at 152 and 154 probably due to Sm as impurity; Tb, only one line 159. Nd contains 143 and 145 in addition to 142, 144, and 146 already known, and these are now shown to be in descending order of abundance.

L. S. T.

Abundance ratio of lithium isotopes Li^7 and Li^6 . L. S. ORNSTEIN, J. A. VREESWIJK, jun., and G. WOLFSOHN (Physica, 1933, 1, 53—59).—Measurements of intensity of the Li resonance line 6708 \AA . lead to the val. 8.1 ± 0.4 for $\text{Li}^7 : \text{Li}^6$, in agreement with previous optical determinations (A., 1931, 992), and contrary to results given by mass-spectrographic methods.

F. L. U.

Suggested nomenclature for heavy hydrogen and its compounds. R. W. WOOD (Science, 1933, 78, 583).—It is suggested that heavy H_2 (I) be called bar-hydrogen, and written as Hydrogen. Compounds of (I) would be bar-benzene, written Benzene, bar-ammonia, written Ammonia, etc.

L. S. T.

Existence of two new α -radiations and a new definite radiation of unknown origin. G. DIECK (Naturwiss., 1933, 21, 896—897).—From Cu sheet, and Cu and Au wires, two new α -radiations were obtained, of ranges in air 0.9 and 1.5 cm. The radiation could not be connected with the U isotope of Wilkins and Rayton. A corpuscular radiation differing in many ways from α -radiation was also found, being probably \bar{H} -particles, not arising from the walls of the cloud chamber, but set free from the gas in the chamber. The origin of this radiation is discussed. The results of Locher (Physical Rev., 1933, [ii], 44, 779) on the corpuscular radiation produced by the action of neutrons on the gas agree with those now obtained.

A. J. M.

Reversed fine structure of the α -rays. A. POLESSITSKY (Nature, 1933, 132, 969).—Theoretical.

L. S. T.

Excitation of the inner shells of atoms by low-energy protons and α -particles. W. HENNEBERG (Z. Physik, 1933, 86, 592—604).—The probability of ionisation of K-shells is calc. and found to vary as the fourth power of the energy for low-energy vals.

A. B. D. C.

Possibility of emission of neutral particles of nul intrinsic mass in β -radioactivity. F. PERRIN (Compt. rend., 1933, 197, 1625—1627).—Pauli's neutrino is discussed, it being regarded as of zero mass, and consequently has always the velocity of light. It is not pre-existent in the nucleus, but formed like a photon at the instant of emission, and has a spin $1/2$.

C. A. S.

Conservation laws and β -emission. G. BECK (Nature, 1933, 132, 967).—Mainly theoretical. The view that U-Z is not a branch product, but a derivative of an unknown isotope of U, is supported.

L. S. T.

Diffusion of hard γ -rays. V. TRKAL (J. Phys. Radium, 1933, [vii], 4, 665—676).—The theory underlying the experimental work of Neukirchen (Z. Physik, 1921, 6, 101) on the absorption of hard γ -rays is developed.

A. J. M.

Investigation of secondary radiation excited by hard γ -rays. T. HETTING (Z. Physik, 1933, 87, 127—138).—Al, Fe, Cu, and Pb when exposed to radiation of 4.7 X all gave a secondary component of wave-length 23.8 X , the intensity of this component varying as the square of the at. no. This secondary radiation is considered to be due to recombination of a positive and a negative electron.

A. B. D. C.

Radioactivity of zinc. H. FESEFELDT (Z. Physik, 1933, 86, 611—614).—The α -particle emission of Zn is $< 1/10$ that observed by Zeigert (A., 1928, 455).

A. B. D. C.

Theory of atomic disintegration. T. SEXL (Z. Physik, 1933, 87, 105—126).—A quant. theory is given for disintegration of nuclei by protons, deuterons, and α -particles.

A. B. D. C.

Half-life period of thorium. H. FESEFELDT (Z. Physik, 1933, 86, 605—610).—The half-life period is 1.3×10^{10} years.

A. B. D. C.

Effective diameters of radioactive nuclei. G. GAMOW and S. ROSENBLUM (Compt. rend., 1933,

197, 1620—1622).—The effective radii of the radioactive elements when plotted against at. wt. for the various α -particles emitted show that elements of the Ra and Th families lie approx. on the same curve; those of the Ac family have comparatively smaller radii (cf. A., 1932, 443).
C. A. S.

Long-range particles from boron liberated on bombardment by protons. F. KIRCHNER and H. NEUERT (Physikal. Z., 1933, 34, 897—898; cf. A., 1933, 551, 1098).—The particles emitted from B of range > 28 mm. have been investigated. The frequency of occurrence of particles with ranges up to 48 mm. has been obtained, the curve showing a very weak max. at 39 mm.
A. J. M.

Excitation of proton emission from boron nuclei by Po α -rays. F. HEIDENREICH (Z. Physik, 1933, 86, 675—693).—Three well-defined groups were observed, and the dependence of their range and intensity on the energy of the primary beam was investigated.
A. B. D. C.

Anomalies in relative amounts of elements and origin of radioactive substances. W. M. ELSASSER and K. GUGGENHEIMER (Compt. rend., 1933, 197, 1627—1629).—The disproportionate rarity of the rare gases is attributed to the action of neutrons (probably from a cosmic cloud) acting on an initial large amount thereof (probably 10^3 to 10^6 kg. per sq. cm.), a neutron being captured by a nucleus with emission of a β -ray, and the process repeated, thus giving rise to other elements. This would be consistent with restriction of radioactive elements to the surface of the earth, and the difference of unity between the masses of radioactive K and Rb and of those of an isotope of A and Kr, respectively.
C. A. S.

Cloud-chamber photographs of the disintegration products of lithium and boron on bombardment with fast protons. F. KIRCHNER (Sitzungsber. bayr. Akad. Wiss., 1933, 129—134; Chem. Zentr., 1933, ii, 1301—1302).

Atomic disintegration by ultra-radiation. W. MESSERSCHMIDT (Physikal. Z., 1933, 34, 896; cf. A., 1933, 551).—The max. of the collision distribution curves (for Pb, Fe, Al, and C) both as regards energy and frequency are displaced towards smaller ion production with increasing at. wt. The collisions observed are identical with the "showers" of Blackett and Occhialini (A., 1933, 441).
A. J. M.

Atomic disintegration by ultra-radiation. E. G. STEINKE, A. GASTELL, and H. NIE (Naturwiss., 1933, 21, 898—899; cf. A., 1933, 995, 1100).—The effect of atm. pressure on disintegration produced by ultra-radiation is surprisingly great, and is probably due to a very soft component of the radiation which is effective in bringing about disintegration, but produces little ionisation. Only the no. of weaker collisions is dependent on atm. pressure. Secondary radiation must also be taken into account. By increasing the thickness of the material through which the radiation must pass the pressure effect is reduced, becoming negligible when a thickness of 30 cm. Fe is interposed.
A. J. M.

New hard component of the cosmic ultra-radiation. A. CORLIN (Nature, 1934, 133, 63).
L. S. T.

Cosmic rays and the new field theory. M. BORN (Nature, 1934, 133, 63—64).—If the assumption of protons be excluded, the high penetrating power observed for cosmic rays supports the new field theory (A., 1933, 1097).
L. S. T.

Experimental evidence for the absence of scattering of light by light. F. L. MOHLER (J. Opt. Soc. Amer., 1933, 23, 386—387).—Certain theoretical relations can be interpreted so that photons will repel and scatter each other at a distance comparable with the wave-length of the radiation. This has been tested experimentally and, if there is any reaction, the scattering radius for photons of visible light is $< 5 \times 10^{-9}$ cm.
W. R. A.

Evidence for the formation of active hydrogen. A. B. VAN CLEAVE and A. C. GRUBB (Nature, 1933, 132, 1001; cf. A., 1931, 805; 1932, 1218).—H, activated by a discharge has properties which do not indicate at. H. With plastic S in the reaction chamber, a definite relation exists between voltage and pressure for the activation of H_2 . Above a crit. pressure, dependent on tube dimensions and proximity of the S, no activity is produced. Coating the tube with syrupy H_3PO_4 gives a less active H_2 , which is contrary to expectations if at. H. is present.
L. S. T.

Electromagnetic mass. M. BORN and L. INFELD (Nature, 1933, 132, 970).—Theoretical.
L. S. T.

Atomic transmutation and stellar temperatures. T. E. STERNE (Nature, 1933, 132, 893).
L. S. T.

Self-forces of elementary particles. II. G. WENTZEL (Z. Physik, 1933, 86, 635—645; cf. this vol., 7).—Theoretical.
A. B. D. C.

Atom factor determinations in the region of anomalous dispersion. II. K. SCHAFER (Z. Physik, 1933, 86, 738—759).—Powders must consist of particles of size $> 10^{-5}$ cm. for atom factor determinations. These were obtained for Fe and Cr.
A. B. D. C.

Hydrogen-like atoms in the classical quantum theory. P. COPEL (J. Phys. Radium, 1933, [vii], 4, 638—645).—Theoretical.
A. J. M.

Model of the electric field and of the photon. (Sir) J. J. THOMSON (Phil. Mag., 1934, [viii], 17, 197—198).—A note on an earlier paper (A., 1933, 441).
H. J. E.

Approximate wave function for the normal helium atom. D. R. HARTREE and A. L. INGMAN (Mem. Manchester Phil. Soc., 1932—1933, 77, 69—90).—Mathematical. A simple approximation to the wave function of the neutral He atom in its normal state is proposed, vals. of parameters are determined, and the function is compared with that due to Hylleraas.
N. M. B.

Attribution of wave functions and "eigenwerten" to the separate electrons of an atom. T. KOOPMANS (Physica, 1933, 1, 104—113).—Mathematical.
J. W. S.

Transparency of the atmosphere and absorption by oxygen. J. DUCLAUX (J. Phys. Radium, 1933, [vii], 4, 625—637).—The limit of transparency of the atm. in proximity to the earth is not given exactly by the theory of mol. diffusion. The atm. contains liquids and solids (e.g., NaCl, NaClO₃, NH₄NO₃, and NH₄NO₂), which considerably increase its absorption. Air at a considerable distance from the surface of the earth has not been washed by rain, and may be impure; coeffs. of absorption measured by solar radiation may therefore be too high. It is difficult to prove that the extinction of the solar spectrum between 2500 and 1850 Å. is due to continuous absorption by O₂.
A. J. M.

Infra-red absorption of ozone. G. HETTNER, R. POHLMAN, and H. J. SCHUMACHER (Naturwiss., 1933, 21, 884).—The spectrum of O₃ from the visible to 27 μ has been investigated. No selective absorption was found in addition to that previously discovered (A., 1933, 763). The bands at 7.6, 7.39, and 11.38 μ, respectively, usually assigned to O₃ do not, in fact, belong to it. If NO₂ is introduced into the tube, bands occur at 7.6 and 11.3 μ which probably belong to N₂O₅. It is suggested that the O₃ usually employed would contain some NO giving rise to the above bands.
A. J. M.

Band spectrum of barium oxide. P. C. MAHANTI (Proc. Physical Soc., 1934, 46, 51—61; cf. A., 1933, 444).—Data and vibrational and rotational analyses are given. The band system is due to a ¹Σ⁺→¹Σ transition.
N. M. B.

New bands in the electronic band spectrum of neutral OH. (Miss) K. CHAMBERLAIN and H. B. CURTIS (Physical Rev., 1933, [ii], 44, 927—930; cf. Johnston, A., 1933, 445).—Data are given for the lines of the λ 2447 (3,0) and λ 2676 (3,1) bands, excited by a high-frequency discharge in a very rapid flow of H₂O vapour through the tube. Additional faint lines were found in the λ 3064 band, and nine lines, probably of the (4,1) band, in the range λ 2539—2565.
N. M. B.

3240 Å. band of NH. R. W. B. PEARSE (Proc. Roy. Soc., 1933, A, 143, 112—123).—A new band attributed to NH has been observed at 3240 Å. near the 3360 Å. band of NH in the spectrum of a heavy-current discharge tube containing H₂ and a trace of N₂. Considerably greater energy is required to excite the 3240 band than the 3360 band. The new band possesses the intensity distribution and no. of "missing lines" characteristic of a ¹Π—¹Δ transition. Vals. of the rotational term differences and rotational consts. are given.
L. L. B.

Spectrum of sulphuryl chloride. H. W. THOMPSON (Nature, 1933, 132, 896).—The absorption spectrum of SO₂Cl₂ has been investigated over the range 5000—2000 Å. at 1—100 mm. pressure. It has certain features in common with the spectrum of CrO₂Cl₂ (A., 1933, 997).
L. S. T.

Absorption spectrum of water vapour and carbon dioxide in the region below 2000 Å. G. RATHENAU (Z. Physik, 1933, 87, 32—56).—New regions of continuous absorption by H₂O were observed at 17.8 and 24.5 volts. Interpretations

are given for bands and continua of H₂O and CO₂, down to 270 Å.
A. B. D. C.

Polyatomic molecules. Structure and activation of benzaldehyde. II. Analysis of the absorption spectrum of benzaldehyde vapour. F. ALMÄSY (J. Chim. phys., 1933, 30, 634—645; cf. A., 1933, 1227).—Vibration frequencies for the normal and three activated states are given. The feeble bands observed in the second portion of the absorption spectrum correspond with a series of Raman frequencies and are attributed to high vibrational levels of the normal mol. Various electronic levels are considered.
R. S.

Vibrational energy levels of hydrogen cyanide. A. ADEL and E. F. BARKER (Nature, 1934, 133, 29).—The bands 4005.6, 4993.9, 5405.0, and 6523.5 cm.⁻¹ have been observed in the infra-red spectrum of HCN vapour.
L. S. T.

Rotational structure of the Raman band (0000) → (020+2) in linear symmetrical molecules YX₂. J. R. NIELSEN (Physical Rev., 1933, [ii], 44, 911—913; cf. A., 1933, 208).—Intensities of rotational lines are calc., confirming the results of Placzek (A., 1933, 446).
N. M. B.

Raman effect in ammonia and some other gases. C. M. LEWIS and W. V. HOUSTON (Physical Rev., 1933, [ii], 44, 903—910).—Interpretation of the Raman rotation spectra of polyat. mols. in terms of the polarisabilities of the mol. allows the calculation of the relative intensities of rotation lines, in good agreement with experimental results, for NH₃, CH₄, C₂H₂, and C₂H₄.
N. M. B.

Raman spectrum of heavy water. R. W. WOOD (Nature, 1933, 132, 970).—Excitation by λ 2536 of 8 c.c. of 18% heavy H₂O gave two Raman bands with an intensity ratio of 1:4, the new one having a mean wave-length of 2713 Å. due to H₂O mols. containing one atom of heavy H. The frequency difference is 2577 cm.⁻¹. Slight indication of the band due to mols. containing 2 atoms of heavy H appeared.
L. S. T.

Raman spectra of some cyclanones. L. PLAUZ (Compt. rend., 1933, 197, 1647—1648).—The Raman spectra of cyclopentanone, 2- and 3-methylcyclopentanones, cyclohexanone, and 2-, 3-, and 4-methylcyclohexanones from 258 to 2972 cm.⁻¹ all show the ketone lines at 1709—1746 (cf. A., 1933, 1144); the absence of lines between 1600 and 1700 indicates almost complete absence of enolic forms (cf. A., 1931, 465).
C. A. S.

Raman effect. T. G. COUVIOMDZELLIS (Praktika, 1932, 7, 242—247; Chem. Zentr., 1933, ii, 669).—New lines in the Raman spectra of C₆H₆, PhMe, PhCHO, PhNO₂, and PhOH are reported. The electrochemical affinity of substituent groups is considered to be an important factor in determining changes in Δν.
A. A. E.

Raman spectrum of fluorobenzene. N. G. PAI (Nature, 1933, 132, 968).—Raman frequencies for PhF are recorded. 1220 cm.⁻¹ appears to be characteristic of the C-F linking. F substitution produces a large shift of the two prominent C₆H₆ frequencies 991 and 3063.
L. S. T.

Raman effect of organic substances. I. Raman effect of a series of esters of benzoic acid and phenyl esters of fatty acids. K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1933, 8, 333—365).—Raman data are tabulated for Me, Et, Pr^a, Bu^a, Pr^b, Bu^b, isoamyl, cyclohexyl, *o*-tolyl, and *n*-octyl benzoates, BzCl, PhOAc, PrCO₂Ph, and *o*-tolyl acetate. The constitutive influences on the frequencies of the C₆H₆ ring were observed. The relation among the frequencies in the region 2860—2980 cm.⁻¹ associated with the C:H linking of alkyl radicals was studied for the benzoates. The intensity and breadth of the line corresponding with the shift of 1450 cm.⁻¹, attributed to the transverse vibration of H atoms in the CH₂ group, increases as the no. of C atoms increases. The frequencies 1720, 1270, 670 cm.⁻¹ in benzoates are probably due to the CO₂ group. Shifts due to inner at. vibrations, group linkings, valency frequencies, and rotations are discussed.

N. M. B.

Molecular light scattering by binary mixtures. R. GANS and H. A. STUART [with W. MÜLLER] (Z. Physik, 1933, 86, 765—777).—Degree of depolarisation was measured for the binary mixtures C₆H₆—C₆H₁₄, CCl₄—C₆H₆, PhNO₂—CCl₄, and PhNO₂—C₆H₁₄. Data necessary for calculation of anisotropic factors are available for C₆H₆—CCl₄, and these divided by density do not show a linear variation with concn. as suggested by Rav (Physical Rev., 1923, 22, 78).

A. B. D. C.

Action of light on rubidium iodide vapour. G. H. VISSER and A. C. S. VAN HEEL (Z. Physik, 1933, 86, 694—696).—A criticism of Desai (A., 1933, 1102).

A. B. D. C.

Thermoluminescence spectra of fluorites. II. Division of the bands of the spectrum into two groups. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 22—33; cf. this vol., 10).—The bands emitted are classified into two groups the relative intensities of which vary with different samples of fluorite. After destruction of thermoluminescence by overheating, it is restored by exposure to X-rays.

D. R. D.

Theory of crystal photo-effect. H. TEICHMANN (Physikal. Z., 1933, 34, 897).—Objections to the theory previously put forward (A., 1933, 209) have been studied. It is not now considered that the equations give improbably high vals. of the ratio of the electron concn. in the crystal in the illuminated and dark condition.

A. J. M.

Liberation of ions from glass and rock-crystal surfaces by the action of radiations from radium. A. FERNAU (Physikal. Z., 1933, 34, 899—900).—If conductivity H₂O is irradiated with β- and γ-rays there is an increase in conductivity even in quartz vessels, which is dependent on the material of the vessel. The conductivity of solutions of H₂O₂ of various concns. was determined. The increase in conductivity cannot be due to the formation of H₂O₂, but must arise from the formation of ions from the material of the vessel.

A. J. M.

Effect of temperature on the energy distribution of photo-electrons. I. Normal energies. L. A. DU BRIDGE and R. C. HERGENROTHER. II.

Total energies. W. W. ROEHR (Physical Rev., 1933, [ii], 44, 861—865, 866—871; cf. A., 1933, 657).—I. Current-voltage curves for the temp. range 300—965° abs. are in good agreement with the distribution theory of normal energies.

II. Current-voltage curves for photo-electrons released from Mo at the centre of a large collecting sphere show good agreement with the Du Bridge theory for the total energy in the temp. range 300—1000° abs.

N. M. B.

Photo-cathode and unidirectional effect. P. GORLICH (Naturwiss., 1934, 22, 11—12).—Experiments with cells with composite cathodes (Cs₂O layers, with Cs and Ag atoms; A., 1933, 999) indicate that such cathodes show the unidirectional effect well.

A. J. M.

Nature of electrical conductivity of α-silver sulphide. II. C. WAGNER (Z. physikal. Chem., 1933, B, 23, 469—472).—Transport and electrolysis experiments have given further support to the theory (cf. A., 1933, 556) that conduction is preponderantly electronic and that the apparent validity of Faraday's law is due to secondary diffusion effects.

R. C.

Direct determination of number of active centres on a crystalline metallic cathode. N. THON (Compt. rend., 1933, 197, 1606—1608).—The attribution of overvoltage to decrease in resistance along the paths of electrons towards "active centres" leads to the expression $1/2-rn\chi$ ($=\eta/i$) for the resistance, where n is the no. of centres, r the radius of one, χ the specific conductivity of the electrolyte, η the overvoltage, and i the c.d. It is shown that n is approx.=the no. of crystals in the deposited metal in the cases of Zn and Cu, and r of the order 10^{-8} cm. when the deposit is near equilibrium with i and η both near zero. If this theory holds for larger vals. of i and η , as seems probable, r must increase with i .

C. A. S.

Electron conductivity in alkali halide crystals. I. Stationary currents. R. HILSCH and R. W. POHL (Z. Physik, 1933, 87, 78—88).—The equalisation of the positive charge at the origin of an electron in motion through a crystal was investigated for NaCl and KCl, and is shown to be attained partly by electrons moving in the reverse direction and partly by an electrolytic dark current.

A. B. D. C.

Contact resistance measurements at low temperatures. R. HOLM and W. MEISSNER (Z. Physik, 1933, 86, 787—791).—Contact resistances were measured for Au, Cu, and Ni.

A. B. D. C.

Current measurements in chloroform, with alternating current. H. EISLER (Z. Physik, 1933, 86, 792—796).—Conductivity decreases with increasing purity, and the breakdown strength is the greater the less is the conductivity.

A. B. D. C.

Electrical properties of sea-water for alternating currents. R. L. SMITH-ROSE (Proc. Roy. Soc., 1933, A, 143, 135—146).—The sp. conductivity of sea-H₂O (English Channel) increases from 3.9×10^{10} e.s.u. at a frequency of 500 cycles per sec. to 5.4×10^{10} e.s.u. at a frequency of 10,000 kilocycles per sec., at 20°. The part played by the dielectric const., ϵ , in determining the current flowing in the H₂O, in the

above frequency range, is negligible compared with the effect of the conductivity. The val. of ϵ is about 80, as for distilled H_2O , the high apparent vals. obtained at audio- and low radio-frequencies being attributed to the effect of polarisation films at the electrodes. The mean temp. coeff. of the conductivity between 0° and 40° is about $+2.7\%$ per degree. A sudden decrease in the conductivity occurs at -2° . L. L. B.

Dielectric polarisation of hydrogen chloride in solution. II. Benzene, ethyl bromide, and ethylene dichloride as solvents. F. FAIRBROTHER (J.C.S., 1933, 1541—1543; cf. A., 1932, 322).—The improved technique includes drying the HCl without possible contamination from $POCl_3$, and new data for C_6H_6 solutions confirm previous vals. Electric moments for HCl in EtBr and $(-CH_2Cl)_2$ are 1.02 and 0.97×10^{-18} e.s.u., which accords with Zahn's val. for HCl gas. The applicability of the Debye equation to solutions of which the solvent is more polar than the solute is considered. J. G. A. G.

Determination of the valency angles of the oxygen and sulphur atoms and the methylene and sulphony-groups, from electric dipole moments. G. C. HAMPSON, R. H. FARMER, and L. E. SUTTON (Proc. Roy. Soc., 1933, A, 143, 147—168).—The electric dipole moments of CH_2Ph_2 , Ph_2O , Ph_2S , and several of their derivatives have been measured, and the angles between the axes of the Ph groups in these compounds have been found to be $115 \pm 5^\circ$, $142 \pm 8^\circ$, and $118 \pm 8^\circ$, respectively. For the anisoles and phenols, the angles have been determined as 150° and 137° , respectively, and the moments of the O-Me and O-H linkings as 2.33 and 2.37. The use of these data gives angles for Me_2O and H_2O of 147° and 134° , respectively. The angle between each pair of valencies in Ph_2SO and its derivatives is about 115° , and the moment of the $S \rightarrow O$ linking 2.63. L. L. B.

Dielectric constant and absorption of several organic fluids at 1.82 metres. W. T. SZYMANOWSKI (J. Chem. Physics, 1933, 1, 809—816).—Using a resonance method at $\lambda = 1.82$ m., dielectric consts. and absorptions were measured for EtOH, Pr^iOH , Pr^oOH , Bu^iOH , Bu^oOH , amyl alcohol, PhCl, $PhNO_2$, and quinoline. For liquids, e.g., ROH and PhCl, the P_∞ of which does not differ from those at normal concn., experimental data are in accord with Debye's theory. For quinoline and $PhNO_2$, Malsch's modification of Debye's formula gives a more satisfactory agreement for the dielectric consts., but not for the absorptions. W. L. A.

Dipole moments of long-chain molecules. J. W. SMITH (J.C.S., 1933, 1567—1570).—From the dielectric consts. and densities of dil. solutions of palmitic (I) and myristic (II) acids and Me myristate (III) in C_6H_6 at 25° , the dipole moments (I) 1.05, (II) 1.02, and (III) 1.74×10^{-18} e.s.u. are calc., neglecting at. polarisation. Existing data and these results accord with the view that the electric doublet is located almost completely in the head of the mol., and the association of the acids in C_6H_6 decreases with increasing mol. wt. J. G. A. G.

Dipole moments of the chlorobenzophenone oximes. G. S. PARSONS and C. W. PORTER (J.

Amer. Chem. Soc., 1933, 55, 4745—4746).—The *cis*- and *trans*-o-oximes have identical dipole moments (161×10^{-18} e.s.u.), whilst in the *m*- and *p*-oximes the higher-melting form has the lower dipole moment (*m* 1.50 and 1.61×10^{-18} ; *p* 2.230 and 2.381×10^{-18} e.s.u.). When the low-melting form is subjected to the Beckmann rearrangement the C_6H_4Cl group shifts to the N atom. The unsubstituted Ph migrates when the high-melting form undergoes the Beckmann change. E. S. H.

Some electrostatic factors which can operate in polar reactions. W. A. WATERS (J.C.S., 1933, 1551—1557; cf. A., 1933, 890, 1124).—Theoretical. Equations are derived for the energy involved in (1) the field or direct effect, which is exerted across space, of ionic charges and permanent dipoles, and (2) the induced effects of these changes and dipoles transmitted through the mol. to the covalent linking which has to be activated. It is suggested that in the experimentally verified equation $E = E_0 + C(\mu + a\mu^2)$ (loc. cit.) the term $C\mu$ corresponds with (1) and Cau^2 with (2). Refractivity data afford linking polarisabilities which show that (2) is $<$ (1), consistent with existing reactivity data. Secondary polarisation and field effects are negligible in org. mols., and hence local electrostatic fields due to mols. will not appreciably alter the frequency of intermol. collisions from that calc. for electrically neutral mols. J. G. A. G.

Refractive indices and refractions of dilute electrolyte solutions. II. Improvement of interferometric method and measurements with thallium chloride and nitrate. A. E. BRODSKI and N. S. FILIPPOVA. III. Refractive indices and refraction values of potassium chloride, bromide, and nitrate, and sodium chloride. A. E. BRODSKI and J. M. SCHERSCHEVER (Z. physikal. Chem., 1933, B, 23, 399—411, 412—427).—II. The interferometric method of determining n previously described (A., 1931, 122) has been improved and the precision increased. The difference in n between solution and solvent, Δn , and its dispersion and temp. coeff. have been measured for 0.001—0.1N-TlCl and 0.01—0.1N-TlNO₃. For both salts $\Delta n/c$ is a linear function of the concn., c .

III. Δn has been measured for aq. solutions of KCl, KNO₃, NaCl, and KBr over a concn. range of 0.001—0.1N at several temp. For all these salts $\Delta n/c$ decreases with increasing c , the decrease being linear except for NaCl. For KCl, KBr, and NaCl the graph of the apparent mol. refraction, R , of the solute against the concn. in mol. per litre is linear only at the higher concns. It is suggested that over the whole concn. range the electric forces of the ionic atm., and not the mutual deformation of the ions or ionic association, are the factors determining the variation of R .

R. C.
Variation with concentration of molecular refraction of electrolytes. K. FAJANS and W. GEFFCKEN (Z. physikal. Chem., 1933, B, 23, 428—430).—Comments on Brodski's papers (cf. preceding abstract). R. C.

Dispersion measurements in the infra-red. R. W. POHL (Z. Physik, 1933, 86, 833).—Grundelach

and Korth (cf. A., 1933, 1001) have used interferometers similar to those of Pfund (Z. wiss. Phot., 1913, 12, 341).

A. B. D. C.

Refractometric constant of the CN group. P. BRUYLANTS and R. MERCKX (Bull. Acad. roy. Belg., 1933, [v], 19, 1003—1016).—From the mol. refractivity of hydrocarbons and nitriles the sp. refractivity of the CN group is 5.434 and 5.459 for the H_a and D lines, respectively, the corresponding vals. for H being 1.026 and 1.037, and for CH , 4.617 and 4.636, respectively.

J. W. S.

Rotatory dispersive power of organic compounds. XXIV. Ascorbic acid. T. M. LOWRY and S. A. PEARMAN (J.C.S., 1933, 1444—1449).—Aq. solutions of ascorbic acid exhibit mutarotation in presence of O_2 and show anomalous dispersion, having a max. in the violet. Dilution or addition of alkali increases the rotatory power of aq. solutions, but the val. for alkaline solutions diminishes after some days, and finally becomes negative on atm. oxidation. Alkaline solutions do not undergo mutarotation in the absence of O_2 , and show simple rotatory dispersion and increased rotatory power.

W. R. A.

Optical rotatory dispersion in the carbohydrate group. II. Ascorbic acid. R. W. HERBERT, E. L. HIRST, and C. E. WOOD (J.C.S., 1933, 1564—1567).—The head of the absorption band, H , of ascorbic acid (I) in dil. aq. and MeOH solutions moves from 260—265 to 240—245 $m\mu$ with rise of concn., c , but in acid solutions H at 240—245 is independent of c . H is at 245 $m\mu$ in dioxan. Although H of Na ascorbate (II) at 265 $m\mu$ is independent of c , it moves to greater λ with increasing alkalinity. The rotatory dispersions, α_λ , of (I) in MeOH and dioxan appear to be simple, but can be represented by two-term equations. Whereas α_λ of (I) in H_2O is very anomalous with a negative term corresponding with λ 2480, α_λ of (II) in H_2O is simple and is controlled by a positive term corresponding with λ 2450. Although the charge on the ion may reverse the sign of circular dichroism without altering the intensity of the observed absorption band, it is likely that the profound change in the dispersion is attributable to instantaneous intermol. change during ionisation.

J. G. A. G.

Mutarotation of α -D-glucose in heavy water. E. PACSU (J. Amer. Chem. Soc., 1933, 55, 5056—5057).—The displaceable H^1 atom of a reducing sugar in H^2H^2O is immediately replaced by H^2 .

E. S. H.

Magnetic birefringence of gaseous oxygen. T. BELLING (Compt. rend., 1933, 197, 1615—1616).—With a field of 45,000 gauss the magnetic birefringence of O_2 is negative and proportional to the pressure from 25 to 100 atm. For 100 kg. per sq. cm. $C_m = -4.8 \times 10^{-14}$, or 0.005 of that deduced from the Langevin-Debye theory, for agreement with which α must = 54° (cf. A., 1933, 663, 765).

C. A. S.

Thermal variation of magnetic birefringence of nitrobenzene, benzene, and carbon disulphide. A. GOLDET (Compt. rend., 1933, 197, 1612—1614).—The variations of the magnetic birefringence with temp. have been determined for $PhNO_2$ (10—100°), C_6H_6 (10—65°), and CS_2 (0—45°); at 20° they are, respectively, 1/144.6, 1/400, and 1/235. Comparison

with results based on Langevin's theory in the case of CS_2 favour de Malleman's invariant, $(n^2-1)(2n^2+1)/n^2d$; in the other two cases it gives no better agreement than the Lorenz-Lorentz theory (cf. A., 1928, 1310).

C. A. S.

Thermomagnetic study of some nickel salts in the solid state. (Mlle.) A. SERRES (Ann. Physique, 1933, [x], 20, 441—477).—As opposed to Ni salts in solution, the solids gave magnetisation coeffs. diverging from the Weiss law, to which a paramagnetism correction const. must be applied. Full data are tabulated and plotted for the various hydrated states of $NiSO_4$, and for $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $NiCl_2$, NiF_2 , $NiBr_2$, and $Ni(CN)_2$. For the last-named no correction is required.

N. M. B.

Ferromagnetism of nickel colloids. S. R. RAO (Physical Rev., 1933, [ii], 44, 850—853).—The intensity of magnetisation of colloidal Ni prepared by an electrical dispersion method, colloid particles being $< 1.5 \mu$ diameter, was $<$ that of the mass metal. The result is discussed with reference to Heisenberg's and Bitter's theories of ferromagnetism.

N. M. B.

Temperature dependence of ferromagnetic saturation. P. S. EPSTEIN (Proc. Nat. Acad. Sci., 1933, 19, 1044—1049; cf. A., 1932, 900).—Theoretical.

R. S.

Magnetic susceptibilities of europium and gadolinium compounds. P. W. SELWOOD (J. Amer. Chem. Soc., 1933, 55, 4869—4875).—Data have been determined from -190° to 70° or 100° for Eu_2O_3 , $Eu_2(SO_4)_3 \cdot 8H_2O$, $EuSO_4$, Gd_2O_3 , $GdCl_3$, and $Gd_2(SO_4)_3 \cdot 8H_2O$. The susceptibility and electronic configurations of Eu^{++} are the same as those of Gd^{++} .

E. S. H.

Diamagnetic susceptibility of atoms. P. GOMBAS (Z. Physik, 1933, 87, 57—61).—Theoretical.

A. B. D. C.

Electronic structure of hexafluorides. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1933, 1427—1429).— SF_6 , SeF_6 , and TeF_6 have identical structures according to parachor determinations, viz., two F attached to the central atom by covalent linkings and the remaining four by semipolar singlet linkings.

W. R. A.

Electronic structure of inorganic complexes. W. A. NOYES (J. Amer. Chem. Soc., 1933, 55, 4889—4893).—Theoretical. The ionic charges of complexes are explained on Sidgwick's assumption that the co-ordinated ions and mols. of the Werner complexes are donors and the central metallic ions acceptors, and that a donor increases its positive valency by 1, whilst an acceptor increases its negative valency by 1. The rearrangement of the negative nitrite and cyanide ions to positive nitro- and carbylamino-groups is discussed.

E. S. H.

"Unshared" electrons and the effects produced by o - p -directive substituents in organic molecules. G. N. BURKHARDT and M. G. EVANS (Mem. Manchester Phil. Soc., 1932—1933, 77, 37—50).—The essentials of the chemical properties ascribed to unshared electrons of N''' , O'' , and halogen atoms, and the interpretation of the origin of o - p -directing power are examined. The cases of Me, NH_2 , and OH

groups, and the ionisation potentials for the various electrons concerned in these linkings are discussed.

N. M. B.

Change from aromatic to metallic electrons in organic compounds. A. R. UBBELOHDE (Nature, 1933, 132, 1002).—Theoretical.

L. S. T.

Constitution of liquid substances. P. BOGDAN (J. Chim. phys., 1933, 30, 581—627).—Theoretical. Mol. association and other properties of liquid are discussed.

R. S.

Quantum-mechanical stability of a benzene molecule. M. MARKOV (J. Chem. Physics, 1933, 1, 784—788).—The C_6H_6 mol. is considered as consisting of six trivalent N-like CH groups. The Heitler-London-Rumer treatment of valency linking yields a matrix of the 34th order which can be decomposed to six matrices of lower order each corresponding with a definite proper val. of the operator which must be < -9 if the model is to be stable mechanically and thermodynamically. The model chosen is proved mechanically but not thermodynamically stable.

W. R. A.

Molecular symmetry and the reduction of the secular equation. H. EYRING, A. A. FROST, and J. TURKEVICH (J. Chem. Physics, 1933, 1, 777—783).—Linking proper functions of any multiplicity may be reduced to a linear independent set; the method of obtaining matrix components for singlet linking proper functions is also extended to all multiplicities. By application of the group theory reduced secular equations are obtained with reference to NH_3 , N_2 , and CH_4 .

W. R. A.

Helium hydride ion. G. GLOCKLER and D. L. FULLER (J. Chem. Physics, 1933, 1, 886—887).—The structure of the ion is considered on the basis of wave mechanics.

N. M. B.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1933, [v], 19, 1140—1152).—Theoretical.

J. W. S.

Inter-atomic distances and forces. ANON. (Nature, 1933, 132, 992—994).—A summary of the British Association discussion.

L. S. T.

Theory of critical phases: generality of properties of zero area. E. JOUGET (Compt. rend., 1933, 197, 1705—1709).—Mathematical. Gibbs' treatment of the phase rule is expanded and generalised in the light of recent work on crit. phenomena.

C. A. S.

Statistics of polyatomic gases. K. SZELL (Z. Physik, 1933, 86, 810—817).—Fermi-Dirac and Bose-Einstein quantum statistics are applied to translation and rotation of mols. with two or three equal moments of inertia.

A. B. D. C.

Capillary depression of mercury in wide tubes. A. KLEMENC and O. BANKOWSKI (Naturwiss., 1934, 22, 10—11).—The capillary depression of Hg in wide tubes has been investigated by an interferometer method. In a tube 30 mm. in diameter, a depression of 0.002 mm. was found. In a tube 40 mm. in diameter, the depression was $< 0.2 \mu$.

A. J. M.

Fine structure of X-ray absorption by molecular gases. H. PETERSEN (Arch. Neerland., 1933,

[iiia], 14, 165—218).—A theory of absorption by polyat. mols. is developed, and that by Cl_2 is discussed.

H. J. E.

Diffuse scattering of X-rays from sodium fluoride. II. Scattering at the temperature of liquid air. G. E. M. JAUNCEY and P. S. WILLIAMS (Physical Rev., 1933, [ii], 44, 794—797; cf. A., 1933, 558).—The ratio of the intensity of X-rays diffusely scattered by a single crystal of NaF at 86° abs. to that at 295° abs. was determined for the angle range 10 — 42° . Results are in good agreement with calc. vals.

N. M. B.

Changes in the X-ray diffraction pattern of nitrobenzene produced by an electric field, changes in temperature, and circulation. F. C. TODD (Physical Rev., 1933, [ii], 44, 787—793).—The intensity change in the diffraction pattern due to a field of 10 kv. per cm. was $-0.02 (\pm 0.06\%)$ over the peak. The change produced by temp. increases in the range 16 — 42° , and by circulating the $PhNO_2$ past the point of X-ray illumination indicates that the mols. associate in pairs and are dissociated by thermal or mechanical agitation.

N. M. B.

Connexion between chemical constitution and K-X-ray absorption spectra. XII. K-X-Ray absorption spectra of stereoisomerides. I. O. STELLING (Z. physikal. Chem., 1933, B, 23, 338—346; cf. A., 1933, 214).—The X-ray absorption spectra of Cl in compounds of the type $[MA_4YCl]X$, where $A = NH_3$ or \downarrow en have been studied. For a given cation the position of the soft edge is const., independent of the anion, and the hard edge is affected by the anion only if this is Cl, when it is softened. In the dihalogenotetrammino-salts the long-wave edge of the *trans* form is softer than that of the *cis* form, whilst if Y is NO_2 or NCS both isomerides have the same spectrum. These observations have been applied to the determination of the configurations of the supposed stereoisomerides of $[Co_3NH_3, H_2O, Cl_2]Cl$ and the corresponding Cr compound.

R. C.

Crystalline structure of the compound $MgPr$. A. ROSSI and A. LANDELLI (Atti R. Accad. Lincei, 1933, [vi], 18, 156—161).—When examined by the powder method $MgPr$ gives a 3.88 \AA . (or an integral multiple thereof), $d^{20} 4.67$, $d_{calc.} 4.65$, a calc. from the at. radii 3.95 \AA .

O. J. W.

Energy content, particle dimensions, and lattice formation of active beryllium oxides. R. FRICKE and J. LUKE (Z. physikal. Chem., 1933, B, 23, 319—329).— BeO prepared from metastable cryst. $Be(OH)_2$ at various temp., from its heat of dissolution in aq. HF, has the higher energy content the lower is the temp. of prep., T . X-Ray study shows that the crystallites decrease in size with fall in T , and that in the direction of the c axis the dimensions lie within the colloidal range. The high energy content of the low-temp. preps. is due, in the main, to imperfect lattice formation.

R. C.

Electron interference experiments with active beryllium oxides. R. FRICKE and J. LUKE (Z. physikal. Chem., 1933, B, 23, 330—337; cf. preceding abstract).—Cathode-ray interferences of BeO pre-

pared from metastable cryst. $\text{Be}(\text{OH})_2$ at various temp. and supported on fine collodion membranes show that the crystallites are plates perpendicular to the c axis. The intensities of the interferences pass through a max. with rise in the temp. of prep., the suggested explanation being that oxides prepared at a low temp. give weak interferences owing to the imperfectly formed lattice and those ignited at higher temp. give weak interferences owing to their crystallites being too thick. R. C.

Investigation of copper oxide films by electron diffraction. C. A. MURISON (Phil. Mag., 1934, [vii], 17, 96—98).—Surface films on Cu heated in air gave diffraction patterns for Cu_2O and a new form of CuO (I) (cf. Thomson and Fraser, A., 1930, 1082). (I) is formed by heating Cu blocks in an air or O_2 stream at 300—500°. H. J. E.

Alkali alkylarsinates. M. G. GILTZ (Bull. Soc. chim. Belg., 1933, 42, 443—447).—Crystallographic measurements of Cs methylarsinate, and Na (+2H₂O) and Rb ethylarsinate have been made. F. R. S.

Realgar and benitoite. H. BUTTGENBACH (Bull. Acad. roy. Belg., 1933, [v], 19, 1019—1033).—The crystal forms of these minerals are discussed in detail. J. W. S.

Molecular orientations in diphenylbenzene crystal. K. S. KRISHNAN and S. BANERJEE (Nature, 1933, 132, 968—969).—Correlation of the principal diamagnetic susceptibilities of the crystal with those of the mols. of $p\text{-C}_6\text{H}_4\text{Ph}_2$ shows that the lengths of the mols. lie in the (010) plane (I), in the acute angle β , making an angle of 14.3° with the c axis, and that the planes of the two mols. are inclined at +56.6° and -56.6°, respectively, to (I). L. S. T.

Crystal structure of s -triphenylbenzene. K. LONSDALE (Nature, 1934, 133, 67).—The crystal class is orthorhombic pyramidal and not orthorhombic bipyramidal. The crystals show a small piezo-electric effect indicating that the crystallographic a axis is a polar axis. The mols. are asymmetric and the plane of the C_6 rings is not coincident with the (001) plane, but makes a small angle with it (cf. this vol., 17). L. S. T.

X-Ray study of s -triphenylbenzene. B. P. ORELKIN (J. Gen. Chem. Russ., 1933, 3, 643—651).—The distances between the o -, m -, and p -C atoms of $s\text{-C}_6\text{H}_3\text{Ph}_3$ are respectively 0.79, 1.12, and 1.38 Å., and the depth of the C_6 ring is 0.46 Å. R. T.

X-Ray investigation of fatty acid esters of cellulose. J. J. TRILLAT (Compt. rend., 1933, 197, 1616—1618).—Debye-Scherrer photographs of cellulose esters from the triacetate to the tristearate show the same larger outer rings throughout the series, indicating a const. reticular distance, d_2 , whilst the inner ring steadily decreases as the length of the aliphatic chain increases, indicating a regular increase in the reticular distance, d_1 , of 1.3 Å. per C atom. d_2 is therefore due to the cellulosic portion, d_1 to the acyl group. Esters up to the butyrate have a cryst. structure; higher ones are mesomorphic and increasingly plastic. The ester chains are approx. perpendicular to the cellulosic, the distance between the latter increasing with the length of the former (cf. A., 1930, 1352). C. A. S.

X-Ray study of konnjakumannan. III. Orientation of micelles by stretching, freezing, and drying. I. SAKURADA and K. HUTINO (J. Soc. Chem. Ind. Japan, 1933, 36, 662B; cf. A., 1933, 1235).—The micelles in β -konnjakumannan are oriented in films, prepared by drying and in cakes formed by freezing, and not only in stretched material. A. G.

Spontaneous orientation of the micelles in unstretched films of cellulose acetate and nitrate. I. SAKURADA and K. HUTINO (J. Soc. Chem. Ind. Japan, 1933, 36, 659—661B).—X-Ray photographs of films of cellulose acetate or nitrate obtained by drying 5% solutions on glass plates show definite orientation when the rays are parallel to the film surface. A. G.

Dynamics of liquid crystals. P. J. BOUMA (Arch. Neerland., 1933, [iiia], 14, 219—284).—The dielectric loss for p -azoxyanisole as a function of frequency has a max. corresponding with the crit. frequency observed by Kast (A., 1931, 1116). Below this frequency the swarms are parallel to the field, and above it are at right angles. The val. rises rapidly with temp. In the solid state, the dielectric loss at high frequencies (e.g., 10^6 hertz) is the same as for the liquid crystals. The time for orientation in a steady magnetic field was measured, and factors affecting it are discussed. In absence of disturbing effects, the time may be several min. H. J. E.

Crystal absorption by substrates. G. I. FINCH, A. G. QUARRELL, and J. S. ROEBUCK (Nature, 1934, 133, 28).—Zn vapour condensed on a cool, polished Cu surface gives rise to a well-defined electron diffraction pattern which initially is brilliant but disappears in a few sec. The rate at which the initial cryst. structure disappears becomes slower with each successive deposit. When Zn is deposited under similar conditions but on to a sputtered or etched Cu, or on to a Cu surface which had been oxidised and reduced, a cryst. film of permanent structure is formed. The results are regarded as an experimental proof of the existence of the Beilby layer. L. S. T.

Oscillation figures of piezo-electric crystals. H. STRAUBEL (Physikal. Z., 1933, 34, 894—896).—An arrangement for obtaining oscillation figures of piezo-electric crystals is described. A. J. M.

Magnetic analysis of nickel films deposited by evaporation. H. N. OTIS (Physical Rev., 1933, [ii], 44, 843—849).—Magnetisation curves for films deposited at various temp., under different degrees of annealing, and on metals with coeffs. of expansion $>$ or $<$ that of Ni are given. Results are explained on Becker's strain theory. N. M. B.

Magnetorotation in non-adiabatic change of the magnetic field. E. BRETSCHER and W. DECK (Helv. phys. Acta, 1933, 6, 229—231; Chem. Zentr., 1933, ii, 1314).

Effect of heat-treatment on production of frictional electric charges on metals. P. A. MAINSTONE (Phil. Mag., 1933, [vii], 16, 1083—1096).—Heating Al or Ni at 300—350° in vac. or in N_2 at 1 atm. lowers the normal frictional charge. Partial

recovery occurs on cooling. The effect of de-gassing was studied. The frictional charge on polished Pd changes from positive to negative when it is de-gassed and heated in H_2 to 250°. Results are correlated with adsorption phenomena. H. J. E.

Elliptic reflexion under normal incidence from a transparent anisotropic substance: superficial birefringence of calcspar. R. DE MALLEMANN and H. COURTILOTT (Compt. rend., 1933, 197, 1610—1612).—The possibility previously adumbrated (cf. Bull. Soc. franç. Phys., 1932, 319, 34) of this phenomenon is demonstrated for the case of calcspar. The observations are explicable on the assumption of a passage layer. C. A. S.

Interference of light in metallic films. J. B. NATHANSON (J. Opt. Soc. Amer., 1933, 23, 388—393).—The interference fringes observed when films of Mn and Pt sputtered cathodically on glass are viewed by reflected light have been investigated. The shape of the fringes depends on the shape of the cathode, being circular for a round cathode and straight for a rectangular cathode. The colours arise most probably from interference of light between the front and rear surface of the films, and from this hypothesis the vol. and mass of the film can be computed. For Mn, but not for Pt, the computed mass agrees fairly well with the mass obtained by weighing the film. The discrepancy with Pt may be due to the uncertainty of the optical consts. for thin Pt films or to occlusion of H₂. W. R. A.

Explanation of a fine structure in the optical absorption bands of metals. R. DE L. KRONIG (Naturwiss., 1934, 22, 11).—Theoretical. An explanation of the results of Smakula (A., 1933, 1226) is based on quantum mechanics. A. J. M.

Flow conditions for crystals. W. BOAS and E. SCHMID (Z. Physik, 1933, 86, 828—830).

A. B. D. C.

Plasticity of rock-salt and its dependence on water. R. B. BARNES (Physical Rev., 1933, [ii], 44, 898—902).—Measurements show that H₂O penetrates into the interior of rock-salt when the latter is placed in H₂O. The influence of H₂O on the increased plasticity and tensile strength (Joffe effect) is discussed. N. M. B.

Physical properties of silicon and ferrosilicon. C. BEDEL (Ann. Chim., 1933, [x], 20, 439—519; cf. A., 1929, 756, 997, 1399; 1930, 437; 1931, 674, 1237; 1933, 217; B., 1933, 151).—A full account of work previously published. F. L. U.

Velocity of sound in gases. F. H. VAN DEN DUNGEN (Bull. Acad. roy. Belg., 1933, [v], 19, 1180—1187).—Theoretical. J. W. S.

Acoustical studies. II. Behaviour of a gas with several independent internal energy states. W. T. RICHARDS (J. Chem. Physics, 1933, 1, 863—879; cf. A., 1933, 217).—Mathematical. N. M. B.

Theory of superconductivity. C. J. GORTER (Nature, 1933, 132, 931; cf. this vol., 19).

Superconductivity of zinc. W. H. KEESOM (Physica, 1933, 1, 123—127).—Zn becomes superconducting at 0.79° abs. Cd and Au are not super-

conducting at 0.73° abs., or Pt at 0.77° abs. Phosphor-bronze is not superconducting at 0.75° abs., so Cu is probably not superconductive at that temp.

J. W. S.

Change of the resistance of single crystals of gallium in a magnetic field. W. J. DE HAAS and J. W. BLOM (Physica, 1933, 1, 134—144; cf. A., 1930, 675, 985, 1102, 1353).—The resistance of a single Ga crystal at 10—20° abs. and in a magnetic field of 5000—22,000 gauss shows similar behaviour to that of a single Bi crystal. The curve of relative change in resistance against inclination of the field to the axis of the crystal is almost sinoidal at low field strengths. The results are in agreement with the rhombic crystal structure of Ga (A., 1932, 987).

J. W. S.

Adiabatic cooling of paramagnetic salts in magnetic fields. W. J. DE HAAS, E. C. WIERSMA, and H. A. KRAMERS (Physica, 1933, 1, 1—13; cf. A., 1933, 1026).—By the adiabatic demagnetisation of CeF₃, Dy(EtSO₄)₃·9H₂O, Ce(EtSO₄)₃·9H₂O, and KCr(SO₄)₂·12H₂O, previously cooled to 1.35° abs., temp. of 0.13°, 0.12°, 0.085°, and 0.05° abs., respectively, have been reached. F. L. U.

Correlation of heat capacity, absolute temperature, and entropy. G. A. LINHART (J. Chem. Physics, 1933, 1, 795—797).—Assuming that at low temp. C is proportional to S , and at high temp. it approaches a limiting val., C_∞ , the following relations connecting C , S , and T are calc.: $C = C_\infty ke^{K \log T} / (1 + ke^{K \log T})$, and $S = 2.3(C_\infty / K) \log C_\infty / (C_\infty - C)$. The validity of these relations is supported by experiment. W. R. A.

Heat capacity and entropy of nitrogen. Heat of vaporisation. Vapour pressures of solid and liquid. Reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ from spectroscopic data. W. F. GIAUQUE and J. O. CLAYTON (J. Amer. Chem. Soc., 1933, 55, 4875—4889).—The heat capacities of N in the two cryst. and liquid forms have been determined from 15° abs. to the b.p. The data recorded are: transition point 35.61° abs.; m.p. 63.14° abs.; b.p. 77.32° abs.; heat of transition 54.71 g.-cal. per mol.; heat of fusion 172.3 g.-cal. per mol.; heat of vaporisation (at 760 mm.) 1332.9 g.-cal. per mol.; entropy at b.p. 36.5 e.u.; abs. entropy at 298.1° abs. 50.154 e.u.; v.p. of solid N (54.78—63.14° abs.) $\log_{10} p(\text{cm.}) = -(381.6/T) + 7.41105 - 0.0062372T$; v.p. of liquid N (63.14—78.01° abs.) $\log_{10} p(\text{cm.}) = -(339.8/T) + 6.71057 - 0.00562867T$; free energy of formation of NO (298.1° abs.) 20.650 g.-cal. per mol. E. S. H.

Low-temperature specific heats. IV. Heat capacities of potassium chloride, potassium nitrate, and sodium nitrate. J. C. SOUTHARD and R. A. NELSON (J. Amer. Chem. Soc., 1933, 55, 4865—4869; cf. this vol., 20).—The heat capacities (g.-cal. per mol. per degree) at 298.16° abs. are: KCl 19.75±0.06, KNO₃ 31.77±0.10, NaNO₃ 27.87±0.08. Measurements have been extended over the range 15—290° abs. The free energies of formation of the salts from the elements are —97,700, —95,000, and —88,300 g.-cal. per mol., respectively. E. S. H.

Specific heats of metals at higher temperatures. XII. Specific heat of rhenium. F. M. JAEGER

and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 786—788).—The sp. heat c_p for Re at 0—1200° is given $0.03256 + 0.6625 \times 10^{-5}t$.
J. W. S.

Variation of specific heat of gases with pressure. E. BURLLOT (Mem. Poudres, 1933, 25, 314—335).—For the calculation of explosion temp. a correction to the quantity of heat liberated is deduced. This applies only when the Clausius-Sarrau equation of state is applicable, and not when the pressure and temp. are both high, as is usually the case. A. G.

Simple calorimeter for heats of fusion. Data on the fusion of ψ -cumene, mesitylene (α and β), hemimellitene, o - and m -xylene, and on two transitions of hemimellitene. F. D. ROSSINI (Bur. Stand. J. Res., 1933, 11, 553—559).—Heats of fusion may be measured quickly, with an accuracy of a few %, by using a vac. flask fitted with a thermoelement as a simple calorimeter. The following vals. have been found for f.p. and mol. heat of fusion in kg.-cal., respectively: ψ -cumene, -44.1° , 2.75 ± 0.06 ; hemimellitene (I), -25.5° , 2.00 ± 0.05 ; α -mesitylene, -44.8° , 2.28 ± 0.06 ; β -mesitylene, -51.7° , 1.91 ± 0.05 ; o -xylene, -25.3° , 3.33 ± 0.07 ; m -xylene, -47.9° , 2.76 ± 0.05 . (I) has two transitions with the following heats of transition: $\gamma \rightarrow \beta$, $-58 \pm 2^\circ$, 0.28 ± 0.04 ; $\beta \rightarrow \alpha$, $-46 \pm 1^\circ$, 0.36 ± 0.04 .
M. S. B.

Butadiene nitriles. G. HEIM (Bull. Soc. chim. Belg., 1933, 42, 461—466).—The b.p., d , n , and mol. dispersion of pure *cis*- and *trans*-crotono- and vinyl-aceto-nitriles have been measured.
F. R. S.

F.p. of organic substances. XIV. Alternation of f.p. in homologous series of symmetrical disubstituted compounds. H. SERWY (Bull. Soc. chim. Belg., 1933, 42, 483—501; cf. A., 1931, 1361).—F.p., b.p., d , coeff. of expansion, viscosity, and n have been determined for a no. of compounds of the type $X \cdot [CH_2]_x \cdot X$ in which $x=1-5$ and $X=Cl, Br, CN, CO_2H$, and CO_2R . The variation of f.p. in homologous series is discussed.
F. L. U.

Thermal expansion of the crystal lattices of silver, platinum, and zinc. E. A. OWEN and E. L. YATES (Phil. Mag., 1934, [vii], 17, 113—131; cf. A., 1933, 1106).—The lattice parameters of Ag and Pt from 0° to 600° have been measured. Vals. for Zn between 20° and 415° along and perpendicular to the hexagonal axis agree with measurements on single-crystal rods of Zn.
H. J. E.

Thermodynamic considerations on a new kind of transition points. O. HALPERN (J. Chem. Physics, 1933, 1, 880—881).—Failure to observe the coexistence of two phases at the new transition point in liquid He (cf. Keesom, A., 1933, 559) can be explained if the two phases do not exhibit a discontinuity in energy.
N. M. B.

Thermodynamic diagrams of liquid helium. W. H. KEESOM and (Miss) A. P. KEESOM (Physica, 1933, 1, 128—133; cf. A., 1933, 894, 1109).—From the data previously recorded, p - T and d - T diagrams are constructed. From these, diagrams have been derived for $(\partial d/\partial p)_T$, $(\partial p/\partial T)_d$, and $(\partial d/\partial T)_p$. Marked discontinuities occur in these differential coeffs.

when passing the transition curve between He I and He II.
J. W. S.

Thermodynamic properties of β -methylpentan- β -ol. F. HOVORKA, H. P. LANKELMA, and C. K. NAUJOKS (J. Amer. Chem. Soc., 1933, 55, 4820—4822).—Data are given for the f.p. ($-103 \pm 1.5^\circ$), surface tension, d , n , viscosity, v.p., parachor, and Eotvos const. of β -methylpentan- β -ol. The b.p. found by interpolation in the v.-p. curve is $121.09 \pm 0.03^\circ$. The calc. heat of vaporisation is about 9700 g.-cal. at the b.p.
E. S. H.

Thermodynamic properties of trichlorotri-fluoroethane and tetrachlorodifluoroethane. F. HOVORKA and F. E. GEIGER (J. Amer. Chem. Soc., 1933, 55, 4759—4761).—The d , n , surface tension, v.p., and viscosity have been measured over the range $28.1-90.0^\circ$ for $C_2Cl_4F_2$ and $0.0-40.0^\circ$ for $C_2Cl_3F_3$. The crit. temp., mol. heat of vaporisation, parachor, and v.p.-temp. equation have been calc.
E. S. H.

Vapour pressure of vinyl acetate. J. MARSDEN and A. C. CUTHBERTSON (Canad. J. Res., 1933, 9, 419—423).—The v.p. has been measured by an isotenoscope method between 0° and the normal b.p. (72.5°). The mol. heat of evaporation is 8211 g.-cal., Trouton's const. is 23.8, and the calc. val. of the crit. temp. is 228.3° .
R. S.

Vapour pressures and heats of vaporisation of normal nitriles. G. HEIM (Bull. Soc. chim. Belg., 1933, 42, 467—482; cf. A., 1932, 1197).—V.p. of saturated normal nitriles C_2-C_8 , and of vinylaceto- and *cis*- and *trans*-crotono-nitriles have been determined. Heats of vaporisation have been calc.
F. L. U.

Process of vaporisation. K. SCHREBER (Z. tech. Physik, 1933, 14, 81—85; Chem. Zentr., 1933, i, 1749).—The temp. difference between liquid and vapour is discussed. In pure liquids it depends only on the velocity of vaporisation.
A. A. E.

Relation between viscosity, vapour pressure, and density. F. HOVORKA (J. Amer. Chem. Soc., 1933, 55, 4899—4900).—The empirical equation $S = \eta P^{1/4} d^{1/2}$, where η is the viscosity, P the v.p., d the density, and S a const. characteristic of the substance, is established for many org. liquids.
E. S. H.

Collision areas of 1 : 3 : 5-mesitylene and of the most highly branched heptanes. W. A. EVERHART, W. A. HARE, and E. MACK, jun. (J. Amer. Chem. Soc., 1933, 55, 4894—4897).—The viscosities of the vapours of 1 : 3 : 5-mesitylene ($100.4-200.0^\circ$) and $\beta\beta\gamma$ -trimethylbutane ($70.3-262.1^\circ$) have been determined over the temp. range indicated. The calc. Sutherland consts. are 136.3 and 257, respectively, and the collision areas 42.4 and 31.1 sq. Å.
E. S. H.

Viscosity, heat conductivity, and diffusion in gas mixtures. XXIV. Determination of the "unpaired viscosity" η_{12} ; application, proof, and various methods of explanation of the viscosity law for binary mixtures. M. TRAUTZ (Ann. Physik, 1933, [v], 18, 816—832).—The relations involved in the formulæ of Maxwell, Enskog, Chap-

man, and Trautz for the viscosity of binary gas mixtures are discussed and compared. A. J. M.

F.p. and densities of binary mixtures of alcohol and ether. LALANDE (Mém. Poudres, 1933, 25, 421—435; cf. A., 1933, 345).—The sp. vol. at 0° of mixtures of EtOH and Et₂O is given by $V - V_1N_1 + V_2N_2 + \Phi_{1,2}N_1N_2$ where N_1 and N_2 are mol. fractions and $\Phi_{1,2} = 2.3 \pm 0.3$. The f.-p. diagram shows a eutectic at -125° and 68.3 mol.-% EtOH. A. G.

Fluidity of dioxan-water mixtures. J. A. GEDDES (J. Amer. Chem. Soc., 1933, 55, 4832—4837).—Viscosities have been measured at 20—80°. The fluidity-concn. curves exhibit inflexion at 5% H₂O. The max. deviation from linearity indicates the presence of approx. 5% of C₄H₈O₂.5H₂O. The variation of the fluidity of dioxan with temp. is given by $\phi = [T - 171.97 + (T^2 - 146.58T + 39,264.2)^{1/2}] \div 0.51894$. E. S. H.

Specific heat of aqueous solutions of phosphoric acid. M. M. POPOV, S. M. SKURATOV, and N. N. FEODOSSJEV (Z. physikal. Chem., 1933, 167, 42—48).—The true sp. heat of aq. H₃PO₄ for concns. up to 89% has been determined at 20.5—22.0°. The mean sp. heat has been determined for concns. up to 60% at 20—100° and for 60—89% solutions from 20° up to near the b.p. R. C.

Heat of formation of binary liquid solutions from their liquid components. J. J. COLEMAN and F. E. E. GERMANN (J. Chem. Physics, 1933, 1, 847—851).—An empirical equation is given which connects the heat of formation with the temp. and composition of the liquid mixtures. The equation is applied to a large no. of binary mixtures. N. M. B.

Distillation. II. Liquid-vapour equilibria in the systems ethyl alcohol-water, methyl alcohol-water, and acetic acid-water. L. W. CORNELL and R. E. MONTONNA (Ind. Eng. Chem., 1933, 25, 1331—1335).—The data have been obtained by distillation and analysis of successive fractions, the initial and final vapour compositions being obtained by extrapolation. Results are compared with those of other workers. C. I.

Physical properties of mixtures of certain organic liquids. V. C. G. TREW and G. M. C. WATKINS (Trans. Faraday Soc., 1933, 29, 1310—1318; cf. A., 1932, 801).—The density, mass susceptibility, n , sp. heat, heats of mixing, and viscosity of mixtures of Bu^oOH with Pr^oOH, Pr^oOH, Bu^oOH, *tert*-amyl alcohol, and of COMe₂ with C₂HCl₃ have been measured at 25°. All give deviations from the mixture law and the max. on the deviation curves vary with the property. H. J. E.

Thermodynamics of mixtures. Ethyl alcohol-water. V. FISCHER (Helv. phys. Acta, 1933, 6, 42—67; Chem. Zentr., 1933, ii, 192).—Accord between theoretical and observed data indicates that for EtOH-H₂O admixture is essentially a physical, and not a chemical, process. A. A. E.

Volume variations of system water-ethyl alcohol-ether. P. BRUN (Compt. rend., 1933, 197, 1637—1638).—The differences between the actual vols. and those derived from the simple mixture rule

are given on a triangular diagram; there is no breach of continuity in the crit. zone (cf. A., 1927, 23).

C. A. S.
Mixed crystals in the sulphate series. I. A. BENRATH and A. BLANKENSTEIN (Z. anorg. Chem., 1933, 216, 41—48).—Data are given for the system MgSO₄-MnSO₄-H₂O. E. S. H.

X-Ray study of the binary alloys of silicon with Ag, Au, Pb, Sn, Zn, Cd, Sb, and Bi. E. R. JETTE and E. B. GEBERT (J. Chem. Physics, 1933, 1, 753—755).—Lattice consts. of the alloys do not differ appreciably from those of the elements, and solid solution formation is therefore very slight. In no case are compounds formed. W. R. A.

Hall effect and some other physical constants of alloys. II. The tin-bismuth series of alloys. W. R. THOMAS and E. J. EVANS (Phil. Mag., 1934, [vii], 17, 65—83; cf. A., 1933, 895).—The Hall coeffs. (I), resistivity, temp. coeff. of resistance, thermoelectric power, and density of annealed Sn-Bi alloys (0—100% Bi) have been measured. A reversal of (I) occurs for some of the alloys at a field strength which depends on the composition. H. J. E.

Surface tension of liquid metals. V. Surface tension of lead-tin alloys. L. L. BIRCUMSHAW (Phil. Mag., 1934, [vii], 17, 181—191; cf. A., 1926, 895).—Measurements have been made at 200—800° on alloys with 0—100% Pb. All the alloys show a negative temp. coeff. It is suggested, on the basis of Schofield and Rideal's relation (A., 1925, ii, 960), that the eutectic has a unimol. surface layer of Pb atoms. H. J. E.

Equilibrium diagrams of binary alloys of alkali metals: Na-Rb alloys. E. RINCK (Compt. rend., 1933, 197, 1404—1406; cf. A., 1933, 771).—The diagram of Na-Rb alloys shows a eutectic containing 75 at.-% Rb, m.p. 4.5°. The formation of Na₃Rb is possible. C. A. S.

Alloys of lithium. II. X-Ray analysis of the system lithium-cadmium. A. BARONI (Atti R. Accad. Lincei, 1933, [vi], 18, 41—44; cf. A., 1933, 18).—Thermal analysis of this system confirms the existence of the three compounds LiCd, LiCd₃, and Li₃Cd. The last-named is not revealed by X-ray analysis, which shows that LiCd has a monometric structure of the body-centred CsCl type with a 3.32 Å., Cd (0, 0, 0), Li ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), d_{calc} . 5.336, and that LiCd₃ is also monometric with 8 mols. per unit cell, a 8.62 Å., d_{calc} . 7.136. O. J. W.

Cadmium-nickel system. C. E. SWARTZ and A. J. PHILLIPS (Amer. Inst. Min. Met. Eng., Contrib. No. 55, 1933, 4 pp.).—The eutectic point in the system is at 0.25% Ni and 318°; the Ni is probably in the form of the compound NiCd, which appears as hard cubes in hypereutectoidal alloys. A. R. P.

Equilibrium diagram of iron-aluminium system. A. ÔSAWA (Sci. Rep. Tohoku, 1933, 22, 803—823).—Photomicrographs and X-ray analyses have given the following results: FeAl, cubic, a 5.78 Å.; n (atoms per unit cell)=16; FeAl₂, rhombohedral, a 6.314, α 74° 9', n 18; Fe₂Al₃, monoclinic, a 9.91, b 10.811, c 8.824, β 124° 59' 53'', n 56; FeAl₃, ortho-

rhombic, a 11.87, b 8.088, c 15.804, n 104. A new phase diagram is constructed. J. G. A. G.

Alloys of gallium with aluminium. N. A. PUSHIN and V. STAJIC (Z. anorg. Chem., 1933, 216, 26—28).—Thermal analysis of alloys containing 0—100% Al has established the existence of three compounds: AlGa_2 (m.p. 281°), AlGa (m.p. 374°), and Al_2Ga (m.p. 467°). Al_2Ga exists in a β form at 447 — 467° and in an α form below 447° . E. S. H.

Structure and origin of the copper-cuprous oxide eutectic. L. W. EASTWOOD (Amer. Inst. Min. Met. Eng., Contrib. No. 59, 1933, 8 pp.).—The $\text{Cu-Cu}_2\text{O}$ eutectic alloy forms large columnar macrograins when cast in an open mould. The grains etch similarly throughout their individual areas but adjoining grains etch differently according to their orientation. Deep etching produces pits of similar orientation throughout each grain but of different orientation in different grains, and slow deformation produces slip bands which are straight and continuous across a grain but change at the grain boundary. From a micrographical examination of sections through the columnar grains at right angles it appears that the Cu is the directing constituent of the eutectic, axes of growth of the Cu portion of the eutectic dendrite (I) spreading into the melt perpendicular to the mould wall; these axes fill out and branches grow from them until they meet adjacent branches of the same or other dendrites. As (I) grows the Cu_2O is pptd. with a definite orientation; the Cu_2O particles are spheroidal with a rapid rate of solidification and rod-shaped with slower cooling, hence the Cu_2O nearest the central portions of the dendrites is spheroidal, whilst that in the more remote portions forms rods inclined at 45° to the direction of axial growth. The form and structure of the eutectic crystals are generally independent of the existence of primary crystals of Cu or Cu_2O unless the rate of cooling favours surfusion when, since Cu surfuses $> \text{Cu}_2\text{O}$, haloes of Cu are formed about the Cu_2O dendrites. Characteristic micro-structures are illustrated.

A. R. P.

Magnesium-zinc-calcium system. R. PARIS (Compt. rend., 1933, 197, 1634—1636).—The thermal diagram for the system Ca-Mg indicates the formation of Mg_5Ca_2 (cf. A., 1911, ii, 611), and that for Ca-Zn indicates Ca_5Zn_2 , and not Ca_5Zn (cf. A., 1908, ii, 278). For Mg-Zn the data agree with previous results (cf. A., 1929, 398). The ternary diagram shows the formation of the following: Ca_3Mg_5 , Ca_5Zn_2 , Ca_3Zn_2 , CaZn_3 , CaZn_{10} , MgZn_2 , MgZn_5 , and $\text{Mg}_5\text{Zn}_5\text{Ca}_5$; the last forms large crystals, not attacked by HNO_3 , and melting at 495° without decomp. Alloys with $>30\%$ Ca oxidise and disintegrate in moist air; those with $>40\%$ Zn are not readily oxidisable, but brittle and unworkable; those rich in Mg are also oxidised with difficulty, are very light, and easy to work, but unless both Ca and Zn are $<1\%$, contain more than one phase.

C. A. S.

Transformations in the solid state of aluminium-magnesium-silicon alloys. A. A. BOCHVAR, K. V. GOREV, and A. M. KOROLKOV (Metallurgist, U.S.S.R., 1933, No. 1, 7—20).—A new constitution

diagram is based on the micro-structures of 47 alloys containing Mg 0—3, Si 0—2.75%. Melts were prepared under a NaCl-KCl-LiCl flux. The alloys were superheated 50 — 150° for 4—18 hr., then kept for 10 days at 200° , 300° , 400° , 500° , or 550° , and quenched in cold H_2O . Max. ageing was observed with max. Mg_2Si . Excess of Si increases the effect of heat-treating if 0.2—0.4% Fe is present, but decreases it if Fe is present in very small quantity. Max. solubility of Mg_2Si in Al is 1% at 500° and 0.45% at 400° ; solubility decreases if excess of Si or Mg is added. CH. ABS.

Iron corner of the system iron-manganese-aluminium. W. KOSTER and W. TONN (Arch. Eisenhüttenw., 1933—1934, 7, 365—366).—Up to 30% Al and 50% Mn only the α - and γ -phases exist; a narrow ($\alpha+\gamma$) field extends from the Fe corner towards the centre of the triangular diagram and is somewhat broader at lower temp. than at $>1000^\circ$. For alloys in the α -field the γ - β Mn transformation begins to be noticeable with $>40\%$ Mn and the alloys become brittle and coarsely crystalline. The ternary α -solid solution is ferromagnetic up to 18% Al.

A. R. P.

The system manganese-tin-mercury. A. N. CAMPBELL and H. D. CARTER (Trans. Faraday Soc., 1933, 29, 1295—1300; cf. A., 1933, 454).—Solubility data for Mn and Sn in Hg at 30° , 55° , and 70° are recorded. The compound Sn_5Mn_2 , stable above 30° , was isolated. Sn, Mn, and Sn_5Mn_2 do not form solid solutions with Hg.

H. J. E.

Interconversion of atomic, weight, and volume percentages in binary and ternary systems. C. S. SMITH (Amer. Inst. Min. Met. Eng., Contrib. No. 60, 1933, 15 pp.).—Tables for facilitating the conversion are given.

A. R. P.

Partly miscible system aniline-water. P. MONDAIN-MONVAL and (ILLE.) H. SCHLEGEL (Compt. rend., 1933, 197, 1632—1634).—The relative densities of the conjugate solutions show inversion at 77° , when the aq. solution becomes the heavier.

C. A. S.

Ternary systems water, pyridine, and salts at 25° . P. M. GINNINGS, B. WEBB, and E. HINOHARA (J. Amer. Chem. Soc., 1933, 55, 4898—4899).—The equilibria can be represented by $y=a+b(10)^{-cx}$, where y is the wt.-% of $\text{C}_5\text{H}_5\text{N}$, x the wt.-% of salt, and a , b , and c are consts. In salt-rich solutions of $(\text{NH}_4)_2\text{SO}_4$ or NaCl the relation $y=a+bx^c$ reproduces the results more satisfactorily.

E. S. H.

Diffusion of gases in liquids under pressure. V. V. IPATIEV, V. P. TEODOROVITSCH, and S. I. DRUSCHINA-ARTEMOVITSCH (Z. anorg. Chem., 1933, 216, 66—74).—A method for determining the diffusion coeff. of gases in liquids under pressure is described, and vals. are determined for the following systems: H_2 in H_2O at 15° , 25° , 35° , and 45° and 40—100 atm., H_2 in liquid NH_3 at 25° and 30° and 35—100 atm., O_2 in H_2O and in 10% and 20% aq. NaOH at 25° and 50 atm. Over the range examined the diffusion coeff. of H_2 is independent of pressure.

E. S. H.

Solubility of inorganic compounds in liquid ammonia. II. M. LINHARD and M. STEPHAN

(Z. physikal. Chem., 1933, 167, 87—102; cf. A., 1933, 456).—The solubility, *s*, of alkali, alkaline-earth, and Ag chlorides, bromides, iodides, and nitrates has been determined at 0°. For the alkali and Ag halides *s* increases with increasing radius of the anion and with decreasing radius of the cation. There is evidence to show that in NH₃ solutions the cations are preferentially solvated, and taking this into account the observed solubilities fit in with Fajans' solubility rule (A., 1923, ii, 750). For the alkali halides *s* generally runs parallel with the tendency to form ammoniates. R. C.

Solubility. XIII. Solubility of iodine in certain solvents. G. R. NORRISH, L. H. DONNALLY, and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1933, 55, 4793—4800).—The solubility of I has been determined in C₂H₄Br₂, SiCl₄, and TiCl₄ at various temp. The relation between solubility and internal pressure is discussed. E. S. H.

Polyiodides. I. Solubility of iodine in potassium iodide solutions and hydration of the iodide ion. S. REICHSTEIN, L. EVENTOV, and I. KASARNOVSKY (Z. anorg. Chem., 1933, 216, 1—9).—The solubility of I in aq. KI (0.055—6.259*M*) has been determined at 25°. At concns. of KI < 2.659*M* addition of sucrose increases the solubility of I, but at higher concns. the reverse effect is observed. In either case the difference of solubility of the I is proportional to the concn. of sucrose added. The *d* of the solutions suggests that I' is hydrated in aq. solution. E. S. H.

Calcium sulphate in sea-water. II. Solubilities of calcium sulphate hemihydrate in sea-waters of various concentrations at 65—150°. T. TORIUMI, T. KUWAHARA, and R. HARA (J. Soc. Chem. Ind. Japan, 1933, 36, 689—690B).—Data for solutions containing 16—97 g. Cl per 1000 g. solution are recorded. The measurements were made with well-formed crystals. J. A. S.

Solubility of the hydrates of nickel chloride in water. E. BOYE (Z. anorg. Chem., 1933, 216, 29—32).—The solubilities of NiCl₂ with 7, 6, 4, and 2H₂O have been determined at temp. up to the b.p. of the saturated solution (117.9°). E. S. H.

Solubilities of amino-acids in water [from 0° to 100°], densities of their solutions at 25°, and calculated heats of dissolution and partial molal volumes. J. B. DALTON and C. L. A. SCHMIDT (J. Biol. Chem., 1933, 103, 549—578).—Data are given for *d*- and *dl*-alanine, *l*- and *dl*-aspartic acid, *d*- and *dl*-glutamic acid, *l*- and *dl*-leucine, di-iodo-*l*-tyrosine, glycine, *dl*-isoleucine, *dl*-norleucine, *dl*-phenylalanine, *l*-tyrosine, and *dl*-valine. It is inferred that *dl*-alanine and *dl*-leucine, and probably also *dl*-aspartic acid, are racemic compounds, whilst *dl*-glutamic acid is probably a racemic mixture. D. R. D.

Solubility of amino-acids in water. M. S. DUNN, F. J. ROSS, and L. S. READ (J. Biol. Chem., 1933, 103, 579—595).—Experimental data at 0°, 25°, 50°, and 75°, and data at 100° (calc. by an extrapolation formula) are given for glycine, *dl*-alanine, -glutamic acid, -valine, -isoleucine, -phenylalanine,

-norleucine, -leucine, and -aspartic acid, *l*-aspartic acid and -tyrosine, and *d*-glutamic acid. D. R. D.

Solubility law for ideal solutions and its application to a salt-water system. A. W. DAVIDSON (J. Chem. Educ., 1933, 10, 234—237).—The observed solubilities of three modifications of NH₄NO₃ in H₂O over the range 169.6° (m.p.)—70° correspond with those calc. from Schroder's equation for solubility in an ideal solution; at < 70° the observed vals. are < the ideal vals. Compound formation occurs to only a small extent. CH. ABS.

Theory of the distribution of electrolytes between a solid crystalline and a liquid phase. A. P. RATNER (J. Chem. Physics, 1933, 1, 789—794).—Equations showing the influence of the composition of the aq. phase on the distribution ratio, and the dependence of the partition const. on the properties of the pure components are deduced thermodynamically. Results for various systems involving the distribution of radio-elements are shown to agree with the theoretical requirements. W. R. A.

Sorption of hydrogen by reduced nickel. I. Determination of the quantities of hydrogen adsorbed by and diffused in pure and spoiled reduced nickel, and of the isothermal adsorption lines and heat of adsorption. II. Adsorption of hydrogen by reduced nickel at low temperatures. S. IJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 285—300; 23, 34—43).—I. Velocity curves indicate that the sorption of H₂ by Ni is due to adsorption followed by diffusion. Adsorption isotherms at 50—300° with *p* < 15 cm. agree with Freundlich's equation and give 16,350 g.-cal. for the heat of adsorption. The latter is reduced considerably (e.g., to 6479 g.-cal.) if the Ni has been contaminated with air, even if the air is removed as completely as possible by heating in vac. for 1 hr. at 400°.

II. Isotherms are given for —183.5° to 100° and pressures from 0.1 mm. to 1 atm. Even at —183.5° the curve is smooth, provided that temporary overheating due to rapid adsorption is avoided (cf. A., 1930, 990). The isobars pass through a min. at about —80° and a max. at room temp., the temp. varying with *p*. There is no indication of compound formation (cf. A., 1926, 673). D. R. D.

Reversible sorption of gases and vapours by potassium benzenesulphonate. W. LANGE and G. VON KRUEGER (Z. anorg. Chem., 1933, 216, 49—65).—NH₃, H₂S, MeCl, N₂O, CO₂, and C₃H₈ are sorbed by PhSO₃K according to the adsorption isotherm, whilst marked deviations occur with SO₂ and Me₂O. In each case there is a saturation val., at which the mol. ratio of the adsorbent to the adsorbed vapour is a simple, whole no. Capillary condensation plays no part, but the gas mols. probably diffuse through the loose structure of PhSO₃K. E. S. H.

Absorption of carbon monoxide by cuprammonium salts. N. M. SHAVORONKOV and P. M. RESCHTSCHIKOV (J. Chem. Ind. Russ., 1933, 10, No. 8, 41—49).—Max. absorption of CO by aq.-ammoniacal Cu^I formate or lactate is obtained at > 20° and at high pressures. 90% of the absorbed CO is evolved on heating at 80°; at higher temp. loss of NH₃ and

separation of free Cu take place. The absorptive capacity increases with the Cu and NH_3 contents.

R. T.

Reciprocal adsorption. IV, V. E. N. GAPON (J. Gen. Chem. Russ., 1933, 3, 660—666, 667—669).—Theoretical.

R. T.

Heat of adsorption of inert gases and carbon dioxide on ionic crystals. F. V. LENEL (Z. physikal. Chem., 1933, B, 23, 379—398).—Data for the adsorption of A and Kr at about 90° and of CO_2 at 200 — 240° abs. by powdered alkali halides have been used to derive the heat of adsorption, Q . In the adsorption of inert gases on ionic crystals the attractive effect is the resultant of (1) the London dispersion forces and (2) an effect due to the creation of an electric moment in the adsorbed gas atom by the ions of the lattice. In the adsorption of a polar gas there is in addition a purely electrostatic effect due to interaction between the charged lattice points and the non-uniformly distributed charges of the adsorbed mol. The three effects have been calc. for the adsorbates studied and from them the adsorption potentials derived and compared with those deduced from the experimental data. For A and Kr the agreement is satisfactory. Throughout (1) (2). For the system A-KCl Q is approx. equal to the latent heat of vaporisation of A.

R. C.

Relation between adsorption, solubility, and nature of the solvent. III. N. SATA and K. KURANO (Kolloid-Z., 1933, 65, 283—290; cf. A., 1932, 991).—For picric (I) and benzoic acids in binary mixtures of H_2O , EtOH, CHCl_3 , Et_2O , COMe_2 , PhNO_2 , PhMe , C_6H_6 , and CCl_4 the curves for the solubility and adsorption by C are antibatic. (I) in COMe_2 is anomalous.

E. S. H.

Capillary ascent or depression of liquids in cylindrical tubes. II. Wide tubes. A. W. PORTER (Trans. Faraday Soc., 1933, 29, 1307—1309; cf. A., 1933, 1002).—Theoretical. Capillary corrections for wide tubes are tabulated.

H. J. E.

Theory of electrocapillarity. II. Thermodynamics of capillarity. S. R. CRAXFORD, O. GATTY, and J. ST. L. PHILPOT (Phil. Mag., 1934, [viil], 17, 54—64; cf. A., 1933, 1248).—Theoretical.

H. J. E.

Oil lenses on water and the nature of unimolecular expanded films. I. LANGMUIR (J. Chem. Physics, 1933, 1, 756—776).—Equations are derived which show that the spreading coeff. can be derived from the radii of large lenses of known vol. A method for introducing hydrophilic mols. into the interface between the lens and the H_2O is described, and the resulting changes are examined with reference to the two-dimensional equation of state of adsorbed mols. at the H_2O -oil interface. The presence of a "kink" in the observed F - a curves is attributed to the sudden appearance of micelles. Vals. of F_0 and a_0 for various substances are determined from Adam's data.

W. R. A.

Effect of reduced pressure on the formation of liquid drops on the surface of the same liquid. L. D. MAHAJAN (Kolloid-Z., 1934, 66, 22—23).—The

effect is difficult to reproduce in air at 431 mm. pressure.

E. S. H.

Surface free energy of liquids and liquid mixtures. Y. MORINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 49—117).—Katayama's equation (A., 1916, ii, 219) and an extension of it to binary mixtures are confirmed by the data for C_6H_6 , PhMe , CCl_4 , PhCl (temp. range 50 — 170°), Et_2O (20 — 110°), EtOAc , MeOH , EtOH , PrOH , and AcOH (20 — 150°), and certain pairs of these. Abnormal results for the alcohols are explained by treating them as binary mixtures of single and triple mols.

D. R. D.

X-Ray spectroscopic experiments on the orientation of palmitic acid at mineral surfaces. E. BERL and B. SCHMITT (Kolloid-Z., 1933, 65, 261—264).—Orientation could not be detected at the surfaces of ZnS , PbS , FeS_2 , CaCO_3 , or PbCO_3 . The existence of a unimol. film is not excluded.

E. S. H.

Structure of surface films. XVIII. Effect of alkalinity in the underlying solution on films of fatty acids. XIX. Influence of alkaline solutions on films with various end groups. N. K. ADAM and J. G. F. MILLER. XX. Surface potential measurements on nitriles. N. K. ADAM and J. B. HARDING (Proc. Roy. Soc., 1933, A, 142, 401—415, 416—422; A, 143, 104—111).—XVIII. Films of the normal fatty acids (12—22 C atoms) on solutions varying from dil. HCl to $2N$ -NaOH have been examined with respect to (a) the lateral adhesion between the mols., indicated either by the temp. at which expansion occurs or by the form of the surface pressure-area relation for the expanded (or gaseous) films; (b) the packing in the condensed films; and (c) the collapse of the films on alkaline solutions.

XIX. Unimol. films of various substances with ionisable end-groups show a marked decrease in lateral adhesion when the alkalinity of the solution is changed so as to ionise the end-groups. This effect is not shown by substances with non-ionisable end-groups. Films of $\text{C}_{17}\text{H}_{33}\text{CO}_2\text{Me}$ are fairly rapidly hydrolysed on $2N$ -NaOH.

XX. Surface potential measurements on unimol. films of long-chain nitriles (14—22 total C atoms in the chain) indicate a max. val. of μ only about $1/7$ of the dipole moment of the CN group as obtained by other methods. The effective "dielectric const." of the surroundings of the film mols. is probably about 7. The transition between condensed and expanded films is heterogeneous.

L. L. B.

Influence of the underlying surface on the cataphoretic mobility of adsorbed proteins. A. DUMMETT and P. BOWDEN (Proc. Roy. Soc., 1933, A, 142, 382—401).—The electrokinetic properties of proteins adsorbed on different surfaces have been studied in aq. solution. For gelatin, the mobility is independent of the nature of the substrate, in agreement with the results of other workers, but in oxy- (I) and carboxy-haemoglobin (II) both the mobility and the isoelectric point vary in a marked degree with the nature of the underlying surface. The surface equilibrium of the protein is attained in a few sec. in conc. solutions, but takes several hr. in dil. solutions. (I) and (II) when adsorbed have identical electro-

kinetic properties, and no evidence is found for two forms of hæmoglobin with different isoelectric points.

L. L. B.

Contact potentials and the effects of unimolecular films on surface potentials. I. Films of acids and alcohols. W. D. HARKINS and E. K. FISCHER (J. Chem. Physics, 1933, 1, 852—862).—Simultaneous measurements of film pressure and surface potential have been made with a form of apparatus which permits the determination of the potential at any point on the surface of the film. Org. substances with homo-heteropolar mols. gave a single smooth curve for surface potential-mol. area at film pressures above that of the gaseous films. For increase of area and reduction of pressure the surface potential becomes variable; it rises rapidly with the no. of C atoms in the hydrocarbon chain, and is higher for alcohols than for acids with the same no. of C atoms. Change of single linking in one film substance to double linking in another lowers the surface potential. Lowering of temp., increase of concn. in the film, or replacement of a basic by an acid solution raises the surface potential. Films in the condensed state show hysteresis with respect to both film pressure and surface potential. The relation between surface potential and mol. moments of mols. constituting the film is discussed.

N. M. B.

Wetting and porosity. Adsorption and total heats of wetting of powders of different particle size. B. ILJIN and A. KISSELEV (Kolloid-Z., 1934, 66, 28—40).—The ordinary calorimeter is unsuitable for determining heats of wetting of powders, as a slow adsorption process is involved. An adiabatic calorimeter has consequently been used to study the heat of wetting of powdered activated wood charcoal of various particle sizes. With decrease in particle size from 0.68 mm. to < 0.15 mm. the amount of adsorbed substance A and the heat of wetting Q (per g. of adsorbent) increase by 4.6% for I and 10% for heptioic acid. The adsorption isotherms are not in accordance with the usual equations, but those for different fractions of adsorbent are related by a simple coeff., which depends on the adsorbed substance. The val. of Q/A_{∞} , where represents max. adsorption, is independent of particle size, indicating that with increasing subdivision the sp. surface of the adsorbent changes, but not its properties. The complete heat of wetting for all fractions of C depends on the wetting liquid; with H_2O it is < with org. liquids and increases with increasing no. of C atoms throughout a homologous series.

E. S. H.

Physical chemistry of wetting phenomena and flotation processes. IX. Influence of adsorption layers of surface-active substances on selective wettability. P. REHBINDER [with M. LIPETZ, M. RIMSKAJA, and A. TAUBMANN]. **X. Dependence of wettability on the adsorption of the flotation reagents. Wetting isotherms at the boundary mineral-water-air.** P. REHBINDER, M. LIPETZ, and M. RIMSKAJA (Kolloid-Z., 1933, 65, 268—283; 1934, 66, 40—50).—IX. A summary and theoretical treatment of published results.

X. Wetting isotherms have been obtained for the boundary malachite-water-air in presence of various

flotation agents. It is shown that the flotation process depends eventually on the alteration of the wetting conditions by the flotation agents. Flotation activities of several agents (Et, isoamyl, and Bu^x xanthates, aliphatic acids and their Na salts, etc.) towards malachite, ZnS , PbS , FeS_2 , and $CuFeS_2$ are given.

E. S. H.

Passage of gases through porous diaphragms. C. PADOVANI and G. MONTI (Acqua e Gas, 1933, 22, 43—45; Chem. Zentr., 1933, ii, 194).—The relation between the difference in pressure Δp and the vol. Q of gas a transferred in unit time is given by $\Delta p = (128l\eta/D^4N)Q + (16\rho/\pi^2D^4N)Q^2$ (or, simplified, $A\eta Q + B\rho Q^2$), where l is the length, D the diam. of the individual capillaries, N their number, η the coeff. of internal friction, and ρ the d of the gas. A and B depend only on the properties of the diaphragm. The influence on linearity of the various factors concerned has been studied.

A. A. E.

Permeability of dried collodion membranes for amino-acids and for organic non-electrolytes. F. E. SCHMENGLER (Pflüger's Archiv, 1933, 232, 591—603; Chem. Zentr., 1933, ii, 1691).—The behaviour of α - and β -alanine, leucine, lysine, asparagine, aspartic acid, betaine (I), and phenylalanine (II) has been compared with that of polyhydric alcohols. As with cells and tissues, the smaller permeability of NH_2 -acids, except (I) and (II), is attributed to their ampholyte nature (existence as zwitterions). (I) has a small dipole moment, whilst (II) exists as zwitterion only to the extent of 10%.

A. A. E.

Stationary, checked, and other states of osmotic systems. III. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 779—785; cf. A., 1933, 900; this vol., 24).—Theoretical.

J. W. S.

Membrane equilibria and the secondary swelling of protein gels. F. G. DONNAN (J. Soc. Leather Trades Chem., 1933, 17, 136—143).—The Donnan equilibrium is considered in relation to the nature of the solutions concerned. The theory is not easily applicable to a micellar system such as skin or natural fibres. In their application of the theory Procter and Wilson neglected to take account of the effect of inorg. salts on the swelling of isoelectric gelatin gel. The interior of the gelatin micelles is penetrated by ions and H_2O mols.

D. W.

Aphorisms of Liesegang rings. B. KISCH (Kolloid-Z., 1933, 65, 316—319).—Examples of the periodic crystallisation of thin films of aq. inorg. salt solutions and of the formation of secondary Liesegang rings are given.

E. S. H.

Acetethylanilide as a cryoscopic solvent, and the mol. wt. of some cellulose ethers dissolved therein. F. GARELLI and G. RACCIU (Atti R. Accad. Lincei, 1933, [vi], 18, 150—155).—Cellulose nitrate, acetate, and Et ether form true dil. solutions in $NPhEtAc$, and give mol. wts. corresponding approx. with the dimeric formula $(C_6)_2$.

O. J. W.

Individuality of osmotic behaviour of alkali halides. G. DAMKOHLER and J. WEINZIERL (Z. physikal. Chem., 1933, 167, 71—86).—The mol. f.-p.

depressions of LiBr, NaBr, KBr, and CsBr have been determined. R. C.

Production of disperse systems by explosion of the vapours of the disperse material in the cold liquid dispersion medium. I. P. P. VON WEIMARN and N. SATA (Kolloid-Z., 1934, 66, 1—11).—A small amount of the substance to be dispersed is placed in a closed, thin-walled capsule, which also contains an electric heating element. Several such capsules are lowered into the cooled liquid dispersion medium. When current is passed through the heating element the substance vaporises, breaks the capsule, and is condensed to colloidal disperse particles in the medium. Stable sols of Hg and Se have been prepared in this way. The concn. obtained is about 0.005% and the stability depends on the presence in the medium of a sol. compound having an atom in common with the disperse phase. S gave a coarsely disperse system as may be expected from its greater solubility. E. S. H.

Condensation aerosols; colloidal dispersed arsenic [trioxide] dust. A. WINKEL and G. JANDER (Kolloid-Z., 1933, 65, 290—294).—Aerosols of As_2O_3 have been prepared by rapid cooling of As_2O_3 vapour. The no. of particles per unit vol. decreases rapidly during the first hr., especially in the more conc. sols (150—500 mg. per cu.m.). The variation of mean particle wt. with concn. after a given ageing period is linear. E. S. H.

Measurement of the concentration and dispersity of suspensions with a photo-electric cell. III. M. MATSUI, T. NODA, and S. IWAI (J. Soc. Chem. Ind. Japan, 1933, 36, 691—692B).—Graphs are given showing the relations between the concn., the extinction ($\log I_0/I$), and the fractional scattering $(I'-I'_0)/I_0$ for suspensions of $CaCO_3$, ZnO , PbO , Fe_2O_3 , and C. I' and I'_0 are the intensities of the light scattered by the suspension and by the suspension medium, respectively. A. G.

Colloidal solutions by hydrolysis of cerium sulphate. A. JANEK and A. SCHMIDT (Kolloid-Z., 1933, 65, 295—297).—Sols containing negatively-charged, hydrophobic particles are prepared by pouring sufficiently conc. aq. $Ce(SO_4)_2$ into a large vol. of H_2O . Addition of Na_2SO_4 causes the initially turbid sol to become clear for a time, but later turbidity reappears and is followed by sedimentation. E. S. H.

Action of ethylene oxide on solutions of the halides of the earth and heavy metals. Preparation of sols and reversible gels of hydrated metal oxides. W. ZIESE (Ber., 1933, 66, [B], 1965—1972).—Addition of $(CH_2)_2O$ (I) to $AlCl_3$ in H_2O yields $Al(OH)_3$ and $CH_2Cl \cdot CH_2 \cdot OH$ (II), the former remaining as a sol until about 90% of the theoretical amount of (I) has been added and subsequently solidifying to a clear gel. Removal of by-products from the sol can be effected by extraction with solvents for (II) or by distillation, when H_2O and (II) pass over together at 97°. The sols of Al, Cr, Zn, and Th may be regarded as containing highly basic salts. They are dried without difficulty to reversible gels which give stable sols when brought in contact with

H_2O , conc. EtOH, or glycerol. Excess of (I) ppt. the metal oxide hydrates as gels after passage through the hydrosol phase. Oxides of bivalent metals (Zn, Mn) frequently have a very unstable sol. phase, pptn. occurring with small amounts of (I). Usually the ppts. are very finely divided and, after thorough washing, readily disperse in H_2O . (I) can be replaced by propylene oxide and H_2O by 96% EtOH. Bromide and iodides can be used in place of chlorides. H. W.

Viscosity of colloidal solutions in relation to concentration. G. BERRAZ (An. Inst. Invest. cient. tecnol., 1930, 1, No. 3, 82—98; Chem. Zentr., 1933, ii, 844).—The viscosity $V = 1 + KSC/(1000 - SC)$, where C is the concn. (g. per litre), S is the vol. of 1 g. of solvatised colloid, and K has different vals. for different systems. When C and S are small Einstein's equation $\mu - \mu_0(1 + 2.5\phi)$ is approached. A. A. E.

Influence of electric charge on the viscosity of hydrophilic colloids. I. SAKURADA and T. NAKASHIMA (Kolloid-Z., 1934, 66, 62—67, and Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 36, 620—621).—The relation between relative viscosity (η_r) and concn. (c) for systems containing particles of any form can be expressed by $\eta_r = 1 + a(\phi c/100)$ (I), or $\eta_r = 1 + a\phi c/(100 - \phi c)$ (II), where ϕ is the sp. vol. of the disperse phase, and a a const. which depends on the form and electric charge of the particle (2.5 for uncharged spheres). The validity of (II) has been established for Na celluloseglycollate (III), starch, and gelatin sols. Colloid particles of (III) appear to be spherical and strongly charged in H_2O . The particles are almost completely discharged by adding small amounts of neutral salts or by rise of temp. Starch particles appear to be spherical and not very highly charged. Gelatin particles are apparently either highly charged or non-spherical. E. S. H.

Behaviour of concentrated ferric hydroxide sols in the capillary viscosimeter. A. RABINERSON and G. FUCHS (Kolloid-Z., 1933, 65, 307—316).—The viscosities of conc. (8—20%), stable $Fe(OH)_3$ sols have been determined at pressures of 15—190 cm. H_2O . Structure viscosity is not observed in freshly prepared, dil. sols, but increases with the age and concn. of the sol. It is always < in most lyophilic colloids. The rate of ageing increases with concn. The crit. Reynolds vals. for conc. $Fe(OH)_3$ sols are < those for H_2O , the deviation increasing with increasing concn. E. S. H.

Importance of dialysis in the study of colloids. I. Colloidal ferric hydroxide. B. N. DESAI and S. K. BORKAR (Trans. Faraday Soc., 1933, 29, 1269—1285).—With progressive dialysis of a $Fe(OH)_3$ sol the cathoretic speed, I , passes through a max. and the viscosity through a min. val. (the two vals. do not correspond), whilst the KCl flocculation val. decreases continuously. The variation of I with the addition of HCl, KCl, $MgCl_2$, H_2SO_4 , K_2SO_4 , and $MgSO_4$, and the effect of dialysis followed by dilution, have been examined. H. J. E.

Elastic properties of collodion during flow. A. PAKSCHVER and M. BUNIN (Kolloid-Z., 1934, 66, 68—75).—Mechanically stressed collodion solutions

(6—20% in EtOH-Et₂O) show thixotropic properties, but regain their original viscosity when kept. Whilst the viscosity is influenced greatly by changes of temp., the elastic limit is unaffected; concn. has a great influence on both properties. The distribution of velocities has been examined for streaming in long and short tubes. E. S. H.

Optics of colourless sols. III. Optical relations in coagulation. T. CASPERSSON (Kolloid-Z., 1933, 65, 301—307; cf. this vol., 26).—Mathematical relations are derived. E. S. H.

Action of electric waves on colloids. E. WILKE and R. MÜLLER (Kolloid-Z., 1933, 65, 257—260).—The colour, viscosity, velocity of electrophoresis, and electrical conductivity of As₂S₃ sols are altered by applying a high-frequency electro-magnetic field (wave-length 105—260 m.). E. S. H.

Electric double layer of colloids. II. Double layer and stability of undialysed silver iodide sols. III. Double layer and stability of dialysed silver iodide sols. E. J. W. VERWEY and H. R. KRUYT (Z. physikal. Chem., 1933, 167, 137—148, 149—163; cf. A., 1929, 136).—II. The adsorptive power of a negative AgI sol for I⁻ decreases with increasing age, the decline being especially rapid immediately after pptn. With positive sols there is a similar, but less marked, fall in the amount of adsorbed Ag⁺. These phenomena are not due to a fall in the degree of dispersity. Ageing apparently consists of two phases, the first a rapid structural change in the individual particles, and the second a slow decrease in the degree of dispersity. X-Ray study shows that lattice changes play at most a secondary part in the first phase, which seems to consist in the recrystallisation of the imperfectly constructed particles formed by pptn. to give a more perfect lattice. It is supposed that during this phase the adsorbed ions constituting the double layer are present only at such points as corners and edges of the crystals and loose places. The peptising power of an ion depends, not on its adsorbability, but on its power to take its place in the lattice of the substance to be peptised; AgI is peptised by Cl⁻, but not by OH⁻.

III. By dialysis and electro-decantation of negative AgI sols, very pure and conc. sols of high stability may be obtained. Adsorption measurements indicate that the charge on the double layer is a linear function of the logarithm of the concn. of free I⁻ in the sol. For these sols the first of the above phases of ageing is particularly important. The counter-ion is largely H⁺. The double layer is present only at active points on the surface, such as crystal edges and loose places, and the particle charge is abnormally small. The charge is zero at [Ag⁺]=about 10⁻⁶, i.e., two powers of 10 on the positive side of the equivalence point. This must involve a systematic error in the potentiometric AgI titration. The physico-chemical behaviour of dialysed AgI sols is completely determined by the distribution of I⁻ between AgI and solution. R. C.

Ageing of arsenic trisulphide sols under the influence of light. Variations in stability of sols with respect to electrolytes. V. KRESTINSKAJA (Kolloid-Z., 1934, 66, 58—62).—Ageing of an As₂S₃

sol may cause either an increase or a decrease of stability towards a particular electrolyte, according as the micelles contain excess of As₂O₃ or of H₂S. Ageing results in a decrease of the amount of disperse phase, an increase in the amount of H₃AsO₃ in the dispersion medium, and the production of colloidal S. The influence of these factors on the stability of the sol varies with different electrolytes.

E. S. H.

Oxidation of arsenious sulphide by atmospheric oxygen in alkaline media, under pressure, and at high temperatures. II. E. P. LOPATINA (J. Appl. Chem. Russ., 1933, 6, 803—807).—S hydrosols result from suspensions of As₂S₃ in 4N-NaOH on heating for 2 hr. at 150° and 25—50 atm. The S, which is pptd. by aq. CO₂ or H₂SO₄, represents 50—75% of that originally present as As₂S₃.

R. T.

Sodium petroselate as a soap. J. MIKUMO (J. Soc. Chem. Ind. Japan, 1933, 36, 632—633b).—Na petroselate closely resembles Na oleate in viscosity, surface tension, and suspending power. R. S.

Determination of the sign of electric charge and isoelectric point of fine fibres. A. DUMANSKI and O. A. DUMANSKI (Kolloid-Z., 1934, 66, 24—28).—Results obtained by observing the deflexion of the fibre, when placed in H₂O between two oppositely-charged unpolarisable electrodes, are in satisfactory agreement with those given by electro-osmotic or streaming-potential measurements. E. S. H.

Electro-kinetics. XIII. Relation between streaming potential and applied pressure. H. B. BULL (Kolloid-Z., 1934, 66, 20—22; cf. A., 1932, 460, 804).—Repetition of the experiments of Ettisch and Zwanzig (A., 1932, 911) has failed to confirm their results. The streaming potential-pressure curves are straight lines, which pass through the origin.

E. S. H.

Electrophoretic mobilities and the isoelectric point of protein-coated particles. O. HALPERN (J. Chem. Physics, 1933, 1, 882—884).—Theoretical considerations support the observation that the electrophoretic potential of protein-coated quartz or glass particles is independent of their size and shape, and that their isoelectric point coincides with that of the protein ions in the solution. N. M. B.

Behaviour of aqueous solutions of the domestic cocoon. XIII. Velocity of electrophoresis of the sericin particle. XIV. Behaviour in sericin gel. H. KANEKO (J. Agric. Chem. Soc. Japan, 1933, 9, 697—704, 737—740).—XIII. Sericin has a negative charge on the alkaline side of the isoelectric point (p_H 4.2; sericin-A, 4.1; -B, 4.3). The velocity of electrophoresis (I) increases in inverse proportion to the concn. and proportionally to the temp. and time of heating. (I) is increased by addition of a small amount of a univalent cation. Sericin has an opposite charge if a small amount of a tervalent cation is added. The electrical behaviour of sericin resembles that of gelatin.

XIV. When an electric current (110 volts) is passed through sericin gel with Pt poles an annular ppt. is formed around the positive pole, due possibly to electrolysis of org. acid adsorbed from sericin-A. If an alkaline-earth or heavy metal is added before gel

formation, a ppt. is formed around the negative pole. The diffusion of org. colouring matters in sericin gel is slower than in gelatin or agar-agar. CH. ABS.

Jellies of zirconium sulphosalicylate. S. PRAKASH (Z. anorg. Chem., 1933, 215, 249—254).—Jellies are obtained when aq. ZrOCl_2 and 5-sulphosalicylic acid are mixed in certain proportions. The effect of dilution, temp., Cl^- , and SO_4^{2-} on the time of gelation has been studied. The sols are positively charged and gelation occurs only in acid solution.

F. L. U.

(A) Lyophilic colloids. (B) Mechanism of gelation of lyophilic colloids. S. M. LIEPATOV (J. Gen. Chem. Russ., 1933, 3, 685—693, 694—697).—A. The solubility of cellulose acetate (I) in CHCl_3 falls with diminishing content of low mol. wt. decomp. products (II) of (I), which act as peptisers. At the same time imbibition of solvent by (I) increases as a result of augmented intramolecular osmotic pressure.

B. Gelation of sols of (I) is ascribed to intramolecular solvation, with consequent retardation of Brownian movements of the micelles, and diminution of the distance between the latter. The velocity of gelation falls with increasing content of (II).

R. T.

Changes in viscosity of cellulose solutions after various treatments. T. NAKASHIMA and M. NEGISHI (J. Soc. Chem. Ind. Japan, 1933, 36, 621—623b).—The change in viscosity of a cuprammonium solution of the treated cellulose is given by $d\eta/dt =$

A. G.

Swelling and dissolution of benzylcellulose in organic liquids. I. SAKURADA and I. KIDO (J. Soc. Chem. Ind. Japan, 1933, 36, 656—659b).—The liquids in which benzylcellulose ($2\text{CH}_2\text{Ph}$ per $\text{C}_6\text{H}_{10}\text{O}_5$) is completely sol. have dipole moments (μ) > 1 and $u/V > 12.7 (\times 10^{-2})$, V being the mol. vol. The alcohols and the lower esters and ketones satisfy these conditions, but are not solvents on account of their strong association.

A. G.

Decomposition of cellulose by hot concentrated aqueous alkalis. N. I. NIKITIN and N. P. NEMTSOVA (J. Appl. Chem. Russ., 1933, 6, 845—849).—The viscosity η of solutions of cotton-wool cellulose which has been immersed for 6 hr. in 20—50% NaOH falls from 9.2—9.4 to 2.0—2.7 when the temp. is raised from 80° to 140°. When the time of immersion is increased to 16 hr. there is little further diminution in η . The Cu val. of the product rises with rising temp. of immersion.

R. T.

Measurements of the diffusion of proteins. A. TISELIUS and D. GROSS (Kolloid-Z., 1934, 66, 11—20).—An optical method is described for following the diffusion of high-mol. colloids, which show absorption of visible or ultra-violet light. Diffusion coeffs. thus obtained at 20° are: R-phycocerythrin 4.00×10^{-7} , R-phycocyanin 4.05×10^{-7} , CO-haemoglobin 6.3×10^{-7} , snail haemocyanin 1.05×10^{-7} , ovalbumin 7.7×10^{-7} cm.² per sec. These vals. are in general $<$ those calc. from mol. wts. or sedimentation velocities.

E. S. H.

Sedimentation constants, mol. wts., and isoelectric points of respiratory proteins.—See this vol., 92.

Physico-chemical study of flocculation of myxoprotein by resorcinol. A. BOUTARIC, M. PIETTRE, and (MLLE.) M. ROY (Compt. rend., 1933, 197, 1413—1415; cf. A., 1933, 966).—The behaviour indicates that myxoprotein adsorbs resorcinol to form a product of gradually decreasing solubility in aq. NaCl. A small residual portion is not affected in this way, and this is probably globulin present as impurity.

C. A. S.

Osmotic pressure of protein solutions. G. S. ADAIR (J. Soc. Leather Trades Chem., 1933, 17, 143—151).—A general consideration of the factors which should be taken into account is the measurement of the osmotic pressure of solutions of proteins.

D. W.

Effect of neutral salts on the swelling of gelatin. F. C. THOMPSON (J. Soc. Leather Trades Chem., 1933, 17, 169—178).—Acid-swollen gelatin is repressed osmotically by neutral salts, and this can be adequately explained by the Procter-Wilson theory. There is also a lyotropic effect on non-ionised neutral gelatin, which is a max. at the isoelectric point. Swelling is favoured by I^- and NO_3^- and inhibited by SO_4^{2-} .

D. W.

Swelling of proteins in weak acids. W. R. ATKIN (J. Soc. Leather Trades Chem., 1933, 17, 220—228).—The evidence of Kuhn (A., 1922, i, 183) against Procter and Loeb's theories of the swelling of proteins is attributed to the ash content of the gelatin (I) used in the experiments. Small quantities of NaCl increase the swelling of (I) in weak acids. Max. swelling of (I) is always obtained when the p_H of the external solution in equilibrium is 2.4.

D. W.

Swelling [of gelatin] in alkaline solutions. R. H. MARRIOTT (J. Soc. Leather Trades Chem., 1933, 17, 178—193).—The first part of the alkaline titration curve p_H 5—8 of gelatin (I) is determined by the lysine and histidine groups, but for $p_H > 8.0$ the curve is due to the arginine groups. The swelling of (I) in alkaline solutions is osmotic and can be explained on the Procter-Wilson theory. A certain amount of H_2O is absorbed owing to the mol. structure of the protein micelles, and this can be calc. for the isoelectric point. Collagen (II) does not swell at $p_H < 9$ and attains a max. about p_H 12. Limed skin, previously dried, shows slight osmotic swelling about p_H 8 and a max. at p_H 12.5. The difference between the swelling of (II) fibres in aq. NaOH and $\text{Ca}(\text{OH})_2$ is explained by the Loeb valency law. The greater swelling of (II) fibres by NaOH is attributed to the larger area covered by the Ca^{++} in the protein. The localised osmotic pressure due to the Na^+ causes localised bulging of the protein structure. The resistance of keratin to swelling is explained by the cystine cross-chains linking up the protein mol. "backbones."

D. W.

Protein swelling and molecular organisation. D. J. LLOYD (J. Soc. Leather Trades Chem., 1933, 17, 208—220).—The swelling of gelatin (I) jellies varies inversely as the concn. of (I) in the jelly at the time of its coagulation. The swelling of protein (II) fibres varies inversely as the concn. of the (II) in the fibres, i.e., the compactness of the fibrous structure. The diminution in swelling with increased concn. is attributed to a reduction of the space available for the

diffusion of non-colloidal ions leading to a mechanical restraint of their movements, to a reduction of the no. of charged centres on the colloidal ion through the formation of cross-linkings between the (II) mols., and to an increase in the rigidity of the protein caused by the cross-linkings. The unequal distribution of diffusible ions is reduced by these factors and (II) swelling is thereby reduced. D. W.

Formation and constitution of protein salts from the viewpoint of modern theories of valency. H. PHILLIPS (J. Soc. Leather Trades Chem., 1933, 17, 151—169).—The factors which influence the polarities of the basic and acid groups in NH_2 -acids, polypeptides, and proteins, and the interaction of gelatin with acids and bases are discussed from the viewpoint of the electronic theory. A true salt is formed by the free NH_2 groups when gelatin reacts with acids, but the latter then combine through the covalencies with the zwitterions in the mol. Swelling is caused by salt formation and is repressed by the covalent combinations. The free CO_2H groups in gelatin form salts in solutions of $p_{\text{H}} < 10$, and combine with the zwitterions in solutions of $p_{\text{H}} < 11$. The zwitterions are converted into NH_2 groups and CO_2H anions. Alkaline swelling occurs in two stages, first when the CO_2H groups become anionic, and then when they associate with metallic cations; the swelling is suppressed by alkaline covalency combinations. D. W.

Elastic properties of glycerol-gelatin gels hardened with formaldehyde. H. J. POOLE (Trans. Faraday Soc., 1933, 29, 1305—1307).—A discussion of Hatzek's results (A., 1933, 1244), supporting the fibrillary theory of gels. H. J. E.

Swelling peculiarities of gelatin sheets, and conclusions derived therefrom concerning the swelling of emulsoid colloids. J. BOLLHAGEN (Kolloid-Z., 1933, 66, 75—83).—Experiments on the swelling in H_2O of thin gelatin sheets, curved and protected on one side with vaseline so that the swelling surface may be concave or convex to the H_2O , show that the swelling is characterised by two stages: (a) alteration in the form of the particles, involving decrease of one dimension and increase of another, (b) increase in vol. of the particles without further change of form. E. S. H.

Influence of electrolytes on the formation and decomposition of urate gels. E. G. YOUNG, F. F. MUSGRAVE, and H. C. GRAHAM (Canad. J. Res., 1933, 9, 373—385).—In the gelation (I) of supersaturated aq. solutions of the urates of NH_2Me , Li, piperazine, and NMe_4 by electrolytes, the cation is the active agent, the order of efficacy being in general $\text{K} > \text{NH}_4 > \text{Rb} > \text{Cs} > \text{Li} > \text{Na}$. The time of (I) varies inversely, and the rigidity of the gel directly, with the concn. of electrolyte up to the pptn. point. Org. diamines and EtOH may cause (I). The thixotropic effect occurs with gels of piperazine urate containing KCl and Li urate with EtOH. H. S. P.

Action of alkaline copper solution on silk fibroin. IV. Fibroin-copper-amine compounds in the system fibroin-copper-amine. I and II. V. Application of conductometric

titration to the fibroin-copper-amine system. VI. Mechanism of the dissolution of fibroin in copper-amine solution. Y. TAKAMATSU (J. Soc. Chem. Ind. Japan, 1933, 36, 596—604B, 662—668B, 668—672B).—IV. When the fibroin-Cu-en compounds I and II are treated with EtOH-KOH, compounds of the composition fibroin : Cu : K = 1 : 1 : 1 : 5 are obtained, and I and II are therefore formulated [fibroin, Cu][Cu en]₂ and [fibroin, Cu]en. If excess of en is added to a fibroin-Cu-en solution, the latter changes from violet to blue, the electrical conductivity is greatly increased, and α diminished. It is probable that $[\text{Cu en}_2](\text{OH})_2$ is formed at the expense of Cu in the fibroin complex.

V. Solutions of $\text{C}_2\text{H}_4(\text{NH}_2)_2$, of $[\text{Cu en}_2](\text{OH})_2$, and complex solutions containing fibroin can be analysed by conductometric titration with H_2SO_4 . Different types of curve are obtained according to whether the solute is [fibroin Cu]en, [fibroin Cu][Cu en]₂, or both of these with or without excess of en.

VI. The rate of dissolution of fibroin in cuprammonium or in $\text{Cu}(\text{OH})_2$ -en is given by $x - kt^n$, where k and n are consts. A. G.

State of caoutchouc in solutions. II. Influence of temperature on the viscosity of solutions of different concentrations. B. DOGADKIN and M. LAVRINENKO (J. Gen. Chem. Russ., 1933, 3, 742—746).—The viscosity η of PhMe and xylene solutions of caoutchouc (I) is const. over the interval 3—60° for $> 0.3\%$ solutions; at higher concn. η varies inversely with temp. The conclusions are reached that (I) is in mol. dispersion up to 0.3%, and in micellar dispersion at higher concn. (up to 10%). In still higher concn. the continuous phase of the emulsions is (I). R. T.

Physical chemistry of starch and bread-making. XIV. Is the starch in starch paste crystalline or amorphous? J. R. KATZ and J. C. DERKSEN (Z. physikal. Chem., 1933, 167, 129—136; cf. A., 1933, 1117).—Starch paste containing $> 67\%$ H_2O gives an amorphous X-ray diagram which is largely the same as that of liquid H_2O . This suggests that the starch in the warm paste is amorphous. On cooling there is partial crystallisation. With *Gramineae* starches there is between the native starch and the amorphous paste an intermediate form with a V spectrum exhibiting sharp crystal interferences; fresh bread at either 80° or room temp. shows the V spectrum. This intermediate form is not observed with potato starch. Any amorphous starch solution or paste dehydrated in the fresh state with EtOH may under certain conditions give a substance with a V spectrum; the starch then crystallises in an α -modification which is unstable at room temp. if the H_2O content is sufficiently large. R. C.

Thermal dissociation of cyanogen into cyanide radicals. G. B. KISTIAKOWSKY and H. GERSHINOWITZ (J. Chem. Physics, 1933, 1, 885).—Corrections (see this vol., 30). N. M. B.

Water-gas reaction in low-pressure explosions. B. W. BRADFORD (J.C.S., 1933, 1557—1563).—The equilibrium const. has been calc. from analyses of the products of explosion of CO and H_2 with in-

sufficient O_2 for complete combustion. K_p decreases continuously with decreasing initial explosion pressure p for a given mixture, and varies with different mixtures at the same p , according to $K_p = \beta p^a$. The variation of K_p is attributed to changing concn. of OH produced by dissociation of H_2O , the equilibrium being chiefly determined by the rate of the reaction $CO + OH \rightarrow CO_2 + H$. R. S.

Chemical equilibria of reactions between hydrocarbons. V. A. A. VEDENSKI, S. G. VINNIKOVA, V. R. SHARKOVA, and B. M. FUNDILER (J. Gen. Chem. Russ., 1933, 3, 718—728).—The equilibrium consts. for the hydrogenation of PhMe, PhEt, and PhPr at 200—300° are given by $\log K = 10,970/T - B$, where the respective vals. of A are 20.387, 20.526, and 20.559, and of B 0.053, 0.049, and 0.105. R. T.

Equilibrium between carbon monoxide, hydrogen, formaldehyde, and methyl alcohol. I. Reactions $CO + H_2 \rightleftharpoons HCOH$ and $H_2 + HCOH \rightleftharpoons CH_3OH$. R. H. NEWTON and B. F. DODGE (J. Amer. Chem. Soc., 1933, 55, 4747—4759).—Reaction (1) in presence of Cu-Zn catalysts yields $K_p = 1.72 \times 10^{-5}$ at 247°. Reaction (2) proceeds readily at 120—200° in presence of Cu-Zn, Cu, Ni, Cu-Ce, Ni-Ce, Cu-Cr, or Zn-Cr, but Os, Pt, or Zn are not active catalysts. Ni tends to promote decomp. of CH_2O into CO and H_2 . Cu tends to give HCO_2Me among the products. For reaction (2) $K_p = 2090$ at 197°. The influence of temp. is given by $\log_{10} K_p = (374/T) - 5.431$ and $\log_{10} K_p = (4600/T) - 6.470$. E. S. H.

Derivation of equations for regular solutions. J. H. HILDEBRAND and S. E. WOOD (J. Chem. Physics, 1933, 1, 817—822).—Mathematical. Menke's probability function (cf. A., 1932, 986) is used for a statistical treatment of the intermol. potentials in solutions of symmetrical mols. for which the entropy of mixing is the same as for an ideal solution of the same composition. Calc. departures of I solutions from the ideal solution laws agree with experimental vals. N. M. B.

Spectroscopic investigation of dissociation relations of mercuric halides in solution. H. FROMHERZ and K. H. LIEB (Z. physikal. Chem., 1933, 167, 103—128).—Extinction curves have been traced between about 180 and 330 m μ . The Hg^{II} halides in aq. solution are practically non-ionised and there is no indication of any polymerisation of the HgX_2 mols. In EtOH solution the band max. are displaced towards the red compared with aq. solutions and are lowered by dilution. The max. of $HgBr_2$ and HgI_2 occupy practically the same position in aq. solution as in the vapour state. In mixed solutions of Hg^{II} and alkali halides there are present complex ions, but with a given pair of halides only one species of complex ion is formed: $HgX_2 + nX' \rightleftharpoons HgX_{n+2}$, where n is probably 1 or 2. The dissociation consts. of the complex ions have been calc. and show the stability to increase in the order $Cl < Br < I$. The ratio of the frequency of the ultra-violet absorption max. of HgX_4^{2-} to that of HgX_2 is approx. the same for all three halides. R. C.

Thermodynamics of aqueous sodium hydroxide solutions from electromotive force measurements. H. S. HARNED and J. C. HECKER (J. Amer. Chem. Soc., 1933, 55, 4838—4849).—Activity coeffs., relative partial mol. heat contents, and heat capacities of NaOH from 0° to 35° have been calc. from the e.m.f. of the cells $H_2|NaOH(M)|Na_2Hg|NaOH(0.05)|H_2$ at 5° intervals. The results agree well with calorimetric data. An equation for extrapolating the partial mol. heat content has been developed. E. S. H.

Dissociation constants of organic acids. VII. Acetic acid: correction. Solvent correction for salts of weak monobasic acids. G. H. JEFFERY, A. I. VOGEL, and (in part) H. V. LOWRY (J.C.S., 1933, 1637—1643; cf. A., 1933, 125).—A method for the accurate measurement of the conductivities of weak acids is described, involving the addition of sufficient $Ba(OH)_2$ to neutralise all impurity calc. as CO_2 in the solvent H_2O . Applied to NaOAc and KOAc, the method gives 40.54 for the limiting mobility of OAc' at 25°. The corr. vals. for the classical and thermodynamic dissociation consts. of AcOH are 1.824×10^{-5} and 1.764×10^{-5} , respectively. R. S.

First dissociation constant of carbonic acid in haemoglobin solutions.—See this vol., 92.

Influence of salts on activity of hydrogen ions. V. CUPR and T. KREMPASKY (Pub. Fac. Sci. Univ. Masaryk, 1933, No. 182, 3—27).— Li_2SO_4 is pptd. by adding EtOH (66%) to the acid solution; in these conditions Na, K, Be, Mg, Ca, and Al sulphates remain in solution. Corrections for the salt error due to NaCl or KCl in the measurement of the $[H^+]$ of aq. HCl using a quinhydrone electrode (I) have been determined for various concns. When two solutions of the same total mol. concn., containing HCl and different chlorides, are mixed, no change takes place in the $[H^+]$ other than that following from the mixture rule; the same applies to sulphate- H_2SO_4 mixtures. The $[H^+]$ of 0.2N- H_2SO_4 increases in presence of equiv. concns. of $MgSO_4$, $BeSO_4$, $ZnSO_4$, and $CdSO_4$ in the order given, and decreases in the series Li_2SO_4 , Na_2SO_4 , and K_2SO_4 . Chlorides increase the $[H^+]$ of 0.05N-HCl, in the order $KCl < NaCl < LiCl < MgCl_2$. R. T.

Theory of concentrated solutions of strong electrolytes. Calculation of the osmotic coefficients. G. B. BONINO and G. CENTOLA (Atti R. Accad. Lincei, 1933, [vi], 18, 145—149).—Theoretical. The osmotic coeffs. of conc. solutions of NaCl and of KCl are calc. O. J. W.

Strong electrolytes. H. D. CROCKFORD (J. Elisha Mitchell Sci. Soc., 1933, 49, 37).—The activity coeffs. of $PbCl_2$ in aq. $Cd(NO_3)_2$ have been determined for various concns. and used to calculate the mean distance of closest approach of ions in dil. solutions of strong electrolytes. CH. ABS.

Amphoteric hydrated oxides. XXI. Iso- and hetero-polymolybdic acids, especially phosphomolybdic acids. G. JANDER and H. WITZMANN (Z. anorg. Chem., 1933, 215, 310—320; cf. A., 1933, 1118).—Measurement of the diffusion coeff. of

Na_2MoO_4 in solutions of different p_{H} indicates that between p_{H} 14 and 6.5 the only anion present is MoO_4^{--} . Between p_{H} 6.5 and 1.5 $\text{HMo}_6\text{O}_{21}^{--}$, $\text{H}_2\text{Mo}_6\text{O}_{21}^{--}$, and $\text{H}_3\text{Mo}_6\text{O}_{21}^{--}$ are progressively formed, and at about 1.25 $\text{H}_7\text{Mo}_{12}\text{O}_{41}^{--}$. At still higher degrees of acidity there are formed, first the slightly sol. "molybdic acid hydrate," and subsequently sol. compounds in which the Mo forms part of a complex cation. In presence of an equimol. proportion of Na_2HPO_4 the behaviour is the same up to p_{H} 1. When the excess acid (HClO_4) reaches 1*N* the max. proportion of yellow $[\text{H}_2\text{PO}_4(\text{H}_3\text{Mo}_6\text{O}_{21})_2]^{--}$ is formed. The latter remains in equilibrium with amounts of the isopoly-anion and the molybdenyl cation which depend on the p_{H} . A study of the optical absorption of the solutions confirms the conclusions based on the diffusion experiments. F. L. U.

Equilibrium $\text{H}_2\text{SO}_4 + \text{HF} \rightleftharpoons \text{HSO}_3\text{F} + \text{H}_2\text{O}$ and the influence of strong acids on it. W. LANGE (Z. anorg. Chem., 1933, 215, 321—332; cf. A., 1933, 1014).—If 37% aq. HF is gradually added to H_2SO_4 at 24°, the amount of HSO_3F formed increases at first, reaches a max., and finally=0. Addition of H_2O to a mixture in equilibrium reduces $[\text{HSO}_3\text{F}]$ more rapidly than the law of mass action would predict. Foreign strong acids displace the equilibrium in favour of HSO_3F , but the action depends on their dehydrating capacity and not on their strength. F. L. U.

Equilibrium relations in slightly soluble basic salts. VI. W. FEITKNECHT (Helv. Chim. Acta, 1933, 16, 1302—1315).—As previously shown by X-ray analysis (A., 1933, 664) the first pptn. products of bivalent metal salts with aq. NaOH are usually well-defined basic salts. These behave as other slightly sol. compounds and the solubility product (I) can be determined. The calc. (I) of basic ZnSO_4 is shown to be fairly const. over a considerable concn. range, and similarly for basic Bi chloride. Equilibrium conditions are deduced for the coexistence of basic salt and hydroxide in solutions containing a second easily sol. salt with the same anion, and it is shown that the (I) of the hydroxide can be deduced. From the equations the val. 1.6×10^{-17} is obtained for the (I) of $\text{Zn}(\text{OH})_2$. This is confirmed by reference to data for aq. ZnCl_2 . Titration curves actually obtained in the pptn. of basic salts by aq. NaOH do not agree with the theoretical curves, probably because the basic salt is only slowly decomposed in presence of excess of alkali. No conclusion can be reached from the position of the end-point as to the composition of the basic salt. There are indications that in aq. ZnSO_4 containing >75% of alkali basic sulphates of composition $\text{ZnSO}_4 \cdot (6-7)\text{Zn}(\text{OH})_2$ are formed with the layered lattice structure observed in the normal basic salts. Similar conclusions apply to ZnCl_2 . M. S. B.

Partial pressure of water vapour and oxides of nitrogen over nitrosylsulphuric acid solutions. A. V. TICHONOV (J. Chem. Ind. Russ., 1933, 10, No. 8, 58—60).—The $\text{NO} + \text{NO}_2$ and H_2O pressures of solutions have been determined at 30—90°. R. T.

Direct determination of dissociation pressure of metal oxides. A. KAPUSTINSKI and L. SCHAMOVSKI (Z. anorg. Chem., 1933, 216, 10—16).—The dissociation pressure of NiO has been determined by measuring the electron emission of a superficially oxidised Ni wire at different temp. Between 1420° and 1610° abs. the course of the reaction can be expressed by $\log K_p = -23,250/T + 10,678$. The calc. heat of formation of NiO is +106.3 kg.-cal.

E. S. H.

Dissociation pressure of strontium carbonate. J. CHIPMAN (Trans. Faraday Soc., 1933, 29, 1266—1269).—Becker's data (cf. A., 1931, 41) are used to calculate the dissociation pressure of SrCO_3 between 650° and 1250°. The calc. heat of dissociation is 53,620 g.-cal. H. J. E.

Temperature-composition relations of the binary system magnesium nitrate-water. W. W. EWING, J. D. BRANDNER, C. B. SLICHTER, and W. K. GRIESINGER (J. Amer. Chem. Soc., 1933, 55, 4822—4824).—The data confirm the existence of the enne-, hexa-, and di-hydrates, and the anhyd. salt.

E. S. H.

Solubility relations of the ternary system magnesium nitrate-nitric acid-water at 25°. W. W. EWING and E. KLINGER (J. Amer. Chem. Soc., 1933, 55, 4825—4827).—The hexa- and di-hydrates and the anhyd. salt can exist as solid phases.

E. S. H.

Temperature-composition relations of the binary system zinc nitrate-water. W. W. EWING, J. J. MCGOVERN, and G. E. MATHEWS, jun. (J. Amer. Chem. Soc., 1933, 55, 4827—4830).—The data confirm the existence of hexa-, tetra-, di-, and mono-hydrates.

E. S. H.

Solubility relations of the ternary system zinc nitrate-nitric acid-water at 25°. W. W. EWING, A. J. RICARDS, W. J. TAYLOR, and D. W. WINKLER (J. Amer. Chem. Soc., 1933, 55, 4830—4832).—The hexa-, tetra-, di-, and mono-hydrates of $\text{Zn}(\text{NO}_3)_2$ can exist in stable equilibrium with HNO_3 at 25°. E. S. H.

Freezing of solutions. X. Mixtures containing [optically] active alkylsuccinic and α -chlorobutyric acids. J. TIMMERMANS and (Mlle.) J. VAN DER HAEGEN (Bull. Soc. chim. Belg., 1933, 42, 448—460; cf. A., 1932, 1205).—*n*-Hexylsuccinic acid (A) and *n*-propylsuccinic acid (B) have been resolved. *d*-A has m.p. 83.2°, $[\alpha]_D^{25} +14.3^\circ$; *d*-B has m.p. 93.9°, $[\alpha]_D^{25} +9.6^\circ$. The two *d*-acids give a continuous series of mixed crystals with min. f.p. *d*-B and *l*-A form an equimol. compound. With *d*- α -hydroxybutyric acid PCl_5 gives the *d*-Cl-acid, whereas PBr_5 gives the *l*-Br-acid. A study of the f.-p. curves of mixtures of the K salts of the respective acids shows that the configuration, as well as the rotation, of the OH-acid is changed by PBr_5 . F. L. U.

System lime-sugar-water. E. SAALMANN (Z. Ver. deut. Zuckerind., 1933, 83, 963—1041).—The conductivity of 0.00023—0.044*N* solutions of $\text{Ca}(\text{OH})_2$ in 0—60% sucrose solutions (I) has been determined. The conductivity of NaCl and BaCl_2 solutions falls linearly as sucrose concn. increases, but for $\text{Ca}(\text{OH})_2$ (and NaOH) the change is parabolic. The difference is due to formation of Ca-sucrose compound, and the

quantity of this in the solutions has been calc. from p_H measurements. The mobility of the saccharate ion lies between 10 and 30. The solubility of Ca(OH)_2 in (I) has been determined when: (a) the Ca(OH)_2 is formed by adding aq. CaCl_2 to (I) containing NaOH ; (b) Ca(OH)_2 is added to (I), and (c) CaO is added to (I). In case (a) colloidal Ca(OH)_2 is formed, and the ppt. consists only of Ca(OH)_2 particles on which sucrose is adsorbed; in (b) mol. dispersion alone occurs, and the Ca concn. in the solution is lower than in (a); in (c) the solubility is much greater, and passes through a max. Viscosity measurements with 10% and 20% (I) containing CaO indicate that colloidal particles are not present. Sucrose is not adsorbed from $\text{C}_5\text{H}_5\text{N}$ by CaO . The theoretical aspects are discussed in reference to van Aken's views. H. F. G.

Equilibrium in the reduction of cobaltous oxide by carbon monoxide. M. WATANABE (Sci. Rep. Tohoku, 1933, 22, 892—901).—The relation $\log(p_{\text{CO}_2}/p_{\text{CO}}) - 2759/T - 1.0643$ is found for the equilibrium $\text{CoO} + \text{CO} \rightleftharpoons \text{Co} + \text{CO}_2$ in the range 563—861° (cf. A., 1930, 861). Thermodynamic quantities are calc. for CoO and the equilibrium $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$ is considered. J. G. A. G.

Oxidation-reduction equilibrium of metallic manganese. S. AOYAMA and Y. OKA (Sci. Rep. Tohoku, 1933, 22, 824—834).—The relation $\log(p_{\text{H}_2}/p_{\text{H}_2\text{O}})(\text{mm.}) = 8504/T - 2.035$ for the equilibrium $\text{Mn} + \text{H}_2\text{O} \rightleftharpoons \text{MnO} + \text{H}_2$ is derived from dynamic experiments at 1048—1460°. The heat and free energy of formation of MnO are $-\Delta H_{298}$ 96,680 and ΔF_{298} -96,240 g.-cal., respectively. J. G. A. G.

Equilibrium in the reduction of silver sulphide by hydrogen. M. WATANABE (Sci. Rep. Tohoku, 1933, 22, 902—914).—The relation $\log(p_{\text{H}_2\text{S}}/p_{\text{H}_2}) = 125.44/T - 0.6449$ is obtained for the equilibrium $\text{Ag}_2\text{S}(\text{cubic}) + \text{H}_2 \rightleftharpoons 2\text{Ag} + \text{H}_2\text{S}$ in the range 453—704°. By calculation, the free energy and heat of formation of Ag_2S (rhombic) are ΔF_{298} -9766 and $-\Delta H_{298}$ 7725 g.-cal., respectively, and the standard electrode potential of S is 0.47 volt. J. G. A. G.

Calcium cyanamide. IV. Nitrogenation equilibria of alkaline earth carbonates with ammonia and of alkaline earth oxides with hydrocyanic acid. H. H. FRANCK and H. BANK (Z. anorg. Chem., 1933, 215, 415—426).—The equilibrium $\text{M}^{\text{II}}\text{CN}_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{M}^{\text{II}}\text{CO}_3 + 2\text{NH}_3$ (Ca , Sr , Ba), determined from the nitrogenation side, agrees with that previously found from hydrolysis (A., 1932, 469). Concordant results from both sides have also been obtained for $\text{M}^{\text{II}}\text{O} + 2\text{HCN} \rightleftharpoons \text{M}^{\text{II}}\text{CN}_2 + \text{CO} + \text{H}_2$. The conventional chemical const. of HCN calc. from the latter equilibria is 3.5 (cf. A., 1931, 807).

F. L. U.

Systems liquid iron-carbon oxides and liquid iron-hydrogen-water vapour. H. C. VACHER (Bur. Stand. J. Res., 1933, 11, 541—551).—The val. 0.0025 previously obtained for the product of C and O, in liquid Fe at 1580° in contact with a mixture of CO and CO_2 at 1 atm. has been confirmed. Equilibrium consts. at 1580° have been determined for the following equations: (I) $\text{FeO}(\text{in solution}) + \text{CO}(\text{gas}) \rightleftharpoons \text{Fe}(\text{liq.}) + \text{CO}_2(\text{gas})$; (II) $\text{Fe}_3\text{C}(\text{in solution}) + \text{CO}_2(\text{gas})$

$3\text{Fe}(\text{liq.}) + 2\text{CO}(\text{gas})$; (III) $\text{Fe}_3\text{C}(\text{in solution}) + 3\text{Fe}(\text{liq.}) + \text{C}(\text{in solution})$; (IV) $\text{FeO}(\text{in solution}) + \text{H}_2(\text{gas}) \rightleftharpoons \text{Fe}(\text{liq.}) + \text{H}_2\text{O}(\text{gas})$. They are, respectively, 27.0, 7.9×10^3 , 0.038, and 110. The vals. for (I), (II), and (IV) are reproducible and can be obtained by approaching the equilibrium from > one direction. The ratio of the consts. of (IV) and (I) is 4.07, in good agreement with the val. 3.95 for the equilibrium const. of the water-gas reaction. The C in liquid Fe appears to be due to slightly dissociated Fe_3C . M. S. B.

Double decomposition in the absence of a solvent. XVII. A. G. BERGMAN and N. S. DOMBROVSKAJA. XVIII. N. S. DOMBROVSKAJA (J. Gen. Chem. Russ., 1933, 3, 729—734, 735—741).—XVII. Theoretical.

XVIII. The fusion diagram for the system $\text{AgCl-NaBr-AgBr-NaCl}$ suggests the formation of solid solutions which contain all four components. R. T.

Phase-rule equilibria of acid soaps. IV. Three-component system potassium laurate-lauric acid-water. J. W. MCBAIN and M. C. FIELD (J. Amer. Chem. Soc., 1933, 55, 4776—4793; cf. A., 1933, 901).—Equilibrium diagrams are given for the range 100—370°. At 100° eleven types of 2- or 3-phase equilibria occur; two types have disappeared at 175°, and only three remain at 250°. E. S. H.

Thermodynamic equilibrium in the crystal state. D. BALAREV [with I. JOTZOV] (Kolloid-Z., 1934, 66, 51—57).—Dissolution and growth of large crystals at the expense of the smaller occur with PbI_2 at room temp. in aq. solution if the thickness of the crystals is about 300 μ . PbI_2 crystals have a mosaic substructure. Powdered crystals of sparingly sol. substances (BaSO_4 , SrSO_4 , PbF_2 , PbI_2 , CaF_2), suspended in H_2O , undergo mol. and submicronic dissolution or peptisation and growth. E. S. H.

Heats of formation of cadmium oxide, cadmium hydroxide, and zinc oxide. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1933, 167, 1—15).—The heats of formation of CdO and ZnO , found by combustion of the metals, are 62.36 ± 0.25 and 83.36 ± 0.21 kg.-cal., respectively, at const. pressure and 20°. The vals. deduced from the heats of dissolution of CdO and ZnO in aq. HCl are 61.04 and 83.54 kg.-cal. The heat of formation of Cd(OH)_2 is 133.41 kg.-cal., giving 4.0 kg.-cal. for the heat of hydration of CdO at 20°. Integral heats of dilution of HCl at 20° are recorded. A method for the complete combustion of metals in the bomb calorimeter is described. R. C.

Heats of formation of niobium and tantalum pentoxides. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1933, 167, 16—18).—The heats of formation of Nb_2O_5 and Ta_2O_5 , determined by combustion of the metals, are 463.1 ± 0.7 and 486.0 ± 0.5 kg.-cal., respectively, at 20° and const. pressure. Ta has d 16.64 at 19.6°. R. C.

Thermodynamic study of lithium sulphate. Y. UEDA (Sci. Rep. Tohoku, 1933, 22, 879—891).—E.m.f. data for Hg , 0.035% $\text{Li}|\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}(\text{sat.})|\text{PbSO}_4 + \text{LiSO}_4 \cdot \text{H}_2\text{O}|\text{Pb}$, Hg , and $\text{Pb}|\text{Hg}|\text{PbSO}_4 + \text{LiSO}_4 \cdot \text{H}_2\text{O}|\text{LiSO}_4 \cdot \text{H}_2\text{O} + \text{H}_2\text{SO}_4|\text{Hg}$ refer to 20—35°. V.-p. data and heats of dissolution and dilution

of $\text{LiSO}_4 \cdot \text{H}_2\text{O}$ and LiSO_4 at 25° are recorded. The heat of hydration is 3018 g.-cal. The free energy and heat of formation of LiSO_4 are ΔF_{298}° -313,614 and $-\Delta H_{298}^\circ$ 338,099 g.-cal., respectively. J. G. A. G.

Heats of dilution of aqueous solutions of zinc, cadmium, and copper sulphates and sulphuric acid at 25° . E. LANGE, J. MONHEIM, and A. L. ROBINSON (J. Amer. Chem. Soc., 1933, 55, 4733—4744).—Data for CdSO_4 , CuSO_4 , and ZnSO_4 (1.0—0.00005*M*) and H_2SO_4 (0.05—0.00005*M*) lead to the following integral heats of dilution: *M*- ZnSO_4 -1314, *M*- CdSO_4 -1973, *M*- CuSO_4 -1590, 0.1*M*- H_2SO_4 -2960 g.-cal. per mol. Relative partial mol. heat contents have been calc. for the concn. range indicated. E. S. H.

Heats of dissolution and dilution of potassium and ammonium phosphates. K. CHOMJAKOV, S. JAVOROVSKAJA, and P. SCHIROKICH (Z. physikal. Chem., 1933, 167, 35—41).—Integral and differential heats of dissolution and differential heats of dilution of KH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ over the complete concn. range are recorded. R. C.

Determination of heat of dehydration of kaolin at 450° . H. E. VON GRONOW and H. E. SCHWIETE (Z. anorg. Chem., 1933, 216, 109—112).—Earlier work is criticised. The val. obtained, 213 g.-cal. per g., is considerably higher than former vals.

E. S. H.

Kohlrausch's theory of moving boundaries. J. MUKHERJEE (Kolloid-Z., 1933, 65, 297—301).—Theoretical. E. S. H.

Conductivity of potassium and sodium hydroxide solutions at high temperatures. P. M. KOROTKOV and N. K. SOKOLOV (J. Gen. Chem. Russ., 1933, 3, 670—678).—The sp. conductivity κ of aq. NaOH is greatest at 50° and 55° in 20%, at 60 — 75° in 22.5%, and at 80° in 25% solutions; for aq. KOH κ is greatest at 50 — 55° in 30%, and at 60 — 80° in 32.5% solutions. R. T.

Activity coefficient and transference numbers of potassium iodide. R. W. GELBACH (J. Amer. Chem. Soc., 1933, 55, 4857—4860).—E.m.f. of cells of the types (a) $\text{KHg}|\text{KI}(m_1)|\text{AgI}|\text{Ag}-\text{Ag}|\text{AgI}|\text{KI}(m_2)|\text{KHg}$, (b) $\text{KHg}|\text{KI}(m_1)|\text{KI}(m_2)|\text{KHg}$, and (c) $\text{Ag}|\text{AgI}|\text{KI}(m_1)|\text{KI}(m_2)|\text{AgI}|\text{Ag}$ have been measured at $25 \pm 0.02^\circ$. The Debye-Hückel consts. and transference nos. have been determined for KI and the activity coeffs. calc. E. S. H.

Dichromic acid. E. CARRIERE and H. SENDRAS (J. Chim. phys., 1933, 30, 628—633).—The equiv. conductivities of K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ between 20° and 30° have been measured and the mobilities of 0.5CrO_4^{2-} and $0.5\text{Cr}_2\text{O}_7^{2-}$ at 20° calc. as 66.9 and 51.8, respectively. The % of H ions formed by dissociation of $\text{H}_2\text{Cr}_2\text{O}_7$ between *M*/60 and *M*/300 has been obtained from these vals. in conjunction with conductivity measurements of the mixtures (a) $2\text{K}_2\text{CrO}_4 + 4\text{HCl} = 4\text{KCl} + \text{H}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O}$, and (b) $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{HCl} = 2\text{KCl} + \text{H}_2\text{Cr}_2\text{O}_7$, at different dilutions. Results from (a) and (b) are in good agreement and indicate that $\text{H}_2\text{Cr}_2\text{O}_7$ is largely ionised. R. S.

Electrochemical and cryoscopic investigation of the ternary systems aluminium bromide-

lithium, copper, and silver bromides-benzene, toluene, or xylene. V. A. PLOTNIKOV, I. A. SCHEKA, and V. A. JANKELEVITSCH (J. Gen. Chem. Russ., 1933, 3, 481—499).—The conductivity of the systems $\text{AlBr}_3\text{-MBr}$ (*M*=Li, Ag, Cu)- C_6H_6 or PhMe increases rapidly with concn. of MBr to a max. val. which corresponds with $\text{MBr} \cdot 2\text{AlBr}_3$. The conductivity increases in the order Cu, Li, Ag. Cu and Ag are deposited on the cathode from the corresponding solutions, and Al from that containing LiBr; the cohesion of the deposits increases in the series $\text{C}_6\text{H}_6 < \text{PhMe} < \text{xylene}$. The decomp. potentials in C_6H_6 are CuBr 1.13, AgBr 1.35, and LiBr 1.60 volts; in PhMe the vals. are 1.40, 1.14, and 2.00 volts. The compounds $\text{MBr} \cdot 2\text{AlBr}_3$ are shown cryoscopically to be highly associated in C_6H_6 to an extent which increases with concn. R. T.

Calomel electrode. K. NOMURA (J. Biochem. Japan, 1933, 18, 301—309).—The potential of a 3.5*M*- $\text{KCl-Hg}_2\text{Cl}_2$ electrode attains a const. val. within 2 days, the vals. for the single electrode being approx. $0.28382t - 0.03988$ (13 — 25°) and $0.30249t - 0.05967$ (25 — 43°). F. O. H.

Antimony electrode. I. Stability of electrode potential and its effect on the relation between p_{H} and electromotive force. T. TOMIYAMA (J. Biochem. Japan, 1933, 18, 285—299).—The prep. of Sb electrodes and the variations of their potential with temp. etc. have been investigated. Before the attainment of equilibrium and when the potential change is 1 mv. per 30 min., the potential against a $\text{N-Hg}_2\text{Cl}_2$ electrode is given by $E = 0.022 + 0.0567p_{\text{H}}$ at 20° . F. O. H.

Mechanism of the oxygen electrode. T. P. HOAR (Proc. Roy. Soc., 1933, A, 142, 628—646).—The kinetics of the processes which occur at the so-called "O₂ electrode" are consistent with the hypothesis that the total electrode process can be represented by the reversible reaction $\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightleftharpoons 4\text{OH}'$, which takes place in stages on the surface of the oxide film with which the inert electrode is covered. Cathodic and anodic polarisation curves have been obtained for O₂ electrodes formed by Pt and Au in various O₂-saturated electrolytes, and the log c.d. bears a linear relation to the electrode potential except at very low c.d. Extrapolation of the anodic and cathodic curves gives a val. of $+1.20 \pm 0.03$ volts at 25° for the reversible O₂ potential referred to H₂ in the same solution, agreeing with the val. $+1.227$ volts calc. from thermal data by Lewis and others. L. L. B.

The cell $\text{Pt}|\text{quinhydrone}, \text{HCl}(0.01M)|\text{AgCl}|\text{Ag}$, and the normal electrode potential of the quinhydrone electrode from 0° to 40° . H. S. HARNED and D. D. WRIGHT (J. Amer. Chem. Soc., 1933, 55, 4849—4857).—The e.m.f. of the cell is reproducible to 0.1 mv. from 0° to 40° , although side reactions destroy the equilibrium after a short time above 30° . Vals. are also given for the cell $\text{Pt}|\text{quinhydrone}, \text{HCl}|\text{H}_2$ with an accuracy of ± 0.1 mv. from 0° to 25° and ± 0.15 mv. from 30° to 40° . E. S. H.

Diffusion potentials. I. V. CUPR and J. ŠPAČEK (Pub. Fac. Sci. Univ. Masaryk, 1933, No. 183, 3—25).—Apparatus for measuring diffusion potential, *E*, and conductivity, *c*, is described. The results ob-

tained with various pairs of solutions agree with Henderson's formula (A., 1907, ii, 426). Büchi's statement that the E between two electrolytes of equal c can be eliminated by interposing a third electrolyte (I) of any concn. (A., 1924, ii, 744) applies only when the concn. of (I) is relatively much $>$ that of the other two. For two solutions $E=0$ when the equiv. c are equal; for mixtures of electrolytes $E=0$ when the ratios of sp. c to ionic strength are equal. R. T.

Liquid junction potentials. I. J. B. CHLOUPEK, V. Z. DANES, and B. A. DANESOVA (Coll. Czech. Chem. Comm., 1933, 5, 469—478).—The e.m.f. of the cells $\text{Hg}|\text{HgCl}_2, 0.1N\text{-KCl}||\text{junction solution}||0.1N\text{-HCl}|\text{Hg}$ with "free diffusion" type of junction have been determined at 25° and 32°. The junction liquids are 0.001—8*N* solutions of twelve salts of several valency types, and in all cases the e.m.f. increases with decreasing concn. J. G. A. G.

Physico-chemical studies of complex formation involving weak acids. VII. Hydroferrocyanic acid, and precipitation of ferrocyanides of silver, lead, copper, zinc, cobalt, nickel, and manganese. H. T. S. BRITTON and E. N. DODD (J.C.S., 1933, 1543—1546).—Titration by the glass electrode method shows $\text{H}_4\text{Fe}(\text{CN})_6$ to be slightly weaker than H_2SO_4 . The pptn. of ferrocyanides from salt solutions has been investigated conductometrically by direct titration and by measurements of solutions in equilibrium with solid phases of known composition. $\text{K}_4\text{Fe}(\text{CN})_6$ ppts. $\text{Pb}_2\text{Fe}(\text{CN})_6$ from $\text{Pb}(\text{NO}_3)_2$, and double ferrocyanides from CuSO_4 , ZnSO_4 , CoSO_4 , NiSO_4 , and MnSO_4 . The first ppt. in AgNO_3 is $\text{Ag}_3\text{Fe}(\text{CN})_6$, which is at once converted into $\text{KAg}_3\text{Fe}(\text{CN})_6$. R. S.

Studies of complex salts by e.m.f. measurement. I. Silver. K. MASAKI (J. Electrochem. Assoc., Japan, 1933, 1, 25—28).—The e.m.f. at 25° of the cell $\text{Ag}|\text{AgNO}_3 (c), \text{alkali or NH}_3 (C)||\text{KCl} (c')|\text{AgCl}|\text{Ag}$ is given by the formula $[0.0591 \log Kc/(C - nc)^n]c'/S$, where K is the dissociation const., S the solubility product, and n the no. of radicals combined with Ag. The formation of $\text{Ag}(\text{CN})_3$, $\text{Ag}(\text{CNS})_4$, AgI_4 , $\text{Ag}(\text{S}_2\text{O}_3)_2$, and $\text{Ag}(\text{NH}_3)_2$ is confirmed. CH. ABS.

Effect of iron on the establishment of the oxidation-reduction potential of alloxantin. E. S. HILL and L. MICHAELIS (Science, 1933, 78, 485—486).—The p.d. for alloxantin (I) at a Pt or Au electrode becomes erratic when the saturated solution of (I) is somewhat diluted. On addition of FeSO_4 (0.1—1.0 mg. per 25 c.c. of solution) the p.d. becomes reproducible and is quickly established even in very dil. solutions of (I) (1 in 10^4). (I) can be reduced to dialuric acid in the electrode vessel by H_2 and colloidal Pt, and after replacement of H_2 by N_2 can be titrated with Br yielding alloxan, but the establishment of a p.d. is sluggish and erratic unless a small quantity of FeSO_4 is added. The titration curve is that of an ordinary dyestuff system with no indication of an intermediate step in the oxidation. The effect of Fe is most marked between p_H 4 and 6, and disappears at p_H 1. Fe cannot be replaced by Cu, Mn, Co, Ni, or org. dyes. An explanation of the effect is discussed. L. S. T.

Current density-potential curves. V. SIHVONEN and O. ENWALD (Suomen Kem., 1933, 6,

74B).—Simultaneous measurements of c.d. and p.d. at electrodes of Fe and Ni in aq. NaOH have led to a formula connecting these vals. E. S. H.

Catalytic hydrogen replacement and the nature of overvoltage. J. A. V. BUTLER (Nature, 1934, 133, 26).—A criticism (cf. this vol., 37). L. S. T.

Rate of decay of hydrogen and oxygen overvoltages. G. ARMSTRONG and J. A. V. BUTLER (Trans. Faraday Soc., 1933, 29, 1261—1266; cf. A., 1932, 700).—An expression is derived for the rate of decay of H and O overvoltages when these are not affected by the electromotive activity of any product of electrolysis. This agrees with the H overvoltage at Hg cathodes when the initial electrode potential is not more negative than -1.0 volt. For the O overvoltage at Pt electrodes agreement is obtained after a period of 100 sec. Deviations under other electrode conditions are discussed. H. J. E.

Decomposition voltages of fused salts. I. Method of determination and decomposition voltage of zinc chloride. Y. KONISHI (J. Soc. Chem. Ind. Japan, 1933, 36, 677B).—A graphite anode, cathode, and neutral electrode were used and the e.m.f. between each pair was measured. The decomp. potentials of fused ZnCl_2 at 408°, 459°, and 498° are 1.94, 1.89, and 1.83 volts, respectively, the vals. calc. from the heat of formation (97.21 kg.-cal.) and the sp. heat (0.1362) being 1.902, 1.880, and 1.843 volts, respectively. A. G.

Reaction rates of the hydrogen isotopes. M. POLANYI (Nature, 1934, 133, 26—27).—The assumption that diplogen (H_2^2) will invariably react more slowly than H_2 is not justified. L. S. T.

Determination of velocity of gas reactions of atomic hydrogen. E. CREMER, J. CURRY, and M. POLANYI (Z. physikal. Chem., 1933, B, 23, 445—468).—The method used consists in allowing an inert gas with which at. H is mixed to issue from a jet in a vessel containing the other reactant, X. The reaction velocity, k , is ascertained by determining in the stationary state the no. of H atoms in the reacting mixture, N , the concn. of X, and the no. of H atoms entering the reaction vessel per sec. N is found by observing the power of the H atoms to transform admixed para- H_2 into normal H_2 . It has not yet been possible to determine k , but only upper or lower limits for the energy of activation, E . CH_2Cl_2 , CHCl_3 , and CCl_4 react much more rapidly than MeCl . Multiple substitution apparently loosens the mol. structure so that both H and C react more readily and H reacts as readily as Cl attached to the same C atom. MeBr reacts more rapidly than MeCl . The reactions with EtI and HBr have also been studied. Comparison with the reactions of the above substances with Na vapour shows that the order of reaction velocity is the same in both reactions, and probably the vals. of E do not differ greatly. R. C.

Combustion of hydrocarbons. W. A. BONE (J.C.S., 1933, 1599—1617).—A lecture. H. S. P.

Combustion pressures. A. PIGNOT (J. Usines Gaz, 1932, 56, 594—599; Chem. Zentr., 1933, i, 1749).—The spontaneous combustion of hydrocarbon-

air mixtures under adiabatic compression has been studied. With increasing compression ratio (3—8) the max. pressure P increases (35—52 kg. per sq. cm.), the ratio P/p (p —pressure at end of compression) and retardation of inflammation diminish, whilst the duration of the reaction is const. (air: cyclohexane—12.04:1 by wt.). With fall in original temp. (100—63°) and const. compression ratio (8.28) the duration of retardation and of the total reaction increase. With increasing hydrocarbon content the max. pressure rises. On addition of 5% of an anti-knock to air- C_6H_{12} mixtures (ratio 17.5:1 by wt.) the duration of the reaction falls in the order (in 0.004 sec.) $PbEt_4$ 2.82, $C_6H_5Me \cdot NH_2$ 2.50, Et_2O 1.96, $MeOH$ 1.47, Et_2S 1.36, no anti-knock 1.06. A. A. E.

Influence of pressure on the spontaneous ignition of inflammable gas-air mixtures. II. Pentane-air mixtures. D. T. A. TOWNEND and M. R. MANDLEBAR (Proc. Roy. Soc., 1933, A, 143, 168—176; cf. A., 1933, 1016).—By increasing the pressure from 1 to 10 atm., the ignition temp. of C_5H_{12} -air mixtures are shown to fall into two groups, one above 490° for pressures < 3 atm., and one below 350° for higher pressures. Transference of an ignition point from the lower to the higher group occurs at a crit. pressure dependent on the composition of the mixture. The presence of $PbEt_4$ raises the ignition points from the lower to the higher group at pressures near the crit. transition pressure, but small amounts of $MeCHO$ at all pressures > 1 atm. produce a transference to the lower group. L. L. B.

Flame speeds during the "inflammation" of moist carbon monoxide-oxygen mixtures. W. A. BONE and J. BELL (Proc. Roy. Soc., 1933, A, 143, 1—15).—When successive $CO-O_2$ media within the range 55 CO :45 O_2 , and 80 CO :20 O_2 are ignited by a small flame at atm. pressure at the open end of a horizontal glass tube, the other end being closed, the max. initial uniform flame speed is reached at the 3 CO + O_2 composition with moist media, saturated at 15°. Partial drying of such media moves the max. flame speed point towards the 2 CO + O_2 composition, until with media containing 4.8 mm. H_2O it is at the composition 70 CO :30 O_2 , approx. Almost complete drying with $CaCl_2$ produces a nearly const. initial uniform flame speed of about 35 cm. per sec. throughout the whole composition range. The initial uniform flame speed observed when an explosive medium is ignited at the open end of a horizontal tube, the other end of which is closed, is shown to have no fundamental significance. L. L. B.

Slow combustion of ethylene. W. A. BONE, A. E. HAFNER, and H. F. RANCE (Proc. Roy. Soc., 1933, A, 143, 16—37).—The reaction between C_2H_4 and O_2 at 300° and atm. pressure is homogeneous and preceded by an induction period, during which a small amount of aldehyde (but no peroxide) appears. The addition of 1% of NO or $MeCHO$ practically eliminates the induction period and accelerates the subsequent reaction; CH_2O shortens the induction without affecting the reaction period, whilst C_2H_4O scarcely affects the former, but retards the latter. The presence of H_2O vapour has no influence on the

reaction. Of all $C_2H_4+O_2$ media, the most reactive is $2C_2H_4+O_2$, C_2H_4O being the initial oxidation product. All the evidence points to the normal course of oxidation being a series of hydroxylations. $CH_2 \cdot CH \cdot OH$ is first formed, any accumulation of this in the medium being transformed rapidly into an equilibrium mixture of the three C_2H_4O isomerides. L. L. B.

Kinetics and mechanism of decomposition of hydrocarbons. I. Thermal decomposition of hexane at atmospheric pressure. A. I. DINTZEZ and A. V. FROST (J. Gen. Chem. Russ., 1933, 3, 747—758).—The reaction commences at 520°, and consists of the primary reactions: C_6H_{14} (I) \longrightarrow C_6H_{12} (II)+ H_2 ; (I) \longrightarrow $C_5H_{10}+CH_4$; (I) \longrightarrow $C_4H_8+C_2H_6$; (I) \longrightarrow $C_3H_6+C_3H_8$, and the secondary reactions (II) \longrightarrow $C_5H_4+C_2H_6$; (II) \longrightarrow $2C_3H_6$; $C_5H_{10} \longrightarrow C_2H_4+C_3H_6$; $C_4H_8 \longrightarrow 2C_2H_4$. The heat of activation of the primary reactions for the interval 525—565° is 64.5—1.5 kg.-cal., and the velocity coeff. is given by $\log K=14.22-14,105/T \pm 0.031$. R. T.

Dynamics and mechanism of aliphatic substitutions. E. D. HUGHES and C. K. INGOLD (Nature, 1933, 132, 933—934).—Dynamical evidence relative to previous theoretical views (A., 1933, 701) is summarised. L. S. T.

Decomposition of formic acid by sulphuric acid. R. E. DE RIGHT (J. Amer. Chem. Soc., 1933, 55, 4761—4764).—Decomp. of HCO_2H by small quantities of H_2SO_4 is apparently unimol. and is inhibited by H_2O . Experiments have also been conducted in excess of H_2SO_4 containing various amounts of SO_3 , but the discussion of results is reserved. E. S. H.

Thermal decomposition of propyl mercaptan. H. A. TAYLOR and E. T. LAYNG (J. Chem. Physics, 1933, 1, 798—808).—The v.-p. curve of $PrSH$ between 12° and 68° is represented by $\log p = -1647/T - 7.7190$. The thermal decomp. of $PrSH$ was investigated between 405° and 435°/100—350 mm. by a static and a dynamic method. It is homogeneous on a poisoned glass surface. An induction period is found and the reactions before and after the point of inflexion are different, the respective energies of activation being 40,000 and 39,000 g.-cal. The induction period is due to the bimol. reaction $2PrSH \longrightarrow Pr_2S+H_2S$ without vol. change. Experiments with Pr_2S showed that $PrSH$ and H_2S remove the induction period. Intermediate additive compounds $SPr_3 \cdot SH$ (I) and $SHPr_2 \cdot SH$ (II) are postulated. Analogues of (I) have been synthesised; they have a very marked instability suggesting the immediate decomp. of (I) to $3C_3H_6+2H_2S$, whilst (II) gives $2C_3H_6+2H_2S$. Subsequently the reaction proceeds thus: $C_3H_6+H_2S \rightleftharpoons Pr^2SH$ (finally in pseudo-equilibrium) and polymerisation of C_3H_6 . W. R. A.

Rates of thermal decomposition of triphenylmethyl alkyl ethers. J. F. NORRIS and A. CRESSWELL (J. Amer. Chem. Soc., 1933, 55, 4946—4951; cf. A., 1930, 470).—The rates of decomp. of $CPh_3 \cdot OMe$ (I), $CPh_3 \cdot OEt$ (II), and $CPh_3 \cdot OPr^s$ (III) at 259—298° in sealed tubes have been studied. At 259° and

269°, the decomp. (up to about 11%) of (II) is unimol.; the rate is doubled for an increase of 10°. Similar results are found for (III) up to about 28% decomp. For (I), the calc. unimol. velocity coeffs. increase rapidly with time; CHPh_3 has a marked accelerating effect on the decomp. The rate of decomp. in air is much $>$ in N_2 . H. B.

Reaction kinetics in films. Hydrolysis of γ -stearolactone. R. J. FOSBINDER and E. K. RIDEAL (Proc. Roy. Soc., 1933, A, 143, 61—75).—Films of γ -hydroxystearic acid and γ -stearolactone (I) have been examined by the surface potential and surface pressure methods. The variation of the electric moment of the acid with compression and temp. indicates that the CH-OH group is probably removed from the surface when under compression. Complexes formed between (I) and substrate are indicated by the vals. obtained for the surface potential equilibrium spreading vals. Information relative to the kinetics of mechanism of the hydrolysis of (I) has been obtained by the method of phase boundary potentials. L. L. B.

Rate of oxidation of hydrogen peroxide by chlorine in presence of hydrochloric acid. B. MACKOWER and W. C. BRAY (J. Amer. Chem. Soc., 1933, 55, 4765—4776).—The rate of the rapid reaction $\text{H}_2\text{O}_2 + \text{Cl}_2 = \text{O}_2 + 2\text{H}^+ + 2\text{Cl}^-$ over the $[\text{HCl}]$ range 0.4—5.2 M agrees with $-d[\text{H}_2\text{O}_2]/dt = \chi_2 [\text{H}_2\text{O}_2] a_{\text{Cl}} a_{\text{H}_2\text{O}}$. When the activity of HCl is $> 2 M$, χ_2 is nearly const. at 5×10^3 at 25°. The step determining the rate involves the bimol. reaction $\text{H}_2\text{O}_2 + \text{HOCl} \xrightarrow{\kappa_2} \text{O}_3 + \text{H}_2\text{O} + \text{H}^+ + \text{Cl}^-$, where $-d[\text{H}_2\text{O}_2]/dt = \kappa_2 [\text{H}_2\text{O}_2][\text{HOCl}]$. This reaction is discussed from the electronic point of view. The bimol. reaction has the max. sp. rate 10^7 at 25°, when $[\text{HOCl}]$ is $\approx 10^{-7}$. At other temp. the coeff. is approx. represented by $10^{10 \pm 1.5} e^{(-4000 \pm 2000)/RT}$. At low $[\text{HCl}]$ and correspondingly high $[\text{HOCl}]$ the law is not obeyed and the coeff. is much smaller. E. S. H.

Conversion of ammonium cyanate into carbamide. Mechanism and kinetic salt effect. J. C. WARNER and F. B. STITT (J. Amer. Chem. Soc., 1933, 55, 4807—4812).—Determination of the rate at different concns. of NH_4CNO with and without addition of other salts support the view that the conversion depends on collisions between NH_4^+ and CNO^- , and not on collisions between undissociated mols. of NH_4CNO . A method for calculating the limiting velocity coeff. when activity coeffs. are known is devised. The coeff. thus obtained is in good agreement with that obtained by extrapolating the ordinary bimol. coeff. to zero ionic concn. E. S. H.

Kinetics of certain reactions of alkyl iodides in hydroxylic solvents. E. A. MOELWYN-HUGHES (J.C.S., 1933, 1516—1580).—The rate of reaction between EtI and $\text{S}_2\text{O}_3^{2-}$ in aq. solution is approx. that calc. for a bimol. reaction if it is assumed that one internal degree of freedom contributes to the energy of activation. A side reaction between EtI and H_2O also takes place. Comparison with analogous reactions indicates that the energy of activation is associated chiefly with the linking between the alkyl radical and the halogen atom. H. S. P.

Influence of poles and polar linkings on the course pursued by elimination reactions. XXI. Dynamics of elimination of the *tert.*-butyl group from sulphonium compounds. E. D. HUGHES and C. K. INGOLD (J.C.S., 1933, 1571—1576; cf. A., 1933, 701).— $\text{SMe}_2\text{Bu}^+\text{OH}$ in aq. solution may decompose to give an olefine or an alcohol. The first reaction is bimol. and the second unimol., depending only on the concn. of the cation. The speed of the second reaction is therefore independent of added OH^- and is identical with that of the analogous decomp. of salts. The effect of replacing H_2O by EtOH as solvent is studied. *Dimethyltert. butylsulphonium iodide*, decomp. 160°, *picrate*, decomp. 132°, and *hydroxide* (obtained in solution, decomp. below b.p.) were prepared. H. S. P.

Preparation and quaternary ammonium decomposition of formocholine. T. D. STEWART and H. P. KUNG (J. Amer. Chem. Soc., 1933, 55, 4813—4819).—The prep. of $\text{NMe}_3\text{Cl-CH}_2\text{-OH}$ (I) and $\text{NEt}_3\text{Cl-CH}_2\text{-OH}$ (II) is described. The rates of decomp. in dil. acid are in accordance with the equations $\text{R}_3\text{N}^+\text{-CH}_2\text{-OH} \rightarrow \text{R}_3\text{N}^+\text{-CH}_2\text{-O}^- + \text{H}^+ \rightarrow \text{R}_3\text{NH}^+ + \text{CH}_2\text{O}$. The first part is fast and the second slow. At const. p_{H} the reaction is of the first order and the rate is inversely proportional to $[\text{H}^+]$. The sp. reaction rates at 25° are given by $\log K = a + p_{\text{H}}$, where a is -4.017 for (I) and -3.213 for (II). E. S. H.

Rate of decomposition of creatine in acid and in alkaline solution. A. T. CAMERON and J. S. GUTHRIE (Canad. J. Res., 1933, 9, 360—372).—The rate of decomp. of creatine (I) in acid and alkaline solution at 37.5° and 50° has been studied. The rate of transformation shows a min. in approx. 0.1 N - HCl and a max. in 0.01 N - HCl , due probably to the catalysis of (I) and its hydrochloride at different rates. The results with alkali support the view that (I) is first transformed into $\text{CO}(\text{NH}_2)_2$ and sarcosine, which reunite to form NH_3 and methylvhydantoic acid. H. S. P.

Unimolecular film in heterogeneous reactions. E. E. AYNSLEY and P. L. ROBINSON (Nature, 1933, 132, 894—895).—The reaction between H_2 and S at 343° remains homogeneous down to pressures of H_2 of approx. 40 mm. At lower pressures the velocities are $>$ correspond with the homogeneous gaseous reaction (I). At 3 mm. pressure there occur the ordinary (I) and a new reaction (II) on the Pyrex surface (III). (II) has an initial velocity independent of $[\text{S}]$ over a wide range, but proportional to the H_2 pressure and to the area of (III). The velocity falls rapidly, however, and (II) ceases when an amount of H_2S sufficient to cover (III) with a unimol. layer has been formed. A unimol. layer of H_2S thus appears to prevent (III) from promoting further union either at low pressures or at pressures up to 760 mm. The contribution of H_2S from (II) is very small compared with that from (I) and is revealed only at low pressures. The results indicate that (i) (I) and (II) proceed independently, (ii) a unimol. film of S is present on (III), and (iii) the mols. in this film and in the liquid S surface are definitely oriented. L. S. T.

Speed of dissolution of potassium minerals. V. E. VILNYANSKI and E. M. MENSHIKOVA (Kali,

U.S.S.R., 1933, No. 1, 17—26).—Vals. of K in $dc/dt = K(S/v)(C-c)$, where S is the surface of the dissolving salt, v is the vol. of solvent, C is the concn. of the saturated solution, t is the time, and c is the concn. of the solution at the given instant, decrease for rock-salt as the concn. of $MgCl_2$ in brine increases; in a conc. solution of $MgCl_2$ K (carnallite) is $> K$ (rock-salt).

CH. ABS.

Crystallisation velocity and number of [crystallisation] centres of tin, bismuth, and lead. G. TAMMANN and H. J. ROCHA (Z. anorg. Chem., 1933, 216, 17—25).—The linear velocity of crystallisation increases with the degree of supercooling and is greater in a thermally conducting tube than in a non-conducting tube. In a tube of Al the max. crystallisation velocity is attained at 2° supercooling. The max. vals. obtained are: Sn 200, Bi, 2, Pb 5 cm. per min. Vals. were also determined for Sn-Cd and Sn-Pb alloys, although max. vals. were not reached. The no. of crystallisation nuclei formed in a given time depends also on the degree of supercooling, but is in order $Pb > Sn > Bi$.

E. S. H.

Inhibitors in the decomposition of hydrogen peroxide by catalase. H. N. ALYEA and J. PACE (J. Amer. Chem. Soc., 1933, 55, 4801—4806).—The decomp. of H_2O_2 by catalase from sheep's liver is inhibited by nineteen org. substances, of which twelve do not appear to deactivate the catalyst, although the remaining seven apparently do so. The relative efficiencies of the inhibitors differ from those for the same substances in the photolysis of H_2O_2 at 75° .

E. S. H.

Enolisation as directed by acid and basic catalysts. I. Acid-catalysed enolisation of menthone. P. D. BARTLETT and J. R. VINCENT (J. Amer. Chem. Soc., 1933, 55, 4992—4997).—The rates of catalytic "inversion" and iodination of *l*-menthone (I) in AcOH containing a little HNO_3 (catalyst) are determined at 30.9° . The results show that (I) gives $79 \pm 5\%$ of Δ^3 -menthen-3-ol.

H. B.

Physico-chemical investigation of the colloidal condition of cholesterol, cholesteryl ester, and lecithin. VIII. Catalytic properties of cholesterol. I. REMESOV and O. SEPALOVA (Biochem. Z., 1933, 266, 330—336).—The catalytic properties of colloidal cholesterol (I) are seen not only in reactions with diamines, but also in the usual reactions for phenolases (pyrogallol, phenol, and naphthol reactions). In N_2 the dehydrogenation reactions of (I) do not occur and atm. O_2 participates in the reaction. The addition of an acceptor to (I) enables its dehydrogenating action to occur in N_2 . Alcohols inhibit the catalytic action of (I). (I) catalyses also the decomp. of H_2O_2 .

P. W. C.

Sulphonation reaction.—See this vol., 178.

Para-hydrogen transformation on carbon surfaces at low temperatures. K. W. RUMMEL (Z. physikal. Chem., 1933, 167, 221—239).—The catalysis is not, in general, due to impurities in the C. Charging with gases which attack the surface atoms; e.g., O_2 at room temp. or above, reduces the catalytic power of the C, whereas molecularly adsorbed gases, e.g., N_2 , have no effect. O_2 at liquid air temp. seems to be

molecularly adsorbed. A large proportion of the C surface is catalytically active, but the activity varies from point to point. A small fraction consists of particularly active centres and is susceptible to poisoning; a part of this has an especially high adsorbent power for H_2 . The transformation follows the unimol. law and is probably brought about by the residual magnetism of surface C atoms. Between -167° and -210° the temp. coeff. of the para-ortho change is small and positive, and that of the ortho-para change negative. The period of half conversion in the ortho-para change is independent of the pressure between 7 and 760 mm., but falls with the pressure below 7 mm. The effect of activation of the adsorbent has been studied.

R. C.

Catalysed reaction of hydrogen with water and the nature of overvoltage. J. HORIUTI and M. POLANYI (Nature, 1933, 132, 931).—Previous observations (this vol., 37) indicate that the rate at which H is ionised depends on the composition of the aq. solution with which the Pt electrode is in contact. This cannot be explained if the inertia (I) of the process is attributed to the reaction of H with Pt, but is readily explicable if (I) is attributed to the transition of the H atoms into the solution. The rate of ionisation of H on Pt-black in different solutions is (H_2O unity) $N-HCl$ 0.7, $N-H_2SO_4$ 0.2, $0.25N-KOH$ 0.4, $EtOH + 2\% H_2O$ 0.4, $EtOH + 2\% H_2O + 0.25N-KOH$ < 0.02 .

L. S. T.

Catalytic oxidation of carbon monoxide. (MME.) L. S. MATHIEU-LEVY and M. GELOSO (Bull. Soc. chim., 1933, [iv], 53, 1039—1050).—The activity of MnO_2 catalysts (I) promoted with Cu, Fe, and Ni is deduced from the differentially determined rise of temp. of the mass during the passage of air-CO (1—7%) mixtures. For a given gas mixture, the activity of (I), previously exposed to air or mixtures containing lower % CO, rises to a max. and falls to a const. val., Δ , finally decreasing very slowly. In general, Δ increases and decreases with the corresponding changes of % CO, but only during the middle portion, M , of the life of (I) are the vals. of Δ reproducible and linearly proportional to % CO. With a new catalyst, the % CO_2 in the effluent gas is $<$ that produced, whilst with an old catalyst, the reverse obtains. During M , the % CO_2 is linearly proportional to the vals. of Δ . These results are related to adsorption phenomena.

J. G. A. G.

Oxidation of phosphorus with water at high pressures and temperatures. V. N. IPATIEV and FREITAG (Z. anorg. Chem., 1933, 215, 388—414).—The reaction $P_4 + 10H_2O \rightarrow P_4O_{10} + 10H_2$ has been studied at 175 — 420° and at 20 — 530 atm. The primary reaction products are PH_3 and H_3PO_3 , each of which then reacts with H_2O to give the end products. The primary reaction is rapid compared with either of the others. All the reactions are accelerated by increase of pressure and rise of temp. Excess of H_2O retards all three; excess of H_2 accelerates the secondary reactions, also the primary reaction if direct contact of H_2 with P is avoided. Free alkali, alkali salts, and free acids have no influence, but H_3PO_3 and H_3PO_4 exercise a retarding effect. Compounds of Co, Ni, Ag, Cu, and Fe have marked catalytic activity, $Ni(NO_3)_2$ in

particular enabling the reaction to reach completion rapidly at 200°. F. L. U.

Poisoning by arsenic of a tin-barium-vanadium catalyst.—See B., 1934, 59.

Poisoning of catalysts for ammonia synthesis.—See B., 1934, 15.

Hydrogenation of naphthalene.—See this vol., 178.

Conversion of acetylene and acetaldehyde into acetone.—See B., 1934, 52.

Catalytic reduction of phenol and *o*-cresol.—See B., 1934, 53.

Hydrogenation of carboxylic acids.—See B., 1934, 53.

Electrolytic production of $\text{H}^2\text{H}^2\text{O}$. H. S. TAYLOR, H. EYRING, and A. A. FROST (J. Chem. Physics, 1933, 1, 823—824).—The prep. is described in detail. N. M. B.

Electrolytic concentration of diplogen. R. P. BELL and J. H. WOLFENDEN (Nature, 1934, 133, 25—26).—A preliminary investigation of the effect of various factors on the efficiency of the concn. of H^2 by electrolysis in alkaline solution has been made. Neither temp. nor nature of the cathodic metal, nor, possibly, c.d. appears to have any effect on the efficiency of separation. L. S. T.

Electrolytic separation of hydrogen isotopes and the mechanism of the process. B. TOPLEY and H. EYRING (J. Amer. Chem. Soc., 1933, 55, 5058—5059).—The relative rates of separation of H^1 and H^2 in the electrolysis of H_2O containing 7% $\text{H}^2\text{H}^2\text{O}$ and 0.5*N*-KOH or H_2SO_4 have been determined, using a Pt anode and cathodes of Pb, Fe, Pt, Cu, Ni, or Ag. Evidence is adduced that the slow cathodic process is not the combination of atoms to mols. E. S. H.

Polarographic studies with the dropping mercury cathode. XXXVI. Catalysis of the electro-deposition of hydrogen due to the presence of the platinum metals. P. HERASYMENKO and I. ŠLENDYK (Coll. Czech. Chem. Comm., 1933, 5, 479—496; cf. A., 1933, 29).—The total catalytic current of H deposition at the dropping Hg cathode from 0.01*N*-HCl increases linearly with concn. of the catalysts, of which the order of increasing efficiency is Pd, Os, Pt, Ir, Rh, Ru. The limiting current increases rapidly with increasing $[\text{H}^+]$ < 0.05*N* and then rises slowly to a max. The current-voltage curves exhibit, in general, three stages which become more clearly defined at high $[\text{H}^+]$ and high concn. of catalyst and are attributed to three types of centres of different activity formed successively by aggregation of the catalyst atoms into polyat. complexes at the Hg surface. The catalytic effects of the several stages can be enhanced or suppressed by varying the rate of dropping of the Hg. The inactivity of Cu, Ag, and Au and the very low val. for Pd are attributed to the strong affinity of these atoms for Hg. J. G. A. G.

Kinetics of electrode processes. III. Behaviour of platinum and gold electrodes in sulphuric acid and alkaline solutions containing oxygen. G. ARMSTRONG, F. R. HIMSWORTH, and

J. A. V. BUTLER (Proc. Roy. Soc., 1933, A, 143, 89—103).—In the anodic polarisation of Pt electrodes a single layer of adsorbed O is formed. Cathodic polarisation effects the reduction of the adsorbed layer simultaneously with depolarisation by dissolved O_2 in the solution. In alkaline solutions Au behaves similarly to Pt, and after long-continued electrolysis the oxidation corresponds with a single layer of O at the surface. In dil. H_2SO_4 , however, a Au electrode on polarisation forms a definite oxide when the potential reaches +1.27 volts. The efficiency of oxide formation (100% in the earliest stages) steadily decreases as electrolysis proceeds and reaches a const. val. of about 0.9%. L. L. B.

Electrolysis of sodium sulphide. W. BOHN-HOLTZER and F. HEINRICH (Z. Elektrochem., 1933, 39, 939—947).—The anode phenomena in electrolysis of Na_2S solutions in a U-tube between Pt wire electrodes were studied from the c.d.—anode potential curves. With increasing applied e.m.f., the anode passes through the following states: (I) bright, with low c.d. and anode potential, when the only reaction is the formation of polysulphides; (II), dull owing to an insulating layer, possibly monoclinic S, resulting in the nearly complete suppression of the current; (III), the coating becomes porous, possibly rhombic S; anode potential rises, but is still small and almost independent of c.d., which may rise to considerable vals. Polysulphides are formed; (IV) anode bright again, low c.d., and formation of sulphate and some dithionate, but no S or polysulphides; (V) coated with S and gas bubbles. High c.d. and production of all possible products; (VI) anode nearly free from S, some O_2 evolution, and notable production of thiosulphate. Periodic electrolysis cannot be explained as due simply to an insulating film, but appears to consist of a cyclic recurrence of stages I, II, IV, and III. D. R. D.

Electrolysis of methyl alcohol solution of cupric chloride. E. GUILLERMET (Compt. rend., 1933, 197, 1608—1610).—When a MeOH solution of CuCl₂ (5 wt.-%) is electrolysed with Pt cathode and Pt or Cu anode, c.d. 1.3—5 amp. per sq. dm., the primary reaction is $\text{CuCl}_2 = \text{CuCl} + \text{Cl}$; some HCl is formed by the interaction of Cl and MeOH, which on electrolysis produces H_2 , thus accounting for formation of Cu at the cathode, the amount of which may vary from nil to 80% of the cathode deposit. The poor yield (sometimes only 8%) is due to direct recombination of CuCl and dissolved Cl_2 (cf. A., 1901, ii, 157). C. A. S.

Electrodeposition of rhodium. G. GRUBE and E. KESTING (Z. Elektrochem., 1933, 39, 948—958).—Rh may be deposited in highly reflecting form from solutions of Rh sulphate, silicofluoride, perchlorate, borofluoride, or oxalate, and the bath may be regenerated by the addition of freshly pptd. $\text{Rh}(\text{OH})_3$. The c.d.—potential curves and the effects of temp. and free acid were studied in the above solutions (except borofluoride) and in solutions of Na_3RhCl_6 and phosphate. Metal deposition is always accompanied by H_2 evolution even at low c.d. D. R. D.

Validity of Faraday's law for electrode processes in electrical discharges in dilute gases. V. SIHVONEN (Suomen Kem., 1933, 6, 71—74b).—A

discussion of the reactions occurring at a graphite anode under electrical discharge in O_2 at very low pressure. Faraday's law holds for short time periods. E. S. H.

Photochemical combination of hydrogen and chlorine in strong light. V. KOKOTSCHASCHVILI (Z. physikal. Chem., 1933, B, 23, 431—444).—By means of an apparatus incorporating a new type of glass-membrane manometer the reaction in the light from Mg flash powder of intensities almost sufficient to cause explosion has been studied. During the flash the velocity, v , first rises rapidly to a max., then falls at first rapidly, and then increasingly slowly. With increasing intensity of illumination the max. v first increases linearly, but after a short period of less rapid increase ultimately increases more rapidly than corresponds with linearity. This last phase is probably the result of chain branching, perhaps through the reaction $HCl^* + HCl^* + Cl_2 = 2HCl + Cl + Cl$. The duration of the chains in the present experiments is ≈ 0.01 sec. R. C.

Photographic properties of silver sulphide. II. Print-out effect: chemical aspect. K. HICKMAN and W. WEYERTS (J. Franklin Inst., 1933, 216, 683—706; cf. B., 1934, 123).— Ag_2S , in contact with certain reducing solutions containing free Ag ions, particularly solutions of (I) Ag_2SO_3 with excess of Na_2SO_3 , and (II) $AgNO_3$ with excess of $NaNO_2$, is sensitive to light and darkens on exposure. This darkening is caused by the deposition of Ag. The yield of Ag is not stoichiometrically related to the amount of Ag_2S or to the loss of S (which is very slight, and of a secondary nature). The spectral sensitivity extends from the violet to 1.4μ , with an apparent max. at 1.1μ . (I) shows a positive, but (II) shows an apparent negative, thermal coeff., probably due to dissolution of Ag by the HNO_3 simultaneously formed. In analogous manner, marked reciprocity failure is found, differing in direction and degree in the two solutions. These experiments have been made on Ag_2S suspensions; the addition of gelatin (III) greatly depresses the intensification process. Any reagent having affinity for Ag ions (e.g., NH_3 , $Na_2S_2O_3$, etc.) practically banishes the sensitivity. Changes in p_H (from 10 to 5) scarcely affect the pure suspensions, but profoundly modify the restraining effect of (III), which is almost removed at p_H 4.8 [the isoelectric point of (III)]. In more acid solutions the Na_2SO_3 decomposes and Ag_2SO_3 is deposited. The mechanism of the reactions in (II) is considered to be relatively simple; in (I) it is known to be complex. J. L.

Photographic summation law and its range of validity. A. VAN KREVELD (Physica, 1933, 1, 60—77).—If three photographic plates are respectively exposed for equal times to two different monochromatic lights and to a mixture of these, the intensities being such that equal photographic densities are produced in each plate, and if the energies associated with the three lights are, respectively, E_a , E_b , and E_m , then $aE_m/E_a + bE_m/E_b = 1$ (in which aE_m and bE_m are the respective contributions of E_a and E_b to E_m) is valid for a range of different emulsions, for different (equal) times of illumination, for any wave-length in the visible spectrum, for any ratio of the monochromatic components, for any selected density, and for different

developers provided single-grain layers are compared. The law is also extended to mixtures of any no. of monochromatic components, i.e., the effects produced by the components of a heterochromatic light are additive. A further corollary is that the Schwarzschild exponent is independent of the wave-length for all densities. F. L. U.

Photochemical action of complex light. M. PADOA and N. VITA (Z. wiss. Phot., 1933, 32, 185—195; cf. A., 1930, 1136; 1933, 791; Winther, *ibid.*, 238).—Winther's criticisms are refuted. From thermoelectric and photographic measurements the transparency of a saturated $NiSO_4$ solution 8.2 cm. thick (diam. of a spherical flask) for the green region in question is about 9.0%, as found before. Reproducible results for the titration of I with $Na_2S_2O_3$, in either neutral or acid solution, are easily obtained if the I solution is sufficiently diluted before titration. The authors' margin of error is much $<$ that of Winther. Several errors in Winther's experiments are pointed out; the passage of a continuous stream of O_2 through the reaction mixture will remove I from the solution. J. L.

Photographic effect of ultra-soft X-rays. M. RENNINGER (Z. Physik, 1933, 86, 382—386; cf. A., 1932, 1184; Prins, A., 1933, 548).—The width of the $K\alpha$ line of C (graphite) is directly proportional to the D_{max} obtained. This confirms the accuracy of the previous results (*loc. cit.*). In the ultra-soft region, a linear relation between exposure time and D_{max} of the line was obtained (on Schleussner "Doneo" film). J. L.

Nomography in photography. G. MAASS (Z. wiss. Phot., 1933, 32, 196—199).—The advantages of graphical representations over tabulated figures are described, with special examples. J. L.

Action of light on iodine in the atmosphere and in the organism. H. KOEPPE (Monatsh. Kinderheilk., 1933, 56, 149—155; Chem. Zentr., 1933, ii, 1645).—Irradiation of aq. I with sun- or Hg-light forms I' and eventually H' and IO_3' , the catalytic power for decomp. of H_2O_2 diminishing. The catalytic activity of KI solutions also diminishes on irradiation in air. Administration of KI increases the blood-catalase. A. A. E.

Catalytic oxidations. IV. **Photochemical oxidation of some ethylenic double linkings.** V. **Oxidation of ergosterol.** K. MEYER (J. Biol. Chem., 1933, 103, 597—606, 607—616).—IV. Chlorophyll (I) and eosin catalyse the photo-oxidation of olive oil, oleic acid, and undecenoic acid by O_2 . *iso*-Chlorophyllin is less active. The autoxidation of bixin and lycopene (II) is accelerated by light in presence of eosin; (I) is active with (II) only. Citronellal, linalool, pulegone, and terpineol all photo-oxidise in presence of (I).

V. Ergosterol (III) autoxidises in the dark, taking up 3 mols. O_2 (approx.); the reaction is slower with highly purified materials and is inhibited by HCN. The rate is markedly affected by solvents and p_H . (III) also photo-oxidises slowly, but in presence of eosin or (I) different reactions occur, the end-point depending on the dye; HCN does not inhibit in this case. D. R. D.

Formation of formaldehyde by the action of ultra-violet light on carbon dioxide and water : application of the Allison magneto-optic apparatus. J. H. YOE and R. E. WINGARD (J. Chem. Physics, 1933, 1, 886).—The formation of CH_2O with a uniform increase in concn. with the time of irradiation was detected. N. M. B.

Reaction between potassium oxalate and iodine and the relation between intensity [of light] and velocity. W. V. BHAGWAT (J. Indian Chem. Soc., 1933, 10, 649—654).—The temp. coeff. of the "dark" reaction is 6.86. Velocities of the photochemical reaction have been measured for different intensities and wave-lengths. F. L. U.

Primary photochemical processes. III. Absorption spectrum and photochemical decomposition of keten. R. G. W. NORRISH, H. G. CRONE, and O. SALTMARSH (J.C.S., 1933, 1533—1539).—Monomeric keten vapour is decomposed by light from a Hg lamp into 2 vols. of CO and 1 vol. of C_2H_2 . The absorption spectrum shows a series of bands between 3700 and 2600 Å. with a max. at 3100 Å. due to the CO group and a region of continuous absorption beginning at 2200 Å. due to the double linking. Energy is probably absorbed by the CO group and transferred to the CH_2 group, causing rupture of the mol. The stages of the decomp. are considered to be $\text{CH}_2\text{:CO} + h\nu = \text{CH}_2 + \text{CO}$, followed by $\text{CH}_2\text{:CO} + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{CO}$. H. S. P.

Chemical reactions brought about by X-rays and their determination. N. WATERMAN and H. LIMBURG (Biochem. Z., 1933, 266, 329).—A table omitted from the author's paper (A., 1933, 1020) is supplied. P. W. C.

Effect of ultra-violet rays on nicotine.—See this vol., 196.

Mitogenetic radiation of gas reactions. E. RUYSSSEN (Acta brev. néerl. Physiol., 1933, 3, 51—52; Chem. Zentr., 1933, ii, 1371—1372).—Emission of mitogenetic radiation has been observed in simple reactions (e.g., $\text{HCl} + \text{NaOH}$) in the liquid phase and in the flames of coal gas- and H_2 - O_2 .

Heavy hydrogen. (LORD) RUTHERFORD (Nature, 1933, 132, 955—956).—An address. A. A. E. L. S. T.

Separation and properties of the isotopes of hydrogen. H. C. ÜREY (Science, 1933, 78, 566—571).—A lecture. L. S. T.

Heavy hydrogen. A. FARKAS and L. FARKAS (Nature, 1933, 132, 894).—The formation of HH^2 from mixtures of H_2 and H^2 ($\leq 95\%$) in contact with a hot Ni wire has been studied. For the reaction $\text{H}_2 + \text{H}^2 \rightleftharpoons 2\text{HH}^2$ at temp. $>$ room temp. K is approx. $\frac{1}{3}$ and independent of temp. Calc. and experimental vals. for the equilibrium concns. of HH^2 in samples of H_2 of known H^2 content are compared. In the diffusion of H_2 through Pd, the gas diffusing at lower temp. has a higher H^2 ratio than the original, but at higher temp. the ratio becomes lower. The residual gas is conc. and the recovered gases contain the equilibrium mixture of the three mols. Some separation of the two isotopes occurs when

they diffuse through a small nozzle at low pressures, e.g., when pumped through a valve. Above 600° , the formation of the equilibrium mixture from H_2 and H^2 proceeds in the homogeneous gas phase: $\text{H} + \text{H}^2 \rightleftharpoons \text{HH}^2 + \text{H}^2$, $\text{H}^2 + \text{H}_2 \rightleftharpoons \text{HH}^2 + \text{H}$, and possibly $\text{H}_2 + \text{H}^2 \rightarrow 2\text{HH}^2$. The energy of activation of this reaction must be > 60 kg.-cal. The formation of HH^2 does not occur at -195° on charcoal. L. S. T.

Separation of hydrogen isotopes by diffusion through palladium. L. HARRIS, W. JOST, and R. W. B. PEARSE (Proc. Nat. Acad. Sci., 1933, 19, 991—994).—A hundredfold decrease in pressure by diffusion is accompanied by a tenfold increase in concn. of H^2 . The rate of pressure decrease is in agreement with the theory of diffusion by atoms. R. S.

Preparation of the pure heavy hydrogen isotope by diffusion. G. HERTZ (Naturwiss., 1933, 21, 884—885).—It is possible to separate Ne^{22} from Ne^{20} by diffusion so completely that the latter can no longer be detected spectroscopically. The same method can be used to separate the H isotopes. H_2O from an electrolysis apparatus was reduced by Mg. The H_2 thus obtained consisted of a mixture of H^1 and H^1H^2 with only a small proportion of H^2 . By passing the electric discharge through the mixture H^1H^2 was broken up into H^1 and H^2 , which, after diffusion, gave H^2 spectroscopically pure. Photographs of the line spectra of H_2 mixtures of various compositions are given. A. J. M.

Isotopic fractionation of water. E. W. WASHBURN, E. R. SMITH, and M. FRANDSEN (Bur. Stand. J. Res., 1933, 11, 453—462).—The variation in d previously observed (this vol., 40) in the residual H_2O on electrolysis has been plotted against change in vol. 0.01N- H_2SO_4 was used. When d 1.001376 was reached for the residual H_2O its physical properties were determined. The temp. of max. d is approx. the same for heavy and for normal H_2O . F.p. for heavy H_2O is 0.053° , b.p. $100.02 \pm 0.002^\circ$, and n for λ 5876 Å. is $<$ for normal H_2O by $(59+1) \times 10^6$. By continuing the electrolysis using $\text{Ba}(\text{OH})_2$, H_2O of d 1.0153 was ultimately obtained. The O_2 and H_2 evolved during this stage were dried and separately combined with normal H_2 and O_2 , respectively. The resulting samples of H_2O contained in one case an increased concn. of O^{18} and perhaps O^{17} and in the other an increased concn. of H^- . H_2 collected at the end had at. wt. 1.012. The method of d determination is described and the relationship between d and isotopic composition calc. The min. val. of the at. fraction of H^2 in normal H_2O is probably 3×10^{-9} . H_2O can be fractionated isotopically by distillation (cf. *ibid.*, 41) and by adsorption on charcoal. M. S. B.

Deuteroammonias. H. S. TAYLOR and J. C. JUNGERS (J. Amer. Chem. Soc., 1933, 55, 5057—5058).— NH_3 (68, 90, and 99%) has been prepared by reaction of H_2O with Mg_3N_2 . The physical properties show a progressive change with increasing concn. of H^2 . The 99% product has m.p. 199° abs., b.p. 242.3° abs.; r.p. have been determined between 202.3° abs. and 238.6° abs. The calc. latent heat

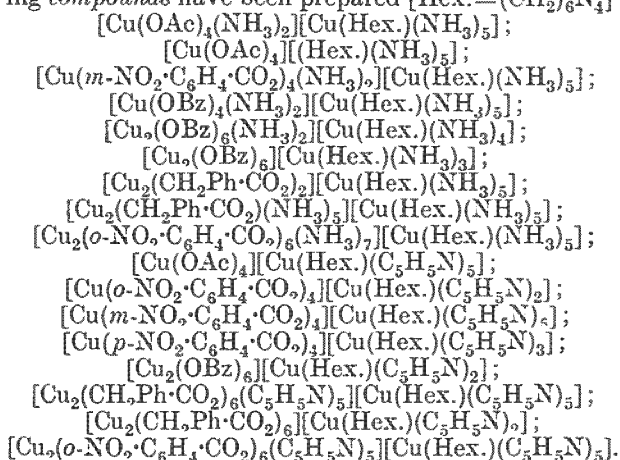
of vaporisation is 5990 g.-cal. per mol. The ultra-violet absorption spectrum has been investigated.

E. S. H.

Additive reactions with H and O atoms at low temperatures. K. H. GEIB and P. HARTECK (Ber., 1933, 66, [B], 1815—1825; cf. A., 1933, 1257).—Additive reactions appear to occur with difficulty when a stable compound can arise from another stable compound by increase in valency of an atom. Addition takes place readily at low temp. in the case of compounds in which a subsidiary valency is chemically active; the union is so feeble that the compounds are not known at room temp. Thus H and HCN at -190° give a product which effervesces at -60° and ultimately affords NH_2Me , HCN, NH_3 , and a yellow oil. C_2N_2 gives products similar to those derived from HCN and, mainly, a substance resembling hydrazalamine. SO_2 yields (?) H_2SO_2 and finally H_2S , SO_2 , S, and H_2O . NH_3 , N_2O , and NH_2Me do not react. C_6H_6 appears to be hydrogenated immediately. C_3H_4 is reduced to C_2H_6 . The intermediate production of C_2H_4 from C_2H_2 is slight. The additive product from C_3H_4 and O decomposes at about -110° , giving finally $(\text{CH}_3)_2\text{O}$, $\text{C}_2\text{H}_2\text{O}$, MeCHO , CO_2 , and liquid materials. The product from C_2H_2 yields CO , $(\text{CHO})_2$, HCO_2H , CO_2 , and H_2O . CO yields about 1.3% of CO_2 , SO_2 slowly produces SO_3 , whilst it remains uncertain whether the production of NO_2 from NO is due to at. O. HCN, N_2O , and H do not appear to yield additive compounds. HCl gives mainly Cl_2 and H_2O with a small proportion of ClO_2 . NH_3 , NH_2Me , and NMe_3 readily add at. O. At -80° , C_6H_6 gives a colourless, glassy material which decomposes into CO_2 , CO , HCO_2H , and H_2O ; quinones appear to be formed. Interaction between Xe and at. O was not observed. H. W.

Formation of amines in aqueous solution.

XI. R. RİPAN (Bul. Soc. Stiinte Cluj, 1932, 7, 60—78; Chem. Zentr., 1933, ii, 1003—1004).—The following compounds have been prepared [$\text{Hex.}=(\text{CH}_2)_6\text{N}_4$]:



A. A. E.

Magnesium sulphite. H. HAGISAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, 12, 63).—The salt forms a hexa- and a tri-hydrate with a transition point at 40° .

A. R. P.

Solid reaction between calcium oxide and silicic acid. K. HILD and G. TROMEL (Z. anorg.

Chem., 1933, 215, 333—344).—The reaction has been studied at 1000° , using equimol. quantities. The time required for completion varies from 5 min. to 400 hr., and is determined by the nature of the reactants and the intimacy of mixing. For reaction times > 20 min. the initial product is $\beta\text{-Ca}_2\text{SiO}_4$, which then reacts with SiO_2 to give $\beta\text{-CaSiO}_3$ (wollastonite). In the most rapid reaction (5 min.) the main product is $\alpha\text{-CaSiO}_3$. In experiments in which quartz was used, the latter was frequently converted into cristobalite in presence of CaCO_3 , but never in presence of CaO . F. L. U.

Calcium oxide-phosphoric acid compounds.

II. M. A. BREDIG, H. H. FRANCK, and H. FULDNER (Z. Elektrochem., 1933, 39, 959—969; cf. A., 1932, 469).—Mixed apatites have been prepared containing the following bivalent groups in place of F: aluminate, ferrite, and cyanamide. Carbonate-mixed-apatite has been characterised by its X-radiogram, and most naturally occurring Ca phosphates consist of it. The materials of bones and teeth are hydroxyoxyapatites. The transformation of the two forms of $\text{Ca}_3\text{P}_2\text{O}_8$ is very sensitive to CaO and H_2O , and this is explained on the basis of the stability of hydroxyoxyapatites.

D. R. D.

Amphoteric behaviour of metal hydroxides.

II. Zincates. R. SCHOLDER and H. WEBER (Z. anorg. Chem., 1933, 215, 355—368; cf. A., 1933, 474).—Conditions of formation and the composition of Na zincates are described. The salt $\text{Na}_2[\text{Zn}(\text{OH})_4]$, the dihydrate of which is known, has been prepared. It forms mixed crystals with $\text{NaOH}\cdot\text{H}_2\text{O}$. Mixed crystals are also formed from $\text{Na}[\text{Zn}(\text{OH})_3]\cdot 3\text{H}_2\text{O}$ and $\text{H}[\text{Zn}(\text{OH})_3]\cdot 3\text{H}_2\text{O}$. Both Na_1 and Na_2 zincates are decomposed by EtOH at room temp., NaOH being abstracted. The following salts are described: $\text{Ba}[\text{Zn}(\text{OH})_4]$, with 1 and 5 H_2O ; $\text{Sr}[\text{Zn}(\text{OH})_4]\cdot\text{H}_2\text{O}$; $\text{Ba}_2[\text{Zn}(\text{OH})_6]$; $\text{Sr}_2[\text{Zn}(\text{OH})_6]$. Constitutional formulæ based on results of experiments on dehydration are proposed. F. L. U.

Chemistry of finely-divided matter. E. BERL and B. SCHMITT (Kolloid-Z., 1934, 66, 87—91).—The superior reactivity of finely-divided substances is illustrated by many examples, which include the flotation of powdered Zn blende by NaCN solutions.

E. S. H.

Halides of the rare earths. VIII. Action of hydrogen on the chlorides of the rare earths.

G. JANTSCH, N. SKALLA, and H. GRUBITSCH (Z. anorg. Chem., 1933, 216, 75—79; cf. A., 1933, 579).— H_2 reduces the trichlorides of the following metals to the free metal at the temp. given: Y 880° , La 880° , Nd 840° , Gd 820° , Tu 650° , Lu 750° ; trichlorides of the following are reduced to dichlorides: Sm 400° , Eu 270° , Yb 560° . In the first series the dichlorides are unstable.

E. S. H.

Existence of lower valencies in the halides of the rare earths. G. JANTSCH and W. KLEMM (Z. anorg. Chem., 1933, 216, 80—84).—Theoretical (cf. preceding abstract).

E. S. H.

Quantitative study of the lanthanum-neodymium separation. P. W. SELWOOD (J. Amer. Chem. Soc., 1933, 55, 4900—4901).—Analysis of the efficiency

of various methods of separation shows that Prandtl's basic NH_3 separation gives the highest efficiency and is followed by the NH_4 double nitrate procedure.

E. S. H.

Mechanism of formation of silane. III. R. SCHWARZ and P. ROYEN (Z. anorg. Chem., 1933, 215, 288—294).—The mechanism previously suggested (A., 1925, ii, 418) is supported by recent observations on unsaturated Ge hydrides (see following abstract).

F. L. U.

Germanium. XIV. Properties of polygermane (GeH_n)_x. P. ROYEN and R. SCHWARZ (Z. anorg. Chem., 1933, 215, 295—309; cf. A., 1933, 579).—By the action of aq. NaOH stepwise replacement of H by OH occurs, the colour of the product changing from yellow to brownish-red with increasing O content. Halogen acids convert the hydroxylated products reversibly into halogen derivatives. HX and NaOH give rise finally to GeX_2 and Na_2GeO_2 , respectively, and the H formed during the change hydrogenates the still intact ' $\text{GeH}_2 \cdots \text{GeH}_2$ ' residues to give a mixture of saturated hydrides, GeH_4 predominating. Pyrolysis of $(\text{GeH}_2)_x$ at 120—220° gives a mixture of GeH_4 , Ge_2H_6 , Ge_3H_8 , and H_2 , with a residue of Ge. The chemical behaviour of $(\text{GeH}_2)_x$ indicates an open-chain structure of high mol. wt., analogous to that of the polyoxymethylenes.

F. L. U.

Preparation and constitution of the thio-stannates. I. Sodium ortho- and meta-thio-stannate. E. E. JELLEY (J.C.S., 1933, 1580—1582).—Monoclinic crystals of $\text{Na}_4\text{SnS}_4 \cdot 18\text{H}_2\text{O}$ have been prepared from aq. $\text{Na}_2\text{Sn}(\text{OH})_6$ and Na_2S . After heating at 200° or drying over P_2O_5 , only $2\text{H}_2\text{O}$ remains, and is considered to form part of a complex anion in which Sn is 6-covalent. When SnS_2 is dissolved in aq. Na_4SnS_4 , tetragonal crystals of $\text{Na}_2\text{SnS}_3 \cdot 3\text{H}_2\text{O}$ are deposited from the hot solution and prismatic crystals of $\text{Na}_2\text{SnS}_3 \cdot 8\text{H}_2\text{O}$ at room temp. Constitutions for these hydrates in which Sn is 6-covalent are advanced.

H. S. P.

Interaction of phosphorus bromide and chloride. III. A. RENC (Rocz. Chem., 1933, 13, 569—577; cf. A., 1932, 1258).—Br and PCl_3 yield yellow crystals of a limiting composition PCl_2Br , whilst Cl_2 and PBr_3 yield a liquid, PClBr , and yellow crystals, PClBr_2 . PCl_2Br is converted at 135° into a cryst. phase, $\text{PCl}_{1.5}\text{Br}_{0.5}$, a deep red liquid, $\text{PCl}_{3.4}\text{Br}_{0.6}$, and a light red liquid, $\text{PCl}_{2.87}\text{Br}_{0.27}$.

R. T.

Ammonia and phosphorus pentachloride. H. MOUREU and P. ROCQUET (Compt. rend., 1933, 197, 1643—1645).—If NH_3 is passed over PCl_5 at -50° and NH_4Cl is removed by washing with liquid NH_3 , PN_3H_4 , probably $\text{P}(\text{NH})_2\text{NH}_2$, is obtained as an intensely hygroscopic white amorphous powder. It begins to evolve NH_3 at 50°, but must be heated for 100 hr. at 350—400° to complete the transformation $\text{P}(\text{NH})_2\text{NH}_2 = \text{PN}_3\text{H} + \text{NH}_3$. At 480° PN_3H begins to evolve NH_3 , $3\text{PN}_3\text{H} = \text{P}_3\text{N}_5 + \text{NH}_3$, but the evolution is completed only at 700°, when dissociation to P and N_2 begins (cf. A., 1907, ii, 541).

C. A. S.

Action of vanadium tetrachloride on anhydrous chlorides. A. MORETTE (Compt. rend., 1933, 197, 1641—1643).— VCl_4 and Cl_2 were passed over various

chlorides at 300—600°; NaCl , LiCl , AgCl , CaCl_2 , SrCl_2 , BaCl_2 , MgCl_2 , ZnCl_2 , MnCl_2 , PbCl_2 , and CrCl_3 were unacted on. KCl , RbCl , and CsCl absorb varying quantities of V and Cl, the max. (at 400—500°) being represented by KCl , $0.315\text{VCl}_{3.14}$, RbCl , $0.330\text{VCl}_{3.10}$ and CsCl , $0.613\text{VCl}_{3.13}$. These alkali chlorides appear to catalyse the reaction $\text{VCl}_4 = \text{VCl}_3 + \text{Cl}$ (cf. A., 1911, ii, 291).

C. A. S.

Existence of pyro- and meta-arsenic acids. V. AUGER (Compt. rend., 1933, 197, 1639—1640).—Repetition of the author's previous work (cf. A., 1908, ii, 489) has confirmed that the only hydrate of As_2O_5 is $\text{H}_5\text{As}_2\text{O}_{10}$, which when heated passes into As_2O_5 without forming any intermediate hydrate (cf. A., 1930, 558).

C. A. S.

Action of solutions of potassium hydroxide on bismuth iodide. F. FRANÇOIS and (Mlle.) M. L. DELWAULLE (Bull. Soc. chim., 1933, [iv], 53, 1104—1106).—The proportion of Bi_2O_3 produced relative to BiOI increases with increased concn. of KOH , but pure BiOI is obtained with excess of BiI_3 . BiI_3 is found in the residual solution of KI only if the liquid is no longer basic.

J. G. A. G.

Properties of the chlorides of sulphur. A. H. SPONG (J.C.S., 1933, 1547—1551).—An iodometric method of determining the total Cl in S chloride mixtures dissolved in CCl_4 has been found to give approx. accurate results. Free Cl_2 in the mixture may be removed by $\beta\text{-C}_{10}\text{H}_{17}\text{OEt}$ and so measured by difference. The composition of the mixture is determined mainly by the equilibrium $2\text{SCL}_2 = \text{S}_2\text{Cl}_2 + \text{Cl}_2$, but also probably by $3\text{S}_2\text{Cl}_2 = \text{S}_3\text{Cl}_4 + \text{S}_3\text{Cl}_4$.

H. S. P.

Intermediate states of reduction of chromic acid. T. R. BALL and K. D. CRANE (J. Amer. Chem. Soc., 1933, 55, 4860—4864).—Investigation by the magneto-optical method has shown that when H_2CrO_4 is partly reduced by FeSO_4 , Hg_2SO_4 , SnCl_2 , or $\text{H}_2\text{C}_2\text{O}_4$, Cr^{IV} is produced as an intermediate product. No evidence of Cr^{IV} has been found. When SnCl_2 is partly oxidised by H_2CrO_4 , evidence has been obtained for the existence of Sn^{III} .

E. S. H.

Influence of temperature on chemical inertia. Action of chlorine on metals. M. LEMARCHANDS and M. JACOB (Bull. Soc. chim., 1933, [iv], 53, 1139—1144; cf. A., 1931, 1016).—The reactions of gases with solids are discussed with reference to surface films and the v.p. of the solids. Min. temp. of interaction of Cl_2 with twelve metals and three non-metals calc. from the b.p. of the elements and their chlorides are, in general, consistent with the data.

J. G. A. G.

Salts of perrhenic acid. E. WILKE-DORFURT and T. GUNZERT (Z. anorg. Chem., 1933, 215, 369—387; cf. A., 1927, 128, 238; 1930, 308).—*Perrhenates* of Ca, Sr, Zn, Cd, $\text{Ag}(\text{NH}_3)_2$, $\text{Zn}(\text{NH}_3)_2$, $\text{Cd}(\text{NH}_3)_4$, $\text{Co}^{\text{II}}(\text{NH}_3)_4$, $\text{Co}^{\text{III}}(\text{NH}_3)_6$, $\text{Cr}(\text{NH}_3)_6$, $\text{Cr}([\text{CO}(\text{NH}_3)_2]_3)$, $\text{Ag}(\text{C}_5\text{H}_5\text{N})_4$, and $\text{Cu}(\text{C}_5\text{H}_5\text{N})_4$, also $(\text{NO})\text{ReO}_4$, are described. Comparison of perrhenates with corresponding salts of HMnO_4 , HClO_4 , and HBF_4 reveals striking differences in solubility, crystal form, and content of H_2O of crystallisation.

F. L. U.

Cementite. P. PINGAULT (Ann. Chim., 1933, [x], 20, 371—438).—Cementite (I) (6.65—6.70% C), con-

taining 0.05% of free C, has been prepared by heating Fe with NaCN at 600–650°; it may also be prepared by electrolysis of fused NaCN with Fe electrodes or by passing coal gas or CH₄ over Fe at 850–975° (in which case much free C is deposited on the surface of the metal). (I) has d^0 7.30, is not attacked by H₂ at 425°, and begins to decompose at about 1000°. The equilibria in the system Fe–(I)–O₂ at 830–1000° have been studied. When Cr is heated at 650° with NaCN an impervious surface film of carbide is formed which prevents further reaction. Mn treated with CH₄ at 950–975° yielded a product containing total C 7.5%, free C 3.55%, but a pure compound could not be obtained. H. F. G.

Internal complex salts of bivalent iron. B. EMMERT and H. G. SOTTSCHEIDER (Ber., 1933, 66, [B], 1871–1874; cf. A., 1931, 825).—The following complex salts are obtained from CH₃Bz₂ and FeSO₄ and the requisite bases, usually in absence of air: C₃₀H₂₂O₄Fe, 2C₅H₅N (I), C₃₀H₂₂O₄Fe, 2C₅H₁₁N (piperidine); C₃₀H₂₂O₄Fe, 2C₁₀H₁₄N₂ (nicotine); C₃₀H₂₂O₄Fe, 2NH₃ which yields C₃₀H₂₂O₄Fe when heated at 120°/0.5 mm. (oxidised to C₄₅H₃₃O₆Fe); C₃₀H₂₂O₄Fe, C₂H₄(NH₂)₂. The dry salts do not absorb NO. In C₆H₆ or PhMe, NO is absorbed by Fe^{II} acetylacetonate with or without presence of C₅H₅N, by Fe^{II} benzoylacetone (+2C₅H₅N) or by (I). CH₃Ac₂, FeSO₄, and *o*-C₆H₄(NH₂)₂ in MeOH–H₂O yield *o*-C₆H₄ $\left\langle \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{CMe} \\ \text{N} \cdot \text{C} \cdot \text{CMe} \end{smallmatrix} \right\rangle \text{CH}_2$, FeSO₄, 1.5H₂O, whence dimethylbenzoheptadiazine, m.p. 132°. H. W.

Salts of iron carbonyl hydride. F. FEIGL and P. KRUMHOLZ (Z. anorg. Chem., 1933, 215, 242–248; cf. A., 1932, 485).—By the action of certain metal ammine salts on Fe(CO)₅ in aq. NH₃ cryst. compounds which are regarded as salts of Fe(CO)₄H₂ are formed. The following compounds are described: Fe(CO)₄Cd(NH₃)₆, Fe(CO)₄Cd(C₅H₅N)₆, [Fe(CO)₄H]₂Ni(NH₃)₆, [Fe(CO)₄H]₂Fe(α'-phen)₃ (phen=phenanthroline), Fe(CO)₄Cd. Dil. mineral acids in all cases liberate Fe(CO)₄H₂. F. L. U.

Formation of amines in aqueous solution. X. Double thiocyanates. R. RİPAN and L. DIMA (Bul. Soc. Stiinte Cluj, 1932, 7, 25–36; Chem. Zentr., 1933, ii, 1003).—The following compounds are described: [M(SCN)₄(C₅H₅N)₂][Fe(Hex.)₂(C₅H₅N)₄], *x*H₂O, where M and *x* are Ni (10, 4) and Co (10, 6); Hex.=(CH₃)₆H₄. M(SCN)₃Fe(SCN)₂2Hex., 8H₂O (M=Ni, Co). [Mn(SCN)₆][Fe(Hex.)₃(H₂O)₃], 6H₂O; [Mn(SCN)₆][Fe(Hex.)₃(C₅H₅N)₅], 12 or 6H₂O. A. A. E.

Decomposition of thiosulphatopentacyanocobaltic acid and isomerism of thiosulphuric acid. P. R. RAY (J. Indian Chem. Soc., 1933, 10, 631–635).—A quant. study of the hydrolysis of the “normal” and “iso” complex acids supports the view put forward previously (A., 1931, 1140) regarding their constitution. The results further indicate that H₂S₂O₃ is capable of existing in two forms, one of which decomposes into H₂S and H₂SO₄. F. L. U.

Dithiosulphato-diethylenediamine cobaltates. P. R. RAY and S. N. MAULIK (J. Indian Chem. Soc., 1933, 10, 655–658; cf. A., 1931, 1140).—The salts

M[Co(S₂O₃)₂en₂] (M=Na, K, Tl) have been prepared in the *cis* and *trans* forms. The former are red, the latter green and more stable. F. L. U.

Thiosulphato-tetramminocobaltic series. II. Constitution of Duff's salt. B. C. RAY and P. B. SARKAR (J. Indian Chem. Soc., 1933, 10, 625–630; cf. A., 1931, 184).—A new structural formula for Duff's salt is proposed. The following compounds are described: thiosulphatoaquo-diethylenediaminocobaltic iodide, nitrate, thiocyanate, and sulphate; [Co(S₂O₃)₂en₂]Na (*cis* and *trans*). F. L. U.

Basic nickel sulphate. G. GIRE (Compt. rend., 1933, 197, 1646).—On adding powdered Mg to 0.25–0.05N-NiSO₄ dissolution proceeds slowly with deposition of a bright green, highly hydrated, efflorescent cryst. salt, which, dried at 100°, contains NiSO₄·4NiO·10H₂O, is non-magnetic, almost insol. in H₂O, but sol. in hot acid. Co behaves similarly (cf. A., 1893, ii, 528). C. A. S.

Non-existence of a higher nickel carbide. J. SCHMIDT [with E. OSSWALD] (Z. anorg. Chem., 1933, 216, 85–98).—Chemical and X-ray analysis fail to reveal a carbide higher than Ni₃C in the products of reaction of Ni with CO at 240–250° or with C₂H₂ at 180–200°. At 260° CH₄ is decomposed by Ni, giving C, but no carbide is formed. E. S. H.

Complex dipyriddy and phenanthroline salts of bivalent metals. P. PFEIFFER and F. TAPPERMANN (Z. anorg. Chem., 1933, 215, 273–287; cf. A., 1933, 400).—The following compounds are described (dipy=dipyriddy, phen=*o*-phenanthroline): Ni phen₂X₂·10H₂O (X=Cl, Br); M phen₂Cl₂ (M=Mn, Ni); Ni phen₂SO₄·14H₂O; Ni phen₂SO₄; Ni dipy₂Cl₂; Co phen₂Cl₂·4H₂O; Mn phen₂SO₄·8H₂O; M phen₂(O·SO₂·C₁₀H₇·β)₂·6H₂O (M=Co, Ni, Fe, Zn, Cd); Ni dipy₂(O·SO₂·C₁₀H₇·β)₂; M phen₂(O·SO₂·C₁₀H₇·β)₂ with 1 H₂O (Cu) and 2 H₂O (Mn); Mn phen₂(O·SO₂·C₁₀H₁₄OBr)₂ (α-bromocamphor-β-sulphonate). F. L. U.

Analogy of ruthenium to iron. Nitric oxide compounds of bivalent ruthenium. W. MANCHOT and H. SCHMID (Z. anorg. Chem., 1933, 216, 99–103).—The prep. and properties of RuI₂NO and RuBr₂NO are described. These compounds undergo a reversible reaction with CO, forming corresponding carbonyls. E. S. H.

Preparation and autoxidation of blue ruthenous solution. W. MANCHOT and H. SCHMID (Z. anorg. Chem., 1933, 216, 104–108).—Solutions of Ru^{II} are prepared by cathodic reduction of RuCl₃ in 4N-HCl, using a Pt cathode. The solution oxidises slowly in presence of air. Addition of NaOH ppts. Ru(OH)₃ immediately, although in absence of O₂ Ru(OH)₂ is pptd. E. S. H.

Factors in sedimentation analysis. E. W. GALLIHER (Amer. J. Sci., 1933, [v], 26, 564–568).—Na oxalate and citrate are more efficient dispersing agents than aq. NH₃. Flocculation is sometimes caused by micro-organisms; it can be prevented by sterilising with PhMe. R. P. B.

Interferences of metal ions in the detection of acids. L. J. CURTMAN and S. M. EDMONDS (J. Chem. Educ., 1933, 10, 567–570). CH. ABS.

Spectrum analysis for traces of elements in ore and rock minerals. H. MORITZ (Chem. Erde, 1933, 8, 321—338).—Tables are given of the sensitive lines for a no. of elements when present in small measured amounts. L. J. S.

Silver electrodes of the "second kind" as comparison electrodes. F. L. HAHN (Z. anal. Chem., 1933, 95, 337; cf. A., 1933, 1027).—A claim for priority (cf. A., 1932, 471). J. S. A.

Micro-quinhydrone electrode.—See this vol., 230.

Eupittone [as indicator]. K. BRAND and E. PERUCHE (Pharm. Zentr., 1934, 75, 8—13).—Eupittone (3 : 5 : 3' : 5' : 3'' : 5''-hexamethoxyaurin) gives a sharp colour change from orange to pure blue at p_H 6.6—7.4, but except in the case of picric acid it offers no advantage over other indicators. S. C.

Indicator properties of *p*-, 2 : 4-di-, and 2 : 4 : 6-tri-nitrophenylacetylhydrazides. A. BLOOM and A. OSOL (Amer. J. Pharm., 1933, 105, 551—553).—The three substances [denoted (1), (2), or (3) according to the no. of NO₂-groups] give good results in titrating strong acids (pale green) with strong bases (brown to orange-brown), but the colours, particularly of (3), are unstable in alkaline solution. The p_H ranges and apparent dissociation consts. (Salm), both determined colorimetrically by means of buffer solutions, are respectively as follows: (1) 6.6—8.0; 7.6, (2) 7.6—9.6; 9.1, (3) 9.0—10.6 approx. The colour of (3) fades too rapidly to permit a measurement of pK_1 . W. S.

System mercuric cyanide-chromithiocyanate as a turbid indicator [in acidimetry and alkalimetry]. R. UZEL (Coll. Czech. Chem. Comm., 1933, 5, 457—465).—0.06 g. of Hg(CN)₂ + 0.01 g. of NH₄NO₃ + 0.002 g. of K₂Cr(CNS)₆ in 1 c.c. added to 25 c.c. of liquid affords at p_H < 4.0 a turbidity due to Hg₃[Cr(CNS)₆]₂ which redissolves at higher p_H . This indicator fails in the presence of I', S₂O₃'', and large quantities of Br' and CNS', but is satisfactory in coloured solutions where other indicators are inapplicable and permits the titration of H₂CrO₄ as a strong monobasic acid. Small quantities of free H₂CrO₄ have been determined in commercial K₂Cr₂O₇. J. G. A. G.

Acid-base titrations in alcohol-water mixtures. II. Indicators in alcohol-water mixtures. H. BAGGESGAARD-RASMUSSEN and F. REIMERS (Dansk Tidsskr. Farm., 1933, 7, 225—272; cf. A., 1933, 1015).—The dissociation exponents and regions of colour change of eleven indicators were determined colorimetrically in 20—85% EtOH. The variation of dissociation exponent with EtOH concn. leads to the conclusion that the azo-indicators are uncharged bases and the sulphonephthaleins uncharged acids. Me-red behaves like the latter, and its isoelectric form must therefore be chiefly uncharged NH₂-acid and not zwitterion. The results are discussed in terms of different theories of colour and structure. The carbinol indicators behave anomalously; a special mechanism is proposed involving reaction with H₂O. The absorption curves of four indicators were measured in acids, bases,

and buffer mixtures. In all cases the absorption curves change with changing EtOH concn.

R. P. B.

Isotopic analysis of water. R. H. CRIST, G. M. MURPHY, and H. C. UREY (J. Amer. Chem. Soc., 1933, 55, 5060—5061).—Determination of n is recommended. E. S. H.

Refractive index of H₂O¹⁸ and the complete isotopic analysis of water. G. N. LEWIS and D. B. LUTEN, jun. (J. Amer. Chem. Soc., 1933, 55, 5061—5062).—By determining n and d the complete isotopic constitution of H₂O can be ascertained from the formulæ $x = 1.370\Delta d - 190.5\Delta n$ and $y = 7.692\Delta d + 180.9\Delta n$, where x is the mol. fraction of H₂O, y the mol. fraction of H₂O¹⁸, Δd and Δn are the differences in d and n of the sample and ordinary H₂O at 25°. E. S. H.

Determination of chlorine in potassium iodide.—See B., 1934, 15.

Determination of bromine in presence of chlorine in mineral waters.—See B., 1934, 59.

Micro-titration of iodides alone or in presence of other halogens. V. STANEK and T. NEMES (Z. anal. Chem., 1933, 95, 240—244; cf. A., 1932, 529, 631).—I' can be accurately titrated with Hg(NO₃)₂, using Na nitroprusside as indicator, provided the solution contains \geq 30 mg. of I in 200 c.c. In presence of Cl' or Br', the I' may be determined by Winkler's method (A., 1932, 487), and the other halogen with Hg(NO₃)₂. F. L. U.

Determination of fluorine. I. Precipitation of fluoride ion as lead chlorofluoride. J. FISCHER and H. PEISKER (Z. anal. Chem., 1933, 95, 225—235).—The influence of degree of acidity, concn., mode of pptn., and the presence of foreign substances on the determination of F' as PbClF has been studied. Procedure is described whereby results accurate within 0.5% may be obtained rapidly and conveniently. F. L. U.

Detection and determination of fluorides. I. M. KORENMAN (Z. anorg. Chem., 1933, 216, 33—40).—Greiff's method (A., 1913, ii, 975) gives low results. A modification of Steiger's procedure (A., 1908, ii, 426) gives good results for 0.05—0.5 mg. HF. Smaller amounts of HF in air (0.002 mg. per litre) can be detected by a reagent paper containing Zr(NO₃)₄ and alizarin. E. S. H.

"Fluorinated" methæmoglobin. Spectrophotometric determination of fluorides.—See this vol., 92.

Conversion of thiosulphuric acid into polythionic acids with the help of catalysts. III. Regularities in the precipitation of arsenic or antimony sulphides. A. KURTENACKER and E. FÜRSTENAU (Z. anorg. Chem., 1933, 215, 257—270; cf. A., 1930, 302).—The pptn. of As or Sb as sulphide by Na₂S₂O₃ is controlled chiefly by the nature and concn. of the acid present. With HCl, H₂SO₄, or HClO₄ the pptn. reaches a max. at about 0.1N-acid, being quant. for Sb and 50—80% for As. Above this concn. the pptn. falls to zero with HCl, whereas it passes through a min. with H₂SO₄ (2—3N) and HClO₄ (1N), and becomes almost quant. at still higher

condens. The observations are interpreted in terms of the conversion of $S_2O_3^{2-}$ into polythionic acids under the influence of mineral acids. F. L. U.

Oxidation of nitric oxide in low concentrations, and its determination. V. PIANKOV (J. Gen. Chem. Russ., 1933, 3, 652—659).—Griess' method is applicable to the determination of 0.1 mg. NO per litre of air. The process of oxidation takes place in two stages: $2NO + O \rightarrow N_2O_3$; $N_2O_3 + O \rightarrow N_2O_4$; the former reaction is practically instantaneous, whilst the velocity of the latter varies with concn. of NO, 95% of 0.06 mg.-% NO being oxidised to N_2O_4 after 2.5 hr., and only 84% of 0.04 mg.-% NO after 20 hr. at 16° . R. T.

Use of diphenylamine azo-dyes as indicators for nitrous acid. A. E. PORAT-KOCHITZ and L. V. TSCHERVINSKAJA (Anilinokras. Prom., 1933, 3, 339—351).—Metanil-yellow, tropaeolin OO, and a no. of other similar dyes prepared from diphenylnitrosoamine or its mono- or di-*p*-sulphonic acids and *o*- $NH_2 \cdot C_6H_4 \cdot SO_3H$, *m*- and *p*- $NH_2 \cdot C_6H_4 \cdot NO_2$, NH_2Ph , *m*- and *p*- $C_6H_4(NH_2)_2$, *o*- and *p*- $C_6H_4Me \cdot NH_2$, and *p*- $C_6H_4Cl \cdot NH_2$ give violet colorations in acid solution, changing to yellow in presence of HNO_2 , and again becoming violet on removal of HNO_2 . The above dyes can be used as indicators in the titration of primary amines by aq. $NaNO_2$. R. T.

Micro-determination of phosphorus as phosphomolybdate. R. H. A. PLIMMER (Biochem. J., 1933, 27, 1810—1813).—The method is adapted to the determination of 0.01—0.1 mg. P by pptn. with a purified MoO_4^{2-} reagent in the presence of 20 c.c. of 10% NH_4NO_3 solution per 1 c.c. of conc. H_2SO_4 added, filtration with a Bertrand asbestos filter, and washing with 50% EtOH. H. D.

Determination of phosphorus in titaniferous material. G. HØRGARD (Z. anal. Chem., 1933, 95, 329—336).—The effect of Ti in hindering the quant. pptn. of PO_4^{3-} as phosphomolybdate may be avoided by addition of 10 c.c. of conc. HCl or $HNO_3 + 10$ g. NH_4Cl or NH_4NO_3 , respectively, for 2 g. of material of low P and Ti content. With > approx. 1% Ti, quant. pptn. is not possible. J. S. A.

Osmium tetroxide as catalyst for the oxidation of arsenious acid by permanganate and ceric sulphate. K. GLEU (Z. anal. Chem., 1933, 95, 305—310).—Oxidation of As_2O_3 in dil. H_2SO_4 solution by $KMnO_4$ or $Ce(SO_4)_2$ is catalysed by the addition of a few drops of 0.01*M*- OsO_4 solution, enabling As_2O_3 to be determined by titration with these reagents in the cold. With $Ce(SO_4)_2$, a $Fe(o\text{-phenanthroline})_3^{3+}$ salt is used as oxidation-reduction indicator. J. S. A.

Use of Bougault's reagent for the gravimetric determination of arsenic in presence of tin and antimony. J. P. PLUCHON (Bull. Trav. Soc. Pharm. Bordeaux, 1932, 70, 140—144; Chem. Zentr., 1933, i, 1816).—25 c.c. of the solution containing approx. 0.1 g. As are mixed with 50 c.c. of Bougault's reagent, heated at $120\text{--}125^\circ$ for 30 min., quickly cooled, filtered on a IG3 Jena glass filter, and washed with cold boiled-out H_2O . Residues containing As are then dissolved by successive treatments with HNO_3 and 5% KOH and the united extracts evaporated to

dryness in porcelain, extracted with 4 c.c. of HNO_3 , and taken to dryness again. Finally, the residue is dissolved in hot H_2O and the As determined as $Mg_2As_2O_7$.

L. S. T.

Microchemical determination of carbonic acid in carbonates. W. REICH-ROHRWIG (Z. anal. Chem., 1933, 95, 315—323).— CO_2 is liberated by the action of 2—3*N*-HCl, in an apparatus described, and swept over in a purified air stream at const. pressure. The gas is freed from H_2S and H_2O by $CuSO_4$ -pumice and P_2O_5 , and the CO_2 absorbed in "ascarite" followed by P_2O_5 . Vals. so obtained are given for Morogoro pitchblendes, showing difference in composition between inner and outer layers. J. S. A.

Errors in determination of carbonate in boiler waters.—See B., 1934, 47.

Evaluation of helium from radioactive minerals and rocks. V. CHLOPIN, E. HERLING, and E. JOFFÉ (Nature, 1934, 133, 28).—The amount of He evolved from different minerals, e.g., uraninite and chlopinite, at a given temp. > a crit. temp. depends on the presence of H_2 and is the greater the higher is the partial pressure of H_2 . Small amounts of H_2 in a gas mixture can be detected by means of this effect. L. S. T.

New reaction for potassium. S. A. CELSI (Anal. Farm. Biochim., 1933, 4, 55—59).—Na cobalthio-sulphate in MeOH, or, better, a mixture of a 14% solution of $Co(NO_3)_2$ in 80% aq. MeOH and 38% aq. $Na_2S_2O_3$, gives a characteristic blue cryst. ppt. with K salts in neutral solution. R. K. C.

Separation and determination of sodium and potassium. L. SZEPELLÉDY and K. SCHICK (Magyar Gyog. Tarsas. Ert., 1933, 9, 40—51; Chem. Zentr., 1933, i, 1817).—In the separation and determination of Na and K as iodide the most suitable solvent is a mixture of equal vols. of anhyd. Bu^iOH and anhyd. Et_2O . The extracted NaI and the residual KI contain only traces of each other, but it is recommended to add 0.6 mg. to the K_2O found and to subtract 0.6 mg. from the Na_2O . Chlorides and sulphates are readily converted into the iodides, carbonates must be converted into chloride, whilst phosphate must be removed prior to the separation. L. S. T.

Volumetric determination of barium and of sulphates. J. C. GIBLIN (Analyst, 1933, 58, 752—753).—The $BaCl_2$ solution (< 1%) is titrated into standard H_2SO_4 , and after mixing, the supernatant liquid is spotted on a filter-paper stained with Na rhodzonate, the end-point being the reddish-brown colour produced with an excess of Ba. The procedure is reversed for the determination of H_2SO_4 . J. G.

Conditions for precipitation of zinc sulphide and aluminium hydroxide, and gravimetric separation of zinc from aluminium. III, IV. J. N. FRERS [with J. KOLLWITZ] (Z. anal. Chem., 1933, 95, 113—142; cf. this vol., 48).—III. Pptn. of $Al(OH)_3$ occurs at p_H between 3 and 7; redissolution in excess of precipitant at $p_H > 9.0$. By neutralisation against phenol-red (p_H 7.5) pptn. is quant. NH_4Cl and NH_4NO_3 have no effect on the pptn.; with $(NH_4)_2SO_4$ some basic Al sulphate, destroyed slowly on ignition, is formed. Wash- H_2O should contain

2% NH_4 salts and be neutralised (phenol-red). A non-hygroscopic Al_2O_3 is formed by ignition at 1200° ; from the variation of hygroscopicity with temp. of ignition, the transition point $\gamma\text{-Al}_2\text{O}_3 \rightarrow \text{corundum}$ is found to be $1010^\circ \pm 5^\circ$.

IV. For the separation of Zn and Al, the solution, containing 4% $(\text{NH}_4)_2\text{SO}_4$, is brought to p_{H} 2.8, using tropæolin OO as indicator. ZnS is pptd. by H_2S , washed with 4% $(\text{NH}_4)_2\text{SO}_4$ of p_{H} 2.8, and ignited in H_2S . Al in the filtrate is pptd. either by addition of aq. NH_3 to give p_{H} 7.5 (phenol-red), or by addition of $\text{Na}_2\text{S}_2\text{O}_3$ followed by aq. NH_3 . J. S. A.

Glycerol complexes in volumetric analysis. H. WAGNER (Z. anal. Chem., 1933, 95, 311—315).—Owing to the formation of complexes with Cu, Co, Ni, Zn, and Cd, by addition of glycerol (I) to solutions of these metals (e.g., plating-bath liquids), free acid may be directly titrated with *N*-NaOH, against Me-orange. Zn may be determined as follows. Alkali-free ZnCO_3 is pptd. by addition of Na_2CO_3 to a cold, slightly acid solution until turbidity appears, heating to boiling, and neutralising (phenolphthalein). The ppt. is dissolved in 0.1*N*-acid, 30 c.c. of (I) are added, and the excess acid is titrated back. Cd may be similarly determined, CdCO_3 being pptd. cold. J. S. A.

Determination of cadmium in presence of zinc.—See B., 1934, 22.

Determination of lead with picrolonic acid. F. HECHT, W. REICH-ROHRWIG, and H. BRANTNER (Z. anal. Chem., 1933, 95, 152—163).—0.01*N*-Picrolonic acid (I) ppts. from neutral Pb solutions at 0° a Pb salt of approx. composition $\text{Pb}(\text{C}_{10}\text{H}_7\text{O}_5\text{N}_4)_2 \cdot 1.5\text{H}_2\text{O}$, containing 27.25% Pb when dried at 130° . Excess of (I) is slowly added to the hot solution, which is cooled to 0° and the ppt. washed with the min. amount of H_2O at 0° . Pb may be accurately determined in the presence of < 5 pts. of Pt (e.g., in Pb from micro-electrolytic depositions). J. S. A.

Volumetric determination of copper and lead in babbitt metal.—See B., 1934, 64.

Potentiometric titration of copper with sodium sulphide and use of a platinum electrode. J. B. JHA (J. Indian Chem. Soc., 1933, 10, 643—647).—Accurate results are obtained when the acidity of the liquid is regulated with AcOH, a Pt wire electrode being used. F. L. U.

Electrolytic analysis of bronzes and brass.—See B., 1934, 22.

Detection of mercury. L. F. VOET (Pharm. Weekblad, 1933, 70, 1336).—The compound is reduced with SnCl_2 , the supernatant liquor poured off, and the pptd. Hg boiled repeatedly with conc. HCl until a globule is formed. S. C.

Determination of mercurous or bromide and chloride ions. L. VON ZOMBORY and L. POLLAK (Z. anorg. Chem., 1933, 215, 255—256).—Good results are obtained in the titration of KBr or KCl by $\text{Hg}_2(\text{NO}_3)_2$ in 0.1*N* solution by using as indicators chlorophenol-red or bromocresol-green. The yellow colour of the ppt. changes to lilac at the equivalence point. F. L. U.

Sources of error in the determination of aluminium. R. RINNE (Chem.-Ztg., 1933, 57, 992).—The quantity of NH_4Cl added to 100 c.c. of solution (2.7% AlCl_3) should be < 3 g. The solubility of $\text{Al}(\text{OH})_3$ in aq. NH_3 does not introduce any considerable error. If the vol. of the $\text{Al}(\text{OH})_3$ on the filter is large, the bulk should be transferred to a beaker and the residue removed by HCl. Appreciable losses arise if a bulky ppt. is treated with HCl on the filter-paper. H. F. G.

Determination of aluminium in corrosion-resisting and plain steels.—See B., 1934, 21.

Mercurimetric determination of chromium. A. IONESCO-MATIU and S. HERSCOVICI (Bull. Soc. chim., 1933, [iv], 1032—1038).— CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are determined by collecting centrifugally the ppt. obtained with $\text{Hg}_2(\text{NO}_3)_2$, dissolving the ppt. in H_2SO_4 , adding KMnO_4 until the liquid is pink, and titrating the Hg^+ with NaCl after pptn. with Na nitroprusside. Cr^{+++} is first pptd. as $\text{Cr}(\text{OH})_3$ by aq. NH_3 and subsequently oxidised to CrO_4^{2-} by hot KOH and H_2O_2 . J. G. A. G.

Volumetric determination of bismuth. G. SPACU and P. SPACU (Z. anal. Chem., 1933, 55, 336—337; cf. A., 1933, 1027).—A claim for priority of prep. of salts derived from H_3BiBr_6 (cf. Mahr, *ibid.*, 924). J. S. A.

Micro-determination of gold. Application to gold-therapy. B. K. MEREJKOVSKY (Bull. Soc. Chim. biol., 1933, 15, 1336—1338).—The material is digested with $\text{H}_2\text{SO}_4 + \text{HNO}_3$; excess of H_2SO_4 is removed, and the pptd. Au dissolved in $\text{HCl} + \text{HNO}_3$. The resulting solution is diluted until the Au content is 0.02—0.002% and then treated with aq. agar followed by dimethylaminobenzylidenerhodanine reagent (A., 1928, 1108). The red colloidal suspension is compared with suitable standards. The reagent will detect 2.5×10^{-6} g. of Au per c.c. F. O. H.

Organic pseudo-compounds as reagents for active atoms in organic molecules.—See this vol., 167.

Simple, sensitive, thermostat regulator. C. E. WOODWORTH (Science, 1933, 78, 536).—Details of a thermo-regulator sensitive to 0.001° between 0° and 35° are given. L. S. T.

Temperature regulation of furnaces and thermostats. R. FONTEYNE (Natuurwetensch. Tijds., 1934, 15, 226—228).—Fouling of Hg contacts by arcing is prevented by using thermionic valves. An apparatus is described. S. C.

Calorimeter for combustion of chlorine and bromine compounds. M. M. POPOV and P. K. SCHIROKICH (Z. physikal. Chem., 1933, 167, 183—187).—Combustion is effected in a bomb containing a neutral aq. solution of As_2O_3 . By rotating the bomb rapid reaction of the solution with free halogen formed in the combustion is ensured. R. C.

Gas furnace for heating tubes to a high temperature. J. VAN DEN BERG (Chem. Weekblad, 1934, 31, 24).—Directions are given for making a small furnace to take tubes 10—20 mm. diam. from kieselguhr bricks. Heating is by a single Teclu burner with a flame spreader, and a temp. of $1000\text{—}1100^\circ$ can

be obtained in a few min. The furnace is extremely economical. S. C.

Sodium glow-lamp. F. H. NEWMAN (Phil. Mag., 1933, [vii], 16, 1109—1114).—A laboratory method of electrolysing Na from a fused NaNO_3 bath into a glow-lamp containing A is described. The Na lamp may be used as a source of D line radiation, A lines being suppressed. H. J. E.

Compensator box for polarimeters. N. DEERR and F. G. STANLEY (Intern. Sugar. J., 1933, 35, 432—433).—Access to the interior of the compensator box is obtained by making the side next to the observer a sliding element. This side carries the observation and scale-reading telescopes, in the former of which is also carried the analysing nicol. When this is slid out, the long wedge, the moving scale, and the vernier scale are exposed. The scale is read directly by transmitted light and the conventional arrangement of inclined mirrors and ground-glass plate is eliminated. J. P. O.

Symmetrically opening optical slit. J. E. SEARS (J. Sci. Instr., 1933, 10, 376—377).—The two halves of the slit are attached at right angles to thin leaf springs, by means of which they are drawn apart as the turning of a micrometer screw moves them longitudinally. C. W. G.

Improvements in the Schlieren method. H. G. TAYLOR and J. M. WALDRAM (J. Sci. Instr., 1933, 10, 378—389).—A more convenient optical system is described in detail. C. W. G.

Transportable apparatus for luminescence analysis. P. W. DANCKWORT (Chem.-Ztg., 1933, 51, 1018).—An apparatus weighing about 3 kg. is described; it is suitable for general fluorescence analysis and for fluorescence photography. H. F. G.

Fluorescence. C. C. PINES (Amer. J. Pharm., 1933, 105, 563—564).—A no. of minerals are examined under a new "argon" lamp, emitting long wavelength ultra-violet light (330—370 $\text{m}\mu$) to which glass is permeable. W. S.

Monochromator with wide field using interference in polarised light. B. LYOT (Compt. rend., 1933, 197, 1593—1595). C. A. S.

Apparatus for X-ray investigation of fine structure. W. E. SCHMID (Z. physikal. Chem., 1933, B, 23, 347—357).—By means of special X-ray tubes the time of exposure required for Debye-Scherrer diagrams can be shortened and up to four cameras can be used simultaneously with one tube. It is advantageous to build up X-ray assemblages from interchangeable elements so that any required combination may readily be obtained. R. C.

Universal camera and "self-indexing" rotating crystal camera. E. SAUTER (Z. physikal. Chem., 1933, B, 23, 370—378).—The construction and mode of operation are described. R. C.

Improvements in the 21-foot normal incidence vacuum spectrograph. G. R. HARRISON (Rev. Sci. Instr., 1933, [ii], 4, 651—655).—Additions to the instrument previously described are given (cf. A.,

1931, 1387); the range is 6000—300 Å., accurate to ± 0.005 Å. N. M. B.

Air ionisation chamber for measuring low-voltage X-ray intensities in rontgens. F. M. UBER (Rev. Sci. Instr., 1933, [ii], 4, 649—650).—A self-contained parallel plate chamber for use in dosage meters is described. N. M. B.

Ring-target X-ray generator adapted to scattering, fluorescence, and irradiation experiments. P. KIRKPATRICK and P. A. ROSS (Rev. Sci. Instr., 1933, [ii], 4, 645—648).—The essential feature is a ring-target approx. 3 in. in diam., along the horizontal axis of which a scatterer can be placed. N. M. B.

Liquids of high refractive index. B. W. ANDERSON and C. J. PAYNE (Nature, 1934, 133, 66—67).—Liquids suitable for refractometry are C_2I_4 and S in CH_2I_2 , n_D 1.81; AsPhI_3 , d^{15} 2.56, n 1.822—1.879 for 6708 to 5106 Å.; Se_2Br_2 , n_{D1} 1.96 \pm 0.1 to 2.02. L. S. T.

Interference scheme for measuring the cell depth of a Siedentopf ultramicroscopic mounting chamber. D. L. GAMBLE and A. H. PFUND (J. Opt. Soc. Amer., 1933, 23, 416—418).—A channelled spectrum is used. C. W. G.

Focalisation of diffused X-rays by plane crystalline plates. (MLLE.) Y. CAUCHOIS (Compt. rend., 1934, 198, 76—78; cf. A., 1933, 450).—Mathematical. An alternative scheme of arriving at the same result as previously described, by means of a circular slit or knife-edge, is worked out. C. A. S.

Focalisation methods in crystal powder analysis. H. HULUBET (Compt. rend., 1934, 198, 79—80).—Mathematical. Illumination of a cryst. powder or of a liquid by a hollow conical beam of X-rays is discussed. C. A. S.

Dipole measurements with very small quantities of material. P. C. HENRIQUEZ (Physica, 1933, 1, 41—52).—A micro-condenser, by means of which dipole moments may be measured accurately with a few mg. of material, is described. The problem is discussed theoretically. F. L. U.

Electrolysis of sodium through Pyrex glass. E. W. PIKE (Rev. Sci. Instr., 1933, [ii], 4, 687).—A method of introducing gas-free Na into a vac. tube by electrolysis through Pyrex glass is described. N. M. B.

Dielectric constant. I. Improved voltage tuning resonance method and its application to aqueous potassium chloride solutions. II. Drude method applied to aqueous solutions of potassium chloride. J. G. MALONE, A. L. FERGUSON, and L. O. CASE (J. Chem. Physics, 1933, 1, 836—841, 842—846).—I. Divergent results for the dielectric consts. of aq. solutions of electrolytes when different types of detection are used indicate that the change in dielectric const. depends on the characteristics of the generating and receiving circuits.

II. Adaptations of the Drude method with three different types of detecting device gave concordant results for the dielectric const. of H_2O and $\text{EtOH-H}_2\text{O}$ mixtures, but divergent results for KCl and

CuSO₄ solutions, indicating dependence on the characteristics of the apparatus. N. M. B.

Simple high resistance. V. DUMERT (*Nature*, 1933, 132, 1005).—The characteristics of C-film and non-metal resistances (this vol., 51) are discussed. A mixture giving resistances of a few thousand to several millions of ohms can be prepared from colloidal graphite (Aquadag) and phenol-resin colloid. It is painted on a rod of insulating material and baked at 150° for 2 hr. The resistor is made variable by immersion in Hg. L. S. T.

Possibilities in connecting up Ostwald's decade rheostats for potentiometric analysis. E. ERBACHER (*Chem.-Ztg.*, 1933, 57, 904—905). A. R. P.

Portable vacuum-tube voltmeter for measurement of glass electrode potentials with examples of p_H determination. F. DE EDS (*Science*, 1933, 78, 556—558).—The apparatus described is suitable for determining the p_H of biological fluids, food products, and soils. The p_H of arterial dog blood was const. at 7.30 for 35 min. 15 min. after administration of dinitrophenol respiration increased and the p_H rose to 7.34, at which val. it remained const. for 30 min. Vals. then fell to 6.94 for a sample taken 1 min. after death. L. S. T.

Laboratory apparatus for esterification. E. GUTTMANN (*Chem.-Ztg.*, 1933, 57, 1001).—A flask is fitted with a plain vertical tube connected at the top and bottom to a condenser parallel to it. A 2-way cock at the bottom of the latter allows the apparatus to be used for refluxing and distillation as desired. C. I.

Laboratory glass filters. P. H. PRAUSNITZ (*Chem.-Ztg.*, 1933, 57, 885—886).—Glass filters of the Büchner type with perforated and sintered porous glass filter plates, and of the ordinary funnel type with channels in the side to assist filtration, are described. A. R. P.

Gas burette. J. HUME (*Chem. and Ind.*, 1934, 37).—A simple apparatus, giving a max. error of < 0.1 c.c. in 100 c.c., is described. E. S. H.

Vessel for acid-alkali titrations. J. JACKSON (*Chem. and Ind.*, 1934, 36). E. S. H.

Kipp apparatus. ANON. (*Chem.-Ztg.*, 57, 1933, 992).—The solid reactant is prevented from falling into the lowest vessel by means of a wide glass sleeve which rests on the bottom and surrounds the central tube to a point slightly above the level of the solid; the external diameter of the sleeve is only very slightly < the internal diameter of the neck between the middle and lowest vessels. H. F. G.

Large-scale laboratory extractions. P. A. ROWAAN (*Chem. Weekblad*, 1933, 30, 771—772).—A large vessel (I) (e.g., 10 litres) is fitted with an upright condenser and a side tube leading from a round-bottomed flask (1 litre) lying horizontally in a H₂O-bath. The neck of the flask is level with the surface of the solvent in (I), and is fitted also with a narrow-bore tube which enters the bottom of (I). Vapour passes from the flask to the condenser, the solvent falls on the material to be extracted, and the

conc. extract flows continuously through the narrow tube to the flask. The apparatus is sturdy, requires little attention, and is inexpensive. H. F. G.

Device for elutriation analysis of small quantities of material. M. VENDL (*Mitt. berg-hüttenmänn. Abt. Hochschule Berg-Forstwes. Sopron*, 1932, 4, 104—119; *Chem. Zentr.*, 1933, i, 1818). L. S. T.

Simple apparatus for exact gas analysis, especially for determination of carbon dioxide and water vapour at low concentration. P. SCHULTAN (*Chem. Fabr.*, 1933, 6, 513—515).—CO₂ is removed by absorption in conc. KOH, and H₂O by freezing at temp. < -55°. The alteration in vol. and pressure of the gas is determined by an inclined capillary manometer. The error is about $\pm 3 \times 10^{-3}$ vol.-%. E. S. H.

Apparatus for azeotropic dehydration. A. DUPIRE (*Bull. Assoc. Chim. Sucr.*, 1933, 50, 373—374).—Laboratory apparatus for esterification, in which the H₂O formed is removed continuously by distillation with an immiscible liquid, is described with a diagram. The reaction mixture, with the immiscible liquid, is boiled in a flask with three necks, one for a thermometer, one for a stirrer with Hg seal, and one leading to a kind of Soxhlet extractor connected with a reflux condenser. The condensate from the last drops into a collecting tube in the bottom of which the H₂O remains, whilst the immiscible liquid overflows and returns to the boiling flask through the Soxhlet extractor, which may contain a dehydrating agent if necessary. This apparatus has been used for the prep. of many boric and arsenious esters (cf. A., 1932, 937) and for the dehydration of many org. and inorg. substances. J. H. L.

Laboratory aids. W. KERCKHOFF (*Chem.-Ztg.*, 1933, 57, 866).—Simple devices made from strips of metal or metal wire are illustrated for supporting crucibles in a desiccator, a beaker in a H₂O-bath, and an extraction thimble below a reflux condenser. A. R. P.

Filtration of hygroscopic substances. G. ROEDER (*Chem.-Ztg.*, 1934, 58, 28).—Apparatus for filtration in an atm. of dry CO₂ is described. A. G. P.

Devices for working with moisture-sensitive substances. H. GRUBITSCH and N. SKALLA (*Z. anal. Chem.*, 1933, 95, 163—165).—Descriptions are given of a weighing bottle with spiral screw thread for opening inside a closed reaction vessel, and of a double-ended weighing tube enabling a boat to be inserted in a combustion tube without exposure. J. S. A.

Collodion membranes in low-pressure ultra-filtration. S. J. FOLLEY (*Biochem. J.*, 1933, 27, 1775—1778).—Details are given of the prep. of collodion tubes of reproducible permeability and of a method of low-pressure ultra-filtration. H. G. R.

Mercury seal for stirrers. D. T. ROGERS (*J. Amer. Chem. Soc.*, 1933, 55, 4901).—Stainless steel is used in place of glass. E. S. H.

More sensitive design of the Geiger-Müller counter. T. R. CUYKENDALL (*Rev. Sci. Instr.*, 1933, [ii], 4, 676—678).—The effective surface is

increased by replacing part of the wall of the counter by Ni vanes from which recoil electrons can escape to ionise the gas in the chamber. N. M. B.

Apparatus for the growth of metal single crystals. M. F. HASLER (Rev. Sci. Instr., 1933, [ii], 4, 656—660).—A furnace is moved mechanically along a glass tube containing the growing trough. Very uniform single-cryst. rods of any orientation can be produced in any gas or in vac. for metals of low m.p. N. M. B.

Phosphoric acid as a drying agent for hydrogen chloride. F. FAIRBROTHER (J.C.S., 1933, 1539—1541).—Dry HCl has no action on P_2O_5 . In presence of a trace of H_2O , HPO_3 is formed and absorption of HCl then occurs in accordance with the reaction $3HCl + HPO_3 = POCl_3 + 2H_2O$. The H_2O thus produced forms more HPO_3 and so the absorption of HCl increases. H. S. P.

Simple pneumator pulsator. C. F. WINCHESTER (Science, 1933, 78, 607—608).—An apparatus to move a liquid in or out of a vessel, or intermittently to move a liquid in a given direction, is described. L. S. T.

Production of high pressures and temperatures. C. RAMSAUER (Physikal. Z., 1933, 34,

890—894).—Compression is effected by a projectile entering the open end of a tube containing the gas. A. J. M.

Rapid elimination of oxygen from water or aqueous solutions.—See B., 1934, 1.

Nomogram for the conversion of potentiometer readings to hydrogen-ion concentration. A. WEBSTER (Chem. and Ind., 1934, 38). E. S. H.

Lecture experiment to illustrate "topsy-turvydom" in induced reactions. K. GLEU (Z. anorg. Chem., 1933, 215, 271—272).—A solution containing H_2SO_4 , $NaVO_3$, As_2O_3 , and a trace of OsO_4 shows the yellow colour of V^V . On adding $KClO_3$, an oxidising agent, reduction of V^V to V^{IV} by the As_2O_3 is induced, and the liquid turns blue. F. L. U.

Survey of progressive science. (SIR) F. G. HOPKINS (Nature, 1933, 132, 878—880).—Presidential address to the Royal Society. L. S. T.

Negative weight of phlogiston. C. SAECHTLING (Angew. Chem., 1933, 46, 754—756).—Most supporters of the phlogiston theory in the latter half of the eighteenth century attributed the increase in wt. of a metal on losing phlogiston to a difference in d between the latter and the surrounding air. A. B. M.

Geochemistry.

Terrestrial abundance of the permanent gases. H. N. RUSSELL and D. H. MENZEL (Proc. Nat. Acad. Sci., 1933, 19, 997—1001).—Theoretical. R. S.

Existence of oxygen in the atmosphere of Mars. D. EROPKIN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 100—101).— O_2 should be detectable through the O_3 absorption bands at 3200—3400 Å. H. J. E.

Electrical conductivity of the air on Mont Dore in August, 1933. G. GRENET (Compt. rend., 1933, 197, 1683—1684).—The mean conductivity of the air at 9.15 a.m., Aug. 2—21, 1933, on Mont Dore (1050 m.) was 4.26×10^{-4} , or approx. double the normal, due probably to the presence of increased emanation. The ratio λ^+/λ^- varied from 0.80 to 1.42, average 0.99. C. A. S.

Catalytic properties and the ages of the mineral waters of Vrnjacka Banja, Arandelovac, and Mladenovac. G. SCHILDER (Kroat. Aerzte-Z., 1932, 54, 243—261; Chem. Zentr., 1933, i, 1825—1826).—Catalytic effects were examined by means of the Glenard reaction (titration with 0.1N- $KMnO_4$ and determination of reaction velocity). Peroxidising effects were examined by means of acid and alkaline benzidine reactions. Fe^{++} was detected and pH measurements were made. L. S. T.

Transparency, colour, and specific conductance of the lake waters of N.E. Wisconsin. C. JUDAY and E. A. BIRGE (Trans. Wisconsin Acad. Sci., 1933, 28, 205—259).—Colour of H_2O from 500 lakes is correlated with org. C in the surface H_2O ; transparency and transmission of solar radiation

are also related. Sp. conductivity at 20° is correlated with the quantity of fixed or bound CO_2 as well as that of Ca and Mg in the surface H_2O . CH. ABS.

Transmission of ultra-violet radiation by water. C. D. HODGMAN (J. Opt. Soc. Amer., 1933, 23, 426—429).—The low transmission of fresh H_2O from lakes is due partly to the presence of dissolved salts and partly to scattering by fine particles. C. W. G.

Radioactivity of waters and natural gases. M. GESLIN and D. CHAHNAZAROFF (Ann. Guébhard-Severine, 1933, 9, 312—351).—Apparatus for the determination of the radioactivity of H_2O and natural gases by the boiling method and the agitation method is described, and examples of the calculation are given. The Curie electroscope is also described. A. J. M.

Petroliferous waters. D. A. CHAHNAZAROFF (Ann. Guébhard-Séverine, 1933, 9, 293—299; cf. A., 1933, 588).—The diminution in quantity, or complete absence, of SO_4 in petroliferous waters may be ascribed to the action of anaerobic micro-organisms, which remove O from the SO_4 . The origin of petroliferous formations is related to that of salt. The factors governing the movement of waters are discussed. A. J. M.

Chemistry of sea-mud. F. KRAUSS and A. KOLLATH (Farben-Chem., 1933, 4, 415—416, 447—452).—A review. S. M.

Formation of the earth. R. PERRIN (Compt. rend., 1934, 198, 105—107).—Regarding the earth

as a metal nucleus surrounded by a slag shell with gaseous envelope, its formation might be attributed to the action of O_2 on the nucleus until further action was stopped by accumulated slag (oxides), but the amount of free O_2 remaining in the air is only such that had a layer of, *e.g.*, Fe only 1 m. thick been oxidised in addition none would have remained. Hence it is suggested that the first materials to condense to the liquid state must have been such as would be in equilibrium with their own vapour, that being low even at a high temp., and with O_2 at very low pressure, and have been formed with evolution of much heat. Such substances are CaO , MgO , Al_2O_3 , and SiO_2 , with which last the others would have combined. These would have been deposited before condensation of the metallic nucleus, and at a temp. at which most metallic oxides would be dissociated. Relative d would then operate.

C. A. S.

Luminescence of minerals in relation to their occurrence and their generation. S. KREUTZ (Bull. Acad. Polonaise, 1933, A, 215—225).—The fluorescence excited by ultra-violet light in specimens of fluorite, apatite, topaz, and calcite varies with the colour of the mineral specimen. This phenomenon is discussed from the point of view of the age of the mineral.

J. W. S.

Activity of materials exposed to the natural electric field. H. GARRIGUE (Compt. rend., 1933, 197, 1619—1620).—The rate of disappearance of radioactivity of samples of metal, rock, and grass exposed to the air at the Pic-du-Midi (2860 m.) indicates the predominance of short-lived elements of the Ra family. A piece of Zn examined within 1 hr. of being struck by lightning was specially active.

C. A. S.

Cooperite and braggite occurring in platiniferous concentrates from the Transvaal. R. H. ADAM (J. Chem. Met. Soc. S. Africa, 1933, 34, 132—136).—Analyses are given.

C. W. G.

Reflectivities of sulphide ore-minerals. F. C. PHILLIPS (Min. Mag., 1933, 23, 458—462).—The reflectivity of simple sulphides, selenides, and tellurides shows a progressive increase with at. no. of the combining metal or of S, Se, Te. "Mol. refractivities" of a large no. of complex S-salt minerals calc. from measured reflectivities agree well with the additive "mol. refractivities" of the constituent simple sulphides. This relation gives a method of calculating the reflectivity of an ore-mineral and a check on the d .

L. J. S.

A new barium plagioclase. S. R. NOCKOLDS and F. G. ZIES (Min. Mag., 1933, 23, 448—457).—An aplitic dike rock from Broken Hill, New South Wales, showing an unusual amount of BaO (9.23 or 4.8%) contains a feldspar which gave SiO_2 44.6, Al_2O_3 33.0, CaO 14.0, BaO 5.7, Na_2O 2.0, K_2O 0.7%, corresponding with anorthite 69.2, celsian ($BaAl_2Si_2O_8$) 13.9, albite 8.9, orthoclase 3.9, carnegieite 4.0%. It has d 2.872, n_α 1.571, 1.580, n_γ 1.585, optic axial angle $2V$ 78° of negative sign.

L. J. S.

Action of mineralisers. W. EITEL and W. WEYL (Chem. Erde, 1933, 8, 445—461).—A discussion

of the action of volatile constituents on the viscosity and crystallisation of magmas.

L. J. S.

Vicinal faces of topaz. S. KREUTZ (Bull. Acad. Polonaise, 1933, A, 169—172).—Goniometric measurements have been made on a no. of specimens of topaz, the results being discussed with reference to the conclusions of Schubnikov and Brunovsky (A., 1931, 788).

J. W. S.

Manganese deposit, Bombay (N.Z.). H. E. FYFE (New Zealand J. Sci. Tech., 1933, 15, 203—207).—Bands of compact amorphous psilomelane (H_4MnO_5) occur in "greywacke" areas. The formation, use, and market val. of these deposits are discussed.

A. G. P.

Occurrence of beryllium in vesuvianites. B. A. SILBERMINTZ and E. W. ROSCHKOWA (Zentr. Min. Geol., 1933, A, 249—254; Chem. Zentr., 1933, ii, 1498).—Be was determined colorimetrically with quinalizarin. Of 19 samples, 13 were free from BeO , 3 contained approx. 0.008%, and others 0.01—0.1, 0.09, and 0.18%. Nepheline syenites were free from BeO .

A. A. E.

Thorium minerals as age indicators. R. C. WELLS (J. Washington Acad. Sci., 1933, 23, 541—544).—More wt. than heretofore should be given to Th minerals as age indicators.

C. W. G.

Geology of the iron deposits of the Sierra de Smataca, Venezuela. G. ZULOAGA (Amer. Inst. Min. Met. Eng., Tech. Publ. No. 516, 1933, 36 pp.).—The Fe ores in this locality and their formation and geology are described and discussed. The ores closely resemble those found in Minas Geraes, Brazil; they have a high Fe content combined with low S, P, SiO_2 , and Mn.

A. R. P.

Barite type and its relations to the monoclinic system. W. GRAHMANN (Neues Jahrb. Min., 1933, A, Bl.-Bd., 66, 155—177; Chem. Zentr., 1933, i, 1754).

Barite deposits at Chapsordag and Taptan-Tursy in the Hakassia district. V. DOMAREV (Min. J. Moscow, 1930, 106, No. 2—3, 150).—Analyses are given.

CH. ABS.

Barite deposits in the Urals. M. GORDIENKO (Min. J. Moscow, 1931, 106, No. 12, 122—126).—Kassinskaja Datscha barite contains 97—98% $BaSO_4$ and appreciable quantities of Au and Ag.

CH. ABS.

Bolivian thioannates. F. AHLFELD and H. MORITZ (Neues Jahrb. Min., 1933, A, Bl.-Bd., 66, 179—212; Chem. Zentr., 1933, i, 1755).—The occurrence of thioannates and germanates is discussed; kyllindrite ($Pb_3Sn_4Sb_2S_{14}$), franckeite ($Pb_5Sn_3Sb_2S_{14}$), argyrodite-canfieldite, and wolfsbergite are described. Wolfsbergite contains Cu 25.65, Sb 48.83, Ge 0.91, S 24.42%.

A. A. E.

Genesis of bauxites in the Sann valley, Yugoslavia. E. DITTLER and O. KUHN (Chem. Erde, 1933, 8, 462—495).—Andesites associated with Triassic limestones have been propylitised by post-volcanic processes and afterwards subjected to weathering, resulting in the loss of alkalis, CaO , and SiO_2 , the last combining with the limestone to form

hornstone. The remaining sesquioxides and TiO_2 were hydrated to allites. L. J. S.

Zeolites. V. Mesolite. M. H. HEY [with F. A. BANNISTER] (Min. Mag., 1933, 23, 421—447).—Five new analyses and X-ray measurements on mesolite from various localities give a unit cell, a 56.7, b 6.56, c 18.44 Å., β 90° 0' (space-group C_{2v}^2), containing $\text{Na}_{16}\text{Ca}_{16}\text{Al}_{48}\text{Si}_{72}\text{O}_{210}\cdot 64\text{H}_2\text{O}$. There may be replacement of Ca by 2Na and of Na by K. Crystallographic, optical, and v.-p. (isohydric) measurements were made. Base-exchange products obtained by fusion with KCNS , LiNO_3 , and AgNO_3 are identical with those obtained with natrolite (A., 1933, 141). Mesolite is an independent species, isostructural, but not isomorphous, with natrolite and scolecite. L. J. S.

Electrolyte contents of two clays. F. K. SCHLÜNZ (Chem. Erde, 1933, 8, 504—506).—The sol. constituents of two clays previously examined (A., 1933, 1030) have been determined. L. J. S.

Clay and bauxitic minerals: statistical classification. S. I. TOMKEIEFF (Min. Mag., 1933, 23, 463—482).—689 analyses taken from the literature are plotted on a triangular diagram. Al_2O_3 - SiO_2 - H_2O and frequency curves are drawn for the ratios $\text{SiO}_2:\text{Al}_2\text{O}_3$, $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$, and $\text{H}_2\text{O}:\text{SiO}_2$. This method indicates the existence of only pyrophyllite ($\text{H}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$) and kaolin and its isomerides

($2\text{H}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$) as definite compounds, other clay minerals, to which many names have been applied, being regarded as mixtures of these with Al and Si hydroxides. A similar plot of 320 bauxitic minerals grading to laterite on a diagram Al_2O_3 - Fe_2O_3 - H_2O and frequency curves give clusters and peaks corresponding with diaspore ($\text{H}_2\text{O}, \text{Al}_2\text{O}_3$) and gibbsite ($3\text{H}_2\text{O}, \text{Al}_2\text{O}_3$). Bauxite ($2\text{H}_2\text{O}, \text{Al}_2\text{O}_3$) does not exist. L. J. S.

Weathering and soil formation in Chile. E. BLANCK, A. RIESER, and E. VON OLDERSHAUSEN (Chem. Erde, 1933, 8, 339—439).—Numerous chemical and mechanical analyses are given of weathered rocks and soils from different climatic zones. L. J. S.

Micro-structure of the coal of certain fossil tree barks.—See B., 1934, 49.

Character of the peat deposits of New York. B. D. WILSON and E. V. STAKER (Cornell Univ. Agric. Exp. Sta. Mem., 1933, No. 149, 20 pp.).—A no. of peat profiles are described. In most cases the deposits were high in Ca^{++} and N, the latter being largely in combination with lignocellulose complexes (I). The org. matter contains higher proportions of hemi-cellulose than of cellulose, although both are exceeded by that of (I). The character of the peats is closely related to the nature of the underlying material.

A. G. P.

Organic Chemistry.

Organic pseudo-compounds as reagents for active atoms in organic molecules. M. REBEK (Bull. Soc. Chim. Yougoslav., 1933, 4, 79—84).—The time t necessary for attainment of max. conductivity κ after mixing COMe_3 or PhNO_2 solutions of hexamethyl-*p*-rosaniline (I) and various ψ -acids varies from 0 for $\text{NH}[\text{C}_6\text{H}_2(\text{NO}_2)_3]_2$ to 55 hr. for $\text{CH}[\text{C}_6\text{H}_3(\text{NO}_2)_2]_3$ (II); for carboxylic acids t varies from 388 min. for maleic to 2652 min. for glutaric acid. The vals. of t are independent of the P_κ of the given acid. Various org. halides react as ψ -acids with (I), the κ - t curves being similar to those obtained with carboxylic acids in the case of CPh_3Cl , and to that given with (II) in the case of picryl chloride, C_2HCl_5 , and C_3HCl_7 ; in the latter cases, the reaction is one of zero order. R. T.

Dynamics and mechanism of aliphatic substitutions.—See this vol., 151.

Pyrolysis of *n*-butane at low decomposition temperatures. C. D. HURD, C. I. PARRISH, and F. D. PILGRIM (J. Amer. Chem. Soc., 1933, 55, 5016—5019).— H_2 (trace), CH_4 , C_2H_6 , C_3H_8 , and C_4H_{10} are obtained when n - C_4H_{10} is passed through a Pyrex tube at 365°, 400°, and 415°; the total decomp. is 0.46, 2.6, and 5%, respectively. Fission at a particular C-C linking does not occur (cf. Norris and Thomson, A., 1931, 1147). H. B.

Pyrolysis of hydrocarbons. Butanes. C. D. HURD and F. D. PILGRIM (J. Amer. Chem. Soc., 1933, 55, 4902—4907; cf. A., 1930, 58).—Decomp. of *n*- (I) and *iso*-butane occurs to the same extent (for a const. temp.) when tubes of widely differing size are used

provided the contact time is the same; variation in the latter alters the amount of decomp. Pyrolysis in Fe, Ni, or quartz tubes at 600° occurs in practically the same manner; monel metal exerts a pronounced catalytic action and the decomp. products are largely C and H_2 . *iso*Butene is not produced from (I) (cf. *loc. cit.*), showing that rearrangement of the C chain does not occur. H. B.

Thermal decomposition of hexane.—See this vol., 151.

Action of aluminium chloride on *n*-hexane and *n*-heptane, alone and in presence of halogen derivatives. Conversion of paraffin into cyclo-paraffin hydrocarbons. C. D. NENITZESCU and A. DRAGAN (Ber., 1933, 66, [B], 1892—1900).—The action of AlCl_3 [freshly sublimed (I) or moist (II)] on *n*-hexane at 68—69° leads to very little combustible gas, a large proportion of β - or γ -methylpentane or a mixture thereof, $\text{C}_{15}\text{H}_{12}$, and dehydrogenated products among which cyclohexane (III) is identified. Compounds boiling at a higher temp. than (III) are not observed. The quantity of (III) depends on the duration of reaction. (III) and AlCl_3 in presence of AcCl give the same products and in approx. the same ratio as in its absence and also saturated fractions b.p. < 248°, including monocyclic hydrocarbons among which 1:3-dimethylcyclohexane (IV) is present and dicyclic compounds, mainly $\text{C}_{12}\text{H}_{22}$. (I) and *n*-heptane (V) yield exclusively saturated products, which are produced in addition to polymerised olefines when (II) is used. With (II) C_7H_8 and *isobutane* are evolved, also obtained with (I) after addition of

H₂O. C₁₅H₁₂, β - or γ -methylpentane, and *iso*-heptane are formed. (IV) and large amounts of dicyclic hydrocarbons, C₁₄H₂₆, are produced. The lower layer formed when (II) is used gives, after addition of H₂O, a heptene or methylcyclohexene and, mainly, a product C₁₄H₂₄; the non-volatile fraction has the approx. composition, (C₇H₁₁)_n. In presence of EtCl, Prⁿ-Cl, Pr^{iso}-Cl, or BuCl (V) reacts very vigorously with AlCl₃, the halide being reduced to hydrocarbon so completely that a preparative method is indicated. (V) is very little converted into simpler hydrocarbons, whereas large quantities of cycloparaffins of higher b.p. and a considerable lower layer containing olefines result. H. W.

Octanes. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1933, 55, 5056).—All the structurally isomeric octanes have been synthesised; references are given. H. B.

Direct preparation of divinyl from alcohol. I. S. V. LEBEDEV (J. Gen. Chem. Russ., 1933, 3, 698—717).—The product obtained by passing EtOH vapour over an unspecified mixed catalyst consists of: H₂ 1.3—1.6, CO 0.2—0.5, CH₄ 0.4—0.6, C₂H₄ 5—8, butene 3—4, divinyl 20—25, pentene, piperilene, hexene, hexadiene, and *p*-xylene each 0.4—0.8, PhMe 0.1—0.2, Et₂O 2—5, EtOBu 0.05—0.1, BuOH 2—4, crotyl alcohol 0.5—1, amyl and hexenyl alcohol 0.5—0.8, octyl alcohol 0.3, MeCHO 2.5—5, PrCHO 0.1—0.2, crotonaldehyde 0.05, COMe, 0.3—0.5, and COMeEt 0.1—0.2%. The mechanism of formation of the above compounds from "nascent" C₂H₄ and MeCHO is discussed. R. T.

Syntheses in the olefine series. V. Hexenes, heptenes, and octenes. I. SCHURMAN and C. E. BOORD (J. Amer. Chem. Soc., 1933, 55, 4930—4935).—CMc₂Prⁿ-OH is dehydrated (anhyd. H₂C₂O₄) to CMc₂:CMc₂, b.p. 72.9—73.2°/760 mm., m.p. -76.4°, and $\beta\gamma$ -dimethyl- Δ^a -butene, b.p. 55.6—56°/760 mm., m.p. -123° to -120°. $\gamma\gamma$ -Dimethyl- Δ^a -butene, b.p. -41.2°/760 mm., $\gamma\gamma$ -dimethyl- Δ^a -pentene, b.p. 76.9°/760 mm. (dibromide, b.p. 95.3—95.6°/10 mm.), $\delta\delta$ -dimethyl- Δ^b -pentene, b.p. 76—76.1°/760 mm. (dibromide, b.p. 92.8—93°/14 mm.), $\delta\delta$ -dimethyl- Δ^b -hexene, b.p. 105.4—106°/760 mm. (dibromide, b.p. 93°/4 mm.), and $\beta\beta$ -dimethyl- Δ^c -hexene, b.p. 100.1°/760 mm. (dibromide, b.p. 96.5—97°/8 mm.), are prepared by the Tschugaev method from CHMeBuⁿ-OH (*Me xanthate*, b.p. 85—87°/6 mm.), methyltert.-amylcarbinol (*Me xanthate*, b.p. 110—112°/8 mm.), CHETBuⁿ-OH (*Me xanthate*, b.p. 92—92.5°/5 mm.), ethyltert.-amylcarbinol (*Me xanthate*, b.p. 118—120°/8 mm.), and CHPrⁿBuⁿ-OH (*Me xanthate*, b.p. 112—114°/8 mm.), respectively. The absence of rearrangement in the preps. is shown by reduction (H₂, PtO₂, EtOH) of the olefines to the corresponding paraffins. H. B.

Ethylenic and saturated hydrocarbons from γ_8 to γ_{10} . M. TUOR (Compt. rend., 1933, 197, 695).—Physical consts. for $\beta\delta$ -dimethyl- Δ -hexene (*loc. cit.*, erroneously given as heptene), b.p. 109°/737 mm.; $\beta\epsilon$ -di-, b.p. 111°/739 mm., and $\beta\gamma\epsilon$ -tri-, b.p. 125°/741 mm., -methyl- Δ^b -hexene; $\beta\delta$ -, b.p. 131°/749 mm., and $\beta\epsilon$ -dimethyl-

Δ^b -, b.p. 137°/747 mm., and $\beta\delta\zeta$ -trimethyl- Δ^c -, b.p. 142°/740 mm., -heptene; $\beta\delta$ -di-, b.p. 154°/752 mm., and $\beta\delta\eta$ -tri-, b.p. 168°/739 mm., -methyl- Δ^b -octene, are given. γ -Methylheptan- γ -ol, b.p. 67°/14 mm., affords γ -methyl- Δ^b -heptene, b.p. 121°/750 mm. Catalytic reduction (Adams) of these affords: $\beta\delta$ -, b.p. 108°/750 mm., and $\beta\epsilon$ -, b.p. 107°/747 mm., -dimethyl-, and $\beta\gamma\epsilon$ -trimethyl-, b.p. 129°/738 mm., -n-hexane; γ -methyl-, b.p. 116.5°/747 mm., $\beta\delta$ -, b.p. 130°/749 mm., and $\beta\epsilon$ -, b.p. 133°/741° mm., -dimethyl-, and $\beta\delta\zeta$ -trimethyl-, b.p. 143°/746 mm., -n-heptane; $\beta\delta$ -di-, b.p. 152.5°/746 mm., and $\beta\delta\eta$ -tri-, b.p. 167.5°/746 mm., -methyl-n-octane. J. W. B.

Mechanism of photopolymerisation of acetylene. W. KEMULA and S. MRAZEK (Z. physikal. Chem., 1933, B, 23, 358—369).—Absorption spectrum measurements during polymerisation have shown the presence of C₆H₆ vapour, C₁₀H₈ derivatives, and C₄H₄. A yellowish-white solid settles out of the gas phase, and analysis of the latter shows the presence of small amounts of C₂H₄ and C₂H₆. The first step in the polymerisation is probably 2C₂H₂ \rightarrow C₄H₄, and the C₁₀H₈ ring is probably synthesised by C₆H₆ + C₄H₄ \rightarrow C₁₀H₁₀. R. C.

sec.-isoAmyl chloride, γ -chloro- β -methylbutane. F. C. WHITMORE and F. JOHNSTON (J. Amer. Chem. Soc., 1933, 55, 5020—5022).—Addition of HCl to CH₃:CHPrⁿ at room temp. (method; Kharasch and Mayo, A., 1933, 805) gives a 90% yield of a 1:1 mixture of γ -chloro- β -methylbutane (I), b.p. 91.8—91.9°/736 mm., and *tert.*-amyl chloride; the latter is removed from the mixture by hydrolysis (H₂O). (I) is unaffected by heating at 100° for 24 hr.; the structure is shown by the formation of CHMePrⁿ-OH from its Grignard reagent and O₂. H. B.

Replacement of strongly positive hydrogen by halogen. III. Reactions of hypohalogenites. F. STRAUS and R. KUHNEL [in part with H. WOLLSCHITT and L. SALZMANN] (Ber., 1933, 66, [B], 1834—1846; cf. A., 1930, 1158).— γ -Methyl- Δ^a -buten- γ -ol (I), b.p. 28.5—29.5°/19 mm. (*p*-nitrobenzoate, m.p. 115°), is converted by alkaline hypobromite into α -bromo- γ -methyl- $\beta\gamma$ -oxidobutane, b.p. 50.5—51.5°/15 mm., transformed by H₂SO₄ at 55° into α -bromo- γ -methylbutane- $\beta\gamma$ -diol, m.p. 48—49° (non-cryst. acetate), which is oxidised by HNO₃ (*d* 1.25—1.26) to α -hydroxyisobutyric acid and by Beckmann's mixture to CH₂Br-CO₂H. Reaction is largely independent of the concn. of alkali provided that non-bleaching solutions are used and the presence of BrO₃' is avoided. Use of excess of KOBr leads to the production of material rich in Br from which CBr₄ is isolated. Addition of I in KI to (I) suspended in KOH-EtOH affords α -iodo- γ -methyl- $\beta\gamma$ -oxidobutane, b.p. 59°/13 mm., converted into α -iodo- γ -methylbutane- $\beta\gamma$ -diol, m.p. 54—55°. (I) does not react with OCl'. Reaction is not universally applicable to *tert.*-allyl alcohols. Thus, γ -ethyl- Δ^a -penten- γ -ol affords α -bromo- γ -ethyl- $\beta\gamma$ -oxidopentane, b.p. 72—73°/12.5 mm., and δ -methyl- Δ^b -penten- δ -ol, b.p. 54°/33 mm., yields CBr₄ and β -bromo- δ -methyl- $\gamma\delta$ -oxidopentane, converted by 1% H₂SO₄ into β -bromo- δ -methylpentane- $\gamma\delta$ -diol, m.p. 96—97°, oxidised

to $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. Reaction does not take place with α -phenyl- γ -methyl- Δ^4 -buten- γ -ol. The intermediate replacement of positive H by OBr' is postulated with formation of a hypobromous ester, which becomes stabilised by isomerisation. $\text{CMe}_2\cdot\text{CHMe}$ is slowly converted by OBr' into $\beta\gamma$ -oxido- β -methylbutane, b.p. $73\text{--}74^\circ/751\text{ mm.}$, and thence into CBr_4 . $\text{CMe}_3\cdot\text{OH}$ and $\text{CMe}_3\text{Et}\cdot\text{OH}$ slowly give CBr_4 ; EtOH is attacked more rapidly than MeOH . $\text{CH}_2\text{Ph}\cdot\text{OH}$ is dehydrogenated by OBr' to PhCHO , which is then rapidly transformed into BzOH ; reactions occur much more slowly with OCl' . Cinnamaldehyde (II) with 2 OBr' yields phenylglycidic acid and brominated products, and is thence degraded to BzOH ; $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ is formed only in minor amount. (II) and OCl' afford PhCHO in 70% yield accompanied by very small amounts of acidic oxidation products. $\text{CH}_2(\text{CO}_2\text{H})_2$ and OCl' give dichloromalononic acid, decomp. $111\text{--}111.5^\circ$ [NH_2Ph salt, m.p. 101.5° (decomp.)]; dianilide, m.p. $129\text{--}130^\circ$, indifferent towards SOCl_2 . $\text{CBr}_2(\text{CO}_2\text{H})_2$, m.p. $130\text{--}131.5^\circ$, is derived similarly. H. W.

Micro-determination of methyl alcohol in presence of large quantities of homologous alcohols. M. FLANZY (Compt. rend., 1934, 198, 94—97).—Accurate micro-determination of MeOH (x mg.) in presence of EtOH (y mg.) and other homologues is effected by conversion of the primary alcohols into their iodides (Zeisel-Fanto) under distillation conditions ($43\text{--}50^\circ$) such that all MeI and some EtI are distilled into aq. AgOAc , whence, by distillation, the alcohols are regenerated. Oxidation of the distillate (50 c.c.) with cold $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ and iodometric determination of excess of CrO_3 gives the oxidation index (p =mg. O required), the wt. of AgI (P mg.) formed being determined after boiling the residue with aq. HNO_3 . Then $x=2\times 32(p/32-P/234.8)$ and $y=3\times 46(P/238.4-p/48)$. By this method 0.1% of MeOH may be determined and its presence in fermented liquors is thus proved.

J. W. B.

Cryoscopic behaviour of alcohol on aqueous solution. E. BERNER (Ber., 1933, 66, [B], 1917—1921).—Mainly a reply to Pringsheim *et al.* (A., 1933, 1144). Re-examination of the behaviour of EtOH and inulin in freezing H_2O at very small concns. does not show any abnormality, and confirms the principle of additivity. The unusual behaviour of α -methylglucoside and sucrose in boiling H_2O at great dilution could not be confirmed.

H. W.

Colour reaction for glycerol. K. TAUFEL and H. THALER (Z. anal. Chem., 1933, 95, 235—239; cf. B., 1932, 849).— $0.5\text{--}1\times 10^{-4}$ g. of glycerol present in a mixture may be detected by conversion into epihydrinaldehyde (I) by way of acraldehyde. (I) is then recognised by the development of a red colour with phloroglucinol. Glycol, mannitol, and various carbohydrates give a negative result. Details are given. F. L. U.

Ascaryl alcohol. F. N. SCHULZ and M. BECKER (Biochem. Z., 1933, 265, 253—259).—Ascaryl alcohol, $\text{C}_{33}\text{H}_{68}\text{O}_4$ (cf. $\text{C}_{32}\text{H}_{64}\text{O}_4$, Flury, A, 1912, ii, 464), m.p. 84° , contains two active H, does not contain

a double linking, gives a *diacetate*, m.p. 52° , without active H, a *dibenzoate*, m.p. 37° , contains glyceryl (I), and gives acraldehyde on heating, but (I) cannot be separated by hydrolysis. P. W. C.

Synthesis of *dl*-mannitol, *allodulcitol*, and *dl*-mannose. LESPIEAU and WIEMANN (Bull. Soc. chim., 1933, [iv], 53, 1107—1110).—Partly reviewed previously (A., 1932, 718; 1933, 47). 100 g. of divinyl glycol give 11 g. of mannitol and 15 g. of *allodulcitol*, new m.p. $149\text{--}150^\circ$ [dibenzylidene derivative, new m.p. $249\text{--}250^\circ$ (block)], but by more prolonged oxidation less alcohols and some *dl*-mannose. R. S. C.

Anhydrides of mannitol. P. BRIGL and H. GRÜNER (Ber., 1933, 66, [B], 1945—1949).—Mannitol $\alpha\zeta$ -dibenzoate is converted at $200^\circ/\text{vac.}$ or preferably in boiling $\text{C}_2\text{H}_2\text{Cl}_4$ into *anhydromannitol dibenzoate* (I), m.p. $137\text{--}138^\circ$, $[\alpha]_D +3.2^\circ$ in abs. EtOH , and *dianhydromannitol dibenzoate* (II), m.p. 133° , $[\alpha]_D +225.7^\circ$ in CHCl_3 . (I) is not an intermediate in the production of (II). (I) does not yield reducing substances with $\text{Pb}(\text{OAc})_4$ and does not condense with COMe_2 , CH_2O , or PhCHO . (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ gives *anhydromannitol dibenzoate di-*p*-toluenesulphonate*, m.p. 142° , $[\alpha]_D +57.9^\circ$ in CHCl_3 , identical with that described by Müller *et al.* (A., 1933, 931). (II) is unaffected by treatment with $\text{Ac}_2\text{O}\text{--C}_5\text{H}_5\text{N}$ or boiling Ac_2O , but with Ac_2O containing H_2SO_4 yields a *compound*, m.p. 140° , containing S. Mannitol $\alpha\beta\zeta$ -tetrabenzoate and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in $\text{C}_5\text{H}_5\text{N}$ give *mannitol $\alpha\beta\zeta$ -tetrabenzoate di-*p*-toluenesulphonate*, m.p. $136\text{--}137^\circ$, $[\alpha]_D -4.8^\circ$ in CHCl_3 , converted by NaOAc and boiling Ac_2O into ill-defined products; similar treatment has no effect on mannitol hexabenzoate. H. W.

Photochemical reactions of *o*-nitrobenzylideneacetals. VIII. (1 : 2 : 5 : 6-Di-*o*-nitrobenzylidenedulcitol.) I. TANASESCU and E. MACOVSKI (Bull. Soc. chim., 1933, [iv], 53, 1097—1102; cf. A., 1933, 393).—1 : 2 : 5 : 6-Di-*o*-nitrobenzylidenedulcitol (I), m.p. $256\text{--}258^\circ$, when illuminated, gives a resin, possibly by partial isomerisation. Its Bz_2 derivative, m.p. 310° , gives 3 : 4-dibenzoyl-1 : 6-di-*o*-nitrosobenzoyldulcitol, m.p. 128° after sintering at $108\text{--}110^\circ$ [corresponding Bz_4 derivative, m.p. about 110° (decomp.)]. These and similar reactions are considered in the light of the fact that (I) has three reactive H atoms. R. S. C.

Ester enolates and keten acetals. XVI. Carbon suboxide tetraethylacetal as intermediate in the transformation of ethyl $\beta\beta$ -diethoxyacrylate into ethyl diethylmalonate. H. SCHEIBLER and H. STEIN (Ber., 1933, 66, [B], 1784—1789).—Et $\beta\beta$ -diethoxyacrylate (I) and CNaPh_3 yield the corresponding enolate; heating of the mixture with EtOBz and extraction of the product with Et_2O leads to the isolation of NaOBz in small amount, thus indicating the incidence of keten acetal fission, the expected product of which could not be isolated. (I) and NaOEt (mol. ratio 2 : 1) at 130° yield EtOH , $\text{CHet}(\text{CO}_2\text{Et})_2$, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and $\text{C}(\text{CO}_2\text{Et})_4$ (II). Carbon suboxide tetraethylacetal appears to be an intermediate in the formation of (II). H. W.

Alkyl and aryl bromosulphites. P. CARRE and D. LIBERMANN (Compt. rend., 1933, 197, 1326—1328).—By interaction of the appropriate alkyl sulphite with SOBr_2 in Et_2O at room temp. are obtained: *Et*, b.p. 67–70°/30 mm., *Pr*, b.p. 90–93°/30 mm., *Pr*^β, b.p. 72–74°/30 mm., *Bu*^a, b.p. 105–107°/30 mm., *β-chloroethyl*, b.p. 118–120°/40 mm. (from *β-chloroethyl sulphite*, b.p. 146–148°/45 mm.), and *Ph*, b.p. 131–134°/40 mm., bromosulphites. All are less stable than the corresponding chlorosulphites (A., 1933, 696), which they otherwise resemble in properties. J. W. B.

Identification of mercaptans with 1-chloro-2:4-dinitrobenzene. II. R. W. BOST, J. O. TURNER, and M. W. CONN (J. Amer. Chem. Soc., 1933, 55, 4956–4957).—The following are prepared as described previously (A., 1932, 719): (a) 2:4-(NO_2)₂ $\text{C}_6\text{H}_3\text{SR}$, where R is *decyl*, m.p. 85° (all m.p. are corr.), *undecyl*, m.p. 90°, *lauryl*, m.p. 89°, *allyl*, m.p. 71–5°, *o-tolyl*, m.p. 101°, *m-tolyl*, m.p. 90–5°, *p-chlorophenyl*, m.p. 123°, *p-bromophenyl*, m.p. 142°, $\alpha\text{-C}_{10}\text{H}_7$, m.p. 176°, $\beta\text{-C}_{10}\text{H}_7$, m.p. 145°, *cyclohexyl*, m.p. 148°, and *β-hydroxyethyl*, m.p. 100–5°; (b) $\alpha\beta\text{-di-2:4-dinitrophenylthioethane}$, m.p. 248°; $\alpha\beta$, m.p. 226°, and $\alpha\gamma$, m.p. 194°, *-di-2:4-dinitrophenylthiolpropanes*; $\alpha\delta\text{-di-2:4-dinitrophenylthiolbutane}$, m.p. 176°; $\alpha\epsilon\text{-di-2:4-dinitrophenylthiopentane}$, m.p. 170°; $\alpha\zeta\text{-di-2:4-dinitrophenylthiohexane}$, m.p. 218°; (c) 2:4-(NO_2)₂ $\text{C}_6\text{H}_3\text{SO}_2\text{R}$, where R is *decyl*, m.p. 93°, *undecyl*, m.p. 97°, *lauryl*, m.p. 101°, *cetyl*, m.p. 105°, *o-tolyl*, m.p. 155°, *m-tolyl*, m.p. 144–5°, *p-chlorophenyl*, m.p. 170°, *p-bromophenyl*, m.p. 190°, and *cyclohexyl*, m.p. 172°. H. B.

Thermal decomposition of propyl mercaptan.—See this vol., 151.

Basis for the physiological activity of -onium compounds. XV. Sulphonium compounds. R. R. RENSHAW and D. S. SEARLE (J. Amer. Chem. Soc., 1933, 55, 4951–4953).—Sulphides are condensed with the appropriate halide and $\text{HgBr}_2(\text{I}_2)$ in COMe_2 or EtOH and the resulting sulphonium halide mercurihalides converted into the stable sulphonium nitrates by treatment with solid AgNO_3 in COMe_2 and subsequent removal of Hg as HgS . The following are described: *dibenzylmethylsulphonium nitrate*, m.p. 79°, and iodide mercuri-iodide, m.p. 155°; *dibenzylcarbethoxymethylsulphonium nitrate*, m.p. 120°, bromide mercuribromide, and bromide mercuri-iodide, m.p. 120°; *diphenylmethylsulphonium nitrate*, m.p. 108°, and iodide mercuri-iodide, m.p. 95°; *dimethyl-β-phenoxyethylsulphonium nitrate*, m.p. 62–65°, and bromide mercuribromide, m.p. 70–71°; *diethyl-β-phenoxyethyl-*, m.p. 78°, and *dibenzylcarbethoxymethyl-*, m.p. 127°, -sulphonium bromide mercuribromides; *dipropylcarbethoxymethylsulphonium bromide*, m.p. 70°. H. B.

Dynamics of elimination of tert.-butyl from sulphonium compounds.—See this vol., 152.

Mixed sulphonic anhydrides. I. Preparation of acetosulphonic anhydrides. A. BARONI (Atti R. Accad. Lincei, 1933, [vi], 17, 1081–1086).—By the action of dry NaOAc or AgOAc on the corresponding sulphonyl chlorides, anhydrides of the follow-

ing acids are obtained (b.p. /20 mm.): *acetomethanesulphonic*, b.p. 100°; *acetoethanesulphonic*, b.p. 115–117°; *acetobenzenesulphonic*, b.p. 160–161°; *aceto-p-toluenesulphonic*, b.p. 186–188°. T. H. P.

Determination of alkyl hydrogen sulphates in dilute solutions. W. KLING and F. PUSCHEL (Textilber., 1934, 15, 21–23).—Alkyl H sulphates and inorg. sulphates are pptd. together from their slightly acid solution by benzidine hydrochloride; after filtration, the benzidine alkyl sulphate is separated from the benzidine sulphate by extraction with hot EtOH and then determined with 0.01N-KOH using bromocresol as indicator. A. J. H.

Halogenation. V. Bromination and iodination of fatty acids. P. S. VARMA and V. T. S. MENON (J. Indian Chem. Soc., 1933, 10, 591–592).— $\alpha\text{-Br-}$ and $\alpha\text{-I-}$ derivatives are obtained when AcOH (or Ac_2O), EtCO_2H , $(\text{PrCO})_2\text{O}$, $\text{Pr}^i\text{CO}_2\text{H}$, and lauric, palmitic, and stearic acids are heated with conc. H_2SO_4 and KBr and I, respectively; the higher acids are dissolved in CCl_4 . The yields are poor with the lower acids; those from AcOH (or Ac_2O) are improved slightly by replacing the H_2SO_4 with a mixture of fuming HNO_3 and nitrosulphonic acid (from HNO_3 and SO_2). H. B.

Determination of acetic anhydride. E. BERL and H. TURCK (Z. anal. Chem., 1933, 95, 143–152).— Ac_2O is determined calorimetrically by measurement of the heat of hydration of a 10-c.c. sample by 200 c.c. of 15% AcOH containing 7% of HCl as catalyst, contained in a Dewar vessel. For the analysis of acetylation mixtures of Ac_2O and H_2SO_4 , Ac_2SO_4 in a portion is converted into sulphoacetic acid by heating at 60°. The difference in the temp. rise produced by this and an untreated sample is a measure of the H_2SO_4 content. J. S. A.

Catalytic reduction of trifluoroacetic anhydride and trifluoroethyl alcohol. F. SWARTS (Compt. rend., 1933, 197, 1261–1264).—With H_2 at 20–40°/45–50 atm. and Pt-black (CF_3CO)₂ O (alone or in Bu_2O solution) affords $\beta\beta\beta\text{-trifluoroethyl trifluoroacetate}$ (I), b.p. 55.0°/760 mm., m.p. –65.5° (main product), $\beta\beta\beta\text{-trifluoroethyl alcohol}$ (II), b.p. 74.05°, m.p. –43.5° (*Ac* derivative, b.p. 77.85°, with AcCl), $\text{CF}_3\text{CO}_2\text{H}$ (III), and $\alpha\alpha\alpha\text{-trifluoroethane}$ (IV), b.p. –46.8°, f.p. –107°: (III) is separated from (II) only as its azeotropic mixture, b.p. 144° [26.3% of (III)], with Bu_2O . With $\text{CrO}_3\text{-H}_2\text{SO}_4$ oxidation of (II) is slow, giving (III) but no aldehyde. With PBr_5 (II) affords $\beta\text{-bromo-}\alpha\alpha\alpha\text{-trifluoroethane}$, b.p. 26.5°, and with H_2SO_4 (followed by BaCO_3) *Ba trifluoroethyl sulphate*, $+\text{H}_2\text{O}$, is obtained. (I) is readily hydrolysed to (II) and (III) by cold H_2O . With Cl_2 in sunlight (IV) gives $\beta\beta\beta\text{-trichloro-}\alpha\alpha\alpha\text{-trifluoroethane}$, b.p. 46°, f.p. 13°. J. W. B.

Odour and constitution of some esters of heptioic and δ-methylhexoic acids. B. ROTHSTEIN (Bull. Soc. chim., 1933, [iv], 53, 1106–1107).—The following *n-heptoates* are described: CH_2Ph , b.p. 157°/14.5 mm., CH_2PhCH_2 , b.p. 167°/14.5 mm., *phenylpropyl*, b.p. 180°/15 mm., *hydratropyl*, b.p. 172°/15 mm., *geranyl*, b.p. 171°/15 mm., and *terpinyl*, b.p. 170°/15 mm. The corresponding $\delta\text{-methylheptoates}$

have b.p. 160°/18 mm., 167°/17 mm., 180°/18 mm., 172°/18 mm., 172°/17 mm., and 170°/18 mm., respectively. The odours of the esters are similar to, but more fatty and feebler than, those of the alcohols.

R. S. C.

Reactions of castor oil with citric acid and phthalic anhydride. R. ODA (J. Soc. Chem. Ind. Japan, 1933, 36, 623—625B).—Castor oil and citric acid (I) at 150—170° or o -C₆H₄(CO)₂O at 190—245° in CO₂ gives multimol. products. Reaction with (I), but not with CH₂Cl·CO₂H, proceeds better at 20—40 mm.

R. S. C.

Phenylmethylhydrazones of glyoxylic acid and its methyl ester. M. BUSCH and W. RENNER (Ber., 1933, 66, [B], 1770—1771).—The compounds described by Meyer (A., 1904, i, 970) as the phenylmethylhydrazone and *p*-nitrophenylhydrazone of Me glyoxylate are derivatives of glyoxylic acid.

H. W.

Reactions and reagents for the identification of organic compounds. II. E. EGGRIWE (Z. anal. Chem. 1933, 95, 323—327; cf. A., 1932, 931).—Colour and fluorescence reactions for the detection of glyceric, lactic, pyruvic, and tartaric acids are given, and the behaviour of certain other OH- and keto-acids is recorded.

J. S. A.

Alkylation of enolates. II. F. ADICKES (Ber., 1933, 66, [B], 1984).—The observations of Wanag (this vol., 77) confirm the author's view (A., 1933, 697) that *C*-alkylation does not necessarily occur through the *O*-ether.

H. W.

Polymerisation and ring formation. XIX. Many-membered cyclic anhydrides. XX. Many-membered cyclic esters. XXI. Physical properties of macrocyclic esters and anhydrides. XXII. Stereochemistry and mechanism in the formation and stability of large rings. J. W. HILL and W. H. CAROTHERS (J. mer. Chem. Soc., 1933, 55, 5023—5031, 5031—5039, 5039—5043, 5043—5052).—XIX. When CH₂(CO₂H)_{*n*} (*n*=4—12 and 16) are heated with c₂O, α-anhydrides (I) are obtained. These are linear polyamides (*M*=3000—5000) of the type $\text{O} \cdot \text{CO} \cdot [\text{CH}_2]_n \cdot \text{CO} \cdot \text{O} \cdot \text{CO} \cdot [\text{CH}_2]_n \cdot \text{CO} \cdot \text{O} \cdot \text{CO} \cdot [\text{CH}_2]_n \cdot \text{CO} \cdot$; with NH₂Ph, they give the anilide, anilic acid, and original acid in the ratio 1:2:1. (I) heated in a mol. still (cf. A., 1932, 601) give volatile β-anhydrides (II) and the more complex ω-anhydrides (III). (II) are cyclic mono- or di-meric anhydrides which when kept, or heated above the m.p., pass into γ-anhydrides (probably large rings) which resemble (I). The monomeric (II) are usually liquids or low-melting solids which polymerise very readily; with NH₂Ph, the anilic acid is the sole product. The dimeric (II) polymerise instantly above their m.p.; with NH₂Ph, they give the same products (in the same ratio) as (I). (III) are tough, opaque solids which can be drawn into pliable, highly-oriented fibres; they are depolymerised by heating in a mol. still to (II). The following derivatives are described: *pinelic α-anhydride*, m.p. 53—55°, and *mono*-, m.p. 108—109°, and *di*-, m.p. 155—156°, *-anilides*; *suberic α-anhydride*, m.p. 65—66°, β-anhydride (dimeric), m.p. 55—57°, and *mono*-, m.p. 128—129°, and *di*-, m.p. 186—187°,

-anilides; *azelaic α-anhydride*, m.p. 53—53·5°, and *mono*-, m.p. 107—108°, and *di*-, m.p. 186—187°, *-anilides*; *nonamethylene-α-dicarboxylic α-anhydride*, m.p. 69—70°, and *mono*-, m.p. 112·5—113°, and *di*-, m.p. 160—161°, *-anilides*; *decamethylene-α-dicarboxylic α-anhydride*, m.p. 86—87°, β-anhydride (dimeric), m.p. 76—78°, and *mono*-, m.p. 123°, and *di*-, m.p. 170—171°, *-anilides*; *undecamethylene-α-dicarboxylic α-anhydride*, m.p. 76—78°, and *mono*-, m.p. 118·5—119·5°, and *di*-, m.p. 160—161°, *-anilides*; *dodecamethylene-α-dicarboxylic α-anhydride*, m.p. 89—91°, and *mono*-, m.p. 124—125°, and *di*-, m.p. 169·5—170°, *-anilides*; *hexadecamethylene-α-dicarboxylic α-anhydride*, m.p. 94—95°, and *mono*-, m.p. 128—129°, and *di*-, m.p. 162—163°, *-anilides*.

XX. (cf. A., 1930, 319). Polymeric polymethylene carbonates are prepared from (CH₂)_{*n*}(OH)₂ (*n*=5, 7—9, 11—14, and 18), Bu₂CO₃, and a little Na at 170—220°; the crude esters are then depolymerised to the monomeric and/or dimeric esters by heating in a vac. Other polymeric esters are similarly depolymerised. The following are described: (a) monomeric esters: *octa*-, b.p. 74—76°/0·5 mm., m.p. 21·5—23°, *nona*-, b.p. 63—64°/0·1 mm., m.p. 34—35°, *deca*-, (I), b.p. 92—93°/1 mm., m.p. 10—11°, *undeca*-, b.p. 104·5°/7 mm., m.p. 40—41°, *dodeca*-, b.p. 118—119°/3 mm., m.p. 11—12°, *trideca*-, b.p. 149—150°/4·5 mm., m.p. 23—24·5°, *tetradeca*-, b.p. 144—146°/2 mm., m.p. 21—22°, and *octadeca*-, b.p. 165—169°/1 mm., m.p. 36—37°, *-methylene carbonates*; *tetraethylene carbonate*, b.p. 128—130°/1 mm., m.p. 42—44°; *deca*-, b.p. 125—126°/0·2 mm., and *undeca*-, b.p. 120—123°/0·5 mm., m.p. 23—24·5°, *-methylene oxalates*; *decamethylene malonate*, b.p. 117—118°/0·5 mm.; *ethylene sebacate*, m.p. 40—41°, and *nonamethylene-α-dicarboxylate*, m.p. 35°; (b) dimeric esters: *penta*-, m.p. 117—118°, *hexa*-, m.p. 128—129°, *hepta*-, m.p. 97—98°, *octa*-, m.p. 116—117°, *nona*-, m.p. 95—95·5°, *deca*-, m.p. 105—106°, *undeca*-, m.p. 97—97·5°, and *dodeca*-, m.p. 93—95°, *-methylene carbonates*; *decamethylene succinate*, m.p. 108—109°; *ethylene sebacate*, m.p. 80—81°, *nonamethylene-α-dicarboxylate*, m.p. 143°, *decamethylene-α-dicarboxylate*, m.p. 95—96°, *undecamethylene-α-dicarboxylate*, m.p. 145—146°, and *dodecamethylene-α-dicarboxylate*, m.p. 102—103°; *trimethylene sebacate*, m.p. 108—110°; *self ester*, m.p. 83—84°, of ξ-hydroxypentadecic acid. Δ¹-*Decen-α-ol*, b.p. 85—86°/2 mm. (*phenylcarbamate*, m.p. 49—50°), has been obtained as a by-product during the prep. of (I). Macrocyclic (*i.e.*, rings of > 7 atoms) esters do not polymerise spontaneously; they polymerise when heated at 200° in presence of a little K₂CO₃.

XXI. The odours of the above monomeric cyclic anhydrides and esters (I) resemble those of ketones and lactones of the same ring size; those containing 14—19 atoms in the ring thus possess musk-like odours. The mol. refractions of (I) show negative exaltation. The m.p. of the monomeric polymethylene carbonates alternate.

XXII. Th. hexadecamethylene-α-dicarboxylate heated in *s*-dixylylethane at 325° for 2 hr. gives a *polyketone*, probably CO₂H·[(CH₂)₁₆·CO]₇·OH, m.p. 126—128° (*Na* salt), which passes at 300—305° in a mol. still into cycloheptadecanone. The synthesis of large

ring ketones is considered to involve the intermediate formation of a linear polyketone which then decomposes; the changes are similar to those found for esters and anhydrides (above). The analogies and differences in the three series can be explained by the nature of the reactions involved and the steric effects of peripheral atoms. Rings of > 5 atoms are not regarded as entirely strainless; the probable nature of the strain in large rings is discussed.

H. B.

Hydrogenolysis of succinates and glutarates. B. WOJCIK and H. ADKINS (J. Amer. Chem. Soc., 1933, 55, 4939—4946).—Reduction (H_2 at 300 atm.; Cu-Cr oxide; 250°) of Et succinate gives $(\cdot CH_2 \cdot CH_2 \cdot OH)_2$ (74%); the yield is lowered by reducing the pressure of H_2 or the ratio catalyst:ester and butyrolactone (I); Et γ -hydroxybutyrate, $PrCO_2H$, and (probably) tetrahydrofuran (II) can be isolated also. $(\cdot CH_2 \cdot CO_2)_2O$ gives (I) (31%), (II) (?), $PrCO_2H$, and $(\cdot CH_2 \cdot CO_2H)_2$; Et α -methylsuccinate affords β -methylbutane- $\alpha\delta$ -diol (72%) and isoamyl alcohol (at 200—300 atm.; at 150 atm., the diol and α -methylbutyrolactone result); Et α -isopropylsuccinate yields β -isopropylbutane- $\alpha\delta$ -diol, b.p. 119—122°/3 mm., $\gamma\delta$ -dimethylamyl alcohol, b.p. 159—162°, isohexyl alcohol (main product using 100 atm. of H_2), and a mixture, b.p. 123—137°, of alcohols; Et α -acetyl- α -butylsuccinate, b.p. 136—138°/4 mm., furnishes β -n-butylbutane- $\alpha\delta$ -diol, b.p. 135—137°/3 mm.; Et α -acetyl- α -benzylsuccinate gives γ -benzylbutyl alcohol, b.p. 103—107°/3 mm., and β -benzylbutane- $\alpha\delta$ -diol, b.p. 162—165°/3 mm.; Et $\alpha\gamma$ -dicarbethoxyglutarate affords pentane- $\alpha\epsilon$ -diol; Et $\alpha\gamma$ -dicarbethoxy- β -methylglutarate yields γ -methylpentane- $\alpha\epsilon$ -diol, b.p. 134—137°/6 mm.; Et $\alpha\gamma$ -dicarbethoxy- β -phenylglutarate furnishes γ -phenylpentane- $\alpha\epsilon$ -diol, b.p. 174—176°/5 mm., γ -phenylpropyl alcohol, and a little γ -phenyl- $\beta\delta$ -dimethylpentane- $\alpha\epsilon$ -diol, m.p. 115—116°; Et $\alpha\gamma$ -dicarbethoxy- β -propylglutarate gives γ -propylpentane- $\alpha\epsilon$ -diol, b.p. 134—136°/10 mm., n -hexyl alcohol, and lower alcohols; Et $\alpha\gamma$ -diacetyl- β -phenylglutarate affords γ -phenyl- $\beta\delta$ -diethylpentane- $\alpha\epsilon$ -diol, b.p. 174—179°/2—3 mm. (diacetate); Et dodecamethylene- $\alpha\mu$ -dicarboxylate yields tetradecane- $\alpha\epsilon$ -diol; Et α -keto- β -methylsuccinate (in EtOH at 200°) gives Et α -hydroxy- β -methylsuccinate, b.p. 109—113°/5 mm., which is reduced further to γ -methylbutane- $\alpha\beta$ -diol, β -methylbutane- $\alpha\delta$ -diol, and lower alcohols; Et α -acetyl- α -ethyladipate affords β -ethylpentane- $\alpha\epsilon$ -diol and alcohols, b.p. 45—90°/4 mm.; Et $\alpha\gamma$ -diacetyl- β -phenylglutarate yields Et $\alpha\epsilon$ -dihydroxy- δ -phenylheptane- $\gamma\epsilon$ -dicarboxylate, m.p. 162—163°; Et α -phenylsuccinate furnishes γ -phenylbutyl alcohol and β -phenylbutane- $\alpha\delta$ -diol, b.p. 162—165°/7 mm.; Et α -acetylsuccinate gives a lactone, $C_6H_{10}O_2$, b.p. 85—87°/5 mm., glycols, and alcohols; Et α -phenylglutarate affords γ -phenylpentane- $\alpha\epsilon$ -diol, b.p. 190—192°/14 mm.; Et α -acetylglutarate yields an inseparable mixture of pentane- $\alpha\epsilon$ -diol and its β -Et derivative. The majority of the above reductions are carried out at 250° under 200—300 atm. of H_2 , using 1 pt. of catalyst to 10 pts. of ester. H_2O and acids diminish the activity of the catalyst. The

effects of various groups on the position of C·C (and C·O) fission are discussed briefly.

H. B.

Derivatives of methoxymalonic acid. J. PRYDE and R. T. WILLIAMS (J.C.S., 1933, 1627—1628).— $OMe \cdot CH_2 \cdot CO_2Me$, $Me_2C_2O_4$, and Na yield *Me* α -keto- β -methoxysuccinate, b.p. 110—120°/1 mm., which on distillation gives *Me* methoxymalonate, b.p. 215°/745.5 mm. [*methoxy-malondiamide*, m.p. 203—204° (slight decomp.), and -malonomethylamide, m.p. 115°].

F. R. S.

Preparation of *l*-tartaric acid by oxidation of *d*-gulonolactone. J. K. DALE and W. F. RICE, jun. (J. Amer. Chem. Soc., 1933, 55, 4984—4985).—Oxidation of *d*-gulonolactone with conc. HNO_3 containing a little Na metavanadate gives *l*-tartaric (13.6% yield), *l*-saccharic, and oxalic acids; details are given for their isolation.

H. B.

Preparation of glycuronic acid from borneol-glycuronic acid. K. T. SWARTZ and C. O. MILLER (J. Biol. Chem., 1933, 103, 651—655).—Hydrolysis of borneolglycuronic acid by Quick's method (A., 1927, 990) is incomplete, but is almost quant. (69% yield of glycuronic acid) if borneol is removed by steam-distillation during hydrolysis with 0.2N- H_2SO_4 : *bornyl borneolglycuronate*, m.p. 96—97°, is obtained as a by-product in either method.

J. W. B.

Preparation of pure thiolacetic acid. F. SCHÜTZ (Angew. Chem., 1933, 46, 780—781).—Use of freshly prepared, pure NaHS gives a 99% yield of $SH \cdot CH_2 \cdot CO_2H$.

R. S. C.

Condensation of sulphamide, dimethylsulphamide, and aniline-*p*-sulphonamide with formaldehyde. F. C. WOOD and A. E. BATTYE (J.S.C.I., 1933, 52, 346—349r).— $SO(NH_2)_2$ (best prepared by Ephraim and Gurewitsch's method, A., 1910, ii, 198) condenses readily with CH_2O (with production of acidity necessitating the presence of a buffer) to form a resin (I) from which clear, hard, light-stable films, sol. in boiling H_2O , may be obtained. Boiling with H_2O converts (I), with production of acidity, into an amorphous substance, which appears to be a derivative of $SO_2[N(CH_2 \cdot OH)_2]_2$. $NH_2 \cdot SO_2 \cdot NMe_2$ condenses with CH_2O (a few drops of HCl in the cold) to give a H_2O -insol., cryst. substance, darkens 175° , m.p. 185° (decomp.), probably $R \cdot N < \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} > O$ or

$R \cdot N < \begin{smallmatrix} CH_2 \cdot O \cdot CH_2 \\ CH_2 \cdot O \cdot CH_2 \end{smallmatrix} > NR$ ($R = SO_2 \cdot NMe_2$), whereas p - $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ gives a resin, analytical data for which correspond with a mixture of $CH_2 \cdot N \cdot C_6H_4 \cdot SO_2 \cdot NH_2$ and $NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_2 \cdot OH$.

J. W. B.

Highly-polymerised compounds. LXXXIV. Constitution of polyoxymethylenes. H. STAUDINGER and W. KERN (Ber., 1933, 66, [B], 1863—1866).—A reply to Walker (A., 1933, 937).

H. W.

Glutaconaldehyde; acetals, oxime, and its ring closure to pyridine 1-oxide. P. BAUMGARTEN, R. MERLÄNDER, and J. OLSHAUSEN (Ber., 1933, 66, [B], 1802—1809).—Treatment of the Na compound (I) of *enol*-glutaconaldehyde in anhyd. MeOH with HCl-MeOH at room temp. and of the product with aq. $CaCl_2$ leads to *glutacondialdehyde di*

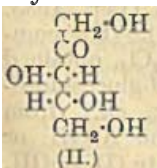
methylacetal (II) ($\delta\delta$ -dimethoxy- Δ^{β} -butenal), b.p. 99—103°/16 mm., which could not be acylated, is moderately stable towards dil. acid, adds 2 Br, and is hydrolysed by aq. NaOH to (I); the *p*-nitrophenylhydrazine (III) has m.p. 160—161°. Treatment of (I) with HCl-MeOH and of the product with conc. aq. K_2CO_3 affords $\alpha\delta\delta$ -trimethoxy- $\Delta^{\alpha\gamma}$ -pentadiene (δ -methoxy- $\Delta^{\alpha\gamma}$ -butadien- α -al dimethylacetal), b.p. 108—112°/18 mm., which rapidly decolorises Br in CCl_4 , gives (III) with *p*-nitrophenylhydrazine, and is hydrolysed by 0.1*N*-HCl at room temp. to (II) and *glutacondialdehyde* *didimethylacetal* ($\alpha\alpha\epsilon\epsilon$ -tetramethoxy- Δ^{β} -pentene), b.p. 115—118°/18 mm., convertible into (III) and hydrolysed by 0.1*N*-HCl to (II); it absorbs cold Br slowly. (I) is transformed by NH_2OH and NH_2OH, HCl in MeOH into *glutacondialdehydedioxime* (IV), m.p. 88°, with a little pyridine 1-oxide (IV) (picrate, m.p. 179°); (V) is formed from (IV) by treatment with boiling EtOH-HCl or directly from (I) by means of HCl and NH_2OH, HCl in MeOH. (V) is also produced from *glutacondialdehydeaniloxime* in boiling $PhNO_2$. δ -Acetoxy-, m.p. 75.5°, and δ -benzoyloxy- (VI), m.p. 118—119°, $\Delta^{\alpha\gamma}$ -butadienal have now been obtained colourless. (VI) affords a phenylhydrazone, *o*-nitrophenylhydrazone, m.p. 183—184°, and an *azine*, m.p. 187°.

H. W.

Determination of mol. wt. of carbohydrates. M. ULMANN and K. HESS (Ber., 1933, 66, [B], 1975—1977).—Irregularities in the behaviour of sucrose (I) in boiling H_2O (cf. Pringsheim *et al.*, A., 1933, 1144), do not occur if (I) has not been dried at too high a temp. and if it is not introduced while H_2O is boiling briskly. Desiccation over P_2O_5 /vac. at room temp. or by means of boiling $CHCl_3$ is adequate. (I) if dried by boiling xylene softens, but does not suffer chemical change. In boiling H_2O it causes no elevation of the b.p., but after cooling to room temp. and again heating, a normal elevation is observed. Pringsheim's objection to the use of isothermal distillation for determining the mol. wt. of Schardinger's α -dextrin is groundless.

H. W.

d-Xyloketoze. O. T. SCHMIDT and R. TREIBER (Ber., 1933, 66, [B], 1765—1769).—*d*-Xylose (I) is boiled with anhyd. C_5H_5N and the resultant mixture is crystallised from 96% EtOH, whereby the bulk of



unchanged (I) is removed. Treatment of the residue with p - $C_6H_4Br-NH-NH_2$ affords *d*-xyloketoze-*p*-bromophenylhydrazone, m.p. 128—129°, $[\alpha]_D^{20} + 23.7^\circ \pm 0.3^\circ$ to $-31.2^\circ \pm 0.3^\circ$ in C_5H_5N in 7 days, transformed by $PhCHO$ into *d*-xyloketoze (II), $[\alpha]_D^{20} - 33.2^\circ \pm 0.4^\circ$ (whence

d-xylosephenylosazone). (II) appears to be the enantiomorphous form of the ketopentose of Levene *et al.* (A., 1914, i, 1027). It is strongly reducing and is affected by KOI (Willstätter-Schudel). It does not give a violet-red colour with 18% HCl and phloroglucinol.

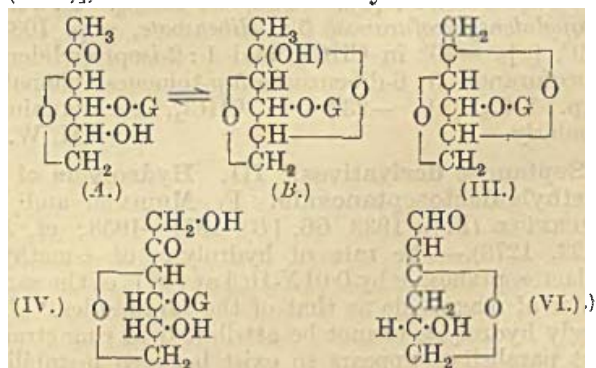
H. W.

Mechanism of carbohydrate oxidation. XVI. Action of aqueous solutions of potassium hydroxide on *l*-rhamnose. G. F. NADEAU, M. R. NEWLIN, and W. L. EVANS (J. Amer. Chem. Soc., 1933, 55, 4957—4963).—The action of aq. KOH on *l*-rhamnose is studied by the method previously described (cf. A.,

1930, 1410) for other sugars at 25°, 50°, and 75°. The amount of lactic acid produced increases with rise in the concn. of KOH (and is max. at about 2*N* at 50° and 75°); more is formed at 50° than at 75° and the yields are intermediate between those from arabinose (*loc. cit.*) and glucose, mannose, and fructose (cf. A., 1928, 1222). The effects of temp. and concn. of KOH on the amount of AcCHO produced are also studied; max. amounts are formed at 50° using approx. 0.5*N*-KOH.

H. B.

Unsaturated reduction products of sugars. XIX. isoGlucal, isolactal, and protoglucal. M. BERGMANN, L. ZERVAS, and J. ENGLER (Annalen, 1933, 508, 25—38).—*iso*Lactal (I), m.p. 218° (corr., decomp., darkens at 193°), $[\alpha]_D^{20} + 88.9^\circ$ in H_2O (modified prep. given; cf. A., 1924, i, 265) [*phenylbenzylhydrazone*, m.p. 145—147° (corr.)], is a 4-galactosido-*isog*lucal, since it is hydrolysed by kefir extract to galactose and *isog*lucal. The presence of the $\cdot CH_2 \cdot CO \cdot$ group is indicated by the amount of NaOI used in oxidation and the non-formation of a lactolide with $CH(OEt)_3$. Acetylation ($Ac_2O-C_5H_5N$) of (I) gives a *penta*-acetate, m.p. 166—167° (corr.) [and not a *hexa*-acetate as stated previously (*loc. cit.*)], hydrolysed (boiling H_2O) to a *tetra*-acetate (II), m.p. 138—139° (corr.), $[\alpha]_D^{20} + 72.6^\circ$ in C_2H_5Cl . (II) and PCl_5 in $CHCl_3$ at -15° afford *isolactal* chlorohydrin tetraacetate, which with Ag_2CO_3 and EtOH gives an ethyl-lactolide tetraacetate, m.p. 160° (softens at 140°), and with C_5H_5N at 100° yields the *tetra*-acetate, m.p. 184—185° (sinters at 182°), $[\alpha]_D^{20} + 141.3^\circ$ in C_2H_5Cl , of *anhydroisolactal* (III), m.p. 243—244° (corr.). The structures (A) \rightleftharpoons (B) ($G=C_6H_{11}O_5$) are assigned to (I). (III) in H_2O and BzO_2H in EtOAc give galactosidoanhydrofructose (IV) [*osazone*, m.p. 184—186° (corr.)], which is not oxidised by alkaline NaOI. *iso*-



Glucal (V) (*loc. cit.*) is formulated as (A, with $G=H$).

*Proto*glucal (VI), b.p. 104—106°/0.4 mm., $[\alpha]_D^{20} + 35^\circ$ in abs. EtOH [*p*-nitrophenylhydrazone, m.p. 152° (corr.)], is formed (in small amount) with (V) when ψ -glucal diacetate is hydrolysed [$Ba(OH)_2$]. (VI) is unsaturated (Br; $KMnO_4$), reduces Fehling's solution in the cold, does not give an osazone, consumes 2 I and 1 mol. of BzO_2H , is oxidised (O_3) to $(CHO)_2$, and absorbs 4 H on reduction (H_2 , Pd-black, AcOH) to give a non-reducing product.

H. B.

Carbohydrates. XVIII. Benzoates of glucofuranose. P. BRIGL and H. GRÜNER (Ber., 1933, 66, [B], 1977—1983; cf. A., 1933, 810).—The tribenzoate (I) (*loc. cit.*) is converted by further treatment with

BzCl and C_5H_5N in $CHCl_3$ into glucofuranose penta-benzoate, m.p. 143—144°, $[\alpha]_D -55.1^\circ$ in $CHCl_3$, and hence is a glucofuranose. The absence of Bz from position 1 follows from the prep. (unpublished) of a *hydrazone*. The occurrence of a 2:3:6-tribenzoate is very improbable, since this would probably give a pyranose derivative on energetic treatment with $Ac_2O-ZnCl_2$ or $AcOH-HBr$. The diacetate tribenzoate obtained from (I) after successive treatment with these reagents and replacement of Br by Ac is syrupy, and not identical with α -, m.p. 162—163°, $[\alpha]_D +140.6^\circ$ in $CHCl_3$, or β -, m.p. 202°, $[\alpha]_D +111.9^\circ$ in $CHCl_3$, *-glucopyranose* 1:4-diacetate 2:3:6-tribenzoate. Hence (I) is *glucofuranose* 2:5:6-tribenzoate. Treatment of isopropylidenglucose 3-acetate 5:6-dibenzoate with $AcOH-H_2O$ -conc. HCl at 50° leads to *glucofuranose* 5:6-dibenzoate (II), m.p. 145—146° after softening at 143°, $[\alpha]_D -19.9^\circ$ (equilibrium val.) in EtOH, transformed by BzCl and C_5H_5N in $CHCl_3$ into α -glucofuranose penta-benzoate, m.p. 119—120°, $[\alpha]_D +60.3^\circ$ in $CHCl_3$. With Ac_2O and C_5H_5N followed by $ZnCl_2$ and Ac_2O (II) gives β -*glucofuranose* 1:2:3-triacetate 5:6-dibenzoate, m.p. 97—98°, $[\alpha]_D -41.6^\circ$ in $CHCl_3$, also obtained from isopropylidenglucose 3-acetate 5:6-dibenzoate. $COMe_2$ containing 1% of HCl transforms (II) into 1:2-isopropylidenglucofuranose 5:6-dibenzoate, m.p. 118°, $[\alpha]_D +41.4^\circ$ in $CHCl_3$, formed as by-product during the prep. of glucose dibenzoate according to Fischer and Noth and differing from Ohle's product (A., 1924, i, 497). Syrupy 1:2-isopropylidenglucofuranose 3-benzoate (III), $[\alpha]_D -26.5^\circ$ in EtOH, is obtained by partial hydrolysis of the diisopropylidene derivative, into which it is smoothly re-converted by $COMe_2$ and $CuSO_4$. (III), Ac_2O , and C_5H_5N afford 1:2-isopropylidenglucofuranose 5:6-diacetate 3-benzoate, m.p. 77—78°, $[\alpha]_D -26.7^\circ$ in $CHCl_3$. 1:2-isopropylidenglucofuranose 3:6-dibenzoate, m.p. 108—109°, $[\alpha]_D -46^\circ$ in $CHCl_3$, and 1:2-isopropylidenglucofuranose 3:6-dibenzoate 5-*p*-toluenesulphonate, m.p. 143°, $[\alpha]_D -23.8^\circ$ in $CHCl_3$, are obtained similarly. H. W.

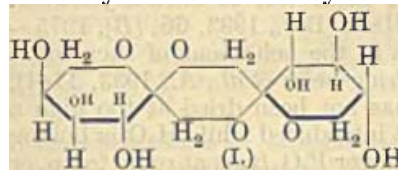
Septanose derivatives. III. Hydrolysis of α -methylgalactoseptanoside. F. MICHEEL and F. SUCKFULL (Ber., 1933, 66, [B], 1957—1958; cf. A., 1933, 1278).—The rate of hydrolysis of α -methylgalactoseptanoside by 0.01*N*-HCl at 95° is of the same order of magnitude as that of the furanosides. The ready hydrolysis cannot be attributed to ring strain, but parallelism appears to exist between instability of the free sugar and ready hydrolysis of its glucosides. Further purification of galactoseptanose penta-acetates leads to the data, m.p. 128.5°, $[\alpha]_D -10.8^\circ$, and m.p. 112°, $[\alpha]_D -103^\circ$, for the α - and β -compounds, respectively. H. W.

Oxidation of fructose by hypiodite. K. BAILEY and R. H. HOPKINS (Biochem. J., 1933, 27, 1965—1974).—The rate of oxidation of fructose (I) by NaOI or $Ba(OI)_2$ (cf. A., 1918, ii, 337) increases with rise of temp., whilst the extent over a range of 1—35° is min. at 15°. Presence of excess of alkali at 17—37° (but not at 1°) enolises (I) and permits a far more extensive oxidation (II). By progressive addition of small amounts of alkali, (II) is increased 4—5 times,

the (II) being independent of the concn. of (I). The products of (II) are *d*-erythronic and oxalic acids. The (II) of (I) in presence of limited amounts of alkali is possibly due to the keto- or the labile (2:5) form of (I). F. O. H.

Specific rotation and stability of (2:5)-fructose from the hydrolysis of sucrose by fructosaccharase. K. BAILEY and R. H. HOPKINS (Biochem. J., 1933, 27, 1957—1964).—Investigations of the progressive changes in $[\alpha]$ during the hydrolysis of sucrose by fructoinvertase (A., 1914, i, 339) indicate that at p_H 4.6—6.1 fructofuranose (I) has $[\alpha]^{17} +15^\circ$ to 17° in H_2O . The change of (I) into equilibrated fructose is unimol., the velocity coeff. $k_{17}^{min.}$ being 0.3. A scheme for the mechanism of the hydrolysis of sucrose is advanced. F. O. H.

Fructose anhydrides. XIII. Synthesis of a *n*-difructose anhydride from fructose. H. H. SCHLUBACH and C. BEHRE (Annalen, 1933, 508, 16—24).—Anhyd. fructose is treated with dry liquid HCl at 14° (sealed tube), the product extracted with EtOH, and the insol. *difructose anhydride* (I), decomp. 250—270° (brown at 150°), $[\alpha]_D^{19} -43.9^\circ$ in H_2O (*hexaacetate*, m.p. 171—173°, $[\alpha]_D^{19} -59.1^\circ$ in $CHCl_3$), crystallised from H_2O . (I) is probably identical with the anhydride described by Pictet and Chavan (A., 1926, 1126). (I) does not reduce Fehling's solution and is hydrolysed only slowly by $N-H_2SO_4$ at 60°.



Methylation (Me_2SO_4 and 35% NaOH followed by MeI and Ag_2O) gives a *Me_6* derivative, m.p. 143—145°, $[\alpha]_D^{20} -46.5^\circ$ in $CHCl_3$, hydrolysed (1.5*N*- H_2SO_4 at 80°) to 3:4:5-trimethylfructose, b.p. 117°/0.4 mm., $[\alpha]_D^{20} -73.5^\circ$ in H_2O (*osazone*). H. B.

Micro-determination of lactose. J. M. CLAVERA and F. M. MARTIN (Bull. Soc. chim., 1933, [iv], 53, 1103).—Priority is claimed (cf. B., 1930, 1129; A., 1933, 732). R. S. C.

Sugars containing sulphur and their derivatives. XVIII. $\beta\beta$ -Diglucosyl sulfoxysulphide. W. SCHNEIDER and A. BANSI (Ber., 1933, 66, [B], 1973—1975; cf. A., 1931, 939).—The compound, m.p. 169°, $[\alpha]_D^{19} -41.91^\circ$ in $C_2H_2Cl_4$, obtained by the action of KNO_2 and AcOH on *d*-glucosido-*S*-thiuronium bromide tetra-acetate (*loc. cit.*), from β -glucothiose tetra-acetate, $NaNO_2$, and AcOH, or from $\alpha\beta$ -diglucosyl disulphide octa-acetate (I), AcOH, and H_2O_2 is identified as $\beta\beta$ -diglucosyl sulfoxysulphide octa-acetate, $C_6H_7O_5Ac_4 \cdot SO \cdot S \cdot C_6H_7O_5Ac_4$. Hydrolysis (Zemplén) and subsequent treatment with $Ac_2O-C_5H_5N$ affords (I). H. W.

Synthesis of glycosides. X. Synthesis of primeverin. E. T. JONES and A. ROBERTSON (J.C.S., 1933, 1618—1620).—The *O*-tetra-acetyl- β -glucoside of Me 4-methoxysalicylate, m.p. 138—139°, $[\alpha]_{D_{561}}^{20} -66.0^\circ$, is obtained from Me 4-methoxysalicylate, Ag_2O , and *O*-tetra-acetyl- α -glucosidyl bromide, and with $MeOH-NH_3$ forms the β -glucoside (+0.5*H_2O*), m.p. 124—126°, $[\alpha]_{D_{561}}^{21} -82.36^\circ$. The

glucoside and $\text{C}_6\text{H}_5\text{N}$ give the 6-O-triphenyl-methyl- β -glucoside, m.p. 120° , $[\alpha]_{\text{D}}^{25} -36.72^\circ$, the triacetate, m.p. $168-169^\circ$, $[\alpha]_{\text{D}}^{25} -103.41^\circ$, of which with $\text{HBr}-\text{AcOH}$ yields the 2:3:4-O-triacetyl- β -glucoside, m.p. 136° , $[\alpha]_{\text{D}}^{25} -40.82^\circ$. Condensation of (I) with O-triacetyl- α -xyloside bromide gives a product, deacetylated ($\text{MeOH}-\text{NH}_3$) to primeverin (the β -primeveroside of Me 4-methoxysalicylate; hexa-acetate, m.p. 125°), identical with the natural product. All rotations are measured in COMe_2 .

F. R. S.

Glucosides. VII. Glucoside of *Sanguisorba officinalis*. S. ABE and M. KOTAKE (Sci. Papers Inst. Phys. Chem. Tokyo, 1933, 23, 44-48).—Extraction of the root with MeOH affords sanguisorbin, $\text{C}_{45}\text{H}_{82}\text{O}_{18}$ (?), m.p. 233° [lit., $272.5-274.5^\circ$ (decomp.)], hydrolysed by warm 5% $\text{MeOH}-\text{HCl}$ to sanguisorbigenin (I), m.p. $266-269^\circ$ [Ac derivative, m.p. $313-316^\circ$ [lit., $272-275^\circ$ (decomp.)], hydrolysed by $\text{MeOH}-\text{KOH}$ to (I)]. (I) with CH_3N_2 in Et_2O affords the Me ester (II), m.p. $201-203^\circ$ [Ac derivative, m.p. $236-238^\circ$, hydrolysed by $\text{MeOH}-\text{KOH}$ to (II)]. (I) at 280° during 20 min. loses CO_2 to give decarboxysanguisorbigenin, $\text{C}_{27}\text{H}_{41}\text{O}$, m.p. $197-199^\circ$ (Ac derivative + $1\text{H}_2\text{O}$, m.p. $180-181^\circ$).

J. L. D.

Reaction of starch with very dilute aqueous sodium hydroxide. M. SAMEC (Bull. Soc. Chim. Yougoslav., 1933, 4, 71-78).—The p_{H} curve obtained on titration of amylopectin (I) with 0.01N-NaOH is of the same type as that obtained with H_3PO_4 . The viscosity varies irregularly with the p_{H} , indicating that the action of alkali depends on neutralisation of H_3PO_4 combined with (I), and also on a modification in the structure of (I).

R. T.

Influence of a quaternary ammonium group on the hydrogen atoms of an adjacent methylene group. A. O. JACKSON and C. S. MARVEL (J. Amer. Chem. Soc., 1933, 55, 5000-5002).—Trimethylcarbethoxymethylammonium chloride (I), m.p. $166-167^\circ$ (lit. $143-144^\circ$), and bromide (II) are not ethylated by EtBr and $\text{EtOH}-\text{NaOEt}$; (I) gives (II) and a small amount of a compound, m.p. $294-295^\circ$, also obtained from (II). The methobromide, m.p. $199-200^\circ$, of $\text{NMe}_2\cdot\text{CH}(\text{CN})\cdot\text{CO}\cdot\text{NH}_2$ is prepared from bromocycanoacetamide, m.p. $176-177^\circ$, and NMe_3 ; it is converted by $\text{EtOH}-\text{NaOEt}$ and EtBr into trimethylcarbamylmethylammonium bromide, m.p. $203-204^\circ$ (also prepared from $\text{CH}_3\text{Br}\cdot\text{CO}\cdot\text{NH}_2$ and NMe_3).

H. B.

Argentometric evaluation of hexamethylene-tetramine. J. VON MIKÓ (Pharm. Zentr., 1933, 74, 642-643).—A 2% solution (5 c.c.) is shaken with 0.1N- AgNO_3 (45 c.c.) and rapidly filtered from the pptd. $2\text{C}_6\text{H}_{12}\text{N}_4\cdot 3\text{AgNO}_3$. The first 15 c.c. of filtrate are rejected and the next 25 c.c., after the addition of 5N- HNO_3 (10 c.c.), are titrated with 0.1N-KCNS.

E. H. S.

Preparation and quaternary ammonium decomposition of formocholine.—See this vol., 152.

Colorimetric determination of glucosamine and chondrosamine. L. A. ELSON and W. T. J. MORGAN (Biochem. J., 1933, 27, 1824-1828).—Glucosamine and chondrosamine are determined by

addition of a solution of CH_2Ac_2 in Na_2CO_3 , heating for 15 min. at 100° , cooling, and adding EtOH and Ehrlich's reagent. After 30 min. the colour is compared with a standard. The max. error was 5% within the range of 0.75-3.0 mg. The optimal concn. of HCl is 5%. The presence of glucose, galactose, fructose, arabinose, histidine, and tryptophan was without significant influence on the determination.

H. D.

Synthesis of peptide-like substances from amino-sugars and amino-acids. III. Acetylated glucopeptides. A. BERTHO and J. MAIER (Z. physiol. Chem., 1933, 222, 139-147; cf. A., 1932, 837, 1118).—Glucosamine tetra-acetate in CHCl_3 , when treated with $\text{C}_5\text{H}_5\text{N}$ and azidoacetyl chloride, gives (N-azidoacetyl)glucosamine tetra-acetate (I), m.p. 131° , $[\alpha]_{\text{D}}^{25} +6.1^\circ$ in CHCl_3 , which with PtO_2 and H_2 affords (N-glycyl)glucosamine tetra-acetate (II), m.p. $161-162^\circ$ (decomp.) [or a product, $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$, m.p. 188° (decomp.)]. With NH_3 in MeOH , (II) gives a non-cryst. product. The corresponding cryst. products obtained with alanylglucosamine tetra-acetate were dehydroalanyl-N-glucosamine anhydride, m.p. $254-258^\circ$, and alanyl-N-anhydroglucosamine anhydride, m.p. 198° . By the same method as (I) were prepared: N-(α -bromopropionylglycyl)glucosamine tetra-acetate (III), m.p. 162° , and N-(α -bromoisohexoylglycyl)glucosamine tetra-acetate (IV), m.p. $174-175^\circ$, N-(α -bromoisohexoylalanyl)glucosamine tetra-acetate, m.p. $169-170^\circ$, N-(α -azidopropionylalanyl)glucosamine tetra-acetate (V), m.p. 139° (decomp.). With PtO_2 and H_2 , (V) affords N-(dialanyl)glucosamine tetra-acetate, m.p. 212° (decomp.). With NH_3 in MeOH , (III) and (IV) give non-cryst. N-alanyl-glycyl- and -leucylglycyl-glucosamine, decomp. 132° , respectively. With $\text{CHMeBr}\cdot\text{COCl}$ and NaOH , chondrosamine hydrochloride gave N- α -bromopropionylchondrosamine, m.p. 181.5° (decomp.), $[\alpha]_{\text{D}}^{25} +68^\circ$ in H_2O falling to 49.5° , which did not afford a glucopeptide anhydride with NH_3 . J. H. B.

Complex compounds formed by certain amino-acids in presence of mercuric chloride and alkali. H. B. VICKERY and W. G. GORDON (J. Biol. Chem., 1933, 103, 543-547).—The best conditions (mols. of HgCl_2 , alkali, p_{H} , and vol. of added EtOH , respectively) for pptn. of the following NH_2 -acids, as insol. HgCl_2 complexes, are: glycine, 1.5, $\text{Ba}(\text{OH})_2$, 9.8, 0, or 1.5, $\text{Na}(\text{Li})\text{OH}$, 9.8, 2; alanine, 1.5, $\text{Ba}(\text{OH})_2$, 9.8, 1; phenylalanine, 1.5, $\text{Ba}(\text{OH})_2$, 8.5, 0; leucine (I), 1.5, $\text{Ba}(\text{OH})_2$, 9.8, 1.5; lysine (II), 2, $\text{Ba}(\text{OH})_2$, 9.3, 0; and glutamic acid, 2, $\text{Ba}(\text{OH})_2$, 9.8, 0. Except for (I) (70%), all pptns. are quant. Except that from (II) ($\text{Hg}:\text{N}:\text{Cl}=4:4:3$ atoms), all pptts. contain $\text{Hg}:\text{N}=3:2$ atoms, in addition to Cl and alkali. Attempts to employ these complexes in the separation of NH_2 -acids were unsuccessful.

J. W. B.

Gas-volumetric determination of amino-nitrogen according to Van Slyke in the case of glycine and peptides containing glycine. O. GERNGROSS and W. DESEKE (Ber., 1933, 66, [B], 1813-1814).—The gas evolved in the determination of glycine and glycylglycine contains > the calc. amount of N_2 for which a correction cannot be introduced.

CO and N₂O are present to the respective extents of 0.4% and 0.6%. H. W.

Serinephosphoric acid obtained on hydrolysis of vitellinic acid. II. P. A. LEVENE and A. SCHOR-MULLER (J. Biol. Chem., 1933, 103, 537—542).—An improved method of isolation of Ba *d*-serinephosphate (I) (A., 1932, 1269) from the hydrolysis products of vitellinic acid (II) involves purification through the brucine salts, two fractions (a), m.p. 89°, decomp. 105° (composition approx. that of the dibrucine salt), and (b), m.p. 120°, decomp. 130° (mixture), being obtained. Under milder conditions of hydrolysis (II) gives a phosphoric ester of serine, and serine is isolated by hydrolysis of (I). In vitellin the serinephosphoric acid is not linked to a dicarboxylic NH₂-acid. J. W. B.

Aminosulphonic acids. II. **Synthesis of taurine derivatives.** B. JOSEPHSON (Biochem. Z., 1933, 265, 448—455).—The following have been prepared by a modification of James' method (J.C.S., 1885, 47, 367): methyl-, m.p. 244°, dimethyl-, m.p. 270° (cf. *ibid.*, 371), *n*-propyl-, m.p. 330°, *n*-heptyl-, m.p. 244°, phenyl-, m.p. 269°, and benzyl-, m.p. 196°, -taurine; β -*p*-carboxyanilinoethanesulphonic acid, m.p. 286°. Their properties differ largely from those of taurocholic acid. P. W. C.

Organic reactions with boron fluoride. VI. **Reaction of acetamide with alcohols and phenol.** F. J. SOWA and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1933, 55, 5052—5053).—NH₂Ac.BF₃ (1 mol.) heated with ROH (1 mol.) gives NH₃, BF₃, and ROAc. Me, Et, Pr^{*n*}, Bu^{*n*}, Bu^{*i*}, and Ph acetates are thus prepared in yields of 71, 69, 32, 50, 38, and 50%, respectively. H. B.

Metallic salts of carboxylic acids. E. C. FRANKLIN (J. Amer. Chem. Soc., 1933, 55, 4915—4917).—Salts, R·CO·NHK, where R is H, Et, Pr^{*n*}, Bu, amyl, pentadecyl, and Ph, are prepared from R·CO·NH₂ and KNH₂ in liquid NH₃; when heated to 250—300°, they decompose to RH+KNCO and RCN+KOH. The salts HCO·NHNa and CHK(CO·NHK)₂ are also described. H. B.

λ -Hydroxystearhydrazide and derivatives. J. VOŘÍSEK (Coll. Czech. Chem. Comm., 1933, 5, 466—468).— λ -Hydroxystearhydrazide, m.p. 115.5—116.5° [hydrochloride, m.p. 162—163°; N-Ac, m.p. 144—145° (warm Ac₂O and EtOH), and ON-Ac₂ derivative (Ac₂O at b.p.)], is formed from the acid and N₂H₄·H₂O at 100°, and with I in EtOH gives *s*-di- λ -hydroxystearylhydrazine, m.p. 153—154°. H. A. P.

Preparation of magnesium crotyl bromide. **Effect of solvents on the yield of magnesium crotyl and allyl bromides.** W. G. YOUNG, A. N. PRATER, and S. WINSTEIN (J. Amer. Chem. Soc., 1933, 55, 4908—4911).—Mg crotyl bromide (I) is obtained in good yield by slow addition of a solution of crotyl bromide (II) to a rapidly stirred mixture of Mg and Et₂O or Bu₂O in N₂. (II) reacts with (I) more readily than does allyl bromide with Mg allyl bromide (III); use of Bu₂O favours these reactions. Slower stirring diminishes the yield of (I) and (III). Much larger ratios of solvent and Mg to bromide

must be used with Bu₂O than with Et₂O to obtain equiv. yields of MgRBr. H. B.

Hydroxypropyldiarsinic acid. K. A. KIRKHGOF (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 73—74).—OH·CH(CH₂Cl)₂ (129 g.) is agitated during 4 hr. with As₂O₃ (200 g.) in H₂O (600 c.c.) and NaOH (240 g.). After 4 days the diluted mixture is boiled and Ca hydroxypropyldiarsinate pptd. with boiling CaCl₂ solution. The acid, decomp. 170—180°, is liberated with boiling dil. H₂SO₄. Reduction with Na₂S₂O₄ and NaOH affords a substance, probably

$$\text{OH}\cdot\text{CH}\begin{array}{c} < \text{CH}_2\cdot\text{As} \\ | \\ \text{CH}_2\cdot\text{As} \end{array}$$

CH. ABS.

Aliphatic germanium derivatives. III. **Germanium ethyl trihalides.** E. A. FLOOD (J. Amer. Chem. Soc., 1933, 55, 4935—4938).—GeI₃ and EtI at 110° for 3 days in absence of air give GeEtI₃ (I), b.p. 281°/755 mm., m.p. -2.5° to -1.5°, which decomposes at > 350° to GeI₄ and gaseous products. (I) and Ag₂O in H₂O afford ethylgermanic oxide (II), (EtGeO)₂O, decomp. > 300°, which with the appropriate HHal gives GeEtF₃, b.p. 112°/750 mm., m.p. -16.5 to -15.5°, GeEtCl₃, b.p. 144°/762 mm., and GeEtBr₃, b.p. 200°/763 mm. (I) is ammonolysed in liquid NH₃ to GeEtN, which is hydrolysed (H₂O) to (II). H. B.

Preparation of germanium diethyl derivatives. L. HORVITZ and E. A. FLOOD (J. Amer. Chem. Soc., 1933, 55, 5055; cf. A., 1932, 606).—GeEtI₃ and an excess of 40:60 Pb-Bi alloy at 150° in absence of air give a product, probably (GeEtI)₂, which with EtI at 125° affords GeEt₂I₂, b.p. 252°/759 mm., m.p. -2° to -1°. GeEt₂Cl₂ has b.p. 175°/758 mm., m.p. -39° to -37°. H. B.

Cracking of naphthene hydrocarbons. I. M. K. DIAKOVA and A. D. PETROV (J. Gen. Chem. Russ., 1933, 3, 679—684).—The stability of decahydronaphthalene and dicyclohexyl at 500—550° is > that of methylisopropyldicyclononane, of amylcyclohexane (I), and of the fractions of Grosny petroleum (II), b.p. 185—248°. A comparison of the *d* and *n* of the products of cracking indicates that (II) consists preponderantly of naphthenes of structure similar to that of (I). R. T.

Application of the electronic theory to the chemistry of organic compounds. I. **Properties of isomeric nitro-compounds from the viewpoint of electronic theory.** A. M. BERKENHEIM and M. I. GOSTEV (J. Gen. Chem. Russ., 1933, 3, 385—410).—An experimental verification by standard methods of org. chemistry of the "electrodynamic" theory of intramol. changes of NO₂-compounds giving rise to different types of N compounds. These changes are possibly of the oxidation-reduction type, involving transformation of N^V into N^{III}, and of ·NO₂ into ·O·N·O. The electronic structure of aromatic compounds is examined, and the position, nature, and firmness of the attachment of NO₂ to the nucleus, as well as the possibility of rearrangements, are demonstrated. With "abnormal" compounds, both electrostatic and electrodynamic rearrangements are possible: in the former case more stable compounds result owing to the migration

of the group in the nucleus, all the charge signs remaining unaltered, whilst in the latter case, new compounds (complex, aromatic nitrous esters) are formed. In the course of such dynamic rearrangements, secondary products appear owing to further transformations of the aromatic nitrites into OH compounds. The aromatic nitrite can be independently prepared and identified by the action of NOCl on the metallic phenoxides. With $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, NOCl gives a nitrite, m.p. 126—131°, and also Me *p*-nitrosalicylate, m.p. 114—115°. Alkalis remove the Me and cause a rearrangement, giving a mixture of *o*- and *p*-nitrosalicylic acids. $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and NOCl give a nitrite isomeric with $o\text{-C}_6\text{H}_4(\text{NO}_2)_2$. Nitration of BzOH gives $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, identical with that obtained by oxidation of PhMe, in accordance with the electronic rearrangement theory; during nitration of BzOH, secondary products, corresponding with those formed when the isomeric nitrite is synthesised, are obtained. The fourth nitrobenzoic acid, m.p. 124—126° (cf. A., 1880, 251), which gave an intense coloration with FeCl_3 , is identical with the aromatic nitrite. M. Z.

1-Chloro-3 : 4-dinitrobenzene series. A. MANGINI and C. DELIDDO (Gazzetta, 1933, 63, 612—629).—The structure of 1-chloro-3 : 4-dinitrobenzene (I), m.p. 38.8°, best made from $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ and $\text{KNO}_3\text{-H}_2\text{SO}_4$, is proved through the following derivatives. 4-Chloro-*o*-phenylenediamine hydrochloride, decomp. 260—270°, yields, with benzil, 6-chloro-2 : 3-diphenyl-1 : 4-quinazoline, m.p. 119—121°, whence 6-chlorobenzotriazole, new m.p. 160° (Ac derivative, m.p. 90°; Ag salt). 3-Chloro-6-nitroaniline (II) (Ac derivative, m.p. 121°) gives 4-chloro-2-acetamidoaniline hydrochloride, decomp. 200°, and 4-chloro-2-acetamidophenol. 5-Chloro-2-nitroanisole gives 4-chloroguaiacol. 5-Chloro-2-nitrophenetole gives the 2-NH₂- (hydrochloride, decomp. 250—260°) and 2-NHAc, m.p. 98°, -compounds. When (I) is treated with $\text{CH}_2\text{Ph}\cdot\text{OH}$, 5-chloro-2-nitrophenyl benzyl ether is formed, reduced to the 2-NH₂-compound [hydrochloride, m.p. 210—218° (decomp.)], whence 5-chloro-2-nitrophenol. With piperidine, (I) forms 1-chloro-4-nitro-3-piperidylbenzene [hydrochloride, m.p. 147—151° (decomp.)]. With N_2H_4 , (I) gives 5-chloro-2-nitrophenylhydrazine, red form, m.p. 160°, yellow form, m.p. 120° (Ac derivative, m.p. 186—187°), which is also obtained from (II), and which with KOH-EtOH yields 6-chloro-3-hydroxybenzimidazole, m.p. 183°, decomp. 188—189°. With $\text{NHPH}\cdot\text{NH}_2$ (I) forms α -phenyl- β -(5-chloro-2-nitrophenyl)hydrazine, m.p. 140—141°. Benzaldehyde-5-chloro-2-nitrophenylhydrazones, m.p. 174°, and acetone- and benzophenone-4[5?]-chloro-2-nitrophenylhydrazones, m.p. 131—132° and 138—139°, respectively, are described.

E. W. W.

Supposed di-ortho-isomerism in benzene. A. CONTARDI and A. DANSI (Rend. R. Ist. lombardo Sci. Lett., 1933, [ii], 66, 203—206; Chem. Zentr., 1933, ii, 1512).—Hodgson's results (A., 1927, 47) are challenged. Substitution of Cl or Br by NH₂ is best attained by heating in a closed tube with EtOH-NH₃ for several hr. at 100°. 3-Chloro-1-bromo-4 : 6-dinitrobenzene from 3-chloro-4 : 6-dinitroaniline is

crystallographically identical with the 1-chloro-3-bromo- from the 3-bromo-1-amino-compound.

A. A. E.

Chloro-derivatives of *p*-xylene. H. WAHL (Compt. rend., 1933, 197, 1330—1332).—3-Nitro-*p*-xylylidine (Noelting *et al.*, A., 1902, i, 313; prep. modified) is converted by the Sandmeyer reaction into 2-chloro-3-nitro-*p*-xylene, b.p. 135°/15 mm., m.p. 56°, reduced by Fe-HCl to 3-chloro-*p*-xylylidine, b.p. 126—127°/15 mm., m.p. 41° (Ac, m.p. 179°, and Bz, m.p. 144°, derivatives; picrate, m.p. 120°), not identical with the chloro-*p*-xylylidine (I), b.p. 132—133°/15 mm., previously obtained (A., 1933, 815) by reduction of the corresponding NO₂-derivative [(II), *loc. cit.*]. (I) is therefore 6-chloro-*p*-xylylidine, and (II) is 6-chloro-2-nitro-*p*-xylene.

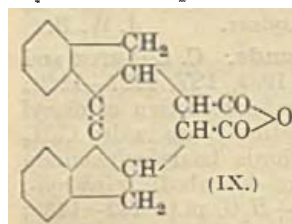
J. W. B.

Arylsulphonium compounds. C. COURTOT and T. Y. TUNG (Compt. rend., 1933, 197, 1227—1229; cf. A., 1932, 506).—Prolonged interaction of diaryl sulfoxides and aromatic hydrocarbons in dry C_6H_6 containing AlCl_3 at 40° affords triarylsulphonium chlorides. The following are described: triphenyl-, m.p. 230—277° (decomp.) [$+\text{H}_2\text{O}$, m.p. 142—143°; $+\text{HgCl}_2$, m.p. 214—215° (decomp.)]; *o*-, an oil, and *m*-xylyldiphenyl-, m.p. 179° ($+\text{H}_2\text{O}$, m.p. 123—124°); phenyldi-*p*-tolyl-, m.p. 193—194° ($+\text{H}_2\text{O}$, m.p. 125—127°; $+\text{H}_2\text{O}$, m.p. 62—63°); tri-*v*-tolyl- ($+\text{H}_2\text{O}$, m.p. 138—140°; $+\text{H}_2\text{O}$, m.p. 51—52°); di-*p*-tolyl-*o*-xylyl-, m.p. 118—120° ($+\text{H}_2\text{O}$, m.p. 56—57°); di-*p*-tolyl-*p*-xylyl-, oil ($+\text{HgCl}_2$, m.p. 86—87°); tolyl-2 : 4 : 2' : 4'-tetramethyldiphenyl-, m.p. 94—97°; tri-*o*-xylyl-, m.p. 102—105° ($+\text{H}_2\text{O}$, m.p. 60—61°); diphenyl-*p*-tolyl-, m.p. 232—234°; phenyl-*p*-tolyl-*o*-xylyl-, m.p. 74—76° ($+\text{H}_2\text{O}$, m.p. 59—60°), and phenyl-*p*-tolyl-*m*-xylyl-sulphonium chloride, m.p. 73—74°.

J. L. D.

Replacement of strongly positive hydrogen by halogen. IV. Reaction of 1 : 1 : 3-trihalogenoindenes. F. STRAUS, R. KUHNEL, and R. HAENSEL (Ber., 1933, 66, [B], 1847—1862; cf. this vol., 168).—Treatment of 1 : 1 : 3-tribromoindene (I) with boiling $\text{COMe}_2\text{-H}_2\text{O}$ affords 3-bromoindone, m.p. 57.5—58°, in 83% yield, converted by Br and Cl_2 in AcOH into 2 : 3-dibromo-, m.p. 123°, and 2-chloro-3-bromo-, m.p. 98°, -indone, respectively. Similarly, 1 : 1 : 3-trichloroindene (II) yields 3-chloroindone, m.p. 57—57.5°, and thence 2 : 3-dichloro-, m.p. 89°, and 3-chloro-2-bromo-, m.p. 111—112°, -indone. Treatment of (I) or (II) with boiling MeOH or MeOH-H₂O gives non-homogeneous products. When heated with NaI in boiling COMe_2 or, less advantageously, with mol. Ag in C_6H_6 , (I) gives 3 : 3'-dibromo-1 : 1'-diindenylenes (III), not molten below 400° after darkening at 300° [tetrabromide, m.p. 179° (decomp.) after darkening at 145°], converted by Zn wool and AcOH in COMe_2 into 3 : 3'-diindenylenes (IV), m.p. 130.5—131.5°. (II) and NaI in COMe_2 yield 3 : 3'-dichloro-1 : 1'-diindenylenes (V), m.p. 231.5—232.5° (decomp.) after darkening at 185°, converted by Cl_2 in CCl_4 into the tetrachloride (VI), m.p. 209—211° (decomp.) after darkening at 155°, with small amounts of a substance $\text{C}_{18}\text{H}_2\text{Cl}_4$, decomp. 160—162°. (VI), Zn wool, and AcOH in MeOH give 3 : 3'-diindenylenes, m.p. 232.5° (decomp.), in 85% yield with only traces of (IV).

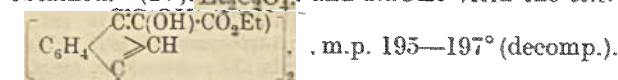
1:1':3:3'-Tetrachloro-1:1'-di-indenyl (VII), m.p. 172.2—173.2°, is an intermediate in the production of (V) and remains dissolved in the COMe_2 ; it is converted by Zn wool and AcOH in COMe_2 into an isomeric 3:3'-dichloro-1:1'-di-indenylene (VIII), m.p. 165.5—166.5°. Trichloroindene is unchanged by Hg in C_6H_6 , but with mol. Ag it yields a small proportion of (VII) and (VIII): with Zn turnings and AcOH in COMe_2 or Et_2O it affords (V) and some indene. Treatment of (III) with Zn dust in boiling EtOH or with Zn dust and AcOH in $\text{C}_6\text{H}_5\text{N}$ gives (IV), stable in light petroleum towards O_2 in the dark but yielding a peroxide when exposed to light, which is oxidised by KMnO_4 to $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and benzil-4:2'-dicarboxylic acid, m.p. 253° (decomp.) (Ag salt; Me ester, m.p. 187.3°). Condensation



of (IV) with maleic anhydride affords the substance (IX), decomp. about 310° (block), accompanied by a colourless (?) stereoisomeric anhydride, m.p. 254—256°, and a yellow material, $\text{C}_{20}\text{H}_{16}\text{O}_3$, m.p. 258.5—261°, probably formed by displacement of H.

(IX) is hydrogenated (Pd) to 1:1'-dihydrindenyl, b.p. 194—195°/14 mm. (IV) and 2 Br in CS_2 afford two dibromides, m.p. 135—136° (decomp.) after darkening, and m.p. 106—106.5° (decomp.), respectively, the former being re-converted into (IV) by Zn dust and EtOH. In individual cases (IV) and 4 Br in CS_2 gave a tetrabromide, m.p. > 250° after darkening at 150°, but usually a third dibromide, m.p. 184—186° (decomp.). Condensation of (IV) with PhCHO affords $\alpha\beta$ -diphenyl-

$\beta\delta\epsilon\zeta$ -diphenyleneoctatetraene (X) ($\text{CHPh}\cdot\text{C}\begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix}$), m.p. 217.5°; analogously, $\alpha\alpha$ -diphenyl- $\delta\epsilon\zeta$ -diphenylene-dodecahexaene, m.p. 251°, and $\alpha\beta$ -di-p-methoxyphenyl- $\beta\delta\epsilon\zeta$ -diphenyleneoctatetraene, m.p. 214°, are obtained. (IV), $\text{Et}_2\text{C}_2\text{O}_4$, and NaOEt yield the ester



1:1'-Di-indenyl is rapidly isomerised to (IV) by NaOMe in EtOH and is transformed by NaOEt and PhCHO in EtOH into (X). H. W.

Hydrogenation of naphthalene. A. MAILLARD (Compt. rend., 1933, 197, 1422—1424).—Catalytic reduction of gaseous C_{10}H_8 (I) with Pt-H_2 < 760 mm. occurs between 20° and 180°. Above 180° C is deposited and CH_4 produced, the proportion of the latter increasing as the H_2 pressure diminishes. At 20° the $\text{C}_{10}\text{H}_{12}$ (II) is reduced more rapidly than (I), the sole reaction being $(\text{I}) - 5\text{H}_2 \rightarrow \text{C}_{10}\text{H}_{18}$ (III), but at > 60° (I) is reduced more rapidly than (II). Thus at 85° the hydrogenation curves for (II) and for (I) in equilibrium with 2H_2 are identical, no (III) being produced until all (I) has disappeared: hence at > 60° two successive reactions $(\text{I}) - 2\text{H}_2 \rightarrow (\text{II})$; $(\text{II}) - 3\text{H}_2 \rightarrow (\text{III})$, occur. J. W. B.

Sulphonation reaction. I, II. I. S. JOFFE (J. Gen. Chem. Russ., 1933, 3, 437—447, 505—512).—Review of the lit. leads to the conclusion that the equations hitherto suggested as representing the

mechanism of sulphonation are somewhat incomplete. The reaction should be represented by the general expression $\frac{dx}{dt} = f(x)(A-x)(S-x) - \phi(x)(H+x)x$, where x is the concn. of the sulphonic acid formed, A that of the compound to be sulphonated, S the H_2SO_4 and H H_2O , whilst $f(x)$ and $\phi(x)$ are hitherto undetermined functions of x . In the sulphonation of C_{10}H_8 , the val. of K as obtained from the above equation falls progressively, indicating the influence of further factors. The following general conclusions are reached, however. Guyot's hypothesis that the limiting factor in sulphonation is the concn. of H_2SO_4 is incorrect. Sulphonation is a reversible reaction, which appears to cease when the two opposing rates are equal. The concn. of the H_2SO_4 is thus dependent on the quantities of the reacting substances present, and therefore has no const. limiting val. Sulphonation with fuming acid depends on the free SO_3 and is according to an equation of the second order. In general, the two opposing reactions are of the second order, becoming of pseudo-first order with large excess of one or other of the reagents. In the formation of 1- and 2- $\text{C}_{10}\text{H}_7\text{-SO}_3\text{H}$ a no. of reactions of varying rates take place simultaneously: sulphonation of C_{10}H_8 to the 1-acid (II) to the 2-acid (III), hydrolysis of (II) and (III). Since (III) is considerably more stable than (II), a const. ratio between them can be reached only under special conditions and after a long period. Since this condition of equilibrium was not attained and since the rates of the various reactions depend on the actual concns. of all the reacting substances, the const., K , calc. in the earlier experiments was found to fall progressively. To give a complete and accurate picture of the sulphonation mechanism, a more detailed series of expressions representing the various interdependent reactions must be developed.

M. Z.

Kinetics of sulphonation and monosulphonation of naphthalene. I. S. JOFFE (Anilinokras. Prom., 1933, 3, 296—304).—The 1- $\text{C}_{10}\text{H}_7\text{-SO}_3\text{H}$ content of the product of sulphonation of C_{10}H_8 at 100° falls from 83% after 8 hr. to 33% after 240 hr. A consideration of the velocity coeff. of the reaction of 1- and 2-sulphonation and of hydrolysis of the products indicates that at equilibrium the product should contain 22.6% of 1- and 77.4% of 2-sulphonic acid.

R. T.

Halogenation. VII. Iodination and bromination of naphthalene and 9-naphthol. P. S. VARMA, D. N. MOZUMDAR, and K. K. RAJAH (J. Indian Chem. Soc., 1933, 10, 595—598: see this vol., 187).—1- $\text{C}_{10}\text{H}_7\text{I}$ is best prepared by addition of a 1:1 mixture (A) of fuming HNO_3 and nitrosulphonic acid to C_{10}H_8 and I in boiling AcOH. A good yield of $\text{C}_{10}\text{H}_7\text{Br}$ is similarly obtained from C_{10}H_8 and Br in CCl_4 : some $\text{C}_{10}\text{H}_7\text{-NO}_2$ is also formed. Experiments using substances (e.g., HNO_3 , CrO_3) other than (A) are described. 3- $\text{C}_{10}\text{H}_7\text{-OH}$ is best iodinated (I in KI) in aq. NH_3 : bromination is best effected in AcOH at 10° in presence of conc. H_2SO_4 or oleum. H. B.

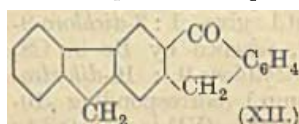
Amyrin. III. Constitution of sapotalin and the hydrocarbon $\text{C}_{14}\text{H}_{16}$. O. BRUNNER, H. HOFER, R. STEIN, and (in part) F. GROF (Monatsh., 1933, 63, 79—98: cf. A., 1932, 1253).—Confirmation that

sapotalin (I) is 1 : 2 : 7- $C_{10}H_5Me_3$ is obtained by oxidation with CrO_3 -AcOH at $>5^\circ$ to the *quinone*, m.p. 113° , oxidised by $KMnO_4$ in H_2O - $COMe_2$ at 0° to 3 : 4-*dimethylphthalic anhydride*, m.p. 126° (*acid*, m.p. 149 — 150° ; *methylimide*, m.p. 98 — 99°), identical with a specimen synthesised by dehydrogenation of the Δ^4 -tetrahydro-compound (Farmer *et al.*, A., 1932, 141) by Br at 200° and subsequent reduction with Na-Hg. Ruzicka's synthesis (A., 1932, 277) of (I) from γ -*p*-tolyl- α -methylbutyric acid (II) is confirmed. Similarly Ruzicka's identification of the hydrocarbon $C_{14}H_{16}$ as 1 : 2 : 5 : 6- $C_{10}H_5Me_4$ (III) (A., 1933, 495) is confirmed by failure to convert it to a quinone, production of mellophanic acid by $KMnO_4$ oxidation, and the following synthesis. 2 : 3-Dimethylbenzonitrile is hydrolysed by conc. aq. KOH-NaOH at 200° to the *acid*, m.p. 145 — 146° (*amide*, m.p. 155 — 156°), the *chloride*, b.p. $128^\circ/22$ mm., of which is converted by Pd-BaSO₄ in xylene into 2 : 3-dimethylbenzaldehyde (*oxime*, m.p. 80 — 82° ; *semicarbazone*, m.p. 222°), condensed with $COMe_2$ (10% NaOH) to 2 : 3-dimethylbenzylidene-acetone, b.p. $166^\circ/16$ mm., m.p. 37° (*oxime*, m.p. 160 — 162° ; *semicarbazone*, m.p. 215° , both in vac.), reduced by H₂ and Pd-BaSO₄ to 3-(2 : 3-dimethylphenyl)ethyl *Me ketone*, b.p. $139^\circ/10$ mm. (*semicarbazone*, m.p. 204° in vac.), reduced (Na in EtOH) to the *carbinol*, b.p. $156^\circ/20$ mm., which is converted by way of the *bromide*, b.p. 151 — 152° , and nitrile into the *acid*, which is cyclised by conc. H_2SO_4 at 100° to 1-keto-2 : 5 : 6-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. This with $MgMeI$ and subsequent dehydrogenation with Se affords (III). Similar dehydrogenation (Br) of 4 : 5-dimethyl- Δ^4 -tetrahydrophthalic anhydride (Diels *et al.*, A., 1929, 819) (*acid*, m.p. 189 — 190° ; *imide*, m.p. 126.5 — 127.5°) affords a ready method of synthesising 4 : 5-dimethylphthalic anhydride (*acid*, m.p. 196° ; *methylimide*, m.p. 150 — 151° ; *ethylimide*, m.p. 89°). J. W. B.

Anthracene derivatives. X. E. DE B. BARNETT, N. F. GOODWAY, and J. W. WATSON (Ber., 1930, 66, [B], 1876—1891).—Condensation of o - $C_6H_4(CO)_2O$ with m - $C_6H_4Cl_2$ yields 2 : 4-dichlorobenzoylbenzoic acid (I) and (?) 3 : 3-di-2' : 4'-dichlorophenylphthalide, m.p. 176° , which, after hydrolysis, could not be reduced by Zn dust and alkali. (I) is reduced by Zn dust, NH_3 , and $CuSO_4$ to o -2 : 4-dichlorobenzylbenzoic acid, m.p. 128° , converted by conc. H_2SO_4 at room temp. into 2 : 4-dichloroanthrone (II), m.p. 161° . (II) is transformed by Ac_2O - C_5H_5N into 2 : 4-dichloroanthranil acetate (III), m.p. 170° , and by Br in CS_2 into 2 : 4-dichloro-10-bromoanthrone (IV), m.p. 157° , whence 2 : 4-dichloro-10-anilinoanthrone, m.p. 187° , and 2 : 4-dichloro-10-piperidinoanthrone, m.p. 154° , -anthrone. (IV), $AlCl_3$, and C_6H_6 at room temp. yield 2 : 4-dichloro-10-phenylanthrone, m.p. 164° , converted by successive treatment with CH_2Ph -MgCl and HCl-AcOH into 2 : 4-dichloro-10-phenyl-9-benzylanthracene, m.p. 175° . 2 : 4-Dichloro-9-benzylanthracene, m.p. 163° , prepared similarly from (II), is transformed by Br in CS_2 at room temp. into 2 : 4-dichloro-9- α -bromobenzylanthracene, m.p. 138° (slight decomp.), whence the corresponding α -piperidino-compound, m.p. 168° . (III) and HNO_3 (d 1.42) in AcOH at 65° afford 2 : 4-dichloro-10-nitroanthrone, m.p. 137° (decomp.), readily decomposed by Ac_2O in cold C_5H_5N . 1 : 3-Dichloro-

anthrone (V), m.p. 194° , obtained by reduction of 1 : 3-dichloroanthraquinone with Al powder and conc. H_2SO_4 [1 : 3-dichloroanthranil acetate (VI), m.p. 200°] yields 1 : 3-dichloro-10-bromoanthrone, m.p. about 180° (decomp.), whence 1 : 3-dichloro-10-anilinoanthrone, m.p. 180° , and, by action of piperidine in $CHCl_3$, 1 : 3 : 1' : 3'-tetrachloro-10-bromo-10 : 10'-dianthranyl, decomp. (indef.) 220 — 230° . (V), CH_2PhCl , and aq. KOH give 1 : 3-dichloro-10 : 10-dibenzylanthrone, m.p. 232° . (V) and CH_2Ph -MgCl give 1 : 3-dichloro-9-benzylanthracene, m.p. 127° , whence by Br in CS_2 1 : 3-dichloro-10-bromo-9-benzylidene-9 : 10-dihydroanthracene, m.p. 197° (decomp.) (corresponding -10-piperidino-compound, m.p. 148°). (VI) is nitrated to 1 : 3-dichloro-10-nitroanthrone, m.p. 158° (decomp.), rapidly transformed by Ac_2O in C_5H_5N at room temp. into 1 : 3-dichloro-10-nitroanthranil acetate, m.p. 207° . 4 : 5-Dichlorophthalic anhydride (VII), o - $C_6H_4Cl_2$, and $AlCl_3$ yield 3 : 4 : 4' : 5'-tetrachlorobenzophenone-2'-carboxylic acid, m.p. 183° (Na salt), converted by conc. H_2SO_4 at 100° into 2 : 3 : 6 : 7- (VIII), m.p. 348° , and 1 : 2 : 6 : 7-, m.p. 242° , -tetrachloroanthraquinone. (VIII) is reduced by Al powder and conc. H_2SO_4 at 30 — 40° to 2 : 3 : 6 : 7-tetrachloroanthrone, m.p. 300° (decomp.). Protracted boiling of (VIII) with $SnCl_2$ and conc. HCl appears to yield a little of the anthraquinol. Reduction and subsequent dehydration of the phthaloyl acid proceeds very slowly, appearing to give small amounts of a trichloroanthrone, m.p. 235° . (VII), o -xylene, and $AlCl_3$ in C_2H_5Cl give 4' : 5-dichloro-3 : 4-dimethylbenzophenone-2'-carboxylic acid, m.p. 184° , transformed by conc. H_2SO_4 at 100° into 6 : 7-dichloro-2 : 3-dimethylantraquinone, m.p. 305° , which is reduced (Al powder, conc. H_2SO_4) to 6 : 7-dichloro-2 : 3-dimethylanthrone (IX), m.p. 295° (6 : 7-dichloro-2 : 3-dimethylanthranyl acetate, m.p. 226°), converted by activated Zn dust and boiling aq. KOH into 6-chloro-2 : 3-dimethylanthrane, m.p. 299° . Bromination of (IX) suspended in CS_2 leads to 6 : 7-dichloro-10-bromo-2 : 3-dimethylanthrone, decomp. 175° , apparently converted by piperidine in $CHCl_3$ into a dianthraquinone. (IX), CH_2PhCl , and KOH in boiling CH_2Ph -OH- H_2O afford 6 : 7-dichloro-10-benzyl-2 : 3-dimethylanthranyl CH_2Ph ether, m.p. 188° , converted by maleic anhydride in boiling xylene into 6 : 7-dichloro-10 : 10-dibenzyl-2 : 3-dimethylanthrone, m.p. 252° . 6 : 7-Dichloro-9-benzyl-2 : 3-dimethylanthrane, m.p. 233° , obtained from (IX) and CH_2Ph -MgCl, is brominated to 6 : 7-dichloro-10-bromo-9-benzyl-2 : 3-dimethylanthrane, m.p. 220° . 2 : 3 : 6 : 7-Tetramethylanthrane, m.p. 299° (cf. Morgan *et al.*, A., 1931, 1282), readily prepared from CH_2Cl_2 , o - $C_6H_4Me_2$, and $AlCl_3$ [9 : 10- Br_2 -derivative, m.p. 290° (decomp.)], is oxidised to the anthraquinone (X), which, contrary to Morgan, is readily reduced if very finely divided. Treatment of (X) with Al powder-conc. H_2SO_4 readily yields 2 : 3 : 6 : 7-tetramethylanthrone (XI), m.p. 271° (2 : 3 : 6 : 7-tetramethylanthranyl acetate, m.p. 241°). (X), CH_2PhCl , and KOH in boiling CH_2Ph -OH- H_2O yield 10 : 10-dibenzyl-2 : 3 : 6 : 7-tetramethylanthrone, m.p. 244° . 9-Benzyl-2 : 3 : 6 : 7-tetramethylanthrane, m.p. 235° , prepared from (XI) and CH_2Ph -MgCl, affords 10-bromo-9-benzyl-2 : 3 : 6 : 7-tetramethylanthrane, m.p. 227° . (VII), C_6H_6 , and $AlCl_3$ in C_2H_5Cl give 4 : 5-

dichlorobenzophenone-2-carboxylic acid, m.p. 208°, converted by conc. H_2SO_4 into 2:3-dichloroanthraquinone, m.p. 265°. 2:3-Dichloro-9-benzylanthracene, m.p. 164°, and its 10-Br-derivative, m.p. 169°, are described. 2:3-Dichloroanthracene is quantitatively obtained from the anthrone by activated Zn dust and 10% KOH. *o*-2-Fluoroylbenzoic acid, m.p. 229°, obtained in > 80% yield from $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$, fluorene, and AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$, is reduced by Zn dust to 2'-fluorylphenylmethane-2-carboxylic acid, m.p. 199°, which is transformed by ZnCl_2 at 180—190° into lin-



indenoanthrone (XII), m.p. 207° (corresponding anthranlyl acetate, m.p. 203°, and Br-derivative, decomp. about 190°). (XII) is oxidised by CrO_3 in dil. AcOH to lin-phthaloylfluorene, m.p. 269° after becoming red, and further in presence of H_2SO_4 to lin-phthaloylfluorenone, m.p. 367°. Reduction of (XII) with activated Zn dust and boiling 10% NaOH leads to lin-naphthafluorene, m.p. 317° [dibromonaphthafluorene, m.p. 245° (decomp.)]. 3:6-Dichlorophthalic anhydride, fluorene, and AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ give dichloro-*o*-2-fluoroylbenzoic acid, m.p. 172°, reduced by Zn dust, KOH, and NH_3 to a compound, (?) $\text{C}_{21}\text{H}_{15}\text{O}_2\text{Cl}$, m.p. 218°. β -Fluoroylpropionic acid (cf. Koelsch, A., 1933, 1284) from fluorene, succinic anhydride, and AlCl_3 in $\text{C}_2\text{H}_2\text{Cl}_4$ or PhNO_2 (yield 80%), is reduced in tetrahydronaphthalene (XIII) (Clemmensen) to γ -fluorylbutyric acid, m.p. 153°, transformed smoothly by ZnCl_2 at 180—210° into ketotetrahydro-lin-benzofluorene, reduced (Clemmensen) in xylene or (XIII) to tetrahydro-lin-benzofluorene, which is dehydrogenated by Se at 280—290° to lin-benzofluorene, m.p. 208°. H. W.

Sulphonation of phenanthrene. Preparation of the monosulphonic acids. I. S. JOFFE (J. Gen. Chem. Russ., 1933, 3, 448—452).—An effective method of preparing phenanthrenesulphonic acids on a technical scale free from disulphonic acids is developed. Large yields of the monosulphonic acids are obtained by shortening the reaction period and avoiding even local excess of H_2SO_4 by adding the acid to molten phenanthrene. Reduction of the quantity on dilution of the acid increases the yield, but lengthens the reaction period. The 9-isomeride can be obtained at higher temp., but rapidly passes into the others by intramol. rearrangement. The 2-isomeride increases in amount with prolongation of the reaction period. A concise scheme of separation of the isomerides from the reaction mixture is given. M. Z.

Polycyclic aromatic hydrocarbons. XII. Orientation of derivatives of 1:2-benzanthracene, with notes on the preparation of some new homologues, and on the isolation of 3:4:5:6-dibenzphenanthrene. J. W. COOK (J.C.S., 1933, 1592—1597).—Oxidation of benzantraquinone derivatives and subsequent esterification affords: *Me*₂ anthraquinone-1:2-dicarboxylate, m.p. 208°; *Me*. anthraquinone-1:2:3-, m.p. 184—185°, -1:2:5-, m.p. 212—213°, -1:2:6-, m.p. 233.5—234.5°, and -1:2:7-, m.p. 204—204.5°, -tricarboxylate; *Me*. anthraquinone-1:2:6:7-, m.p. 193—194°, and

1:2:7:8-, m.p. 237—239°, -tetracarboxylate. 1-Benzoyl-2:3-dimethylnaphthalene when heated affords 4-methyl-1:2-benzanthracene, m.p. 124.5—125.5° (picrate, m.p. 149—150°). 5-Keto-5:6:7:8-tetrahydro-1:2-benzanthracene and MgMeI give 5-methyl-1:2-benzanthracene, m.p. 157.5—158.5° (picrate, m.p. 163—163.5°), oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$) to -benzantraquinone, m.p. 173.5—174.5°. α - $\text{C}_{10}\text{H}_7\text{COCl}$, 2:3- $\text{C}_{10}\text{H}_6\text{Me}_2$, and AlCl_3 give 1- α -naphthoyl-2:3-dimethylnaphthalene, m.p. 191° (1- β -, m.p. 129—130°), which on heating forms 4-methyl-1:2:5:6-dibenzanthracene, m.p. 184—185° (dipicrate, m.p. 200—201°). Oxidation of 1- α -naphthoyl-2:6-dimethylnaphthalene with H_2SeO_3 yields 1- α -naphthoyl-6-methyl-2-naphthaldehyde, m.p. 185—186°. 9:10-Dihydro-1:2:5:6-dibenzanthracene, m.p. 196—198°, obtained by hydrogenation of the dibenzanthracene, is oxidised to 1:2:5:6-dibenz-9:10-, and some -3:4-anthraquinone, m.p. 326—327° (decomp.) (azine, m.p. > 300°), also formed from the oxidation of 1:2:5:6-dibenzanthracene. Separation of the mixture of acids resulting from the Pschorr reaction with di- α -*o*-aminobenzylidene-*p*-phenylenediacetic acid (Weitzenbock and Klinger, A., 1918, i, 494) gives a product oxidised to 3:4:5:6-dibenzphenanthra-1:2:7:8-diquinone, m.p. > 360° (diazine, m.p. > 360°) (decarboxylated to 3:4:5:6-dibenzphenanthrene, m.p. 177—178°), and 1:2:5:6-dibenzanthraquinone-4:8-dicarboxylic acid, m.p. > 360°. F. R. S.

Isomerisation of the hydrocarbons $\text{C}_{42}\text{H}_{30}$, isomeric with 1:3:4':3'-tetraphenyl-1:1'-dihydorubene. A. WILLEMART (Compt. rend., 1933, 197, 1429—1432).—Fusion of the hydrocarbon $\text{C}_{42}\text{H}_{30}$ (I), m.p. 179° (A., 1927, 355), converts it into a colourless isomeride, + solvent, m.p. 250°, solvent-free, m.p. 317—318°, and a yellow isomeride, m.p. 249°, identical with the yellow substance (*loc. cit.*, m.p. 245°) formed with (I), and with the yellow "satellite" of rubrene (A., 1930, 594). J. W. B.

Rubenes: a colourless hydrocarbon with violet fluorescence derived from diphenylditolylrubene. L. ENDERLIN (Compt. rend., 1933, 197, 1332—1334).—By shaking the monoxide (A., 1932, 216) of the above rubene with 90% H_2SO_4 in C_6H_6 , or boiling it [or the corresponding $(\text{OH})_2$ -compound] with AcOH , is obtained a colourless hydrocarbon $\text{C}_{44}\text{H}_{30}$, m.p. 375° (block), which is the di-*p*-tolyl analogue of the hydrocarbon $\text{C}_{42}\text{H}_{26}$ previously obtained (*loc. cit.*). A trace of a yellow substance was sometimes obtained in the reaction. J. W. B.

Halogenation of the condensation products of *N*-alkyl-*o*-toluidines with chloral hydrate and nitration of the resulting compounds. A. H. ADVANI (J. Indian Chem. Soc., 1933, 10, 621—624).—5-Trichloro- α -hydroxyethyl-*N*-methyl-*o*-toluidine (I) is brominated (under various conditions) to the 3-Br-derivative (II), m.p. 150°, the ON- Ac_2 derivative, m.p. 130°, of which is oxidised (aq. KMnO_4) to 3-bromo-4-*N*-acetmethylamido-5-methylphenylglyoxylic acid, m.p. 201°. (I) and Cl_2 in C_6H_6 give the 3-Cl-derivative (III), m.p. 132—133° (Ac_2 derivative, m.p. 112°). 5- $\beta\beta$ -Trichloro- α -hydroxyethyl-*N*-ethyl-*o*-toluidine similarly affords 3-Br-, m.p. 115° (Ac_2

derivative, m.p. 150—152°), and 3-*Cl*-, m.p. 116—117° (*Ac*-, derivative, m.p. 155—156°), -derivatives. (II) and (III) are converted by conc. HNO_3 into 6-bromo-, m.p. 230° (decomp.) (*Ac* derivative, m.p. 107°), and 6-chloro-, decomp. 230° (*Ac* derivative, m.p. 113°), -2-methyl-4- $\beta\beta\beta$ -trichloro- α -hydroxyethyl-phenyl-*N*-methylnitroamine, respectively; 6-bromo-, m.p. 198° (decomp.) (*Ac* derivative, m.p. 127°), and 6-chloro-, m.p. 181° (*Ac* derivative, m.p. 132°), -2-methyl-4- $\beta\beta\beta$ -trichloro- α -hydroxyethylphenyl-*N*-ethyl-nitroamine are similarly prepared. 6-Nitro-2-methyl-4- $\alpha\beta\beta\beta$ -tetrachloroethylphenyl-*N*-methylnitroamine, m.p. 199°, is obtained from the 4- $\beta\beta\beta$ -trichloro- α -hydroxyethyl derivative (A., 1933, 497) and SOCl_2 . H. B.

Chloro-derivatives of *p*-xylene. H. WAHL (Compt. rend., 1934, 198, 100—102).—6-Nitro-*p*-xylidine (Sonn, A., 1916, i, 391) is converted by the Sandmeyer reaction into 2-chloro-6-nitro-*p*-xylene (I), reduced (Fe-HCl) to 6-chloro-*p*-xylidine, identical with the amine, m.p. 40°, obtained (this vol., 177) by reduction of the NO_2 -compound [identical with (I)] isolated from the nitration products (II) of chloro-*p*-xylene. Fractional distillation of the amines obtained by reduction of (II), or fractional crystallisation of their hydrochlorides, effects isolation of 3-chloro-*p*-xylidine (*loc. cit.*). The proportions of 5-, 6-, and 3- NO_2 -derivatives in (II) are, approx., 60, 15, and 10%, respectively. J. W. B.

Introduction of the thiocyano-group into aromatic compounds by means of chloroamines. II. M. V. LICHOSCHERSTOV and A. A. PETROV (J. Gen. Chem. Russ., 1933, 3, 759—764).— $\text{o-C}_6\text{H}_4\text{Me-NH}_2$ (I) reacts with NH_4CNS and NH_4Cl (II) in AcOH to yield the 5-SCN-derivative of (I) [*N*-*Ac*-, m.p. 140.5°; 3-*Cl*-, m.p. 82—83.5°; 3-*Br*-derivative, m.p. 98—99.5° (*Ac* derivative, m.p. 150°)]. Under analogous conditions, *m*- $\text{C}_6\text{H}_4\text{Me-NH}_2$ yields the 6-SCN-derivative (*N*-*Ac*-, m.p. 189°; 4-*Cl*-, m.p. 95—97°; 2-bromo-4-chloro-, m.p. 105°; 2:4- Cl_2 -, m.p. 105—106°; 4-*Br*-, m.p. 78°; 2:4-*Br}_2*-, m.p. 103.5°; 4-bromo-2-chloro-, m.p. 98°; 4-*I*-derivative, m.p. 86—87°), using 1 equiv. of (II) or of dichloro-carbamide, whilst using 2 equivs. the product is the 4:6-(SCN) $_2$ -derivative, m.p. 142—143° [2-*Br*-derivative, sinters at 162°, m.p. 241° (decomp.)], which on prolonged heating in aq. HCl solution undergoes conversion into 6-thiocyano-2-amino-5-methylbenzthiazole, m.p. 210°. The 3-SCN-, m.p. 56°, and 3:5-(SCN) $_2$ -derivatives of *p*- $\text{C}_6\text{H}_4\text{Me-NH}_2$, obtained as above, undergo spontaneous conversion into the corresponding benzthiazole derivatives.

R. T.

Diazotisation of aromatic nitro-amines and prevention of diaryl formation in Sandmeyer reaction. H. H. HODGSON and J. WALKER (J.C.S., 1933, 1620—1621).—Diazotisation of weak bases such as 2- and 4-nitro- and 2:4-dinitro- α -naphthylamines is rapid and complete when a solution of the amine in abs. AcOH is added to NaNO_2 in conc. H_2SO_4 . Addition of the resulting solution to cold CuCl-HCl , CuBr-HBr , or saturated aq. KI gives the corresponding halogeno-compound in > 80% yield, no diaryl formation being observed. 4:4'-

Dichloro-3:3'-dinitrodiphenyl may thus be prepared (80% of theory; cf. J.C.S., 1913, 103, 2074). Prior dilution of the diazo-solution with H_2O or ice results in tar formation or a different course of reaction [e.g., 4-nitronaphthalene-1-diazo-2-oxide from 1:2:4- $\text{NH}_2\cdot\text{C}_{10}\text{H}(\text{NO}_2)_2$]. Addition of EtOH to the diazo-solution and gradual heating to 80° eliminates the diazo-group. 1-Bromo-, m.p. 160°, and 1-iodo-2:4-dinitronaphthalene, m.p. 183°, are described.

H. A. P.

Action of nitrous acid and nitrosyl chloride on β -phenylpropylamine. Method of separating primary, secondary, and *tert.*-phenyl chlorides and phenylcarbinols. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1933, 103, 373—382).—Contrary to earlier results (A., 1930, 1287), *l*- α -phenyl-*n*-propyl alcohol (I), $[\alpha]_D^{25}$ -1.75°, is obtained from *d*- α -phenylpropionic acid, either by reduction of its Et ester, or by the action of HNO_2 on the amine derived from it. In mixtures of primary (II), *sec.* (III), and *tert.* (IV) phenylated carbinols, and of their respective chlorides (V), (VI), and (VII), (II) and (III) give esters with $\text{o-C}_6\text{H}_4(\text{CO})_2\text{O}$ and are thus separated from (IV) which gives unsaturated hydrocarbons, and only (III) and (IV) give their chlorides with aq. HCl . With AgOAc only (VI) gives the *Ac* derivatives of (III), (VII) again yielding unsaturated hydrocarbons, and thus (V) is separated, then (VI) and (VII) are determined by conversion, by way of the acetates, into (III) and (IV), and (III) is separated as its *H* phthalate. By these methods it is shown that *l*- β -phenyl-*n*-propylamine, b.p. 85°/12 mm., $[\alpha]_D^{25}$ -3.49° (H_2 - PtO_2 reduction of nitrile), with HNO_2 affords 66% of β -phenyl-*n*-propyl alcohol and 34% of $\text{CPhMe}_2\cdot\text{OH}$, but with NOCl in Et_2O at -50° it gives 90% of *l*- α -chloro- β -phenylpropane, b.p. 71°/2 mm., $[M]_D^{25}$ -1.2°, 8% of CMe_2PhCl , and 2% of secondary chlorides. Prolonged keeping of $\text{CHMePh}\cdot\text{CH}_2\text{Cl}$ at room temp. causes 16% conversion into secondary and/or *tert.* chlorides. All vals. of $[\alpha]$ are for the homogeneous substance. J. W. B.

Optical activity of a diphenyl derivative, dissymmetry of which is caused by space effect of only one group. (Miss) M. S. LESSLIE and E. E. TURNER (J.C.S., 1933, 1588—1592; cf. A., 1933, 388).—2-Nitro-*NN'*-dicarbethoxybenzidine (A., 1928, 283) is converted by Br in AcOH into the 3-bromo-2'-nitro-derivative, m.p. 145—147°, hydrolysed by aq. H_2SO_4 to 3-bromo-2'-nitrobenzidine, m.p. 155—156° (corr.), which is readily deaminated to 3-bromo-2'-nitrodiphenyl (I), m.p. 69—70°, b.p. 195°/11 mm., by heating the bisdiazoborofluoride (II) with abs. EtOH and conc. H_2SO_4 . Reduction of (I) with $\text{SnCl}_2\text{-HCl}$ gives the -2'- NH_2 -compound, m.p. 69—70° (corr.), the *N*- Me_2 derivative of which, m.p. 47—48°, b.p. 176—178°/9 mm. (*platinichloride*), forms quaternary salts only with difficulty; the *methiodide* is formed by heating at 175° for 8 hr. with a large excess of MeI . Attempts at optical resolution of this failed. The corresponding *As* compound was therefore prepared. 3'-Bromodiphenyl-2-arsinic acid, m.p. 189—190° (corr.), is obtained from (II) and Na_2AsO_3 in presence of CuSO_4 . It is reduced by SO_2 , HCl , and I to the dichloroarsine, which is treated with MgMeI in C_6H_6 ;

the resulting product with MeI in EtOH gives 3-bromo-diphenyl-2-trimethylarsonium iodide, m.p. 183—184° (corr.). By crystallisation of the d- α -bromocamphor- π -sulphonate of this a d-isomeride, m.p. 184—185°, $[\alpha]_{D}^{20} +46.8^\circ$, was isolated; the d-camphorsulphonate, m.p. 219—220°, has $[\alpha]_{D}^{20} +19.6^\circ$ to 21.8° . Mesityldimethylarsine, b.p. 138—139°/20 mm. (from Mg mesityl bromide and AsMe₃I), gives a methiodide, m.p. 219—220°, and an ethiodide, m.p. 174—175° (corr.) (cf. dimethylmesidine, A., 1872, 1021). H. A. P.

Ammonolytic reactions. E. C. FRANKLIN (J. Amer. Chem. Soc., 1933, 55, 4912—4915).—CN·NR₂ (I) (R=Et, Prⁿ, Buⁿ) (1 mol.) and KNH₂ (II) (2 mols.) in liquid NH₃ at 35° give NHR₂, NH₃, and CN·NK₂. NN'N''-Triphenylguanidine and NH₄Cl in liquid NH₃ at 200° afford guanidine (III) and NH₂Ph. (I) (1 mol.) and (II) (1 mol.) in cold liquid NH₃ give NR₂·C(NH)·NHHK; the K salts where R₂ is Me₂, Et₂, Prⁿ₂, Buⁿ₂, and disoamyl and the Na salts where R₂ is Et₂ and Buⁿ₂, are described. Ammonolytic decomp. of NH₂·CO·NHMe affords CO(NH₂)₂ (IV), NH₂Me, and (III) [formed from (IV)], whilst CO(NHPh)₂ gives (III), (IV), and NH₂Ph. NH₂Ac or NH₄OAc heated with NH₄Cl in liquid NH₃ affords acetamidine (V); diphenylacetamidine similarly gives (V) and NH₂Ph; diphenylbenzamidine yields benzamidine and NH₂Ph; NPhAc furnishes (V) and NH₂Ph. CPhCl₃ and liquid NH₃ at room temp. give PhCN; at 100°, uni- and ter-mol. PhCN result.

H. B.

Triarylaminoethylenes. VI. Coloured by-products formed during the synthesis of triarylaminoethylenes. R. SHIBATA and T. NISHI (J. Soc. Chem. Ind. Japan, 1933, 36, 625—630B; cf. A., 1933, 1286).—The by-product (I), m.p. 141°, obtained in the synthesis of tri-*p*-tolylaminoethylene (II) is C₆H₄Me·N:C(NH·C₆H₄Me)·CH:N·C₆H₄Me, since it yields (II) with Na-Hg and EtOH or when hydrogenated (Pd-black) in Et₂O, and is formed from (II) by PbO₂ and CaCl₂ in boiling C₆H₆, by KMnO₄ in hot COMe₂, by O₂ in hot PhMe-20% NaOH emulsion, by heating in high-boiling solvents, e.g., decahydronaphthalene, or by heating above the m.p. (which gives also a small amount of a substance, m.p. 207°). (II) with ZnCl₂ at 180° gives a substance, m.p. 100—101°, and with S at 140—150° gives tri-*p*-tolylaminothioethylene, m.p. 137°, and a trace of dithio-ox-*n*-toluidide, m.p. 201°. NH₂Ph and C₂HCl₃ give a red and a yellow compound, m.p. 115—117°. β -C₁₀H₇·NH₂ gives tri- β -naphthylaminoethylene, m.p. 200°.

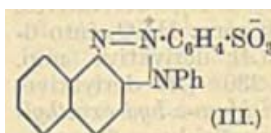
R. S. C.

Preparation of *p*-azoxyanisole. B. M. BOGOSLOVSKI (Anilinokras. Prom., 1933, 3, 304—307).—96% yields of *p*-azoxyanisole, m.p. 117°, are obtained by heating *p*-nitroanisole with Na and MeOH at 65—67° during 6 hr.

R. T.

Sensitivity to light of aryl- β -naphthylamine-azo-dyes. F. KROLLPFEIFFER, C. MÜHLHAUSEN, and G. WOLF (Annalen, 1933, 508, 39—51).—Exposure of a dil. (1 : 10,000) aq. solution of 1-*p*-sulphobenzene-azo-*N*-phenyl- β -naphthylamine (I) to sunlight gives ang-naphthphenazine (II) and (mainly) the betaine (III), m.p. about 360° (decomp.), of 3-phenyl-2-*p*-

sulphophenyl- α - β -naphth-1 : 2 : 3-triazolium hydroxide.



Aq. solutions of (III) show strong green fluorescence; treatment with alkaline reducing agents regenerates (I). (III) is also prepared by oxidation (amyl nitrite or K₂Cr₂O₇ in AcOH) of (I). Exposure of 1-benzeneazo-*N*-phenyl- β -naphthylamine (IV) (on cotton; immersed in H₂O) gives (after concn. of the extract and treatment with picric acid) 2 : 3-diphenyl- α - β -naphth-1 : 2 : 3-triazolium picrate, m.p. 244—245°; (II) is not produced. The *N*-Bz derivative of (IV) is much more stable to light; it is oxidised (H₂O₂, AcOH) to the *N*-Bz derivative, m.p. 173—174° (decomp.), of 1-benzeneazoxy-*N*-phenyl- β -naphthylamine, m.p. 132—133°, which is converted by AcOH-HCl at 150° into 2 : 3-diphenyl- α - β -naphth-1 : 2 : 3-triazolium chloride. 2 : 3-Diphenyl- (V), decomp. 305°, 3-phenyl-2-*p*-chlorophenyl-, decomp. 278—279°, 3-phenyl-2-*p*-nitrophenyl-, m.p. 215° (decomp.), 2-phenyl-3-*p*-tolyl-, decomp. 270°, and 2-phenyl-3-chlorophenyl-, decomp. 237—238°, - α - β -naphth-1 : 2 : 3-triazolium nitrates are prepared by oxidation (amyl nitrite, AcOH) of the requisite 1-aryloxy-*N*-aryl- β -naphthylamines and subsequent treatment with a little conc. HNO₃. Successive treatment of wool or cotton with these salts and alkaline Na₂S₂O₄ gives the azo-dye on the fibre; e.g., (IV) is thus prepared from (V). Diphenyl-4 : 4'-bis-(1-azo-*N*-phenyl- β -naphthylamine) (VI), m.p. 281—282° (from tetrazotised benzidine and β -C₁₀H₇·NHPh), is oxidised (as above) to 2 : 2'-(4 : 4'-diphenyl)bis-(3-phenyl- α - β -naphth-1 : 2 : 3-triazolium nitrate) [corresponding picrate, m.p. 320—321° (decomp.)]. 2 : 2'-(3 : 3'-Dichloro-4 : 4'-diphenyl)-bis-(3-phenyl- α - β -naphth-1 : 2 : 3-triazolium nitrate), decomp. 250—260° (corresponding picrate, m.p. 305—306°), is similarly prepared. (VI) (on cotton) is bleached rapidly by sunlight in air or O₂; in N₂, bleaching is very slow. Azo-dyes from *N*-alkyl- β -naphthylamines are not so readily convertible into triazolium salts and are much more stable to light. Bleaching of, e.g., (IV) probably involves initial oxidation of >NH.

H. B.

Action of halogens on nitrophenylazobenzoylacetones. F. D. CHATTAWAY and D. R. ASHWORTH (J.C.S., 1933, 1624—1627).—Action of Cl₂ in CHCl₃ on *p*-nitrobenzeneazobenzoylacetone (I), m.p. 143°, replaces the COMe group with formation of ω -chlorophenylglyoxal-*p*-nitrophenylhydrazone, m.p. 243°; in AcOH in presence or absence of NaOAc nuclear substitution also occurs giving ω -chlorophenylglyoxal-2-chloro-4-nitrophenylhydrazone, m.p. 183°. Similarly, from *o*-nitrobenzeneazobenzoylacetone (II), m.p. 145°, ω -chlorophenylglyoxal-*o*-nitro-, m.p. 151°, and 4-chloro-2-nitro-phenylhydrazone, m.p. 157°, are formed. ω -Bromophenylglyoxal-*p*-nitrophenylhydrazone, m.p. 247° (decomp.), is formed from (I) and Br in AcOH in presence of NaOAc only; in CHCl₃ or boiling AcOH substitution of the CH₃ group occurs with formation of δ -bromo- (III), m.p. 172° (decomp.), and δ -di-bromo- α - γ -triketo- α -phenylbutane- β -*p*-nitrophenylhydrazone (IV), m.p. 190° (decomp.). Action of KOAc in boiling EtOH on (III) and (IV), respectively, gives

4-hydroxy- (V), m.p. 211.5°, and *o*-bromo-4-hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole, m.p. 167°. Cl_2 in CHCl_3 converts (V) into 5 : *o*-dichloro-3-benzoyl-1-*p*-nitrophenyl-4-pyrazolone, m.p. 145°, which with aq. HI gives 5-chloro-4-hydroxy-3-benzoyl-1-*p*-nitrophenylpyrazole, m.p. 177°, and with boiling EtOH gives *Et* $\alpha\beta\gamma$ -triketo- γ -phenyl-*n*-butyrate- β -*p*-nitrophenylhydrazone (VI), m.p. 135° [free acid, m.p. 154° (cold dil. NaOH)]. (VI) is also formed from diazotised $\text{p-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and Et sodiobenzoylpyruvate. The following are similarly prepared from (II) : δ -bromo- $\alpha\beta\gamma$ -triketo- α -phenylbutane- β -*o*-nitrophenylhydrazone, m.p. 155° (decomp.); 4-hydroxy-3-benzoyl-1-*o*-nitrophenylpyrazole, m.p. 121° (5-Cl-derivative, m.p. 120°); 5 : 5-dichloro-3-benzoyl-1-*o*-nitrophenyl-4-pyrazolone, m.p. 166°; Et, m.p. 108°, and Me $\alpha\beta\gamma$ -triketo- γ -phenyl-*n*-butyrate- β -*o*-nitrophenylhydrazone, m.p. 119°. Many of the above are dimorphous, but the stable form only is described.

H. A. P.

Manufacture of azo dyes.—See B., 1934, 89.

Azo-derivatives of methyleneindoline.—See this vol., 195.

Replacement of diazo- by acetoxy-group. H. L. HALLER and P. S. SCHAFER (J. Amer. Chem. Soc., 1933, 55, 4954—4955).—*m*-Chlorobenzenediazonium borofluoride heated with AcOH gives about 50% of $\text{m-C}_6\text{H}_4\text{Cl}\cdot\text{OAc}$. *p*-Acetamidobenzenediazonium borofluoride and Ac_2O similarly give about 52% of diacetyl-*p*-aminophenol; AcOH can be used, but the product is less pure.

H. B.

Preparation of trihydroxyarylsulphonium derivatives of *o*- and *p*-substituted phenols and arylsulphonium bases. D. LIBERMANN (Compt. rend., 1933, 197, 1425—1427).—Thermal decomp. of aryl chlorosulphites (A., 1933, 48; reacting as $\text{HO}\cdot\text{Ar}\cdot\text{SOCl}$) in a suitable solvent affords tri(hydroxy-aryl)sulphonium chlorides (I) isolated as the Bz_4 derivative of the corresponding hydroxides, PhOH yielding tribenzoyloxyphenylsulphonium benzoate $+\text{H}_2\text{O}$. Similar derivatives are obtained from *p*-cresol, m.p. 53°, *p*-chlorophenol, m.p. 57—58°, and guaiacol, m.p. 51°. Treatment of conc. solutions of (I) in EtOH at 95° with NaCN affords tri-(*p*-hydroxyphenyl)-, m.p. 235°, and tri(hydroxytolyl)- (from *o*-cresol), m.p. 264°, -sulphonium hydroxides. The aryl derivatives of orthosulphurous acid obtained by Richter (A., 1919, i. 73) are also sulphonium bases.

J. W. B.

Germicidal action of 2-chloro-4-*n*-alkylphenols. F. F. BLICKE and R. P. G. STOCKHAUS (J. Amer. Pharm. Assoc., 1933, 22, 1090—1092).—The phenol coeffs. of homologous 2-chloro-4-*n*-alkylphenols (cf. Klarmann *et al.*, A., 1933, 817) increase progressively from Me to C_7H_{15} . The m.p. of their α -naphthoates are, respectively : 108—110°, 70—72°, 71—73°, 44—46°, 63—65°, 43—45°, 45—47°. The following are also mentioned : *p*-tolyl α -naphthoate, m.p. 61—63°, and diphenyl-*p*-carboxylate, m.p. 122—124°; *m*-chloro-*p*-tolyl *p*-nitrobenzoate, m.p. 88—90°, diphenyl-*p*-carboxylate, m.p. 111—113°, and benzoate, m.p. 67—68°; 2-chloro-4-ethylphenyl benzoate, m.p. 44—46°; 2-chloro-4-*n*-hexoyl-, m.p. 79—81°, 4-*n*-

hexoyl-, m.p. 61—62°, and 2 : 6-dichloro-4-*n*-hexylphenol, b.p. 308—310°/745 mm.

W. S.

Derivatives of *o*-aminophenol. L. GALATIS (Ber., 1933, 66, [B], 1774—1779).—Treatment of *o*-benzylidenaminophenol (I) with Ac_2O in presence or absence of NaOAc at 110—120° affords the *O*-Ac derivative and *N*-acetyl-2-phenylbenzoxazoline (II),

$\text{C}_6\text{H}_4\langle\text{N}^+\text{Ac}\rangle\text{CHPh}$, m.p. 98.5°, in 50% yield. The intermediate production of *o*-hydroxyacetbenzylamidophenol is established by the formation of PhCHO , $\text{o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NHAc}$, and 2-methylbenzoxazole when the product obtained from the cold reactants is treated with dil. HCl; addition of AcOH to $\text{N}^+\text{C}\langle$ does not occur in absence of Ac_2O . (II) is converted by conc. HCl into the hydrochloride of a compound, m.p. 245—255°. (I) is very readily hydrolysed by acid, whereas the corresponding *p*-derivative is stable.

H. W.

Organic compounds of sulphur. XXIV. "Free" radicals with univalent sulphur. A. SCHÖNBERG, E. RUPP, and W. GÜMLICH (Ber., 1933, 66, [B], 1932—1945; cf. A., 1933, 291, 487).—Solutions of di- α -thionaphthoyl disulphide (I) in $\text{C}_2\text{H}_4\text{Br}_2$ at 97°, PhOMe at 100°, C_{10}H_8 at 100°, phenanthrene at 110°, xylene, and Ph_2O do not obey Beer's law. Similar observations are made with Ph_2S_2 (II) in C_{10}H_8 , PhOMe , and $\text{C}_2\text{H}_4\text{Br}_2$ at 100°, whereas diphenylene disulphide (III) behaves normally. The behaviour is explained by the hypothesis of radical dissociation of (I) and (II) and the normal behaviour of (III) is expected, since dissociation, if occurring, does not lead to an increase of the no. of mols. in the dissolved phase. Solutions of (I) and (III) are markedly thermochromic. The following chemical evidence in favour of radical dissociation is adduced. (II) and CPh_3 afford $\text{SPh}\cdot\text{CPh}_3$. Solutions of the Na derivative (IV) of $\text{C}_6\text{H}_4\text{Ph}\cdot\text{COPh}$ are almost instantaneously decolorised by (I) and (II). (I) reacts instantaneously with CH_2N_2 , but the nature of the amorphous product could not be established. (II) and CPh_2N_3 yield $\text{CPh}_2(\text{SPh})_2$. (I) in boiling COMe_2 or $\text{COMe}_2\cdot\text{CHCl}_3$ readily dissolves Ag or Zn with formation of $\text{Ag} (+0.5\text{C}_5\text{H}_5\text{N})$ and $\text{Zn} (+\text{C}_5\text{H}_5\text{N})$ α -dithionaphthoate. Solutions of (I) and (II) are stable towards atm. O_2 . Determination of mol. wt. does not give evidence of radical dissociation in any case, but experiments have not been made in media of high b.p. on account of the danger of thermal decomp. Solutions of (I) in C_{10}H_8 at 100° are not electrolytes. Solutions of Ph_2Se_2 are strongly thermochromic and with (IV) produce $\text{C}_6\text{H}_4\text{Ph}\cdot\text{COPh}$ and NaSePh .

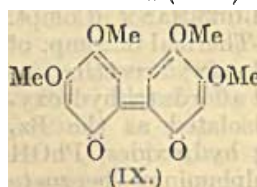
H. W.

Constitution of resorcinol and acetylacetone viewed from the Raman effect. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 16—21; cf. A., 1933, 764).—A reply to criticism (*ibid.*, 1144). Further work confirms the existence of the diketone-form of $\text{m-C}_6\text{H}_4(\text{OH})_2$ in equilibrium with the phenolic form in MeOH solution. Repetition of the work on CH_2Ac_2 revealed lines previously overlooked, but the main conclusions are unaltered thereby. The data for $(\cdot\text{CH}_2\text{Ac})_2$ are further discussed. D. R. D.

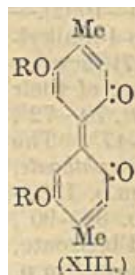
Formation of complex oxidation and condensation products of phenols. Origin and nature of humic acid. I. Reactivity of simple monocyclic quinones. II. Coupling of simple phenols and quinones to diphenyl derivatives. III. Rearrangements of oxidation-reduction type in the diquinone group. IV. Termolecular polymerisation products of *p*-benzoquinone, toluquinone, and α -naphthaquinone. H. G. H. ERDTMAN (Proc. Roy. Soc., 1933, A, 143, 177—191, 191—222, 223—228, 228—241).—I. The reactivity of various methoxyquinones towards Ac_2O - H_2SO_4 (I) and oxidative coupling is in qual. agreement with the predictions of electronic theory. Methoxybenzoquinone [prep. by oxidation of methoxyquinol (Ac_2 derivative, m.p. 95—96°) with PbO_2 - MgSO_4 in hot dry C_6H_6 described] with Ac_2O containing 2 wt.-% H_2SO_4 affords 2:4:5-triacetoxyanisole, m.p. 142°, hydrolysed (H_2SO_4 -MeOH in H_2) and methylated to 1:2:4:5-tetramethoxybenzene, oxidised by HNO_3 to 2:5-dimethoxybenzoquinone, which, like the 2:6-compound, is unattacked by (I). 2:3-Dimethoxybenzoquinone similarly affords 1:2:3-triacetoxy-3:4-dimethoxybenzene, m.p. 96—97°, *m*- and *p*-xyloquinones giving 2:4:5-triacetoxy-*m*-, m.p. 103—104° (lit., m.p. 99°), and 2:3:5-triacetoxy-*p*-xylene, respectively. 5-Methoxytoluquinone (II) gives 2:3:5-triacetoxy-4-methoxytoluene, m.p. 91—92°, hydrolysed and methylated to 2:3:4:5-tetramethoxytoluene, m.p. 51—52°, identical with a specimen similarly prepared from the Ac_4 derivative of Thiele and Winter (A., 1900, i, 504), the phenol obtained by these authors being, therefore, 2:3:4:5-tetrahydroxytoluene. With AcCl - AcOH (II) similarly affords 3-chloro-2:5-diacetoxy-4-methoxytoluene, m.p. 126°. Thymoquinone with (I) gives a mixture of 2:3:6-, m.p. 87—88° (38%), and 2:3:5-, m.p. 136—137° (57%), -triacetoxy-1-methyl-4-isopropylbenzene, separated by fractional crystallisation from EtOH, and synthesised by the action of Ac_2O - AcOH and Zn on 3- and 6-hydroxythymoquinone, respectively; 3:5:3':5'-tetramethyldibenzoquinone (Auwers *et al.*, A., 1905, i, 219) similarly gives 2:4:4'-triacetoxy-3:5:3':5'-tetramethyldiphenyl, m.p. 141—142°. With Br in AcOH creosol gives its 6-*Br*-derivative, b.p. 270—275° (slight decomp.), m.p. 82—83° (Br entering *p* to OMe), converted by Me_2SO_4 into 6-bromohomoveratrole.

II. All bishydroxyquinols in the lit. obtained by oxidative coupling of hydroxyquinols are derivatives of 2:4:5:2':4':5'-hexahydroxydiphenyl. The dipyrrogallol obtained by Harries (A., 1902, i, 771) by autoxidation of pyrogallol (III) in aq. $\text{Ba}(\text{OH})_2$ is 2:3:4:2':3':4'-hexahydroxydiphenyl (IV), darkens 280°, m.p. 310—320° (decomp.) (Ac_6 derivative, m.p. 163—164°), the Me_6 ether, m.p. 123° (Br_2 -compound, m.p. 110—111°), of which is identical with a specimen synthesised by heating 4-iodopyrogallol Me_3 ether (Graebe and Suter, A., 1905, i, 703) with Cu powder. With NaOH in place of $\text{Ba}(\text{OH})_2$ the sole product is the humic acid which also accompanies (IV), and no (IV) is obtained by anodic oxidation of (III) in $\text{N-H}_2\text{SO}_4$, but such oxidation of the Me_3 ether of (III) gives 2:6-dimethoxybenzoquinone and tarry products. Partial oxidation of methoxybenzoquinone (from vanillin and H_2O_2 -NaOH) with FeCl_3 -HCl at

30—40°, or the action of H_2SO_4 - AcOH affords a coupled product (V), probably 4:4'-dimethoxydiquinhydrone, sinters 210°, decomp. 230°, also obtained (with methoxyquinol) by thermal decomp. of methoxyquinhydrone, m.p. 97° (rapid heating) (prepared from its components), at 95—100°. When oxidised with dil. CrO_3 (V) gives 4:4'-dimethoxydiquinone (VI), decomp. 212—214°, converted by prolonged action of (I) into 2(?) : 3 : 6 : 2' (?) : 3' : 6'-hexa-acetoxy-4:4'-dimethoxydiphenyl, m.p. 200°, which when demethylated and acetylated gives only a trace of an unidentified Ac derivative, m.p. 264—266°. Passage of HCl into a CHCl_3 - AcOH suspension of (VI) gives a chlorophenol (probably 6:6'-dichloro-2:4:2':4'-tetrahydroxy-4:4'-dimethoxydiphenyl), dissociating into its components on heating and giving an Ac_2 derivative, m.p. 232°, with cold 1% H_2SO_4 in Ac_2O . With hot Ac_2O the main product is (VI) together with an (?) anhydride, m.p. 253°. Reduction of (VI) with SO_2 in H_2O suspension at 100° gives (V), but with HI and NHPh-NH_2 , 4:4'-dimethoxydiquinol, m.p. 210° (decomp.) [oxidised to a humic acid in alkaline solution, and by HNO_3 to (VI)], the Ac_4 derivative, m.p. 186—187°, of which is hydrolysed and methylated to 2:4:5:2':4':5'-hexamethoxydiphenyl (VII), m.p. 177—179°, identical with the products obtained by Fabinyi and Szeki (A., 1910, i, 837) and Schuler (A., 1907, i, 700), whereas HBr followed by Ac_2O - $\text{C}_5\text{H}_5\text{N}$ gives the corresponding (OAc)₆-derivative (Barth and Schreder, A., 1885, 520) and 2:3:6:7-tetra-acetoxydiphenylene oxide, m.p. 262° (Brezina, A., 1901, i, 700). With ICl, or I+HgO, the Me_3 ether (VIII) of hydroxyquinol gives (VII) as its labile additive compound with I, but anodic oxidation of (VIII) in acid solution, or CrO_3 followed

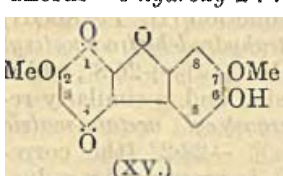


Zn dust, gives (VII), and a small yield of the indigoid quinone (IX) (bluish-violet), m.p. 185—187°, converted by conc. HNO_3 into (VI). With 3% H_2O_2 and NaOH followed by acetylation dehydrodivanillin (Elbs and Lerch, A., 1916, i, 315) gives the Ac_4 derivative (X), m.p. 176—178° (6:6'- Br_2 -derivative, m.p. 207—208°), of 3:3'-dimethoxydiquinol which cannot be isolated owing to its rapid polymerisation to a humic acid, but hydrolysis and methylation gives 2:3:5:2':3':5'-hexamethoxydiphenyl, m.p. 119—120° [6:6'- Br_2 - (XI), m.p. 271—272°, and 6:6'-(NO_2)₂-, m.p. 300—301°, -derivatives]. Cold conc. HNO_3 converts (XI) into 6:6'-dibromo-3:3'-dimethoxydibenzoquinone, sinters 236°, m.p. 240—242° (decomp.). The Me_2 ether (XII) of toluquinol (improved prep.) with HNO_3 (*d* 1.42)- AcOH gives its 5- NO_2 -derivative, m.p. 117—118°, and with I-HgO at 85—95° affords its 5-*I*-derivative, m.p. 85°. The ditoluquinone (XIII, R=Me) of Nietzki and Bernard (A., 1898, i, 529) with Zn- Ac_2O gives tetra-acetoxyditolyl (XIV), converted into 2:5:2':5'-tetramethoxydi-*p*-tolyl, m.p. —136°, identical with a specimen obtained from 4-iodotoluquinol Me_2 ether and Cu powder at 210°, thus proving the above struc-



ture for (XIII). Spica's "toluquinone polymeride" (A., 1882, 196) also gives (XIV) by reductive acetylation. Reduction (SO_2 in boiling EtOH) of Nietzki's quinone and subsequent ethylation (EtI-NaOEt) affords 5:5'-dimethoxy-2:2'-diethoxydi-p-tolyl, m.p. 116—118°, not identical with 2:2'-dimethoxy-5:5'-diethoxydi-p-tolyl, m.p. 94—96°, similarly obtained by reduction and methylation of the diquinone obtained by Noelting and Werner (A., 1891, 209) from toluquinol Et_2 ether. Noelting's diquinone is therefore (XIII, $\text{R}=\text{Et}$). With (I) ditoluquinone gives 2(?):3:6:2'(?):3':6'-hexa-acetoxydi-p-tolyl, m.p. 202—203°, and with HCl affords a chlorophenol analogous to that obtained from (VI). Reduction of nitroquinol (CH_3Ph) $_2$ ether affords the corresponding NH_2 -compound, m.p. 100—102° (Ac, m.p. 86—87°, and p-nitrobenzylidene, m.p. 105°, derivatives). With the appropriate aldehyde 2-iodo-4-nitroaniline affords its p-, m.p. 194—196°, and m-, m.p. 177—178°, -nitrobenzylidene derivatives.

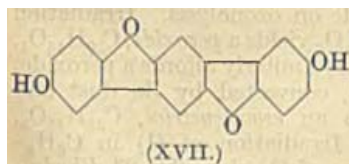
III. When heated at 250—280° in 1- $\text{C}_{10}\text{H}_7\text{Br}$ (VI) affords 6-hydroxy-2:7-dimethoxydiphenylene oxide-



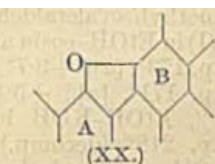
(XV.)

1:4-quinone (XV), sinters 242°, m.p. 250° (Ac derivative, m.p. 252—254°), reduced by Zn-AcOH to 1:4:6-trihydroxy-2:7-dimethoxydiphenylene oxide, decomp. 210° (tri-p-nitrobenzoyl derivative, m.p. > 300°), the Ac_3 derivative, m.p. 232—233°, of which with 2% $\text{H}_2\text{SO}_4\text{-MeOH}$, followed by methylation, affords 1:2:4:6:7-pentamethoxydiphenylene oxide, m.p. 109—110°. Ditoluquinone undergoes a similar rearrangement to give 6-hydroxy-2:7-dimethoxydiphenylene oxide-1:4-quinone, m.p. 218—220°, converted by reductive acetylation into 1:4:6-triacetoxy-2:7-dimethoxydiphenylene oxide, m.p. 168—171°, and a trace of the Ac_4 derivative of 4:4'-dimethoxydiquinol.

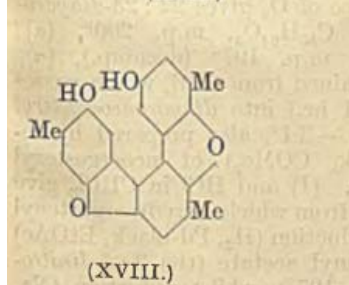
(IV). With cold conc. $\text{H}_2\text{SO}_4\text{-AcOH}$ p-benzoquinone (XVI) affords quinol (about 50%) and a dark-coloured ppt. which, after reductive acetylation, gives dihydroxytriphenylene dioxide $\text{C}_{18}\text{H}_{10}\text{O}_4$ (XVII), m.p. 336—340°, isolated and purified as its Ac_2 derivative, m.p. 236—237°, together with amorphous products. With



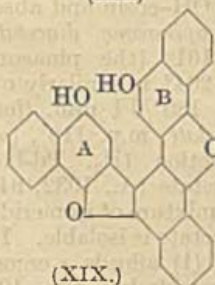
(XVII.)



(XX.)



(XVIII.)



(XIX.)

$\text{Me}_2\text{SO}_4\text{-NaOH}$ in H_2 (XVII) affords a Me₂ ether, m.p. 210—211° (Br_2 -derivative; decomp. about 300°).

Analysis of the products of reductive acetylation or methylation of the quinone humic acids obtained by polymerisation of (XVI) in NaOH indicates a lower C content than is present in the amorphous products of acid polymerisation. Similar acid polymerisation of toluquinone affords a dihydroxytriphenylene dioxide $\text{C}_{21}\text{H}_{16}\text{O}_4$, + $2\text{H}_2\text{O}$ and anhyd. (XVIII), m.p. > 300° (rapid heating) [Ac_2 derivative, m.p. 285—286°; Me_2 ether, m.p. 233—234° (Br_2 -m.p. 274—275°, and NO_2 -m.p. 305°, -derivatives)], identical with the substance given the composition $(\text{C}_7\text{H}_5\text{O})_x$ by Brunner (A., 1889, 996). Polymerisation of α -naphthaquinone occurs more slowly, but with $\text{AcOH-H}_2\text{SO}_4$ at 40—50° is isolated the Ac_2 derivative $\text{C}_{34}\text{H}_{20}\text{O}_6$, m.p. 340—343° (sol. in quinoline), of a bisanhydrotetrinaphthaquinol, probably (XIX), and the trioxide $\text{C}_{30}\text{H}_{12}\text{O}_6$ (XX), sublimes at 300—330°/high vac., charring > 400° (insol.). The above structures are assigned on the basis of the previous results. J. W. B.

Alkyl-substituted aromatic hydroxy-compounds.—See B., 1934, 54.

1-Cyano- Δ^1 -cyclohexene. R. VAN COILLIE (Bull. Soc. chim. Belg., 1933, 42, 419—426).—1-Hydroxy-1-cyanocyclohexane, b.p. 119.5°/10 mm., 132°/20 mm., m.p. 26° (lit. 29°), and SOCl_2 first in the cold and then at 100° (bath) give 2-chloro-1-cyanocyclohexane (I), b.p. 121—121.4°/12 mm., m.p. 22.4—23°, a stereoisomeride (II), b.p. 109—110°/12 mm., m.p. —8° to —6°, and a product (A), b.p. 75—76°/12 mm., which consists mainly of (III) (below) and could not be freed from Cl by repeated distillation. PCl_5 gives similar products. (A) absorbs dry HCl to yield (I). (I) and $\text{C}_5\text{H}_5\text{N}$ at 100° afford 1-cyano- Δ^1 -cyclohexene (III), b.p. 73.9—74.2°/11.5 mm., also formed (together with a little of the corresponding amide) from (I) or (II) and 5% NaOH at 100° (bath). Contrary to Cocker *et al.* (A., 1931, 1037), (I) is unaffected by boiling H_2O . H. B.

β -2-Naphthylethyl alcohol and 2-vinylnaphthalene. (MILLER) D. SONTAG (Compt. rend., 1933, 197, 1130—1132).— β -2-Naphthylethyl alcohol, m.p. 67.5—68° [prepared from 2- $\text{C}_{10}\text{H}_7\text{-MgBr}$ and $(\text{CH}_3)_2\text{O}$, in small amount from 2- $\text{C}_{10}\text{H}_7\text{-CH}_2\text{-MgBr}$ and CH_3O , and by reduction (Bouveault) of 2- $\text{C}_{10}\text{H}_7\text{-CH}_2\text{-CO}_2\text{Et}$], heated with KOH gives 2-vinylnaphthalene, b.p. 135—137°/18 mm., m.p. 66° (dibromide, m.p. 84.5—85°). Dehydration of α -2-naphthylethyl alcohol [by reduction (Na-Hg) of 2- $\text{C}_{10}\text{H}_7\text{Ac}$] with NaHSO_4 gives a small amount of a liquid product. H. B.

Displacement in the allyl group. J. MEISENHEIMER and G. BEUTTER (Annalen, 1933, 508, 58—80).—The amounts of α -phenylallyl acetate (I) formed when cinnamyl chloride (II) is treated with various metal acetates (1.5 equivs.) in AcOH (containing about 3.5% H_2O) at 100° (bath) are: Li, about 9%; Na, 20%; K, 22%; Mg, 0; Ca, about 6%; Ba, 21%; Pb, 30%; the amount of "abnormal substitution" increases with increased at. wt. of the metal. The change (I) \rightarrow cinnamyl acetate (III) occurs more rapidly in AcOH alone at 100° (bath) than in presence of metal acetates; retardation is most marked with the most electropositive metals. Addition of H_2O to the AcOH causes acceleration either in absence or presence of acetates. The "abnormal substitution"

with (II) and KOAc in AcOH is diminished by addition of H_2O ; normal substitution [formation of (III)] is favoured. Increase in the concn. of KOAc (or LiOAc) favours "abnormal substitution" and suppresses the change (I) \rightarrow (III). (II) also reacts with AcOH alone forming about 16% of the theoretical amount of HCl: $CHPh:CH:CH_2Cl + AcOH \rightarrow CHPh:CH:CH_2OAc$ (or $OAc:CHPh:CH:CH_2$) + HCl. The reaction between (II) and KOAc in AcOH and Ac_2O is studied kinetically; reaction occurs about ten times as fast in AcOH, but in Ac_2O (III) is the sole product. The reaction in AcOH is considered to involve direct participation of the solvent and to be termol. H. B.

Law of periodicity. IX. Constitution of triarylmethyl compounds. L. PETRENKO-KRITSCHENKO (Ber., 1933, 66, [B], 1771—1774; cf. A., 1933, 1048).—A reply to Hantzsch *et al.* (*ibid.*, 1158). H. W.

Rates of thermal decomposition of triphenylmethyl alkyl ethers.—See this vol., 151.

Preparation of higher ethers.—See B., 1934, 54.

Production of α -*p*-aminophenyl- β -methylamino-*n*-propyl alcohol.—See B., 1934, 54.

Catalytic oxidations. IV. Photochemical oxidation of some ethylenic double linkings. V. Oxidation of ergosterol.—See this vol., 155.

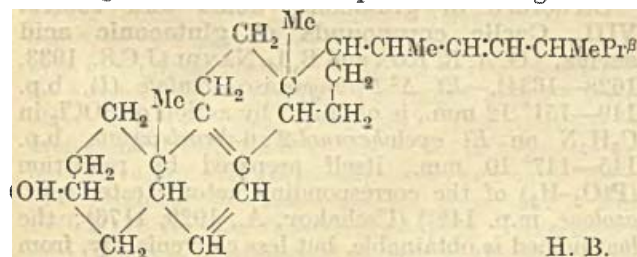
Ergosteryl acetate-maleic anhydride and its hydro-derivatives. H. H. INHOFFEN (Annalen, 1933, 508, 81—88).—Ergosteryl acetate (I) and maleic anhydride (II) in xylene at 135° give the adduct *ergosteryl acetate-maleic anhydride* (III), m.p. 216° , $[\alpha]_D^{25} -19^\circ$ (all rotations are in $CHCl_3$) (*dibromide*, m.p. $252-253^\circ$), which differs from that obtained by Windaus and Lüttringhaus (A., 1931, 840) from ergosterol-maleic acid and Ac_2O . (III) is hydrolysed (EtOH—conc. H_2SO_4) to *ergosterol-maleic anhydride*, m.p. 202° (5—10% yield), re-acetylated (Ac_2O) to (III). Hydrolysis (10% MeOH—KOH) of (III) gives ergosterol-maleic acid, m.p. $198-199^\circ$ (decomp.) [Me_2 ester (IV), m.p. 163° , the *acetate*, m.p. 164° , of which is also obtained from (III), Me_2SO_4 , and alkali with subsequent acetylation]. (III) distils practically unchanged at $240^\circ/0.0002$ mm.; at 220° /about 15 mm., almost quant. fission into (I) and (II) occurs. Reduction (H_2 , Pd-black, $COMe_2$) of (III) gives 22:23-*dihydroergosteryl acetate-maleic anhydride* (V), m.p. $202-203^\circ$ (sinters at $172-174^\circ$), $[\alpha]_D^{25} -9.1^\circ$, which does not absorb Br and affords no α -methylisovaleraldehyde on ozonolysis. Similar reduction of (IV) and subsequent acetylation gives 22:23-*dihydroergosteryl acetate-Me maleate*, m.p. $116-117^\circ$, also obtained by successive hydrolysis, esterification, and acetylation of (V). Reduction (H_2 , Pt, AcOH) of (III) yields *tetrahydroergosteryl acetate-maleic anhydride*, m.p. $187-187.5^\circ$, $[\alpha]_D^{25} -25.4^\circ$, which does not undergo thermal fission; hydrolysis (EtOH—KOH) gives tetrahydroergosterol-maleic acid, m.p. $218-220^\circ$ (decomp.) [Me_2 ester *acetate*, m.p. 138° , $[\alpha]_D^{25} -69.8^\circ$]. Structures for (III) are suggested. H. B.

Adducts from maleic anhydride and dehydroergosterol and their hydrogenation products. H. HONIGMANN (Annalen, 1933, 508, 89—104).—The

adduct dehydroergosteryl acetate-maleic anhydride (I) [*dibromide*, m.p. 245° (decomp.)], prepared by Murke's method (Diss., Gottingen, 1931; cf. A., 1931, 840), is usually obtained with m.p. $220-240^\circ$ (decomp.) (according to rate of heating); in two cases, the m.p. was 205° (as found by Murke). (I) distils at $210-220^\circ/0.0004$ mm., but at $240^\circ/0.1$ mm. the components are regenerated. Hydrolysis (10% MeOH—KOH) of (I) gives dehydroergosterol-maleic acid, m.p. $170-175^\circ$ (decomp.), $[\alpha]_D^{25} +67.5^\circ$ (all rotations are in $CHCl_3$) [Me_2 ester *acetate*, m.p. 180°]. (I) is reduced (H_2 , Pd-black, $COMe_2$) to *dihydrodehydroergosteryl acetate-maleic anhydride* (II), m.p. 216° , $[\alpha]_D^{25} +81.6^\circ$, which when distilled at about 15 mm. affords 22:23-*dihydrodehydroergosteryl acetate* (III), m.p. 128° , $[\alpha]_D^{25} +219.9^\circ$, the absorption curve of which resembles that of dehydroergosteryl acetate. *Dihydrodehydroergosterol-maleic acid* ($+0.5H_2O$) [Me_2 ester *acetate*, m.p. 163° (sinters about 155°)] has m.p. 180° (decomp.). Reduction (Na, EtOH) of (III) gives a *tetrahydrodehydroergosterol* ($+H_2O$), m.p. 132° , $[\alpha]_D^{25} -12.5^\circ$ (*acetate*, m.p. 141° , $[\alpha]_D^{25} -9.7^\circ$), which contains two double linkings (BzO_2H). Reduction (H_2 , Pt, AcOH) of (I) or (II) yields *tetrahydrodehydroergosteryl acetate-maleic anhydride*, m.p. 197° , $[\alpha]_D^{25} +26.8^\circ$, which does not undergo thermal fission and is similarly reduced to *hexahydrodehydroergosteryl acetate-maleic anhydride* (IV), m.p. 187° , $[\alpha]_D^{25} -22.2^\circ$ [the corresponding Me_2 ester, m.p. 138° , is prepared by reduction (H_2 , Pt-black, AcOH) of *tetrahydrodehydroergosteryl acetate-Me maleate*, m.p. 135°]. *Tetrahydrodehydroergosterol-maleic acid* has m.p. 180° (decomp.), $[\alpha]_D^{25} +63^\circ$. (IV) is identical with tetrahydroergosteryl acetate-maleic anhydride (preceding abstract). Structures are suggested for the above adducts. H. B.

22:23-Dihydroergosterol. A. WINDAUS and R. LANGER (Annalen, 1933, 508, 105—114).—22:23-*Dihydroergosteryl acetate* (I), m.p. $157-158^\circ$, $[\alpha]_D^{25} -74.8^\circ$ (all rotations are in $CHCl_3$), is obtained when its adduct with maleic anhydride (Inhoffen, see above), is heated at 220° /about 15 mm. and then distilled in a high vac. Hydrolysis (EtOH—KOH in N_2) affords 22:23-dihydroergosterol (II), m.p. $152-153^\circ$, $[\alpha]_D^{25} -109^\circ$, which does not give α -methylisovaleraldehyde on ozonolysis. Irradiation of (I) in EtOH—eosin and O_2 yields a *peroxide*, $C_{30}H_{48}O_4$, m.p. 173° , $[\alpha]_D^{25} +9.7^\circ$ [(II) similarly affords a *peroxide*, m.p. 171° , $[\alpha]_D^{25} +5.4^\circ$], converted by Zn dust and 10% EtOH—KOH into an *ergostenetriol*, $C_{28}H_{48}O_3$, m.p. 218° (decomp.). Irradiation of (I) in C_6H_6 —EtOH—eosin and absence of O_2 gives 22:23-*dihydroergopinacone diacetate*, $C_{60}H_{94}O_4$, m.p. 200° , $[\alpha]_D^{25} -161^\circ$ [the *pinacone*, m.p. 197° (decomp.), $[\alpha]_D^{25} -204^\circ$, is similarly obtained from (II)], which passes at $180^\circ/0.1$ mm. (for 1 hr.) into *dihydroergosteryl acetate*, m.p. 118° , $[\alpha]_D^{25} -3.1^\circ$, also prepared by reduction (H_2 , Pd-black, $COMe_2$) of neoergosteryl acetate (A., 1932, 944). (I) and HCl in $CHCl_3$ give a mixture of isomerides from which dehydroergosteryl acetate is isolable. Reduction (H_2 , Pd-black, EtOAc) of (I) affords α -ergostenyl acetate (the 3:5-*dinitrobenzoate* has m.p. $196-197^\circ$), whilst reduction (Na, PrOH) of (II) yields γ -ergostenol, m.p. $145-146^\circ$, $[\alpha]_D^{25} \pm 0^\circ$ [*acetate*, m.p. 157° , $[\alpha]_D^{25} -5.3^\circ$; *benzoate*

(III), m.p. 179°; 3:5-dinitrobenzoate, m.p. 209—210°. (III) is isomerised by $\text{HCl}-\text{CHCl}_3$ to a mixture containing β -ergostenyl benzoate (Heilbron and Wilkinson, A., 1932, 845). When γ -ergostenol is shaken with H_2 and Pt- or Pd-black, α -ergostenol is produced. Ultra-violet irradiation of (I) gives product possessing antirachitic properties. The following constitution is now preferred for ergosterol.



Constitution of cholesterol and ergosterol. A. WINDAUS (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 92—102; Chem. Zentr., 1933, ii, 1366—1367).—A discussion. A. A. E.

Oxidation product of α -ergostenol. T. ACHTERMANN (Z. physiol. Chem., 1933, 222, 70—72).—Oxidation of ergostenone with CrO_3 in 90% AcOH gave the unsaturated ketone, $\text{C}_{28}\text{H}_{44}\text{O}_2$, m.p. 183°, $[\alpha]_D^{25} +105.9^\circ$ in CHCl_3 , which on catalytic reduction gave α -ergostenol. No product $\text{C}_{21}\text{H}_{32}\text{O}_2$ (?) was isolated (cf. Heilbron *et al.*, A., 1932, 845).

J. H. B.
Cerevisterol: composition, properties, and relation to other sterols. E. M. HONEYWELL and C. E. BILLS (J. Biol. Chem., 1933, 103, 515—519).—New analytical data for cerevisterol (I) and its Ac_2 derivative confirm the composition $\text{C}_{28}\text{H}_{46}\text{O}_3$ (two double linkings). Two O are present as OH, and the third is not present in a CHO, CO, OR, CO_2H , or lactone group, or in the ring structure, and is tentatively located to a *tert.*-alcohol group, failure to acetylate it being ascribed to steric hindrance. (I) does not form an insol. digitonide, but, like ergosterol, gives a positive reaction with $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ (Rosenheim). J. W. B.

Halogenation. VI. Bromination and iodination of benzonitrile. P. S. VARMA and N. B. SENGUPTA (J. Indian Chem. Soc., 1933, 10, 593—594).—Careful addition (not mixing) of PhCN to conc. H_2SO_4 followed by KBr gives $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CN}$, a little $o\text{-C}_6\text{H}_4\text{Br}\cdot\text{CN}$, BzOH , and NH_2Bz ; o - and $p\text{-C}_6\text{H}_4\text{I}\cdot\text{CN}$, BzOH , and NH_2Bz are similarly obtained using KI . H. B.

Addition of alkali alkoxides to acid esters.
VIII. Sodium alkoxides and esters at higher temperatures. F. ADICKES, S. VON MULLENHEIM, and W. SIMSON (Ber., 1933, 66, [B], 1904—1909).—Prolongation of the action of EtOBz and NaOEt at 100° in absence of H_2O does not lead to a marked increase of the NaOBz produced, thus rendering improbable Scheibler's explanation that the effect is due to the change, ester+alkoxide=salt+ C_6H_5 +alcohol. The interaction of MeOBz (I), PrOBz , $\text{CH}_2\text{Ph}\cdot\text{OBz}$ (II), PhOBz , $o\text{-C}_6\text{H}_3(\text{CO}_2\text{Et})_2$, $o\text{-C}_6\text{H}_4(\text{CO}_2\text{CH}_2\text{Ph})$, (III), $\text{CO}(\text{OEt})_2$, and $\text{CO}(\text{OCH}_2\text{Ph})_2$ (IV) with the corresponding Na

alkoxide has been investigated at about 180°. With (I), (II), (III), and (IV) production of ethers is observed, but subsidiary changes occur leading to production of H_2O , and hence of hydrolysis of the esters, since the yield of ethers attains only 50—83% of that expected from the amount of acid produced and 50—100% of the missing ether appears as alcohol. Repetition of Scheibler's experiments with EtOBz and NaOEt shows that CO is evolved in addition to C_6H_4 (ratio 20 : 1), and that there is no equivalence between NaOBz and C_6H_5 ; COPhMe and CH_2Bz_2 are obtained, the latter derived from the former, EtOBz , and NaOEt . In the case of $o\text{-C}_6\text{H}_3(\text{CO}_2\text{Et})_2$, CH_2O is produced, which is partly condensed to methylenebisindandione. PrOBz reacts in the same manner as EtOBz , whereas $\text{CO}(\text{OEt})_2$ does not react at atm. pressure. PhOBz does not react sufficiently rapidly at 250—270°. Ether is not formed and partial resinification affords the H_2O necessary for hydrolysis of the ester. p -Hydroxybenzophenone is formed to the extent of 8%. H. W.

Syntheses with acids of the type $\text{CHR}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and mixed organomagnesium derivatives. D. IVANOV and G. PCHÉNITCHNY (Compt. rend., 1933, 197, 1230—1231; cf. A., 1931, 483).—Interaction of $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (I) with $\text{MgPr}^\text{F}\text{Cl}$ or $1\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ followed by CO_2 affords *styrylmalonic acid*, m.p. 133° (decomp.). (I) with *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$, and MgPhBr affords respectively β -hydroxy- α -phenyl- β -m., m.p. 138—139°, and *p*-tolyl-, m.p. 165°, and β -*diphenyl*- α -styryl- Δ^5 -hexenoic acid, m.p. 142—143°. Similarly, interaction of Δ^5 -hexenoic acid (II) with $\text{MgPr}^\text{F}\text{Cl}$ and CO_2 affords Δ^5 -butenylmalonic acid, m.p. about 100°. MgPhBr and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ with (II) afford, respectively, β -hydroxy- β -phenyl-, m.p. 145°, and β -*p*-tolyl- α -(Δ^5 -butenyl)- Δ^5 -octenoic acid, m.p. 124.5°. (I) and (II) afford no Na derivatives with NaOEt .

J. L. D.
Fixation of SbO_2H by aromatic monohydroxy-monobasic acids. DUQUÉNOIS (Compt. rend., 1933, 197, 1335—1336; cf. A., 1933, 1142).—Only α -OH-aromatic acids react with Sb_2O_3 , max. fixation occurring with an equimol. mixture of the acid and its neutral salt, and max. reaction velocity with *tert.*-OH ($\text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$). The following are described: *K* antimonylmandelate (cf. A., 1933, 948); *Na*, m.p. 257°, and *K*, m.p. 231°, antimonyl- β -phenyl-lactate $\text{Sb}(\text{OH})[\text{O}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}][\text{O}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{K}]$, and *Na*- H_2O and anhyd., m.p. 235° (decomp.), *K*+ $2\text{H}_2\text{O}$, and NH_4 , giving anhydride at 135°, decomp. 140°, antimonylbenzilate, of type $\text{Sb}(\text{OH})(\text{O}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H})(\text{O}\cdot\text{CPh}_2\cdot\text{CO}_2\text{M})$. J. W. B.

Components of the Kawa root. XIV. Ethyl cinnamoylacetate. W. BORSCHÉ and M. LEWINSOHN [with, in part, R. SCHIFFNER] (Ber., 1933, 66, [B], 1792—1801; cf. A., 1933, 829).—Treatment of *Et* cinnamoylacetate (I) with 75% AcOH at 100° leads to *Et* cinnamoylacetate (II), m.p. 46° (*Cu* compound, m.p. 185—187°; 2:4-dinitrophenylhydrazones, m.p. 170—171°), $\text{CHPh}\cdot\text{CH}\cdot\text{COMe}$, and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$. (II) and $\text{NHPh}\cdot\text{NH}_2$ in AcOH at 100° yield 3-styryl-1-phenylpyrazol-5-one, m.p. 148—149°. Distillation of (II) under 15 mm. gives

3-cinnamoyl-6-styryl-2:4-pyrone, m.p. 162° after softening at 158°. Treatment of (I) with $m\text{-C}_6\text{H}_4(\text{OH})_2$ or of its Na derivative (III) with $\text{COPh}\cdot\text{CH}_2\text{Br}$ leads to ill-defined products, whereas with chloro-2:4-dinitrobenzene and $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$, respectively, (III) gives *Et* α -2:4-dinitrophenylcinnamoylacetate, m.p. 120—121° (hydrolysed by H_2O at 130° to 2:4-dinitrobenzyl styryl ketone, m.p. 152—153°), and *Et* dicinnamoylacetate, m.p. 129° (hydrolysed at 120—130° to dicinnamoylmethane, m.p. 142°). Hydrogenation ($\text{Pd}\text{--EtOH}$) of (I) affords *Et* β -keto- δ -phenylvalerate (IV), b.p. 170—171°/13 mm. (*Cu* compound; 2:4-dinitrophenylhydrazone, m.p. 78°), and 3- β -phenylpropionyl-6-styryl-2:4-pyrone, m.p. 95°, transformed by fuming HCl at 120° into 2:6-di- β -phenylethyl-4-pyrone, m.p. 140°. (IV) is transformed by $m\text{-C}_6\text{H}_4(\text{OH})_2$ and conc. H_2SO_4 into 7-hydroxy-4- β -phenylethylcoumarin, m.p. 175—176°, and by Na in Et_2O followed by $\text{COPh}\cdot\text{CH}_2\text{Br}$ into non-cryst. *Et* $\alpha\delta$ -diketo- $\alpha\zeta$ -diphenyl- n -hexane- γ -carboxylate, which yields *Et* iminoketo- $\alpha\zeta$ -diphenylhexane- γ -carboxylate, m.p. 147°, with $\text{NH}_3\text{--MeOH}$ at room temp. and *Et* 2- β -phenylethyl-1:5-diphenylpyrrole-3-carboxylate, m.p. 139—140°, with $\text{NH}_2\text{Ph}\text{--AcOH}$ at 100°. (IV), NaNH_2 , and $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$ give *Et* β -keto- α -cinnamoyl- δ -phenylvalerate, m.p. 57° (*Cu* compound, m.p. 204—205°), whence $\gamma\epsilon$ -diketo- $\alpha\eta$ -diphenyl- Δ^4 -heptene, m.p. 84—85° (*Cu* derivative, m.p. about 200°). Hydrogenation (colloidal $\text{Pd}\text{--EtOH}$) of (I) leads to *Et* β -keto- α -acetyl- δ -phenylvalerate (V), b.p. 130°/0.6 mm. (*Cu* compound, m.p. 136°), converted by 2:4-dinitrophenylhydrazine into *Et* 1-2':4'-dinitrophenyl-3- β -phenylethyl-5-methylpyrazole-4-carboxylate, m.p. 144—145°, and a small amount of 4-acetyl-1-2':4'-dinitrophenyl-3- β -phenylethylpyrazol-5-one, m.p. 178°. Hydrolysis of (V) gives $\gamma\epsilon$ -diketo- α -phenyl- n -hexane, b.p. 153—155°/14 mm. [converted by $m\text{-C}_6\text{H}_4(\text{OH})_2$ and HCl in AcOH into the benzopyrylium chloride, $\text{C}_{18}\text{H}_{17}\text{O}_2\text{Cl}$, isolated as the compound $\text{C}_{18}\text{H}_{17}\text{O}_2\text{Cl}\cdot\text{FeCl}_3$, m.p. 154°], better obtained by hydrogenation of $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\text{Ac}$.

3:4-Methylenedioxy innamic acid (VI) and SOCl_2 in C_6H_6 yield 3:4-methylenedioxy-cinnamoyl chloride, m.p. 143° (corresponding amide, m.p. 183°), converted by *Et* sodioacetacetate in Et_2O into *Et* methylenedioxy-cinnamoylacetate (VII), m.p. 104° (*Cu* derivative, m.p. 208°), a little regenerated (VI), and a substance $\text{C}_{15}\text{H}_{16}\text{O}_4$, m.p. 132°. (VII) and 2:4-dinitrophenylhydrazine in MeOH give a pyrazole $\text{C}_{22}\text{H}_{18}\text{O}_8\text{N}_4$, m.p. 212°, and methylenedioxy-cinnamoyl-acetonedinitrophenylhydrazone, m.p. 200°. Boiling 75% AcOH transforms (VII) almost exclusively into (VI), whereas saturation with NH_3 of a solution of (VII) in $N\text{--NaOH}$ leads to *Et* 3:4-methylenedioxy-cinnamoylacetate, m.p. 58—60° (*Cu* derivative, m.p. 222°; 2:4-dinitrophenylhydrazone, m.p. 204°). The non-cryst. *Et* β -keto- α -acetyl- δ -3:4-methylenedioxyphenylvalerate (*Cu* compound, m.p. 173°) is transformed by 2:4-dinitrophenylhydrazine into a pyrazole $\text{C}_{22}\text{H}_{20}\text{O}_8\text{N}_4$, m.p. 175°, and $\gamma\epsilon$ -diketo- α -3:4-methylenedioxyphenylhexane-2':4'-dinitrophenylhydrazone, m.p. 116°. α -Phenylcinnamic acid is converted through the chloride into non-cryst. *Et* α -phenylcinnamoylacetate (VIII) (*Cu* derivative, m.p. 125°, or, on an isolated occasion, m.p. 185°),

hydrolysed by H_2O at 130° to $\gamma\epsilon$ -diketo- $\alpha\beta$ -diphenyl- Δ^2 -hexene, m.p. 81°. Treatment of (VIII) with 75% AcOH at 100° gives *Et* α -phenylcinnamoylacetate, m.p. 91° (*Cu* derivative, m.p. 213°), hydrolysed to γ -keto- $\alpha\beta$ -diphenyl- Δ^2 -butene, m.p. 56°. H. W.

Substitution products of aminobenzoyl- α -benzoic acid.—See B., 1934, 54.

Structure of glutaconic acids and esters.
VIII. Cyclic compounds of glutaconic acid series. G. A. R. KON and B. L. NANDI (J.C.S., 1933, 1628—1634).—*Et* Δ^2 -tetrahydroisophthalate (I), b.p. 149—151°/12 mm., is obtained by action of SOCl_2 in $\text{C}_5\text{H}_5\text{N}$ on *Et* cyclohexanol-2:6-dicarboxylate, b.p. 145—147°/10 mm., itself prepared by reduction ($\text{PtO}_2\text{--H}_2$) of the corresponding ketonic ester (pyrazolone, m.p. 148°) (Uschakov, A., 1929, 1176); the last-named is obtainable, but less conveniently, from cyclohexanone and $\text{Et}_2\text{C}_2\text{O}_4$ in presence of NaOEt . The corresponding free acid, m.p. 197—198°, is also produced by condensing *Et* tetrahydrobenzoate with $\text{Et}_2\text{C}_2\text{O}_4$ (NaOEt), hydrolysing the resulting *Et* 3-carbethoxy- Δ^2 -cyclohexenylglyoxylate, m.p. 105°, with alkali [*H* ester, m.p. 178°; free acid, m.p. 224° (decomp.)], and finally oxidising the alkaline solution with H_2O_2 . It is unaffected by prolonged contact with 25% KOH at 100°, but rapidly isomerised to the Δ^3 -acid by HCl at 180—190°. The ester (I) on ozonisation gives glutaric acid and on ethylation gives *Et* 1-ethyl- Δ^2 -cyclohexene-1:3-dicarboxylate, b.p. 149—150°/9 mm. (free acid, m.p. 162°). Me_2 (cf. J.C.S., 1894, 67, 950) and Et_2 (II), b.p. 136—139°/23 mm., Δ^1 -cyclobutene-1:2-dicarboxylates are unaffected by the corresponding Na alkoxides and on ozonisation give the corresponding $\alpha\alpha'$ -diketo adipates. Et_2 1:2-dibromocyclobutane-1:2-dicarboxylate, b.p. 150—158°/14 mm., gives (II) with Zn and EtOH , but not with KI in EtOH or COMe_2 . Attempts at prep. of the Δ^2 - and Δ^3 -acids corresponding with (II) failed. The Na derivative of $[\text{CH}(\text{CO}_2\text{Et})_2]_2$ with $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in C_6H_6 gives (?) Et_4 cyclobutan-3-one-1:1:2:2-tetracarboxylate (phenylhydrazone, m.p. 128°) and the liquid fraction of the crude product with $\text{H}_2\text{--PtO}_2$ gives (?) 3-hydroxycyclobutane-1:1:2:2-tetracarboxylic acid, m.p. 191°, in poor yield. Et_2 Δ^1 -cyclopentene-1:2-dicarboxylate gives Et_2 $\alpha\alpha'$ -diketopimelate on ozonisation and is not isomerised, giving only the *Et H* ester, b.p. 135—140°/13 mm., by NaOEt ; the free acid is unaffected by 25% KOH at 100° or hot conc. HCl . Δ^2 -Tetrahydrophthalic acid (Et_2 ester, b.p. 155°/12 mm.) is conveniently prepared by dehydrating the cyanohydrin, b.p. 147—150°/10 mm., of *Et* cyclohexanone-2-carboxylate with SOCl_2 and $\text{C}_5\text{H}_5\text{N}$ and hydrolysing the resulting *Et* 1-cyanocyclohexene-2-carboxylate, b.p. 135—137°/10 mm., with aq. alcoholic KOH . Et_2 Δ^1 -tetrahydrophthalate, b.p. 160°/14 mm. (from the Ag salt of the acid), like the Δ^2 ester does not react with Cl_2 or Br, and is unaffected by distillation/1 atm. Hot $\text{NaOEt}\text{--EtOH}$ causes addition of EtOH . The anhydride of the Δ^1 -acid is hydrolysed by alkali to the Δ^2 -acid (approx. 75% at equilibrium). The latter is unaffected by 25% KOH at 100°. H. A. P.

3-Chlorophthalic acid. J. C. SMITH (J.C.S., 1933, 1643—1644).—3-Chlorophthalic acid (modified prep. from 3-nitrophthalic anhydride and PCl_5) has

m.p. 202° (decomp.) (lit. 184—186°) [anhydride, m.p. 126° (lit. 122°)]. R. S. C.

Formation of rings attached to *m*-position of benzene nucleus. S. G. P. PLANT (J.C.S., 1933, 1586—1588).—Stereochemical considerations demand that a ring joining the *m*-positions of the C_6H_6 nucleus should be at least 10-membered, and that a *p*-ring should be 14-membered. Attempts at cyclisation of δ -*o*-amino-2-methoxybenzoylvaleric acid (I), m.p. 118° [*Ac* derivative (+H₂O), m.p. 112° (decomp.)], its hydrochloride, m.p. 168° (decomp.), and *Bz* derivative, m.p. 146°, however, failed. (I) is prepared by nitration (HNO₃, *d* 1.5, at -5° to 0°) of δ -*o*-methoxybenzoylvaleric acid (prep. improved) and reduction of the resulting 5-NO₂-compound, m.p. 112°, with Fe(OH)₂. Its structure is proved by converting it into the 5-Cl-compound, m.p. 94°, by the Sandmeyer reaction, and synthesis of this by methylation (Me₂SO₄-KOH) of δ -5-chloro-2-hydroxybenzoylvaleric acid (II), m.p. 136°. (II) is obtained among other products by hydrolysis of 6-chloro-2:3-dihydroxypentachromone, m.p. 129—130°, b.p. 233—235°/23 mm., prepared by condensation of *p*-C₆H₄Cl·OH with Et cyclopentanone-2-carboxylate in presence of P₂O₅ (cf. A., 1933, 511).

H. A. P.

Pyrolysis of hydrogenated diphenic acids. Blanc's rule. F. VOCKE (Annalen, 1933, 508, 1—11).—Reduction (H₂ at 200—250 atm., Ni, and methylcyclohexane at 230—240°) of Me diphenate [and subsequent hydrolysis (20% MeOH-KOH)] gives two hexahydrodiphenic acids, m.p. 242° (I) and 220° (II), and two perhydrodiphenic acids, m.p. 245° (III) and 213° (IV); the former are separable from the latter through their Ba salts. Further reduction of (I) or (II) affords (III) and (IV) in each case. (I) heated at 300° in N₂ passes into (II), which at > 300° is converted into hexahydrofluorenone (V) [semicarbazone, m.p. 220° (darkening and decomp.)]. (II) and boiling Ac₂O give an anhydride, m.p. 120°, which when distilled at atm. pressure passes largely into (V). (III) heated at 300—325° gives a small amount of a ketone [semicarbazone, m.p. 215° (darkening and decomp.)], also formed [together with an anhydride (VI), C₁₄H₂₀O₃, m.p. 115°, re-solidifying with m.p. 265°] when the anhydride (VII), m.p. 265° [from (III) and Ac₂O], is heated at 300—310°. (VI) passes into (VII) when heated above its m.p.; both are hydrolysed (alkali) to (III). (IV) and its anhydride, m.p. 86°, are practically unaffected under similar conditions. The above results are in accordance with Blanc's rule.

Reduction (H₂, Pt-black, AcOH) of diphenic acid is slow and gives a mixture of stereoisomeric acids from which a dodecahydrodiphenic acid, decomp. 273° (*Me* ester, m.p. 57°), is isolated. Distillation of this with Ac₂O affords dodecahydrofluorenone, m.p. 37° [semicarbazone, m.p. 209—210° (decomp.)]; oxime, m.p. 172°]. H. B.

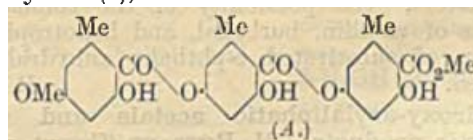
Condensation of benzylpyruvic acid with phenylacetonitrile. P. CORDIER (Compt. rend., 1933, 197, 1427—1429).—In KOH-EtOH, CH₂Ph·CN (I) condenses with CHPh·CH(OH)·CO·NH₂ (which affords CH₂Ph·CH₂·CO·CO₂H *in situ*) to give α -hydroxy- γ -phenyl- α -cyanobenzyl-*n*-butyric acid, m.p. 192° (decomp.), decomposed by boiling alkalis to give

(I), but converted by cold alkali or HCl into β -phenyl- α -(β -phenylethyl)malamic acid, NH₂·CO·CHPh·C(OH)(CH₂·CH₂Ph)·CO₂H, m.p. 198—200° (decomp.), hydrolysed by HCl-AcOH to an anhydride [CH₂Ph·CH₂·C(=O)Ph·CO-O (II) or the isomeride with an exocyclic double linking], m.p. 74°, of the corresponding maleic acid. Warm KOH-C₅H₁₁·OH converts (I) into a mixture of this ethylenic acid, m.p. 180° (insol. in C₆H₆) and an anhydride, m.p. 80° (sol.), isomeric with (II). J. W. B.

Constituents of *Filix Mas*. II. Synthesis of filicic acid. A. ROBERTSON and (the late) W. F. SANDROCK (J.C.S., 1933, 1617—1618).—Et *H* dimethylmalonate, b.p. 135—136°/19 mm., and PCl₅ give dimethylmalonyl chloride Et ester, b.p. 74—78°/19 mm. (anilide, m.p. 47—48°), which with Et sodioacetone-dicarboxylate affords Et β -methylhexane- γ , δ -dione- β , δ -tricarboxylate, b.p. 175—180°/5 mm., converted by NaOEt into Et 1:1-dimethylcyclohexane-2:4:6-trione-3:5-dicarboxylate, m.p. 147—148°. Hydrolysis and decarboxylation of this ester yields filicic acid, identical with the natural product (cf. Boehm, A., 1902, i, 37; 1904, i, 405). F. R. S.

Bile acids. XLI. M. SCHENCK (Z. physiol. Chem., 1933, 222, 131—138; cf. A., 1933, 1161).—The gel C₂₄H₃₃O₉N (A., 1932, 1132) prepared by the action of HNO₃ on bilianic acid dioxime or NO-compound is the 7-NO₂-compound (I), cryst. from hot 40% AcOH, darkens 220°, m.p. 256—258° (decomp.). With 10% NaOH, (I) gives bilianic acid, and with HNO₂, bilidanic acid. Reduction with Zn dust and AcOH affords the 7-monoxime. J. H. B.

Lichen substances. XXXII. Tenuiorin, a methyl gyrophorate monomethyl ether. Y. ASAHINA and M. YANAGITA. XXXIII. Enzymic fission of lichen depsides and related compounds. Y. ASAHINA and T. HIGUTI (Ber., 1933, 66, [B], 1910—1912, 1959—1964).—XXXII. The thalli of *Lobaria pulmonaria*, Hoffm., *f. tenuior Hue*, are extracted successively with hot COMe₂ and EtOH, the extract from the latter affording *d*-mannitol in 1.6% yield. Tenuiorin (I), m.p. 178—180°, and decomp. 238° after re-solidification, obtained from the COMe₂ extract in 0.5% yield, is neutral, contains 2 OMe, and is scarcely coloured by FeCl₃ or CaOCl₂ in EtOH. It is transformed by CH₂N₂ in COMe₂ into Me gyrophorate Me₄ ether, m.p. 195°, and is hydrolysed by KOH-MeOH to evernic acid, its Me ester, and Me orsellinate. Partial methylation of gyphoric acid yields (I), which is therefore A.



XXXIII. Most lichen depsides are hydrolysed by tannase from *Aspergillus niger* or the enzyme from *A. oryzae*, technical takadiastase (I) being very suitable. The alkali salts of the depsides in H₂O are treated with (I) at 37° and *p*_H 7.0—8.5. Incidence of hydrolysis is marked by the appearance of turbidity due to the phenolcarboxylic acid (II) and liberated

depside (III). The original p_H is restored, and more (I) is added, and the operation is continued until further change is not observed. Acidification of the solution yields a mixture of (II) and unchanged (III), which are usually readily separated from one another. Difficulties in the separation of individual phenol-carboxylic acids from one another are obviated by use of the Me ester of (III). Ready fission is observed of lecanoric, gyrophoric, evermic, olivetoric, sekikaic, divaricatic, squamatic, and salicylsalicylic acid, atranorin, and the tannin from Chinese oak galls. Diffractaic, benzoylsalicylic, and 4-4'-hydroxybenzoyloxybenzoic acids and Me gallate and salicylate are more resistant. Depsides containing a free OH in *o*- or *m*-position to the CO of the depside linking appear, therefore, to be more readily hydrolysed. H. W.

Elimination of the aldehydic group as formic acid from aromatic aldehydes. II. Polynitrobenzaldehydes. G. LOCK (Ber., 1933, 66, [B], 1759—1765; cf. A., 1933, 1295).—Treatment of 2:4-dihydroxybenzaldehyde with molten KOH affords only traces of HCO_2H and a nearly molar proportion of H_2 . Reaction therefore does not consist in elimination of CHO , but in hydroxylation and dehydrogenation to K 2:4-dihydroxybenzoate, which, under these conditions, affords K_2CO_3 and $m\text{-C}_6\text{H}_4(\text{OH})_2$. In consequence of decomp., the amount of CO_2 invariably exceeds that expected. Similar behaviour is shown by 2-, 3-, and 4-hydroxy-, 3:4-dihydroxy-, and 2:4:6-trihydroxybenzaldehyde and by 2-hydroxy-naphthaldehyde. 2:4-Dinitrophenol and HCO_2H are obtained when 2:6-dinitro-3-methoxy- or 4:6-dinitro-3-methoxy- (I) benzaldehyde is treated with 5% NaOH at 100° ; (I) is best prepared by methylation of 4-nitro-3-hydroxybenzaldehyde and nitration of the Me ether. Similarly, 2:6-dinitrovanillin affords HCO_2H and 3:5-dinitroguaiacol. 4:6-Dinitro- yields HCO_2H , whereas 4:6-dibromo-3-hydroxybenzaldehyde suffers the Cannizzaro change. 2:4-Dinitrobenzaldehyde gives nearly the calc. amount of HCO_2H without apparently yielding $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$. The conversion of 2:4:6-trinitrobenzaldehyde into $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$ by NH_4Ph , EtOH-NH_3 , or aq. NaOH is accompanied by evolution of HCO_2H . The presence of 2 NO_2 in *o*- and *p*-position has the same effect on CHO as 2 Cl in positions 2 and 6. H. W.

Synthesis of valuable aromatic aldehydes from new sources. A. L. RUSCHTSCHINSKI (Compt. rend. Acad. Sci. U.R.S.S., 1933, 118—123).—The CHO group can be introduced into carbohydrates, phenols, and their ethers by condensation with mesoxalic esters. The possibility of the commercial synthesis of vanillin, burbonal, and heliotropin by reduction of substituted *o*-phthalic anhydrides is envisaged. R. T.

β -Hydroxy-arylaliphatic acetals and their hydrolytic products. M. ROXBART (Compt. rend., 1933, 197, 1225—1227).—Interaction of bromodiethylacetal with Na arylalkoxides (cf. A., 1933, 1037) affords β -arylalkoxy-diethylacetals. The following are described: benzyloxy- (cf. A., 1932, 384); anisyl-oxy-, b.p. $181^\circ/16$ mm.; β -phenylethoxy-, and β -phenylpropoxy-diethylacetal, b.p. $130\text{--}132^\circ/5$ mm., which are hydrolysed by dil. (up to 7%) H_2SO_4 to

the corresponding aldehydes, b.p. $109\text{--}111^\circ/11$ mm. (semicarbazone, m.p. 119°), b.p. $157\text{--}160^\circ/15$ mm. (semicarbazone, m.p. $160\text{--}160.5^\circ$), b.p. $120\text{--}122^\circ/15$ mm. (semicarbazone, m.p. 88.5°), b.p. $134\text{--}136^\circ/16$ mm. (semicarbazone, m.p. $89\text{--}89.5^\circ$). α -Phenylethoxy-diethylacetal, b.p. $138\text{--}140^\circ/15$ mm., is hydrolysed by 1% H_2SO_4 to give CHPhMe-OH , but no aldehyde. Similarly, phenyldimethyl-, b.p. $138\text{--}140^\circ/15$ mm., and benzyldimethyl-methoxy-diethylacetal, b.p. $115\text{--}118^\circ/2$ mm., are hydrolysed to alcohols rather than to aldehydes. Et α -phenylethyl and α -anisylmethyl ether are hydrolysed under the same conditions as the above, indicating that the behaviour of the acetals is not exceptional. J. L. D.

Replacement of groups by hydrogen in substituted methanes. $\omega\omega\omega$ -Tribromoacetophenones. C. H. FISHER (J. Amer. Chem. Soc., 1933, 55, 5003—5008).— $\omega\omega\omega$:3:5-Pentabromo-2:4:6-trimethylacetophenone (I) and its 1:1 compound with ω :3:5-tetrabromo-2:4:6-trimethylacetophenone (II) are converted by KI in COMe_2 into the ω :3:5- Br_3 -derivative, m.p. $126\text{--}127^\circ$, which is prepared from 3:5-dibromoacetomesitylene and Br (1 mol.) in AcOH . (I) is converted into (II) by MgEtBr , $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, PhOH , or COPhMe ; COMe_2 and cold 10% KOH have no action. Alkali-sol. products are formed from (I) and hot aq. KOH; a pure compound could not be isolated. 4-Chloro- $\omega\omega$ -dibromoacetophenone and aq. 10% KOH give *p*-chloromandelic acid; $\omega\omega$ -dibromo-2:4:6-trimethylacetophenone reacts much more slowly to give an unidentified substance. H. B.

Molecular rearrangement of $\alpha\beta$ -unsaturated ethers. W. M. LAUER and M. A. SPIELMAN (J. Amer. Chem. Soc., 1933, 55, 4923—4930).—The following are prepared by the methods previously described (A., 1931, 710): β -bromo- α -phenylethyl Me, b.p. $117\text{--}118^\circ/15$ mm., P_1^a , b.p. $146\text{--}148^\circ/27$ mm., Bu^a , b.p. $165\text{--}166^\circ/32$ mm., and isoamyl, b.p. $140\text{--}143^\circ/12$ mm., ethers; β -bromo- α -*p*-chlorophenylethyl Me ether, b.p. $154\text{--}156^\circ/26$ mm.; α -*n*-butoxystyrene (I), b.p. $134.5\text{--}135.5^\circ/26$ mm.; *p*-chloro- α -methoxystyrene (II), b.p. $118\text{--}121^\circ/23$ mm., which with semicarbazide acetate in aq. EtOH gives *p*-chloroacetophenonesemicarbazone, m.p. $202\text{--}204^\circ$. α -Methoxystyrene (III) heated at about 300° for 2 hr. gives COPhEt (main product), $\alpha\beta$ -dibenzoylpropane (IV) (dioxime, m.p. $166\text{--}167^\circ$), and CH_4 . (IV) is dehydrated (conc. HCl) to 2:5-diphenyl-3-methylfuran, m.p. $57\text{--}58^\circ$, and is synthesised from $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ and $\text{COPh}\cdot\text{CHMeBr}$ (with subsequent hydrolysis). (IV) is probably formed [from (III)] thus: $\text{CH}_3\cdot\text{CPh}\cdot\text{OMe} + \text{COPhEt} \rightarrow \text{CHMeBz}\cdot\text{CH}_2\text{Bz} + \text{CH}_4$. In agreement with this view, (III) or α -ethoxystyrene (V) heated with an excess of COPhMe gives (CH_2Bz), whilst (V) and COPhEt similarly afford (IV). (V) heated at 300° for 1 hr. affords COPhPr^a , $\alpha\beta$ -dibenzoylbutane, b.p. $234\text{--}245^\circ/20$ mm., C_2H_6 , and a little C_6H_4 ; α -*n*-propoxystyrene similarly yields COPhBu^a , C_2H_6 , and C_3H_8 ; (I) furnishes Ph *n*-amyl ketone; (II) gives *p*-chloropropiophenone (semicarbazone, m.p. $175\text{--}176^\circ$) and some $\alpha\beta$ -di-*p*-chlorobenzoylpropane, m.p. $116.5\text{--}117^\circ$; α -isoamyloxystyrene affords Ph isohexyl ketone, b.p. $145\text{--}148^\circ/18$ mm. (semicarbazone, m.p. $144\text{--}145^\circ$),

COPhMe, ($\cdot\text{CH}_2\text{Bz}$)₂, isopentane, and isopentene. The formation of the above olefines indicates that the change $\text{CH}_2\text{:CPh}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{R} \rightarrow \text{COPhMe} + \text{CH}_2\text{:CHR}$ occurs to some extent. When (I) and (II) are heated together at 265°, a mixture of products (from which COPhEt is isolable as its semicarbazone) results; an intermol. exchange of radicals must occur. A reaction mechanism [similar to that formulated by van Alphen (A., 1928, 57) for the rearrangement of phenol ethers] is advanced. Rearrangement of $\text{CHMc:CPh}\cdot\text{OMe}$, $\text{CHEt:CET}\cdot\text{OMe}$, and $\text{OEt}\cdot\text{CMc:CH}\cdot\text{CO}_2\text{Et}$ could not be effected. H. B.

Oxidation products of benzophenoneoxime. W. H. HUNTER and W. S. DYER (J. Amer. Chem. Soc., 1933, 55, 5053—5055; cf. von Auwers and Wunderling, A., 1933, 505).—Oxidation [alkaline $\text{K}_3\text{Fe}(\text{CN})_6$] of $\text{CPh}_2\text{N}\cdot\text{OH}$ (I) in EtOH gives COPh_2 (II), a compound (III), $\text{C}_{26}\text{H}_{20}\text{ON}_2$, m.p. 156—157°, and a substance (IV), $(\text{C}_{13}\text{H}_{10}\text{ON})_4$, m.p. 193° (decomp.). Hydrolysis (conc. HCl) and attempted reduction of (III) affords (II). (IV) is reduced to (I)+(II), is decomposed slowly by COMe_2 to (I)+(II), and is converted by PCl_5 into (II) and NHBzPh . I oxidation of the Na salt of (I) in absence or presence of C_6H_6 gives (II) and tarry material. With Ag_2O in C_6H_6 , (I) gives (II) and a little (IV); in Et_2O , (II) and (III) (?) result. H. B.

Dipole moments of chlorobenzophenone oximes.—See this vol., 131.

Oxidation-reduction reaction of desyl chloride, and the supposed tolane oxide. G. RICHARD (Compt. rend., 1933, 197, 1432—1434).—Contrary to Madelung and Oberwenger (A., 1932, 62), the action of dry, powdered KOH on $\text{COPh}\cdot\text{CHClPh}$ yields BzOH , $\text{CHPh}_2\cdot\text{CO}_2\text{H}$ (I) (as salts), $\text{COPh}\cdot\text{CH}_2\text{Ph}$ (II) (unattacked by HCl at 120°), and benzil, the supposed tolane oxide (*loc. cit.*) probably being impure (II). $\text{CPh}_2\cdot\text{CO}$ is probably the intermediate from which (I) is obtained, and in one case an orange substance, transformed into tetraphenylcyclobutane-1:3-dione by heating, was isolated. J. W. B.

Condensation of *m*-iodoacetophenone with nitrobenzaldehydes. W. KRASZEWSKI and S. KOTOWICZÓWNA (Rocz. Chem., 1933, 13, 601—606).—*m*-Iodophenyl o-, m.p. 123° (*Br*-derivative, m.p. 145°; phenylhydrazone, m.p. 50°), *m*-, m.p. 147° (*Br*-derivative, m.p. 164°; phenylhydrazone, m.p. 54°), and *p*-nitrostyryl ketone (I), m.p. 164° (*Br*-derivative, m.p. 148°; phenylhydrazone, m.p. 92°), are produced when *m*-iodoacetophenone and the appropriate $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ interact in EtOH in presence of NaOH; in the case of *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, *m*-iodophenyl β -hydroxy- β -*o*-nitrophenylethyl ketone (II), m.p. 82° (*Bz* derivative, m.p. 127°), is also formed at 16°, but not at 0°. The *m*-, m.p. 92° (*Bz* derivative, m.p. 158°), and *p*- NO_2 -isomerides of (II), m.p. 108° (*Bz* derivative, m.p. 168°), are prepared analogously to (I) in aq. EtOH in presence of NaOH and K_2CO_3 , respectively. (II) is decomposed by aq. NaOH to yield indigotin and *m*- $\text{C}_6\text{H}_4\cdot\text{I}\cdot\text{CO}_2\text{H}$. R. T.

Action of the Grignard reagent on benzanthrone. Case of 1:6-addition. M. NAKANISHI (Proc. Imp. Acad. Tokyo, 1933, 9, 394—397).—Benz-

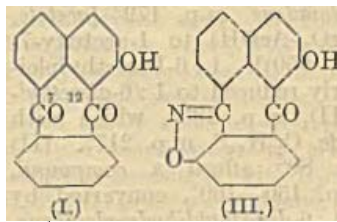
anthrone and an excess of MgPhBr in Et_2O give *Bz*-3-phenylbenzanthrone (I), m.p. 186°, the structure of which is proved by its yellowish-brown colour, reddish-brown halochromy in conc. H_2SO_4 , oxidation by $\text{Na}_2\text{Cr}_2\text{O}_7\text{-AcOH}$ to anthraquinone-1-carboxylic acid, formation of a *Br*-derivative which with NaOEt gives a blue isoviolanthrone, and synthesis of 1-phenylbenzanthrone, m.p. 182° (oxidised to 1-benzoylanthraquinone; the *Br*-derivative does not give an isoviolanthrone), from anthrone and $\text{CH}_2\text{Bz}\cdot\text{CH}_2\text{Cl}$. Benzylidenanthrone and MgPhBr give analogously anthra-fuchson. MgBu^tI gives probably *Bz*-3-*n*-butylbenzanthrone, m.p. 96°. (I) and KMnO_4 give a colourless substance, $\text{C}_{22}\text{H}_{16}$, m.p. 242°. R. S. C.

Preparation of phenylacetylcarbinol and its ethers. (MLLE.) M. DARMON (Compt. rend., 1933, 197, 1328—1329).—With $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ in Et_2O at 40°, $\text{OH}\cdot\text{CH}_2\cdot\text{CN}$ (I) gives a 15% yield of $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, similar treatment of the Me and Et ethers of (I) affording, respectively, benzyl methoxymethyl, b.p. 139—140°/27 mm. (semicarbazone, m.p. 127—128°), and ethoxymethyl, b.p. 116—118°/1 mm. (semicarbazone, m.p. 100°), ketone; the corresponding benzoyloxymethyl compound, b.p. 235°/40 mm. (semicarbazone, m.p. 105°), is similarly obtained from $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ (by the action of NH_3 on the mixed esters from $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ on $\text{CH}_2\text{Ph}\cdot\text{ONa}$). J. W. B.

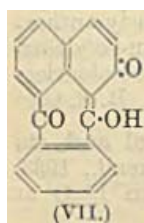
Beryllium benzoylacetate. R. W. BAILEY, F. M. BREWER, and H. M. POWELL (J.C.S., 1933, 1546—1547).—Beryllium benzoylacetate, $\text{Be}(\text{C}_{10}\text{H}_5\text{O}_2)_2$, m.p. 210°, is prepared by interaction of $\text{CH}_2\text{Bz}\cdot\text{COMe}$ with basic Be carbonate in boiling EtOH. Crystallographic data are given.

H. A. P.

Reaction of phthaloylnaphthol with hydroxylamine and diazomethane. L. F. FIESER (J. Amer. Chem. Soc., 1933, 55, 4963—4976).—1:8-Phthaloyl- β -naphthol (=1-hydroxy-7:12-pleiadenedione) (I) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in hot EtOH-NaOH (small amount) give the 7-oxime (II), m.p. 243° (diacetate, m.p. 237°), which passes at 300—320°/vac. into the dehydro-derivative, probably (III), m.p. 260° (acetate, m.p. 208°). (II) is converted by 82% H_2SO_4 at 200° into an isomeric substance, m.p. 251°. Similar oximation of (I) using more alkali gives (II) and (mainly) the 12-oxime (IV), m.p. 262° (with loss of H_2O) (diacetate, m.p. 174°), which is readily dehydrated (conc. acids; Ac_2O ; aq. NaOH) to the (1:12-)anhydro-derivative, m.p. 227°. The anhydro-derivative of 1:6-dihydroxy-7:12-pleiadenedioneoxime has m.p. 292°. (I) and NH_2OH in aq. NaOH room temp. give an additive 1:1 compound (V), decomp. about 135°, which regenerates its components when treated with AcOH, and with cold $\text{Ac}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ affords a little of the acetate of (I) and (mainly) a diacetate, m.p. 163°, of (IV). (V) heated with $\text{C}_5\text{H}_5\text{N}$ gives (II) and (IV). The production of (V) is considered to involve both CO groups of (I), viz., $\text{OH}\cdot\text{C}_7\cdot\text{O}\cdot\text{C}_{12}\cdot\text{NH}\cdot\text{OH}$. Similar



additive compounds are obtained from 1:2- and 1:6-dihydroxy-, 1-hydroxy-2:6-dimethyl-, and 1-hydroxy-4:5-benz-7:12-pleiadenediones. An additive compound is also obtained from (I) and N_2H_4 ; it is acetylated ($Ac_2O-C_5H_5N$) to a *hydrazone diacetate* (?), m.p. 199—200°. (V) and $Et_2O-MeOH-CH_2N_2$ give (I) and its Me ether (VI). (VI) is not obtained from (I) and CH_2N_2 (see below); its formation from (V) suggests that (V) undergoes decomp. to an unstable modification [which must be formulated as



the 1-OH derivative, i.e., (I)] of the phthaloylnaphthol; the stable form may be (VII). (I) does not react with CH_2N_2 in Et_2O ; in $C_2H_2Cl_4$, a compound (VIII), $C_{20}H_{14}O_3$ (alternative structures suggested), m.p. 208°, is formed by addition of two CH_2 groups. (VIII) contains OMe and CO groups and one active (enolic) H, and is reduced (Zn dust, AcOH) to a

dihydro-derivative, m.p. 245° (acetate, m.p. 184°).

H. B.

Derivatives of pleiadene. L. F. FIESER (J. Amer. Chem. Soc., 1933, 55, 4977—4984).—3:7-Dimethyl- β -naphthol (1 pt.), $o-C_6H_4(CO)_2O$ (I) (10 pts.), and $AlCl_3$ (2 pts.) at 200° give 1-hydroxy-2:6-dimethyl-7:12-pleiadenedione, m.p. 209° (acetate, m.p. 205°); 2:3- $C_{10}H_6(OH)_2$ and 2-phenanthrol similarly afford 1:2-dihydroxy-, m.p. 233°, and 1-hydroxy-4:5-benz-, m.p. 240° (acetate, m.p. 227°), -7:12-pleiadenedione, respectively. 3:7-Dimethyl- β -naphthyl Me ether, m.p. 82°, (I), and $AlCl_3$ in $C_2H_2Cl_4$ give small amounts of o-6-methoxy-3:7-dimethyl-1(or 2)-naphthoylbenzoic acid, m.p. 212° [converted by 82% H_2SO_4 at 100° (bath) into 3'-methoxy-4:2'-dimethyl-1:2-benzanthraquinone, m.p. 235°], and o-2-methoxy-3:7-dimethyl-1-naphthoylbenzoic acid (?), m.p. 223°. 3:7-Dimethyl- α -naphthyl Me ether, m.p. 58°, and (I) similarly give a little o-4-methoxy-2:6-dimethyl-1-naphthoylbenzoic acid, m.p. 261°, reduced (Zn dust, aq. NaOH) to the -1-naphthylmethylbenzoic acid, m.p. 236°, which is cyclised (82% H_2SO_4 at 100°) to 4-methoxy-2:6-dimethyl-12-pleiadone, m.p. 241°. This is demethylated ($AlCl_3$ in C_6H_6) to the 4-OH-derivative, m.p. 286°. 2:7- $C_{10}H_6(OMe)_2$ and (I) afford o-2:7-dimethoxy-1-naphthoylbenzoic acid, m.p. 201° (Me ester, m.p. 114°); the -1-naphthylmethylbenzoic acid, m.p. 161°, is cyclised to the Me₂ ether, m.p. 201°, of 1:6-dihydroxy-12-pleiadone, m.p. 233° (diacetate, m.p. 220°). Reduction (H_2 , Cu chromite, EtOH) of 1:8-phthalovl- β -naphthol gives 1-hydroxy-7:12-dihydropleiadene, m.p. 179° [acetate, m.p. 136°, oxidised (CrO_3 -AcOH) to 1-acetoxy-7-pleiadone (cf. A., 1933, 950)]. 1:6-Dimethylpleiadone (loc. cit.) is similarly reduced to 1:6-dimethyl-7:12-dihydropleiadene (II), m.p. 133°, which with S at 260° gives a sulphide, $C_{20}H_{16}S$, m.p. 217°. (II) and Br in AcOH at 80° afford a compound, $C_{20}H_{17}Br$, AcOH, decomp. 150—160°, converted by cold C_5H_5N into a bromo-1:6-dimethyldihydropleiadene, m.p. 179°.

H. B.

Reaction of o-phenylenedi(phenylglyoxal) and the retrograde benzilic acid change. Preparation of 1:4-dihydroxy-2:3-diphenylnaphthalene. R. WEISS and K. BLOCH (Monatsh., 1933, 63,

39—51).—An improved prep. of dibenzylidene-phthalan (I), $o-C_6H_4(CO-CBr_2Ph)_2$ (II), decomp. 114°, and $o-C_6H_4(COBz)_2$ (III) (A., 1932, 396) is given. With Cl_2 in AcOH (I) affords s-dichlorodi(dichlorobenzyl)phthalan (IV), m.p. 242—248°, similar treatment with I in AcOH giving 2-phenyl-3-benzylindone. With Zn in hot AcOH both (II) and (IV) give 1:4-dihydroxy-2:3-diphenylnaphthalene (V), softens 220°, m.p. 236—243°, oxidised in AcOH by air or $Na_2Cr_2O_7$ to 2:3-diphenyl-1:4-naphthaquinone (VI). With Zn and $Ac_2O-H_2SO_4$ (III) affords the Ac_2 derivative, m.p. 200—202°, of (V), which is obtained by hydrolysis with dil. HCl at 150°. Distillation of (V) with excess of Zn dust gives a little 2:3-diphenyl- α -naphthol (VII), the main product being a mol. compound $C_{44}H_{30}O_3$, m.p. 133—136°, of (VI) and (VII), also obtained by heating these together in AcOH, and resolved into its components by hot KOH-EtOH. The substance, m.p. 193° (decomp.), obtained by the action of amyl nitrite on $o-CH_2Ph-CO-C_6H_4-CH_2Bz$ in presence of NaOEt, previously designated 4-hydroxy-3-phenyl-1-benzylisoquinoline (A., 1925, i, 937), is actually 4-nitroso-2:3-diphenyl- α -naphthol. When heated with KOH in EtOH (III) affords diphenylphthalancarboxylic acid, $C_6H_4<\begin{smallmatrix} CPh(CO_2H) \\ CHPh \end{smallmatrix}>O$ (VIII), m.p. 200—202° (decomp.) (Me ester, m.p. 197°, by CH_2N_2), converted by heating with Ac_2O into diphenylindone [also obtained by distilling (VIII) at 265—275°/18 mm.] and o-benzoylbenzilic acid (IX), m.p. 176° (decomp.), probably $C_6H_4<\begin{smallmatrix} CPh(OH)-CO \\ CPh(OH)-O \end{smallmatrix}>$, since it does not react with CH_2N_2 , and forms a salt only with KOH-EtOH. Reduction of either (VIII) or (IX) with red P and HI in AcOH affords s-diphenylhomophthalide, m.p. 166°.

J. W. B.

Synthesis of brazilinic acid. J. N. RAY, S. S. SILOOJA, and P. R. WADHA (J. Indian Chem. Soc., 1933, 10, 617—620).—Et m-methoxyphenoxypropionate, veratroyl chloride (I), and $AlCl_3$ in cold $PhNO_2$ give 2-hydroxy-4:4':5'-trimethoxy- (II), m.p. 141°, and a little 4-hydroxy-2:4':5'-trimethoxy- (III), m.p. 175°, -benzophenone; the structures are assigned from the colours with $FeCl_3$. (II) and (III) are also obtained in approx. equal amounts from (I), m-OMe- C_6H_4-OH , and $AlCl_3$ in $PhNO_2$. (II) and HNO_3 (d 1.42) in AcOH-conc. H_2SO_4 at 48—52° give the 2'- NO_2 -derivative, m.p. 211° (oxidised to nitroveratric acid), which is converted through the 2'- NH_2 - (hydrochloride, m.p. 240°) and 2'-CN- (IV), m.p. 152—154°, -derivatives into 2-hydroxy-4:4':5'-trimethoxybenzophenone-2'-carboxylic acid, m.p. 203°. Condensation of this with CH_2Cl-CO_2H gives brazilinic acid, also obtained from (IV) and CH_2Cl-CO_2H with subsequent hydrolysis.

H. B.

Lipins of tubercle bacilli. XXXVII. Synthesis of phthiocol, the pigment of the human tubercle bacillus. R. J. ANDERSON and M. S. NEWMAN (J. Biol. Chem., 1933, 103, 405—412).—2-Methyl-1:4-naphthaquinone (oxime, m.p. 166—168°) heated with Zn- Ac_2O -AcOH-NaOAc gives the Ac_2 derivative of 1:4-dihydroxy-2-methylnaphthalene, converted by NaOEt-EtOH into 3-hydroxy-2-

methyl-1:4-naphthaquinone, m.p. 173—174° (isolated in 12% yield by acidification and steam-distillation), identical with phthiocol (A., 1933, 1083), and oxidised by H_2O_2 -0.1N-NaOH to $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$. J. W. B.

Methyl ether and bromine derivatives of α -elemolic and α -elemonic acids. H. LIEB and M. MLADENOVIC [with A. REZEK and M. SOBOTKA] (Bull. Soc. Chim. Yougoslav., 1933, 4, 85—99).— α -Elemolic acid (I) or its Ac derivative on heating during 5—6 hr. with 4% H_2SO_4 in MeOH yields the *Me ether* (II) of (I), m.p. 242° (Ac derivative, m.p. 224°); the reaction consists in addition of MeOH to the ethylenic linking of (I), as is shown by the non-addition of Br or HBr to (II). The *Me ether* of α -elemonic acid (III), m.p. 280—281° (*oxime*, m.p. 243°), is prepared analogously to (II) from (III), or by oxidising (II) with CrO_3 in AcOH. The Br_2 -derivative (IV), m.p. 235°, of (III) is prepared directly from Br and (III), or by oxidising the Br_2 -derivative of (I), and the *Br*-derivative (V), m.p. 273°, of (III) by oxidising the *Br*-derivative (VI) of (I), or from (IV) and KOMe. The presence of OH in (VI) is demonstrated by preparing its Ac derivative, m.p. 260°. (VI) and (V) with Pd- H_2 yield, respectively, dihydro-derivatives of (I) and (III). R. T.

Sapic acid, a constituent of American pine resin. F. VOCKE (Annalen, 1933, 508, 11—15).—When the fresh resin is kept in absence of air, crystals of *sapic acid* (I), $\text{C}_{20}\text{H}_{30}\text{O}_2$, m.p. 143°, $[\alpha]_D^{25}$ -123° (all rotations are in 96% EtOH for Hg green), separate. (I) is reduced (H_2 , PtO_2 , EtOH) to a *dihydro*-derivative, m.p. 195°, $[\alpha]_D^{25}$ +28.7°, and thence to a non-homogeneous *tetrahydro*-derivative, m.p. 173° (not sharp), $[\alpha]_D^{25}$ +28.3° [probably identical with the product similarly prepared from abietic acid (II)]. (I) rearranges to (II) when boiled with AcOH. Irradiation of (I) gives a non-cryst. product, $[\alpha]_D^{25}$ +35°. (I) may be identical with the similar acid isolated from European pine resin (Ruzicka and Schinz, A., 1923, i, 818). A reply is made to Ruzicka (A., 1933, 279, 820). H. B.

Plant heart-poisons. I. Constitution of uzarin. R. TSCHESCHE. II. Dehydrogenation of uzarigenin with selenium. R. TSCHESCHE and H. KNICK (Z. physiol. Chem., 1933, 222, 50—57, 58—62).—I. Catalytic hydrogenation of the acetate of α -dianhydrouzarigenin, m.p. 263—265°, $[\alpha]_D^{25}$ -29.5° (cf. lit.), gave as acetates α_1 - (I), m.p. 217°, $[\alpha]_D^{25}$ +11.4° (acetate, m.p. 248°, $[\alpha]_D^{25}$ +3.9°), and α_2 - (II), m.p. 230°, $[\alpha]_D^{25}$ +20.2° (acetate, m.p. 205°, $[\alpha]_D^{25}$ +20.2°), -*hexahydrodianhydrouzarigenins*, $\text{C}_{22}\text{H}_{36}\text{O}_3$. Oxidation of (I) and (II) with CrO_3 in AcOH afforded the α_1 - (III), m.p. 248—249°, $[\alpha]_D^{25}$ +39.3° (*oxime*, decomp. 275—278°), and α_2 - (IV), m.p. 216—217°, $[\alpha]_D^{25}$ +42.5° (*oxime*, m.p. 251—253°), -*ketones*, $\text{C}_{22}\text{H}_{36}\text{O}_3$. Clemmensen reduction of (III) and (IV) gave the *lactones*, $\text{C}_{22}\text{H}_{36}\text{O}_2$, α_1 -, m.p. 178°, $[\alpha]_D^{25}$ +11.3°, α_2 - (V), m.p. 180°, $[\alpha]_D^{25}$ +24.3°, which are oxidised by CrO_3 to the *dicarboxylic acids*, $\text{C}_{22}\text{H}_{34}\text{O}_6$, α_1 -, m.p. 270°, $[\alpha]_D^{25}$ +37.6° (*Me*₂ ester, m.p. 134—135°, $[\alpha]_D^{25}$ +18.7°), α_2 - (VI), m.p. 245—246°, $[\alpha]_D^{25}$ +38.5° (*Me*₂ ester, m.p. 146—147°, $[\alpha]_D^{25}$ +25.0°). When heated with Ac_2O , (VI) gives a *pyroketone*, $\text{C}_{22}\text{H}_{32}\text{O}_3$, m.p. 215°, $[\alpha]_D^{25}$ +150.9° (*oxime*, decomp. 248—250°), indicating that

the secondary OH group of uzarigenin (VII) occurs in a 6-C ring. (V) is probably identical with octahydro-trianhydroperiplogenin, showing that (VII) has the same C skeleton as the other heart-poisons. From the crude dianhydrouzarigenin (VIII), there was isolated a β -*isomeride*, m.p. 236—237°, $[\alpha]_D^{25}$ +4.95° (acetate, m.p. 167—168°, $[\alpha]_D^{25}$ +4.9°). All rotations are in CHCl_3 .

II. Se dehydrogenation of (VIII) gives a mixture of hydrocarbons from which Diels' hydrocarbon, $\text{C}_{16}\text{H}_{16}$, obtained from cholesterol, was isolated, indicating for (VII) the same skeleton as in the sterols and bile acids.

J. H. B.

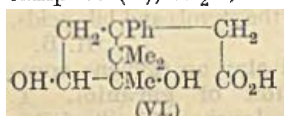
Action of Japanese acid clay on terpene compounds. IV. Isomerisation of geraniol. T. KUWATA (J. Soc. Chem. Ind. Japan, 1933, 36, 583—585B; cf. A., 1933, 830).—In COMe_2 at 60° α -terpineol, other terpenes, and polymerised products (I) are formed. In MeOH less (I) and much terpeneol *Me ether* are formed. R. S. C.

Acid-catalysed enolisation of menthone.—See this vol., 153.

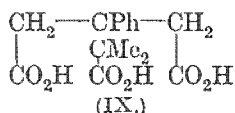
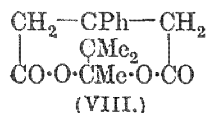
***d*-epiCamphor.** Y. ASAHINA and M. ISHIDATE [with T. JOYAMA] (Ber., 1933, 66, [B], 1913—1917).—Passage of CO_2 at 0° through a mixture of KCN in H_2O and *d*-5-ketocamphor in Et_2O leads exclusively to addition of HCN at 5-CO with production of a mixture of hydroxy-nitriles, hydrolysed by fuming H_2SO_4 (30% SO_3) to α - (I), m.p. 248—249°, $[\alpha]_D^{25}$ -1.24° in EtOH, and β - (II), m.p. 190—191°, $[\alpha]_D^{25}$ +44.79° in EtOH, -5-hydroxycamphor-5-carboxylamide. (I) is hydrolysed by 10% HCl at 100° to α -5-hydroxycamphor-5-carboxylic acid, m.p. 151—152°, b.p. about 250°/20 mm., $[\alpha]_D^{25}$ -6.48° in EtOH [semicarbazone (III), m.p. 267° (decomp.); quinine salt, m.p. 178°], oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 in H_2O to 5-ketocamphor (IV). Similarly, (II) affords β -5-hydroxycamphor-5-carboxylic acid, m.p. 153°, $[\alpha]_D^{25}$ +21.58° in EtOH [semicarbazone, (V), m.p. 225° (decomp.); quinine salt, m.p. 219°], oxidised to (IV). Treatment of (III) with NaOMe at 180° leads to α -5-hydroxycamphane-5-carboxylic acid (VI), m.p. 151°, $[\alpha]_D^{25}$ -59.2° in EtOH, whereas the corresponding β -compound (VII) has m.p. 130°, $[\alpha]_D^{25}$ -39.8° in EtOH. Oxidation of (VI) or (VII) with CrO_3 and a little H_2SO_4 at 100° affords *d*-epicamphor, m.p. 183—184°, $[\alpha]_D^{25}$ +50.0° in EtOH [semicarbazone, m.p. 236° (decomp.)], transformed by Br in CHCl_3 at 100° into *bromo-d*-epicamphor, m.p. 133—134°, $[\alpha]_D^{25}$ -86.9° in EtOH. H. W.

Degradation of 4-phenylcamphor to phenylisocamphoronic acid. M. BREDT-SAVELSBERG and J. BUCHKREMER (Ber., 1933, 66, [B], 1921—1932).—Phenylcamphoroxime (I), m.p. 143°, is transformed by boiling Ac_2O into its *acetate*, b.p. 150—160°/0.35 mm., which partly resinifies and partly yields AcOH and *phenyl- α -campholenonitrile* (II), m.p. 80°, better obtained by heating (I) with H_2SO_4 (*d* 1.18). With 50% H_2SO_4 (I) gives a compound containing S and N and (?) *phenyl- β -campholenolactone*, b.p. 143—145°/0.3 mm., m.p. 52—53°. The best method for the prep. of (II) consists in treating (I) with PhSO_2Cl in $\text{C}_5\text{H}_5\text{N}$, whereby *phenyl- α -campholenolactone*, m.p. 203—204°, unchanged by boiling 50% H_2SO_4 , scarcely attacked by molten KOH, and transformed by 30% KOH-MeOH at 180° in small amount into *phenyl- α -camphol-*

enic acid (III), results. Hydrolysis of (II) by KOH-H₂O-EtOH at 150° leads to *phenyl-α-campholenamide*, m.p. 126—127° after softening, and (III), m.p. 123—124° [Ag salt and thence by EtI the Et ester, b.p. 125—126°/0.2 mm.; Me ester (IV), b.p. 122.3—123°/0.4 mm., from (III) and CH₃N₂]. (III) is obtained in poor yield by the action of molten KOH on *phenylcamphor-ω-sulphonic acid*, m.p. 239—240° (decomp.) after darkening at 200°, obtained from phenylcamphor (V), Ac₂O, and conc. H₂SO₄. (III) is very



stable towards HNO₃, but smoothly oxidised by KMnO₄ to *dihydroxy-phenyldihydro-α-campholenic acid* (VI), m.p. 252—253° [Ag and Na (+2H₂O) salts]. (VI) is unchanged by Pb(OAc)₄, molten KOH, HNO₃ (d 1.3), or CrO₃-H₂O. CrO₃ in AcOH converts it into a *keto-lactone* (VII) C₁₆H₁₈O₃, m.p. 177—178° [semicarbazone, m.p. 200° (decomp.)], also obtained by treatment of (VI) with Pb(OAc)₄ and subsequently with CrO₃, whereas dihydroxydihydro-α-campholenic acid and its esters give *isoketocamphoric* and *isocamphoronic* acid when treated similarly. (VII) is converted by KOH-MeOH into the monobasic acid C₁₆H₁₈O₄, m.p. 205—206°, which does not react with NH₂OH or NH₂·CO·NH·NH₂ and is transformed by Br-KOH into the dibasic acid C₁₆H₁₈O₆, m.p. 240—241° (decomp.). (VII) is accompanied by a (?) *phenylterpenylic acid* C₁₄H₁₆O₄, m.p. 185°. Ozonisation of (III) leads to BzOH as sole recognisable product, whereas similar treatment of (IV) yields *phenylisoketocamphorodilactone* (VIII), m.p. 207—208° (the corresponding acid being stable as its salts), and a honey-like mass from which two *oximino-acids*, m.p. 290° (decomp.) and



m.p. 133—134°, are isolated. Oxidation of (VIII) by Br and KOH affords *phenylisocamphoronic acid* (IX), m.p. 184° [K₃ salt (+H₂O)], thereby locating Ph at 4 in the phenylcamphor.

Reasons are advanced for considering that the Nametkin transformation depends primarily on the camphane bridged ring. H. W.

Hydrogenation of the furan nucleus using osmium catalyst. N. D. ZELINSKI and N. I. SCHUIKIN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 60—65).—When the vapour of 2-methylfuran mixed with H₂ is passed over an Os-asbestos catalyst at 80—82° the tetrahydro-derivative is obtained. Using Pt catalyst the product consists chiefly of acyclic alcohols. R. T.

Attempted synthesis of primetin. S. SUGASAWA (J.C.S., 1933, 1621—1624).—5 : 6-Dimethoxyanthranilic acid affords 6-bromo-2 : 3-dimethoxybenzoic acid, an oil (*anilide*, m.p. 135—137°), which with NaOAc and Cu(OAc)₂ gives only veratric acid (I). 6-Iodo-2 : 3-dimethoxybenzoic acid (II), m.p. 137—138° (similarly prepared), with CH₃Ph·ONa and Cu in CH₃Ph·OH at 130—150° gives 6-benzyloxy-2 : 3-di-

methoxybenzoic acid, m.p. 128—129°, the *chloride*, m.p. 75—76°, of which with ZnMeI yields 6-benzyloxy-2 : 3-dimethoxyacetophenone, m.p. 90—91°. This with AcOH-HCl at 100° affords (?) 5-hydroxy-8-methoxyflavone, m.p. 129—130° (Ac derivative, m.p. 146—147°), demethylated by HI-Ac₂O to (?) 5 : 8-dihydroxyflavone, m.p. 179—180°, not identical with primetin. Hydrogenation (Pd-CaCO₃) of (II) in EtOH-KOH gives (I). The Et ester, an oil, of (II) (prepared by way of the chloride) with Cu at 250° gives Et. 3 : 4 : 3' : 4'-tetramethoxydiphenate, m.p. 124—125°, which resisted hydrolysis. R. S. C.

Synthesis of tricrin. K. C. GULATI and K. VENKATARAMAN (J.C.S., 1933, 1644).—Identity of 5 : 7 : 4'-trihydroxy-3' : 5'-dimethoxyflavone and tricrin is confirmed. R. S. C.

2 : 3-Dichlorodioxan. W. BAKER and A. SHANNON (J.C.S., 1933, 1598).—A pure form, m.p. 30°, b.p. 97—98°/20 mm. (isolated by distillation), of 2 : 3-dichlorodioxan (I) gives with (·CH₂·OH)₂ a mixture of ethylenedioxydioxans (eutectic, m.p. 86°, contains 77% of the form, m.p. 111°), inversion occurring during the reaction. Cl₂ and boiling 1 : 3-dioxacyclopentane give an inseparable mixture of the 2- and some 4-Cl-derivatives. Attempts to prepare 2 : 3-dicyanodioxan from (I) failed. R. C. S.

Rotenone, the active constituent of *Deris* root.
XI. Rotenone resin. Determination of rotenone and deguelin in rotenone resin. S. TAKEI, S. MIYAJIMA, and M. ONO (Ber., 1933, 66, [B], 1826—1833; cf. A., 1933, 512; Clark, A., 1931, 357, 1065, 1208; 1932, 950).—Agitation of rotenone resin (I) in Et₂O with 2% NaOH followed by dil. H₂SO₄ leads to l-deguelin, m.p. 163°, [α]_D²⁰ -23.22° in C₆H₆. Treatment of the crude mixture of rotenone (II) and deguelin with H₂ in EtOH-KOH (Pd-BaSO₄) and removal of the portion sol. in alkali affords readily dl-deguelin (III), m.p. 166° (oxime, m.p. 220°; isooxime, m.p. 149°). Hydrogenation (Pd-BaSO₄ in EtOAc) of (III) gives dihydrodeguelin, m.p. 170°, identical with Clark's β-dihydrorotenone; in KOH-EtOH, (III) does not absorb H₂ (Pd-BaSO₄), thereby differing from (II). (III) is transformed into deguelinol I, m.p. 197°, and deguelinol II, m.p. 251°, identical with tephrosin and isotephrosin of Clark. The deguenols are transformed by H₂SO₄-EtOH into dehydrodeguelin, m.p. 227°, which with boiling KOH-EtOH affords *deguelic acid* C₂₃H₂₄O₈, m.p. 177°. Hydrolysis of (III) gives β-tubaic acid, m.p. 161°, in poor yield, hydrogenated to dihydro-β-tubaic acid, m.p. 170°, identical with the product obtained from β-dihydrorotenone. Towards *Cobitis fossilis* (III) is approx. one half as toxic as (II) in 0.02—0.002% solution; at lower concns. its toxicity diminishes more rapidly. At high concn. (I) has about the same toxicity as (II), but loses its effect more rapidly with increasing dilution. The non-cryst. components of (I) are not more toxic than colophony. (II) and (III) are determined in (I) by treating its solution in EtOH-NaOH with O₂ and weighing the dehydro-mixture (IV) thus produced. (IV) is hydrogenated (Pd-BaSO₄ in EtOH-NaOH) and the dehydrodeguelin and isodihydrodehydrorotenone so formed are weighed. H. W.

Complex compounds of bivalent silver of new type. G. A. BARBIERI (Atti R. Accad. Lincei, 1933, [vi], 17, 1078—1081).—Red *Ag dipicolinate*, $\text{Ag}(\text{C}_5\text{H}_4\text{N}\cdot\text{CO}_2)_2$, obtained from the normal salt by treatment with persulphate or by electrolytic oxidation, is highly stable and forms mixed crystals with the analogous Cu compound (cf. Ley and Ficken, A., 1917, i, 706). T. H. P.

Complex iron compounds of 2-pyridylhydrazine. B. EMMERT and O. SCHNEIDER (Ber., 1933, 66, [B], 1875—1876).—Gradual addition of Et_2O to 2-pyridylhydrazine and FeCl_2 in MeOH in absence of O_2 ppts. the salt $\left[\begin{array}{c} \text{C}_5\text{H}_4\text{N} \\ \text{NH}\cdots\text{NH} \end{array} \right]^{2+} \text{Fe} \left[\text{Cl}_2 \right]$, oxidised by air in presence of HCl to the compound, $\text{C}_{15}\text{H}_{21}\text{N}_5\text{Cl}_2\text{Fe}$. H. W.

Poly-membered ring systems. II. Improved syntheses of hexamethyleneimine. K. ZIEGLER and P. ORTH (Ber., 1933, 66, [B], 1867—1871; cf. A., 1933, 951).—Equiv. quantities of $\alpha\zeta$ -dibromohexane (I) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}_2$ (II) are dissolved in hot BuOH and treated gradually with 0.5 atom of Na in BuOH. After removal of excess of (I) and (II), *p*-toluenesulphon- ζ -bromohexylamide (III) is obtained in 65—70% yield. Slow addition of equiv. solutions of (III) and Na in BuOH to boiling BuOH gives *p*-toluenesulphonylhexamethyleneimine (IV), b.p. $164^\circ/0.3$ mm., m.p. 75° , in 70% yield. A 74% yield is obtained when the solutions are slowly run into $\text{CH}_2\text{Ph}\cdot\text{OH}$ at 170° so that the BuOH distils continuously. Hydrolysis of (IV) is effected conveniently by 48% HBr. H. W.

Azo-derivatives of methyleneindoline. (SIGNA.) E. GIUGI (Gazzetta, 1933, 63, 701—708; cf. A., 1924, i, 420, 1002).—*COMePr*^s *o*-tolylhydrazone, b.p. $176^\circ/33$ mm., when treated with ZnCl_2 in EtOH forms 2 : 3 : 3 : 7-tetramethylindolenine (I), b.p. $135^\circ/22$ mm., of which the 1-methiodide (II) (new m.p. 245° ; cf. A., 1905, i, 718) gives with $\text{NHPh}\cdot\text{NH}_2$ a substance $\text{C}_{19}\text{H}_{22}\text{N}_3\text{I}$, m.p. 232° (decomp.). The last is decomposed by picric acid to the *picrate*, m.p. 208° , of 1 : 3 : 3 : 7-tetramethyl-2-benzeneazomethyleneindoline, m.p. 146° , also obtained by action of PhN_2Cl on 1 : 3 : 3 : 7-tetramethyl-2-methyleneindoline. Similarly *COMePr*^s *m*-tolylhydrazone, b.p. $190^\circ/50$ mm., yields 2 : 3 : 3 : 6-tetramethylindolenine, m.p. 61 — 62° , b.p. $140^\circ/27$ mm., which forms a *picrate*, m.p. 169° , a *Bz* derivative, m.p. 186° , and a *methiodide*, m.p. 230° , whence the compound $\text{C}_{19}\text{H}_{22}\text{N}_3\text{I}$, m.p. 250° , and the *picrate*, m.p. 200° , of 1 : 3 : 3 : 6-tetramethyl-2-benzeneazomethyleneindoline (hydrochloride, m.p. 240°), also obtained by action of PhN_2Cl on 1 : 3 : 3 : 6-tetramethyl-2-methyleneindoline. 1 : 3 : 3-Triethyl-2-methyleneindoline and PhN_2Cl form 1 : 3 : 3-triethyl-2-benzeneazomethyleneindoline (*picrate*, m.p. 168°). W W

Quinoline synthesis. G. A. KIRKHOFF and M. FEDOTOV (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1930, 40—41; cf. Russ. Pat. 29,173).— NH_2Ph (1 mol.), 94% glycerol (2 mols.), H_2SO_4 (*d* 1.84, 1.44 mols.), and PhNO_2 (0.55 mol.), with $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (34 g.) + infusorial earth (10 g.) as catalyst, are heated to 136° , PhNO_2 and H_2O evaporating being condensed and the former returned to the reaction vessel. The

mixture is then kept at 150 — 154° for 4—5 hr. The cold product is diluted with ice and H_2O and nitrite is added until N oxides are liberated. After steam-distillation the residue is made alkaline and the quinoline distilled with steam. The yield is 85% on NH_2Ph and 42—43% on glycerol. CH. ABS.

Cytisine group. I. Attempted synthesis of Ewins' structure for cytisine. S. CHAKRAVARTI and A. VENKATASUBBAN (J. Annamalai Univ., 1933, 2, 227—237).—Unsuccessful attempts to synthesise a compound having Ewins' cytisine formula (J.C.S., 1913, 103, 97) are described. Attempted oxidation of $\omega\omega'$ -dibromomesitylene to the dialdehyde with different reagents and by conversion into the $(\text{NHPh})_6$ -compound and oxidation with KMnO_4 failed. Nitration of *m*-tolualdehyde and subsequent condensation with $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ (+ $\text{C}_5\text{H}_{11}\text{N}$) gives a mixture of 2- (I) and 6-nitro-3-methylcinnamic acid (II), m.p. 224° ; 6-nitro-*m*-tolualdehyde-*p*-tolil has m.p. 89° . *m*-Methylcinnamic acid with HNO_3 (*d* 1.48) at $<0^\circ$ gives the 4- NO_2 -compound, m.p. 251° (*Me* ester, m.p. 124°), (I), and (II). The mono-*p*-tolil, m.p. 161° , of 1 : 4 : 3 : 5- $\text{C}_6\text{H}_2\text{Me}(\text{OH})(\text{CHO})_2$ with $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ gives 2-hydroxy-3-aldehyde-5-methylcinnamic acid, m.p. 212° (*Me* ester, m.p. 129°). Attempts at cyclisation of 1-nitroso-6 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline between the 1 : 8-groups failed. Diazotised 8-amino-6-methylquinoline with KCN - CuCN gives only a small amount of substance, m.p. 90° . 6-Methylquinoline-8-carboxylic acid, m.p. 169° , obtained from 4-amino-*m*-toluonitrile by the Skraup reaction, is reduced by Sn - HCl to the H_1 -compound, m.p. 190 — 191° , the 1- NO -derivative, m.p. 138° (decomp.), of which loses the NO group when reduced with Zn dust and AcOH . Na-Hg and NH_4 sulphide also failed to give the expected hydrazine or its cyclisation product. H. A. P.

Acridones. V. 3-Nitrophenylanthranil. I. TANASESCU and E. RAMONTIANU (Bull. Soc. chim., 1933, [iv], 53, 918—923; cf. A., 1933, 956).—3-Nitrophenylanthranil (I), m.p. 174 — 175° (0.5 HgCl_2 compound, m.p. 190° after decomp. from 185°), is isolated from the reaction product of 2 : 4-dinitrobenzaldehyde (II), C_6H_6 , and H_2SO_4 . It is reduced by SnCl_2 to the 3- NH_2 -compound (III), m.p. 135 — 136° (HgCl_2 compound, m.p. 192° ; *Bz* derivative, m.p. 260° after decomp.), also obtained similarly from (II). (I), (II), or (III) with Zn dust and CaCl_2 gives 2 : 4-diaminobenzophenone, m.p. 132° (*Bz*, derivative, m.p. 201°). R. S. C.

Isolation of amino-acids as carbamido-acids and hydantoins. I. Derivatives of monoaminomonocarboxylic acids. W. J. BOYD (Biochem. J., 1933, 27, 1838—1848).—The properties of the carbamido-acids (I) and hydantoins (II) corresponding with the NH_2 -acids present in protein hydrolysates were investigated with a view to the isolation and determination of NH_2 -acids. Many vals. of m.p. (lit.) are corr. Separation of (I) by EtOH at p_H 4 and conversion into (II) permits the removal of the derivatives of leucine, isoleucine, valine, phenylalanine, alanine, proline, and hydroxyproline by Et_2O or CHCl_3 , whilst that of tyrosine is obtained from the residue insol. in Et_2O . Separation of (II) by solvents

appears to be possible. New compounds described are: α -carbamido-*sec*.-butylacetic acid, m.p. 205°; *sec*.-butylhydantoin, m.p. 145—150° (hydrate, m.p. 95°). F. O. H.

Tautomerism of pyrazoles. K. VON AUVERS (Annalen, 1933, 508, 51—58).—The following compounds are shown (from their sp. exaltations) to be entirely or largely homogeneous: 3-phenyl- and 3-phenyl-5-methyl-pyrazoles; Me 3-phenyl- and 3-phenyl-1-methyl-pyrazole-5-carboxylates; Me 5-phenyl-1-ethylpyrazole-3-carboxylate; the constitutions are assigned from the spectrochemical data. The 3- and 5-positions in pyrazole can no longer be regarded as equiv. H. B.

2-Benzoylglyoxaline. A. SONN and P. GREIF (Ber., 1933, 66, [B], 1900—1903).—*d*-Tartaric acid is converted by fuming HNO_3 and conc. H_2SO_4 into dinitrotartaric acid, which is dissolved in Et_2O and treated successively with $\text{CH}_2\text{Ph}\cdot\text{CHO}$ and $\text{EtOH}\cdot\text{NH}_3$, thus leading to 2-benzoylglyoxaline-4 : 5-dicarboxylic acid (I), decomp. 248° (NH_4 salt). Decarboxylation of (I) in anthracene at 300° gives 2-benzoylglyoxaline, m.p. 125—126° (picrate, m.p. 172°), oxidised by CrO_3 in AcOH to 2-benzoylglyoxaline (III), m.p. 161—162°, not identical with the product of Oddo *et al.* (A., 1927, 1098). (II) is transformed by Br in CHCl_3 into 4 : 5-dibromo-2-benzoylglyoxaline, m.p. 218—220°, and its *perbromide*, m.p. 117—120°. Hydrogenation ($\text{Pd}\text{--}\text{AcOH}$) of (II) affords 2- α -hydroxybenzoylglyoxaline, m.p. 199—201°. H. W.

Bis- β -halogenoethylamines. III. N-Phenylpiperazine. V. PRELOG and G. J. DŘÍZA (Coll. Czech. Chem. Comm., 1933, 5, 497—502).—Interaction of NH_2Ph with $\beta\beta'$ -dichlorodiethylamine hydrochloride or $\beta\beta'$ -dibromodiethylamine hydrobromide in MeOH gives N-phenylpiperazine (I), b.p. 162—164°/22 mm. [hydrochloride, m.p. 247° (decomp.); hydrobromide, m.p. 250—252°; Ac, m.p. 96° (hydrochloride, m.p. 213—214°), Bz, m.p. 96—97° (hydrochloride, m.p. 244°), and *p*-toluenesulphonyl derivative, m.p. 199—200°; *p*-nitrobenzeneazo- (brownish-red), decomp. about 250°, and *p*-sulphobenzeneazo-derivative (Na salt, decomp. about 210°)], and a little $\beta\beta'$ -dianilindithylamine, b.p. 268—276°/22 mm. (hydrochloride, m.p. 237°). (I) has marked physiological action. H. A. P.

Spontaneous resolution of a racemic compound (histidine monohydrochloride). R. DUSCHINSKY (Chem. and Ind., 1934, 10; cf. A., 1928, 653).—A hot solution of 660 g. of *dl*-(I) and 340 g. of *l*-histidine hydrochloride (II) when rapidly cooled to 20° affords pure (II); the mother-liquor with $\text{EtOH}\text{--}\text{Et}_2\text{O}$ at 0° gives pure (I). Concn. of the second filtrate and rapid cooling gives the *d*-isomeride (46 σ) $[\alpha]_D^{25} +38^\circ$ to $+39.5^\circ$. J. L. D.

Complex dipyridyl and phenanthroline salts of bivalent metals.—See this vol., 159.

Oxidation of uric acid in presence of glycine. FREREJACQUE (Compt. rend., 1933, 197, 1337—1339).—Oxidation of uric acid with O_2 in alkaline solution in presence of MnO_2 and glycine (I) (cf. A., 1932, 67) affords the *K* salt, $+\text{H}_2\text{O}$

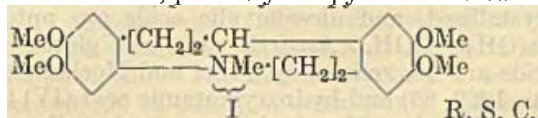
$\text{CO} < \begin{array}{c} \text{NH}\cdot\text{CH} \\ \text{NH} \end{array} \text{C}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K})\cdot\text{NH} > \text{CO}$ (II), of isoallantoylglycine (III) [double Cu, $\text{CuR}_2\cdot 2\text{CuSO}_4\cdot 11\text{H}_2\text{O}$; $\text{CuR}_2\cdot \text{CuCl}_2\cdot 3\text{H}_2\text{O}$; and Ag, $\text{AgR}\cdot \text{AgNO}_3$, salts ($\text{R} = \text{C}_6\text{H}_5\text{O}_4\text{N}_5$)]. With dil. AcOH (II) gives an equimol. double salt, $+\text{H}_2\text{O}$, of (II) and (III), hydrolysed by mineral acids completely to (I) and allantoin. Using $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ in place of (I) gives the *K* salt $+\text{3H}_2\text{O}$, of isoallantoylalanine. J. W. B.

Reductions with zinc dust in pyridine. III. Reversible hydrogenation and dehydrogenation of chlorophylls. R. KUHN and A. WINTERSTEIN (Ber., 1933, 66, [B], 1741—1745; cf. A., 1932, 1138).—Chlorophyll *a* or *b* or methylchlorophyllide is rapidly reduced by Zn dust in presence of $\text{C}_5\text{H}_5\text{N}$ and AcOH , giving brown solutions which become green with red fluorescence on exposure to air. Chromatographic treatment of the solution in light petroleum with sucrose removes decomp. products; the regenerated dyes are identical with the initial materials. Similar treatment of phaeophorbide *a* or phaeophytin *a* + *b* gives leuco-compounds converted by air into complex Zn compounds. Haemin is not decolorised. The bearing of the observations on photosynthesis is discussed. H. W.

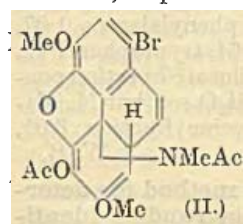
Effect of ultra-violet rays on nicotine. V. A. GANT (J. Pharm. Exp. Ther., 1933, 49, 408—427).—Irradiation of 0.1% nicotine (I) destroys its basicity in 105 min. and causes slight acidity in 150 min. At the neutral point the solution has a slight vasopressor activity. The product contains nicotinic acid (II), NH_2Me (III), and unchanged (I). After 12 hr.' exposure a 0.1% solution becomes neutral again, corresponding with the destruction of (II), malonic acid (IV), and (III); traces of NO_3' , NO_2' , and NH_3 are found. (II) on irradiation gives similar end products; 70% of a (IV) solution is destroyed and 73% of a (III) solution giving NO_3' , NO_2' , and NH_3 as end-products. H_2O_2 produces the same series of changes. H. D.

Synthesis of *dl*-homolaudanosoline and its dehydrogenation. S. SUGASAWA and H. YOSHIKAWA (J.C.S., 1933, 1583—1585).—Homoveratrylamine and β -veratrylpropionyl chloride in $\text{Et}_2\text{O}\text{--}\text{aq. NaOH}$ at 0° give β -3 : 4-dimethoxyphenylpropiono- β -3' : 4'-dimethoxyphenylethylamide, m.p. 99—100°, which with POCl_3 in PhMe at 120—130° yields 6 : 7-dimethoxy-1- β -3' : 4'-dimethoxyphenylethyl-3 : 4-dihydroisoquinoline (I), m.p. 96—97° (lit. 94°; hydrochloride). Diveratrylideneacetone (modified prep.; 85% yield), m.p. 84°, is quantitatively hydrogenated (PtO_2) to di- β -3 : 4-dimethoxyphenylethyl ketone, m.p. 84°, the oxime, m.p. 138—139°, of which with POCl_3 in PhMe at 120—130° gives (I). (I) with MeI in hot MeOH gives *dl*-homolaudanosine methiodide, decomp. 132.5—133.5° (perchlorate, decomp. 183—185°); the corresponding methochloride affords, when hydrogenated, the *tert.* base, which with $\text{HI}\text{--}\text{Ac}_2\text{O}$ at 150° gives *dl*-homolaudanosoline (II) [perchlorate, m.p. 183—185° (decomp.)]. The hydriodide, amorphous, hygroscopic, of (II) with chloranil in hot AcOH yields 2 : 3 : 11 : 12-tetrahydroxy-8-methyl-6 : 7 : 15 : 16-tetrahydro-5 : 18 : 9 : 14-dibenzyrpyridocolinium iodide, decomp. 252—253°, methylated (Me_2SO_4) in H_2 to

2 : 3 : 11 : 12 - tetramethoxy - 6 : 7 : 15 : 16 - tetrahydro - 5 : 18 : 9 : 14 - dibenzpyridocoline methiodide, decomp. 237—238°; the corresponding crude methochloride, decomp. 204—205°, at 220—230° gives a substance, m.p. 153.5—154.5°, probably the pyridocoline base



Sinomenine. XXXVII. Acetolysis of 1-bromosinomenine. K. GOTO, K. IIDA, and H. SHISHIDO (Bull. Chem. Soc. Japan, 1933, 8, 366—370).—1-Bromosinomenine (I) is converted by Ac_2O and NaOAc at the b.p. into 1-bromodiacylsinomenine, m.p. 135° (sinters 125°), to which formula



(II) is assigned, and which on further treatment (e.g., hydrolysis, reduction) is converted into amorphous products. De-*N*-methyl - 1 - bromosinomenine, however, on acetolysis gives 90% of theory of 1-bromodiacylsinomenol (III) (1-bromo-4 : 6 - diacetoxy - 3 : 7 - dimethoxy - phenanthrene), m.p. 187°, converted by catalytic reduction into diacylsinomenol, m.p. 151°. (III) is also obtained similarly but in poor yields from 1-bromosinomenine methiodide (IV), and the hydrochloride, methiodide, and de-*N*-methyl derivative of 1-bromosinomenine. De-iodination of (IV) by AgOAc in AcOH and acetolysis of the product gives 1-bromo-4 : 6 : 7 (?) - triacetoxy - 3 - methoxyphenanthrene, m.p. 216°, which is also formed by acetolysis of 1-bromosinomenine ketone, and on catalytic reduction gives 4 : 6 : 7 (?) - triacetoxy - 3 - methoxyphenanthrene, m.p. 168°. H. A. P.

Asymmetric quaternary arsonium compounds and attempted fission into their optically active components. G. KAMAI (Ber., 1933, 66, [B], 1779—1783).— AsMeEtI is converted by MgPhBr into phenylmethylethylarsine, b.p. 89—90.5°/12 mm., which with CH_2PhI affords phenylbenzylethylarsonium iodide (I), m.p. 140°. Ethyl-*n*-propylphenylarsine (II), b.p. 245°/760 mm. (compound $\text{C}_{11}\text{H}_{17}\text{AsCuBr}$, m.p. 134°), and CH_2PhCl at 140° yield phenylbenzylethyl-*n*-propylarsonium chloride (III), m.p. 156°. (II) does not give cryst. derivatives with $\text{COMe}\cdot\text{CH}_2\text{Cl}$ or $\text{COPh}\cdot\text{CH}_2\text{Br}$. *p*-Tolylethyl-*n*-propylarsine, b.p. 127—128°/10 mm. (compound $\text{C}_{12}\text{H}_{19}\text{AsCuBr}$, m.p. 117—118°), and CH_2PhI at room temp. yield *p*-tolylbenzylethyl-*n*-propylarsonium iodide (IV), m.p. 119—120°. α -Naphthylethyl-*n*-propylarsine, b.p. 181°/10 mm. (additive compounds with Br and CuBr), affords α -naphthylbenzylethyl-*n*-propylarsonium iodide (V), m.p. 154—155°, and α -naphthylphenylethyl-*n*-propylarsonium bromide (VI), m.p. 136—137°. (I), (III), (V), and (VI) give non-cryst. products with $\text{Ag d-}\alpha$ - and d - α - (VII) - bromocamphorsulphonates. (IV) and (VII) give a salt which can be separated into fractions of differing $[\alpha]_D$; treatment of the first fraction, m.p. 137°, with aq. KI leads to *d*-*p*-tolylbenzylethyl-*n*-propylarsonium iodide, m.p. 120°, $[\alpha]_D^{25} + 9.86^\circ$ in COMe , which rapidly becomes inactive. H. W.

Asymmetric arsenic atom. Attempts to prepare optically active arsenicals. J. D. A. JOHNSON (J.C.S., 1933, 1634—1637).—2-Methyl-10-*n*-propyl-5 : 10-dihydrophenarsazine and CH_2PhBr or CH_2BzBr (I) at 100° give 10-benzyl-, m.p. 206—207° [*d*-camphor- β -sulphonate, m.p. 262° (decomp.), $[\alpha]_D^{25} + 21^\circ$, irresolvable], and 10-phenacyl-2-methyl-10-*n*-propyl-5 : 10-dihydrophenarsazonium bromide, respectively. $\text{CH}_2\text{Ph}\cdot\text{MgBr}$ and 10-chloro-2-methyl-5 : 10-dihydrophenarsazine give $(\text{CH}_2\text{Ph})_2$ and 10-benzyl-2-methyl-5 : 10-dihydrophenarsazine, m.p. 132.5°, which with (I) gives 10-phenacyl-10-benzyl-2-methyl-5 : 10-dihydrophenarsazonium bromide, m.p. 203° (*d*-camphor- β -sulphonate, m.p. 187—188°, $[\alpha]_D^{25} + 17.5^\circ$ in EtOH , irresolvable). The corresponding iodide, m.p. 179°, with Ag_2O in hot H_2O gives (?) 10-benzyl-2-methyl-5 : 10-dihydrophenarsazonium dihydroxide (II), m.p. indefinite. 10 : 10'-Bis-5 : 10-dihydrophenarsazinyll (III) and EtBr at 100° give (?) 10 : 10-diethyl-5 : 10-dihydrophenarsazonium bromide, m.p. 129—132° (decomp.), also obtained similarly from 10-ethyl-5 : 10-dihydrophenarsazine. 10-Chloro-5-acetyl-5 : 10-dihydrophenarsazine and H_3PO_2 in hot $\text{EtOH}\cdot\text{COMe}$, afford 10 : 10'-bis-5-acetyl-5 : 10-dihydrophenarsazinyll, unchanged by EtBr . (III) and $(\text{CH}_2)_5\text{Br}_2$ give a substance, m.p. 166° (decomp.). R. S. C.

Additive products of *p*-phenoxyphenyldialkylphosphines and carbon disulphide. W. C. DAVIES and C. J. O. R. MORRIS (Bull. Soc. chim., 1933, [iv], 53, 980—986).—*p*-Phenoxyphenyldichlorophosphine and the appropriate Grignard reagent give the *p*-phenoxyphenyldialkylphosphines, $p\text{-OPh}\cdot\text{C}_6\text{H}_4\cdot\text{PR}_2$, which with CS_2 give additive compounds (A) (1 mol. of each), in which $\text{R} = \text{Me}$, m.p. 87.5°, *Et*, cryst. (with MeI gives the phosphine methiodide, m.p. 163°), and *Pr*, m.p. 57°. (A) are partly dissociated in solution and are considered to contain a co-ordinate C-P linking. *p*-Chlorophenyldi-*n*-propylphosphine and CS_2 give a red colour, but no ppt. R. S. C.

Preparation of selenophen. Attempts to prepare tellurophen. F. A. McMAHON, T. G. PEARSON, and P. L. ROBINSON (J.C.S., 1933, 1644).—Selenophen (CHPh_3 derivative, m.p. 57°, decomposes into its components when heated) is best obtained from C_2H_2 , Se, and roasted bauxite at 400°; it is formed in traces from P_2Se_3 and Na succinate (cf. A., 1910, i, 187). Tellurophen, probable b.p. 136°, could not be obtained pure; mixtures containing it are formed from C_2H_2 , roasted bauxite, and Te, or better Al_2Te_3 , at 400°. R. S. C.

Antimonial analogues of the acridine series. Dihydrostibacridines. G. T. MORGAN and G. R. DAVIES (Proc. Roy. Soc., 1933, A, 143, 38—47).—2-Aminodiphenylmethane is converted by the Bart-Schmidt process into diphenylmethane-2-stibinic acid (I), reduced by SO_2 in presence of HCl and a trace of KI to diphenylmethane-2-dichlorostibine (II), m.p. 129—130°, converted by $\text{NaI}\cdot\text{COMe}_2$ into the corresponding I_2 -compound, m.p. 95°, and by aq. $\text{NH}_3\cdot\text{COMe}_2$ (or EtOH) at 0° into the stibine oxide (III), m.p. 82—83°, which with HBr (*d* 1.3) affords the Br_2 -compound, m.p. 121°. Ring-closure of (I) with warm AcOH —

H_2SO_4 gives *sibacridinic acid* $\text{CH}_2\langle\text{C}_6\text{H}_4\rangle\text{SbO}_2\text{H}$, converted by HCl at 0° into *sibacridine trichloride*, reduced by SO_2 to 10-chloro-9:10-dihydro-sibacridine, m.p. 105° , whence the corresponding 10-Br-, m.p. 112° , and 10-I- (IV), m.p. $160\text{--}162^\circ$, -derivatives, and 10:10'-bis-9:10-dihydro-sibacridine oxide, softens 211° , sinters 215° , are obtained. With MgMeI (IV) gives 10-methyl-9:10-dihydro-sibacridine, softens 98° , m.p. 101° (dichloride, m.p. $177\text{--}178^\circ$; Br_2 - and I_2 -compounds unstable), the corresponding 10-Ph derivative (using MgPhBr) being isolated only as its dichloride, m.p. $221\text{--}223^\circ$. With excess of warm aq. NH_3 in COMe_2 (II) gives tetrakis(diphenylmethane-2-sibine oxide) $[(\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4)_2\text{Sb}]_2\text{O}$, m.p. 117° , from which by similar methods are obtained bis(diphenylmethane)-2-chloro- (V), m.p. $87\cdot5^\circ$, -2-bromo-, m.p. $86\cdot5^\circ$, and -2-iodo-, m.p. $73\text{--}75^\circ$, -sibine. With Cl_2 in CH_2Cl_2 (V) gives a trichloride (VI), m.p. 129° , converted by warm dil. aq. NH_3 into bisdiphenylmethane-2-sibinic acid, m.p. 248° , also obtained by oxidation of (III) with H_2O_2 . Heated at $150\text{--}180^\circ/18\text{--}20\text{ mm.}$ (VI) gives 10:2'-diphenylmethane-9:10-dihydro-sibacridine dichloride, m.p. $220\text{--}224^\circ$ (decomp.), purified through the corresponding oxide, softens at $158\text{--}160^\circ$. J. W. B.

Thermolysis of neutral, aqueous solutions of polypeptides with increasing chain-length in relationship to the thermolysis of proteins. O. GERNGROSS and W. DESEKE (Ber., 1933, 66, [B], 1810—1813).—The progress of the hydrolysis of alanyl-glycyl- and -diglycyl-glycine, of leucyl-di- and -tetra-glycylglycine in neutral aq. solution at 100° is followed by determination of NH_3 (Van Slyke). The rate in the case of the initial members of analogously constituted series increases with increasing chain-length, but rapidly tends to a const. val. There is no evidence that polypeptides with increasing chain-length become more resistant towards hydrolysis in H_2O at 100° . Immediately after dissolution it is considered that gelatin exists in more or less intact micelles; the peptide linking is protected for a time from hydrolysis, since the partial valencies are saturated with the corresponding groups of vicinal mols. in the micelle. The peptide chain does not suffer more rapid hydrolysis until it is severed completely from the micelle. H. W.

Formalin titration of proteins. D. W. STEUART (Analyst, 1933, 58, 754—755).—Vals. of total N (c.c.)/formol titration (0.1N-NaOH) are: ordinary milk 23 (calc.), gelatin 40, casein 22, albumin 33, peptone 16 and 17, pepsin 11, and pancreatin 5 (cf. B., 1933, 1080). As these vals. decrease, buffer action (for growth of lactic bacteria) increases, and the action of pepsin on casein produces a better buffered peptone than Witte's peptone. J. G.

Basic amino-acids of casein. H. B. VICKERY and A. WHITE (J. Biol. Chem., 1933, 103, 413—415).—Determination of the basic NH_2 -acids from casein by the Ag. pptn. method (A., 1928, 511) gives histidine 1.83, arginine 3.85, and lysine 6.25%. J. W. B.

Fractionation of the amino-acids of livetin. T. H. JUKES (J. Biol. Chem., 1933, 103, 425—437).—

A method for fractionating NH_2 -acids (protein hydrolysis) is described. Humin, NH_3 , and basic NH_2 -acids are first removed and determined by Vickery's methods (cf. *inter alia*, A., 1928, 511; 1932, 1148), and from the combined mother-liquors tyrosine (I) is crystallised, and dicarboxylic acids are pptd. with $\text{Ba}(\text{OH})_2\text{--EtOH}$. Aspartic (II) and glutamic (III) acids are determined by Jones and Moeller's method (A., 1929, 85) and hydroxyglutamic acid (IV) is pptd. as its Ag salt. Monoamino-monocarboxylic acids are then converted into Cu salts and fractionated (Brazier, A., 1930, 1458, modified). Application of this method to hen's yolk livetin (containing 15.5% N; hydrolysed with 20% HCl) affords 87% recovery of total N, 56% of which is allocated thus: NH_3 8.3, histidine 1.62, arginine 11.6, lysine 6.15, (III) 4.18, (II) 2.04, (IV) (?) trace, (I) 1.80, leucine 7.29, phenylalanine 1.07, alanine 6.3, proline 1.71, cystine 2.64, tryptophan 1.11, and glucosamine 0.4%. The unallocated portion consists of Cu salts, H_2O -insol. 10.1, H_2O -sol. but MeOH -insol. 19.7, MeOH -sol. 17.7; glycine fraction 3.01, valine + isoleucine fraction 7.18%. J. W. B.

Elementary microanalytical method for determination of halogens and nitrogen and for identification of organic substances. V. STANEK and T. NEMES (Z. anal. Chem., 1933, 95, 244—260).—The method previously described (A., 1932, 529) has been elaborated so as to give accurate quant. results for C, H, N, and halogens. 3—10 mg. of substance are used. In trials with eight pure substances the max. error on any element was $<0.4\%$. F. L. U.

Micro-determination of sulphur in organic compounds. Modification of ter Meulen's method. H. C. GOSWAMI and P. B. SARKAR (J. Indian Chem. Soc., 1933, 10, 611—615).—Ter Meulen's method (A., 1922, ii, 311; 1930, 357) is adapted for use with about 2—10 mg. of substance. H. B.

Determination of the impurities in ethyl ether produced by autoxidation. L. SZÁHLENDER (Magyar Gyóg. Taras. Ert., 1932, 8, 425—435; Chem. Zentr., 1933, i, 1820).—To 100 c.c. of 20% H_2SO_4 and 5 c.c. of starch solution are added 5 g. of coarse-grained KHCO_3 , 0.5 g. of KI, and 1 g. of KHCO_3 , and shortly before the end of the evolution of CO_2 , 5 c.c. of the Et_2O . The mixture is well shaken and after 10 min. the liberated I titrated with 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$. Degree of oxidation (II) = no. of c.c. of 0.01N- $\text{Na}_2\text{S}_2\text{O}_3$ required for 10 c.c. of Et_2O , oxidation no. = (II) \times 1.27—mg. of I. Samples of Et_2O for narcosis gave vals. of 0.0, 0.0, 0.36, and 1.57 for (II), whilst other samples gave vals. >100 . L. S. T.

Differentiation between and determination of formaldehyde and acetaldehyde in mixtures of the two. M. V. IONESCU and H. SLUSANSCHI (Bull. Soc. chim., 1933, [iv], 53, 909—918).— CH_3O , MeCHO , and (if the total aldehyde content is known) mixtures of the two are determined by the time taken for formation of a ppt. with dimethyldihydroresorcinol under defined conditions. R. S. C.

Aminometry. D. VORLÄNDER [with J. FISCHER and F. WILDNER] (Ber., 1933, 66, [B], 1789—1792).—The term "aminometry" is applied to the volumetric determination of amines with acids with as complete

as possible exclusion of aq. and alcoholic solvents and of all conditions under which amines become bases. A solution of HCl in CHCl_3 is employed which is standardised (daily) by titration with $\text{N}(\text{CH}_2\text{Ph})_3$ in presence of dimethylaminoazobenzene (I) as indicator or by agitation with H_2O and titration of the emulsion with 0.05N-Ba(OH) $_2$ or NaOH in presence of phenolphthalein. The indicator solution, 0.05 g. of (I) in 100 c.c. of CHCl_3 , is permanent. Titration is effected directly or with volatile amines by dissolution in excess of acid and back titration with $\text{N}(\text{CH}_2\text{Ph})_3$. $\text{C}_5\text{H}_5\text{N}$ does not give a satisfactory endpoint. With *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ the mean errors are -4.4%, -4.0%, and -2.5%, respectively. Errors < 1% are observed with *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NMe}_2$, *as-m*-xylidine, ψ -cumidine, and α - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$. Dibasic alkaloids react accurately with 2 HCl when the titration is slowly performed. The method is inapplicable to technical aromatic amines on account of their colour. HBr offers no advantage over HCl, whilst $\text{H}_2\text{C}_2\text{O}_4$ and $\text{CCl}_3\cdot\text{CO}_2\text{H}$ do not give sharp colour changes if (I) is used.

H. W.

Analysis of mixtures of amines. A NELUBINA (Anilinokras. Prom., 1933, 3, 355).—Good results for determination of NH_2Ph in its mixtures with NHPhMe and NPhMe_2 are obtained by using a modification of Linke's method (A., 1932, 1149).

R. T.

Determination of *o*-toluidine. S UENO and H. SEKIGUCHI (J. Soc. Chem. Ind. Japan, 1933, 36, 613—615B).—This is effected by the m.p. of the dehydrated hydrochloride (216°), figures for the depression by the *m*- and *p*-isomerides being given. Similar figures are given for the hydrobromide, m.p. 198-7°.

R. S. C.

Azo-compounds in volumetric analysis. E. ROZTOVTSEVA (Anilinokras. Prom., 1933, 3, 308).—Better results are obtained in titration of β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ by standard PhN_2Cl by adding gelatin or gum arabic, which prevents flocculation of the dye formed.

R. T.

Gasometric determination of cysteine and cystine. W. C. HESS (J. Biol. Chem., 1933, 103, 449—453).—Addition of glucose to mixtures of NH_2 -acids free from cysteine (I) gives positive results for (I) by the Baernstein gasometric method (II) (A., 1931, 108) [10 mg. glucose=1.64 mg. of (I)], but not by the Sullivan, Okuda, or Folin-Marenzi methods. $(\cdot\text{CHO})_2$ and AcCHO give negative results, but AcCO_2H [10 mg.=1.0 mg. of (I)] gives a positive reaction, and the presence of carbohydrates in protein matter may thus explain the discrepancies observed between (II) and other methods for determination of (I).

J. W. B.

Reactions of terpenes with antimony trichloride. V. E. LEVINE and E. RICHMAN (Biochem. J., 1933, 27, 2051—2054).—The reaction has been studied both with and without the addition of Ac_2O . Reactivity is greatest in presence of CHO, OH, CO, and general unsaturation. The camphane group is the least and the olefine group the most reactive.

H. G. R.

Shear's aniline-hydrochloric acid reaction for vitamin-D. I. Furan and derivatives. V. E. LEVINE and C. L. SEAMAN. II. Terpenes. V. E.

LEVINE and E. J. SHAUGHNESSY (Biochem. J., 1933, 27, 2047—2048, 2048—2050).—I. The colour reactions given by Shear's reagent (cf. A., 1927, 282) for furan and derivatives are tabulated.

II. Terpenes do not, generally, react in the cold, and Sexton's conclusion (A., 1928, 1161) that the coloration is due to the CO group was not confirmed. The reaction is given by the fat-sol. vitamins, carotene, and irradiated ergosterol.

H. G. R.

Micro-determination of histidine; method for the separation of histidine and tyrosine. K. LANG (Z. physiol. Chem., 1933, 222, 3—5).—The separation of histidine (I) and tyrosine depends on the pptn. of (I) with Hg mixture (Hinsberg and Laszlo, A., 1930, 494). (I) is determined by step-photometer after dissolving the ppt. in 5% aq. NaCN, adding aq. Na_2CO_3 and the diazo-reagent of Kocessler and Hanke (A., 1920, ii, 67).

J. H. B.

Determination of nicotine by the silicotungstate method. L. BENVENIN (Mitt. Lebensm. Hyg., 1933, 22, 217—220; Chem. Zentr., 1933, ii, 1402).—100 c.c. of the solution (approx. 1% nicotine) and 10 c.c. of 50% KOH are distilled in steam, the distillate (375 c.c.) being collected in 25 c.c. of 10% HCl. 12 c.c. of 10% silicotungstic acid solution are added to the receiver, stirred, left for 24 hr., filtered (Gooch crucible), dried for 2 hr. at 120°, and weighed ($\times 0.1012$ =nicotine). $\text{C}_5\text{H}_5\text{N}$, if present, is removed before addition of KOH by distillation in presence of 40 c.c. of glacial AcOH.

A. A. E.

Determination and separation of alkaloids from *Peganum harmala*. N. I. BUNTZELMAN (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 71—72).—The ground seeds are left over-night in contact with 15% AcOH; the extract is filtered through cotton and then through paper moistened with 15% AcOH. Filtrate corresponding with 0.8 g. of seeds is mixed with 20 c.c. of 30% KOH and extracted six times with Et_2O . The residue from Et_2O is dissolved in 5 c.c. of 0.1N- H_2SO_4 and 15—20 c.c. H_2O , the excess of acid being titrated with 0.1N-NaOH (Mered); 1 c.c. of 0.1N- H_2SO_4 =0.0213 g. of alkaloids. Harmine is separated from harmaline by mixing 20 c.c. of a solution of the base (< 0.1%) in 2% AcOH with 0.5 c.c. of 30% NaOH, neutralising (phenolphthalein) with N-NaOH, acidifying with AcOH, neutralising with 0.1N-NaOH, and adding 0.4 c.c. in excess. After 5—10 min. on a H_2O -bath the crystals which appear are collected on a dry, hot filter; the harmine is dissolved in hot 2% AcOH and reprecipd. with 0.1 c.c. excess of 0.1N-NaOH. The combined filtrates are treated with 25 c.c. of 30% NaOH and extracted four times with Et_2O ; on titration, 1 c.c. of 0.1N- H_2SO_4 =0.0214 g. of harmaline. The harmine on the filter is dissolved in hot 2% AcOH and determined in the usual manner; 1 c.c. of 0.1N- H_2SO_4 =0.0212 g.

CH. ABS.

Analysis of emetine hydrochloride. B. A. KLYACHKINA and F. D. ZILBERG (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 103—109).—Pharmacopœial methods for the separation of Na cephaeline are inaccurate. Et_2O extraction of emetine (I) from aq. NH_3 solutions is incomplete, whilst cephaeline (II) is extracted unless the NaOH concn. is high. 1.5

times the calc. quantity of NH_3 should be used. CHCl_3 extracts psychotrine as well as (II). For the separation of (I) from (II) the alkaline mixture is treated with aq. NH_3 after acidifying, followed by repeated Et_2O extraction; the residue after evapor-

ation of the Et_2O consists of (II). To the neutralised aq. solution of (I) hydrochloride and (II) NaOH is added to approx. 50% and the alkaline liquid is shaken 2—3 times with Et_2O , (I) being left on evaporation of the Et_2O .
CH. ABS.

Biochemistry.

Respiratory exchange of the adult white mouse. Effect of external temperature. L. CHEVILLARD (Compt. rend. Soc. Biol., 1933, 113, 181—184).—The smaller is the mouse the greater is the effect of low environmental temp. (I) in increasing the energy exchange. The ratio (II) loss of H_2O by evaporation : O_2 consumption is the same at any fixed temp. for mice of various wt. As (I) is lowered (II) becomes smaller. At temp. below thermic neutrality, (II) in mice is > in larger animals. NUTR. ABS. (m)

Continuous gas analysis. Determination of basal metabolic rate. H. W. BANSI (Deut. med. Woch., 1933, 59, 729—730).—The expired air (I) is measured and its composition determined by comparing its density with that of atm. air (II). The comparison is made in an apparatus which gives a differential measurement of the kinetic energies of (II) and (I) moving at equal velocity in opposite directions. A complete determination requires 6 min. and an accuracy of $\pm 0.02\%$ CO_2 and $\pm 0.07\%$ O_2 is claimed. NUTR. ABS. (m)

Clinical model of the Haden-Hausser hæmoglobinometer. R. L. HADEN (J. Lab. Clin. Med., 1933, 18, 1062—1065). CH. ABS.

Normal hæmoglobin level during the first year of life. H. M. M. MACKAY (Arch. Dis. Child., 1933, 8, 221—225).—Revised figures are given for a proposed standard normal hæmoglobin curve for the first year of life. The average hæmoglobin vals. of breast-fed infants (I) and of those (II) bottle-fed from the second month are compared. (II) show a progressive fall from 80 in the first to second month to 69.1 at 12—13 months; the lowest val. for (I) is 72.8 at 10—11 months. NUTR. ABS. (m)

Hæmoglobin content of chicken blood. A. D. HOLMES, M. G. PIGOTT, and P. A. CAMPBELL (J. Biol. Chem., 1933, 103, 657—664).—The hæmoglobin (I) content of young cocks fed on a high-grade diet increased from 9.6 to 10.1 g. per 100 c.c. of blood in 63 days and that of pullets from 9.3 to 9.7. Restriction of the dietary H_2O failed to influence the (I) vals. H. D.

Refraction of the hæmoglobins of different animals. S. SCHONBERGER (Biochem. Z., 1933, 267, 57—63).—The average n of solutions of horse, dog and ox hæmoglobin (I), expressed as multiples (10^5) of the const. used by Stoddard and Adair (A., 1924, ii, 76), are, respectively, 194, 203, and 209. For solutions of oxyhæmoglobin (II) the val. is the same in H_2O , dil. aq. NaHCO_3 , and dil. aq. NH_3 . Horse (I) gives reproducible results only after 3 crystallisations. CO -(I) shows the same val. as (II). W. McC.

Absorption of light by neutral solutions of oxy- and carbon monoxide-hæmoglobin. V. SEBESTA

and A. HERZOG (Biochem. Z., 1933, 267, 157—166; cf. A., 1933, 622, 1180).—The curve of light absorption of neutral solutions of cryst. oxyhæmoglobin (I), exhibits max. at 575.2 and 541.3 $\text{m}\mu$ and that of solutions of cryst. natural or synthetic CO -hæmoglobin (II) exhibits max. at 566 and 537 $\text{m}\mu$. The curve of (II) exhibits a min. at 551 and that of (I) a false min. at 557.5 $\text{m}\mu$. Horse (II) does not differ in the respect concerned from ox (II). One crystallisation of (II) suffices to give correct results, which are confirmed by determination of other optical consts. W. McC.

Physiological degradation of blood-pigment. R. NOTHHAAS (Z. klin. Med., 1933, 124, 490—496; Chem. Zentr., 1933, ii, 1386).—Hæmoglobin is very sensitive to the action of H_2O_2 when catalase has been removed from the blood. Bingold's observation that blood treated with Na silicate and heated requires less H_2O_2 for decolorisation than normally is presumably due to removal of catalase. A. A. E.

Prosthetic group of blood-pigments. H. FISCHER and K. ZEILE (Z. physiol. Chem., 1933, 222, 151—154).—The hæmin prep. of Herzog (A., 1933, 1180) was impure owing to drying at 100° and retention of NH_3 ; hence his conclusions are not justified. J. H. B.

Carbon content of prosthetic group of blood-pigment. Methyl and ethyl esters of hæmoprostheticin. A. HERZOG (Biochem. Z., 1933, 267, 48—56).—The composition of the mono- and dimethyl and -ethyl esters of hæmoprostheticin (I) prepared by Küster's method (A., 1913, i, 110, 1005) and of the substance $\text{C}_{34}\text{H}_{33}\text{N}_4\text{O}_4\text{Fe}$ shows that (I) has 33 C. If removal of globin (II) is incomplete substances similar to (I), but containing C atoms from (II) in addition, are obtained. W. McC.

"Normal" carbon monoxide content of the blood. A. O. GETTLER and M. R. MATTICE (J. Amer. Med. Assoc., 1933, 100, 92—97).—Average vals. for city (min. exposure) and rural residents were 0.27 and 0.24 vol.-%, respectively. Street-cleaners gave 0.69 and taxicab drivers 1.47—4.33 vol.-%. Tobacco-smoking increases blood- CO . CH. ABS.

Significance of copper and iron in blood restoration. C. A. ELVEHJEM (Amer. J. Pub. Health, 1933, 23, 1285—1289).—A discussion.

Hæmoglobin production. IV. Evaluation of therapeutic agents in anæmia due to milk diets, based on study of blood and bone marrow of rats from birth to maturity. T. FITZ-HUGH, jun., G. M. ROBSON, and D. L. DRABKIN (J. Biol. Chem., 1933, 103, 617—628).—The blood hæmoglobin (I), erythrocytes (II), reticulocytes (III), and the degree of hyperplasia (IV) of the marrow in the long bones of

rats were used as criteria of the anaemia produced on a milk diet. At weaning the rats studied were anaemic. On the milk diet (I) fell more rapidly and reached a relatively lower level than (II). (III) increased from 17 to 35% of (II) in 20 days; at 70 days the count was 15%, and at 130 days 40%. A small increase in marrow-(IV) was observed. Fe alone fed to anaemic rats produced a small increase in (I) and a greater increase in (II); the (III)-crisis reached its peak after 20 days, but never subsided to normal levels corresponding with a continued (IV) of the marrow. With Fe-Cu therapy recovery of (I) and (II) was almost complete; the peak of the (III)-crisis occurred on the eleventh day, followed by a normal subsidence of (III) and a return to the normal cellular state of the marrow. Fe + Na glutamate gave generally more complete returns to normal states, the (III)-crisis reaching its peak in 3—8 days. H. D.

Blood grouping by means of preserved muscle. W. C. BOYD and L. G. BOYD (Science, 1933, 78, 578).—Dried human muscle and even muscle preserved at necropsy and several years old contains agglutinogens and can be used to determine the blood groups of individuals. L. S. T.

Influence of fasting on the concentration of blood-lipins in the rat. B. SURE, M. C. KIK, and A. E. CHURCH (J. Biol. Chem., 1933, 103, 417—424).—There is a decrease in the fatty acids and lecithin, but no change in the cholesterol. H. G. R.

Micro-determination of fatty acid in blood. M. E. SMITH and M. C. KIK (J. Biol. Chem., 1933, 103, 391—398).—The methods of Bloor, Pelkan, and Allen and of Stoddard and Drury (A., 1930, 103) have been combined and modified for use with 0.5 ml. of blood. H. G. R.

Micro-determination of oxalic acid in blood. S. IZUMI (Japan. J. Med. Sci., 1933, 2, 195—204).—Blood or serum (4.0 c.c.) is deproteinised with $\text{CCl}_3\cdot\text{CO}_2\text{H}$, brought to p_H 2.5—3.0, and $\text{H}_2\text{C}_2\text{O}_4$ pptd. by 0.25% aq. CeCl_3 . The ppt. (I) is washed, dissolved in 5 c.c. of $N\text{-H}_2\text{SO}_4$, and titrated at 70—80° with 0.01N- KMnO_4 . Alternatively (I) is dissolved in 1 c.c. of $N\text{-H}_2\text{SO}_4$, and 1 c.c. of 30% aq. K_2CO_3 and H_2O_2 are added, giving a brown solution for colorimetric determination. F. O. H.

Distribution of sugar and rate of glycolysis in blood of some mammals. M. SOMOGYI (J. Biol. Chem., 1933, 103, 665—670).—There is no correlation between the rates of glycolysis (I) and the distribution ratios of sugar in the serum and erythrocytes of various mammals. (I) conform to the Engelhardt-Liubimova (A., 1931, 108) series of phosphate cleavage. H. D.

Diurnal variations in blood-sugar level of lactating cow. W. M. ALLCROFT (Biochem. J., 1933, 27, 1820—1823).—A rhythmic variation in the blood-sugar of lactating cows, absent in dry cows, is observed. H. D.

Comparison of sugar-tolerance curves obtained on venous and capillary blood. J. W. CAVETT and S. R. SELJESKOG (J. Lab. Clin. Med., 1933, 18, 1103—1107).—Vals. for finger-tip blood are slightly > those for venous blood only during hyperglycaemia. CH. ABS.

Determination of blood-sugar. C. BIRT (J. Roy. Army Med. Corps, 1933, 61, 401—411).—A simple technique for the Hagedorn-Jensen method is described. R. K. C.

Diazo-reaction, especially of blood. I, II. Serum and urine. III. Red blood-corpuscles. G. NAKAYAMA (Japan. J. Med. Sci., 1933, 2, 215—227, 229—235, 237—244).—I. Human and animal blood gives Leimdorfer's modification of the diazo-reaction (I) (A., 1924, i, 1126), which is due to the erythrocytes and not to the plasma. Pathological urine frequently yields a marked (I), whilst the corresponding blood response is normal or even negative. The blood-(I) is not influenced by fever or starvation, but acute inflammation causes a decrease. No relation exists between (I) and the blood content of bilirubin, urobilin, or residual N. The reactant of (I) is stable to acids, readily destroyed by alkalis, extracted by dil. AcOH or $\text{CCl}_3\cdot\text{CO}_2\text{H}$, and pptd. by phosphotungstic acid. Extracts of adrenal glands, spleen, and liver frequently give a positive (I).

II. In uraemic blood (II) a urochromogen present is probably the cause of the characteristic response of (II) to (I) (cf. A., 1925, i, 726). Indican is also frequently present in (II), whilst a further substance (probably histidine) takes part in the response of (II) and of the urine of consumptives to (I).

III. The intensity of (I) of the corpuscles of various animals is approx. proportional to the content of residual N and, more particularly, to that of ergothioneine. Substances such as tryptophan, glyoxaline derivatives, and cyclic compounds may be involved. F. O. H.

Colloid-osmotic (oncotic) pressure. XXIX. Serum-albumin and -globulin. E. KYLIN (Arch. exp. Path. Pharm., 1933, 173, 549—552).—The colloid-osmotic pressures (A., 1932, 540) of 1% aq. serum-albumin and -globulin (horse, man) are 55—75 and 17—30 mm. of H_2O , respectively. F. O. H.

Determination of bases of serum and whole blood. P. M. HALD (J. Biol. Chem., 1933, 103, 471—494).—Serum is ashed in a muffle furnace with H_2SO_4 and $\text{Fe}_2(\text{SO}_4)_3$; the SO_4^{--} formed is pptd. with benzidine in the Fe-free filtrate, and determined by titration with NaOH or gravimetrically. No appreciable loss of Mg occurs after heating at 750° for 9 hr. The sparingly sol. residue from the ashing of whole blood consists of FePO_4 . In the determination of Ca, Mg, K, and Na in the dissolved ash Ca is pptd. as CaC_2O_4 , and determined with KMnO_4 ; Mg is pptd. as MgNH_4PO_4 , and determined colorimetrically by the Benedict-Theis method (A., 1924, ii, 700). The P is then removed by $\text{Fe}_2(\text{SO}_4)_3$ and aq. NH_3 . The supernatant fluid is ashed and the SO_4^{--} of one portion of the solution of the ash pptd. with benzidine and in the other the Na and K platinichlorides are pptd. The Na salt is dissolved in 80% EtOH and determined by the Barber-Kolthoff method (A., 1928, 859) and the K salt is determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$. In several cases the total acid of normal human serum exceeded the total base. H. D.

Serum-calcium in normal boys. M. MOLITCH, S. WEINSTEIN, and R. F. COUSINS (Amer. J. Med.

Sci., 1933, 186, 378—382).—From 8 to 20 years the serum-Ca ranged from 7.6 to 12.5 mg. per 100 c.c., irrespective of age, nationality, or race. CH. ABS.

Calcium content of ultrafiltrates of plasma and the influence of changes in hydrogen- and hydrogen carbonate-ion concentration on it. L. M. DILLMAN and M. B. VISSCHER (J. Biol. Chem., 1934, 103, 791—799).—The Ca in the plasma of dog's blood becomes more completely dialysable as acidity increases, when the acidity is produced by increase in CO_2 tension. At p_{H} 7.0, 59%, and at p_{H} 7.7, 45%, is dialysable. W. O. K.

Diffusibility of plasma-calcium following parathormone administration. Comparison of the calcium, phosphate, and protein concentrations of serum and oedema fluids. D. R. GILLIGAN, M. C. VOLK, and M. D. ALTSCHULE (J. Biol. Chem., 1934, 103, 745—756).—In many pathological conditions, administration of parathormone produces a rise in the Ca and a fall in the inorg. P concn. of oedema and ascitic fluid closely parallel to that occurring in the serum. The change in P precedes that in Ca. The Ca and P concns. of the cerebrospinal fluid (I) remains approx. const. and thus (I) is not a simple dialysate of serum. W. O. K.

Relation of filterable to non-filterable calcium in chicken blood. J. T. CORRELL and J. S. HUGHES (J. Biol. Chem., 1933, 103, 511—514).—Whilst the serum-Ca (I) of laying hens is 25.1 as against 12.0 and 11.7 mg. per 100 c.c. for non-laying hens and cocks, respectively, their ultrafilterable Ca is the same (approx. 6.4 mg. per 100 c.c.), so that the ratio of filterable to total (I) decreases as (I) rises. H. D.

State of calcium and phosphate of the blood. D. M. GREENBERG, W. E. CORN, and E. V. TUFTS (Proc. Soc. Exp. Biol. Med., 1933, 30, 1005—1007).—The loss of Ca during ultrafiltration (I) reported by Smith and Sternberger (A., 1932, 635) is negligible except when the serum-Ca is considerably > normal. There is then adsorption of PO_4''' also, so that it becomes partly non-diffusible. Possibly a colloidal compound of Ca, PO_4''' , and (possibly) CO_3 is formed. Adsorption of ions does not occur, since there is no loss of Mg during (I). NUTR. ABS. (m)

Forms of calcium and inorganic phosphorus in human and animal sera. III. Comparison of physiological and experimental hypercalcaemia. H. R. BENJAMIN and A. F. HESS (J. Biol. Chem., 1933, 103, 629—641).—By methods previously described (A., 1933, 521) the serum-Ca is resolved into four components. In hypercalcaemia (I) in laying hens the two filterable fractions remain const., whilst each of the non-filterable fractions (II) rises, together with the serum-proteins. There is no correlation between the serum-cholesterol and the adsorbable (II) fraction. In (I) produced by parathyroid extracts and vitamin-D in dogs, the 4 Ca fractions tend to maintain their normal proportions, except for a small increase in (II); the total P is raised, its filterability is diminished, and up to 2.5 mg. per 100 c.c. of the adsorbable P becomes non-filterable. H. D.

Normal range of calcium and inorganic phosphorus in the serum of healthy non-preg-

nant women. J. W. MULL and A. H. BILL (J. Lab. Clin. Med., 1933, 18, 1034—1041).—Serum-Ca in women is normally 10—11.5 mg. per 100 c.c., and is unaffected by age or diet if the Ca intake is adequate. Serum-inorg. P is 3.2—4.4 mg. at < 30 years and 2.6—4.2 mg. at > 30 years. There is no seasonal variation in Ca or inorg. P. CH. ABS.

Normal serum-calcium and -magnesium of the rat; their relation to sex and age. E. WATCHORN (Biochem. J., 1933, 27, 1875—1878).—The serum-Ca (I) of females is slightly < (I) of males, and of adults (11.77 mg./100 c.c.) < (I) of young (12.16 mg./100 c.c.). The serum-Mg of young males (5.36 mg./100 c.c.) is > that of adult males and all females (4.4 mg./100 c.c.). A. L.

Magnesium in serum and milk. H. R. BENJAMIN, A. F. HESS, and J. GROSS (J. Biol. Chem., 1933, 103, 383—390).—Mg is adsorbable from sera and ultrafiltrates on BaSO_4 and may be separated into (1) a filterable, adsorbable form (I), (2) a filterable, non-adsorbable form containing Mg^{++} , (3) a non-filterable form, possibly bound to protein. In hypercalcaemia, (I) is reduced to a negligible amount. The concn. of (I) varies directly with P and inversely with Ca content, suggesting that it is adsorbed in combination with P. The presence of (I) in milk could not be demonstrated. H. G. R.

Biochemistry of copper. I. Colorimetric micro-determination. II. Determination in blood. U. SARATA (Japan. J. Med. Sci., 1933, 2, 247—260, 261—275).—I. The red colour given by Cu salts with "cryogenine" (*m*-benzamidosemicarbazide) is used for the determination of 0.0005—0.02 mg. of Cu with an accuracy of $\pm 1.5\%$. The reaction is sp.

II. Blood (1 c.c.) is digested with $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$, the digest is neutralised (using MgCl_2 as indicator) and re-acidified with H_2SO_4 , Cu is pptd. as CuS , the ppt. is dissolved in dil. HNO_3 , and Cu is determined in the filtered solution. In addition to data for the blood-Cu of various fishes, the following vals. (in mg. per 100 c.c.) were obtained: man, 0.073—0.081; ox, 0.125—0.171; horse, 0.103—0.133; rabbit, 0.070—0.104; pig, 0.062—0.098. F. O. H.

Determination of bromine in blood. E. D. YATES (Biochem. J., 1933, 27, 1763—1769).—A method for the determination of Br in amounts of $5\text{--}1000 \times 10^{-6}$ g. accurate to within 2×10^{-6} g. is described. H. G. R.

Fibrinogen and a plasma-globulin producing clotting. A. SCHMITZ (Z. physiol. Chem., 1933, 222, 155—160).—Hammarsten's fibrinogen (I) differs from Mellanby's (II) in composition. (I) is not homogeneous, but cannot be fractionated by salting out with $(\text{NH}_4)_2\text{SO}_4$, which separates (II) into true fibrinogen (III) and a protein which produces clotting and is apparently identical with Mellanby's prothrombasc. The flocculation max. is at p_{H} 5.3—5.6. The clotting rate of (III) is independent of its concn. J. H. B.

Hæmolysis by Australian snake venoms. I. Comparative hæmolytic power. II. Peculiarities in behaviour. C. H. KELLAWAY and F. E. WILLIAMS (Austral. J. Exp. Biol. Med., 1933, 11,

74—80, 81—94).—I. The venoms are of two types: those which hæmolyse directly without serum activation (black, copperhead), and those which have a negligible action on washed cells (death adder, tiger).

II. Hæmolysis depends on a lecithinase acting at the limiting surface of the corpuscle and is subject to the same ionic effects as cobra venom. Complement effect is insignificant. Inhibition by serum is frequent. Venoms are adsorbed on red blood-corpuscles at 0° and cause hæmolysis when warmed. Blood-lipins alone activate the process, but the natural protein-lipin complex causes inhibition.

CH. ABS.

Relationship between structure of antigen and specificity of anti-body. VIII. Changes in the specificity of cholesterol on its conversion into a complex antigen. E. BERGER (Biochem. Z., 1933, 267, 143—150; cf. A., 1933, 1066).—Anti-sera (I) obtained by coupling diazotised cholesteryl amino-benzoate (II) with pig-sera do not react with cholesterol (III) nor with (III) coupled with horse- or hen-sera. (I) have reduced or no immunological relationship with the native protein with which the product used is condensed for immunisation (IV). Structural specificity is exhibited by (I) solely towards products obtained from the interaction of (II) with the serum-protein of the complex antigen used for (IV). (I) to (III) obtained by (IV) with mixtures of (III) with serum do not react with (II) coupled with sera. The changes in serological specificity which (III) undergoes on conversion into (II) followed by coupling with protein (sera) (V) chiefly concern (III), but also affect (V).

W. McC.

Chemistry of the antigen of brain. II. Purification. H. RUDY (Biochem. Z., 1933, 267, 77—88; cf. A., 1932, 765).—The antigen (I), further purified by a method described, contains N and combined sugar, but no P, and is stable towards alkali. The purification is accompanied by increasing solubility in H₂O and acquisition of the ability to dialyse. Solutions of (I) in EtOH are acid. Crude (I), which is probably adsorbed on lipins, is sol. in lipins, scarcely sol. in H₂O, and incapable of dialysing. (I) is not a sterol or cerebroside nor is it identical with creatine.

W. McC.

Antigen nephelometer solidified with pectin. H. R. BAKER and G. L. BAKER (J. Amer. Vet. Med. Assoc., 1933, 36, 472—473).—For the agglutination test for pullorum disease antigen turbidity standards can be preserved in pectin gel.

CH. ABS.

Oxygen affinity of muscle-hæmoglobin. R. HILL (Nature, 1933, 132, 897—898).—Dissociation curves showing that muscle-hæmoglobin (I) has a higher affinity for O₂ than blood-hæmoglobin have been obtained by a spectroscopic method. The distinctive properties of (I) are due to its protein, globin. The presence of (I) in muscle cells will be advantageous in O transport. (I) can be the intermediate carrier of mol. O₂ from blood to the oxidase-cytochrome system in the cells.

L. S. T.

Chemical composition of living organisms and periodic system. A. VINOGRADOV (Compt. rend., 1933, 197, 1673—1675).—The % of each element in animal and vegetable bodies, based on analyses of some 2000 and 5000 species, respectively, is plotted

against the at. no. in two curves, for odd- and even-numbered elements, respectively, the curve for the latter being above that for the former, and both steadily declining as at. no. increases; above elements nos. 1 and 2 there is a max. at every sixth element in both curves.

C. A. S.

Determination of dry matter in the retina.

R. W. J. MÜLLER (Biochem. Z., 1933, 267, 43—44).—The retina (I) in the ox, pig, sheep, and guinea-pig contains about 12% of dry matter; in the dog and rabbit it contains about 16%. In all these animals the average thickness of (I) is 0.22—0.31 mm.

W. McC.

Brain-creatine. M. MATSUMOTO (Japan. J. Med. Sci., 1933, 2, 205—213).—Pig's brain is hydrolysed, the hydrolysate pptd. by CCl₃·CO₂H, the filtrate neutralised and treated with Al(OH)₃, and the final filtrate extracted with Et₂O. The Et₂O extract contains some creatinine (I) (which is extracted with H₂O and combined with the main aq. layer) and a substance (also present in egg-lecithin etc.) which responds to the Jaffé reaction. Results (0.08—0.09% as creatine) are < previous vals.

F. O. H.

Cetacea. XLIV. Isoelectric flocculation of porphyrins. Y. OKAHARA (Japan. J. Med. Sci., 1933, 2, 189—194).—Hæmato- and uro-porphyrin are isoelectrically flocculated in PO₄''' or OAc' buffer at p_H slightly > 5; a somewhat less marked region occurs at p_H 3.9—4.2 and 2.2—2.9, respectively. The porphyrin from whale's intestine (A., 1927, 85) flocculates between p_H 5.66 and 6.64 and again at p_H 7.66; a secondary region appears at p_H 3.2—3.8. The coagulation is a function of the salts present as well as of [H⁺].

F. O. H.

Reactivity of the sulphur linking in wool.

J. B. SPEAKMAN (Nature, 1933, 132, 930).—Supercontraction is associated with the breakdown of ·S·S· linkings in wool, so that when strained fibres are exposed to steam the first reaction which occurs is $R·S·S·R + H_2O \rightleftharpoons R·SH + R·S·OH$. The hypothesis is supported by the fact that wool heated with H₂O even at 55° in presence of Hg vapour is rapidly contaminated by HgS. The rebuilding of new linkings probably takes place according to the reaction $R·S·OH + R·NH_2 = R·S·NH·R + H_2O$, for when fibres are treated with saturated Ag₂SO₄ to convert ·S·S· into R·SO₃H, their power to assume a permanent set is reduced.

L. S. T.

Body-fats of the pig. III. Influence of body temperature on composition of depôt-fats. H. K. DEAN and T. P. HILDITCH (Biochem. J., 1933, 27, 1950—1956).—The back fat of a sow fed on a diet of maize meal, thirds, and whey was divided into five layers and the constituent fatty acids were determined. The acids of the three layers under the "streak" were identical, whilst the outermost layer contained less palmitic and stearic and more oleic acids.

H. D.

Iodine-containing substance of the thyroid gland. III. Ultra-filtration and dialysis of thyroid press-juice. G. LUNDE, K. WÜLFERT, and P. LALAND (Endokrinol., 1933, 13, 29—35; Chem. Zentr., 1933, ii, 1697—1698).—Most of the I-containing substance does not pass through the filter. Pptn. with

COMe, affords a substance (I 0.225%) which contains practically all of the I. Electrodialysis afforded ppts. (I 0.329%) containing 77% of the total I. Biological tests on the mouse were performed. A. A. E.

Iodine content of foetal, new-born, and infants' thyroid glands. Z. LELKES (Endokrinol., 1933, 13, 35—40; Chem. Zentr., 1933, ii, 1697).—I can be detected from the fourth month onwards; the I content is greatest in winter. The abs. I content increases, and the relative I content decreases, until birth occurs. Afterwards the wt. of the thyroid diminishes; hence its relative I content suddenly increases.

A. A. E.

Functional significance of the structural elements of the thyroid gland. W. GRAB (Klin. Woch., 1933, 12, 1102—1103; Chem. Zentr., 1933, ii, 1538).—The colloidal fraction (60—70%) of the sheep's and cat's thyroid contains 0.065—0.074% I (on undried colloid); 50% is thyroxine-I and the remainder probably di-iodotyrosine. The epithelial tissue contains 0.0072—0.0094% I, of which 33% is thyroxine-I. 95% of the I content of medicinal dried thyroid preps. consists of colloidal I compounds. Stimulation of the thyroid gland, e.g., with thyrotropic hormone, diminishes the quantity of colloid and its I content (to 0.012%), but the ratio total: thyroxine-I is unaltered. Epithelial total I and I distribution are practically unchanged.

A. A. E.

Block-staining of nervous tissue with silver. IV. **Embryos.** H. A. DAVENPORT, W. F. WINDLE, and R. H. BEECH (Stain Tech., 1934, 9, 5—10).—Fixation of embryos in a solution containing 4% CH_2O and 0.5% $\text{CCl}_3\text{CO}_2\text{H}$ improved the staining of neural elements by Bielschowsky's method. Ranson's $\text{C}_5\text{H}_5\text{N}$ -Ag method was modified slightly for staining neurofibrillar elements.

H. W. D.

Marchi's staining method. R. L. SWANK and H. A. DAVENPORT (Stain Tech., 1934, 9, 11—19).—The actions of the various reagents used by Marchi for staining degenerating myelin have been studied.

H. W. D.

Staining of neuroglia. F. PROESCHER (Stain Tech., 1934, 9, 33—38).—The exposure of the section, after staining with Victoria-blue (Heidelberger's method), to sunlight induces an oxidative process. Artificial ultra-violet rays, or chemical oxidising agents, produce the same effect. Victoria-blue may be replaced by Me-, Et-, or crystal-violet.

H. W. D.

Cerebrospinal fluid. I. Chemical and spectrographic detection of lead. II. Occurrence of lead in cerebrospinal fluid. I. M. RABINOVITCH, A. DINGWALL, and F. H. MACKAY (J. Biol. Chem., 1934, 103, 707—723, 725—732).—I. The Behrens-Kley triple nitrite reaction ("Mikrochemische Analyse," 1915), detects Pb reliably in cerebrospinal fluid (I), the sensitivity being 10^{-4} mg. The results were controlled by spectrographic methods of which the sensitivity is 1 in 10^9 , with 6 c.c. of fluid.

II. Pb was found in the (I) in every case definitely diagnosed as Pb poisoning, but with one exception, > traces ($1:5 \times 10^4$) were present where there had been no exposure to Pb. The production of an acidosis by administration of NH_4Cl increased the rate of

excretion of Pb in the urine as the result of mobilisation of stored Pb. Acidosis occasionally also caused small quantities of Pb to appear in the (I) where previously absent.

W. O. K.

Natural pigments of raw silk of the domestic cocoon. V. Detection of violaxanthin in the yellow cocoon. VI. Decolorisation of the yellow cocoon. M. OKU (J. Agric. Chem. Soc. Japan, 1933, 9, 580—586, 587—592).—V. Violaxanthin, m.p. 185° , and a red resin were obtained from the mother-liquor after separation of lutein.

VI. Decolorisation in air is due to the oxidation of xanthophyll.

CH. ABS.

Influence of chlorides and phosphates of saliva on its amylolytic activity. W. L. ADAMS and V. C. MYERS (J. Dental Res., 1933, 13, 311—322).—The amylolytic index of human saliva is 25—50; it is unusually const. in a normal person and is closely related to salivary Cl and total P. It may decrease by 50% in severe "colds."

CH. ABS.

Sugar content of semen. K. YAMADA (Japan. J. Med. Sci., 1933, 2, 245).—Human semen contains sugar (probably fructose), three samples yielding 62.5, 83, and 140 mg. per 100 c.c., respectively. The prostatic fluid is free from reducing substances.

F. O. H.

Gastric-juice colloids and their determination by the gold number. F. DELHOUGNE (Arch. exp. Path. Pharm., 1933, 174, 92—95).—The Zsigmondy Au no. of normal gastric juice (I) (induced by histamine) varies between 0.8 and 2.0 mg., the no. being approx. proportional to the acidity (II). This is true for (I) of subnormal (II) due to disease. The correlation of the colloidal secretion of the gastric mucous membrane and (II) is discussed.

F. O. H.

Gastric secretion during pharmacological tests. C. DIENST (Klin. Woch., 1933, 12, 741—744).—Changes in the acidity of gastric juice (I) are explained on the assumption that they depend on the ratio of a const. acid (II) and a const. alkaline (III) secretion. (II) is determined as total Cl', (III) is indicated by the N content of (I). Histamine stimulates (II), pilocarpine (III). When these are given together the Cl' and the N content of (I) increase and more (I) can be recovered than after each alone. Ingestion of HCl produces an increase in the N content, whilst NaHCO_3 produces an increase of Cl' in (I).

NUTR. ABS. (m)

Osmotic relations between blood and body-fluids. IV. **Pancreatic juice, bile, and lymph.** A. GILMAN and G. R. COWGILL (Amer. J. Physiol., 1933, 104, 466—469).—The blood, hepatic bile, lymph (from the thoracic duct), and pancreatic juice collected simultaneously from dogs under amytal anaesthesia are approx. isotonic (Hill's method) and remain so even following extreme variations in the osmotic pressure of the blood brought about by injecting NaCl or H_2O .

NUTR. ABS. (m)

Relation between sugar content, chlorine content, and serum refraction of milk. T. SUNDBERG (Svensk Kem. Tidskr., 1933, 45, 253—275; cf. B., 1932, 45).—Tables are given for calculating the "osmotic factor" of milk from its lactose (I) and Cl

content. Gravimetric and polarimetric methods of determining (I) are compared. The (I) and Cl contents and "osmotic factors" are given for 100 samples of milk, and compared with the n of the serum. The n and Cl content can be used as a preliminary test for dilution with H_2O . R. P. B.

Composition of the "isotonic diluent" in samples of milk low in solids-not-fat. W. L. DAVIES (J. Dairy Res., 1933, 4, 273—278).—In milks having low solids-not-fat contents, the caseinogen-N bears a lower proportion to the total N than in normal milks (76%). Such milk may be represented as containing two fractions: (a) true milk, (b) an "isotonic diluent" (I). From analytical data obtained, the proportion and distribution of N in the diluent are calc. The composition of (I) resembles that of a modified blood-serum or lymph-serum or a caseinogen- and lactose-free lacteal secretion. The Cl content conforms more nearly to that of a lymph-serum.

A. G. P.

Cow's milk poor in non-fatty solids. G. L. PESKETT and S. J. FOLLEY (J. Dairy Res., 1933, 4, 279—284).—The presence of blood serum-albumin (I) in normal milks is demonstrated. In many cases milks poor in solids-not-fat (II) have an increased proportion of (I). Deficiency of (II) in milks may be due to dilution of normal secretion by a fluid resembling oedema fluid (cf. preceding abstract).

A. G. P.

Phospholipins in milk. I. Distribution among some milk products. G. E. HOLM, P. A. WRIGHT, and E. F. DEYSHER. II. Phospholipins in skim milks and their effect on the accuracy of the various fat tests. P. A. WRIGHT and G. E. HOLM. III. Phospholipins in buttermilk and their effect on the accuracy of various fat tests. P. A. WRIGHT, E. F. DEYSHER, and G. E. HOLM (J. Dairy Sci., 1933, 16, 445—454, 455—459, 460—466).—I. Up to 45% of the total phospholipin (I) content of creams passed into the butter. The amounts concerned were sufficient to be of significant val. in fat determinations. Acidity is probably not an important factor influencing the distribution of (I) in milk products.

II. The (I) of skim milk averaged 0.13%. The Rose-Gottlieb method (II) removes \approx 20% of the natural (I). In samples containing 0.10% of fat the error due to extraction of (I) is approx. 15%. The Babcock method and its various modifications remove negligible amounts of (I), but give low vals. for skim milks (cf. Thurston and Peterson, B., 1928, 942).

III. The (I) content of sweet cream buttermilks averaged 0.27%. Only insignificant amounts of this are removed by the various Babcock methods. Results of (II) were 6—17% high owing to the inclusion of (I) in the extract. A. G. P.

Blood-lipins and milk-fat production. J. MARCQ and A. DEVUYST (Bull. Inst. Agron. Gembloux, 1933, 2, 101—126).—The coeff. of correlation between the total lipins and the lecithin of the blood (0.684 ± 0.062) is the only significant factor to serve as an index of productive capacity (measured in terms of butter-fat), although the coeffs. of correlation between mean total blood-lipins and milk-fat production per

lactation (0.1904 ± 0.161) and mean blood-lecithin and total butter-fat production (0.144 ± 0.195) are slightly positive.

NUTR. ABS. (m)

Effect of organotherapy on the production of fat in the milk of cows. G. MONNOT (Compt. rend., 1934, 198, 119—120).—Daily oral administration of a mixture of bovine serum and organotherapeutic products to cows during their lactation period causes a 25—40% increase (especially after the first month) in the milk-fat and increase in body-wt. of the animal, without otherwise affecting the quality of the milk.

J. W. B.

Nutritive value of proteins for milk production. I. Comparison of proteins of beans, linseed, and meat meal. S. MORRIS and N. C. WRIGHT (J. Dairy Res., 1933, 4, 177—196).—Replacement of bean meal (I) by equiv. proportions of meat meal (II) or linseed meal (III) in a ration of minimal protein content resulted after 4—18 days in a reduced milk yield. In the intervening period body-N was utilised in maintaining milk production. Wastage of N (urinary N) with the (I) ration was low, with (II) high, and with (III) intermediate.

A. G. P.

Loss of minerals through the skin of infants. W. W. SWANSON and L. V. IOB (Amer. J. Dis. Children, 1933, 45, 1036—1039).—The skin secretions of infants aged 2—28 weeks contain: Cl 0.22—1.48, Na 0.17—0.94, K 0.24—1.86, Ca 0.07—0.23, and P 0.01—0.26 g. for six-day periods. Loss of K through the skin reaches 38% of the calc. retention.

NUTR. ABS. (m)

Constituents of the sweat, urine, and blood; gastric acidity and other manifestations resulting from sweating. X. Basic metals. G. A. TALBERT, C. HAUGEN, R. CARPENTER, and J. E. BRYANT (Amer. J. Physiol., 1933, 104, 441—442).—100 c.c. of sweat contain: K 40—50 (occasionally 28.3—145.4); Ca 0—11.8 (average 5); Mg 0—4.5 mg.

NUTR. ABS. (m)

Urinary acidity. II. S. MORGULIS (J. Biol. Chem., 1934, 103, 757—761).—Analysis of the P of urine by the $CaSO_4$ method of Kugelmass (A., 1924, ii, 275) gives results agreeing with those calc. from the p_H , provided the latter is < 6.0 , whilst when H_2PO_4' and HPO_4'' are added to urine, analytical results are satisfactory. The hypothesis of Berg that phosphates, especially H_2PO_4' , undergo substantial changes in urine and other body-fluids thus receives no support.

W. O. K.

[Determination of urinary ammonia.] Action of ammonia on phenols. B. HARROW, I. M. CHAMBLIN, and H. WAGREICH (Science, 1933, 78, 514).—Orr's work on the colorimetric determination of NH_3 in urine by $PhOH$ and $NaOCl$ (A., 1925, i, 184) has been confirmed. The method gives results in good agreement with those obtained by Folin's acration method.

L. S. T.

Colorimetric determination of urinary cholesterol. I. A. MIRSKY (J. Lab. Clin. Med., 1933, 18, 1068—1071).—Cholesterol (I) is pptd. with protein by H_2WO_4 and extracted with $EtOH-Et_2O$ (3:1). Total (I) is determined colorimetrically in one portion, and free and combined (I) in another, free (I) being fixed as the digitonide.

CH. ABS.

Determination of bilirubin in urine. K. FELLING and K. MENKES (Wien. klin. Woch., 1933, 46, 133—134; Chem. Zentr., 1933, i, 1819).—A modification of Franke's method (A., 1932, 1158). 5 c.c. of non-icteric urine are coloured a definite blue by 1—2 drops of 2% methylene-blue (I). Icteric urine becomes green and is coloured blue only by the addition of further amounts of (I). The use of a comparison fluid, prepared from alcoholic (I) and $K_2Cr_2O_7$, is recommended. L. S. T.

Preparation of homogentisic acid from urine. G. MEDES (Proc. Soc. Exp. Biol. Med., 1933, 30, 751).—5—6 g. $Pb(OAc)_2$ are added to each 100 c.c. of boiling urine, which is then filtered and the p_H of the hot filtrate adjusted to about 5.6 with aq. NH_3 . On cooling, Pb homogentisate separates. Recrystallisation from hot H_2O is conducted similarly. The Pb salt is decomposed with H_2S ; the solution is conc. under reduced H_2 pressure and saturated with SO_2 . The acid rapidly separates on cooling.

CH. ABS.

Dietary acidosis in dairy cattle. A. E. PERKINS and C. F. MONROE (J. Dairy Sci., 1933, 16, 413—426).—The feeding to cattle of lactic acid or AcOH in amounts > those likely to be eaten in silage (1.5—1.75 lb. daily) produced no urinary symptoms of acidosis (I), but marked acidosis followed the ingestion of 2—3 oz. daily of HCl , H_2SO_4 , or H_3PO_4 . Silage fed alone produced no (I), and prevented or delayed acidic effects when fed in conjunction with rations producing these. All leguminous diet had a definitely alkaline action on urine. Timothy hay resembled silage in this respect. Exclusive grain rations reduced the HCO_3^- and increased the NH_3 of the urine. The protein of the grain had no influence on the acidic symptoms thus produced. Alkaline mineral supplements did not correct (I) satisfactorily. A. G. P.

CH. ABS.

Blood-sugar in allergic persons. J. H. BLACK (Texas State J. Med., 1933, 29, 257—260).—Blood-sugar and -P are frequently low in allergy.

CH. ABS.

Digestion of protein in gastric anacidity. D. C. HINES (Amer. Med. J. Sci., 1933, 185, 684—695).—In patients with gastric anacidity without response to histamine and without cancer or anaemia there is no increase in faecal N either on high-N (I) or low-N diet. On (I) positive N balance is present. When ground beef is given, increase in the urea-N of the urine occurs in the normal time.

NUTR. ABS. (m)

Composition of the globin of normal and anæmic persons. K. LANG (Arch. exp. Path. Pharm., 1933, 174, 63—68).—Whilst the contents of the main constituent NH_2 -acids [tyrosine (I), tryptophan, cystine, arginine, and histidine (II)] of human globin (A., 1930, 948) differ in normal individuals [the most const. being (I), 2.75—3.38%, and (II), 7.58—8.33%], variations occur in anaemia (III) which are characteristic of (III) and also to some extent of the type of (III).

F O H

Blood regeneration in dogs as influenced by liver and iron preparations. A. E. MEYER (J. Lab. Clin. Med., 1933, 18, 1127—1135).—Colloidal Fe is an important factor in regeneration of hæmoglobin

(I) in experimental hæmorrhagic anaemia in dogs. Purified liver extract stimulates erythropoiesis, but does not affect the formation of (I). CH. ABS.

Blood of normal human subjects during foetal liver feeding. O. S. WALTERS and P. H. WOODWARD (Amer. J. Physiol., 1933, 104, 364—370).—The statistically significant variations in hæmoglobin vals. and erythrocyte counts (I) found in normal subjects remain unchanged in individuals who consume the equiv. of 300 g. of fresh foetal calf liver (II) daily for a period of 10 days. (II) has a high Cu content. Discontinuance of liver feeding is followed, after about 12 days, by a fall of (I) below control val. A similar tendency is noted after feeding stomach and ox-liver extract.

NUTR. ABS. (m)

Blood formation. I. Arsenic in relation to blood formation. Testing therapeutic agents in anaemia. WICHELS and I. HOFER (Klin. Woch., 1933, 12, 591—593).—Reticulocytes (I) increase considerably within a few days in healthy subjects (II) receiving daily 0.0075—0.015 g. of As. The increase is accompanied by toxic symptoms. The increase of (I) in (II) is suggested as a suitable test for antianæmic agents.

NUTR. ABS. (m)

Lack of copper as a cause of disease in animals and plants. B. SJOLLEMA (Biochem. Z., 1933, 267, 151—156).—In farm animals (I) lack of Cu in the diet and in crops (wheat, rye, oats) or such lack in the soil leads to disease which is cured by administration of, or manuring with, $CuSO_4$, respectively. The action of the Cu in (I) is probably direct, although the blood of the diseased (I) is often low in hæmoglobin.

W. McC.

Presence, in the urine of cancerous subjects, of a principle having an action on the adrenal cortex. M. ARON (Compt. rend., 1933, 197, 1702—1704).—Although injection of large vols. of normal urine is without effect, injection of urine from a cancer subject into rabbits causes a large excretion of lipins of the adrenal cortex. The active substance is contained in the material pptd. from the urine by $COMe_2$.

J. W. B.

Therapeutic application of amino-acids in spontaneous cancer in mice. F. VLES and A. DE COULON (Compt. rend., 1933, 197, 1779—1781).—By suitable treatment with NH_2 -acids and endocrine gland preps. a disappearance of spontaneous tumours was obtained in two strains of mice in 40% of the cases.

P. G. M.

Blood chemistry of hens bearing Rous sarcoma No. 1. H. M. DYER and J. H. ROE (Amer. J. Cancer, 1933, 18, 888—898).—Intramuscular inoculation produces mild hyperglycaemia, lowered glucose tolerance, increase in glycolytic activity, and slight decrease in CO_2 -combining power, fatty acid, and carotene of the blood. Numerous other constituents are unchanged.

CH. ABS.

Effect of enzymes on the pathogenicity of Rous and Fujinami tumour viruses. A. PIRIE (Biochem. J., 1933, 27, 1894—1898).—The enzyme, present in preps. of dried pancreas (I), responsible for the inactivating effect on the agents of Rous and Fujinami tumours is unstable at 0° in glycerol solutions. It is adsorbed by $Al(OH)_3$ B at 4.0 together

with lipase, but is not lipase. The protease and carboxypeptidase present in (I) are inert. A. L.

Calcium metabolism and malignant tumours. M. TABANELLI (Riv. Patol. sper., 1933, 10, 234—252).—With malignant tumours at an early stage of development, Ca vals. (blood, urine, faeces) remain normal, but when the cancer (I) is well advanced, there is a considerable fall (II) in the blood-Ca, and a corresponding fall in the urinary Ca. (II) also occurs in diseases other than (I), and is due, not to the tumour itself, but to the general lowering of health occurring in the later stages of the disease. NUTR. ABS. (m)

X-Ray therapy. I. Insulin and adrenaline. F. EICHHOLTZ, H. G. ZWERG, and L. KLUGE (Arch. exp. Path. Pharm., 1933, 174, 210—216).—The growth-inhibiting action of X-rays on rats' sarcoma is increased by previous subcutaneous injection of insulin, whilst that of adrenaline reverses the action to a growth-promoting one. The phenomena are probably related to changes induced by the hormones in the lactic acid content of the tumours. F. O. H.

Immunological reactions in dental caries. G. G. MACPHEE (J. Dental Res., 1933, 13, 273—274). CH. ABS.

Metabolic studies of children with dental caries. J. D. BOYD, C. L. DRAIN, and G. STEARNS (J. Biol. Chem., 1933, 103, 327—337).—Incidence of dental caries (I) is not dependent on serum-Ca and -P, the acid-base relationship, dietary deficiency of P, or the inorg. constituents of the saliva. A definite relation exists between the retention of Ca and P, the metabolic efficiency of the body as a whole, and the resistance to (I). (I) depends primarily on factors operating from within the tooth. H. G. R.

Cholesterosis of the gall-bladder in Indians. A. C. GHOSE (Indian J. Med. Res., 1933, 20, 939—949).—Cholesterosis (I) of the gall-bladder (II) occurs in (II) diseases. Lipins are present in the various coats of (II). There is a definite rise in the blood- and bile cholesterol content. NUTR. ABS. (m)

Hydrogen-ion concentration of nasal secretion in children with acute coryza. M. C. HILL and A. R. HARNES (J. Lab. Clin. Med., 1933, 18, 1029—1032).—In the early stages the p_H is 7.69 ± 0.039 ; the normal val. is 7.02 ± 0.021 . CH. ABS.

Kidney-function during diabetes insipidus. Action of pituitary extract and of adrenaline. [Glomerular] filtration. P. IVERSEN, E. JACOBSEN, and J. BING (Arch. exp. Path. Pharm., 1933, 174, 69—76).—Injection of pituitary extract into a patient with diabetes insipidus and one kidney removed produced a diminution of the glomerular filtration (I) and an increase in the ratio of urine- to blood-creatinine due to a sp. action on the tubules affecting the re-absorption of H_2O . The excretions of PO_4 -P and Cl were partly proportional to (I), whilst that of PO_4 appeared to have a threshold val. The (I), which was not influenced by adrenaline, amounted to 111.5 litres for the one kidney in 24 hr. F. O. H.

Metabolism of galactose in diabetes mellitus. W. G. KARR and T. V. LETONOFF (Amer. J. Med. Sci., 1933, 185, 596—597).—Galactose disappears very

quickly from the blood of diabetics, probably owing to ready formation of glycogen. Insulin does not aid the removal of galactose from the blood-stream.

CH. ABS.

Sorbitol (sionon) for diabetics. W. W. PAYNE, R. D. LAWRENCE, and R. A. MCCANCE (Lancet, 1933, 225, 1257—1258).—*d*-Sorbitol (I) can be used as a sweetening agent for diabetics (II), since it does not enter directly into carbohydrate metabolism. Administration of (I) to (II) produces only a slight rise in blood-sugar. Less $COMe_2$ is excreted in urine when (I) is given. (I) has no effect in relieving insulin hypoglycaemia, and fails to increase the glycogen in the liver of starved rats. L. S. T.

Utilisation of sorbitol. A. ROCHE and A. RAYBAUD (Compt. rend. Soc. Biol., 1933, 113, 320—322).—Sorbitol does not act as a source of glycogen in the young guinea-pig. In normal and diabetic man and in the insulinised rabbit it is not metabolised; in the phloridzinised animal it apparently produces hexose. NUTR. ABS. (m)

Influence of vitamin-B on carbohydrate metabolism. M. LABBE, F. NEVEUX, and J. D. GRIGNOIRE (Bull. Acad. Med., 1933, [iii], 109, 689—702; Chem. Zentr., 1933, ii, 1391).—In diabetes, administration of vitamin-B diminishes glycosuria and glycaemia, raises the carbohydrate tolerance, improves the general condition, and increases the body-wt. The improvement appears slowly, and combination at first with insulin is recommended. A. A. E.

Methylglyoxal in the urine and cerebrospinal fluid of infants with toxic dyspepsias and of dogs and rats in experimental vitamin-B₁ deficiency. I. A. GEIGER and A. ROSENBERG (Klin. Woch., 1933, 12, 1258—1260).—Laboratory animals require more vitamin (I) when kept at high temp. than when kept cool. The pathological findings in dogs suffering from (I)-deficiency resemble those in infants (II) suffering from certain types of acute dyspepsia (III). AcCHO occurs regularly in the urine of dogs and rats in (I)-deficiency and is also found in the urine and cerebrospinal fluid of (II) with toxic (III). Such (II) often respond dramatically to the giving of (I) and the AcCHO rapidly disappears from the urine. NUTR. ABS. (m)

Acid-base equilibrium of the blood in epilepsy. F. L. McLAUGHLIN and R. H. HURST (Quart. J. Med., 1933, [ii], 2, 419—429).—Between fits variations in alkaline reserve (I) and lactic acid (II) are normal, but the p_H tends to be slightly high. (I) falls during and after a fit owing to accumulation of (II). CH. ABS.

Experimental production of simple goitre. A. W. SPENCE, F. H. A. WALKER, and E. F. SCOWEN (Biochem. J., 1933, 27, 1992—1997).—Thyroid hyperplasia (I) is produced in rabbits by feeding cabbage when the diet is free from antigoitrogenic substances, e.g., hay or oats. Small doses of MeCN also produce (I), the mechanism being different from that of the diminished resistance to MeCN poisoning on administration of thyroxine. F. O. H.

Iodine metabolism in disease of the thyroid gland. L. SCHEFFER (Klin. Woch., 1933, 12, 1285—

1286; Chem. Zentr., 1933, ii, 1697).—Much I may be excreted through the skin and the intestines as well as in the urine. In exophthalmic goitre there is no equilibrium between I ingested (I) and I excreted (II); (II) > (I). In some cases the I excreted through the skin (III) = $10 \times$ that excreted through the kidneys (IV). In hyperthyrosis and simple goitre (III) and (IV) diminish, whilst faecal I is high: (II) < (I).

A. A. E.

Cretinism and hypothyroidism in childhood. I. P. BRONSTEIN (J. Amer. Med. Assoc., 1933, 100, 1661—1663).—In hypothyroid children the blood-cholesterol (I) is markedly > in healthy children. The improvement wrought by thyroid extract is reflected by a fall in (I).

NUTR. ABS. (m)

Lipins of spleen and liver in various types of lipinosis. H. SOBOTKA, D. GLICK, M. REINER, and L. TUCHMAN (Biochem. J., 1933, 27, 2031—2034).—In Gaucher's disease a shift from the phosphatide fraction (I) to neutral fat (II) together with the presence of considerable amounts of kersin was observed. Niemann-Pick's disease was characterised by increase in (I) with almost complete absence of (II). These changes in lipin distribution are explained by a deficiency of liver-esterase.

H. G. R.

Fluorescent substance in human urine. P. NIEDERHOFF and G. HOLLAND (Klin. Woch., 1933, 12, 1184; Chem. Zentr., 1933, ii, 1700).—A substance exhibiting strong sky-blue fluorescence is usually present in malaria, obstructive conditions, and high fever.

A. A. E.

Lactic acid of the cerebrospinal fluid in meningitis. A. G. DE SANCTIS, J. A. KILLIAN, and T. GARCIA (Amer. J. Dis. Children, 1933, 46, 239—249).—The increased concn. varies directly with the leucocyte count and is > and independent of that of the blood.

CH. ABS.

Carbohydrate metabolism and acid-base equilibrium in experimental intestinal obstruction. U. FOGLIANI (Riv. Patol. sper., 1933, 10, 261—280).—In rabbits, when the pylorus is obstructed, blood-sugar (I) falls, lactic acid (II) vals. vary, and the alkali reserve (III) rises, but when the intestine is obstructed at levels lower than the duodenum (IV), (I) rises and (II) and (III) fall. In dogs, when (IV) is obstructed, (I) and (III) rise, and (II) falls, but with obstruction at lower levels, (III) still rises and (I) and (II) fall.

NUTR. ABS. (m)

Experimental dermatitis (pellagra) in rats. M. KELLOGG and W. H. EDDY (Science, 1933, 78, 609).—Pellagra develops most uniformly in rats fed on a diet in which low or sub-min. amounts of vitamin-B₃ are coupled with high or adequate amounts of -B₁.

L. S. T.

[Rapid decolorisation of iodine solutions by pellagra blood.] C. H. CAMPBELL (Amer. J. Med. Sci., 1933, 186, 266—270).

CH. ABS.

Carbohydrate metabolism in pregnancy and the puerperium. B. KRIS and S. HIRSCHHORN (Wien. klin. Woch., 1933, 46, 616—617).—In pregnant women and in women early in the puerperium ad-

ministration of glucose (2 × 50 g.) causes disturbance in the functional capacity of the islets of the pancreas.

NUTR. ABS. (m)

Endocrine factors in the causation of the creatinuria of pregnancy. I. SCHRIRE and H. ZWARENSTEIN (Nature, 1934, 133, 27—28).

L. S. T.

Occurrence of the melanophore-dilating factor in the urine in certain diseases. R. COLLIN and P. L. DROUET (Bull. Acad. Méd., 1933, [in], 109, 794—802; Chem. Zentr., 1933, ii, 1538).—Urine of menstruating women, but not normal urine, frequently gives the (frog) melanophore reaction. The reaction is frequently obtained in hyperthyroidism, and sometimes in pituitary tumour and in Cl retention.

A. A. E.

Porphyria without porphyrinuria. A. A. H. VAN DEN BERGH and W. GROTEPASS (Klin. Woch., 1933, 12, 586—589).—In a case of chronic porphyria the urine contained a normal amount of porphyrin (I) [exclusively coproporphyrin (II)]. The (I) content of the red cells was raised only slightly, but the serum was very rich in (I) (6.1 mg. per 1000 c.c.). Duodenal juice contained 35 mg. of (II) and 20 mg. of protoporphyrin (III) per 100 c.c. (II) was derived from aetioporphyria I, not from haemoglobin. The source of the (III) in the faeces is unknown.

NUTR. ABS. (m)

Occurrence of protoporphyrin in urine. I. BOAS (Klin. Woch., 1933, 12, 589—591).—In a significant no. of liver and bile-duct diseases involving porphyria, besides coproporphyrin, a CHCl₃-sol. porphyrin spectroscopically identical with protoporphyrin is found in the urine.

NUTR. ABS. (m)

Blood-sugar in relation to resection of the stomach. F. W. LAPP and H. DIBOLD (Klin. Woch., 1933, 12, 547—548).—Ingestion of glucose (100 g.) by patients with resected stomach causes a more rapid rise in the blood-sugar level and an earlier decline to a lower level than is normal (lowest val. 42 mg. per 100 c.c. after 2 hr.). This alteration is not due to a significant alteration in carbohydrate metabolism, but to changed conditions in gastroduodenal passage.

NUTR. ABS. (m)

Mineral metabolism in renal disease. III. Regulative excretion of minerals by the kidney on acid and basic diet. H. GLATZEL (Z. ges. exp. Med., 1933, 88, 454—477).—In nephritis (I) the first and occasionally only sign of impaired renal function is reduction in the ability to concentrate all minerals (hyposthenuria). In advanced renal impairment the excretion of minerals depends almost entirely on the vol. of H₂O secreted. The renal regulation of acid-base equilibrium in (I) depends on changes in the excretion of Na, Ca, Cl, and P. In health (II) on the acid diet there is at first increase in the output of NH₄, Na, and Ca, but later a decrease in Na and further increase in NH₄ and Ca. The increase in NH₄, Na, and Ca is much less marked in (I) where K supplies a large part of the extra base required; Cl and P output in (I) is > in (II) probably due to inefficiency in dealing with HCO₃' and org. acids. On the alkaline diet the output of Cl, P, Na, and more especially K in (I) is > in (II).

NUTR. ABS. (m)

Concentration test of renal function. II. Measurement of proteinuria. F. H. LASHMET and L. H. NEWBURN (J. Amer. Med. Assoc., 1933, **100**, 1328).—A suspension formed with 1 c.c. of 0.1N-NaOH and 0.16 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 125 c.c. can replace Folin and Denis' standard of turbidity. CH. ABS.

Cereals and rickets. IV. Effect of immaturity of the maize kernel on its rachitogenic properties. V. Effect of germination and autolysis on the rachitogenic properties of the maize kernel. V. M. TEMPLIN and H. STEENBOCK (Biochem. J., 1933, **27**, 2055—2060, 2061—2068).—IV. Immature maize (I) gives better calcification than mature (I). Canned sweet (I) is also better than the seed. The variation in the P content was not sufficient to account for the observed differences.

V. Germination and heating to 50° did not affect the antirachitic activity of (I), whereas autolysis decreased it. H. G. R.

Calcium-phosphorus ratio in the genesis of experimental and human rickets. G. MOURIQUAND and A. LEULIER (Compt. rend., 1934, **198**, 208—210).—The Ca/P ratio is approx. the same in cow's (I) and human milk. The possibility of human rickets being due to an incorrect Ca content of (I) is thus eliminated. R. S. C.

Calcification of teeth and bones on rachitic and non-rachitic diets. M. KARSHAN (J. Dental Res., 1933, **13**, 301—304).—A severe rachitic diet (Ca : P = 7.27) decreased rats' tibia-ash, -Ca, and -P, but had no influence on these constituents of teeth. Addition of KH_2PO_4 and cod-liver oil did not affect vals. for teeth in 30—45 days, but in 64—80 days the teeth-Ca and -P were slightly > in rats receiving the basal diet with KH_2PO_4 . CH. ABS.

Correlation of chemical and pathological changes in teeth and bones on rachitic and non-rachitic diets. M. KARSHAN and T. ROSEBURG (J. Dental Res., 1933, **13**, 305—310).—A high-Ca, low-P diet affected the ash, Ca, and P of bone, but not of teeth. Low Ca, with low or high P, affected both teeth and bone. CH. ABS.

Phosphorus metabolism in rickets. VIII. Quantitative relationship of glycerol- and hexosediphosphatase in human faeces in rickets, spasmophilia, intestinal infantilism, and febrile hypophosphatæmia. W. HEYMANN (Z. Kinderheilk., 1933, **55**, 92—100).—The glycerophosphatase (I) and hexosediphosphatase (II) contents of faeces are greater in the youngest individuals, the vals. for infants, children, and adults being in the ratios 72 : 42 : 15 and 70 : 38 : 15, respectively. In uncomplicated rickets of infancy the average (I) is 59, and the average (II) 56; when tetany is present the vals. are 81 and 86; during the healing phase of rickets the vals. are 71 and 69. In coeliac disease the vals. are 15 and 16, indicating very defective enzyme production by the alimentary mucosa. In non-rachitic hypophosphatæmia associated with fever, the vals. are normal. NUTR. ABS. (m)

Scurvy in the seventeenth and eighteenth centuries. E. G. T. LIDDELL (Nature, 1934, **133**, 67).—Historical. L. S. T.

Silica content of the lungs of a group of tunnel workers. C. S. SMITH and H. L. WIKOFF (Amer. J. Public Health, 1933, **23**, 1250—1254).—Analyses of the lungs of 9 men who worked in the same tunnel show correlation between the severity of silicosis (I) as determined histologically and the % SiO_2 in the dried lung substance. The latter varied from 0.33 to 5.09% and is regarded as a better criterion of the intensity of (I) than is the % SiO_2 in the total ash. C. J.

Enzyme biology and enzyme diagnosis of syphilis. A. MARCHIONINI and B. OTTENSTEIN (Arch. Dermatol. Syphilis, 1933, **167**, 244—278; Chem. Zentr., 1933, i, 1792).—The diastase content of skin dialysate (Ottenstein) is high in syphilis; the effect is detectable in the primary period. Neurosyphilis affords particularly high vals. Similar high vals. are found in diabetes. A. A. E.

Diastase content of cerebrospinal fluid in syphilis. A. MARCHIONINI and B. OTTENSTEIN (Klin. Woch., 1932, **11**, 1424—1426; Chem. Zentr., 1933, i, 1792).—Vals. are : normal, 11—40 (sometimes > 80); syphilitic, < 10 (often 0) mg. per 100 c.c. The various forms of syphilis are related to the frequency with which this disappearance of diastase is observed. The effect is independent of the result of the Wassermann blood-reaction. A. A. E.

Calcium of whole blood, serum, and plasma in human diseases, including tetany. F. K. HERBERT (Biochem. J., 1933, **27**, 1975—1977).—With various diseases, including three cases of tetany of non-parathyroid origin, Ca was absent from the red blood-corpuses. Comparison of plasma from citrated blood with serum from defibrinated blood did not indicate the passage of abnormal amounts of Ca into the fibrin coagulum (cf. A., 1925, i, 857; 1930, 1319). F. O. H.

Mechanism of chemotherapeutic action. XI. "Immunising effect" in treatment of experimental trypanosomiasis with neoarsphenamine. L. REINER and C. S. LEONARD (Arch. Int. Pharm. Ther., 1933, **44**, 434—445).—Blockade (with Indian ink) or splenectomy (or both) decreases the efficiency of chemotherapeutic treatment of rats infected with *T. equiperdum* (I), but influences very little, or not at all, the course of infection produced by (I) which have been treated *in vitro* with the therapeutic agent. Blockade inhibits the production of immune bodies (II), and thus interferes with the treatment of an infection with neoarsphenamine, which normally leads to the production of (II). A. W.

Action of lipins of healthy mammalian organs on evolution of experimental tuberculosis in guinea-pig and rabbit. L. NEGRE (Ann. Inst. Pasteur, 1933, **51**, 697—706).—Repeated subcutaneous injections of COM_2 -extracted fats of the lung, liver, and kidney of the guinea-pig (I), rabbit (II), or man favour the development of experimental tuberculosis (III) in (I) and in (II). The evolution of (III) in (I) is not modified by repeated injections of aq. suspensions of defatted organs of (I). Since in (III) the lipin content of the organs increases progressively, the conditions will become more and more suitable for the growth of the bacilli. A. W.

Total and diffusible serum-calcium and calcium of cerebrospinal fluid in human cases of hypo- and hyper-calcaemia. F. K. HERBERT (Biochem. J., 1933, 27, 1978—1991).—During hyper- and hypo-calcaemia (I), the cerebrospinal fluid-Ca (II) remains relatively const. The level of (II) is no criterion of that of the diffusible serum-Ca (III), (III) being $>$ (II) during hyperparathyroidism [when the normal ratio of (III) to total Ca is maintained] and $<$ (II) during some cases of uraemia. Normal vals. of (III) occur with the (I) associated with low serum-protein and normal -inorg. PO_4 , whilst with severe (I) of uraemia, (III) is subnormal and tetany [during which the relation of (III) to total Ca is variable] may occur. F. O. H.

Relation between respiration, gelatinase content, and pigmentation of skin. S. BLAZSÓ (Biochem. Z., 1933, 267, 11—17).—The respiration of non-pigmented (I) rabbit skin does not differ from that of pigmented (II). The gelatinase content of (I), determined by a capillary method described, is 50—80% $>$ that of (II). Histologically (I) differs greatly from (II). W. McC.

Effect of carbohydrates on respiration of tissues. B. KISCH (Biochem. Z., 1933, 267, 32—42; cf. A., 1932, 1281).—The alterations in the respiration of retina (I), heart, diaphragm, liver, and kidney (II) of ox, sheep, guinea-pig, rat, and rabbit caused by arabinose, xylose, rhamnose, glucose, fructose, galactose, lactose, maltose, sucrose, mannose, and glucosamine vary in the same tissue (III) with the carbohydrate (IV) used, with the same (IV) when different (III) of the same animal are used, and in the cases of (I) and (II) with the species of animal when the same (III) and (IV) are used. W. McC.

Influence of *l*- and *d*-lactate on oxygen consumption of rabbits. K. W. BUCHWALD, C. F. CORI, and R. E. FISHER (J. Biol. Chem., 1934, 103, 763—776).—Na *l*-lactate (I) administered to rabbits intravenously increases the O_2 consumption to an extent which accounts for only 25% of the lactate which disappears (70% of that administered). Of *d*-lactate (II) only 10—30% is removed, but all the removed fraction is accounted for by the increase in O_2 consumption. It appears that (I) is partly oxidised and partly converted into glycogen (III), whilst (II), although capable of oxidation, is not converted into (III). W. O. K.

Metabolism of sea urchins' eggs. I. Influence of dyes on respiration and lactic acid formation. A. W. H. VAN HERK (Arch. neerl. Physiol., 1933, 18, 578—602).—The addition of methylene-blue (I), chrysoidine (II), or Janus-green (III) to unfertilised sea-urchins' eggs (*Sphaerechinus granularis*) greatly increases respiration; with fertilised eggs the increase is less. Before and after fertilisation, the R.Q. is the same, but whilst (I) and (II) are without effect, (III) causes an increase with the unfertilised eggs. Mature eggs leaving the ovary have a relatively high lactic acid (IV) content which decreases rapidly aerobically, remaining unchanged under anaerobic conditions. The amount of O_2 taken up is, however, much $<$ that required for the oxidation

of (IV). The presence of (I), (II), or (III) increases the formation of (IV) both anaerobically and aerobically. A. L.

Metabolism of surviving tissue, especially of the thyroid gland. B. WALTHARD (Endokrinol., 1933, 13, 5—9; Chem. Zentr., 1933, ii, 1696).—The respiration of normal thyroid tissue is high; aerobic (I) and anaerobic glycolysis and Warburg's coeff. are zero. In exophthalmic goitre respiration is increased, but (I) is 0; administration of I causes return to normal respiration and slight (I) is observed. Malignant tumours behave as regards respiration and glycolysis like those of other organs. A. A. E.

Oxidation of fatty acids in the liver. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1933, 27, 1753—1762).—Fatty acids (I) increase the respiration of guinea-pig liver, each (I) having an optimum concn., above which there is a fall in Q_{O_2} (cu. mm. of O_2 produced per hr., per mg. dry wt. of tissue) and in production of ketonic substances, which are formed only with (I) containing an even no. of C atoms. Crotonic and isocrotonic acids yield $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ (II), which is not broken down appreciably to COMe_2 and CO_2 in the liver. Neither glucose nor lactic acid affects Q_{O_2} or Q_{III} for PrCO_2H (III), but EtCO_2H lowers Q_{O_2} and Q_{III} , and increase in PO_4''' concn. lower both Q_{O_2} and Q_{III} , and replacement of Locke solution by saline lowers the oxidation of (III). Minced liver cannot oxidise (I). H. G. R.

Metabolism of azelaic acid. H. G. SMITH (J. Biol. Chem., 1933, 103, 531—535).—When azelaic acid was fed to dogs in quantities from 10 to 45 g. in 6-day periods, an average of 60% was recovered in the urine. H. D.

Nutritive value of fatty acid esters. W. M. COX, jun. (J. Biol. Chem., 1934, 103, 777—790).—The mixed Et esters of the fatty acids of coconut oil are utilised by rats and promote growth practically as well as the original fat, but the individual esters are relatively inefficient. When 77% of the cal. of the diet are in the form of the pure esters, death occurs with butyrate and hexoate as the result of refusal to eat them; palmitate and stearate are hydrolysed in the intestine, but the fatty acids are largely unabsorbed; deoate and laurate usually cause death within two weeks. The higher, but not the lower (up to C_{10}), fatty acids accumulate in the depot fats. W. O. K.

Role of phosphoaminolipins in the metabolism of fats. II. Oral administration of iodised fats. C. ARTOU and G. PERETTI (Arch. internat. Physiol., 1933, 36, 351—370).—Iodised fat (I), after oral administration as emulsions to rabbits, is fixed by the liver during the succeeding 44 hr. Most of the lipin-I is sol., a smaller part is insol., in COMe_2 . In the blood, (I) increases up to 20 hr. after ingestion and then decreases. A considerable portion of this (I) is insol. in COMe_2 . At the peak of absorption, the concn. of lipin-I in the corpuscles is $>$ in the plasma, the difference being largely in I precipitable by COMe_2 . Much of the I administered is liberated in the liver and is present as non-lipin I in the blood. The

phosphoaminolipins of liver and blood probably participate in the intermediate metabolism and transport of fatty acids. NUTR. ABS. (m)

Diet and blood-lipins. II. Effect of occasional over-feeding on the post-absorptive level. W. R. BLOOR (J. Biol. Chem., 1934, 103, 699—705).—In dogs on const. diet the level of the plasma-lipins in the post-absorptive state remains const.; single over-feeding with fat or carbohydrate but not with protein, to the extent of half the cal. intake of the ordinary diet, usually produces high plasma-phospholipins and often high fat vals., whilst the cholesterol level is not affected. The high vals. generally last \approx 2—3 days. W. O. K.

Accumulation of lipins in the gall-bladder. J. BERENDES (Arch. klin. Chirurg., 1933, 175, 266—282).—Storage (I) of lipins in the wall of the gall-bladder (II) is the result of absorption. It is not due to a primary disturbance of cholesterol metabolism of the whole animal, and there is no causal relationship between it and the production of gall-stones, although a relationship between (I) and inflammatory processes cannot be excluded. (I) results from an accumulation of cholesteryl esters in (II) bile and slowing of the lymph stream from (II) also appears important. NUTR. ABS. (m)

Effect of cholesterol feeding on lipins of rat livers. R. OKEY (Proc. Soc. Exp. Biol. Med., 1933, 30, 1003—1005).—Rats fed on a standard diet containing cholesterol show a marked increase in the fatty acid (I) content of the livers and a very considerable increase of sterol as ester (II). Free sterol is not increased. Litter mates fed vitamin-B+cholesterol at the 10% fat level show 16.6% of (I) and 6.0% of (II) for livers of males and 23.2% of (I) and 6.6% of (II) for females, whilst those deprived of vitamin-B show 11.9% of (I) for males, 13.9% for females, and 4.5 and 2.5% of (II) for males and females, respectively. NUTR. ABS. (m)

Synthesis and destruction of cholesterol in the organism. R. SCHOENHEIMER and F. BREUSCH (J. Biol. Chem., 1933, 103, 439—448).—On a bread diet mice synthesised in a month as much cholesterol (I) as was initially contained in their bodies. When (I) was fed in quantity, much was destroyed. Fat and carotene had no effect on the (I)-balance, but bile acids increased the destruction of (I). H. G. R.

Nerve metabolism. VII. Rôle of lactic acid. T. H. CHANG and R. W. GERARD (Amer. J. Physiol., 1933, 104, 291—297).— $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ (I) gradually depresses the respiration and abolishes the action potentials of nerve. The presence of lactate (II) antagonises and delays these effects. (I) also causes breakdown (III) of phosphocreatine (IV) [max. effect at 0.005*M*-(I)]. With split nerves, presence of (II) largely prevents (III). The loss of (IV) due to tetanisation of the nerve is not, however, increased by the presence of (I). It is improbable that (II) is produced and removed during conduction, but more probable that it can be oxidised as part of the resting metabolism of the nerve. NUTR. ABS. (m)

Production of lactic acid in the auricle of the rabbit heart. F. GOTTDENKER and M. WACHSTEIN

(Biochem. Z., 1933, 267, 192—201).—The average time of survival of the stræ in N_2 is 6, in Tyrode's solution (I) 17, in (I) containing glucose 37 min. Anaerobic conditions lead to increased production (II) of lactic acid (III), most of which diffuses into the nutrient medium (IV). (II) is independent of the nature of the (IV). In presence of O_2 (III) disappears after about 8 hr. W. McC.

Liver- and muscle-carbohydrate of wild and domesticated ducks. S. SUZUKI (Japan. J. Med. Sci., 1933, 2, 277—283).—During winter the carbohydrate (I) of the liver of wild ducks (II) diminishes, whilst the muscle-(I) remains unchanged. With both wild and tame (II) the pectoral muscle contains more (I) than the leg muscle. F. O. H.

Carbohydrate metabolism of dogs during continuous carbohydrate ingestion. L. FALIN (Arch. exp. Path. Pharm., 1933, 174, 12—27).—Continuous ingestion (2×50 g. daily for 19—125 days) of sucrose (I) or glucose by dogs produces with each dosage a mild hyperglycæmia (II) followed by a hypoglycæmia, the levels of both of which vary with the period of treatment. A second administration 30 sec. after the first results in less marked deviations of the blood-sugar from normal. With dogs treated for 53 days with (I), the extent of (II) is small, whilst after 83 or 120 days, the (II) resembles that occurring with normal dogs. The (II) due to adrenaline and the sensitivity to insulin are also modified. The correlation of these findings with changes in the secretion of insulin is discussed. F. O. H.

Carbohydrate metabolism. I. Effect of previous diet on utilisation of glucose injected intravenously. J. A. JOHNSTON (Amer. J. Dis. Children, 1933, 46, 309—321).—The amount of glucose injected intravenously is directly related to that available in the basal oxidised mixture. CH. ABS.

Cutaneous blood-sugar curves after administration of fructose, mannose, and xylose. V. J. HARDING, T. F. NICHOLSON, and A. R. ARMSTRONG (Biochem. J., 1933, 27, 2035—2042).—Administration of fructose (I) produces an increase in blood-glucose, and small quantities of (I) can be detected in blood (II) and urine (III). Mannose, owing to slow absorption and rapid utilisation, was not found in (II), but was detected in (III) after administration. Large amounts of xylose are found in both (II) and (III) after ingestion. H. G. R.

Carbohydrate metabolism with partial exclusion of liver. F. MEYTHALER and T. NAEGELI (Klin. Woch., 1933, 12, 596—597).—Dogs with Eck's fistula receiving a diet rich in carbohydrates show increased hyperglycæmia after ingestion or injection of glucose. When only the blood of the pancreaticoduodenal vein passes through the liver, normal blood-sugar curves are obtained. NUTR. ABS. (m)

Glycogen synthesis in the small intestine. E. A. HORNE and H. E. MAGEE (J. Physiol., 1933, 78, 289—294).—There is no evidence that glycogen is synthesised in the small intestine (dog, rabbit, cat, rat) during glucose absorption. NUTR. ABS. (m)

Relation of the chemical change in frog's muscle to the degree of tension. O. RIESSER and

R. MIURA (Pflüger's Archiv, 1933, 232, 513—538; Chem. Zentr., 1933, ii, 1708).—In anaerobic excitation of frog's muscle *in vitro* the formation of lactic acid (I) is max. at moderate tension. *In situ* all tensions and performances result in the same increase in (I). The "all or nothing" rule appears to hold.

A. A. E.

Chemical changes accompanying muscular contraction and overheating. I. Analytical methods. T. CAHN, J. HOUGET, and R. JACQUOT (Ann. Physiol. Physicochim. biol., 1933, 9, 205—243; Chem. Zentr., 1933, ii, 1708).—Methods for the determination of muscle-, blood-, and liver- H_2O , total reducing substances, lactic acid, phosphate, creatine-, adenylypyro-, and hexose-phosphoric acids, total acid-sol. P, total P, total fat, fatty acids, unsaponifiable matter, lipin-P, urea, NH_3 , creatine, creatinine, nuclein-P, Na, K, and Ca are discussed. A. A. E.

Regulation of nitrogen metabolism by nervous centres. C. RICHEL and J. DUBLINIAU (J. Physiol. Path. gen., 1933, 31, 64—81).—In fatal cerebral puncture in rabbits N retention in the blood-stream occurs, accompanied by increased urea excretion (I). (I) also occurs with less severe lesions. Sometimes, however, there is no disturbance of N metabolism.

NUTR. ABS. (m)

New-formed hæmoglobin and protein catabolism. Conservation of intermediates in the anæmic dog on protein-free diet. F. S. DAFT, F. S. ROBSCHT-ROBBINS, and G. H. WHIPPLE (J. Biol. Chem., 1933, 103, 495—510).—Normal (I) and anæmic dogs (II) were fasted for 3 days; and after a week's feeding on carbohydrate were given 400 mg. Fe. In (I) the urea and NH_3 fraction of urine decreased by 38% and in (II) by 62%. The total hæmoglobin (III) produced [112 g. in (II)] was > accounted for by the diminished N excretion. Before Fe feeding (II) excreted more N than (I); the excretion of creatine and uric acid was also high. The total N excretion of (II) fed for 3 weeks with sugar without Fe decreased by 36% and (III) formation was 36 g., whilst with sugar+Fe it decreased by 53% and (III) formation was 128 g.

H. D.

Availability of mesocystine for promotion of growth in connexion with cystine-deficient diets. H. S. LORING, R. DOREMANN, and V. DU VIGNEAUD (J. Biol. Chem., 1933, 103, 399—403).—Mesocystine (I) is capable of supporting growth in absence of L-cystine. This is probably due to formation of L-cysteine by reduction of (I). It is confirmed that D-cystine does not promote growth (this vol. 89)

H. G. R.

Cystine requirements of fleece growth. A. T. KING and J. E. NICHOLS (Nature, 1933, 132, 966).—A discussion.

L S

Cow's milk as a balanced food for mammals. R. JACQUOT (Compt. rend., 1933, 197, 1755—1757).—Cow's milk has a high coeff. of digestive utilisation in the calf (92%) young pig (97%), but the lactosuria is greater in the latter (49 g. *per diem*). The coeff. of N retention in the calf is 60—70%, but in the pig only ~%, no retention occurs in young rats, which will subsist but not grow, on a cow's milk diet; hedgehogs die within 10 days.

P G M

Nutritive value of boiled and raw milk in infant feeding. N. MORRIS and S. GRAHAM (Lancet, 1933, 225, 1314—1315).—Retention of N, Ca, and P appears to be greater when infants are fed on pasteurised as compared with raw milk.

L. S. T.

Growth and development. XXVI. Energy increment of standing over lying and the cost of getting up and lying down in growing ruminants (cattle and sheep): comparison of pulse rate, respiration rate, tidal air, and volume of pulmonary ventilation during lying and standing. W. C. HALL and S. BRODY. XXVII. Endogenous urinary nitrogen and total creatinine excretion in rats as functions of dietary protein level, time on N-free diets, age, body-weight, and basal metabolism. XXVIII. Decline of endogenous nitrogen excretion per unit weight with increasing weight in growing rats, and its relation to the decline in basal metabolism. Decline in live weight, nitrogen and energy metabolism with the advance of the period of nitrogen starvation, and of the influence of live weight and of preceding level on protein intake on these declines and on the survival periods. XXIX. Age curves of creatinine and urinary nitrogen coefficients in dairy cattle and their relations to energy metabolism. U. S. ASHWORTH and S. BRODY. XXX. Partition of digestible nitrogen intake between growth, milk secretion, and urinary excretion in growing dairy cattle. S. BRODY and A. C. RAGSDALE. XXXI. Influence of the plane of nutrition on the utilisability of feeding stuffs. Review of literature and graphic analysis of published data on the net energy and specific dynamic action problems. S. BRODY and R. C. PROCTER (Missouri Agric. Exp. Sta. Res. Bulls., 1933, No. 180, 31 pp. No. 189, 68 pp.; No. 190, 19 pp.; No. 191, 18 pp.; No. 192, 28 pp.).—XXVII. The average creatinine-N (I) coeff. (15.1) was practically independent of age and protein intake. The limiting max. val. of the ratio total (I): total endogenous N (II) was approx. 15% and the average val. 11%. The ratio of cal. (basal metabolism) to mg. total (I) declines with increasing wt. at approx. the same rate as the ratio cal.: body-wt. The cal. per mg. of urinary (II) approaches 1.5 for young rats with high basal metabolism and 0.8 g.-cal. for heavier animals. A greater proportion of adipose tissue in rats on high-proteins diet is associated with lower (I) and (II) coeffs.

XXVIII. The total (I) coeff. of rats is const. between 20 and 600 days of age, but the total urinary (II) coeff. falls with increasing live wt. Prolonged feeding with a N-free diet (III) reduces the energy metabolism to the same level as prolonged abs. starvation. The time taken to reach the endogenous level of N excretion is a function of the level of protein intake prior to N starvation (IV). The faecal N on (III) is a nearly const. proportion of the total N excretion, increasing slightly with prolonged (IV). The ratio of faecal N to food intake increases as (IV) proceeds. The time-live wt. curve on (III) indicates the utilisation of tissues in successive stages.

XXIX. The preformed (I) coeff. of growing dairy

cattle is the same as for man and remains const. over the age 7—40 months. The ratio of basal energy metabolism to creatinine excretion declines with increasing live wt. in approx. the same manner as the ratio of basal metabolism to live wt.

XXX. Under dietary conditions examined, the % of the digestible N intake excreted in urine varied from 45 to 92% after the age of 10 months. High vals. were obtained between 12 and 20 months and low vals. during the last months of gestation and during the flush of lactation. Data showing the efficiency of diets in producing live-wt. increases are given for varying ages of cattle. A. G. P.

Acid-base equilibrium of inhabitants of the tropics. I. Acid-base ratio in the 24-hours' urine. II. Alveolar CO_2 tension, concentration of hydrogen ions, and CO_2 content of blood. G. M. STREEF and J. V. KLERKS (Arch. neerl. Physiol., 1933, 18, 415—535, 536—577; cf. A. 1932, 1277).—I. Analyses of the urine of Europeans (I), students (II), and native servants (III) are given. In comparison with the urine of (I), that of (III) has a lower p_{H} , less PO_4''' and fixed alkali, and more NH_3 .

II. [With W. RADSMAN.] Measurements of the alveolar CO_2 tension and the p_{H} of the blood of (I), (II), and (III) indicate that the acidity increases in this order. A. L.

Effect of nutritional status on the phosphorus content of protein of tissue. O. H. FULCHER (J. Lab. Clin. Med., 1933, 18, 1144—1148).—Dog's muscle- and liver-protein-P increases after prolonged fasting. Human liver-protein-P is high in malnutrition. Cretinism in pigs is not attended by such changes. CH. ABS.

Calcium precipitation and alkalisation in aerobic tissue cultures. W. C. HUEPER and M. A. RUSSELL (Amer. J. Med. Sci., 1933, 186, 383—390).—The pptn. of Ca in tissue cultures does not depend on the formation of excess of lactic acid. It has been observed in Carrel flask cultures with supernatant fluid having p_{H} 8.2—9.0. Alkalisation of the supernatant fluid and plasma medium occurs in cultures of normal and malignant cells grown under aerobic conditions, whilst acidification is observed in anaerobic conditions. CH. ABS.

Calcium and phosphorus in the chick. C. A. ELVEJHEM and B. E. KLINE (J. Biol. Chem., 1934, 103, 733—744).—The whole blood of chicks 1—2 days old contains 12 mg. Ca/l per 100 g. When the vitamin-D (I) supply is adequate, it increases to 13—14 mg. during the first week, then falls to 10—11 mg. at 3—6 weeks. With (I)-deficiency it falls to 9—10 mg. during the first week, rises during the second week, and then falls at four weeks. With adequate (I) the inorg. P decreases from 9 mg. during the first week to 6—7 mg. at six weeks, but with inadequate (I) it falls to 5 mg. at four weeks until death from rickets ensues. On a ration low in PO_4 it falls to 7 mg. at one week and decreases to 5 mg. at six weeks in presence of (I), slightly lower vals. being obtained with (I)-deficiency. On the rachitogenic diet, the ash content of the bones decreases

from 30—32% at one week to 27—29% at five weeks, whilst with ample (I) the ash increases to 36% during the first week and reaches 40—42% in six weeks. A low-P diet with adequate (I) may slightly reduce the ash, but seems not to disturb calcification.

W. O. K.

Sexual differences in calcification of chicks and effect on assays. C. H. SCHROEDER (Poultry Sci., 1933, 12, 256—260).—The proximal end of the metatarsi of cockerels (I) showed 81% of the calcification in female chicks (II). The tibia-ash of (I) is 96.4% of that of (II). CH. ABS.

Magnesium in animal diets. Influence of the level of dietary magnesium on the magnesium and calcium contents of the bones, the bodies, and the blood-serum of rats. I. J. CUNNINGHAM (New Zealand J. Sci. Tech., 1933, 15, 191—198).—Diets containing subnormal proportions of Mg lowered the Mg content of the bones and the blood-serum. Introduction of Mg salts into such diets raised the vals. in some instances > normal. The increase was greater with higher amounts fed and greater with carbonate than with chloride, sulphate, or phosphate. The Mg content of bones was not greatly affected by the level of Mg feeding, but the blood-Ca fell slightly when Mg vals. were high. The calcification of bones proceeded normally with low-Mg feeding; with higher proportions the ash, CO_3'' , and SO_4'' contents of bones decreased and the H_2O content increased. A. G. P.

Action of salt-free diets. Partition of calcium in the blood. H. SCHWARZ (Arch. exp. Path. Pharm., 1933, 173, 558—570).—The total serum-Ca of rabbits fed on either NaCl-rich (I) or -poor diets (II) remains const. Deprivation of NaCl by means of (II) and administration of diuretin produce an increase in the protein-bound Ca and a decrease in the free Ca, whilst (I) produces the opposite effect. F. O. H.

Deprivation of chlorine from the organism. I.—III. J. MICHELSEN (Arch. exp. Path. Pharm., 1933, 173, 737—745, 746—749, 750—758).—I. Diuresis (I) induced in rabbits produces a markedly negative Cl balance, the threshold of Cl being independent of that of H_2O . The assimilated N exceeds the excreted N with normal animals, but *vice versa* during (I), when the increased N and Cl excretions are directly related. Deprivation of Cl therefore appears to result in increased protein decomp.

II. The urea- and residual N are increased during (I) due to endogenous renal deficiency. Lack or excess of Cl in the organism produces an increased formation of protein catabolites and an impairment of the N-concn.-regulating properties of the kidney.

III. The acid-base equivalence is displaced during (I), the deprivation of Cl producing a marked acidosis due to accumulation of lactic and other org. acids. A concomitant hyperglycemia indicates disturbances in the fat and carbohydrate metabolism parallel with those occurring in diabetes. The changes in the distribution of Cl between plasma and corpuscles are discussed. F. O. H.

Distribution and fate of ethyl alcohol in the organism of the dog. E. M. P. WIDMARK (Biochem.

Z., 1933, 267, 128—134).—A formula expressing the relationship between amount of EtOH consumed and its concn. in the blood in man (cf. Kungl. Fysiogr. Sällskapetets Handl., N.F. 41, No. 9; Mellanby, M.R.C. Spec. Rept., 1919, No. 31) can be applied also to the dog. By considering only the post-resorptive period (I) and calculating the body-vol. in which the concn. of EtOH would everywhere be the same as in the blood, results more significant than those of Mellanby are obtained. In (I) the EtOH disappears from the blood more slowly in the dog than in man. Variations amongst dogs are > those in men and dogs are less suitable than men for such experiments. W. McC.

Effect of diet on the alcohol content of the blood. E. M. P. WIDMARK (Biochem. Z., 1933, 267, 135—142; cf. this vol., 105).—The improbabilities of explanations, other than that previously given, of the fact that the EtOH content of the blood is lower when glycine or alanine is administered with the EtOH than when it is given alone, are demonstrated. W. McC.

Absorption of ethyl alcohol and alcohol habituation. G. JUNGMICHEL (Arch. exp. Path. Pharm., 1933, 173, 388—397).—The blood-EtOH (I) (A., 1922, ii, 789) is a suitable criterion of the rate of absorption (II) of orally administered EtOH. With normal fasting persons, (II) is complete 40—60 min. after ingestion, but the rate is influenced by the state of the person and by the amount and form of the EtOH. The changes in (I) with chronic alcoholism are not significantly different from the normal; with intravenous injection, however, a more rapid combustion of EtOH is indicated. F. O. H.

Inhibition of local anæsthesia due to alcohol habituation. K. BALODIS (Arch. exp. Path. Pharm., 1933, 173, 589—594).—Continuous ingestion of EtOH produces a gradual diminution in the sensitivity of the corneal reflex to local anæsthetics, probably related to the change in Ca distribution. F. O. H.

Influence of orally administered alkali and acid on cocaine anæsthesia of the cornea. E. RENTZ (Arch. exp. Path. Pharm., 1933, 173, 595—604).—Oral administration of aq. HCl or NaH₂PO₄, but not of Na₂CO₃, to guinea-pigs diminishes the corneal anæsthesia (I) due to cocaine. Acute alkalinisation or acidification by intravenous injection does not produce any marked change in (I). The above and similar phenomena are probably related to changes in the Ca distribution. F. O. H.

Quantitative applications of the modified Turk test [for narcotics]. J. C. MUNCH, H. J. PRATT, and A. M. DE PONCE (J. Amer. Pharm. Assoc., 1933 22, 1078—1080).—Using a period of 60 sec. immersion, and a sufficient no. of frogs (*Rana pipiens*), it is possible to detect variations of $\pm 10\%$ in the concns. of local anæsthetics etc. W. S.

Poisoning by barbitone and allied drugs (SIR) J. PURVES-STEWART and (SIR) W. H. WILLCOX (Lancet, 1934, 226, 6—7). L. S. T.

Gaseous metabolism during cardiac insufficiency. II. Barbituric acid derivatives and avertin. A. RUHL (Arch. exp. Path. Pharm., 1933 174, 96—110, cf. A., 1933, 1323).—With heart-lung

preps., the cardiac insufficiency (I) due to numal, somnifen, pernocton, or avertin is accompanied by a marked diminution of O₂ consumption (II) (due to œdematous changes in the capillaries) despite the increased dilation of the heart. This lack of O₂ produces an increase in the R.Q. For a given amount of work, the (II) with (I) is < that of the normal heart. F. O. H.

Alteration of the blood-[H⁺] and mineral metabolism during narcosis. III. Influence of alkalosis and acidosis on narcosis. J. BEČKA (Arch. exp. Path. Pharm., 1933, 174, 173—181; cf. A., 1933, 977).—With the exception of morphine (which produces an alkalosis), all the narcotics (I) tested produce in rabbits an acidosis (II) which can be corrected by parenteral administration of colloidal Mg(OH)₂. Such an inhibition of (II) results in an increase (100—200%) in the efficacy of (I), whilst the post-narcotic disturbances are avoided. That veronal is an exception is probably due to the formation of a non-dissociated alkali salt. When the acidosis is emphasised by treatment with glucose, H₃PO₄, or NH₄Cl, the narcosis is deeper and frequently lethal. F. O. H.

Fate of morphine in the body. E. KEESER, H. A. OELKERS, and W. RAETZ (Arch. exp. Path. Pharm., 1933, 173, 622—632).—Subcutaneous injection of single doses of morphine (I) into guinea-pigs is followed by its appearance in the kidney (II), liver (III), and, to a smaller extent, in the muscle, blood, and brain; 24 hr. after injection it is found only in (II) and (III). With continuous injection for 3—6 weeks, (I) occurs in all tissues except muscle. After injection for 4 days, the total amount administered may be recovered from the tissues, urine, and faeces. With mice injected for long periods, approx. 90% of the (I) injected is found in the excreta. Hence (I) is not catabolised in the organism, its action being one of reversible adsorption and inhibition of enzyme action. F. O. H.

Absence of morphine from the stomach following parenteral administration. P. ELLINGER and H. SEEGER (Arch. exp. Path. Pharm., 1933, 174, 168—172).—Subcutaneous injection of morphine (I) into dogs [both normal and habituated to (I)] with gastric fistulæ produced a complete inhibition of gastric secretion within 2—3 hr., followed by a slow return to normal. In no instance was (I) detectable in the gastric juice. F. O. H.

Determination of morphine in excreta, secretions, and tissue. P. ELLINGER and H. SEEGER (Arch. exp. Path. Pharm., 1933, 174, 160—167).—The methods depending on the pptn. of morphine (I) by phosphotungstic acid (A., 1924, ii, 794; 1929, 846) have an accuracy of $\pm 3\%$ when applied to pure aq. (I). A method for the recovery (90—95%) of (I) from gastric juice, urine, faeces, and tissue is described. F. O. H.

Physiological action of *l*- and *d*-derivatives of morphine alkaloids. K. GOTO and T. TAKEBE (Proc. Imp. Acad. Tokyo, 1933, 9, 390—393).—The *d*-derivatives of sinomenine are mainly convulsive poisons and show neither the tail reaction

nor the analgesic action characteristic of the corresponding morphine *l*-derivatives (I); the action on respiration is also less. The action of (I) depends not only on constitution but also on configuration.

F. O. H.

Effect of narcotic gases on brain oxidations. M. BULOW (Biochem. J., 1933, 27, 1832—1837; cf. A., 1932, 424).—The inhibition of the O_2 uptake of brain tissue by narcotic gases (I) (C_2H_2 , C_2H_4 , $CHMc:CH_2$) is not due to their solubility in the tissue-lipins (cf. A., 1932, 1284). With tissue depleted of its substrate by washing with H_2O and in presence of glucose, lactate, or succinate, no inhibition occurs. With tissue washed with Ringer's solution, without added substrate and in presence of (I), the O_2 consumption is partly inhibited by C_2H_2 , but not by CH_4 or $CHMc:CH_2$ (cf. *loc. cit.*). This inhibition is irreversible and is due to the toxic action following prolonged exposure to C_2H_2 .

F. O. H.

Biological evaluation of a new *Digitalis* hybrid. V. AUGUSTIN (Magyar Gyog. Taras. Ert., 1933, 9, 69—73; Chem. Zentr., 1933, i, 1811).—In *D. Ujhelyii*, a hybrid from *D. lutea* (I) and *D. lanata* (II), the morphological characters of (I) are modified by (II), but the pharmacological properties of (I) are unaltered.

L. S. T.

"Senso," a drug from the dried cutaneous secretion of the toad. I. Y. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1933, 9, 552—555).—Many derivatives of ψ -bufotalin (I) have a digitalis-like action on the isolated frog heart. A concn. of 1 in 10^9 of (I) is detected.

J. L. D.

Influence of sinomenine and parasinomenine on the excretion of total nitrogen, creatine, creatinine, ammonia, and urea in the urine of rabbits in comparison with the influence of quinine. Y. ARAKAWA (Folia Pharmacol. Japon., 1933, 16, No. 2, 182—193).—In large quantities (0.1—0.15 g. per kg.) all three drugs decrease the total N; urea, creatinine, and creatine are decreased in that (diminishing) order. Small quantities (0.05 g. per kg.) have no effect on the N.

CH. ABS.

Influence of sinomenine and parasinomenine on the excretion of total sulphur, neutral sulphur, total inorganic sulphur, and ethereal sulphuric acid in the urine of rabbits in comparison with the influence of quinine. Y. ARAKAWA (Folia Pharmacol. Japon., 1933, 16, No. 2, 194—206).—0.05 g. per kg. has no effect. > 0.1 g. per kg. decreases the total S; decrease in inorg. S is > that in neutral S. With > 0.15 g. per kg. there is a change in the form in which S is excreted.

CH. ABS.

[Physiological] activity of maize smut (*Ustilago maidis*). S. S. BARJAKTAROVIC and S. B. BOGDANOVIĆ (Arch. exp. Path. Pharm., 1933, 173, 381—387).—Subcutaneous injection of aq. extracts of fresh (but not of old) spores produces a mild hyperglycaemia (I) in rabbits. When extracts of either fresh or old spores are injected before or just after administration of adrenaline (II), the (I) due to (II) is partly or completely inhibited and the return of the blood-sugar to normal levels occurs more rapidly.

Hence the spores contain a substance which has an ergotamine-like action on the (I) due to (II).

F. O. H.

Effect of smoking on blood-carbon monoxide. H. B. HANSON and A. B. HASTINGS (J. Amer. Med. Assoc., 1933, 100, 1481).—In a small no. of individuals the % saturation of haemoglobin was for non-smokers and smokers, respectively, 1.5 and 3—4%.

CH. ABS.

Effect of intravenous administration of lecithin and sodium chloride on blood-sugar. D. E. GREGG (Amer. J. Physiol., 1933, 104, 344—346).—In dogs, injections of 100 c.c. of hypotonic saline increase the blood-sugar (I) up to a max. of 20% above the fasting level. Other saline solutions or 3% lecithin in saline have no effect on (I).

NUTR. ABS. (m)

Dependence of the action of oxytocic substances (histamine and ergotamine) on concentration and temperature. W. LIPSCHITZ and F. KLAR (Arch. exp. Path. Pharm., 1933, 174, 223—244).—The latent period, its temp. coeff., and the time of the contraction itself of the same guinea-pig uterus prep. with histamine (I) are markedly < those with the oxytocic pituitary principle (II). The temp. coeff. of the rapidity of contraction with (I), however, is approx. = that with (II). The concn.-activity curve of (I) resembles in some respects that of (II), the differences being more marked at 19—24° than at 37°. The contraction curve of ergotamine in general resembles those of (I) and (II), indicating that it induces pendulum- and not tetanus-motion of the uterus.

F. O. H.

Neosine. O. FLOSSNER and P. VON MILLER (Z. Biol., 1933, 94, 307—311).—Neosine has a choline-like action on blood-pressure, heart, uterus, and intestine (I). The activity on (I) is 2000 times that of choline and 400 times that of γ -homocholine.

R. K. C.

Substances that decrease blood-pressure. II. Yeast-nucleic acid. M. TOKI and T. MIYOSHI (J. Agric. Chem. Soc. Japan, 1933, 9, 705—714).—Aq. (Boehringer's) yeast Na nucleate, or the hydrolytic products of nucleic acid, when administered to rats by injection or orally, decreased the blood-pressure.

CH. ABS.

Blood-sugar-reducing properties of aqueous extract of brewers' yeast. L. BINET, R. FABRE, and D. BARGETON (Compt. rend. Soc. Biol., 1933, 113, 235—236).—The blood-sugar level of the depancreatized dog is reduced by injection of the extract.

NUTR. ABS. (m)

Action of halogenated substances on lactic acid fermentation in normal and cancerous animal tissues, *in vivo* and *in vitro*. J. BRISON (Compt. rend. Soc. Biol., 1933, 112, 1391—1393).—Non-toxic doses of CH_2BrCO_2H and other halogenated acids greatly diminish the production of lactic acid in rats' tissues (particularly kidney).

NUTR. ABS. (m)

Catalytic processes in the liver. F. DELHOUGNE (Arch. exp. Path. Pharm., 1933, 174, 88—91).—The icterus in dogs or rabbits due to ligation of the bile duct or to poisoning by P or tolylenediamine produces

a decrease in the total glutathione (I) of the liver (II) which is most marked when (II) has a low content of glycogen (III). Similarly, the levels of both (I) and (III) in (II) are diminished in phloridzin diabetes. Hence the catalytic processes of (II) are dependent on the carbohydrate content.

F. O. H.

Acceleration of tissue respiration by a nitrophenol. E. C. DODDS and G. D. GREVILLE (Nature, 1933, 132, 966).—4:6-Dinitro-*o*-cresol produces a large increase in the respiration of thin slices of surviving rat tissues when added in suitable concn. ($10^{-5}M$) to the medium supporting respiration. The respiration of kidney tissue in the presence of glucose is increased in HCO_3^- but not in PO_4^{4-} containing media.

L. S. T.

Diuresis. I. Assay of antidiuretic substances. H. MARX (Arch. exp. Path. Pharm., 1933, 173, 526—535).—A method of assay, based on the amount and NaCl content of urine excreted by rats suffering from excess H_2O dosage, is described.

F. O. H.

Absorption of salicylic acid after oral and rectal administration. W. BLUME and F. S. NOHARA (Arch. exp. Path. Pharm., 1933, 173, 413—430).—Following oral or rectal administration (rabbit), salicylic acid (I) appears in the urine within approx. 1 hr. and in the blood within 2 min. The total amount excreted varies from 50% to 80% of that administered. Traces of (I) are detectable in the blood 7—8 hr. after administration. The blood-(I) after administration of (I) into the mouth (cf. A., 1931, 1087), intestine, and rectum indicates that the rates of absorption from these sites are in the ratio of 3:6:8.

F. O. H.

Action of germanin. I, II. B. VON ISSEKUTZ (Arch. exp. Path. Pharm., 1933, 173, 479—498, 499—507).—I. Whilst neosalvarsan (I), trypanflavine, etc. diminish the respiration of *Trypanosoma Brucei* (II) *in vitro* and, with very dil. cultures, are lethal, germanin (Baeyer 205) (III) has no action. Also with (I) but not with (III), the serum of rabbits injected 24 hr. previously exhibits a trypanocidal action. *In vivo* (rats) injection of (III) eliminates (II) within 24 hr.; with (II) removed from such animals 9 hr. after injection, active movement is shown, but their respiration and glycolysis are depressed, their period of survival at room temp. (but not at body temp.) being, however, > that of the *in-vivo* (II). Hence (III) yields *in vivo* a substance trypanocidal only at body temp.

II. With infected rats treated with (III), (II) separated from the serum contains 0.005—0.0105% of (III), whilst the serum contains 0.024—0.042%. The O_2 consumption of (II) grown in serum-Ringer solution is not affected by (III), whilst the virulence is diminished but not totally eliminated.

F. O. H.

Gastric hunger-mechanism. IV. Influence of experimental alterations in blood-sugar concentration on the gastric hunger-contractions.

ARULINOS (Amer. J. Physiol., 1933, 104, 371—). In dogs with gastric fistulae spontaneous or experimental increases in blood-sugar (I) do not affect gastric motility. Insulin (II) given intravenously

decreases it temporarily and then increases it when (I) falls. This hypermotility (III) is depressed by oral or intravenous glucose. Starvation or diabetes causes (III). Adrenaline (temporarily) or atropine depresses the hyperactivity induced by food, starvation, saline injections, diabetes, and (II).

NUTR. ABS. (m)

Influence of vagotomy on stimulation-hyperglycaemia. F. HOGLER and F. ZELL (Arch. exp. Path. Pharm., 1933, 173, 674—679).—The hyperglycaemia (I) induced by adrenaline after either uni- (II) or bi-lateral vagotomy (III) is of more rapid onset and of longer duration than normal. The (I) due to pyrimidone or $MgSO_4$ is not affected by (II) or (III). Hence the influence of the vagi on insulin production appears to be over-emphasised.

F. O. H.

Influence of the nervous system on the sugar excretion threshold. M. B. HANDELSMAN and K. OBERDISSE (Arch. exp. Path. Pharm., 1933, 174, 81—87).—Complete denervation of the kidney in dogs has no effect on the alimentary glycosuria following injection of glucose, whilst the kidney threshold val. is unchanged.

F. O. H.

Influence of vago-sympathetic stimulation on the gaseous exchange in the lungs. H. BECKER, M. HOCHREIN, and K. MATTHES (Arch. exp. Path. Pharm., 1933, 173, 466—478).—In dogs, electric stimulation of the vago-sympathetic nerves increases the O_2 -saturation of the arterial blood. The mechanism of this phenomenon is discussed.

F. O. H.

Absorption of essential oils by the skin. H. PAFFRATH (Arch. exp. Path. Pharm., 1933, 174, 143—150).—Methods of determining essential oils (I) in expired air (II) or urine (III), based on Et_2O extraction and steam-distillation, are described. Inunction of the chest with a balsam containing (I) results in the appearance of significant amounts of (I) in (II) and, to a smaller extent, in (III).

F. O. H.

Chemistry of the production of oedema of the lungs after contact with poison gases. A. KLING (Compt. rend., 1933, 197, 1782—1784).—The presence of free cholesterol enables a fat to be penetrated by H_2O . Saturation (by Cl_2 or Br) and esterification (by $COCl_2$) destroy this property, and are responsible for the oedema of the lungs produced by the action of these gases.

P. G. M.

Permeability of animal membranes to aluminium salts. G. KARBEL (Arch. exp. Path. Pharm., 1933, 173, 697—709).—Aq. $AlCl_3$, $K_2Al_2(SO_4)_4$, and $Al(OH)(OAc)_2$ do not significantly permeate frog's or toad's skin, whilst aq. $AlCl_3$ or $Al(NO_3)_3$ permeates cat's intestine to only a slight extent. The permeability of aq. $AlCl_3$ is not markedly influenced by saponin, whilst that of neutral aq. Na Al tartrate is not appreciably increased by bile.

F. O. H.

Action of acute and chronic acid and alkali administration on the organism. E. RENTZ (Arch. exp. Path. Pharm., 1933, 173, 605—613).—The various effects of the administration of acid and alkali and their correlation with changes in the distribution of Ca in the organism are discussed.

F. O. H.

Influence of small amounts of arsenic on metabolism. F. DELHOUGNE (Arch. exp. Path. Pharm., 1933, 174, 77—80).—Rats receiving $1-3 \times 10^{-4}$ mg. of As daily for 14—20 days experience a decrease in body-wt. and an increase in liver- (I) and muscle-glycogen (II). No significant changes occur in the urine- or organ-N and in the liver- or muscle-fat. With toxic doses of As, (I) and (II) do not increase, whilst with acute As poisoning (I) diminishes.

F. O. H.

Catalytic action of iron. F. EICHHOLTZ and A. ORTEGA (Arch. exp. Path. Pharm., 1933, 174, 217—222).—When injection of aq. FeSO_4 or Na ferricitrate into mice is followed by that of normally harmless doses of Na pyrogalloldisulphonate, convulsions and other symptoms of toxicity appear. The degree of toxicity being parallel with the general catalytic action (I) of the administered Fe in the body, the phenomenon affords a method for the determination of (I). The normal body-Fe has no detectable (I).

F. O. H.

Pharmacology of indium. H. STEIDLE (Arch. exp. Path. Pharm., 1933, 173, 458—465).—The action of $\text{In}_2(\text{SO}_4)_3$, $\text{In}(\text{NO}_3)_3$, and InCl_3 was investigated. Rats tolerate oral administration of 2 g. of $\text{In}_2(\text{SO}_4)_3$ per kg. body-wt., but rabbits are killed by that of 1.3—2.0 g. per kg. The min. lethal dose by subcutaneous injection into rats is 0.15 g. per kg.

F. O. H.

Storage of halogens in hens' eggs and animal tissues. II. B. PURJESZ, L. BERKESY, and K. GONCZI (Arch. exp. Path. Pharm., 1933, 173, 553—557; cf. A., 1933, 979).—Small amounts (approx. 0.0001%) of Br normally occur in the tissues [greatest in muscle (I) and smallest in blood (II)] and eggs of hens. Intravenous injection of aq. NaBr into hens is followed by storage of Br in the liver, (I), (II), and especially in the brain, whilst the Br content of the eggs increases.

F. O. H.

Affinity between various parts of the brain and "physiological" amounts of bromine. A. BIER (Arch. exp. Path. Pharm., 1933, 173, 508—512).—Following oral administration of NaBr and Na monobromo-oleate (I) to rabbits, Br is found not only in the cerebral cortex but in the mid-brain, cerebellum, and medulla oblongata. For a definite amount of Br administered, the Br contents of the various parts of the brain are higher with (I) than with NaBr. This is probably due to the lipin-solubility of (I).

F. O. H.

Effect of fluorine on growth, calcification, and parathyroids in the chicken. H. M. HAUCK, H. STEENBOCK, J. T. LOWE, and J. G. HALPIN (Poultry Sci., 1933, 12, 242—249).—0.15% NaF in the diet produces no unfavourable effect; 1.2% is toxic. 0.6—1.2% lowered serum-Ca in young chicks. NaF has no significant effect on bone-ash, kidney-phosphatase, or size and structure of parathyroids.

CH. ABS.

Action of light on iodine in the atmosphere and in the organism.—See this vol., 155.

Physiological effect of heavy water and ice water. T. C. BARNES and E. J. LARSON (J. Amer. Chem. Soc., 1933, 55, 5059—5060; cf. A., 1933,

1329).—A filament of 31 cells of *Spirogyra nitida* in "heavy" H_2O (d 1.000061) (I) exposed to northern light at $10-14^\circ$ had 43 cells (3 dead) after 6 days; no cell division occurred in "ordinary" H_2O (II). In ice- H_2O (III) renewed twice daily, a filament of 50 cells showed 15 abnormal after 5 days; in freshly condensed H_2O , all the cells died. *Oscillatoria* spread more extensively in (I) probably owing to its p_{H} of 6.77. A solution of pancreatic amylase in (I) (which has been kept for 24 hr.) does not digest starch as readily as in (II). A 10% decrease in the amount of CO_2 evolved during fermentation with zymase [exposed to (I) for 66 hr.] is found. Oxidation of guaiaconic acid (IV) by the peroxidase-oxygenase system is increased if the solution is made in fresh (III) and allowed to warm to room temp. When a solution of (IV) and peroxidase is frozen, oxidation occurs when the ice melts.

H. B.

Intervention of thermal phenomena in the biological action of ultrasonic (vibrations). E. BIANCANI, H. BIANCANI, and A. DOGNON (Compt. rend., 1933, 197, 1693—1695).—When submitted to ultrasonic vibrations in a const.-temp. bath, fats and lipins (e.g., tap-grease, liver, brain matter) exhibit a considerable rise in temp., whereas no such increase is observed with sols and gels (agar, ovalbumin).

J. W. B.

Catalysis of hydration of carbon dioxide and dehydration of carbonic acid by an enzyme isolated from erythrocytes. W. C. STADIE and H. O'BRIEN (J. Biol. Chem., 1933, 103, 521—529).—The velocity coeffs. for the hydration, k_{CO_2} , and dehydration of CO_2 , $k_{\text{H}_2\text{CO}_3}$, are determined by mixing solutions of $\text{HPO}_4^{''}$ and CO_2 and solutions of NaHCO_3 and AcOH buffer all saturated with quinhidrone, and observing the p_{H} at different times with a calomel electrode. The enzyme is prepared by adding a 3 : 1 $\text{EtOH}-\text{CHCl}_3$ mixture and then 95% EtOH to the diluted cells, and extracting the evaporated filtrate with 50% EtOH . KCN and heating at 70° inactivate the enzyme. In a $\text{HPO}_4^{''}-\text{CO}_2$ mixture, addition of washed corpuscles or the enzyme prep. increases k_{CO_2} , linearly with the concn. The effect of the enzyme on k_{HCO_3} is approx. 38% of that on k_{CO_2} , and is less the greater is the concn. of CO_2 in the substrate.

H. D.

Yeast-catalase. M. MATSUYAMA (J. Fac. Agric. Hokkaido, 1933, 32, 109—199).—Bottom- and top-yeast catalase, respectively, had optimum p_{H} 6.6, 6.3; optimum temp. for 15—20 min. reaction 15° , 22° ; optimum p_{H} for max. heat-stability 7.0, 6.8; inactivation temp. (1 hr.) 55° , 55° . Aeration in the early stages of growth increased the catalase in both.

CH. ABS.

Digestibility of raw starch. E. POZERSKI (Bull. Soc. sci. Hyg. aliment., 1933, 21, 1—29; Chem. Zentr., 1933, ii, 1368).—Heated, but not raw, starch is digested by saliva and pancreatic juice. Raw starch can be digested with the aid of large quantities of amylase. Comminution produces a digestible substance.

A. A. E.

Physiological importance of mineral elements in plants. VI. Influence of potassium chloride on rate of diastatic hydrolysis of starch. W. O. JAMES and M. CATTLE (Biochem. J., 1933, 27, 1805—

1809).—The rate of destruction of Lintner's starch by enzyme extracts from potato tubers (I), sprouts, and large shoots is increased in all cases by 5% KCl, whereas sugar formation is increased only in the case of (I). Sugar formation from dextrin is uninfluenced by KCl in all cases. The hydrolysis of starch involves two enzymes, only one being activated by KCl.

H. D.

Amylases. VI. Mechanism of activation of the ampholytic action of pancreatin by ethylamine hydrochloride. F. CAUJOLLE and S. LAFITE (Bull. Sci. pharmacol., 1933, 40, 213—219; Chem. Zentr., 1933, ii, 1691).—Salts or salt mixtures containing free Na^+ or NH_4Et^+ ions as well as Cl^- activate the amylolytic action of pancreatin.

A. A. E.

Amylosynthase. XIV, XV. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 688—692, 740—744).—XIV. Amylosynthase (I) polymerises dextrin from malt amylase, but not that obtained by heating starch. β -Glucosidomaltose is polymerised by (I) to a non-reducing substance.

XV. Lower-mol. dextrin was acetylated and then deacetylated; the product was polymerised by (I) to a substance giving a bluish-white colour with I-KI. The hydrolytic products of amylopectin, but not of amylose, was polymerised by (I). CH. ABS.

Enzymic hydrolysis of maltose- and lactose-carboxylic acids. P. PRATESI (Biochem. Z., 1933, 267, 238—242).—The acids $\text{C}_{13}\text{H}_{21}\text{O}_{13}$ (Ba and Na salts) are hydrolysed, the first to glucose by maltase from yeast to the extent of 40% (32% in 48 hr.), the second to galactose by *Saccharomyces fragilis* (38% in 48 hr.) and by emulsin (30%).

W. McC.

Phosphatase content of the whole rat and of the vasoligated kidney. F. W. KINARD and A. CHANUTIN (J. Biol. Chem., 1933, 103, 461—470).—Phosphatase (I) in the whole rat increased from birth to a max. in 13—20 days, when it decreased to remain const. after about 60 days. Irradiated ergosterol caused an increase after 15—20 days, but had no effect on the adult rat. Ligation of the kidney caused an immediate decrease in (I), which reached zero after 16 days.

H. G. R.

Kinetics of the action of kidney-phosphatase. II. E. JACOBSEN (Biochem. Z., 1933, 267, 89—101; cf. A., 1932, 882).—Between p_{H} 6.9 and 9.2 the rate (I) of hydrolysis by the phosphatase varies with the concn. of enzyme, substrate, and phosphate (II) as expressed in a formula given. (II) causes a relative (III) and an abs. (IV) inhibition, (III) being dependent on the ratio substrate:orthophosphate. As $[\text{H}^+]$ decreases (IV) decreases, but (III) increases. To a certain limit (I) increases with increasing substrate concn.; at 9 the increase is great, whilst at 8.5 it is scarcely perceptible.

W. McC.

Kinetics of ester hydrolysis by enzymes. V. Behaviour of esterases towards acid anhydrides such as lactic acid lactide and lactyl-lactic acid. Cause of the relative specificity of lipases. E. BAMANN, E. SCHWEIZER, and M. SCHMELLER (Z. physiol. Chem., 1933, 222, 121—130; cf. A., 1931, 392).—Lactide and (less readily) glycolide are

hydrolysed by esterase to the ester anhydride stage, whereas diphenylglycolide, benzilide, tetra- and polysalicylide are not attacked owing to lack of affinity between the enzyme and these substances. No intermediate compounds are formed with the simple ester anhydrides lactyl-lactic, acetylmandelic, acetyl- and salicylo-salicylic acids. The hydrolysis of Ph esters of aromatic acids is even slower than that of Me and Et esters. The enzyme-binding power of the ester group of a substrate is controlled by the electrochemical nature of the adjacent groups. J. H. B.

Comparison of esterases from human pancreas and liver. R. AMMON and E. TABOR (Biochem. Z., 1933, 267, 26—31).—Human pancreas-esterase (I) preferentially hydrolyses the *l*-form in *dl*-Me and *dl*-Pr mandelates, but its action is not affected by addition of strychnine or by the initial concn. of the substrate. (I) synthesises Bu butyrate and oleate from their constituents. Heat alters the specificity of (I). In a mixture of (I) with human liver-esterase (I) acts independently on Me mandelate.

W. McC.

Directive influences in biological systems. III. Effect of proteases on lipase actions. K. G. FALK (J. Biol. Chem., 1933, 103, 363—372).—Lipase action was decreased in every case by trypsin. Papain was variable in its effect, giving decreased actions with esters other than glyceryl triacetate (I). The addition of inactive proteins greatly increased the hydrolysis of (I).

H. G. R.

Are there two separate enzymes—rennin and pepsin? I. S. KLEINER (Hahnemannian Monthly, 1933, 68, 610—613).—A conc. rennin, 1 part of which coagulates 1.45×10^6 parts of skimmed milk, has no proteolytic power; it differs from cryst. pepsin in behaviour on dialysis, and response to pptn. and colour reactions. Apparently rennin is a thioprotease and pepsin a simple protein.

CH. ABS.

Adsorption of pepsin on tricalcium phosphate. L. UTKIN (Biochem. Z., 1933, 267, 64—68).—The pepsin of fresh autolysed gastric mucous membrane is preferentially adsorbed by suspensions of $\text{Ca}_3(\text{PO}_4)_2$ at p_{H} 5.0—5.5, although the adsorption is independent of the concn. of the enzyme and separation from impurities is incomplete.

W. McC.

Ultracentrifugal study of crystalline pepsin. J. ST. L. PHILPOT and I. B. ERIKSSON-QUENSEL (Nature, 1933, 132, 932—933).—The velocity method gives a sedimentation const. (I) of $3.3 \pm 0.15 \times 10^{-13}$, and the equilibrium method a mean mol. wt. of 35,500. Comparison of these vals. shows that the pepsin (II) mol. is spherical. Northrop's cryst. pepsin thus belongs to the same class of proteins as ovalbumin, Bence-Jones protein, and insulin. The homogeneity of the preps. was determined by the ultracentrifuge. Exposure of (II) to *N*-HCl for 10 min. followed by 0.1*N*-HCl + 0.1*N*-NaCl had little effect on (I), indicating that a low p_{H} has no instantaneous effect on mol. wt., but causes only slow acid hydrolysis. Exposure to p_{H} 9 for 10 min. produces approx. 50% of an aggregate having a (I) of approx. 12.

Heat-inactivation of crystalline pepsin ; critical increment of the process. W. J. LOUGHLIN (Biochem. J., 1933, 27, 1779—1788).—Heat-inactivation (I) of pepsin is unimol. and varies with the p_H , having a min. at p_H 3—4.5. Temp. has a very marked effect, the crit. increment (II) being of the order 80,000 g.-cal. (II) varies with the p_H and is max. (96,000 g.-cal.) where (I) is min. (I) is analogous to the heat-denaturation of proteins, except in the location of the min. speed. H. G. R.

Isolation of a crystalline protein from pancreas and its conversion into a new crystalline proteolytic enzyme by trypsin. M. KUNITZ and J. H. NORTHROP (Science, 1933, 78, 558—559).—Fresh pancreas is extracted with $M/8\text{-H}_2\text{SO}_4$. The extract (I) has no measurable proteolytic activity but becomes highly active when enterokinase (IV) or relatively large amounts of trypsin (V) are added. (I) contains a protein (III), called chymo-trypsinogen, sol. in 0.4 saturated $(\text{NH}_4)_2\text{SO}_4$ (II), but insol. in 0.7 saturated (II). (III) can be crystallised from (II) at p_H 5.0. It cannot be activated by (IV), but becomes very active when a small amount of (V) is added. The crude (I) and the mother-liquor from crystals of (III) are completely activated by (IV), but not by small amounts of (V), owing to the presence of an inhibitor. (IV) forms sufficient active (V) to overcome this inhibition. The active protein formed from (III), chymo-trypsin, has been crystallised. L. S. T.

Preparation of protaminase. E. WALDSCHMIDT-LEITZ and E. KOFRANYI (Z. physiol. Chem., 1933, 222, 148—150).—Protaminase (I) (A., 1931, 984) is freed from tryptic proteinase (II) by pptn. of the peptidase-free mixture with COMe_2 in presence of ovalbumin (III). (II) is pptd. with the (III), leaving (I) in solution. The activity of (I) is not increased by added enterokinase. J. H. B.

Muscle autolysis. III. Changes in reaction, surface tension, viscosity, and refraction. I. A. SMORODINCEV, N. V. SCHIROKOV, and N. N. KRYLOVA (Biochem. Z., 1933, 267, 18—21; cf. this vol., III).—During autolysis the p_H of muscle (I) falls, reaching a min. after 24 hr., but the η of (I) extracts (II) remains unaltered. The η of (II) reaches a min. and the γ a max. in 12—24 hr. after death. Change of temp. (4—25°) during storage slightly checks the fall of p_H and causes slight decrease in γ and increase in η ; the ratio $\eta : \gamma$ remains unchanged. The coeff. of the ratio $p_H : \gamma$ reaches a min. between the 12th and 24th hr. W. McC.

Activation of arginase. E. WALDSCHMIDT-LEITZ and W. KOCHOLATY (Naturwiss., 1933, 21, 848).—Whilst arginase is partly inhibited by $\text{Fe}^{II} + \text{cysteine}$ (I) in H_2 and, to a smaller extent, by $\text{Fe}^{III} + \text{cystine}$ in air, it is accelerated by labile systems, e.g., $\text{Fe}^{III} +$ (I) in air (cf. A., 1932, 85; 1933, 315). This activation, which is optimal at p_H 5 and appears to be due to an oxidation rather than a reduction process, is also effected by Fe-alloxan or oxyhæmoglobin, but not by methæmoglobin. Oxidation-reduction systems may play a part in intracellular proteolysis. F. O. H.

Action of metals on enzymes. III. M. JACOBY (Biochem. Z., 1933, 267, 167—168; cf. A., 1933, 865).

—No irreversible oxidative destruction of urease (I) occurs when it is shaken in air with Se or Se compounds. The inactivation of (I) by metals is probably due to production of inactive complex compounds. W. McC.

Influence of preservatives on enzymic reactions. B. BLEYER, W. DIEMER, and K. LEONHARD (Arch. Pharm., 1933, 271, 539—552).—The inhibitory influence of a no. of preservatives on the action of amylase, pepsin, trypsin, lipase, the dehydrase of muscle, and crude peroxidase varies widely. $(\text{CH}_3)_6\text{N}_4$ and H_2O_2 are generally ineffective, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $o\text{-CO}_2\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2$ most effective. Some substances are in certain cases activators. R. S. C.

Effects of radiations from a mercury-vapour arc in quartz on enzymes. H. J. FULLER (Ann. Missouri Bot. Gard., 1932, 19, 505—531).—Taka-diastase and Difco invertase are partly inactivated. Injury of bean and tomato plants by ultra-violet rays increases the activity of amylase, invertase, peptase, and catalase. When mycelium of *Fusarium lini*, Bolley, is killed by ultra-violet rays there is no effect or a slight increase in the activity of amylase and peptase. CH. ABS.

Effects of monochromatic light on fermentation products of yeast. II. R. MURAKAMI (J. Agric. Chem. Soc. Japan, 1933, 9, 672—679).—EtOH production was max. at 6130 Å., and of MeCHO at 4000—5500 Å. Ester production was generally high at long λ . In the first stage of the fermentation much acid was produced at long λ ; the reverse held in the last stage. CH. ABS.

Butylene glycol as a fermentation product. J. ŠTASTNÝ (Vestník českoslov. Akad. Zemed., 1932, 8, 687—692; Chem. Zentr., 1933, i, 1861).—The oxidation method with Ni dimethylglyoxime reveals only traces of $\beta\gamma$ -butylene glycol (I) in distillery mash, chiefly that of potatoes. Fellenberg's method (II) gives higher vals. which, however, do not correspond with (I). (II) is thus unsuitable and previous statements concerning the ratio between (I) and glycerol (III) are untrustworthy. The (III) content in (I) varies between limits wider than 1 : 3. L. S. T.

[Fermenting power of] yeast maceration juice. A. C. VAN WIJK and F. M. MULLER (Biochem. Z., 1933, 267, 102—118).—The fermenting power (I) of bottom yeast depends on the treatment which it has undergone, being greater when kept at 1° for 24—48 hr. after pressing than when used at once. Increased duration of maceration (II) has a very favourable effect on (I) in initially poor samples. Destructive proteolysis does not occur during (II) of ordinary duration, but in very long-continued (II) the zymase is destroyed by proteolytic enzymes. Anti-proteolytic power (III) is conferred on (II) juice by boiling, and addition of boiled juice results in increased rate and extent of fermentation. Hexose diphosphate, which has no (III), increases the rate, but not the extent. W. McC.

Utilisation of pentoses by the yeast *Oospora* No. 208. E. A. PLEVAKO and N. I. ALTOVSKAYA (Schr. zentr. biochem. Forschungsinstit. Nahr.-

Genusssm., Moscow, 1932, 2, 212—220).—According to time and temp., 40—99% of xylose is utilised. Without aeration oxidation proceeds to CO_2 ; with aeration 10% each of EtOH and glycerol are formed. CH. ABS.

Carotenoids of red yeast. E. LEDERER (Compt. rend., 1933, 197, 1694—1695).—Differential absorption from a ligroin extract of the unsaponifiable pigment of *Torula rubra* by Al_2O_3 affords β -carotene, a new carotenoid hydrocarbon *torulene*, decomp. 180° (bands at 566, 522, 491, and 461 m μ in CS_2), and a third unstable hydrocarbon, not obtained pure. A fourth acidic or lactonic carotenoid (600—535 m μ in CS_2), sol. in alkaline EtOH and closely resembling astracene, is also present. J. W. B.

Concentration of ionisable benzene derivatives by yeast-cells and the spontaneous conversion of salicylic acid. F. AXMÄCHER (Arch. exp. Path. Pharm., 1933, 173, 722—736).—The adsorption (I) of C_6H_6 derivatives (II) by yeast-cells is proportional to their degree of dissociation and to the $[\text{H}^+]$ of the medium, the acidic (II) being more readily adsorbed in acid and the basic more readily in alkaline media. The extent of (I) is not related to the partition of the substance between olive oil and H_2O . The (I) of $\text{o-HO-C}_6\text{H}_4\text{-CO}_2\text{H}$ (III) is not proportional to its initial concn., being relatively lower at lower concns., whilst with dead cells (I) is considerably lowered. With (III), (I) is reversible and produces a liberation of NH_3 in the medium, probably from hydrolysis of CO-NH_2 groups of complexes of the cell-wall proteins or by ionic exchange with intracellular NH_3 . Multivalent anions and cations respectively inhibit and increase (I). F. O. H.

Products of fermentation of the *Mucor* group. II. Products of fermentation in the presence of calcium carbonate. T. TAKAHASHI and T. ASAI (Zentr. Bakt. Par., 1933, II, 89, 81—84).—Of five species examined four produced, from glucose, MeCHO, EtOH, AcCO_2H (one exception), succinic acid, and traces of lactic acid (one exception). A. G. P.

Products of fermentation by *Penicillium*. G. IITTO (J. Agric. Chem. Soc. Japan, 1933, 9, 552—562).—Oxalic, citric, gluconic, glycuronic, fumaric, l-malic, and succinic acids were found. Some varieties produce a yellow material, separable with CHCl_3 into a sol. yellowish-brown substance, m.p. $92-94^\circ$, and an insol. reddish-brown substance, m.p. $226-229^\circ$. CH. ABS.

Biochemistry of micro-organisms. XXXV. Metabolic products of *Byssoschlamys fulva*. Olliver and Smith. H. RAISTRICK and G. SMITH (Biochem. J., 1933, 27, 1814—1819).—*B. fulva* grown on Czapek-Dox solution at 24° produces *byssoschlamic acid*, $\text{C}_{18}\text{H}_{20}\text{O}_6$, m.p. 163.5° , $[\alpha]_{\text{D}}^{25} +127^\circ$ in CHCl_3 , a tetrabasic acid, toxic to mice; the main metabolic product is mannitol in amounts up to 30% of the glucose utilised. H. D.

Fermentation products of moulds. X. *Aspergillus glaucus*. 4. Y. SUMIKI (J. Agric. Chem. Soc. Japan, 1933, 9, 714—716).—A monobasic acid, "glaucic acid," $\text{C}_{17}\text{H}_{22}\text{O}_5$, m.p. $237-238^\circ$, containing no OH or OMe, was found. CH. ABS.

Reaction of *Aspergillus repens* on ammonium nitrate: production of ammonia. D. BACH and D. DESBORDES (Compt. rend., 1933, 197, 1772—1774).—In a medium of initial p_{H} 1.89 the mould liberates NH_3 at the expense of the NO_3 of NH_4NO_3 , the reaction attaining a max. at about p_{H} 5.0. As the medium becomes more alkaline, NH_3 again begins to penetrate the cells. P. G. M.

Nutritive value of the mycelium of moulds. J. T. SKINNER, W. H. PETERSON, and H. STEENBOCK (Biochem. Z., 1933, 267, 169—178).—The moulds (I) (*A. fischeri*, *A. oryzae*, *A. sydowi*, and *P. chrysogenum*) are not markedly toxic to rats, but their N contents, although assimilable, are inadequate for maintenance of life and growth. The mycelium of (I), given in amounts of $\leq 20\%$ of the diet, contains sufficient vitamin-B to prevent polynneuritis and maintain growth. W. McC.

Amylopectin as a nutrient medium for moulds. H. HÄRDTL (Biochem. Z., 1933, 267, 6—10).—Amylopectin serves well as a C source (I) for the growth of *Aspergillus niger* (II), little acid being produced. The assimilation of N depends as to extent and course on (I). In the degradation of starch by (II) it is chiefly the grains which are attacked; the more resistant envelope is attacked later. W. McC.

Effect of vitamins on the growth of fungi in pure culture. W. G. SOLHEIM, S. S. SEARS, and R. C. ROLLINS (Phytopath., 1933, 23, 929—930).—Addition of vitamins- B_1 and $-B_2$ to culture media increased the fructification of certain fungi and in the case of *Aspergillus niger* and *Penicillia* induced yellow pigmentation. A. G. P.

Effect of vitamins on the reproduction and toxin formation of diphtheria bacilli. I. ANNÓK and J. BUCHGRABER (Magyar orvosi Arch., 1933, 34, 220—223; Chem. Zentr., 1933, ii, 1535).—Toxin formation is increased by vitamins, particularly by $-B$ and least by $-A$. Colonv size was less affected. A. A. E.

Growth of *Clostridium botulinum* on synthetic media. W. BURROWS (J. Infect. Dis., 1933, 52, 126—137).—Cystine, leucine, and proline are essential; lysine and glycine are active in growth promotion, but not essential. Leucine and proline can be replaced by isoleucine and hydroxyproline. *C. welchii*, *C. chauvaxi*, *C. sporogenes*, *C. histolyticum*, and *C. tetani* did not grow on the medium. CH. ABS.

Relation of gastrointestinal poison to other toxic substances produced by staphylococci. O. C. WOOLPERT and G. M. DACK (J. Infect. Dis., 1933, 52, 6—19).—A gastrointestinal poison, a hæmolysin, dermatotoxin, and killing toxin were produced when the organisms were grown on a semi-solid medium in a partial CO_2 atm. CH. ABS.

Acidity produced in *Brucella* cultures. S. H. McNUTT and P. PURWIN (J. Infect. Dis., 1931, 48, 292—294).—Broth or peptone solution without sugar became strongly alkaline. When glucose (I), fructose (II), galactose (III), xylose (IV), or arabinose (V) was added the medium still became alkaline. When (I)—(IV) was added to nutrose solution *Brucella* pro-

duced acid; with (V) the quantity was greater. When sugar is the only source of C, growth took place in (IV) and (V). CH. ABS.

Delayed sugar utilisation by bacteria. A. G. WEDUM (Proc. Soc. Exp. Biol. Med., 1933, 30, 693—695).—Certain organisms grow in carbohydrate liquid media for several days without utilising sugar (I); sudden utilisation of (I) was accompanied by decrease in p_H . CH. ABS.

Influence of the origin of bacterial strain on the amount of nitrogen in aerobic cultures. M. LEMOIGNE and R. DESVEAUX (Compt. rend., 1933, 197, 1697—1699).—The loss of (Kjeldahl) N caused by bacteria in peptone media (A., 1926, 979) is irregular. This effect is the smaller the longer is the period during which the strain has been conserved on sugar-gelose. J. W. B.

Mechanism of respiration of pneumococci. II. M. G. SEVAG (Biochem. Z., 1933, 267, 211—237; cf. A., 1933, 1333).—At first at p_H 8 all the O_2 absorbed is converted into H_2O_2 , which then reacts with $AcCO_2H$ to give $AcOH$, H_2O , and CO_2 , and in another way. Results obtained by adding $AcCO_2H$, catalase, and KCN confirm those previously obtained, and, with other evidence, permit distinction between virulent and non-virulent types as well as between members and different strains of the same type. W. McC.

Dehydrogenases of *Bacterium coli*. I. Effect of dilution; existence of a co-enzyme of glucose dehydrogenase. J. YUDKIN (Biochem. J., 1933, 27, 1849—1858).—The product, activity \times dilution, is const. (within certain limits) for formic- (I) and succinic- (II), but not for glucose-dehydrogenase (III) of *B. coli* (cf. A., 1924, i, 913; 1925, i, 1015, 1217). (I), (II), and (III) are not affected by keeping for 1 hr. at 40°; (I) is unaffected by 5 hr. with methylene-blue (IV) or 1 hr. with $PO_4^{'''}$ buffer (V). (II) is slowly poisoned to an extent of 40% by (IV), especially in presence of (V) or succinate, and (III) to an extent of 80% by (IV), especially in presence of (V) or glucose. The action of PhMe and of Ag⁺ indicates that the acceleration of (III) by glucose is due to the production of H donators from glucose by activation by *B. coli*. The accelerating action by heated *B. coli* on the reduction indicates the presence of a thermostable co-enzyme of (III). F. O. H.

Dehydrogenase activity of *B. coli communis* on higher aliphatic acids. F. P. MAZZA and A. CIMMINO (Atti R. Accad. Lincei, 1933, [vi], 17, 1086—1091).—Stearic acid and, to smaller extents, oleic and palmitic acids are rapidly dehydrogenated by *B. coli*. As the mol. wt. increases in the aliphatic acid series, the velocity of the action falls up to the C_6 — C_9 members, and later increases. As regards the action of F⁺ and CN⁻, and the influence of p_H , the bacterial enzyme behaves similarly to that of the liver. The velocity is proportional to the no. of bacteria present. If the bacteria are killed by PhMe, the action ceases after a relatively short time (cf. Mazza and Stolfi, A., 1933, 747). T. H. P.

Bacterial production of histamine from *l*-histidine. K. HIRAI (Biochem. Z., 1933, 267, 1—5).

—Strains of *B. coli* which produce tyramine from tyrosine (and one strain which produced $p\text{-OH}\cdot C_6H_4\cdot C_2H_4\cdot CO_2H$ from tyrosine) produce small amounts of histamine (I) from *l*-histidine (II) [0.9 g. of (I) hydrochloride from 10 g. of (II)]. W. McC.

Production of hydrogen peroxide by *Bacillus bulgaricus*. C. FROMAGEOT and J. ROUX (Biochem. Z., 1933, 267, 202—203; cf. A., 1933, 1206; Bertho and Glück, A., 1932, 654).—In presence of O_2 , production of H_2O_2 accompanies the fermentation (I) of glucose by *B. bulgaricus*, the amount of H_2O_2 increasing with that of O_2 . (I) is brought to an end by accumulation of H_2O_2 . W. McC.

Enzymic formation of hydrogen sulphide by certain heterotrophic bacteria. H. L. A. TARR (Biochem. J., 1933, 27, 1869—1874).—Yields of H_2S > 75% are obtained from cultures of *Proteus vulgaris* (I) and *Serratia marcescens* (II) when cysteine (III), cystine, and compounds of these are used as substrates. Substituted (III) compounds and α -thiol-carboxylic acids yield only small amounts, other org. S compounds examined giving no H_2S . S as substrate gives small amounts of H_2S , neither $SO_3^{''}$ nor $SO_4^{''}$ is reduced, and $Na_2S_2O_3$ gives H_2S with (I), but not with (II). The production of H_2S from (III) is possible in the case of aerobes, facultative anaerobes, and strict anaerobes, but is not effected by *S. lutea*. A. L.

Nutrition of trypanosomides and hæmophilic bacteria: Baudisch's "active iron." M. LWOFF (Ann. Inst. Pasteur, 1933, 51, 707—713; cf. A., 1933, 983).—Protohæmin (or protoporphyrin) is indispensable for the multiplication of *Strigomonas fasciculata*; it cannot be replaced by deuterio- or meso-hæmin, by hæmato- or meso-porphyrin, or by Baudisch's "active Fe" (I). It seems doubtful if (I) can play any role in the nutrition of hæmophilic organisms. A. W.

Trypano-agglutinins and -lysins and their production with killed trypanosomes. L. REINER and S. S. CHAO (Amer. J. Trop. Med., 1933, 13, 525—534).—Rats immunised with vaccines prepared by the action of *p*-benzoquinone or neoarsphenamine on *T. equiperdum* (I) show a marked but not abs. immunity to (I). The serum of these immunised rats agglutinated, and if sufficient complement was present, dissolved, (I). A marked parallelism between agglutinating and sensitising (lytic) powers indicates that the same antibody is responsible for the two functions. A. W.

Fluorescence of synthetic pyocyanine. C. DHÉRE (Compt. rend., 1934, 198, 126—128).—Pyocyanine and its hydrochloride (I), which do not fluoresce in aq. or buffered solutions, develop intense green fluorescence (in violet or ultra-violet light) when reduced (various reagents), especially in alkaline solution, fluorescence in visible light being observed in the aq. layer after shaking with $C\text{-}H_{11}\text{-OH}$. α -Hydroxyphenazine behaves similarly. J. W. B.

Evidence of the particulate nature of bacteriophage. R. F. FEEMSTER and W. F. WELLS (J. Exp. Med., 1933, 58, 385—391).—Bacteriophage closely

follows the laws of chance distribution of particles in suspension. CH. ABS.

Selective action of crystal-violet and of brilliant-green on bacteriophages. A. Y. WELLS and N. P. SHERWOOD (J. Infect. Dis., 1933, 52, 209—213). CH. ABS.

Refractometric examination of purified antitoxins. C. SIEBENMANN (Biochem. J., 1933, 27, 1745—1752).—Globulins (I) and total solids may be determined in antitoxins (II) by a single refractometer reading. (II) of diphtheria, tetanus, scarlet fever, and erysipelas did not alter the n of (I) solutions. H. G. R.

Lithium chloride media for preservation and recovery of the typhoid bacillus in faeces. L. C. HAVENS and C. R. MAYFIELD (J. Infect. Dis., 1933, 52, 157—166).—Advantages are described. CH. ABS.

Illuminated counting chamber for plate cultures. A. T. R. MATTICK and E. R. HISCOX (J. Sci. Instr., 1933, 10, 373—376).—"Daylight" electric lamps are used. C. W. G.

Germicidal action of 2-chloro-4-*n*-alkylphenols.—See this vol., 183.

Energetic basis of endocrine actions. IV. Role of the growth hormone in the metabolism of liver and kidneys. M. REISS, A. HOCHWALD, and H. DRUCKREY (Endokrinol., 1933, 13, 1—4; Chem. Zentr., 1933, ii, 1696).—The O_2 requirement of liver- and kidney-tissue of young rats is diminished by hypophysectomy. Injection of growth hormone produces normal or high vals. Anaerobic glycolysis increases; in the liver aerobic glycolysis is observed. The prep. of the hormone is described. A. A. E.

Action of thyroxine, di-iodothyronine, and di-iodotyrosine on the gaseous metabolism of normal and castrated rats. L. DE CARO and M. GIANI (Arch. exp. Path. Pharm., 1933, 173, 398—404).—The differences between the actions of thyroxine and di-iodothyronine on gaseous metabolism (I) are most marked with small doses, the duration of action being more significant than the max. val. attained. Di-iodotyrosine produces a slight increase in (I) followed by a fall to subnormal vals. Negative variations in (I) are produced by all three substances, the effects of which are diminished by castration. F. O. H.

Influence of hormones on the metabolism of surviving thyroid tissue. H. PAAL (Arch. exp. Path. Pharm., 1933, 173, 513—525).—Thyroid tissue (I) of normally fed guinea-pigs (II) has an average val. of Q_{O_2} = 8.2—7.35, an R.Q. = 1.1, and exhibits neither aerobic nor anaerobic glycolysis. The metabolism of (I) is increased by approx. 200% with (II) previously treated with anterior pituitary (III) or thyroxine preps. (IV), whilst prolactin and preps. of castrin, posterior pituitary gland, vitamin-A, and carotene are inactive. (III) and (IV) also increase the metabolism of (I) on addition *in vitro*. The metabolism of (I) once activated by (III) or (IV) *in vivo* is not changed by further treatment *in vitro*. F. O. H.

Standardisation of thyroid preparations. G. ROTTER and E. SOOS (Arch. exp. Path. Pharm., 1933, 173, 614—621).—The analytical method of Leland and Foster (A., 1932, 432) fails to give trustworthy vals.; that of Harington and Randall (A., 1930, 504) is satisfactory. F. O. H.

Detoxification of the thyroid hormone by metals and natural springs. E. HESSE (Klin. Woch., 1933, 12, 1060—1061; Chem. Zentr., 1933, ii, 1384).—Medicinal water from Bad Kudowa has a similar protective action to metallic salts in respect of thyroid intoxication in dogs. The effect is due chiefly to the Fe and As. A. A. E.

Total and thyroxine-iodine content of thyroid gland after injection of saline anterior pituitary extracts. G. L. FOSTER, A. B. GUTMAN, and E. B. GUTMAN (Proc. Soc. Exp. Biol. Med., 1933, 30, 1028—1032).—Intraperitoneal injections of saline anterior pituitary extract cause decrease in total I content of the thyroid gland of the sheep, with a proportionate decrease in thyroxine. NUTR. ABS. (m)

Diabetes-producing effect of anterior pituitary extract. B. A. HOUSSAY (Klin. Woch., 1933, 12, 773—775).—Daily administration of 7 c.c. per kg. of alkaline extract (I) of the anterior lobe of the pituitary (1.5 g. fresh gland) produces, within 3—7 days, hyperglycaemia (II), glycosuria, and acetonuria in fed dogs. The same effect is produced by (I) after the removal of the pituitary or the thyroid or both. Blood-sugar returns to normal within 2—3 days after stopping (I) or when the dogs fast. In fasting dogs (I) causes no (II). After partial pancreatectomy, smaller doses of (I) suffice to produce similar changes. NUTR. ABS. (m)

Standardisation of posterior pituitary extracts. K. SCHÜBEL and W. GEHLEN (Arch. exp. Path. Pharm., 1933, 173, 633—641).—A method is described for the assay of extracts depending on the constancy of the min. dose per kg. necessary to produce contraction of the uterus (*in situ*) of cats 2—4 days *post partum*. A standard pituitary extract is not necessary and an accuracy of $\pm 15\%$ is claimed. F. O. H.

Assay of the oxytocic principle of commercial posterior pituitary preparations. K. SCHÜBEL and W. GEHLEN (Arch. exp. Path. Pharm., 1933, 173, 642—651).—The assay (cf. preceding abstract) of eleven commercial preps. indicated only one of the strength claimed. F. O. H.

Complexes containing oxytocic principle. K. SCHÜBEL and W. GEHLEN (Arch. exp. Path. Pharm., 1933, 173, 652—661).—Admixture of quinine (I) with pituitary extracts (II) approx. doubles the oxytocic activity, whilst the pressor action is inhibited, the complex slightly diminishing the blood-pressure. Combinations of "gravitol" with (I) or (II) exhibit no additive or synergising effects. The absorption of (I) appears to be accelerated by (II). F. O. H.

Lack of maturity hormone in the pituitary of the infantile rat. O. SWEZY (Nature, 1933, 132, 898).—A discussion. L. S. T.

Influence of a decrease or an increase in blood-calcium on the action of pituitrin, secacornin, and hydrastine on the uterus. F. YAGI (*Folia Pharmacol. Japon.*, 1933, 16, No. 2, 113—125).—The action is diminished; it is not similar to that of adrenaline. CH. ABS.

Effects of adrenalectomy and cortico-adrenal extract on renal excretion and tissue-fluids. H. SILVETTE and S. W. BRITTON (*Amer. J. Physiol.*, 1933, 104, 399—411).—In bilaterally adrenalectomised rats (I) which lost wt. there was a normal phenol-sulphonaphthalein excretion, but lowered H_2O excretion (II), which was more striking after H_2O injections. Excretion of urea and chlorides ran parallel with that of H_2O ; small injections of urea proved fatal. The H_2O content (III) of the liver and muscles of (I) was $>$ that of controls, the (III) of the blood lower, and that of the skin and brain the same. Probably (II) is not renal in origin.

NUTR. ABS. (m)

Influence of protein amino-acids on adrenaline action. I, II. H. NISHIYAMA (*Folia Pharmacol. Japon.*, 1933, 16, No. 2, 141—158, 159—181).—The effect of various NH_2 -acids on the depressant action of adrenaline on the isolated mouse uterus is reported.

CH. ABS.

Effect of adrenal cortex on resorption of sugar. W. WILBRANDT and L. LENGYEL (*Biochem. Z.*, 1933, 267, 204—210).—In rats from which the adrenal glands (I) have been removed resorption (II) of glucose in the intestine is reduced to the level of that of xylose, (II) of which remains unaltered. The alteration is due not to the removal of adrenaline, but to that of a substance (or substances) found in extracts of cortex of (I) ("eucortone"). W. McC.

Effect of diet on response to parathyroid extract and vitamin-D. I. Relation of calcium and phosphorus of the diet to the response in rats. A. F. MORGAN and J. G. FIELD. II. Effect of high-calcium-low-phosphorus diets in dogs. A. F. MORGAN and E. A. GARRISON. III. Effect of low-calcium-high-phosphorus diets in dogs. A. F. MORGAN, E. A. GARRISON, and M. J. HILLS. IV. Effect of diets of normal calcium and phosphorus contents in dogs. A. F. MORGAN, E. A. GARRISON, F. GILLUM, and M. J. HILLS (*Amer. J. Physiol.*, 1933, 105, 585—595, 596—607, 608—620, 621—634).—I. On a high-Ca-low-P diet (Steenbock), only those rats receiving vitamin-D (I) show a rise in serum-Ca (II) after injection with parathyroid extract (III), whereas on a low-Ca-high-P diet the reverse is the case. On a diet with normal Ca the rise in (II) is greater for rats without (I) than for those receiving it. (III) treatment does not affect the ash content of the femora.

II. With high-Ca-low-P diets, (III) produces hypercalcaemia (V) only in those dogs receiving (I). Serum-inorg. P rises whether (I) is given or not. Dogs on these diets deprived of (I) have low val. for serum-Ca and -P. The first is raised by giving (I) and the second by giving (I) and PO_4''' . Addition of Ca to the low-Ca-low-P diet decreases the response to parathormone (IV).

III. Severe bone deformity, tetany, and muscular

paralysis are produced in dogs on a low-Ca-high-P diet without (I). When cod-liver oil is given, the symptoms are similar, but less severe, although the Ca and inorg. P content of the serum is normal. First doses of (IV) give (V), but subsequent doses have no effect unless they are much increased in amount. There is increased retention of Ca when (I) is given. (III) reduces P retention, but does not affect Ca retention in the presence or absence of (I).

IV. Young dogs fed on a diet of normal Ca : P ratio respond to injection of (III) with (V) unless deprived of (I). NH_4Cl in the diet tends to reduce, and NaCl to increase, (V). (III) injection lowers the retention of P in dogs receiving (I). The response to (III) injection depends on the amount and availability of a Ca reserve, and is therefore affected by the ingestion of (I) and by the amount and ratio of Ca and P in the diet.

NUTR. ABS. (m)

Comparative pharmacology of calcinosis factor and parathyroid hormone. II. Observations on man. F. HOLTZ, J. GÜRSCHING, and H. KRAUT (*Arch. exp. Path. Pharm.*, 1933, 174, 51—62; cf. A., 1932, 1068).—Both oral administration of the calcinosis factor (I) and subcutaneous injection of parathyroid hormone' (II) produce calcification (III) of the tissues (especially of the kidneys), and increase the blood-Ca and -Si. The differences in the toxic symptoms and in (III) of tissue cultures indicate, however, that the action of (I) is independent of (II).

F. O. H.

Detection of a substance resembling acetylcholine in the blood of the portal vein. W. FELDBERG and P. ROSENFELD (*Pflüger's Archiv*, 1933, 232, 212—235; *Chem. Zentr.*, 1933, ii, 1700).—Portal venous blood from the dog which has received physostigmine (I) intravenously contains a substance which behaves like acetylcholine (II). The depressor and contractile (leech muscle) activities are rapidly lost when (I) is not employed. Arterial, or femoral or jugular venous, blood does not behave similarly. (II) appears to be formed continuously at the gastric and intestinal walls and to be hydrolysed to choline unless the hydrolysis is arrested by (I). A. A. E.

Crystalline insulin. I. Mode of application and duration of insulin action. M. BÜRGER and H. KOHL. II. Preparation and properties. E. BRUCH. III. Action of intrathecally injected insulin in rabbits. H. KOHL. IV. Action on the diabetic metabolism. M. BÜRGER and A. PATZOLD. V. Inactivation by blood. M. BÜRGER and H. KOHL (*Arch. exp. Path. Pharm.*, 1933, 173, 431—438, 439—451, 452—457; 174, 118—129, 130—142).—I. The extent of the diminution in blood-sugar (I) is not a sufficient criterion of the activity of insulin (II), which is more fully indicated by the area between the (I) curve and the abscissa through the fasting val. of (I). This "area of activity" indicates that intraperitoneal injection of either amorphous or cryst. (II) into rabbits is more effective than intravenous injection, and that with both routes cryst. (II) differs in activity from the amorphous (II) from which it was prepared.

II. Analytical data are given for various preps. of (II). (II) is oxidised by aq. $NaOH + K_3Fe(CN)_6$,

1 mg. of (II) being equiv. to 2.093 mg. of $K_3Fe(CN)_6$ [or to 0.0509 mg. of O_2 , only 0.0116 mg. of which is necessary for complete inactivation of (II)]. When heated at 96° in 0.01N-NaOH, the liberation of NH_3 and the decrease in reducing power of (II) are not related to the concomitant inactivation.

III. Following intrathecal injection into rabbits, both amorphous and cryst. (II) are absorbed and produce a fall in (I) (cf. A., 1927, 994), the onset being later and the duration longer than with intravenous injection. With the latter route, however, hypoglycaemic convulsions are less evident.

IV. Administration of cryst. (II) to diabetics produces a two-phase action. The first corresponds with a compensatory equalisation of lack of (II), resulting in a more rapid utilisation of the available carbohydrate and to an increase in O_2 consumption (III) which, after 30 min., returns to normal for approx. 1 hr. The second corresponds with a deficiency in the body-carbohydrate and is indicated by a rise in (III), in the CO_2 output, and in (I) and by a fall in the R.Q.

V. (II) is inactivated by anaerobic incubation for 10–20 hr. at 37° with blood and, to a smaller extent, with serum. The inactivation (IV) is especially marked with the leucocyte-rich blood of patients with leucemia, the extent of (IV) decreasing with decreasing concn. of leucocytes. With blood or serum heated to 56° , however, (IV) does not occur. F. O. H.

Action of insulin. N. A. NIELSEN (Skand. Arch. Physiol., 1933, 66, 19–49; Chem. Zentr., 1933, ii, 1698–1699).—In order to exhibit activity in the liver, cryst. insulin requires an accessory substance present in muscle. A. A. E.

Influence of insulin on body-temperature. L. DUNNER (Arch. exp. Path. Pharm., 1933, 173, 710–721).—Insulin-hypoglycaemia (I) in guinea-pigs and in men is accompanied by a fall in body-temp. (II), which persists when the blood-sugar (III) returns to normal, and hence is not a symptom of (I). The decrease is probably partly dependent on the utilisation of carbohydrate reserves. Administration of luminal or novocaine lowers (II) without changing (III). Exposure to cold produces hyperglycaemia ("cold diabetes"). Insulin inactivated by dil. NaOH or H_2O_2 has no action on (II). F. O. H.

Purification of insulin. A. V. MOGILSKI (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 111–113).—Known methods are applied. CH. ABS.

Callicrein. VIII. Identification and occurrence of callicrein in blood. H. KRAUT, E. K. FREY, and E. WERLE (Z. physiol. Chem., 1933, 222, 73–99; cf. A., 1932, 547).—Callicrein (I) forms, with a substance present in blood (II), two inactive compounds. From one (A), (I) is liberated quickly (in 2 min.) on acidification, from the other (B), slowly and incompletely. On mixing (I) with (II), A is first formed and passes slowly into B, which is therefore regularly present in (II). Treatment of serum or plasma with $COMe_2$ activates an enzymic reaction which liberates all the (I) in 24 hr. The velocity of the reaction is dependent on temp., substrate concn., and p_H , and is max. at 7–9. The inactivator

present in lymphatic and salivary glands differs from that in (II), since the complex formed only liberates (I) on acidification, not on $COMe_2$ treatment. It is found in small amount in (II) of ruminants. Human serum contains 2.6 units of inactive (I) per c.c., pig serum more, ape, ox, horse, and dog sera less.

J. H. B.

Influence of the follicular hormone on blossom and yield of plants. H. GOEBEL (Arch. Pharm., 1933, 271, 552–558).—Addition of the hormone in H_2O hastens growth and improves the yield and quality of blossom (and fruit) of hyacinths, *Calla althiopica*, maize, tomatoes, and other plants.

R. S. C.

Action of folliculin and prolan on the reproductive organs of the bat during hibernation. B. ZONDEK (Lancet, 1933, 225, 1256–1257).—Prolan (I) can also produce rupture of the follicle in bats during winter. Folliculin and (I) produce all the phases of the generative process in winter.

L. S. T.

Endocrine factors concerned in the control of the ovarian cycle. II. *Rana temporaria* as test animal. III. Action of anterior pituitary extracts on the ovary. C. W. BELLERBY (Biochem. J., 1933, 27, 2022–2025, 2025–2030).—II. Ovulation without oviposition, which is never complete and occurs in only a few animals, can be induced by injection of saline suspensions of anterior pituitary (I) in *R. temporaria* (II). As the ovary remains undeveloped for several months (II) can be used to determine the effect of the extract on development of the ova.

III. Alkaline extracts of (I) in equiv. dosage are as effective as acid extracts in producing ovulation (III) in the toad. Keeping the animals at 23 – 31° reduces the time between injection and (III) from 18 to 9 hr. without any effect on the sensitivity.

H. G. R.

Mechanism of the metabolism-stimulating effect of ovarian hormone. A. VON ARVAY (Endokrinol., 1933, 13, 9–16; Chem. Zentr., 1933, ii, 1694–1695).—Injection of ovarian hormone increases the gaseous metabolism of female rats.

A. A. E.

Hormones in colostrum. S. KONSULOV (Endokrinol., 1933, 13, 27–29; Chem. Zentr., 1933, ii, 1694).—The effect of injection of colostrum of pregnancy into the infantile mouse is described; *post-partum* colostrum has no effect. It is presumed that the hormone is consumed during parturition.

A. A. E.

Vitamin-A and visual purple. F. HAUROWITZ (Med. Klinik, 1933, 29, 1148–1149; Chem. Zentr., 1933, ii, 1703).—The $SbCl_3$ reaction for vitamin-A is given by frog's retina before or after extraction of the visual purple (I). (I) and its decolorised products do not give the reaction.

A. A. E.

Carotene and vitamin-A (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932–1933, 19).—Manuring appears to have no effect on the carotene content (I) or vitamin-A activity of cumbu leaves, and under all conditions of growing, (I) decreases with the age of the crop.

NUTR. ABS. (m)

Association of nutritional conditions for plants with nutritional factors for animals (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932—1933, 17).—Different conditions of manuring appear to have no appreciable effect on the vitamin-A and -B content of cumbu grains, or on the digestibility of the protein.

NUTR. ABS. (m)

Production of vitamins in plants. I. A. I. VIRTANEN, S. VON HAUSEN, and S. SAASTAMOINEN (Biochem. Z., 1933, 267, 179—191).—The total amount of vitamin-A (I) (carotene) and -C (II) in plants (wheat, peas, clover, grasses) increases with growth until the time of flowering (III) and then decreases, the max. being attained at the time of most vigorous growth. For (I) the highest % content is attained when soil acidity is optimal and N supply most favourable. The decrease in the (II) content after (III) is less certain than that of (I).

W. McC.

Fat-soluble vitamins. XXXVIII. Micro-organisms and the synthesis of carotene and vitamin-A. C. A. BAUMANN, H. STEENBOCK, M. A. INGRAHAM, and E. B. FRED (J. Biol. Chem., 1933, 103, 339—351).—Certain micro-organisms (I) can synthesise carotene (II), which accounts for the whole of their vitamin-A (III) activity. Transformation of (II) into (III) by (I) failed, and it is improbable that (III) as such is present in bacteria. H. G. R.

Stability of carotene in ethyl esters of fatty acids and in liver and vegetable oils. F. G. McDONALD (J. Biol. Chem., 1933, 103, 455—460).—Carotene (I) decomposed rapidly in solution in Et butyrate, laurate, and palmitate and peanut oil under all conditions. The loss of (I) in cod-liver, maize, and Wesson oils was retarded at 5° and in absence of O₂ at 37°.

H. G. R.

Vitamins of Californian and Asiatic dates. A. F. MORGAN (J. Home Econ., 1933, 25, 603—611).—Both varieties (I) (grown in California) contain about 300 international units of vitamin-A (II) per lb., but very little vitamin-D. Antiscorbutic activity is absent from pasteurised (I), but pasteurisation decreases the (II) activity only slightly.

NUTR. ABS. (m)

Coastal movements of the cod and vitamin content of Norwegian cod-liver oil. E. POULSSON (Nord. med. Tidsskr., 1933, 6, 886—890).—The vitamin (A and D) content of the liver oil (I) of the cod depends on the state of nourishment of the fish, and hence on the season at which fishing takes place. (I) from Norwegian cod is as potent as, or more potent than, (I) from Newfoundland cod with respect to vitamin-D.

NUTR. ABS. (m)

Colorimetric determination and detection of vitamin-A. E. ROSENTHAL and J. ERDELYI (Biochem. Z., 1933, 267, 119—123).—For the detection and determination of vitamin-A (I) 1 c.c. of a freshly-prepared 0.5% solution of pyrocatechol in CHCl₃ and 3 c.c. of a saturated CHCl₃ solution of SbCl₃ are added to 1 c.c. of a CHCl₃ solution of the material and the mixture is immediately heated at 60° for 1—2 min. The intense reddish-violet colour (II) (initially blue) produced is compared with that of 0.01% aq. KMnO₄. (II), which is not given by carotene, lycopene,

zeaxanthin, capsanthin, physalene, ergosterol (III), irradiated (III), or (I) irradiated with X-rays or ultra-violet light, exhibits characteristic absorption bands (e.g., those with max. at 552 and 476 mμ).

W. McC.

Determination of vitamin-A. A. W. DAVIES (Biochem. J., 1933, 27, 1770—1774).—The alkali digestion method has been simplified for rapid working. Vitamin-A in liver preps. is more stable if stored in 5% KOH.

H. G. R.

Sterility in males on diets deficient in vitamin-A or -E. V. KORENCHESKY (Proc. Roy. Soc. Med., 1933, 26, 1187—1192).—Histological degenerative changes in the testes of rats on a vitamin-A-deficient diet closely resemble those in rats on a diet deficient in vitamin-E.

NUTR. ABS. (m)

Significance of the passage of vitamin-A into milk. H. FASOLD and H. PETERS (Munch. med. Woch., 1933, 80, 1427—1429).—Vitamin-A, administered to lactating rats, passes into the milk.

NUTR. ABS. (m)

Transmission of vitamin-A from parents to young in mammals. II. Carotene and vitamin-A content of cow's colostrum. W. J. DANN (Biochem. J., 1933, 27, 1998—2005; cf. A., 1932, 1175).—Carotene (I) and vitamin-A (II) may be separated from milk by heating with aq. KOH and extracting with Et₂O+EtOH. The concns. of (I) and (II) in colostrum are frequently 70 and 10—100 times, respectively, those in later milk from the same cows. The sources of (II) for the young calf are discussed.

F. O. H.

Cockroaches as test animals in the quantitative analysis of vitamins in foodstuffs. V. MOSKALENKO (Nutr. U.S.S.R., 1933, 2, No. 4, 28—32).—Vitamin-C is not essential for development of the cockroach larvæ which require, however, vitamin-A and the -B complex, the necessary part of the latter being probably vitamin-B₁. As a source of fat-soluble factors, Et₂O extract of wheat germ is most potent.

NUTR. ABS. (m)

Relation of serum-calcium to pathological calcifications of hypervitaminosis-D. A. HAM and B. C. PORTUONDO (Arch. Path., 1933, 16, 1—14).—In rats receiving single large doses of irradiated ergosterol, the serum-Ca (I) reaches its max. about 72 hr. later; deposition (II) of Ca in the tissues (aorta and coronary vessels) takes place as the level begins to decline. (II) in hypervitaminosis-D depends more on the state of (I) than on its abs. level, and is attributed to the release of Ca from the fraction controlled by the parathyroid hormone.

NUTR. ABS. (m)

Effect of sources of vitamin-D on storage of the antirachitic factor in the egg. G. M. DEVANEY, H. E. MUNSELL, and H. W. TITUS (Poultry Sci., 1933, 12, 215—222).—Cod-liver oil (I), fed to Rhode Island Red hens, produces its optimal effect on the vitamin-D content (II) of the egg-yolks when the dose is 2% of the basal feed. With viosterol (20D) (III) the (II) increases with increasing dosage (up to 2%). At the optimal level for (I) feeding (II) is stored more efficiently than from (III). As regards

storage of (II) in the egg, irradiation of the hen for 15 min. daily with a carbon arc lamp is equiv. to adding 1% of (I) to the feed. NUTR. ABS. (m)

Sparing action of fats on the vitamin-B of animal tissues. A. R. KEMMERER and H. STEENBOCK (J. Biol. Chem., 1933, 103, 353—362).—1 unit of vitamin-B (I) is present in 2 g. of rat or chicken muscle, 0.25—0.5 g. of rat or chicken liver, 0.25 g. of pork ham. (I) in dark chicken muscle was > in the light muscle. Rats on low-(I), high-fat diets maintained a higher caloric intake than those on a low-(I), low-fat diet. Muscle and liver of rats, chicken, and pigs on a low (I), high-fat diet contained no more (I) than those on a low-(I), low-fat diet; the better maintenance on the former diet may be due either to a better caloric nutrition or to a ketogenic effect. H. G. R.

Apparent increased resistance of vitamin-B-deficient rats to an acute infection. L. REINER and J. B. PATON (Proc. Soc. Exp. Biol. Med., 1932, 30, 345—348).—Albino rats fed on a vitamin-B-complex-free diet (I) lived longer than control animals after infection (II) with *Trypanosoma equiperdum*. This effect appears to be due to lack of B_1 , but some slight effect was observed with diets containing B_1 but no B_2 . No difference was observed in the development of the (II), and the delayed death of infected rats on (I) may be due to secondary changes in the intermediate metabolism of the animals. Subsequent feeding of the infected deficient rats with B complex did not change the course of (II), but cured polyneuritis. Rats on vitamin-A-deficient diet died earlier after (II) than did control animals. A. W.

Relation of vitamin-B requirement to metabolism. W. A. HENDRICKS (Amer. J. Physiol., 1933, 105, 678—683).—In growing chickens the metabolism is proportional to the $5/3$ power of the live wt. (I). Since Cowgill has suggested that the vitamin-B (B_1) requirement (II) bears a similar relation to (I), it follows that (II) is proportional to the metabolism. NUTR. ABS. (m)

Effect of vitamin-B₁ on respiratory quotient of brain tissue. H. M. SINCLAIR (Biochem. J., 1933, 27, 1927—1934).—The R.Q. of normal pigeon brain-tissue (I) in PO_4''' -buffered lactate was approx. 0.90. The R.Q. of (I) from birds in opisthotonus due to vitamin-B₁ (II) deficiency was approx. 0.68 and was raised nearly to normal by cryst. (II). The R.Q. of (I) from birds showing no symptoms but fed on polished rice is scarcely affected by the feeding of (II). In CO_2-HCO_3' media the R.Q. of normal brain is approx. 0.81. In avitaminous brain addition of PO_4''' and (II) raises the R.Q. > does the addition of (II) alone. H. D.

Avian carbohydrate metabolism. Action of catatorulin in brain. R. A. PETERS and H. M. SINCLAIR (Biochem. J., 1933, 27, 1910—1925).—The effect on the O_2 uptake of avitaminous pigeon's brain of a no. of substances with and without vitamin-B₁ (I) was determined. Purified hexose diphosphate (II) has no great influence and the (I) effect is reduced. Impure (II) has a slightly greater effect. α -Glycerophosphate (III) raises the respir-

ation level with and without (I). $Na_4P_2O_7$ (IV) at p_H 7.3 produces a steady respiration for 2—3 hr. and enhances the (I) effect. From this it is concluded that the interaction of (IV), lactic acid, and (I) constitutes the basis for the catatorulin effect (V). Mixtures of (IV), (I), and (III) have a considerable effect; adenylyl pyrophosphate is without effect. The (V) is reduced from a max. at p_H 7.3 to a min. at p_H 6.6; (IV) restores the (I) effect at p_H 6.6, hence it is inferred that free P_2O_7''' is split off in surviving respiration at p_H 7.3. 0.01M-NaF inhibits (V). H. D.

Growth of blow-fly larvæ on blood and serum.
I. Response of aseptic larvæ to vitamin-B₁. R. P. HOBSON (Biochem. J., 1933, 27, 1899—1909).—Blow-fly larvæ hatched from aseptic eggs show deficient growth on aseptic blood; addition of yeast extract or marmite or the use of unsterilised blood produces normal growth. The H_2O -sol. fraction of marmite, Peters' antineuritic concentrate, and at least two heat-stable growth factors in yeast are all required for growth. It is concluded that vitamin synthesis is carried out by symbiotic micro-organisms in blood-sucking insects. H. D.

Action of formaldehyde on a vitamin-B₁ preparation (tiki-tiki). J. MALCOLM (Quart. J. Exp. Physiol., 1933, 23, 83—88).— CH_2O destroys or inactivates the vitamin-B₁ of tiki-tiki.

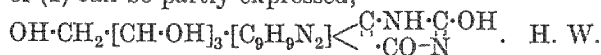
NUTR. ABS. (m)
Does adenine sulphate have the action of vitamin-B₁ when irradiated by ultra-violet light? R. YAMAMOTO and T. YAMAGISHI (J. Agric. Chem. Soc. Japan, 1933, 9, 749—751).—Avitaminosis-B₁ in pigeons was not cured. CH. ABS.

Irradiated adenine as a source of vitamin-B₁. B. SURE (Biochem. J., 1933, 27, 2043—2046).—Irradiated adenine sulphate, up to doses of 1 mg. per rat daily, does not exhibit vitamin-B₁ activity. H. G. R.

New nutritional factors required by chicks. J. A. KEENAN, O. L. KLINE, C. A. ELVEHJEM, E. B. HART, and J. G. HALPIN (J. Biol. Chem., 1934, 103, 671—685).—Chicks reared on a diet of caseinogen (24%), dextrin (63.5%), salt mixture (2.5%), yeast (8%), and cod-liver oil (2%) show defective growth and develop paralysis accompanied by brain degeneration, but not when the ration is supplemented by dried liver. Two factors are concerned: a H_2O -insol. heat-stable growth-promoting factor and a H_2O -sol. heat-labile antiparalytic factor (I), probably identical with vitamin-B₄ (cf. A., 1929, 1203; 1930, 380). Kentucky blue-grass and lucerne both contain (I). W. O. K.

Distribution of lyochromes and vitamin-B₂. E. ADLER and H. VON EULER (Svensk Kem. Tidskr., 1933, 45, 276—280).—The fraction of the COMe₂ extract sol. in light petroleum from animal organs, blood, and sarcoma tissue is shaken with H_2O ; the ultra-violet fluorescence of the aq. solutions determines the lyochrome content (I). Estimates of (I) per kg. include: fish-eyes, 13.5 mg.; ox-liver and kidney, 10 mg.; ox-blood, 0.025 mg. Vitamin-B₂ potency and (I) are parallel. R. K. C.

Lactoflavin (vitamin-*B*₂). R. KUHN, H. RUDY, and T. WAGNER-JAUREGG (Ber., 1933, 66, [B], 1950—1956; cf. A., 1933, 847).—Lactoflavin (I), m.p. 274° (corr., decomp.), $[\alpha]_D^{25} > -9.80^\circ$ in H₂O, after further purification through the *TH* salt, is C₁₇H₂₀O₆N₄. The biological activity is unchanged and the identity of (I) with vitamin-*B*₂ appears established. The compound obtained from (I) and Ac₂O in C₅H₅N is an Ac₄ derivative; under like conditions lumilactoflavin (II) is unchanged. Comparison of the formulae C₁₇H₂₀O₆N₄ and C₁₃H₁₂O₂N₄ indicates that photolysis involves the removal of 4 acetylable OH distributed among 4 C atoms. Oxidation of (I) with Pb(OAc)₄ gives 0.775 mol. CH₂O, whereas (II) does not afford a volatile aldehyde. Hence the hydroxylated portion of the mol. has the structure $[\text{CH}(\text{OH})_3]\text{CH}_2\text{OH}$. Treatment of (I) with Na₂S₂O₄, Pt+H₂, Zn dust in acid solution, or H₂S in Na₂CO₃ leads to leucolactoflavin, re-converted into (I) by agitation with air, whereas irradiation of (I) in H₂O in high vac. gives *deuteroleucolactoflavin*, converted by air into *deuterolactoflavin*, sharply differentiated from (I), since it becomes sol. in CHCl₃ after treatment with NaOH in the dark. Protracted irradiation of (I) in neutral aq. solution in presence of air leads to almost complete decolorisation and production of a *compound*, m.p. >360°, containing 26% N. (II) has the composition C₁₃H₁₂O₂N₄, m.p. 328° (corr., decomp.), $[\alpha] +0^\circ$ (red Ag salt), contains 1 OH, and gives 1 mol. of AcOH when oxidised with CrO₃. It is sol. in H₂O and dil. AcOH to a yellow solution with intense green fluorescence; in dil. alkali the former remains, whilst the latter is lost, whereas the colour lightens and fluorescence disappears in dil. acid. Treatment with Ba(OH)₂ eliminates urea. Boiling 2*N*-NaOH yields pale yellow acidic products, the chief of which is C₁₂H₁₂O₃N₂ (III), sol. in NaHCO₃. When heated, (III) loses CO₂ and yields the *compound* C₁₁H₁₂ON₂ (IV), m.p. 174° (corr.). Distillation of (III) or (IV) with Zn dust affords a cryst. base of low m.p. which gives sparingly sol. ppts. with picric acid, AuCl₃, HgCl₂, and phosphotungstic acid. The constitution of (I) can be partly expressed,



Vitamin-*B*₂. I. Yeast and liver preparations as source. R. J. BLOCK and L. R. FARQUHAR (J. Biol. Chem., 1933, 103, 643—649).—Rats were fed on a basal diet containing sufficient of vitamins-*A*, -*B*₁, -*D*, and -*E*. The addition of liver or yeast concentrates, or heated or unheated yeast produced good growth. Digestion of a liver concentrate with gastric juice did not increase its growth-promoting activity. Another concentrate with a high content in pernicious anaemia factor contained no vitamin-*B*₂.

H. D.

Vitamin-*C* in the adrenal medulla. L. J. HARRIS and S. N. RAY (Biochem. J., 1933, 27, 2006—2010).—The medulla (I) as well as the cortex (II) of the adrenal gland is very rich in vitamin-*C* (III), (I) being twice and (II) thrice as active (wt. for wt.) as standard lemon juice. When assayed biologically or by titration with 2:6-dichlorophenol-indophenol, ox (I) contains 1.1—1.2 mg. of (III)

per g. The staining with AgNO₃ is not a certain criterion of the presence or absence of (III). Rats, which synthesise their own (III), do not develop scurvy when adrenalectomised and fed on a (III)-free diet. The adrenal gland [which in rats contains approx. 0.6% of (III)] is not a storehouse for (III).

F. O. H.

Identification of vitamin-*C* and its derivatives. N. BEZSSONOFF and A. DELIRE (Compt. rend., 1933, 197, 1774—1776).—Ascorbic acid (vitamin-*C*) can be determined in biological media by means of the Bezssonoff colour reaction, after treatment with Pb(OAc)₂ at *p*_H 3.5. It is not present in vegetable juices as the free acid. In young males a considerable quantity is excreted in the urine.

P. G. M.

Distribution of vitamin-*C* in plant and animal tissues, and its determination. O. A. BESSEY and C. G. KING (J. Biol. Chem., 1934, 103, 687—698).—Vitamin-*C* may be determined by titration with 2:6-dichlorophenol-indophenol. For plant and animal tissues, extracts made with AcOH (8%) and CCl₃·CO₂H (8%), respectively, may be employed. In animals the highest concn. is in the adrenals and corpus luteum (1.4—2.3 mg. per g.). The distribution in the human body is similar to that in animals. In *C*-avitaminosis general tissue depletion occurs before symptoms of scurvy appear.

W. O. K.

Indophenol-reducing capacity and vitamin-*C* content of extracts of young germinated peas. S. W. JOHNSON (Biochem. J., 1933, 27, 1942—1949).—PO₄''' (I), PO₄'''-CN' (II), H₂SO₄, CCl₃·CO₂H, and aq. extracts of peas have similar reducing capacities (III) as determined by indophenol titration. The (I) and (II) extracts are less antiscorbutically active than the peas from which they are derived, and < would be expected from their (III). H₂S does not increase the titration of the extracts, indicating the absence of an active oxidised form of the vitamin. It is concluded that other substances are present in the extracts which reduce indophenol and that the methods of extraction were insufficient to remove the vitamin completely.

H. D.

Antiscorbutic potency of ascorbic acid. L. J. HARRIS and S. N. RAY (Biochem. J., 1933, 27, 2016—2021).—Using the tooth-protection method, 3 c.c. of orange juice are equiv. to 2 mg. of ascorbic acid (I), agreeing with the val. obtained by titration. The (I) content of lemon juice varies from 0.19 to 0.69 mg. per c.c. (average, 0.47±0.11 mg. per c.c.).

H. G. R.

Antiscorbutic activity of compounds resembling ascorbic acid. O. DALMER and T. MOLL (Z. physiol. Chem., 1933, 222, 116—120).—"Maurer's acid" (A., 1933, 936), tested on guinea-pigs, has weak antiscorbutic properties, but 40 times and 20 times the ascorbic acid dose for oral and subcutaneous administration, respectively, are necessary for the same effect. Hydroxytetrone acid is inactive.

J. H. B.

Polyploidy and vitamin-*C*. F. W. SANSOME and S. S. ZILVA (Biochem. J., 1933, 27, 1935—1941).—The juice from tetraploid forms of the strains of tomato obtained by the induction of polyploid method is about twice as strongly antiscorbutic to

rats as that of the diploid forms. Similar results are obtained by indophenol titration. H. D.

Influence of vitamin-C on the gaseous metabolism of normal and scorbutic guinea-pigs. J. MOSONYI and L. RIGÓ (Z. physiol. Chem., 1933, 222, 100—104).—The gaseous metabolism (I) of scorbutic guinea-pigs (II) is $>$ that of normal (II). After administration of ascorbic acid, the (I) of scorbutic (II) decreases and of normal (II) increases; the R.Q. rises in both cases, but in normal (II) only slightly. J. H. B.

Excretion of vitamin-C in human urine and its dependence on the dietary intake. L. J. HARRIS, S. N. RAY, and A. WARD (Biochem. J., 1933, 27, 2011—2015).—Normal individuals excrete 30—33 mg. of vitamin-C (I) daily in the urine, but this increases 8- to 10-fold after ingestion of a massive dose of (I) and then rapidly falls to normal. This daily loss is slightly $>$ the reputed min. daily requirement for man. H. G. R.

Formation and decomposition of chlorophyll in the leaves of winter and spring cereals. M. S. TSCHAILACHJAN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 127—130).—The velocity of formation of chlorophyll in winter wheat and barley sprouts is $>$, and that of its decomp. is $<$, in spring cereals. R. T.

[H⁺] necessary for the germination of pollen and vital coloration of their vacuoles. HUREL-PY (Compt. rend., 1934, 198, 195—197).—For a no. of plants in sucrose solution the p_H must be < 5 . R. S. C.

Ionising action of fresh pulp of vegetable tissues, and mitogenetic radiations. L. PETRI (Atti R. Accad. Lincei, 1933, [vi], 17, 1041—1043).—Pulped vegetable, especially embryonal, tissue determines slight ionisation of the air. Fresh potatoes, containing active oxidising enzymes, show this phenomenon, which, however, fails with cooked potatoes, in which oxidation processes are very slow. T. H. P.

Transpiration of tobacco plants in relation to radiant energy in the visible and infra-red. J. M. ARTHUR and W. D. STEWART (Contr. Boyce Thompson Inst., 1933, 5, 483—501).—The effects of radiation of varying intensity, of temp., and of humidity on transpiration rates are examined. A. G. P.

Growth-differentiation balance versus carbohydrate-nitrogen ratio. W. E. LOOMIS (Proc. Amer. Soc. Hort. Sci., 1932, 29, 240—245).—Variations in the form, composition, and growth behaviour of a genotype are explained on the basis of variations in the growth-differentiation balance. CH. ABS.

Accumulation of carbohydrates in apple foliage, bark, and wood as influenced by moisture supply. J. R. MAGNESS, L. O. REGEIMBAL, and E. S. DEGMAN (Proc. Amer. Soc. Hort. Sci., 1932, 29, 246—252).—Carbohydrate synthesis in apple foliage is reduced under conditions of H₂O shortage. The starch content of storage tissues is reduced, but the sugar content of plant juices is increased. CH. ABS.

Starch in the young orange tree. S. H. CAMERON (Proc. Amer. Soc. Hort. Sci., 1932, 29, 110—114).—Only the root-bark shows marked fluctuations throughout the year. CH. ABS.

Relation between leaf area and size of fruit, chemical composition, and fruit-bud formation in Elberta peaches. J. H. WEINBERGER and F. P. CULLINAN (Proc. Amer. Soc. Hort. Sci., 1932, 29, 23—27).—Increasing the no. of leaves per fruit from 10 to 80 increased the total sugar from 7.2 to 12.3% (fresh wt.). Leaf-sugar and -starch, and twig-sugar, also tended to increase. CH. ABS.

Influence of leaf area on fruit growth and quality in the peach. I. D. JONES (Proc. Amer. Soc. Hort. Sci., 1932, 29, 34—38).—Increase in the no. of leaves per fruit increased the total solids, total sugars, acidity, and EtOH-sol. fraction. CH. ABS.

Relation of leaf area to fruit size and food reserves in apple seeds and branches. A. E. MURNEEK (Proc. Amer. Soc. Hort. Sci., 1932, 29, 230—234).—Carbohydrate storage in the branches increased with increasing area of foliage per fruit. Total N decreased in the new growth of twigs but increased in the older wood. CH. ABS.

Growth rate and composition of the Hiley peach from stone formation to flesh maturity. R. V. LOTT (Proc. Amer. Soc. Hort. Sci., 1932, 29, 1—7).—Physiological maturity is reached in the order: stone, flesh, kernel. CH. ABS.

Assimilation and caoutchouc formation in the Tau-sagiz plant. V. A. NOVIKOV, A. I. GRET-SCHUSCHNIKOV, J. P. BARMENKOV, and A. K. NOSOV (Compt. rend. Acad. Sci. U.R.S.S., 1933, 78—82).—The metabolism of the plant and the formation of caoutchouc (I) vary with the temp., the H₂O content of the leaves, and the intensity of incident light. (I) formation ceases completely in misty weather; under optimum conditions ($\pm 77\%$ H₂O in the leaves, in direct sunlight and at 28°) the daily production of (I) is 4 g. per 500 g. of leaves. R. T.

Inducing caoutchouc formation by ultra-violet light. V. A. NOVIKOV and E. C. GERBER (Compt. rend. Acad. Sci. U.R.S.S., 1933, 131—136).—The catalase activity of Tau-sagiz (I) seeds is increased 1600% by ultra-violet irradiation (II); the caoutchouc (III) content of the leaves of (I) and of *Asclepius* soaked in 3% aq. sucrose increases during 3 days after (II) from 0.8 to 2%, and from 1.6 to 4.5%, respectively. The (III) content of the roots of (I) grown from irradiated seeds is approx. 3 times that in normal plants, and the leaves are less subject to insect infestation. R. T.

Daily variations in weight and powder-volume of the dry substance of leaves. R. KOKETSU, T. FUJITA and K. HANADA (Proc. Imp. Acad. Tokyo, 1933, 9, 419—421).—The cellulose and ash contents of leaves vary but little from day to day and hence may be used as reference standards for wt. changes in other constituents. The powder-vol. of the dried leaves is less influenced than the dry wt. by changes in the rate of assimilation. F. O. H.

Iodine content of agar. A. ITANO (Proc. Imp. Acad. Tokyo, 1933, 9, 398—401).—Sea-weeds with 430—796 p.p.m. of I yielded agars with 24.5—101.9 p.p.m. Commercial preps. had 11.8—42.8 p.p.m. The I content can be controlled by the method of prep. whilst washing the agar with H₂O reduces it.

F. O. H.

South Indian pastures. I. Seasonal variation in the mineral and nitrogen content of spear-grass (*Andropogon contortus*). P. V. RAMIAH (Indian J. Vet. Sci., 1933, 3, 65—84).—The N, total ash, SiO₂, Ca, K, and P contents of the grass show considerable seasonal variations. The N and P curves are roughly parallel, whilst the Ca curve varies inversely. The main factor affecting the variation appears to be the period of growth. Max. and min. (dry-matter basis) are CaO 0.990, 0.234; K₂O 2.150, 0.568; P₂O₅ 0.588, 0.235; protein 11.48, 1.78%.

NUTR. ABS. (m)

Nitrogen, phosphoric acid, and potassium contents of different varieties of wheat. L. MAUME and J. DULAC (Compt. rend., 1934, 198, 199—202).—15 varieties of wheat growing under identical conditions have, at the time of efflorescence, N 0.54—1.26, P₂O₅ 0.28—0.49, and K₂O 1.13—3.32% (calc. on dry matter), a rough parallelism existing between the three vals.

R. S. C.

Determination of inorganic phosphate in vegetable substances. T. LITYNSKI (Rocz. Chem., 1933, 13, 578—584).—The substance is shaken during 3 hr. with 1% HCl, the filtrate is deproteinised with OCl₂·CO₂H, inorg. P is pptd. as NH₄MgPO₄, which is dissolved in 25% HNO₃, and P is determined as phosphomolybdate.

R. T.

***Laurus camphora*, Nees. (*Cinnamomum camphora*).** V. E. VORONTZOV (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 88—93).—The tree (30 years) afforded the following percentages of camphor and essential oil, respectively: leaves and young branches 2.07, 0.13 (on dry substance); older branches 0.53, 0.13; trunk 2.14, 0.53; roots 1.65, 1.30. Storage only slightly affects the yields.

CH. ABS.

***Achillea millefolium*, Linné. Constituents of the light petroleum extract of the blossoms.** R. L. McMURRAY (Amer. J. Pharm., 1933, 105, 573—582).—The fatty oil (1.86% from the dry flowers) had: acid val. 37, sap. val. 112, I val. 57, unsaponifiable matter 22.75% (triacontane, ceryl alcohol, sterol, m.p. 135°), and fatty acids 52.5% [myristic, palmitic, cerotic, undetermined (? lignoceric), linoleic, and oleic].

E. H. S.

Isolation of *n*-triacontanol from lucerne wax. A. C. CHIBNALL, E. F. WILLIAMS, A. L. LATNER, and S. H. PIPER (Biochem. J., 1933, 27, 1885—1888).—The principal component of the wax from lucerne leaves is identified as *n*-triacontanol, m.p. 86.3—86.5°, by reduction to *n*-triacontane, m.p. 65.6—65.8°, and oxidation to *n*-triacontanoic acid, m.p. 93.6—93.9°. The wax also contains a mixture of paraffins, m.p. 65.6°, and fatty acids, no ketone being present.

A. L.

Isolation of *n*-octacosanol from wheat wax. A. POLLARD, A. C. CHIBNALL, and S. H. PIPER

(Biochem. J., 1933, 27, 1889—1893).—The principal component of the wax from blades of young wheat is identified as *n*-octacosanol, m.p. 83.2—83.4°, by reduction to *n*-octacosane, m.p. 61.3—61.5°, and by oxidation to *n*-octacosic acid, m.p. 90.8—91.1°. The wax also contains a mixture of paraffins, m.p. 66°, and fatty acids.

A. L.

Proteins of grasses. II. Method of preparation. A. C. CHIBNALL, E. J. MILLER, D. H. HALL, and R. G. WESTALL (Biochem. J., 1933, 27, 1879—1884).—The Et₂O-H₂O extraction method (A., 1932, 662) for the prep. of the proteins of leaves is modified, Et₂O-H₂O already used for cytotoxicity of leaf material being used in place of fresh Et₂O-H₂O. Improved yields of protein are obtained from several pure-strain grasses and forage crops.

A. L.

Occurrence of cyanogenetic glucosides in Nelson pasture plants. T. RIGG, H. O. ASKEW, and E. B. KIDSON (New Zealand J. Sci. Tech., 1933, 15, 222—227).—The proportion of HCN obtainable from red clover, alsike, subterranean clover, and *Lotus major* averaged 0.0001—0.0005% of fresh material and from white clover 0.0016—0.0124% (average 0.0045%).

A. G. P.

Determination of hydrocyanic acid in white clover. H. O. ASKEW (New Zealand J. Sci. Tech., 1933, 15, 227—233).—Best results were obtained by grinding the fresh sample and steeping in H₂O for 20 hr. at room temp. or warming at 45° for 5 hr. Addition of acid to produce >0.001N reduced the yield of HCN from the mixture but NaOH to give 0.01N had little effect. The extract is distilled and the distillate titrated with AgNO₃ in the presence of KI and aq. NH₃. The HCN content of stems is > that of leaves.

A. G. P.

Kuromamin, the colouring matter of "*Kuromame*." II. C. KURODA and M. WADA (Proc. Imp. Acad. Tokyo, 1933, 9, 517—520; cf. A., 1933, 544).—The H₂O-sol. and -insol. portions of the seed-coat of Kuromame from many sources affords (improved prep.) a cryst. monoglucoside of cyanidin chloride.

J. L. D.

Phytochemistry. II. Carbohydrates of vegetable downs. E. VOTOCEK and J. ZVONICEK (Coll. Czech. Chem. Comm., 1933, 5, 448—456).—The cleaned, degreased fibre is extracted with H₂O to remove sol. sugars (a), hydrolysed with 3% H₂SO₄ at 100° to remove hemicelluloses (b), and the residual cellulose hydrolysed. In each case a true cellulose giving glucose only on hydrolysis was obtained. The constituents of the other fractions are: flax (*Eriophorum angustifolium*), (a) 28% xylose (I), 72% galactose (II); (b) 83—91% (I), (II); thistle (*Carduus acanthoides*), (a), (I), fructose (III), (b) (I), (II); dandelion (*Taraxacum officinale*), (a) pentoses, (b), (I), and a little unidentified hexose; *Asclepius syriaca*, (a), (I), (III), (b), (I); poplar (*Populus nigra*), (a), mannose, (IV), and a little (I), (b), 85% (I), 15% (IV).

H. A. P.

Methods of staining plant tissues for differentiating natural plant oils from petroleum spray oils. P. W. ROHRBAUGH (Stain Tech., 1934, 9, 1—3).—A combination of Nile-blue sulphate and

"oil-red O" is used. This imparts a brownish-black colour to the plastids and to most natural oils whilst the petroleum is coloured red, after the sections have been treated with either KOH or Bouin's solution.

H. W. D.

Chromic fixation in alcoholic media. H. C. WATERMAN (Stain Tech., 1934, 9, 23—31).—I is suggested as a quick-killing adjuvant in chrome-alum-alcohol-acetic acid fixatives. The application of such mixtures to the study of chromosomes in the root-tips of *Vicia faba* is described.

H. W. D.

Inhibition of root-growth of *Lens esculenta* by radium. A. SARTORY, R. SARTORY, J. MEYER, and ERNST (Compt. rend., 1933, 197, 1760—1762).—Tubes of Ra were used either in contact with or at a distance of 10 mm. from the roots. The curve of mitosis shows a steady diminution on successive days of the treatment; the max. always occurs about mid-day. The effect \propto the time of application of the Ra.

P. G. M.

Inhibition of root-growth of *Lens esculenta* by radium; modification of the minimum inhibitory dose by antagonistic ions. A. SARTORY, R. SARTORY, J. MEYER, and ERNST (Compt. rend., 1934, 198, 197—199).—Isotonic KCl and, more so, MgSO_4 weaken the inhibitory action of Ra, doses of 10·16 and 11·015 millicuries, respectively, being needed to produce the effect of 7·8 millicuries in distilled H_2O .

R. S. C.

Death as the result of change of living matter within the plant cell. J. DUFRENOY (Science, 1933, 78, 494—500).—A lecture.

L. S. T.

Fever of *Arum*. L. BLARINGHEM (Compt. rend., 1933, 197, 1551—1554).—Absorption of O_2 by the whole inflorescence of *A. italicum* and *A. maculatum* is nearly doubled during the period when a higher temp. is observed. During ripening the male organs first consume 5—10 times the amount of O_2 absorbed by the (normal) female organs (the intensity and time of this crisis varying with individuals), then, later, a smaller increase occurs in the sterile papillae, and finally a two-fold increase in the O_2 absorption of the female organs.

J. W. B.

Biochemical changes accompanying curly top of tomato. F. B. WANN and H. L. BLOOD (Phytopath., 1933, 23, 929).—In comparison with healthy plants diseased specimens had higher proportions of dry matter in the pulp and of sugars and solids in the juice. The titratable acidity of the leaf juice was lowered and that of stem juice increased. In the leaves, sugar increased and total N declined. In stems the total sugars and starch increased and the total N decreased in some, but not all, varieties.

A. G. P.

Relationships between type of infection and the growth and course of metabolism of plants resulting from changes in mineral nutrition. K. BONING with E. BÖNING-SEUBERT (Zentr. Bakt. Par., 1933, II, 89, 85—106).—The influence of nutrient conditions and the composition of the sap of tobacco plants on infection by a no. of disease organisms indicate close relationships between plant metabolism and resistance to infection and injury.

A. G. P.

Possible chemical nature of tobacco mosaic virus. E. BARTON-WRIGHT and A. M. MCBAIN (Nature, 1933, 132, 1003—1004).—Vinson and Petre's work (A., 1931, 1201) has been confirmed and their conclusion that the virus disease of tobacco mosaic is a chemical compound and not an organism is supported. The mixed phosphate eluate is highly infectious, and contains protein. At p_H 5, COMe_2 ppts. a white, infectious material (I) containing protein. (I) can be separated into a white, cryst. solid (II) and a gelatinous protein portion (III). (III) produced disease and the virus could not be separated from protein. (II) consists mainly of phosphate with some org. matter. It contains no N, and is infectious. The addition of a 1% solution of safranin (IV) to the phosphate eluate produces a slow pptn. After removal of (IV) the aq. solution of the ppt. is infectious, but contained no N, P_2O_5 , or protein.

L. S. T.

Accessory factor necessary for the growth of *Nematospira gossypii*. III. Preparation of concentrates of the second accessory factor. H. W. BUSTON and S. KASINATHAN (Biochem. J., 1933, 27, 1859—1868).—The second factor (I) (A., 1931, 1458) occurs in lentils combined with an inactive nitrogenous base or associated with proteins and is liberated on hydrolysis. (I), which is pptd. by $\text{Hg}(\text{OAc})_2$ reagent and (when in the combined state) by phosphotungstic acid, appears to be a weak acid. With most active preps. 1·2 mg. per 100 c.c. of medium promotes full growth of the fungus. The first factor (*D*-inositol) cannot be replaced by quercitol, quebrachitol, *l*- or *d*-inositol, or sennitol.

Belling's green-light method for critical microscopy. H. C. WATERMAN (Stain Tech., 1934, 9, 21—22).—Practical advice is given.

H. W. D.

Continuous extraction apparatus. S. E. OWEN and W. L. OLSEN (J. Lab. Clin. Med., 1933, 18, 1072—1073).—An apparatus suitable for small quantities of biological material is described.

CH. ABS.

Micro-quinhydrone electrode. T. MIKAWA (Biochem. J., 1933, 27, 1829—1831).—The fluid (0·01—0·1 c.c.) is mixed with quinhydrone and sucked into a suitably insulated Au tube of 1 mm. diameter which serves as the metal electrode. The electrode is applicable to serum, urine, etc. but not to whole blood or tissue fluids *in vivo*.

F. O. H.

Micro-determination of gold. Application to gold therapy.—See this vol., 162.

Determination of furfuraldehyde-yielding constituents of plant materials. H. REYNOLDS, O. L. OSBURN, and C. H. WERKMAN (Iowa State Coll. J. Sci., 1933, 7, 443—451).—The sample is distilled with 100 c.c. (replenished) of 20% HCl, 200 c.c. being collected in 1 hr. The distillate, or a part thereof, is treated with excess of a saturated solution of 2 : 4-dinitrophenylhydrazine in cold 2N-HCl. After 3 hr. at room temp. or 2 hr. at 0° the ppt. is collected, dried for 1 hr. at 100°, and weighed. Arabinose (30—300 mg.) afforded 73—68% recovery; xylose (30—300 mg.) afforded 87·5—82·9% recovery.

CH. ABS.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1934.

General, Physical, and Inorganic Chemistry.

Theory of hyperfine structures. E. FERMI and E. SEGRÈ (Mem. R. Accad. d'Italia Sci. fis., 1933, 4, 131—158).—A theoretical discussion of the hyperfine structure of the spectral lines of Li, Na, Cu, Ga, Rb, Cd, In, Cs, Ba, Au, Hg, Tl, Pb, and Bi. The theory of the nuclear magnetic moment is discussed.

O. J. W.

Spectrum of atomic nitrogen, N I. D. SEFERIAN (Compt. rend., 1934, 198, 68—69).—An arc is struck between parallel W wires 3 mm. diam. and 2—3 mm. apart, N₂ at the rate of 800—1000 litres per hr. being passed around them. With a.c. of 46—50 amp. at 110 volts the spectrum of N I is obtained (cf. A., 1929, 1116; 1932, 103), and also two different continuous spectra, one due to W, the other to either W or N.

C. A. S.

Spectrum of atomic nitrogen (N I) in ammonia and in mixtures of hydrogen and nitrogen. D. SEFERIAN (Compt. rend., 1934, 198, 358—460; cf. preceding abstract).—N₂ was replaced by (a) H₂, (b) NH₃, (c) N₂—H₂ mixtures, (d) air. (a) confirms previous results (cf. A., 1930, 387) and gives the "raies ultimes" of W; (b) and (c) give identical spectra of N I, whilst (d) shows that the two continuous spectra are due one to the incandescent electrodes, the other to the W atom.

C. A. S.

Continuous spectrum of neon. N. T. ZE and V. S. LING (Compt. rend., 1934, 198, 356—358).—The intensity of the continuous spectrum of Ne relatively to that of H₂ (cf. A., 1931, 275), and hence absolutely, increases with λ to λ 3400, remains approx. stationary to λ 4200, and afterwards increases again. With increase in pressure of Ne the intensity of the continuous spectrum increases, that of the line spectrum diminishes.

C. A. S.

Effect of pressure on high terms of alkaline spectra. E. AMALDI and E. SEGRE (Nature, 1934, 133, 141).

L. S. T.

Remarkable optical properties of the alkali metals. R. DE L. KRONIG (Nature, 1934, 133, 211—212).—A discussion based on Zener's interpretation (this vol., 124).

L. S. T.

Seeing in sodium-vapour light. M. LUCKIESH and F. K. MOSS (J. Opt. Soc. Amer., 1934, 24, 5—13).—The relation of the spectral quality of Na vapour and W filament light to physiological effects is examined.

N. M. B.

Band spectrum of magnesium hydride. A. GUNTSCH (Z. Physik, 1934, 87, 312—322).—Rotation and dissociation consts. are given for various levels.

A. B. D. C.

Infra-red grating spectra and spectral series (Al II, Al I, He I and II, Zn I and II). F. PASCHEN and R. RITSCHL (Ann. Physik, 1933, [v], 18, 867—892).—A comprehensive analysis of the grating spectrum of Al II is made. With a specially luminous hollow cathode arrangement new infra-red lines beyond 1μ are tabulated and an extended analysis is given for Al I, He I and II, Zn I and II.

W. R. A.

Arc spectrum of silicon in the red and infra-red. C. C. KIESS (Bur. Stand. J. Res., 1933, 11, 775—782).—130 new lines have been measured in the arc spectrum of Si between 6125 and 11,290 Å. These include the strongest previously unidentified Fraunhofer line (6155 Å.) and other solar spectral lines. Most have been classified as combinations, including terms arising from 4p, 4f, and 5f electron configurations.

J. W. S.

New calculation of the term system of Si IV. B. EDLEN and J. SÖDERQVIST (Z. Physik, 1933, 87, 217—219).

A. B. D. C.

Absorption spectra due to excitation of inner electrons. V. The doublet in potassium vapour due to excitation of the (3p)⁶-shell. (K I^b resonance lines.) H. BEUTLER and K. GUGGENHEIMER (Z. Physik, 1933, 87, 188—191).

A. B. D. C.

Relative intensities of the components of the a^3F — γ^3F^0 multiplet of Fe I. J. PIERAND (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 16—19).—The intensities of the weaker components relative to those of the stronger members of this multiplet are > would be anticipated from the Sommerfeld formulæ (cf. Proc. Nat. Acad. Sci., 1932, 18, 590).

J. W. S.

Ionisation potential of Fe II. J. C. DOBBIE (Physical Rev., 1934, [ii], 45, 76—78).—New high terms e^6D (77861.4) and e^4D (79439.3) are reported in the spark spectrum of Fe. Combination multiplets with low terms are tabulated. The val. 16.16 volts is found for the principal ionisation potential of Fe II.

N. M. B.

Spectrum of fluorine. F II, F III, F IV. I. S. BOWEN (Physical Rev., 1934, [ii], 45, 82—86).—Full data and classifications for the region 125—620 Å. and corr. classifications of additional lines in the longer wave-length regions are tabulated. The ionisation potentials are: F II 34.81, F III 62.35, F IV 87.34 volts.

N. M. B.

Absorption spectra due to excitation of inner electrons. IV. Zn spectrum from 1150 to 700 Å. due to excitation of the (3d)¹⁰-shell (Zn I^b). Comparison of terms and their values for Hg I^b,

Cd I^b, and Zn I^b. H. BEUTLER and K. GUGGENHEIMER (Z. Physik, 1933, 87, 176—187; cf. this vol., 124). A. B. D. C.

Fine structure in the spectrum of arsenic II. S. TOLANSKY (Z. Physik, 1933, 87, 210—217).—Lines reported by Rao to have fine structure (A., 1933, 880) are single. A. B. D. C.

Mechanical moment of the nucleus of caesium. D. A. JACKSON (Proc. Roy. Soc., 1934, A, 143, 455—464).—The hyperfine structure of the lines 4555 and 4593 Å. of Cs has been examined. The intensity ratio is 1.27 ± 0.02 for both doublets, which establishes the val. $7/2$ for the mechanical moment of the Cs nucleus. L. L. B.

Continuous absorption of light in caesium vapour. H. J. J. BRADDICK and R. W. DITCHBURN (Proc. Roy. Soc., 1934, A, 143, 472—481).—A detailed account of work already noted (A., 1933, 200). L. L. B.

Temperature of the mercury arc. W. ELENBAAS (Physica, 1934, 1, 211—224).—The calc. temp. at the centre of a contracted discharge (5.5 amp., 8.8 volts per cm.) was $6000^\circ \pm 800^\circ$ abs. H. J. E.

Hyperfine structure absorption in optically excited mercury vapour. M. L. POOL and S. J. SIMMONS (Physical Rev., 1933, [ii], 44, 997—1001).—The absorption, with high and low dispersion, of the Hg 4047, 2967, and 2752 Å. lines in optically excited Hg vapour was investigated for various lengths of excited vapour, and various pressures of admixed N₂. N. M. B.

Structure of the band spectrum of mercury vapour. S. MROZOWSKI (Z. Physik, 1934, 87, 340—355).—The variation of structure of the Steubing band series with exciting wave-length is due to deviation of the rotational energy distribution from that of Maxwell's law. Polarisation and other effects are investigated on this hypothesis. A. B. D. C.

Multiplet and hyperfine structure analyses of Bi IV. Discussion of perturbation effects. A. B. McLAY and M. F. CRAWFORD (Physical Rev., 1933, [ii], 44, 986—996).—Classifications of 360 lines of Bi IV excited in an electrodeless discharge are tabulated. Hyperfine structure intervals of several terms are evaluated, and agree with theoretical separations consistent with the multiplet analysis. N. M. B.

Stark effect of the Lyman series. R. FRERICHES (Ann. Physik, 1934, [v], 19, 1—8).—The Stark effect was investigated for the first three lines of the Lyman series. The no., position, and polarisation of the components agree with conclusions based on quantum mechanics. The intensities of the components, however, show some deviations from theory. A. J. M.

Wave-lengths and spectral laws. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1933, No. 30, 12 pp.).—The accuracy of wave-lengths and wave-no. is discussed. A. J. M.

Emission spectrum of the night sky in the ultra-violet. J. DUFAY (Compt. rend., 1934, 198, 107—109). 67 emission bands observed in the night sky at Courbons (Basses-Alpes) by exposure of 24 hr.

on 13—18 Sept., 1925, are tabulated; of these 27 are new, and 29 referable to N₂⁺ or N₂⁻ (cf. A., 1932, 105). C. A. S.

Spectral analysis of the night sky at the Pic du Midi. J. CABANNES and J. DUFAY (Compt. rend., 1934, 198, 306—309).—With a new form of spectro-scope 91 lines, 36 new and 8 found only on re-examining an old plate (see above), were measured between $\lambda\lambda$ 3891 and 5204, and their relative intensities shown in many cases to vary from night to night and in different parts of the sky. Some of the lines indicate O, N, A, para- and ortho-He. C. A. S.

Explosive potentials in argon. H. GUIMOT (Ann. Guebbard-Severine, 1933, 9, 306—311).—The current flowing in a discharge tube containing A, at various potentials, has been measured for different gas pressures and electrode separations. A. J. M.

Significance of broadening effects of spectral lines due to foreign gases. M. KULP (Z. Physik, 1933, 87, 245—254).—These effects are qualitatively explained by means of potential curves. A. B. D. C.

Gas discharge with diffusion and transverse forces. W. FUCHS (Z. Physik, 1933, 87, 139—153).—Equilibrium conditions for steadily burning discharges are given, and are discussed with respect to min. cross-section and current. A. B. D. C.

Vibrational isotope effects in three-particle systems. I. A. ADEL (Physical Rev., 1934, [ii], 45, 56—58).—Mathematical. N. M. B.

Anomalous dispersion and absorption of X-rays. E. J. WILLIAMS (Proc. Roy. Soc., 1934, A, 143, 358—376).—The anomalous dispersion of X-rays is calc. from the experimental data for photo-electric absorption. The results for Fe and Cu are compared with experiment. The theoretical reasons for the observed val. of the oscillator strength are considered, and in particular the equivalence of the $2K$ electrons to about 1.3 classical electrons. L. L. B.

Spectroscopy of ultra-soft X-rays. II. M. SIEGBAHN and T. MAGNUSSON (Z. Physik, 1934, 87, 291—310; cf. A., 1930, 1229).—Wave-lengths are given for C, N, and O $K\alpha$ lines, for Li, Be, and B K lines, and L lines from K to Na. A. B. D. C.

Quantum scattering of X-rays. H. HULUBEL (Ann. Physique, 1934, [xi], 1, 5—71).—Bands due to multiple scattering with change of wave-length, additional to normal and Compton scattering, when $K\alpha$ radiation of Mo and Rh was scattered by paraffin or Li, were investigated for the angular range 0° — 130° . An expression is found for the displacement limits of bands for n -fold scattering. Double scattering ($n=2$) was found in all cases, with some indications of triple scattering. An electronic Raman effect (partial absorption) on the direction of the primary beam was not confirmed. N. M. B.

Spatial distribution of photo-electrons ejected from the atomic K shell. J. A. VAN DEN AKKER (Physical Rev., 1934, [ii], 45, 49—55).—The longitudinal space-distribution of electrons ejected from the K level of Cu by Mo $K\alpha_1$ radiation shows asymmetries differing by 10% from the wave-mechanical asymmetries. N. M. B.

K absorption discontinuities of the elements zirconium to iodine. P. A. ROSS (Physical Rev., 1933, [ii], 44, 977—983).—All except Cd showed, on the high-frequency side of the discontinuity, faint fine structure appearing as narrow bands of slightly decreased absorption. The width of the main discontinuity increased with at. no. The wave-lengths of the discontinuity, accurate to $\pm 0.02 \text{ \AA.}$, corresponding with the inflexion point in the main absorption curve are tabulated. N. M. B.

Quadrupole transitions and other new weak lines in the K spectra of elements 48 Cd and 50 Sn. III. E. C. INGELSTAM (Z. Physik, 1934, 87, 283—291; cf. Carlsson, A., 1933, 881).

A. B. D. C.

Relative intensities of certain L-series X-ray satellites in cathode-ray and in fluorescence excitation. F. R. HIRSH, jun., and F. K. RICHMYER (Physical Rev., 1933, [ii], 44, 955—960).—Using a special X-ray tube the relative intensities of satellites and their parent $L\alpha_1$ line were measured for cathode-ray excitation by 20-kv. electrons and for fluorescence excitation by the radiation from a Ag target bombarded by 20-kv. electrons for Zr, Mo, Ru, Rh, Pd, and Ag. Fluorescence results indicate LM ionisation as the origin of $L\alpha$ satellites, but cathode-ray excitation indicates peripheral electron structure influence on satellite production. N. M. B.

Natural widths of the L-series lines in the X-ray spectra of elements 74—83. J. H. WILLIAMS (Physical Rev., 1934, [ii], 45, 71—75).—Data for the widths at half-max. of the $L\alpha_1, \beta_1, \beta_2, \gamma_2$ lines of Bi, Pb, Tl, Au, Pt, Ir, and W and for the relative wave-lengths of neighbouring lines are given. Relations with the at. no. and electron transitions, and the effects of alloys of the elements, are discussed.

N. M. B.

Measurement of X-ray emission wave-lengths in the M-series by means of the ruled grating. E. G. PURDOM and J. M. CORK (Physical Rev., 1933, [ii], 44, 974—976).—Results are tabulated for Hf, Ta, W, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U. Wave-lengths are $>$ those found by the crystal method. N. M. B.

Townsend coefficients for ionisation by collision. F. H. SANDERS (Physical Rev., 1933, [ii], 44, 1020—1024).—The photo-electric current between parallel plates in dry air was measured as a function of plate distance for const. field strength and pressure for plate distances of 1—7 cm. at 1 mm. pressure of Hg. The relation of results to the Townsend coeffs. is discussed. N. M. B.

Effect of alkali ions on the photo-electric emissivity of tungsten. A. K. BREWER (Physical Rev., 1933, [ii], 44, 1016—1019; cf. A., 1931, 1106).—Curves are given for the effect on photo-emission of W excited by various Hg lines and the fraction of W surface covered by $\text{Na}^+, \text{K}^+, \text{Rb}^+$, and Cs^+ ions. Effect of temp. and variation of the work function are discussed. N. M. B.

Production of secondary electrons by argon positive ions and by argon atoms. C. J. BRASEFIELD (Physical Rev., 1933, [ii], 44, 1002—1005).—

Positive A ions of energy up to 150 equiv. volts were much less efficient than A atoms of equal kinetic energy in producing secondary electrons from a lamp-blackened Ni collector. The efficiency of production by these probably metastable atoms was approx. 3.5%. It is concluded that positive ions have negligible influence in producing electrons for the maintenance of a cold cathode discharge in gases. N. M. B.

Electron orbits in crossed electric and magnetic fields. A. E. SHAW (Physical Rev., 1933, [ii], 44, 1006—1011).—Focussing properties were investigated. Polarisation layers form on the plates of the electric field, reducing the effective deflecting potential. The abs. magnitude of the layers, measured for Au and bronze, depends on plate material, gas pressure, and electron intensity. Permanent insulating layers, vitiating e/m determinations, may be formed if electrons bombard a metal surface.

N. M. B.

Elastic scattering of high-velocity electrons by mercury atoms and the agreement with Mott's theory. E. B. JORDAN (Physical Rev., 1934, [ii], 45, 47—48; cf. A., 1933, 202).—The distribution in the angular range 8—48° of electrons scattered elastically by single Hg atoms for electron volt energies of 900, 1160, 1600, and 2000 gave curves differing widely from Mott's curve in the 900-volt case, but showing progressively closer agreement at the other voltages. N. M. B.

Study of the transformation of metals by [measuring] secondary electron emission. K. HAYAKAWA (Sci. Rep. Tohoku, 1933, 22, 934—958).—At the A3 transformation point of Fe the secondary electron emission-temp. curve shows a break which is independent of the voltage of the exciting electrons. The variation in electron emission during the magnetic transformation depends on the exciting voltage, changing sign at a certain "crit." val. of the latter. Similar changes are observed in the magnetic transformation of Co, Ni, and Fe-Ni alloys. The existence of the crit. voltage is explained on the basis of Richardson's structure electrons. F. L. U.

Light excitation in hydrogen canal rays. R. DÖPEL (Z. Physik, 1934, 87, 356—360).—Balmer series emitted by canal rays are due to direct excitation, neutralisation of the proton being probably radiationless. A. B. D. C.

Atomic collision. I. Production of slow atomic rays by recharging, and their determination by the thermo-element. O. BEECK. II. Ionisation of argon by neutral argon. O. BEECK and H. WAYLAND (Ann. Physik, 1934, [v], 19, 121—128, 129—142).—I. A method of producing a bundle of monochromatic, slow at. rays of considerable intensity is described. The construction and calibration of a thermo-element, suitable for determining the intensity of neutral rays, are described.

II. The above method is used to find the ionisation function, N , of A, by A rays of 350—650 ion-volt-equivalents. In this range, N increases from 4.5 to 6.5. The efficiency is four times that for collisions of K^+ with A, and exceeds to an even greater extent the efficiency of collisions of A with A. The effective

cross-section of A^+ in A is const. over the velocity range 350—650 volts. A. J. M.

Masses of the proton and electron. (SIR) A. EDDINGTON (Proc. Roy. Soc., 1934, A, 143, 327—350; cf. A., 1933, 107).—The mass m of a proton or electron is given by $10m^2 - 136mm_0 + m_0^2 = 0$, where $m_0 = h\sqrt{N/2\pi c\rho}$, N being the no. of such particles in the universe, and ρ the radius of curvature of an empty region, $=\sqrt{(3/\lambda)}$, where λ is the cosmical const.

L. L. B.

Thermal data and the at. wt. of krypton. W. HEUSE and J. OTTO (Physikal. Z., 1934, 35, 57—59; cf. A., 1929, 1226; 1931, 1004).—Using a gas-thermometric method, previously described, the 0° isotherm, and the expansion and compressibility coeffs. for Kr in the region of 1 m. pressure, have been determined. The density of Kr determined by direct weighing is 3.743 ± 0.001 g. per litre, and its at. wt., 83.66 ± 0.01 .

A. J. M.

Periodic system of chemical compounds of the type A_mB_n . H. G. GRIMM (Angew. Chem., 1934, 47, 53—58).—Binary compounds are divided into the classes salts, at. mols., diamond-like substances, metallic compounds, noble gases, and substances with two types of linking. Starting from the periodic arrangement of the elements it is shown that these various types of compounds recur at corresponding places in the table. The table provides new assumptions for the study of the relation between the properties of atoms and those of their compounds, and suggests fresh problems.

A. G.

Names for the hydrogen isotopes. H. C. UREY, F. G. BRICKWEDDE, and G. M. MURPHY (Science, 1933, 78, 602—603, and Nature, 1934, 133, 173).—Wood's nomenclature (this vol., 127) is considered unsatisfactory owing to the difficulty in naming the three waters, four ammonias, and thirteen benzenes now possible. Objections to the name diplogen (cf. this vol., 156) are discussed. Deuterium is the name and H^2 the symbol preferred for heavy H.

L. S. T.

Suggested nomenclature for heavy hydrogen and its compounds. F. C. WHITMORE (Science, 1933, 78, 603).—Deuterium is preferred to the "bar" nomenclature suggested by Wood (this vol., 127).

L. S. T.

Designation of heavy hydrogen. H. E. ARMSTRONG (Nature, 1934, 133, 173).—Deutrydrogen is suggested.

L. S. T.

Isotope report. Chemical elements and types of atoms according to isotope investigation. (Report on the work from end of 1932 to end of 1933.) O. HAHN (Ber., 1934, 67, [A], 1—8).—The work on H, Li, Be, B, C, O, F, Ne, Cl, Ga, Ge, Rb, Cd, and Hg is reviewed.

H. W.

Distribution of the radioactive thallium isotope Th-C'' in thallium salt solutions. J. ZIRKLER (Z. Physik, 1934, 87, 410).—Th-C'' distributes itself in Tl^+ ions in proportion to the $[Tl^+]$, but does not distribute itself equally between Tl^+ and Tl^{++} ions.

A. B. D. C.

Periodic series of biogenetic elements in the periodic system. K. HRYNAKOWSKI (Rocz. Chem., 1933, 13, 541—545).—Certain numerical relation-

ships between the biologically active elements N, O, Na, Mg, P, S, K, and Ca are pointed out. R. T.

Amendment to the law of multiple proportions. E. A. VUILLEUMIER (Science, 1934, 79, 13).

L. S. T.

New type of radioactivity. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1934, 198, 254—256; cf. A., 1933, 762).—The emission of positive electrons as previously described continues after removal of the source of α -particles for times that vary according to the irradiated element; the intensity of such emission decreases exponentially, the periods for Al, B, and Mg being respectively 3.25, 14, and 2.5 min. The initial intensity increases with the time of irradiation up to an approx. equal limit. No such effect is observed with H, Li, C, Be, N, O, F, Na, Ca, Ni, or Ag. Absorption by Cu screens indicates energies of 2.2×10^6 ev. for the positive electrons from Al, and 0.7×10^6 ev. for those from B and Mg. The emission is probably explained by $Al^{27} + He^4 = P^{30} + n_0^1$, P^{30} being radioactive with period 3.25 min. ($P^{30} = Si^{30} + e^+$); B and Mg would yield similarly N^{13} and Si^{27} of similar short periods.

C. A. S.

Radioactivity of samarium. M. CURIE and F. JOLIOT (Compt. rend., 1934, 198, 360—363; cf. A., 1933, 4, 442).—When examined in a Wilson's expansion chamber a thick layer of $Sm_2(C_2O_4)_3 \cdot 10H_2O$ emits per sq. cm. approx. 7 α -particles per min., with path probably > 1.5 cm.; the period of Sm is about 10^{12} years. The disintegration suggested is $^{147}Sm = ^{144}Nd + ^4He + 0.0030$.

C. A. S.

Recoil atoms in gaseous media. L. GOLDSTEIN (Compt. rend., 1934, 198, 363—365; cf. A., 1933, 761).—With an electrode negatively charged in an atm. of Rn and (a) H_2 , (b) Br vapour, the % of atoms of Ra-A remaining charged at the end of their recoil path varied, in (a) from 36 to 32.5 when pressure varied from 140 to 250 mm. Hg, or, deducting the activation of the electrode by direct recoil, 32%, as for the rare gases; in (b) the % was 79, or approx. the same as in air or O_2 (83).

C. A. S.

Radium-uranium ratio and the number of actinouranium isotopes. A. E. RUARK and F. WESTERN (Physical Rev., 1934, [ii], 45, 69—70).—An expression for the ratio is found. Evidence indicates the existence of only one Ac-U isotope.

N. M. B.

Gamow's theory of radioactive decomposition. H. CASIMIR (Physica, 1934, 1, 193—198).—Theoretical.

H. J. E.

Measurement of natural α -particles ejected from solids. R. D. EVANS (Physical Rev., 1934, [ii], 45, 29—37).—Mathematical. From an analysis of empirical ionisation curves, expressions and their graphical integration for ionisation due to α -particle emission are given.

N. M. B.

Complex radiation excited in aluminium by α -particles. P. SÁVEL (Compt. rend., 1934, 198, 368—370).—When the radiation produced from Al by the impact of α -particles from Po is examined in a high-pressure (A or H_2 , 25 atm.) ionisation chamber (cf. A., 1933, 659), both the γ -radiation and neutrons are found to be complex. The γ -radiation (mainly photons) consists of two varieties with $\mu/\rho_{Fe} = 0.17$,

energy 0.55×10^6 ev., and $\mu/\rho_{\text{Pb}} = 0.045$, energy 2.10×10^6 ev. Similarly the neutrons include two varieties the intensities of which are reduced to half by 1.7 mm. and 1.53 cm. Pb, respectively, the energy of the more rapid being 2×10^6 ev. To excite the γ -radiation the min. energy of the incident α -particles is $3-3.1 \times 10^6$ ev., and for the neutrons $4-4.3 \times 10^6$ ev., penetration to the Al nucleus being by a resonance level. The softer γ -radiation is attributable to the annihilation of $+$ electrons of Al (cf. this vol., 126, 127), the harder to disintegration of the Al atom (cf. A., 1932, 318). C. A. S.

Ionisation curves of α -rays. R. NAIDU (Ann. Physique, 1934, [xi], 1, 72-122).—Using a new apparatus to eliminate the effect of multiple scattering, normal Bragg curves are constructed for α -rays of Po and Ra-C'. A proportionality between energy loss and ionisation energy is shown for Po rays, but rather less so for Ra-C' rays. Regarding energy transformation into ionisation energy as complete in He the same was found true for Ne, but for A and air there is a loss of 20 and 50%, respectively, due to excitation or dissociation of atoms or mols.

N. M. B.

Suggested explanation of β -ray activity. M. N. SAHA and D. S. KOTHARI (Nature, 1933, 132, 747; 1934, 133, 99).—Theoretical. L. S. T.

Radioactive radiations from the surfaces of solids and the measurement of the thorium content of rocks. R. D. EVANS (Physical Rev., 1934, [ii], 45, 38-42).—Ionisation due to α - and γ -radiation from granite and representing the combined effect of the U, Ac, and Th series can be corr., by emanation measurements, for contributions due to U and Ac; hence the Th content of rocks can be obtained.

N. M. B.

Zero method for the γ -radiation strength of radium preparations. A. PICCARD and L. MEYLAN (J. Phys. Radium, 1933, [vii], 4, 715-718).—An improved precision form of Rutherford's method is described, in which the position on a graduated scale is found at which the sample neutralises the ionisation due to a standard sample, using two identical ionisation chambers.

N. M. B.

γ -Rays of radium-B+C and of thorium-C+C'. C. D. ELLIS (Proc. Roy. Soc., 1934, A, 143, 350-357).—A re-measurement has been made of the Ra-B+C spectrum, and all the energies have been recalcd. using $C = 2.9980 + 10^{10}$ and $e/m = 1.760 \times 10^7$. The results are in excellent agreement with the α -ray measurements (A., 1933, 1224). Certain measurements on the Th-C+C' spectrum are described. L. L. B.

Slow neutrons emitted by beryllium under the action of α -rays. P. AUGER (J. Phys. Radium, 1933, [vii], 4, 718-724).—Photographs of tracks, due to the action on a chamber of moist H_2 , when Be was bombarded by α -rays were obtained. Tracks for high-speed protons under the action of high-energy neutrons, and others for slow protons arising from collisions with slow neutrons were distinguished. The slow neutrons are attributed to excitation of the Be nucleus by α -particles, without capture of the latter, emission being due to excitation energy. N. M. B.

Combination of proton and neutron. D. E. LEA (Nature, 1934, 133, 24).—Scattering experiments with paraffin wax suggest that in some of the collisions between neutron and proton the particles combine to form H^2 with emission of energy in the form of γ -radiation. L. S. T.

Radiative collisions of neutrons and protons. H. S. W. MASSEY and C. B. O. MOHR (Nature, 1934, 133, 211).—Calculation of the probability of a radiative combination of a neutron (I) and proton (II) to form a dipion shows that for the range of energies involved in the experiments of Lea (see above) combination should not take place more frequently than 1 in 10^3 collisions, which is $<$ the observed frequency of 1 in 4. The calc. probability of a (II) radiating in the impact without combination taking place is even smaller. Assuming (I) to be a complex particle consisting of (II) and electron and that there are exchange forces between (I) and (II) of the type suggested by Heisenberg, a smaller probability (1 in 10^6) of combination is obtained. These results indicate the need for additional information concerning the (I)-(II) collision. L. S. T.

γ -Rays produced by passage of neutrons across hydrogenated substances. P. AUGER (Compt. rend., 1933, 198, 365-368; cf. Lea, above).—If a proton and neutron unite to form a deuteron, the latter should move off in nearly the direction of the initial motion of the neutron, but this is not the case (cf. A., 1933, 551; but cf. also *ibid.*, 1100). Measurements of e/m by a magnetic field also give no indication of the presence of deuterons. It is therefore suggested that the mass of the neutron is $>$ that of the proton (1.011 or 1.009), the proton being a combination of a neutron and a positron with loss of mass $= 2-4 \times 10^6$ ev. The impact of a neutron on such a proton would excite the proton and cause emission of a γ -ray of energy $2-4 \times 10^6$ ev., whilst the trajectory of the proton would be more inclined to the initial direction of the neutron than in the case of an elastic collision. C. A. S.

Action of X-rays on atomic nuclei. G. I. POKROVSKI and V. K. KORSUNSKI (J. Exp. Theor. Phys., U.S.S.R., 1932, 2, 141-153).—Theoretical conclusions regarding conditions for disintegration of unstable nuclei agree with results obtained with Pb, Sn, W, and Al. CH. ABS.

Cloud photographs of cosmic-ray stosse. G. L. LOCHER (J. Franklin Inst., 1933, 216, 673-682).—The large instantaneous increments in the ionisation by cosmic rays were photographed stereoscopically in ionisation chambers containing A and surrounded by a large mass of metal, the chamber being operated automatically. The origin and mechanism of production of the stosse are discussed. Neutrons arising from disintegration processes appear to be generated or liberated. N. M. B.

Hoffmann stosse and the origin of cosmic-ray ionisation. W. F. G. SWANN (Physical Rev., 1933, [ii], 44, 1025-1027).—Mathematical. It is shown that nearly the whole of observed cosmic-ray intensity may be attributed to bursts of Hoffmann stosse in the

atm., but, as observed by Geiger counters, the effect will be only that of single rays at random.

N. M. B.

Ionisation by cosmic-ray particles and swift β -particles. G. L. LOCHER (J. Franklin Inst., 1934, 217, 39—58).—Suggestions are put forward to account for the discrepancies between the results of the Geiger counter and cloud-chamber methods of determination of the ionisation along cosmic-ray tracks. J. W. S.

Ionisation per centimetre of path by individual secondary cosmic rays. W. F. G. SWANN (Physical Rev., 1933, [ii], 44, 961—968).—Results for A, N₂, and O₂ are 89, 61, and 57 ions per cm., respectively, at atm. pressure. The existence of multiple rays, contributing 2/3 of the total ionisation, is verified. N. M. B.

Distribution of low-energy cosmic rays in the atmosphere. W. E. DANFORTH and M. R. LIPMAN (J. Franklin Inst., 1934, 217, 73—78).—By using thin-walled Geiger counters it has been found that the energy spectrum of cosmic-ray secondaries extends at least as far as 5×10^6 ev., and that the intensity between 5×10^6 and 10^7 ev. is about one eighth of the total intensity above 10^7 ev. J. W. S.

Dematerialisation of pairs of electrons. F. JOLIOT (Compt. rend., 1933, 198, 81—83; cf. this vol., 126).—Positrons from an Al plate irradiated by α -particles from Po and conc. magnetically fell on a Pb radiator placed above a Geiger-Müller counter. All such are stopped by 1.5 mm. Pb with production of γ -rays, of $\mu/\rho = 0.19$ — 0.32 , whilst the average energy of a photon is 485 ± 60 ekv. in agreement with Dirac's theory. There are three possible methods of dematerialisation: (i) an electron and a positron meet, resulting in production of two photons of equal energy (0.5×10^6 ekv.). This can occur only when the positron has been stopped in absorbing material, and implies an average life for a positron in H₂O of 4×10^{-10} sec. (ii) A positron meets an electron strongly bound in an at. nucleus, resulting in production of one photon of energy 10^6 ekv. These are both in accordance with Dirac's theory. Comparison with the emission from Ra implies the production of 1.6—3 photons per positron, i.e., favours (i). (iii) A neutrino (cf. this vol., 127), which, having no intrinsic mass, has no effect on the counter, and one photon of energy 0.5×10^6 are produced, which Thibaud's results seem to favour. As positrons dematerialise only when they have lost most of their velocity, their average life may be much $>$ supposed by Thibaud. C. A. S.

Materialisation of æther. V. POSEJPAL (Compt. rend., 1934, 198, 59—61).—The discovery of the positron has extended the author's theory (cf. A., 1932, 1187) of the ether as consisting of inert mass of at. no. zero, with nucleus of combined proton and electron, to include any pair of such particles provided they are of opposite sign; the formation of an ether particle in this way is accompanied by production of two photons of quanta $h\nu = m_{\text{re}}c^2/2$. Conversely, access of photons of at least similar energy should split an ether particle into its constituents, materialising it into a proton and an electron; such separation should become complete in vac. in presence of a sufficiently

powerful electric field. This has been demonstrated by maintaining an intense field between a cylindrical electrode and a Pd wire along its axis as cathode, the whole in vac. Production of protons was inferred from the increase of 1.7—7.5% (increase greatest with wire of least diam.) in the resistance of the Pd wire caused by their absorption, the process being unaccompanied by production of light, whereas when the field was reversed the Pd wire was ruptured with emission of sparks (cf. A., 1932, 892). C. A. S.

[Materialisation of æther.] A. COTTON (Compt. rend., 1934, 198, 61—62; cf. preceding abstract).—It is suggested that in spite of all precautions the protons thought to be produced were really present *ab initio* in the tube, as, e.g., a trace of H₂O. C. A. S.

The photon. L. DE BROGLIE (Compt. rend., 1934, 198, 135—138; cf. A., 1932, 1184; this vol., 7).—It is shown mathematically that the photon is not simple, but consists of a "corpuscle of light" accompanied in its movements by an "anticorpuscle" related to it as the positive to the negative electron in Dirac's theory of holes. In presence of matter the photon would yield to the matter energy $h\nu$, the corpuscle of light falling into the hole that accompanies it. Such corpuscle of light would be identical with the neutrino (cf. this vol., 127). C. A. S.

Quantum mechanics of photons. A. PROCA (Compt. rend., 1934, 198, 54—56).—Regarding the photon as a particle of zero mass and charge, the limitations of the application thereto of a method analogous to the relativistic form of Schrodinger's mechanics are considered. C. A. S.

Representation of radiation reaction in wave mechanics. W. F. G. SWANN (J. Franklin Inst., 1934, 217, 59—71).—Mathematical. J. W. S.

Energy distribution of a surface lattice of atoms with electronic orbital angular momentum. H. LUDLOFF and G. REYMANN (Z. Physik, 1933, 87, 154—175).—The total angular momentum is on the average zero, and does not contribute to ferromagnetism. The "proper" val. spectrum is discussed in relation to degeneracy and zero point entropy. A. B. D. C.

Negative result of an attempt to combine light quanta. C. J. GORTER (Physica, 1934, 1, 199—200).—Sunlight (5000—6000 Å.) was conc. on H₂O or aq. NiCl₂. No indication of light of twice the incident frequency was found in the radiation scattered at right angles. H. J. E.

Electron theory of metals. A. SOMMERFELD (Naturwiss., 1934, 22, 49—52).—Theoretical. The Thomson effect for the alkali metals, and the Richardson effect, are considered. A. J. M.

Isotope of hydrogen. III. P. ZEEMAN and J. DE GIER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 2—3; cf. A., 1933, 1099; this vol., 4).—The mass differences between He and H¹H², HeH¹, and H¹H³, HeH², and as measured by the parabola method using a mixture of He with H₂ containing 10% H², agree to 1—1.5% with the vals. calc. from the data of Bainbridge (cf. A., 1933, 203). Parabolas corresponding with m/e vals. of 41 and 42 are attributed to AH¹ and AH², respectively. J. W. S.

Existence of negatively-charged proton ; constitution of the nucleus of the isotope H^2 . I. I. PLACINTEANU (Bul. Soc. Romane Fiz., 1933, 35, 95—102; cf. A., 1933, 995).—Theoretical. The nucleus of H^2 of mass 2.013 is formed by the union of two neutrons and a positive electron. H. J. E.

"Mottled" hydrogen. W. GERLACH (Z. Physik, 1934, 87, 409).—A criticism of Günther-Schulze and Betz (A., 1933, 759), particularly with regard to introduction of this term. A. B. D. C.

Equilibrium between the three hydrogens. D. RITTENBERG, W. BLEAKNEY, and H. C. UREY (J. Chem. Physics, 1934, 2, 48—49; cf. this vol., 30).—Mass-spectrographic analysis of H_2 made by the decomp. of HI (used previously) at 25°, 397°, and 468° gave abundance ratios of H_2 , H^1H^2 , and H_3 at these temp. of approx. 1 : 21 : 134, 1 : 13.3 : 46, and 1 : 2.69 : 1.93, respectively. The observed and calc. vals. for the equilibrium $H_2 + H_3 \rightleftharpoons 2H^1H^2$ agree. H. J. E.

Atomic and molecular radii. V. POSEPAL (J. Phys. Radium, 1933, [vii], 4, 741—748).—A theory previously developed (cf. A., 1932, 1187) is applied to the calculation of the at. radius and mean at. collision durations of H, He, N, O, Ne, Cl, A, Br, Kr, I, and Xe. Results are in good agreement with available data. N. M. B.

Value of c/m from the Zeeman effect. L. E. KINSLER and W. V. HOUSTON (Physical Rev., 1934, [ii], 45, 104—108).—A high-precision repetition of previous work (cf. A., 1932, 444) gives the val. 1.7570 ± 0.0010. N. M. B.

Approach to an explanation of the surface work functions of pure metals. J. F. CHITTM (J. Physical Chem., 1934, 38, 79—84).—A formula is deduced for the net surface work function of a metal. The intrinsic potentials are calc. for many metals and compared with the arbitrary experimental vals. The agreement is satisfactory. M. S. B.

Electron terms of the nitrogen molecule. A. RECKNAGEL (Z. Physik, 1934, 87, 375—398).—An approx. solution is obtained for the Schrödinger equation; this gives good approximations to the lower terms as determined empirically, and is applied to allocation of the higher terms. A. B. D. C.

Quantised molecules formed of excited mercury atoms and methane molecules. G. GLOCKLER and F. W. MARTIN (J. Chem. Physics, 1934, 2, 46).—Four diffuse fluorescence bands between 2554.2 and 2542.6 Å., attributed to quantised states of a CH_4 -Hg complex, were observed on illuminating a mixture of CH_4 (1 atm.) and Hg vapour with a Hg (Ne) discharge tube. Raman scattering is excluded. Oldenberg observed similar bands with excited Hg and rare gas atoms (A., 1928, 346). H. J. E.

Large electronic isotope effects in molecular spectra. H. L. JOHNSTON (Physical Rev., 1934, [ii], 45, 79—81).—Measurements of fine structure in the isotopic OH bands confirm a large electronic isotope effect in the spin coupling of $^2\Pi$ terms. For BO and OH the observed increase in the doublet spacings, in the mol. with the heavier isotope, agree with theory.

A large electronic isotope effect in A doubling is also observed for OH. N. M. B.

Rotation-vibration coupling in diatomic molecules. C. L. PEKERIS (Physical Rev., 1934, [ii], 45, 98—103).—Mathematical. N. M. B.

Zeeman effect for the absorption lines of the ruby. H. LEHMANN (Ann. Physik, 1934, [v], 19, 99—117).—The transverse Zeeman effect for the absorption lines R_1 and R_2 is dependent on the orientation of the crystal lattice with respect to the magnetic field and plane of polarisation down to -190°. The variation of the splitting follows the symmetry of the crystal lattice. The optic axis is one of six-fold symmetry. A. J. M.

Photometric and spectrophotometric studies. X. Influence of adsorption on the absorption spectra. K. SCHAUM and K. MAENNCHEN (Z. wiss. Phot., 1934, 32, 201—221).—The extinction coeff. of aq. $KMnO_4$ does not decrease uniformly with dilution, and other anomalies are found; the absorption curve is flattened somewhat but not shifted on addition of SiO_2 sols. Detailed results are given of the changes in absorption of various dyes (methylene-blue, rhodamine, pinacyanol, etc.) in admixture with hydrophile colloids (gelatin, agar, etc.), in acid and alkaline solutions. J. L.

Predissociation in the Angstrom bands of CO. D. COSTER and F. BRONS (Physica, 1934, 1, 155—160).—Predissociation of the upper level of the Angstrom bands occurs at $v=0$ and $J=38$. The dissociation energy of normal CO is 9.82 ev. H. J. E.

Absorption spectra of the sulphides of zinc, cadmium, and mercury, from 7000 to 1900 Å., and the heat of dissociation of sulphur. P. K. SEN-GUPTA (Proc. Roy. Soc., 1934, A, 143, 438—454).—The vapours of ZnS, CdS, and HgS absorb light continuously from a long-wave limit, resulting in photochemical dissociation into two normal atoms, thus: $MS + h\nu_1 = M + S (^3P)$. After the first absorption there is a re-transmitted patch and a second absorption corresponding with $MS + h\nu_2 = M + S (^1D_2)$. For HgS there is another re-transmitted patch and a third absorption corresponding with $MS + h\nu_3 = M + S (^1S_0)$. It is postulated that in the vapour state these compounds are ionic in nature, of the type $M^{++}S^{--}$. The heat of dissociation of S_2 into S atoms is 102.9 kg.-cal. L. L. B.

Temperature dependence of the absorption spectrum of chromium oxychloride. P. K. PEERLKAMP (Physica, 1934, 1, 150—154; cf. A., 1933, 997).—With rise of temp. the diffuse bands between 6000 and 5300 Å. weaken, and disappear at 220°, whilst the general absorption increases. Between 5300 and 2300 Å. absorption is continuous. Predissociation occurs in all vibrational levels of the upper electronic state. SO_2Cl_2 shows diffuse absorption bands between 3200 and 2800 Å., and continuous absorption at greater frequencies (cf. this vol., 129). H. J. E.

Ultra-violet absorption of binary liquid mixtures. III. System propaldehyde-ethyl alcohol. M. PESTEMER and (FRL.) P. BERNSTEIN (Monatsh., 1933, 63, 236—243).—Although the absorption spectrum of a EtCHO-EtOH mixture shows

no distinctive absorption bands due to acetal formation, the deviations of the val. of ϵ from the additive law are a max. for an equimol. mixture and indicate that $\text{OH}\cdot\text{CHEt}\cdot\text{OEt}$ is formed, but not $\text{CHEt}(\text{OEt})_2$.

D. R. D.

Spectral differentiation of pure hydrocarbons : near infra-red absorption study. U. LIDDEL and C. KASPER (Bur. Stand. J. Res., 1933, 11, 599—618).—The absorption spectra of 36 hydrocarbons have been measured over the range 5500—9000 cm^{-1} by means of an automatic recording infra-red glass spectrograph, the results being recorded in graphical form. The absorption bands are correlated and discussed with reference to the mol. structures.

J. W. S.

Absorption spectra of monohalogen derivatives of saturated aliphatic hydrocarbons. J. LECOMTE (Compt. rend., 1934, 198, 65—67).—The infra-red spectra (λ 20.4—6.9 μ , ν 490—1450 cm^{-1}) of 20 compounds have been determined. Where comparison is available, agreement with Raman spectra is good. Differences *inter se* in homologous series are sufficient to make the method suitable for analysis. Frequencies in corresponding bands are in the order $\text{Cl} > \text{Br} > \text{I}$, a pair of fundamental frequencies characteristic of the halogens in straight-chain derivatives with $\text{C} < 3$ lying, respectively, between 650 and 725, 560 and 645, and 505 and 595 cm^{-1} (cf. A., 1933, 208).

C. A. S.

Structure of the ultra-violet absorption spectrum of formaldehyde. I. G. H. DIEKE and G. B. KISTIAKOWSKY (Physical Rev., 1934, [ii], 45, 4—28).—Wave nos., intensities, rotational analyses, and combination relations are tabulated for the 3530, 3430, 3390, 3370, 3295, and 3260 \AA . bands.

N. M. B.

Absorption and fluorescence of alcoholic solutions of phenanthrene. R. TITEICA (Bul. Soc. Romane Fiz., 1933, 35, 149—155).—The absorption and fluorescence spectra in solutions of various concns. have been measured. New bands were found with max. at 3096 and 2420 \AA .

H. S. P.

Effect of ultra-violet rays of the ultra-violet absorption spectrum of aqueous methylene-blue solution. C. E. NURNBERGER and L. E. ARNOW (J. Physical Chem., 1934, 38, 71—77).—Max. absorption in the ultra-violet by methylene-blue occurs at 2920 and 2460 \AA ., but on continuous exposure there is a decrease in the absorption bands in both visible and ultra-violet regions, the most active wave-lengths in decreasing the bands being those $< 2700 \text{\AA}$., so that this absorption cannot be used to measure radiation intensity in the "physiologically active" region 2900—3100 \AA . p_{H} change has no effect on the spectrum, but irradiation causes the greatest change in solutions of highest p_{H} .

M. S. B.

Ultra-violet absorption of thin blown glass. S. CRISTESCU and S. VENCOV (Bul. Soc. Romane Fiz., 1933, 35, 75—87).—The transmission of Jena and Thurmger glass, 2.5—300 μ thick, has been measured. For very thin plates it extends to 2300—2500 \AA .

H. J. E.

Infra-red bands and molecular constants of HBr . E. K. PLYLER and E. F. BARKER (Physical Rev., 1933, [ii], 44, 984—985).—Vals. obtained by re-

measurement of the fundamental band and examination of the harmonic band under high resolution are : $\nu_0 = 2649.74 \text{ cm}^{-1}$, $I_0 = 3.2634 \times 10^{40} \text{ g. cm}^2$, $r_0 = 1.4096 \times 10^{-8} \text{ cm}$. Separations of isotopic components were in agreement with those calc. from the isotopic masses of Br.

N. M. B.

Harmonic and combination bands in CO_2 . E. F. BARKER and T. Y. WU (Physical Rev., 1934, [ii], 45, 1—3).—The 5.0, 1.43, 2, and 1.6 μ bands have been resolved.

N. M. B.

Influence of foreign gases on the intensity of infra-red absorption. P. C. CROSS and F. DANIELS (J. Chem. Physics, 1934, 2, 6—10).—The effect of He, A, O_2 , N_2 , C_2H_6 , CO_2 , and H_2 on the N_2O and CO bands at 4.5 μ and 4.66 μ , respectively, and on infra-red absorption by EtBr , has been measured. The foreign gas enhances the absorption. To explain the effects, collision diameters related linearly to the gas-kinetic diameters must be assumed. The vals. are not related to those which must be taken for explaining the influence of the same gases on the thermal decomp. of N_2O (cf. Volmer and Froehlich, A., 1933, 30). The applicability of Beer's law is discussed.

H. J. E.

Infra-red absorption of benzene vapour. R. TITEICA (Bul. Soc. Romane Fiz., 1933, 35, 89—91).—ands between 1 μ and 17 μ resemble closely the absorption bands of liquid C_6H_6 in the same region, but have a different intensity distribution. The C—H distance in C_6H_6 is 1.04 \AA . The C—C and the C:C linkings are both indicated.

H. J. E.

Infra-red absorption of organic substances. III. A. ROTH (Z. Physik, 1933, 87, 192—204).— $\text{Pr}^{\text{III}}\text{Cl}$, $\text{Pr}^{\text{III}}\text{Br}$, $\text{Pr}^{\text{III}}\text{I}$, HCO_2H , HCO_2Me , HCO_2Et , PhCCl_3 , BzCl , MeOBz , anisole, and anisaldehyde were investigated from 0.8 to 2.6 μ .

A. B. D. C.

Infra-red absorption spectra of some plant pigments. R. STAIR and W. W. COBLENTZ (Bur. Stand. J. Res., 1933, 11, 703—711).—The infra-red absorption spectra of chlorophyll, carotene, xanthophyll, ethylchlorophyllide, phytol, phaeophytin, and Cu phaeophytin have been measured as far as 15 μ , and the changes in absorption spectrum accompanying the oxidation of carotene examined in detail.

J. W. S.

Raman spectrum of water. J. CABANNES and J. DE RIOLS (Compt. rend., 1934, 198, 30—32).—This consists of (1) a large band around 3450 cm^{-1} , with max. at 3224, 3436 (most intense), and 3525, all three polarised, ρ for 3436 = 0.3; (2) a narrow band at 1650, also polarised, ρ = 0.4; and (3) a weak band at 350—750. Lines or bands corresponding with (1) and (2) occur in aq. NaNO_3 , and in H_2O vapour, those in the latter (3654 and 1648) being the symmetrical lines n_2 and n_3 of the angular mol. H_2O , whilst the anti-symmetric line n_1 is probably concealed by 3654, with which 3625 in liquid H_2O corresponds. 3411 and 3495 in gypsum are attributed to the double mol. $(\text{H}_2\text{O})_2$.

C. A. S.

Raman spectrum of heavy water. R. W. WOOD (Nature, 1934, 133, 106; cf. this vol., 129).

L. S. T.

The OH Raman band of nitric acid. L. MÈDARD and (Mlle.) T. PETITPAS (Compt. rend., 1934, 198,

88—89).—Using pure HNO_3 renewed every 3 hr. to avoid photochemical decomp., and exposing for 30 hr. to $\text{Hg } \lambda 4046.5$ filtered through aq. CoCl_2 , a dissymmetric band around 4685 \AA . (i.e., $3215\text{--}3485 \text{ cm}^{-1}$) was observed (cf. A., 1931, 1111; A., 1933, 1228). A similar band occurs in a solution of NH_4NO_3 in HNO_3 , the Raman spectra of which and of a HNO_3 solution of KNO_3 resemble each other. C. A. S.

Molecular spectra of some indium and gallium halides. E. MIESCHER and M. WEHRLI (Z. Physik, 1934, 87, 310—311).—A criticism of Petrikal and Hochberg (this vol., 7). A. B. D. C.

Molecular spectra of some indium and gallium halides. A. PETRIKALN and J. HOCHBERG (Z. Physik, 1934, 87, 311).—A reply to the above. A. B. D. C.

Raman effect. XXVIII. Isomeric paraffin derivatives. IV. K. W. F. KOHLRAUSCH and F. KOPPL (Monatsh., 1933, 63, 255—270).—Data are recorded and discussed for five *n*-paraffin halides, three mercaptans, six alcohols, and one amine with branched chains. D. R. D.

[Raman] spectra of some acetylenic alcohols. (MLLE.) B. GRÉDY (Compt. rend., 1934, 198, 89—91).—The Raman spectra of $\text{CR}:\text{C}:\text{CH}_2\cdot\text{OH}$ and $\text{CR}:\text{C}:\text{CHMe}\cdot\text{OH}$ ($\text{R}=\text{n-C}_5\text{H}_{11}$, $\text{n-C}_6\text{H}_{13}$, *cyclo-C}_6\text{H}_{11}, CH_2 , and Ph) have been determined. Replacement of R' (not Me) in $\text{CR}:\text{CR}'$ by $\text{CH}_2\cdot\text{OH}$ has practically no effect on the characteristic frequencies (cf. A., 1933, 886), but replacement by $\text{CHMe}\cdot\text{OH}$ increases them by $20\text{--}25 \text{ cm}^{-1}$, greatly reducing the intensity of the second line. Ph has its usual effect. The following are described: Δ^2 -decinen- β -ol, b.p. $110\text{--}112^\circ/16 \text{ mm.}$, δ -cyclohexyl- Δ^2 -butinen- α -ol, b.p. $134^\circ/17 \text{ mm.}$, ϵ -cyclohexyl- Δ^2 -pentinen- β -ol, b.p. $133^\circ/17 \text{ mm.}$, Δ^2 -Noninen- β -ol (Mourcu, Bull. Soc. chim., 1905, 33, 155) has b.p. $100^\circ/16 \text{ mm.}$ C. A. S.*

Raman effect of furan and furfuraldehyde. G. GLOCKLER and B. WIENER (J. Chem. Physics, 1934, 2, 47).—Data are given. A Raman line 1567 cm^{-1} due to the C:C linking occurs for furfuraldehyde, but not for furan, thus favouring a centric formula for the latter mol. H. J. E.

Raman effect of multiple linkings between C and N in organic molecules. G. B. BONINO and R. MANZONI-ANSIDEI (Mem. R. Accad. d'Italia Sci. fis., 1933, 4, 759—776).—The Raman spectra of various aliphatic and aromatic aldoximes and ketoximes have been measured. The aliphatic oximes have a characteristic frequency about $1650\text{--}1660 \text{ cm}^{-1}$, and the aromatic oximes about 1625 cm^{-1} , attributed in both cases to the C:N linking. In the Na salts of the aromatic compounds the C:N frequency is displaced to $1540\text{--}1550 \text{ cm}^{-1}$. The nature of the C:N linking in oximes and in other compounds is discussed. O. J. W.

Raman spectra of some unsaturated nitriles. M. DE HEMPTINNE and J. WOUTERS (Ann. Soc. Sci. Bruxelles, 1933, 53, B, 215—218).—Vinylaceto-, crotono- (I), and isocrotono-nitriles (II) all show an intense Raman frequency of about 2250 cm^{-1} , attributed to the $\cdot\text{C}:\text{N}$ vibration, as well as the frequencies 1407 and 2921 cm^{-1} of the $\cdot\text{CH}_2$ and $\cdot\text{CH}$

groups. The C:C vibration frequency is higher for (I) (1645) than for (II) (1628 cm^{-1}). J. W. S.

Photoluminescence of sodium and potassium hydroxides. A. GRUMBACH and (MLLE.) M. RIBALLIER (Compt. rend., 1934, 198, 70—72).—The fluorescence of freshly cut KOH is green, of NaOH blue; after heating to fusion the fluorescence is at first more brilliant, but changes to yellow, and on prolonged heating disappears. The blue and green fluorescence appears to be due to formate, the change to yellow to formation of carbonate in addition. The fluorescence is restored to the calcined product on addition of formate, but not by carbonate. C. A. S.

Phosphorescence of eosin solutions. Influence of temperature. J. CHLOUPEK (Chem. Listy, 1933, 27, 493—497).—The duration of luminescence of eosin dissolved in glycerol is diminished by addition of H_2O or by raising the temp., to an extent proportionate to the change in viscosity of the medium, indicating that the phenomenon is one of true phosphorescence. R. T.

Extinction of fluorescence by organic compounds. K. WEBER and M. L. SAVIC (Z. physikal. Chem., 1934, B, 24, 68—74).—The extinction of the fluorescence of solutions by foreign substances and the part played by the solvent in the extinction have been studied. For a given foreign substance and fluorescing substance change of the solvent usually causes a parallel shift of the extinction curve in a direction which is the same whatever the foreign substance, X. The order of increasing effectiveness of a group of foreign substances varies with the fluorescing substance, Y. The order of magnitude of the dimensions of the sphere of action is determined by the properties of Y and is independent of X. R. C.

Coloration of fluorides of different elements by cathode rays. H. NAGAOKA, Y. SUGIURA, and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1933, 9, 486—489).—The colours observed when Ca, Li, Na, Mg, Al, Ti, Mn, Cr, Zn, and Pb fluorides are subjected to the radiation from a heated W filament are described. The curves relating the ratio of intensities of reflected and incident light to voltage $V^{2/3}$ are almost linear at low voltages, but change slope abruptly at 660 volts owing to the excitation of the *K* radiation of F, and subsequently when the *M* and *K* radiations of the cations appear. No direct evidence was obtained of dissociation, since when, e.g., Ca and CaF_2 are heated at 800° colorations similar to those caused by bombardment are produced. H. F. G.

Thermo-luminescence spectra of fluorites. III. Thermo-luminescence spectra of fluorites from Wilberforce. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 153—161; cf. this vol., 10, 130).—Three specimens of different appearance each gave eleven bands in almost identical positions. The bands at wave-lengths $> 3840 \text{ \AA}$. are attributed to Tb and those in the ultra-violet region to Gd, the proportions of these impurities varying in the three specimens. J. W. S.

Artificial production of the blue fluorescence of fluorite. H. HABERLANDT, B. KARLIK, and K. PRZIBRAM (Nature, 1934, 133, 99—100).—Experi-

ments with synthetic materials show that a rare-earth element, probably Eu, is responsible for the blue fluorescence band shown by fluorite. L. S. T.

Polarised photoluminescence of adsorbed molecules of dyes. A. JABŁOŃSKI (Nature, 1934, 133, 140).—The degree of polarisation of fluorescence and phosphorescence from Cellophane films coloured by Kautsky's method has been investigated.

L. S. T.

Rectification. W. C. VAN GREL and H. EMMENS (Z. Physik, 1933, 87, 220—230).—Experiments on electrolytic rectifiers show that these act according to the emission theory, although electron emission is complicated by electrons having to be freed from hydrated ions before passing into the barrier layer.

A. B. D. C.

Role of intervening layer in rectification by imperfect contact. QUINTIN (Compt. rend., 1934, 198, 347—349).—A plate of polished Si in contact with graphite shows no rectifying effect, but if separated by a thin mica plate with a hole so that a film of air 10^{-3} — 10^{-5} cm. thick intervenes such effect appears. Current-p.d. curves are given and also for similar contacts with Si and Cu and Si and Sn. With Si-C and Si-Cu the current passes most easily with Si +; with Si-Sn and Si-Cd, which are less stable, the reverse is the case.

C. A. S.

Mechanism of the cupric sulphide-magnesium rectifier. J. CAYREL (Compt. rend., 1934, 198, 64—65).—The author has shown that in a Cu sulphide rectifier the rectifying action is due mainly to CuS, Cu₂S being responsible only for subsidiary effects.

C. A. S.

Crystal photo-effect. H. TEICHMANN (Z. Physik, 1933, 87, 264—272).—Experiments on the temp. variation of the crystal photo-effect indicate that a purely electronic theory (cf. A., 1933, 209) is untenable.

A. B. D. C.

Influence of water on some rectifying contacts. R. AUDUBERT and J. ROULLEAU (Compt. rend., 1934, 198, 344—346).—Current-p.d. curves for the couple Si/SiO₂/PbO₂/C show that for low p.d. the current passes most easily with Si +, but for higher p.d. is reversed; the inversion p.d. rises greatly if the intervening substance, PbO₂, etc., is dried, being initially 0.5—3 volts for PbO₂, CuI, Fe₂O₃+CuI, Ag₂S, MnO₂, or PbS, but 12 volts with thoroughly dried PbO₂ (cf. A., 1927, 1145).

C. A. S.

Conductivity of thin layers of insulating or slightly conducting liquids: variations with temperature. (M.L.E.) T. MEYER (Compt. rend., 1934, 198, 160—163).—Working with layers of liquid 20 μ thick the following conductivities were determined: (10^{-12} ohm⁻¹) vaseline 0.8, decalin 0.8, C₆H₆ 1, CCl₄ 1, PhMe 1.3, xylene 1.8, Et₂O 2, C₂H₅Cl₂ 2, C₂HCl₃ 2, pinene 3, C₂H₅Cl₄ 400, PhCl 500, CHCl₃ 600; (10^{-8} ohm⁻¹) NH₂Ph 2, glycol 4.5, glycerol 5, COMe₂ 600; EtOH (95%) 2×10^{-4} ohm⁻¹. Resistivity increases with the current; it also increases slowly as temp. falls and rapidly at the f.p., abruptly where this is definite (e.g., NH₂Ph), more gradually where there is a pasty stage (e.g., from -10° to -40° for glycol). The conductivity is probably due to impurities.

C. A. S.

Heating in the high-frequency condenser field on account of abnormal absorption. H. HAASE (Physikal. Z., 1934, 35, 68—76).—A method is described for determining the heating caused in dipole liquids by abnormal absorption in the high-frequency condenser field. The substances used in various concns. were C₆H₁₃·OH in C₆H₆, and C₆H₁₁·OH in C₆H₆ and in xylene. The pure alcohols and their bromides were also used. The extent of the absorption decreases, and the max. is displaced towards the higher frequencies, with increasing dilution. In general the results agree with Debye's theory, but the wavelength of the max. for the pure alcohols was twice the theoretical val., and the displacement of the max. due to change of viscosity was smaller than expected.

A. J. M.

Electrical properties of liquid hydrocarbons. C. SALCEANU and D. GHEORGHIU (Bul. Soc. Romane Fiz., 1933, 35, 103—116).—The electrical conductivity of "petroleum spirit" and its mixtures with paraffins, C₈H₁₈, C₁₀H₁₈, and Ph₂ has been measured by the electroscopie leak method. No connexion exists between the vals. for the liquid fuels and their anti-knock characteristics.

H. J. E.

Determination of dielectric constant and electric moment by electrical-resonance method. (Preliminary test.) K. S. CHANG and Y. T. CHA (J. Chinese Chem. Soc., 1933, 1, 107—115).—The dielectric consts. of dil. solutions of PhNO₂ in C₆H₆ have been determined to $\pm 2.5\%$. The calc. mol. polarisation and electric moment of PhNO₂ are 32.77 c.c. and 3.82×10^{-18} e.s.u., respectively.

E. S. H.

Relation between dipole moment and cohesive forces. V. A. E. VAN ARKEL and J. L. SNOEK (Rec. trav. chim., 1933, 53, 91—94).—The dipole moments of pyrazine, 2:5- and 2:6-dimethyl- and tetramethyl-pyrazine, 2:3-dimethyl- and 2:3-dichloro-quinoxaline, and 2-methylquinoxaline are, respectively, < 1, 0, 0.53, < 0.45, < 0.3, 3.2, and 2.2×10^{-18} e.s.u. The measured vals. are compared with those obtained by the vectorial addition of the group moments. 2:6-Dimethylpyrazine has b.p. 155.6°, m.p. 39°.

H. S. P.

Free rotation [in molecules]. P. C. HENRIQUEZ (Chem. Weekblad, 1934, 30, 2—15).—The theoretical aspects, and means of experimental investigation of the problem of the relative rotation of two parts of a mol. are discussed. Measurement of the dipole moment and X-ray determination of interat. distances are regarded as the most promising methods of attack.

H. F. G.

Molecular polarisations of nitrobenzene in various solvents at 25°. H. O. JENKINS (Nature, 1934, 133, 106).—Data for dil. solutions of PhNO₂ in *n*-C₆H₁₄, cyclohexane, dekaline, CCl₄, C₆H₆, CS₂, and CHCl₃ are recorded.

L. S. T.

[Variation with time of] properties of liquids. J. R. POUND (Chem. and Ind., 1934, 71—76).—The changes of d and n of liquids stored in bottles in the dark for 11 years are small except for esters and BzCl (where change is ascribed to absorption of H₂O and hydrolysis) and for fatty oils and terpene oils where change is due to polymerisation and oxidation.

CHCl_3 is stable in presence of H_2O but not when dry. $[\alpha]$ varies for terpenes but not for amyl esters.

D. R. D.

[Refractive] index of water by interferometric method. (MLLE.) O. JASSE (Compt. rend., 1934, 198, 163—164).—Measurements have been made for $\lambda\lambda$ 5790, 5770, 5460, and 4360 Å., at some 30 temp. between 0° and 94° , accuracy $\pm 2-8 \times 10^{-6}$.

C. A. S.

Refractive index of water for waves of length 3—3.6 mm. M. M. ALIMOVA and N. S. NOVOSILZEV (Ann. Physik, 1934, [v], 19, 118—120; cf. A., 1929, 1129).—The previous work has been extended up to waves of length 3.6 mm. There is no anomalous dispersion over the wave-length range 2.2—3.6 mm.

A. J. M.

Refractive indices of *l*-ascorbic acid. S. B. HENDRICKS (Nature, 1934, 133, 178; A., 1932, 987).—*l*-Ascorbic acid from pepper has n_D 1.465, n_D 1.600 \pm 0.006, and n_D 1.747 for 5780 Å.; m.p. 188° . The results substantiate Cox's deduction of a plane configuration for the mol. in accord with the accepted furanose ring structure.

L. S. T.

Rule of shift (Verschiebungsgesetz). P. A. LEVENE and G. M. MEYER (J. Amer. Chem. Soc., 1934, 56, 244—245).—Data for the max. mol. rotations of the free acid, Et ester, and *p*-nitrophenyl esters of configuratively related acids are inconsistent with the rule of shift: $\text{CHMcEt} \cdot \text{CO}_2\text{H}$ series -18.0 , -22.9 , -52.5 , $\text{CHMcBu} \cdot \text{CO}_2\text{H}$ -24.3 , -30.7 , -65.7 , $\text{CHMcEt} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ -10.4 , -11.5 , -20.0 , $\text{CHMcPr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ $+3.6$, $+0.7$, $+5.0$, $\text{C}_5\text{H}_{11} \cdot \text{CHMc} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ $+8.1$, $+4.2$, $+11.2$.

E. S. H.

Optical rotation of unpolarised light. I. A. LANGSDORF, jun., and L. A. DU BRIDGE. II. R. W. WOOD (J. Opt. Soc. Amer., 1934, 24, 1—3, 4).—I. One part of an unpolarised beam was passed through a dextrorotatory and the other through a levorotatory solution, the sum of the rotations being 90° ; the emergent beams showed no interference fringes, in agreement with theory.

II. A note on the above.

N. M. B.

Rotatory dispersion of sparteine in aqueous solution. C. LAPP and (MLLE.) G. ZALC (Compt. rend., 1934, 198, 177—178).— $[\alpha]$ at 18° for a solution containing, as sulphate, 1.09% sparteine was plotted against p_H (2—11) for $\lambda\lambda$ 5890, 5780, 5460, 4920, and 4360. The curves show the two base functions at p_H 4—5 and > 7 . To determine sparteine the solution is brought to p_H 4 (bromocresol-green) or p_H 5 (bromocresol-purple) and $[\alpha]$ determined. For the above $\lambda\lambda$ and 1.242% sparteine solution it is, respectively, -34.2° , -37.0° , -41.3° , -49.6° , and -64.0° . Agreement with results of the silicotungstic acid method is within 1%.

C. A. S.

Thermal variation of magnetic birefringence and dispersion of ethyl phenylsuccinate. R. LUCAS, M. SCHWOB, and A. GOLDET (Compt. rend., 1934, 198, 72—74).—Thermal variation (-6° to 107.5°) of the magnetic birefringence, and the dispersion thereof for $\lambda\lambda$ 5461 and 4358, of Et phenylsuccinate indicate the presence of \leq three isomerides,

the birefringence of one or more being negative (cf. A., 1933, 765, 1103).

C. A. S.

Magnetic investigation of organic radicals. H. KATZ (Z. Physik, 1933, 87, 238—244).—Magnetic susceptibilities have been measured for org. compounds containing N^{III} , $\text{N}^{\text{IV}+}$, N^{II} , $\text{N}^{\text{III}+}$, and N^{IV} , and these are in agreement with Lewis' electron pair theory and Bose's theory of magnetism (A., 1927, 805).

A. B. D. C.

Anomalies in the variation with temperature of the magnetic susceptibilities of salts. G. BOZZA (Gazzetta, 1933, 63, 778—786).—Mainly mathematical. In view of the large deviations from Curie's law exhibited by most salts, it is suggested that two forms of these compounds, of different magnetic properties, coexist; that a majority of the mols. are mutually compensated magnetically, and that Curie's law is applicable to each form.

H. F. G.

Structure and magnetic susceptibility of complex ferric salts. L. CAMBI and A. CAGNASSO (Gazzetta, 1933, 63, 767—778).—The susceptibilities at temp. between 84° and 350° abs., and the temp. coeffs. have been determined for a no. of Fe^{III} derivatives of oximinoketones (anhyd., and with H_2O and $\text{C}_5\text{H}_5\text{N}$ of crystallisation), glyoximes, and pyridine-, quinoline-, and quinoxaline-carboxylic acids. The following compounds are described: $\text{K}_2\text{Fe}_2(\text{C}_3\text{H}_5\text{O}_2\text{N})_2$ and $\text{Fe}(\text{C}_3\text{H}_4\text{O}_3\text{N}_3)_2 \cdot 3\text{C}_5\text{H}_5\text{N}$, from isooximinomalonomide; $\text{Fe}(\text{C}_4\text{H}_2\text{O}_4\text{N}_3)_2 \cdot 3\text{C}_5\text{H}_5\text{N}$, from violuric acid; and $\text{Fe}(\text{C}_{10}\text{H}_6\text{O}_2\text{N}_2)_2 \cdot \text{H}_2\text{O}$, from quinoline-2-carboxylic acid.

H. F. G.

Effect of crystalline electric fields on the paramagnetic susceptibility of cupric salts. O. M. JORDAHL (Physical Rev., 1934, [iii], 45, 87—97).—The paramagnetic susceptibility of the Cu ion in $\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is calc., assuming for the cryst. field monoclinic symmetry deviating only slightly from cubic symmetry. The calc. variation of the magnitudes of the principal susceptibilities with temp. agrees with experimental data. The observed and calc. variations of the direction of the principal axes with temp. are discussed.

N. M. B.

Interaction between the magnetogenic atoms in a paramagnetic crystal. H. A. KRAMERS (Physica, 1934, 1, 182—192).—Theoretical.

H. J. E.

Weiss constant of paramagnetic ions in the S-state. A. BOSE (Nature, 1934, 133, 213).—In aq. solutions of MnCl_2 (I) and $\text{Mn}(\text{NO}_3)_2$ (II) the susceptibility of Mn $^{2+}$ obeys the simple Curie law. The Curie consts. of Mn $^{2+}$ in (I) and (II) are 4.19 and 4.11 per g. ion, respectively, corresponding with 28.8 and 28.5 Weiss magnetons.

L. S. T.

States of aggregation. K. F. HERZFELD and M. GOEPPERT-MAYER (J. Chem. Physics, 1934, 2, 38—45).—Theoretical.

H. J. E.

Theory of the structure of CH_4 and related molecules. III. J. H. VAN VLECK (J. Chem. Physics, 1934, 2, 20—30; cf. this vol., 13).—The ^5S state of C is probably 5—8 ev. above the ground state. A formula is derived for the energy of the "valency state" of the C atom, characteristic of C^{IV} compounds

with four electron pair linkings. It involves an increase of about 7 ev. in the internal energy of C over that in the ground state. Consequently the observed linking energy is < the gross or true interat. val. The gross energy per linking is probably greater in CH_3 than in CH_4 , although the reverse is true of the observed vals. The Slater-Pauling theory of directed valency and the Heitler-Rumer non-directional theory are compared. It is shown to be accidental that the linking energy in CH is almost exactly four times that in CH_4 . H. J. E.

Symmetric states of atomic configurations. F. SEITZ and A. SHERMAN (J. Chem. Physics, 1934, 2, 11—19).—Theoretical. H. J. E.

Form of molecules. H. J. BACKER (Chem. Weekblad, 1934, 31, 71—73).—Substances with spherical or compact mols. are characterised by stability of the cryst. phase, high m.p., low b.p., low heats of fusion and vaporisation, small temp. range and high mobility of the liquid phase, volatility, penetrating camphoraceous odour, and relatively high density. These properties are most marked with radial compounds, CX_4 , the compactness depending on the size and shape of X. Similar properties are shown by some *s*-polysubstituted, chain mols. (C_2H_6 derivatives) and tricyclic, cage-like mols. (camphor). Long-chain mols. have opposite characteristics. Rigid, long-chain mols. of limited but definite length tend to orient themselves in parallel directions with the formation of liquid crystals. S. C.

Oxygen molecules as radicals. W. STEINER (Trans. Faraday Soc., 1934, 30, 34—39; cf. A., 1933, 5).—Existing data relating to absorption spectra of gaseous, liquid, and solid O disclose the occurrence of spin-interaction between O_2 mols. which is not, however, associated with sufficient energy to justify their being regarded as free radicals. F. L. U.

Relation between chemical and physical theories of the source of stability of organic free radicals. C. K. INGOLD (Trans. Faraday Soc., 1934, 30, 52—57; cf. A., 1933, 1151).—Applying the rule that, in neutral dissociations, coupled electrons move in divergent directions, it is shown that perturbation mechanisms analogous to all those involved in the degeneracy of either ion must co-exist in the degeneracy of a CAR_3 radical. The relative stability of such radicals may be predicted with a knowledge of the degree of complexity of the degeneracy, as is illustrated by a series of triarylmethyls. This chemical theory is closely related to the physical theories of Huckel and of Pauling, and, although qual., is of wider scope. F. L. U.

Nature of the covalent linking, and formation of free radicals. M. W. TRAVERS (Trans. Faraday Soc., 1934, 30, 100—102).—It is suggested that the changes involved in the (chemical) condensation of B_2H_6 may be similar to those which C_2H_6 undergoes on pyrolysis. There is no evidence for dissociation of the latter into CH_3 radicals, nor for production of CH_2 from C_2H_4 . The structure of B_2H_6 is discussed. F. L. U.

Applications of molecular rays technique to the study of free radicals. R. G. J. FRASER

(Trans. Faraday Soc., 1934, 30, 182—184).—The possibility of carrying out a qual. analysis of mol. rays is indicated, the constituents being characterised by their ionisation potentials and/or magnetic properties. F. L. U.

Electronic levels of polyatomic molecules. I. Levels of the C:C double linking. C. P. SNOW and C. B. ALLSOPP (Trans. Faraday Soc., 1934, 30, 93—99).—The fine structure observed in spectra of vapours of C_2H_4 , C_2HMe_3 , and cyclohexene indicates a common origin for the band system of C_2H_4 derivatives at about 2100 Å. and for the C_2H_4 band at slightly shorter wave-lengths. It is probable that the effective permitted states of C:C derivatives of lower symmetry than V_h are in general the same as for C_2H_4 . F. L. U.

Potassium superoxide and the three-electron linking. E. W. NEUMAN (J. Chem. Physics, 1934, 2, 31—33).—The oxide is paramagnetic, the susceptibility corresponding with a Bohr magneton no. of 2.04. The formula must therefore be KO_2 , containing O_2' ions in a $^2\Pi$ state ($:\ddot{\text{O}}:\ddot{\text{O}}'$) and not K_2O_4 , which probably contains the O_4'' ion ($:\ddot{\text{O}}:\ddot{\text{O}}:\ddot{\text{O}}:\ddot{\text{O}}:$). H. J. E.

Hydrides of lithium, boron, and beryllium. J. TUTIN (Chem. and Ind., 1934, 65).—In B_2H_6 the assumption of H^Π is preferred to that of B^IV . E. S. H.

Thallic oxide. [Lead suboxide.] F. HALLA, H. TOMPA, and L. ZIMMERMANN (Z. Krist., 1934, 87, 184; cf. A., 1933, 1106).—Two corrections concerning Ti_2O_3 . Regarding the existence of Pb_2O , the grey layer formed on the slow oxidation in air at room temp. of a saturated Pb amalgam consists of PbO and Hg. C. A. S.

Carbon-halogen linking energy and the molecular structure as related to halogen alkyls. Y. HUKUMOTO (J. Chem. Physics, 1934, 2, 46; cf. this vol., 8).—From absorption spectra the C-halogen linking energy increases in the order $\text{I} < \text{Br} < \text{Cl}$, and increases with the length of the C chain. It diminishes with multiple substitution of halogens. Results harmonise with Raman spectra data. H. J. E.

Energy relations in the dissociation of the water molecule into its atoms. O. RIECHEMEIER, H. SENFTLEBEN, and H. PASTORFF (Ann. Physik, 1934, [v], 19, 202—217).—A mixture of water vapour and Hg was irradiated with Hg (2537 Å.) with an energy of 4.9 volts, causing dissociation. The extent to which the process has occurred can be found by determining the partial pressure of H_2 after other products have been removed by cooling in liquid air. The increase in dissociation with temp. to be expected since the no. of effective collisions of energy > 4.9 volts increases with temp. has been observed. The difference between the heat of dissociation of the H_2O mol. and the energy imparted to the mol. by the radiation is 0.21 ± 0.04 volts. The heat effect of the reaction $\text{H}_2\text{O} = \text{H} + \text{OH}$ is 5.11 ± 0.04 volts ($117.9 + 0.9$ kg.-cal. per mol.), agreeing with previous vals. The heat of dissociation of the OH mol. ($\text{OH} = \text{H} + \text{O}$) is 5.29 ± 0.14 volts. A. J. M.

Atomic parachors of carbon and hydrogen. A. I. VOGEL (Chem. and Ind., 1934, 85).—The Me and Et esters of *n*-dibasic acids yield a mean parachor increment of 40.3 units per CH_2 ; the val. 39.0 was deduced by Sugden from other series (cf. A., 1924, ii, 662). D. R. D.

Electron diffraction and the imperfection of crystal surfaces. L. H. GERMER (Physical Rev., 1933, [ii], 44, 1012–1015).—Bragg reflexions were obtained by scattering fast electrons (0.05 Å.) from the etched surfaces of (100) Fe, (111) Ni, and (110) W single crystal faces. A given reflexion is found for glancing angles varying up to 1° from the calc. Bragg val. The accuracy with which this glancing angle must be adjusted is a measure of the degree of crystal imperfection. Widths of half max. of electron rocking curves are 0.8° , 1.5° , and approx. 1° for the Fe, Ni, and W crystals, respectively. Corresponding X-ray rocking curves are much narrower. It is concluded that the degree of misalignment is much greater at the surface than deep down in the crystal. N. M. B.

Scattering of electrons by stibnite and galena. A. G. EMSLIE (Physical Rev., 1934, [ii], 45, 43–46).—The patterns for 20–60-kv. electrons are discussed. Results indicate that the stibnite crystal has relatively large mosaic units, and that collisions with atoms, involving small energy losses, cause high absorption of the primary beam as it penetrates the crystal. N. M. B.

Fine structure of X-ray absorption edges and the influence of the polar character of the compound. D. COSTER and G. H. KLAMER (Physica, 1934, 1, 145–149).—Fine structure of the *K* edge of K and Cl in KCl and KClO_3 has been photographed. There is no resemblance between that of K and Cl, although they are in the same crystal lattice. For metal alloys the type of fine structure depends mainly on the lattice (cf. Veldkamp, A., 1932, 979; 1933, 760). H. J. E.

Determination of Debye-Scherrer X-ray structure of non-cubic systems. V. NESKUCHAEV (J. Tech. Phys., U.S.S.R., 1931, 1, 105–110).—Formulae are given for tetragonal, hexagonal, and rhombohedral systems. CH. ABS.

Crystal lattice of nickel and the sudden change in magnetic properties. B. DEL NUNZIO (Atti R. Ist. Veneto Sci. Lett., 1933, 92, 541–549; Chem. Zentr., 1933, ii, 1850).—Ni is face-centred, with *a* 3.56 Å. X-Ray analysis does not elucidate changes in magnetic behaviour. A. A. E.

Crystal structure of α -(β -)tungsten. E. EBERT and H. HARTMANN (Z. Krist., 1934, 87, 183; cf. A., 1933, 665).—Neuberger's work is criticised, and the proposed interchange of the names of α - and β -tungsten is deprecated. C. A. S.

Crystal structure of NdAl. C. W. STILLWELL and E. E. JUUKOLA (J. Amer. Chem. Soc., 1934, 56, 56–57).—NdAl has the CsCl type of structure and 3.73 ± 0.01 Å. E. S. H.

Structure of calcium boride. L. PAULING and S. WEINBAUM (Z. Krist., 1934, 87, 181–182; cf. A., 1933, 116, 891).— CaB_6 is cubic with *a* 4.145 Å., and

one mol. in the unit cell; each B is equidistant, 1.716 Å., from each of five other B, forming a rigid 3-dimensional network in the interstices of which are the Ca atoms. C. A. S.

Crystal structure of copper sulphate. C. A. BEEVERS and H. LIPSON (Nature, 1934, 133, 214).— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has *a* 6.12, *b* 10.7, *c* 5.97 Å., α $82^\circ 16'$, β $107^\circ 26'$, γ $102^\circ 40'$, 2 mols. per unit cell. The Cu atoms lie on the centre of symmetry at (000) and ($\frac{1}{2}$, $\frac{1}{2}$, 0) and the S atoms on the general position (0.01, 0.29, 0.64). Each Cu is surrounded by an octahedron consisting of 4 H_2O and 2 O, suggesting direct linkings from Cu to O. The odd H_2O touches 2 O of different SO_4 groups and 2 H_2O of different octahedra, and appears to play an important part in maintaining the structure. L. S. T.

Crystal structure of $\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$. S. B. HENDRICKS (J. Physical Chem., 1933, 37, 1109–1122).—The crystallographic and optical consts. of triclinic crystals of $\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$ have been measured and the crystal structure has been partly determined from X-ray diffraction data. M. S. B.

Crystal structure of cadmium hydroxy-chloride. J. L. HOARD and J. D. GRENKO (Z. Krist., 1934, 87, 110–119).— $\text{CdCl} \cdot \text{OH}$, prepared by heating CdO in a solution of CdCl_2 for several days at 210° , is hexagonal, *a* 3.66, *c* 10.27 Å., with 2 mols. in the unit cell, space-group C_{6h}^{2h} —*C6mc*. Each Cd^{++} is surrounded octahedrally by 3 Cl' and 3 $(\text{OH})'$, each of which is shared among 3 Cd^{++} , the whole forming neutral layers parallel to the basal plane of composition $\text{CdCl} \cdot \text{OH}$. C. A. S.

Structure of the hypophosphite group as determined from the crystal lattice of ammonium hypophosphite. W. H. ZACHARIASEN and R. C. L. MOONEY (J. Chem. Physics, 1934, 2, 34–37).— $\text{NH}_4\text{H}_2\text{PO}_2$ is orthorhombic-holohedral (*a* 3.98, *b* 7.57, *c* 11.47 Å.; 4 mols. in unit cell; space-group *Acmn* V_h^n). The H_2PO_2 group forms a distorted tetrahedron, with O atoms at two corners and H at the other two. The P–O distance is 1.51 Å., and the P–O linkings are at 120° . The P–H distance is 1.5 Å., with the linkings at 92° . Each NH_4^+ is surrounded by 4 O at 2.81 Å. and by 4 H at 3.08 Å. The NH_4 group probably is not rotating and its H atoms are probably linked to the surrounding O atoms. H. J. E.

Structure of thallous and potassium thiocyanates. W. BUSSEM, P. GUNTHER, and R. TUBIN (Z. physikal. Chem., 1934, B, 24, 1–21; cf. A., 1933, 666).— TlCN crystallises in the rhombic system, and probably has the space-group V_h^n and *a* 6.80, *b* 6.78, *c* 7.52 Å.; the unit cell contains 4 mols. KCN has the space-group V_h^n and *a* 6.67, *b* 6.65, *c* 7.54 Å.; unit cell contains 4 mols. From the at. arrangements in both salts the SCN chain is probably bent, making an angle of 125 – 130° , but the possibility of a straight chain is not excluded. R. C.

Crystal structure of potassium osmyl chloride. J. L. HOARD and J. D. GRENKO (Z. Krist., 1934, 87, 100–109).— $\text{K}_2\text{OsO}_2\text{Cl}_4$ is face-centred tetragonal, *a* 6.99, *c* 8.75 Å., with 2 mols. in the unit cell, space-group D_{2h}^{2h} —*I4/mmm*. The structure is ionic, with a

fluorite-like grouping, in which $2K^+$ and $[OsO_2Cl_4]^{2-}$ are situated as F_2^{2-} and Ca^{2+} , respectively; $[OsO_2Cl_4]^{2-}$, symmetry D_{4h} , is octahedral with Os in the centre and $Os-Cl=2.28$, $Os-O=1.85$, $Cl-Cl=3.22$, and $O-Cl=2.94$ Å. C. A. S.

Crystal morphology of ammonium tetroxalate. H. HIMMEL (Zentr. Min. Geol., 1933, A, 209—214; Chem. Zentr., 1933, ii, 1867).—16 forms have been measured. $a:b:c=0.5995:1:0.6860$. A. A. E.

Crystal structure of enargite (Cu_3AsS_4). K. TAKANE (Proc. Imp. Acad. Tokyo, 1933, 9, 524—527).—The cell dimensions are a_0 6.39 ± 0.05 , b_0 3.68 ± 0.03 , c_0 6.15 ± 0.05 Å.; 1 mol. per unit cell; space-group V_h^1 . H. F. G.

The Si_3O_8 chains in space-groups V_h^{10} and C_{2h}^{50} . T. IBO (Proc. Imp. Acad. Tokyo, 1933, 9, 528—530).—The structure of eudidymite (rhombic $HNaBeSi_3O_8$) may be derived from that of epididymite (the monoclinic form) on the assumption that both are built of Si_3O_8 groups connected by centres of symmetry. Epididymite has a 12.63, b 7.32, c 13.58 Å.; space-group V_h^{10} ; 8 mols. per unit cell. H. F. G.

New determination of the lattice constant of carbon dioxide. W. H. KEESOM and J. W. L. KOHLER (Physica, 1934, 1, 167—174).—The lattice is cubic (space-group T_h^h). At -190° the lattice const. is 5.575 ± 0.005 Å. The C—O distance is 1.13 ± 0.02 Å. H. J. E.

X-Ray diffraction in long-chain liquids. B. E. WARREN (Physical Rev., 1933, [ii], 44, 969—973).—Mathematical. Vals. are calc. by the Zernicke-Prins method for the fatty acid, n -alcohol, and n -paraffin series. N. M. B.

X-Ray diffraction by gaseous benzene derivatives. W. C. PIERCE (J. Chem. Physics, 1934, 2, 1—5).—The scattering of X-rays by o - and p - $C_6H_4Cl_2$ vapours has been studied. Correction was made for C—C and C—Cl scattering from measurements on $PhCl$, and vals. of the Cl—Cl distance of 3.0 and 6.25 Å., respectively, were deduced. The structure of $C_6H_4Cl_2$ forms a planar hexagon, with the Cl atoms in or near the plane. H. J. E.

X-Ray behaviour of sodium cellulose II, washed with dilute sodium hydroxide and when dehydrated. C. TROGUS and K. HESS (Cellulosechem., 1934, 15, 1—3).—Na-cellulose II produced by treating cellulose fibres with $> 21\%$ aq. NaOH give somewhat diffuse X-ray diagrams, but if subsequently treated with more dil. (6.6—15%) aq. NaOH the spots are sharper. It is proposed to restrict the name Na-cellulose II to the latter product. This substance is changed by dehydration with NaOH in MeOH to Na-cellulose II'. A. G.

X-Ray investigation of elastic tissue. H. KOLPAK (Naturwiss., 1934, 22, 72).—Submicroscopic changes in the fine structure of elastic tissue, with and without stretching, have been investigated. On stretching, extensive orientation occurs. The diagram for damp, unstretched tissue shows two "amorphous" rings, of which the inner shows four max. A. J. M.

Orientation of the micelles in unstretched agar films. I. SAKURADA and K. HUTINO (Sci.

Papers Inst. Phys. Chem. Res., Tokyo, 1934, 23, 162—163; cf. A., 1933, 1235).—Debye-Scherrer photographs of hydrated agar films suggest that the micelle is of needle or plate form. J. W. S.

Limits of validity of the law of electric forces in metals; Volta's second law. O. SCARPA (J. Phys. Radium, 1933, [vii], 4, 725—731).—It is shown theoretically and experimentally that Volta's law for metallic circuits is not valid when, in addition to electrons, the metals contain mobile ions; this is the case for liquid metals, and probably also for solid metals at high temp. Cu—Cd—Hg—Pt—Cu and Cu—Zn—Hg—Pt—Cu contacts were investigated. N. M. B.

Non-conducting modifications of metals. J. KRAMER (Ann. Physik, 1934, [v], 19, 37—64).—Modifications of certain metals (Fe, Ni, Pt, Zn, Sn, Cd, and Sb) which possess very low conductivity can be made by vaporisation or cathodic sputtering. The temp. (t) at which the abnormal changes to the normal form are Fe 440° , Ni 336° , Pt 510° , Zn 133° , Sn 180° , Cd 150° , and Sb 446° (all temp. abs.). The normal conductivity is determined by t and the no. of conductivity electrons. It is supposed that the poorly conducting layers are amorphous phases, which are formed from the above metals when the atoms come together at $< t$. The change to the normal metal takes place with the formation of the lattice, and liberation of conductivity electrons. With Sb the transition can be followed experimentally by the Debye-Scherrer method. The large temp. coeff. of conductivity of amorphous metals is due to the increase in the no. of free conductivity electrons at the higher temp. The conductivity of the amorphous forms of Fe, Ni, and Sb can be increased by light. With Sb the increase is related to the absorption spectrum. After transition, the layers are no longer sensitive to light. A. J. M.

Electrical properties of thin metallic layers obtained by cathode sputtering. Y. MASLAKOVETZ (J. Tech. Phys., U.S.S.R., 1931, 1, 401—427).—Vals. are tabulated. Layers of Pt, Au, Ag, Cu, and Ni swell on absorption of H_2O , Et_2O , or benzene. CH. ABS.

Hardening phenomena in compressed metal powders. W. TRZEBIATOWSKI (Z. physikal. Chem., 1934, B, 24, 75—86).—The hardness, H , and d of specimens prepared by compressing Au and Cu powders in moulds under pressures up to 30×10^3 atm. have been studied. Max. hardnesses of 180 Brinell with Cu and 145 Brinell with Au have been observed. X-Ray examination showed widening of the interference lines and increase of the diffuse scattering due to the compression, but the fibre diagrams showed that in the compressed mass the crystallites retained the same random orientation as in the loose powder. On heating the compressed material H falls rapidly above about 200° , which is ascribed to recovery and recrystallisation. At about 400° the internal strains in the lattice have disappeared. It is concluded that hardening and recrystallisation effects play a decisive part in the production of synthetic masses of metal (cf. A., 1933, 450). The changes in d on heating such masses depend on the loss of gas sorbed by the powder, the ease of which decreases with increasing compression, and on sintering. R. C.

Electrical conductivity of compressed masses of metal powder. W. TRZEBIATOWSKI (Z. physikal. Chem., 1934, B, 24, 87—97).—The resistance, R , of specimens prepared by compressing powdered Au and powdered Cu has been measured at 18—600°. The temp. coeff. of R is positive up to about 100°, negative between about 100° and 300°, and positive above about 300°. Dilatometric measurements show that between 100° and 300° there is only slight sintering; the principal cause of the fall in R seems to be the evolution of adsorbed gas, which is continuous at 100° and a max. at the temp. between 350° and 500° at which the X-ray diagram shows the first signs of grain growth. In the variation of R with temp. compressed metal powders resemble thin films of metal (cf. A., 1933, 893). R. C.

Electric resistivity of peranthracites. P. LEBEAU and P. CORRIEZ (Compt. rend., 1934, 198, 170—172).—Using material powdered to pass 120-mesh, subjected to 50 kg. per sq. cm. pressure, the resistivity of ten samples varied from 0.65 to 556.0 ohms, the order of increase being the same as that in amount of gas (21.78—147.51 cu. m.) evolved at 1000°, and almost the same as that in H content (0.67—1.93%). Similarly determined resistivities of graphites varied from 0.030 to 0.036 ohm. C. A. S.

Cause of the increase of the electrical conductivity of crystalline substances on approaching the m.p. M. LE BLANC and E. MOBIUS (Z. Elektrochem., 1934, 40, 44—46).—The rise in conductivity of AgNO_3 on approaching the m.p. becomes sharper and occurs closer to the m.p. with progressive purification. Firmly-held H_2O causes the phenomenon. 0.1% Ag_2SO_4 gives a similar effect. The increase in the sp. heat of AgNO_3 just below the m.p. is also due to impurities. H. J. E.

Electrical conductivity of nickel oxide. H. H. VON BAUMBACH and C. WAGNER (Z. physikal. Chem., 1934, B, 24, 59—67).—At 800—1000° the conductivity, κ , of NiO varies with the O_2 pressure, p , in the surrounding gas atm., when p lies between 2×10^{-4} and 1 atm., according to $\kappa = kp^{1/n}$, where n is about 4 and k is a const. The conduction is nearly all electronic. It is inferred that the conduction is of the electron deficiency type (cf. A., 1933, 888), a conclusion confirmed by thermo-e.m.f. measurements. The excess of O_2 over the stoichiometric proportion is too small for direct determination, but is estimated from data for diffusibility and the rate of formation of surface oxide films. R. C.

Conduction of electricity in solid silver sulphide, selenide, and telluride. C. TUBANDT and H. REINHOLD (Z. physikal. Chem., 1934, B, 24, 22—34).—Experiments have been made on the combination of Ag with X (X—S, Se, or Te) in an arrangement in which Ag is separated from X by layers of two or three of the corresponding compounds. The results in conjunction with those of new transport measurements show that $\alpha\text{-Ag}_2\text{S}$, $\text{-Ag}_2\text{Se}$, and $\text{-Ag}_2\text{Te}$ are mixed conductors and that < 1% of the total conduction is electrolytic (cf. A., 1933, 467). R. C.

Presence of a negative minimum in the resistance hysteresis loop of nickel in longitudinal

magnetic fields. M. S. ALAM (Z. Physik, 1933, 87, 255—257).—This min. does not appear with fields of max. 200 gauss, and cannot be due to incomplete initial demagnetisation as suggested by Stierstadt (A., 1931, 898). A. B. D. C.

Change in magnetic susceptibility in metals and alloys caused by internal stress. Y. SHIMIZU (Sci. Rep. Tohoku, 1933, 22, 915—933; cf. A., 1931, 154; B., 1931, 1054).—The paramagnetic susceptibility of Cu, Ag, Au, Al, Pt, and of their binary alloys decreases, and the diamagnetic susceptibility increases, with increasing residual internal stress, the latter being measured by the decrease in density caused by working. F. L. U.

Stern-Gerlach experiment with iron. W. KLABUNDE and T. E. PHIPPS (Physical Rev., 1934, [ii], 45, 59—61).—The at. ray trace was found to be widened when the ray was subjected to a magnetic field, indicating that Fe in the vapour state has a magnetic moment. N. M. B.

Refraction and dispersion of crystals. VIII. Refraction measurements of crystals; comparison of isomorphous salts with cations similar to and dissimilar from inert gases. P. WULFF and D. SCHALLER. IX. Molecular refraction, dispersion, and absorption of isomorphous salts of strontium, barium, lead, and thallium. P. WULFF and A. KING (Z. Krist., 1934, 87, 43—71, 72—99; cf. A., 1933, 765).—VIII. The regularities in ΔR (difference between the additively calc. and the experimental vals. of the mol. refractivity) existing in the case of salts with inert gas-like ions (cf. A., 1924, ii, 372; 1929, 13), and due to the electrostatic effect of neighbouring ions, are shown to be present in the Ag halides of NaCl type, but not in the Ti^{II} halides. Revised vals. of d and n are given for NaBr , Na_2SO_4 , NaOAc , $3\text{H}_2\text{O}$, CsCl , Ag_2SO_4 , TiClO_4 , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, CaSO_4 , and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

IX. ΔR are compared for sulphates and nitrates of Pb, Ca, Sr, and Ba, some halides of these and of Rb, Cs, and Ti^{II} . The connexion of ΔR and of the dispersion and absorption curves of some of the salts with the structure of the salts and the electronic structure of their cations is discussed. ΔR for $\text{Pb}(\text{NO}_3)_2$ agrees with the results for salts with inert gas-like ions (cf. A., 1931, 24, 669), but for PbSO_4 and the Pb halides ΔR is greater, indicating increased influence of the stronger electrostatic field due to the double charge of the cation. The non-ionic lattice of PbCl_2 is confirmed. Revised vals. of d^{20} and n_D^{25} are given for $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$. C. A. S.

Latent energy remaining in a metal after cold-working. G. I. TAYLOR and H. QUINNEY (Proc. Roy. Soc., 1934, A, 143, 307—326).—Measurements have been made of the latent energy remaining in metal rods after severe twisting. As the total amount of cold work which has been done on a specimen increases, the proportion which it absorbs decreases. Although saturation was not completely reached even with twisted rods, the experimental results for Cu show that it would have been reached at a plastic strain very little > the strain of fracture. The cold

work necessary to saturate Cu with latent energy at 15° is slightly > 14 g.-cal. per g. L. L. B.

Indifferent and critical points. E. JOUGET (Compt. rend., 1934, 198, 218—222; cf. this vol., 133).—A previous investigation is extended to the case of n independent constituents in one phase, or in two phases, the constituents passing from one to the other. C. A. S.

Effect of high-frequency currents on the transition point of superconductors. E. F. BURTON, J. O. WILHELM, A. PITT, and A. C. YOUNG (Canad. J. Res., 1933, 9, 630—636).—The modified technique shows that the temp. of transition to superconductivity of thin films of Sn does not vary within the frequency range $0-3 \times 10^7$ cycles with small currents, but the min. of a.c. resistance (I) is nearer 0° abs. than is that of d.c. resistance (II). D.c. has no effect on the a.c. point, but a.c. superimposed on d.c. lowers the temp. at which (II) suddenly falls, and this effect depends on the strength of the a.c. only (cf. A., 1932, 684, 1193). With solid Ta wires, the initial change of (I) at the transition point is a slight increase which is absent with thin films of metal. The phenomena are related to variation, with frequency, of current distribution in the wire and magnetic effects. J. G. A. G.

Current stability in a superconductor. L. BRILLOUIN (J. Phys. Radium, 1933, [vii], 4, 677—690; cf. A., 1932, 1005).—Difficulties arising from the effect of perturbations on electron distribution in the interpretation of superconductivity are discussed. The influence of inductive forces for electrons in metals (cf. Frenkel, A., 1933, 769), and conditions for transition from the resistant to the superconductive state, are considered. N. M. B.

Measurements with liquid helium. XXIII. Superconductivity of vanadium. W. MEISSNER and H. WESTERHOFF (Z. Physik, 1933, 87, 206—209).—Superconductivity sets in between 4.3° and 4.4° abs.; resistance measurements are given between this and 0° . A. B. D. C.

New methods of attaining low temperatures. E. JUSTI (Z. Physik, 1933, 87, 273—276).—Simon's isothermal adsorption and subsequent adiabatic desorption method (A., 1927, 100) does not work in practice, but might be used to obtain uniform intermediate temp. A. B. D. C.

Dependence of the volume and f.p. of carbon tetrachloride on the thermal pretreatment. W. BRULL (Z. Elektrochem., 1934, 40, 8—10; cf. A., 1932, 1194).—Retention of air by CCl_4 and hysteresis of the Beckmann thermometer caused the change in physical properties with pretreatment previously reported. Nieuwenhuis' method is criticised (A., 1933, 1109). H. J. E.

Transition point of carbon tetrachloride as a fixed point in thermometry. M.p., heats of transition and of fusion. H. L. JOHNSTON and E. A. LONG (J. Amer. Chem. Soc., 1934, 56, 31—35).—Data obtained with CCl_4 containing $< 1 \times 10^{-3}$ mol.-% of impurities are: transition point $-47.66 \pm 0.05^\circ$, m.p. $-22.87 \pm 0.05^\circ$, heat of transition 1080.8 ± 3 g.-cal. per mol., heat of fusion 577.2 ± 1 g.-cal. per

mol. The transition in solid CCl_4 is sharp and reproducible and provides a satisfactory secondary fixed point for the calibration of thermometers.

E. S. H.

F.p. and triple points with water. W. P. WHITE (J. Amer. Chem. Soc., 1934, 56, 20—24).—An ice point at atm. pressure, const. to 0.0001° , can be made with good commercial ice by carefully protecting against melting from external sources and removing impurities in the ice from the surfaces by washing with thoroughly chilled H_2O . This ice point is more convenient for continuous work than the triple point.

E. S. H.

Atomic heats and heats of fusion and of transformation of gallium, indium, and thallium. W. A. ROTH, I. MEYER, and H. ZEUMER (Z. anorg. Chem., 1934, 216, 303—304).—Corrections to a previous paper (A., 1933, 1237). F. L. U.

Specific heat of thallium at liquid helium temperatures. W. H. KEESOM and J. A. KOK (Physica, 1934, 1, 175—181).—Measurements have been made from 1.3° to 4.2° abs. The at. heat falls from 0.01325 to 0.01177 at the transition point. No latent heat was observed at this point. H. J. E.

Series of coefficients occurring in some phenomena dependent on thermal agitation. P. WEISS (Compt. rend., 1934, 198, 302—304).—The vals. of ζ in the equation of state of fluids (cf. A., 1918, ii, 354); of the factor F (or T_1) in the law of discontinuous distribution of Curie and of m.p. (cf. A., 1932, 449, 452); and of the temp. at which discontinuous increases occur in the resistance of Pt-black (cf. A., 1933, 893) are all expressible with fair accuracy by the terms of arithmetical progressions with common difference approx. 0.0465. No explanation is suggested. C. A. S.

Thermodynamic derivation of the Boltzmann equation. N. BARBULESCU (Bul. Soc. Romane Fiz., 1933, 35, 69—73).—Theoretical. H. J. E.

Isothermals of helium at temperatures of 0° , 20° , and 100° and pressures from 5.5 to 16.5 atmospheres. W. H. KEESOM and J. J. M. VAN SANTEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 813—821).—The second virial coeffs. of Onnes' equation of state for He, deduced from p - v data, are B_0 , 0.5028×10^{-3} , B_{20} , 0.4989×10^{-3} , and B_{100} , 0.4814×10^{-3} , from which $B_{100} - B_0 = -0.0214 \times 10^{-3}$ and hence, in conjunction with α_A 0.00366130, 0° abs. = -273.127° . J. G. A. G.

Relation between the maximum vapour tensions in some organic series. I. E. LUCATU (Bul. Soc. Romane Fiz., 1933, 35, 127—128).—At fixed temp. between 0° and 130° the ratio of the saturation v.p. for neighbouring members in various homologous series (e.g., hydrocarbons, alcohols, or esters) is approx. const. It increases linearly with rise of temp. H. J. E.

Density discontinuities at the critical temperature. [Propylene and methyl ether.] C. A. WINKLER and O. MAASS (Canad. J. Res., 1933, 9, 613—629; cf. A., 1933, 1237).—With an improved technique it was found that in a vertical tube of either C_3H_8 or Me_2O a sharp discontinuity (I) of d persisted

above the crit. temp. in the zone from which the meniscus vanished. (I) became sharper and its magnitude decreased as the ratio of the vol. of the container to the wt. of fluid increased. In general, (I) was not changed by stirring, but was eliminated by appropriate thermal treatment. The results are discussed. J. G. A. G.

Density of propylene in the liquid and vapour phases near the critical temperature. C. A. WINKLER and O. MAASS (Canad. J. Res., 1933, 9, 610—612; cf. A., 1933, 1105).—The data refer to the range 66—92°. J. G. A. G.

Barometric formula for real gases and its application near the critical point. R. RUDNY (Canad. J. Res., 1933, 9, 637—640).—Theoretical. From equations of state (e.g., van der Waals) it is shown that in a short column of fluid maintained throughout its length at the crit. temp. marked variations of d may exist, especially near the layer which is at the crit. d , and to obtain uniform d a temp. gradient must be applied. These phenomena are not necessarily inconsistent with the theory of the continuity of state (cf. A., 1933, 1237). With isotopes, e.g., Ne, of almost identical crit. temp., the concn. of heavier mols. tends to rise near the layer which is at the crit. point. Vals. of crit. temp. derived from experiments in closed tubes are not, in general, trustworthy. J. G. A. G.

Physical properties of compressed gases. IV. Entropies of nitrogen, carbon monoxide, and hydrogen. W. E. DEMING and (Mrs.) L. S. DEMING (Physical Rev., 1934, [ii], 45, 109—113).—Previous work is extended (cf. A., 1932, 799) to the calculation of the change of S and abs. S along isotherms for the temp. range —75° to 600° and pressure range 25—1200 atm. Full data for N₂, CO₂, and H₂ are tabulated and deviations from results for an ideal gas are discussed. N. M. B.

Entropy diagram of liquid helium. W. H. KEESOM and (Miss) A. P. KEESOM (Physica, 1934, 1, 161—166).—The diagram is described and discussed. H. J. E.

Specific volumes of saturated vapours. C. H. MEYERS (Bur. Stand. J. Res., 1933, 11, 691—701).—A formula is derived for the sp. vol. of a saturated vapour in terms of the v.p., sp. vol. of the liquid, and two empirical consts., one of which is the same for all the 23 substances tested. The formula holds for pressures up to one fourth of the crit. pressure. An equation of state, for a limited range, for superheated vapours is developed from this formula. J. W. S.

Thermal expansion of bismuth by X-ray measurements. A. H. JAY (Proc. Roy. Soc., 1934, A, 143, 465—472).—X-Ray measurements on the expansion of the Bi lattice from 18.5° to 268° have been made. The vals. are compared with those given by optical methods. No evidence is found of the discrepancy recorded by Goetz and Hergert (A., 1932, 681, 796), and the lattice expansion agrees with that of the specimen as a whole. The characteristics of the expansion curve are a steady expansion from 20° to 70°, a sudden rise between 70° and 80°, a linear expansion up to 240°, and a decrease above 250°. L. L. B.

Glass. VIII. Coefficient of thermal expansion of boron trioxide. M. E. SPAGHT and G. S. PARKS (J. Physical Chem., 1934, 38, 103—110).—The cubical coeff. of thermal expansion for viscous liquid B₂O₃ is > ten times that for the glassy state. Between these there is a state of transition extending over the temp. range 200—260°, approx. The form of the expansion coeff.-temp. curve in this region depends mainly on the extent of annealing during the initial formation of the glass. M. S. B.

Density and viscosity of titanium tetrachloride. T. SAGAWA (Sci. Rep. Tohoku, 1933, 22, 959—971).—The viscosity has been measured at 20° and 25° (0.007921 and 0.007458 c.g.s. unit, respectively), and d in the range —18.1° to 109.6°. F. L. U.

Viscosity of air at 200 atmospheres pressure. A. G. NASINI and G. PASTONESI (Gazzetta, 1933, 63, 821—832).—The viscosity η of air has been determined at 14° and pressures (p) up to 200 atm. in a new form of apparatus. The error is $\pm 0.5\%$. [185.6 + 0.295(p - 70)] $\times 10^{-9}$. H. F. G.

Thermal conductivity of gaseous mixtures. O. RIECHEMEIER, H. SENFTLEBEN, and H. PASTORFF (Ann. Physik, 1934, [v], 19, 218—224).—The thermal conductivity (I) of pure H₂O vapour is increased by irradiation with λ 2537 Å., when some of the H₂O is dissociated. (I) of the H₂ in the dissociated mixture is < that of H₂O vapour at the same pressure. It is thus not possible to determine (I) of a mixture from a knowledge of the partial pressures of the constituents. A. J. M.

Viscosity, heat conductivity, and diffusion in gas mixtures. XXIV. Viscosity laws in binary mixtures. M. TRAUTZ (Ann. Physik, 1933, [v], 18, 833—866).—Theoretical. W. R. A.

Density of aqueous hydrofluoric acid. L. DOMANGE (Compt. rend., 1934, 198, 469—471).—New vals. have been obtained for solutions with the use of a bakelite container. The wt.-% and d_{15}^{15} vals. recorded are: 5.06, 1.017; 10.1, 1.035; 15.3, 1.054; 20.25, 1.072; 26.4, 1.097; 29.8, 1.1085; 36.4, 1.134; 39.9, 1.149; 42.4, 1.1595; 47.3, 1.179; 53.8, 1.205 (cf. B., 1898, 578; A., 1902, ii, 287). C. A. S.

Specific gravity of acetone-water mixtures. W. YOUNG (J.S.C.I., 1933, 52, 449—450r).—COMe₂ purified by repeated drying and distillation had b.p. 56.25°/760 mm., d_4^{20} 0.79061. Further purification by the NaI method followed by drying and distillation gave a product of b.p. 56.25° \pm 0.05°/760 mm., d_4^{20} 0.79053. A table gives the d of COMe₂-H₂O mixtures from 0 to 100% COMe₂.

Densities of molten inorganic nitrate mixtures. K. LAYBOURN and W. M. MADGIN (J.C.S., 1934, 1—7).—The densities of various molten binary mixtures of K, Na, Sr, Ba, and Pb nitrates and of ternary mixtures of K, Ba, and Sr nitrates have been determined at a no. of temp. to an accuracy of ± 0.001 . The T - d and sp. vol.-composition curves are almost linear. D. R. D.

F.p. of mixtures of waters H₂O and H₂O. V. K. LA MER, W. C. EICHELBERGER, and H. C. UREY (J. Amer. Chem. Soc., 1934, 56, 248—249).—Vals. of f.p. and d are recorded. F.p. is a linear function of d

up to 20% of H_2O , but a deviation is perceptible at 40%. E. S. H.

Partial pressures of water in equilibrium with aqueous solutions of sulphuric acid. E. M. COLLINS (*J. Physical Chem.*, 1933, 37, 1191—1203).—An isotenoscope is described which permits the measurement of v.p. of solutions without change in the concn. This has been used to determine aq. partial pressures for 0—70% H_2SO_4 at 20—140°. The heats of vaporisation of H_2O from solutions of the same range of concn. and temp. have been calc.

M. S. B.

Azeotropic mixtures in the system hydrogen chloride–water–chlorobenzene–phenol. W. PRAHL and W. MATHES (*Angew. Chem.*, 1934, 47, 11—13).—The following const.-boiling mixtures are recorded: H_2O 90.79%, PhOH 9.21% (b.p. 99.57°); HCl 5.3%, H_2O 20.2%, PhCl 74.5% (b.p. 96.90°); HCl 15.8%, H_2O 64.8%, PhOH 19.4% (b.p. 107.3°). Apart from these and the binary mixtures of HCl and PhCl with H_2O , there are no other azeotropic mixtures in the system HCl – H_2O – PhCl – PhOH . The application of these results to the separation of PhOH manufactured by catalytic hydrolysis of PhCl is discussed.

H. F. G.

B.-p. curves of systems TiCl_4 – CCl_4 , TiCl_4 – SiCl_4 , and TiCl_4 – SnCl_4 . N. NASU (*Sci. Rep. Tohoku*, 1933, 22, 987—996, and *Bull. Chem. Soc. Japan*, 1933, 8, 392—399; cf. *A.*, 1933, 1012).—B.-p.-composition curves are of simple type for all three systems.

F. L. U.

Vapour pressure of fused mixtures of aluminium and sodium chlorides. V. A. PLOTNIKOV, N. S. FORTUNATOV, and V. S. GALINKER (*J. Appl. Chem. Russ.*, 1933, 6, 1025—1028).—Data are recorded for 700°.

R. T.

Electrical conductivity and related properties in binary aggregates. K. LICHTENECKER (*Z. Elektrochem.*, 1934, 40, 11—14).—A discussion of the applicability of the logarithmic mixture law.

H. J. E.

Structure of gold–copper alloys. W. BRONIEWSKI and K. WESOŁOWSKI (*Compt. rend.*, 1934, 198, 370—372).—Curves relating composition to m.p., electric conductivity, temp. coeff. of resistance, thermoelectric power and its temp. coeff., and elongation all indicate that slowly cooled alloys contain AuCu and AuCu_3 , both of which form solid solutions. Mixtures occur only with 62—65.5% Au in which AuCu has a martensitic and other Au – Cu alloys have a polyhedral structure. Alloys cooled suddenly from 650° give no indication of either compound. There is no evidence for the existence of Au_2Cu_3 (cf. *A.*, 1931, 1224, 1364; 1932, 989).

C. A. S.

X-Ray analysis of the crystal structure of the thallium–tin alloys. H. J. C. IRETON, J. P. BLEWETT, and J. F. ALLEN (*Canad. J. Res.*, 1933, 9, 415—418).—The Sn lattice const. shows a max. at the eutectic point. Addition of Sn to Tl induces the change $\alpha\text{-Tl}$ — $\beta\text{-Tl}$ (cf. *A.*, 1928, 1181). Unusual superconductivity phenomena have been observed at low temp.

R. S.

System copper–lead. M. NISHIKAWA (*Suiyokai-shi*, 1933, 8, 239—243).—The system has been studied by thermal and microscopical methods. At 13—48% Cu a monotectic reaction, liquid + Cu liquid, occurs at 957°.

CH. ABS.

Röntgenographic determination of the phase boundaries in the copper–zinc diagram. A. JOHANSSON and A. WESTGREN (*Metallwirt.*, 1933, 12, 385—387; *Chem. Zentr.*, 1933, ii, 1747).—The results in general confirm those of Owen and Pickup (*A.*, 1932, 990) except where the latter differ from those obtained microscopically.

A. A. E.

Mechanism of age-hardening of silver–copper single crystals. P. WIEST (*Z. Metallk.*, 1933, 25, 238—240).—Measurements of the hardness (H) and lattice parameter (a) of 5% Ag – Cu single crystals during ageing at 350—470° after quenching from 780° show that the ageing process passes through three stages, in all of which H first increases and then decreases with time of ageing. In the first stage a remains unchanged, in the second a slight broadening of the interference points in the X-ray photograph occurs, and in the third this becomes more marked and a large decrease in a takes place due to the rejection of the dissolved Ag atoms from the Cu lattice. The increase of H in the first two stages is attributed to at. movements preparatory to pptn.

A. R. P.

Behaviour of graphitic silicon in aluminium at high temperatures. C. SCHAARWACHTER (*Z. Metallk.*, 1933, 25, 250—251).—Owing to its slow rate of diffusion graphitic Si does not dissolve in Al at temp. < 540°, even after prolonged annealing, but above the eutectic temp. (577°) it dissolves rapidly.

A. R. P.

Active oxides. LXIX. Variation of the magnetic properties of mixtures of ferric and beryllium oxides on heating. G. F. HÜTTIG and H. KITTEL (*Gazzetta*, 1933, 63, 833—844).—Neither the variations of susceptibility nor the X-ray diagrams afford any evidence of the formation of a compound when an equimol. mixture of BeO and Fe_2O_3 is heated (for 200 hr.) at temp. up to 1000°. The susceptibility of a CaO – Fe_2O_3 mixture passes through a max. at about 400°, and a min. at about 475°, and with further rise of temp. increases very rapidly.

H. F. G.

Dia- and para-magnetism in metallic mixed crystal series. II. E. VOGT and H. KRUEGER. **III. Atomic magnetic moments of the transition metals in dilute mixed crystal solutions.** E. VOGT (*Ann. Physik*, 1933, [v], 18, 755—770, 771—790).—II. The magnetism of Au – Ni mixed crystals containing 1, 2, 4, and 6% Ni has been examined. Ni occurs in the Au lattice up to the solubility limit, with a paramagnetism which is const. between 200° and 300° abs., and equal to $+380 \times 10^{-6}$ per g.-atom of Ni . Below 200° abs. there is an increase in the paramagnetism, the rate of which increases with falling temp. If this is ascribed to Ni^+ ions, these form at the most 1% of the dissolved Ni . The superstructure and magnetism of the alloys CuPd , Cu_3Pd , and Cu_3Pt after various heat-treatments were also examined.

III. The magnetic properties of mixed crystal series of the transition metals dissolved in Cu , Ag , and Au

have been examined at various temp. The strong interaction between the ionic moments of the transition metals gives rise to ferromagnetism or causes the effect of temp. on paramagnetism to be very small. When, however, the transition metals are dissolved in the diamagnetic noble metals to form dil. mixed crystals the presence of free, or almost free, moments is found. The Curie-Weiss law for paramagnetism is obeyed only when the dissolved transition metal has a d -shell of < 10 electrons. Diamagnetism is shown with Pd alloys and with Cu-Pt; in other cases the addition of foreign metal produces little or no change in the effect of temp. on paramagnetism. Ni dissolved in Au shows an increase in paramagnetism at low temp., and the results agree with the fact that at $-185^\circ < 1\%$ of the Ni exists as Ni^+ . The results of Linde, which show that the at. resistance of the noble metals is increased by addition of the transition metals, are in agreement with the magnetic observations. A. J. M.

Lattice dimensions of some solid solutions in the system $\text{MgO-Al}_2\text{O}_3$. G. L. CLARK, E. E. HOWE, and A. E. BADGER (J. Amer. Ceram. Soc., 1934, 17, 7—8).— $\text{MgO, Al}_2\text{O}_3$ (I) has a_0 8.064 ± 0.002 Å., and for solid solutions of $\alpha\text{-Al}_2\text{O}_3$ in (I) this decreases progressively with increase in Al_2O_3 content. MgO does not form a solid solution and therefore does not distort the lattice. Attempts to ppt. (I) by mixing solutions of $\text{K}_2\text{O, Al}_2\text{O}_3$ and Mg(OH)_2 were unsuccessful. J. A. S.

Approximate composition of the lowest fusing mixture of barium oxide, magnesium oxide, and silica. C. H. TURNER (J. Amer. Ceram. Soc., 1934, 17, 14—15).—The mixture with the lowest softening point (pyrometric cone equiv. 1115°) corresponds approx. with $\text{BaO } 46, \text{MgO } 8, \text{SiO}_2 \text{ } 46\%$. J. A. S.

Does the change in lattice constant in mixed crystal formation depend on particle size? E. SCHMID and G. SIEBEL (Metallwirt., 1932, 11, 685; Chem. Zentr., 1933, i, 1733).—Data for Al-Mg, Zn-Mg, and Mg-Al alloys do not support a particle-size effect, whilst a Cu-Al alloy (5% Cu) shows no difference between single and poly-crystals. The effect described by Wiest (A., 1932, 330) for Ag-Cu alloys could not be observed. L. S. T.

Does the change in lattice constant in mixed crystal formation depend on particle size? U. DEHLINGER and P. WIEST (Metallwirt., 1933, 12, 2—3; Chem. Zentr., 1933, i, 1733; cf. preceding abstract).—The difference in lattice consts. (I) of single and poly-crystals of Ag-Cu is confirmed by additional data; it exists also for the system Ag-Au (II). Further, (I) are different for cast and recryst. particles in (II). L. S. T.

Foreign material which added to a solution is able to modify the form of crystals of the solute. L. ROYER (Compt. rend., 1934, 198, 185—187; cf. A., 1932, 682; 1933, 369).—The spacing characteristics of the added substance must be related to those of the solute if the cryst. form of the latter is to be affected. C. A. S.

Separation and rate of growth of crystals of inorganic salts in extracts and other colloidal

media of so-called second consistency. H. KUNZ-KRAUSE (Apoth.-Ztg., 1933, 48, 57—60; Chem. Zentr., 1933, i, 1732). L. S. T.

Crystallisation of eutectic mixtures. G. TAMMANN (Z. Metallk., 1933, 25, 236—238).—The linear rate of crystallisation (R) of eutectic mixtures (I) depends on the degree of undercooling as is the case with homogeneous melts (II). In (II) the flow of heat from the ends of the crystal filaments (F) determines R , whereas in (I) the separation of the constituents into individual F , which proceeds by diffusion, affects R . By increasing R the thickness of the F may be decreased until they cannot be detected by the microscope. Thus, even with a high R , the relatively slow rate of diffusion is sufficient to cause separation of the constituents, and therefore the max. val. of R for (I) must be much $<$ that of either of the constituents. This has been proved for the $\text{NHPhAc-OH-C}_6\text{H}_3(\text{NO}_2)_2$ and azobenzene-benzil eutectics. A. R. P.

Accelerated and retarded diffusion in aqueous solution. J. W. MCBAIN and C. R. DAWSON (J. Amer. Chem. Soc., 1934, 56, 52—56).—The mutual influence of ions in altering the usual rates of diffusion is illustrated by experiments on the KCl-HCl system. Very high rates of diffusion were found for all constituents when glycine diffused against HCl. E. S. H.

Diffusion of water in a zeolite crystal. A. TISELIUS (Nature, 1934, 133, 212—213).—The diffusion of H_2O in heulandite has been determined by observation of the change in optical properties of dehydrated crystals in an atm. of H_2O vapour. L. S. T.

Diffusion of potassium into glass. B. VON LENGYEL (Z. physikal. Chem., 1933, 167, 295—311).—The diffusion of K from various molten K salts into glass has been studied. Irrespective of the Na content of the glass, the amount of K diffusing into the glass and the resulting increase, R , in the resistance of the glass are both proportional to the square root of the time of diffusion, t . This result may be deduced theoretically, assuming the validity of Fick's law, and shows the mobilities of Na^+ and K^+ in the glass to be independent of the concn. The temp. coeff. of R/\sqrt{t} is small and negative, which agrees with theoretical deductions. No diffusion occurs from K_2SO_4 dissolved in conc. H_2SO_4 . R. C.

Exchange of heavy hydrogen atoms between water and molecular hydrogen. K. F. BONHOEFFER and K. W. RUMMEL (Naturwiss., 1934, 22, 45; cf. A., 1933, 1233; this vol., 37).—Heavy H_2O and ordinary H_2 were shaken together, under pressure, in the presence of Pt-black. The equilibrium attained agrees with theory. A. J. M.

Solubility of hydrogen in water at $0^\circ, 50^\circ, 75^\circ$, and 100° from 25 to 1000 atmospheres. R. WIEBE and V. L. GADDY (J. Amer. Chem. Soc., 1934, 56, 76—79).—Data for the range indicated show a min. similar to that of N_2 in H_2O . E. S. H.

Solubility equation of hydrated salts. J. PERREU (Compt. rend., 1934, 198, 172—174; cf. A., 1889, 752).—Evidence for certain relations shown by

hydrated salts is discussed in reference to the data for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. C. A. S.

Aqueous solubility of salts at high temperatures. II. Ternary system Na_2CO_3 – NaHCO_3 – H_2O from 100° to 200°. W. F. WALDECK, G. LYNN, and A. E. HILL (J. Amer. Chem. Soc., 1934, 56, 43–47; cf. A., 1932, 457).—Four solid phases are involved: (1) $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, (2) $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ (stable up to $195 \pm 5^\circ$), (3) $3\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3$ (stable over this temp. range), (4) NaHCO_3 . The solubility of NaHCO_3 under the natural pressure of the system increases from $19.1 \pm 0.2\%$ at 100° to 43.0 ± 1.0 at 200°. E. S. H.

Solubility of silver bromate in mixtures of alcohols and water. E. W. NEUMANN (J. Amer. Chem. Soc., 1934, 56, 28–29).—The solubilities of AgBrO_3 in binary mixtures of MeOH, EtOH, PrOH, and Pr^iOH with H_2O have been determined at 25°. The data are incompatible with the Born electrostatic formula. E. S. H.

Solubility of inorganic salts in liquid ammonia at -33.9° . W. C. JOHNSON and O. F. KRUMBOLTZ (Z. physikal. Chem., 1933, 167, 249–259).—Solubilities of alkali salts have been determined with a special apparatus permitting direct measurement. With the more sol. salts the results are reproducible to 0.5%. R. C.

Solubility of glucose in methyl alcohol. J. GILLIS and H. N. NACHTERGAELE (Rec. trav. chim., 1933, 53, 31–33).—The solubility of glucose in MeOH has been measured from 0° to 128.5° . The transition temp. S_{trans} — $b + L$ is 108° . H. S. P.

Solubility of acet-*o*-toluidide in various solvents. J. L. HALL, A. R. COLLATT, and C. L. LAZZELL (J. Physical Chem., 1933, 37, 1087–1094).—The solubility of *o*- $\text{C}_6\text{H}_4\text{MeNHAc}$ (I) in MeOH, EtOH, Pr^iOH , Pr^nOH , Bu^iOH , Bu^nOH , COMe_2 , CHCl_3 , CCl_4 , C_6H_6 , Et_2O , and H_2O has been determined by the synthetic method between 25° and the m.p. (110.3°). With H_2O two liquid phases are obtained over a wide range of temp. and a triple point is shown at approx. 79.6° . According to the solubility data the mol. heat of fusion of (I) is approx. 5700 g.-cal. From this val. the ideal solubility curve has been plotted. M. S. B.

Solubility of trinitrotrimethylenetriamine. T. URBANSKI and B. KWIATKOWSKI (Rocz. Chem., 1933, 13, 585–587).—The solubility in MeOH, EtOH, *iso*- $\text{C}_5\text{H}_{11}\text{OH}$, COMe_2 , Et_2O , CCl_4 , C_6H_6 , and PhMe has been determined between 0° and the b.p. of the solvent. R. T.

Solubility of pentaerythritol tetranitrate. T. URBANSKI and B. KWIATKOWSKI (Rocz. Chem., 1933, 13, 740–741).—Data are given for MeOH, EtOH, Et_2O , COMe_2 , C_6H_6 , and PhMe, between 0° and the b.p. R. T.

Validity of mass law. II. Determination of solubility of radium sulphate in sodium sulphate solutions and in water. B. NIKITIN and P. TOMATSHEV (Z. physikal. Chem., 1933, 167, 260–272; cf. A., 1932, 223).—The solubility at 20° of RaSO_4 in H_2O and in 10^{-4} to $10^{-2}N$ - Na_2SO_4 shows that in all these

solutions the solubility product in terms of activities of RaSO_4 has approx. the same val., 4.25×10^{-11} . The solubility of RaSO_4 is 2.1×10^{-4} g. per 100 c.c. of H_2O . R. C.

Influence of conditions of precipitation of zinc sulphide on its solubility in hydrochloric acid. T. KROKOWSKI (Rocz. Chem., 1933, 13, 561–568).—The solubility of ZnS (I) increases in the order: (I) pptd. by H_2S from aq. ZnSO_4 (II) at $75^\circ < \text{at } 25^\circ < \text{from aq. Zn(OAc)}_2 < \text{(I) pptd. by } (\text{NH}_4)_2\text{S}$ from (II) < from ammoniacal (II). R. T.

Diffusion of hydrogen through palladium. V. LOMBARD and C. EICHNER (Bull. Soc. chim., 1933, [iv], 53, 1176–1206; cf. A., 1933, 218).—The diffusion of H_2 through heated Pd for pressures varying from 1 atm. to a few mm. into a vac. has been shown in three cases to be expressed by the formula D (rate of diffusion) $= K \cdot P^{0.56}$ and in a fourth by $D = K \cdot P^{0.5}$ at 493° , 470° , and 617° . The latter is the formula found for other metals. For the same sample the rate of diffusion from a high to a low pressure is given by $D = K(P^{0.5} - p^{0.5})$. The influence of temp. on the normal sp. rate of diffusion, D_{SN} , for 350 – 850° is expressed by $D_{SN} = 20.737^{70} e^{-2022/T}$ (D_{SN} is the val. of D for 1 mm. thickness of Pd). The permeability of Pd is strongly influenced by its state of purity. M. S. B.

Measurement of diffusion velocities in dissolution of gases in solids. H. DUNWALD and C. WAGNER (Z. physikal. Chem., 1934, B, 24, 53–58).—The formulæ used are reviewed. R. C.

Chemisorption on charcoal. II. Acid constituent of charcoal. A. KING (J.C.S., 1934, 22–26; cf. A., 1933, 898).—The quantity of $\text{H}_2\text{C}_2\text{O}_4$ formed is independent of the pressure of O_2 or time of treatment, and proportional to the mass of charcoal. Repetition of the treatment on the same C without drying the C yields less $\text{H}_2\text{C}_2\text{O}_4$, but, if dried in air at 120° , the normal yield is obtained. No $\text{H}_2\text{C}_2\text{O}_4$ is produced when dried org. liquids replace H_2O , but with 5% or more H_2O in EtOH the yield is the same as with pure H_2O . Activated birch C gives a slightly higher yield. Intensively dried C saturated with dry O_2 yields almost pure CO on heating in vac., the greater part being evolved at 370° . Such C yields little $\text{H}_2\text{C}_2\text{O}_4$ with air-free H_2O , and after shaking with dil. H_2SO_4 , the latter gives no coloration with starch-KI solution. It is suggested that O_2 is adsorbed in two different ways. D. R. D.

Adsorption of carbon tetrachloride on carbon and the activation of carbon. W. LEMCKE and U. HOFMANN (Angew. Chem., 1934, 47, 37–43).—The adsorption isotherms for CCl_4 on activated carbons, lampblacks, graphites, and CO carbon have been determined with an automatic apparatus. Capillary condensation occurs only when the air is nearly saturated with CCl_4 ; at lower pressures a two-dimensional film is formed. The effect of activation on the adsorption of CCl_4 is parallel to its effect on the adsorption of methylene-blue and PhOH from aq. solution, and the increase is due to a reduction in the crystal size. Adsorption by Ceylon graphite is less after activation, which smooths the surface and destroys the smaller sizes. A. G.

Sorption of vapours by activated, highly evacuated sugar charcoal over long periods of time. J. W. MCBAIN and R. F. SESSIONS (J. Amer. Chem. Soc., 1934, 56, 1—4).—Sorption experiments with 10 vapours show that, when evacuation of the C is adequate, sorption is nearly complete at infinitesimal pressures. Equilibria are established rapidly and then remain almost const. for periods of 4—5 years. E. S. H.

Absorption of gases at low pressure by active carbon and silica gel. O. WINKLER (Z. tech. Physik, 1933, 14, 319—332; Chem. Zentr., 1933, ii, 1853).—Measurements have been made with N_2 and H_2 at 10^{-2} and 10^{-5} mm. and at the temp. of liquid O_2 or N_2 . A. A. E.

Adsorption. Relation of water held by charcoal at zero pressure to the ash content. L. J. BURRAGE (J. Physical Chem., 1933, 37, 1095—1101).—The ash content of a no. of different charcoals has been compared with the amounts of H_2O held at zero pressure. To explain this and other data it is suggested that the ash plays no part in the retention of the H_2O at zero pressure, but that the latter is held in a quasi-chemical manner by the active centres and C_xO_y complex. M. S. B.

Adsorption of hydrogen atoms and iodine on calcium fluoride. J. H. DE BOER and J. J. LEHR (Z. physikal. Chem., 1933, B, 24, 98—102).—Under favourable conditions thin vac.-sublimed films of CaF_2 can adsorb twice as many H atoms as I_2 mols. With larger amounts of CaF_2 the adsorbability of H atoms seems to decline. Owing to the lamellar structure of thicker films (cf. A., 1933, 672) it is possible that the inner parts of the salt surface become inaccessible to H atoms but not to other gases. R. C.

Adsorption of neon on glass at liquid hydrogen temperatures. W. H. KEESOM and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 825—832).—The fraction of wall covered, q , increases regularly with increasing pressure, p , until at about the saturated v.p., p_s , a complete unimol. layer is produced. The adsorption isotherms in the range 14.45 — 20.28° abs. are given, approx., by $q^3 = p/[0.7(p_s - p) + p]$. J. G. A. G.

Adsorption of helium on glass at liquid helium temperatures. W. H. KEESOM and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 832—835).—In the range 3.56 — 1.13° abs., the adsorption isotherms of He on glass are given by $q^4 = p/[0.26(p_s - p) + p]$, where q is the fraction of wall covered at pressure p and p_s is the saturated v.p. Below 0.8° abs. the error in the temp. determined by the He thermometer is liable to be $> 1\%$ owing to adsorption; this is not adequately diminished by previously forming a unimol. layer of Ne. J. G. A. G.

Thermodynamic basis of adsorption of gas mixtures. I. KRITSCHIEVSKI (Z. anorg. Chem., 1934, 216, 253—262).—Three-component systems (two gases + adsorbent) are treated. F. L. U.

Base-exchange equilibria in clays. C. E. MARSHALL and R. S. GUPTA (J.S.C.I., 1933, 52, 433—443r).—The various methods of formulation of base-

exchange reactions are discussed. Putnam clay (beidellite) and bentonite (montmorillonite) have been examined in relation to the systems: Na clay + KCl; Na clay + $CaCl_2$; Na clay + $AgNO_3$; H clay + $AgNO_3$; H clay + Tl_2SO_4 . The results show little agreement with the equations proposed. In the Na clay + $AgNO_3$ and H clay + $AgNO_3$ systems electrometric measurements of Ag^+ activities were made and the dissociation of Ag clays in absence of electrolyte was studied. It is shown that bentonite has a comparatively high dissociation. In the H clay + Tl_2SO_4 systems electrometric measurements of both H^+ and Tl^+ were made. The results confirm those of the Ag^+ measurements. It is inferred that the substitution of ionic activities for concns. does not suffice to make valid the formulations of base-exchange reactions so far proposed. The dissociation of clays is shown to present certain important anomalies, when compared with ordinary electrolytes.

Adsorption of copper sulphate by sphalerite and its relation to flotation. S. F. RAVITZ and W. A. WALL (J. Physical Chem., 1934, 38, 13—18).—With sphalerite (I) particles larger than 37μ the amount of $CuSO_4$ giving the best flotation recovery is that required to form a unimol. film of CuS. For smaller particles it is less. This probably depends on the fact that the wt. of a particle decreases more rapidly than its surface area. The amounts of Cu adsorbed by (I) of various particle size from a $0.02M$ - $CuSO_4$ solution are equiv. to surface films of CuS many mols. thick. This layer decreases in thickness as the particles become smaller. The results are explained by the mosaic theory of the structure of crystals and agree with the assumption that the unit blocks of (I) are approx. 0.37μ in length. M. S. B.

Capillary activity and association of aqueous solutions. H. CASSEL (Naturwiss., 1934, 22, 60).—Measurements of adsorption at the interface water/air, by the bubble method, give vals. for solutions of p - $C_6H_4Me-NH_2$ and isoamyl alcohol which are about double those obtained by calculation from the Gibbs equation. The activity of the solute does not correspond with the simple osmotic equation. The effect of association in the aq. phase on the Gibbs equation is considered. A. J. M.

Interfacial tension at the surface of two non-miscible liquids. III. C. BELCOT (Bul. Soc. Romane Fiz., 1933, 35, 119—125; cf. A., 1928, 472).—The author's drop method has been applied to measure the surface tension of aq. HCl. The vals. are correlated with the ionic concns. The surface tension method can be used to measure salt hydrolysis (e.g., for $PhONa$ or $NaHCO_3$). H. J. E.

Surface tension at the surface of two non-miscible liquids. IV. C. BELCOT (Bul. Soc. Romane Fiz., 1933, 35, 157—159; see preceding abstract).—Theoretical. From a study of aq. solutions of NH_3 and KOH, evidence is adduced that the activity coeffs. are not equal to the degree of ionisation except at low concns. H. S. P.

Effect of dissolved electrolytes on the boundary tension of water. W. G. EVERSOLE and D. S. DEDRICK (J. Physical Chem., 1933, 37, 1205—1214).—

An apparatus for the very accurate measurement of interfacial tensions (I) by the drop vol. method is described. At low concns. NaOAc and HCO_2Na tend to lower (I) of oil- H_2O systems, but this is probably due to the formation of free acid by hydrolysis. At higher concns. (I) is raised and this latter effect has been explained on the basis of the Langmuir theory of mol. orientation and the increased interionic attraction in the interface due to the dielectric const. gradient in the interfacial layer. The effect of strong electrolytes in general on boundary tension may be similarly explained. M. S. B.

Effect of sodium acetate on the interfacial tension of the benzene-water system at 40° . D. S. DEDRICK and M. H. HANSON (J. Physical Chem., 1933, 37, 1215—1221).—A very high concn. of NaOAc in the system C_6H_6 - H_2O produces a secondary lowering of the tension not previously observed (cf. preceding abstract). The effect is considered to be due to the tendency of the electrolyte as a whole to pass through the boundary layer into the non-aq. phase as doublets or undissociated mols. M. S. B.

Unimolecular films of polyesters. S. A. MOSS, jun. (J. Amer. Chem. Soc., 1934, 56, 41—43).—Polymeric acid and neutral ethylene succinates, when dissolved in CHCl_3 and spread on 0.01N-HCl, form stable unimol. films, which are similar to vapour-expanded films of fatty acid esters. The mol. chains are flexible and can be packed closely before immersion on compression occurs. The closeness of approach is 5.85 Å. E. S. H.

Spreading of ovalbumin. G. T. PHILIPPI (Rec. trav. chim., 1933, 53, 81—90).—The spreading of ovalbumin has been studied in relation to the potential differences at an air- H_2O interface. For certain ranges a coherent unimol. layer of surface 1.3 sq. m. per mg. is formed, but for others a compressed film of surface 0.7 sq. m. per mg. is obtained. In the latter the polypeptide backbones lie tightly packed in the surface and the NH_2 -acid groups (I) protrude from the surface, whilst in the coherent films (I) also lie tightly packed in the surface. H. S. P.

Spreading of insulin and of zein. E. GORTER and J. VAN ORMONDT (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 922—926).—Max. spreading is found at the isoelectric point. C. W. G.

Origin of osmotic pressure and its theoretical calculation. K. FREDENHAGEN (Z. Physik, 1933, 87, 62—77).—The kinetic conception of osmotic pressure is criticised, and shown to be self-contradictory. Solvation of the solute mols. is supposed to be the primary cause of osmotic pressure. A. B. D. C.

Microcryoscopic measurements by Rast's method. II. Cryoscopic constant of retene. T. W. JEZERSKI (Rocz. Chem., 1933, 13, 720—724).—Retene has m.p. 100.5° ; the mol. depression for a no. of substances is 12.16. Certain modifications of Rast's method are proposed. R. T.

[Cryoscopic] determination of hydration of ions of calcium chloride. F. BOURION and E. ROUYER (Compt. rend., 1934, 198, 175—176; cf. A., 1933, 777).—The hydration of the ions in 0.5M- and

0.25M- CaCl_2 corresponds with $\text{CaCl}_2 \cdot 27\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 30.6\text{H}_2\text{O}$, respectively. C. A. S.

Structure of arginine in aqueous solution. G. DEVOTO (Z. physiol. Chem., 1933, 222, 227—228).—The dielectric coeff. of δ -arginine (+62) indicates that it is δ -polar in aq. solution. J. H. B.

Apparent molecular volume of dissolved electrolytes. II. Pressure coefficient of apparent molecular volume. W. GEFFCKEN (Z. physikal. Chem., 1933, 167, 240—244).—The relation between apparent mol. compressibility, β , and concn. pointed out by Gucker (A., 1933, 901) is derived theoretically. The order of magnitude of β at infinite dilution may also be calc. R. C.

Influence of concentration on the compressions of aqueous solutions of certain sulphates. Representation of the compressions of aqueous solutions as a function of pressure. R. E. GIBSON (J. Amer. Chem. Soc., 1934, 56, 4—14).—Compressions of aq. solutions of the sulphates of Li, Na, Cs, Mg, Zn, Cd, Be, NH_4 , Cu, Ce^{III} , and H have been determined over a pressure range of 1—1000 bars and over the entire range of possible concns. The bulk compressions of solutions of the same mol. concn. are approx. equal, when the sulphates are not greatly hydrolysed. A deviation function, A , giving the difference between the sp. compression of H_2O alone and H_2O in any solution is expressed by $A = am + bm^2$, where m is the mol. concn. and a and b are consts., which vary with the solute. The sp. compressions of H_2O and aq. solutions are discussed as a function of pressure. E. S. H.

Polarimetric examination of complex ferritartrates. PARISELLE and DELSAL (Compt. rend., 1934, 198, 83—85).—Polarimetric observations indicate the formation of the compounds: $\text{H}[\text{C}_4\text{H}_2\text{O}_6\text{Fe}]$, which is pptd. as an ochre-coloured powder in neutral solution; $\text{Na}[\text{C}_4\text{H}_2\text{O}_6\text{Fe}]$; $\text{Fe}[\text{C}_4\text{H}_5\text{O}_6]_3$; $\text{Fe}[\text{C}_4\text{H}_4\text{O}_6\text{Na}]_3$; $\text{Fe}[\text{C}_4\text{H}_3\text{O}_6\text{Na}_2]_3$; $\text{Fe}[\text{C}_4\text{H}_4\text{O}_6\text{Na}]_3$; and $\text{H}[\text{C}_4\text{H}_2\text{O}_6\text{Fe}]$. C. A. S.

Brownian movement according to Fermi statistics. M. SATÔ (Z. Physik, 1933, 86, 667—674).—Theoretical. A. B. D. C.

Action of electric field on stratified diffusion of alkali carbonates in gelatin. (MLLE.) S. VEIL (Compt. rend., 1934, 198, 258—260; cf. A., 1929, 1382; 1933, 224).—The rings formed by a drop of aq. K_2CO_3 placed on a sheet of gelatin some 10 cm. sq., when subjected to an electric field, move towards the anode and the rings on the cathode side gradually disappear. The effect is due to the action of the field on both the gelatin and the electrolyte, and varies with the nature of the latter. C. A. S.

Congruence of colloid correlation principle and a recognised relationship. S. C. BLACKTIN (Chem. and Ind., 1934, 64—65).—Theoretical. The increased freedom of disperse particles on rarefaction of a gaseous dispersion medium is compared with the relation between mean free path and life-tendency of particle size comprehended under the colloid correlation principle. E. S. H.

New theory of ferric oxide hydrosols. W. F. FAIR, jun. (J. Physical Chem., 1934, 38, 19—34).—

The purities of Fe hydrosols at incipient pptn., as measured by the ratio Fe/equiv. anion, are in agreement with the hydrolytic definition of sols, but the val. for weak acids is not much > 1 , whilst for strong acids it may be 20–30. A chemical theory of sol pptn., based on the solubility product concept, is developed mathematically and shown to be supported by experimental data. The results are in agreement with the chemical complex theory of hydrosols.

M. S. B.

Colloidal properties of coconut milk. A. CLEMENTE and M. VILLACORTE (Univ. Philippines Nat. Appl. Sci. Bull., 1933, 3, 7–10).—The fresh milk is an emulsion of coconut oil (I) in H_2O ; the emulsifying agents are colloiddally dispersed proteins, adsorbed at the oil- H_2O interface, and sugar, chiefly dissolved in the aq. phase. The average diam. of the oil globules is 0.72 μ . The surface tension of the fresh milk is about 46.65 dynes per cm. Starch or gelatin coagulates the emulsion. Pure (I) can be extracted from the milk by a centrifugal method.

CH. ABS.

Coagulation of colloids. VI. Viscosity variations during coagulation. S. S. JOSHI and T. M. MENON (J. Indian Chem. Soc., 1933, 10, 599–609; cf. A., 1933, 1011).—Rates of change of viscosity of As_2S_3 sols when coagulated by different electrolytes in the "slow" region are recorded.

F. L. U.

Electric double layer of colloids. IV. Sorption of ions of flocculating electrolytes by particles of silver iodide sol. E. J. W. VERWEY and H. R. KRUYT (Z. physikal. Chem., 1933, 167, 312–328; cf. this vol., 143).—In general the amount of cation, x , taken up from an indifferent electrolyte by colloiddally dispersed AgI is equiv. to the amount of counter-ion (I) displaced. With increase in the concn. of electrolyte x rises, but in many cases attains a const. val., corresponding with complete displacement of (I), before the amount of electrolyte is sufficient to cause pptn. In such instances, pptn. does not occur when the amount of cation taken up is equiv. to the total charge on the disperse phase. Metal cations can be displaced again by a large excess of H^+ . The cation adsorption by a mass m of adsorbent may be represented by $x/m = f(c/m)$, where c is the equilibrium concn. The sorption of oppositely charged ions by colloiddal AgI thus belongs to the class of exchange phenomena, and is of no significance for a general theory of pptn. Each member of the series $Ce^{+++} > UO_2^{++} = Pb^{++} > Ba^{++} > H^+ > Cs^+ > K^+$ is adsorbed more readily and displaced less readily than the one following it. The older Freundlich theory of pptn. is untenable. Exchange will lead to pptn. only if the ion taken up is completely incorporated in the immobile part of the outer coating of the double layer, as may occur with large highly polar (organic) ions. This mode of pptn. is thus restricted to ions constituting exceptions to the Hardy-Schultze rule.

R. C.

Lecithin. III. Electrophoretic behaviour of lecithin-cholesterol dispersions. C. W. PRICE (Biochem. J., 1933, 27, 1789–1792).—Since the mobility- p_H relationship and the position of the isoelectric point are const., the formation of the lecithin-

cholesterol complex is not attributable to the amphoteric groups of the lecithin or to those on which ion adsorption occurs.

H. G. R.

Electro-deposition of shellac. N. MURRY and M. SREENIVASAYA (Chem. and Ind., 1934, 35–36).—Colloiddal particles of shellac in NaOH, Na_2SiO_3 , $Na_2B_4O_7$, or aq. NH_3 are negatively charged and can be electrodeposited, preferably on a Pt anode. Ni, Cu, or Pb anodes are attacked during the deposition. Anions such as Cl^- and SO_4^{--} have a polymerising effect on the deposit.

E. S. H.

Summary of the isoelectric points of proteins. A. W. THOMAS (J. Amer. Leather Chem. Assoc., 1934, 29, 3–16, 52).—A list of proteins with the isoelectric points, the method of determination, and a bibliographical reference to the source of information is given.

D. W.

Interaction of boron compounds with lyophilic colloids. S. I. INOZENTZEV (Chemis. Social. Agric., Russia, 1933, No. 3, 214–216).—Na borate, and particularly H_3BO_3 , causes gelatin to congeal more rapidly than Na_2SO_4 or NaI. The swelling is lowest with $B_4O_7^{--}$, and highest with I^- .

CH. ABS.

Nature and amount of non-diffusible calcium in protein sols. W. G. EVERSOLE, L. A. FORD, and G. W. THOMAS (J. Biol. Chem., 1934, 104, 107–114).—Gelatin (I) decreases the activity of Ca^{++} in a solution of $Ca(OAc)_2$ as measured by a Corten-Esternman electrode (A., 1928, 1205), the amount of Ca bound increasing with $[Ca^{++}]$. A solution of NaCl and $Ca(OAc)_2$ was dialysed against an identical solution containing (I), and Cl^- and Ca determinations were made for both solutions. The $[Ca^{++}]$ in the (I) solution was calc. and the bound Ca obtained by difference. Vals. obtained by the latter method are $>$ those given by the former unless a correction is made for the vol. occupied by (I).

H. D.

Interrelationships between the effect of electrolytes on the swelling of, and their permeability through, gels. M. VON DELLINGSHAUSEN (Planta [Z. wiss. Biol.], 1933, 21, 51–97).—In permeable, homogeneous gels, e.g., gelatin, agar, adsorbed ions favour swelling according to their hydrophilic character ("direct ion effect"). The reverse effect of non-adsorbed ions corresponds with their H_2O affinities ("indirect effect"). The action of adsorbed ions on swelling effects is controlled by the hydrophilic nature of the micelles. Increasing concn. of electrolyte solutions intensifies the "direct ion effect" in permeable gels and the "indirect effect" in impermeable gels. The mobility of ions in gelatin follows the same order as that in free solutions, unless the gel is in equilibrium with the electrolyte solution, when the order of mobility becomes $KCl < NaCl < LiCl$ and $AlCl_3 < MgCl_2 < CaCl_2$. The effect of varying concns. of electrolytes on a no. of other membranes is examined.

A. G. P.

Aggregation of gelatin. W. GIEDROYC (Rocz. Chem., 1933, 13, 686–703).—The optical rotation of gelatin (I) sols is at 40° proportional to the concn. of (I) over the range p_H 1–10. Mutarotation does not take place at any p_H at $> 40^\circ$. The val. of α for a given and concn. varies inversely with the temp.

At 20° the increment in the val. of α after 20 hr. increases from p_H 2 to p_H 4.8, then falls to a min. at p_H 6.6, and rises to a second max. at p_H 7.35. The velocity of fall of a steel sphere in 1% sols and gels previously kept at 20° during 20 hr. falls with increasing p_H to a min. at p_H 4.4, then rises to p_H 5, again falls to p_H 6.23, rises abruptly to p_H 7.5, and falls sharply to a third min. at p_H 7.7, above which it rises continuously. Solutions of (I) are regarded as polydisperse sols, in which (I) exists in two forms, differing only in their degree of dispersion. The transition point varies for different samples of (I) from 35° to 40°.

R. T.

Rhythmic precipitation with organic precipitants. J. E. HECK and M. G. MELLON (J. Physical Chem., 1934, 38, 85—93).—The formation of ppts. in SiO_2 (I) and agar (II) gels by the action of org. precipitants on metal salts has been investigated under different conditions of acidity and alkalinity. Different types of structure were obtained, bands being formed in certain cases only. 8-Hydroxyquinoline gave very good bands with ZnSO_4 , CdSO_4 , and CuSO_4 in (II) but less good in (I). In other cases there was either no ppt. or a continuous structure. Discrete structures or fern-like growths were also obtained. Nitron nitrate was the only ppt. not giving noticeable bands in at least one type of gel. Better results were always obtained by putting the org. compound in the gel. Light had no influence on the type of structure.

M. S. B.

Harmony [between ionic concentrations]. J. STRAUB [with KLOPPERT] (Chem. Weekblad, 1933, 30, 790—792).—The mechanism of the biological processes which lead to "harmony," as opposed to equilibrium, between ionic systems on either side of a membrane, as in white and yolk of egg, yeast cells and their culture media, and blood corpuscles and serum, is discussed. The distribution of the ions is not altered by the diffusion of non-electrolytes, and is re-established after being disturbed by addition of, e.g., H_2O ; if NH_4NO_3 is added to the white of an egg, it undergoes "harmonious" distribution between the white and yolk.

H. F. G.

Dissociation constant of nitrogen-nitrogenase in azotobacter.—See this vol., 329.

Calculation of equilibrium constants for the reaction $\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow \text{C}_2\text{H}_8$ from spectroscopic data. A. V. FROST (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 161—164).—The equilibrium consts. calc. for the range 300—1000° abs. assuming free rotation of the Me groups in C_2H_8 are consistent with existing experimental data. Considerable deviations occur if absence of free rotation is assumed.

J. G. A. G.

Electrostatic theory of ionic equilibria. I. Chemical equilibrium in aqueous solution as an electrostatic problem. J. V. CHODAKOV (Z. physikal. Chem., 1934, B, 24, 35—52).—The theory developed is mathematically similar to Kossel's theory of complex compounds, but differs from it fundamentally in its primary postulates, the principal one of which is that a complex ion of approx. spherical symmetry is electrostatically equiv. to an elementary ion of the same radius. By means of the theory, a

quantity P , characteristic of the potential energy, may be derived for a system of ions or mols. from at. radii data. From vals. of P ionic equilibria may be qualitatively calc., examples of the application to the strength of acids and bases being reproduced. Ionic radii calc. from dissociation consts. agree within 3—4% with the vals. obtained from considerations of crystal structure.

R. C.

Theory of concentrated solutions of strong electrolytes. I. Theoretical considerations. G. B. BONINO. II. Calculation of activity coefficients. G. B. BONINO and G. CENTOLA. III. Calculation of the lowering of the v.p. of the solvent. G. B. BONINO and M. ROLLA (Mem. R. Accad. d'Italia Sci. fis., 1933, 4, 415—444, 445—464, 465—479).—I. The Debye-Hückel theory and its limitations are discussed, and the expression for the activity of an ion is modified by substituting for D_0 (the dielectric const. of the solvent) a function which depends on D_0 , on temp., and on the nature of the solvent and of the ions present. The activity of an ion, f_i , is then given by an expression of the form $\log f_i^0 + \log f_i^*$, where f_i^0 is the activity on the Debye-Hückel theory and f_i^* is the correction term due to the theory put forward.

II. The activity coeffs. of LiCl , NaCl , KCl , CaCl_2 , SrCl_2 , and BaCl_2 calc. from the above formula agree well with experimental data, even for conc. solutions.

III. The v.p. of conc. aq. solutions of LiCl , NaCl , and KCl are calc. and shown to agree very well with experimental data.

O. J. W.

Dissociation constant of hippuric acid. B. A. JOSEPHSON (Biochem. Z., 1933, 267, 74—76; cf. A., 1933, 1012; this vol., 28).— $K = 15.7 \times 10^{-5}$.

W. McC.

Dissociation constants of glycine at various temperatures. B. B. OWEN (J. Amer. Chem. Soc., 1934, 56, 24—27).—E.m.f. determinations give the following vals. for the acid and basic dissociation consts.: K_A 4.47×10^{-3} , K_B 6.04×10^{-5} . The calc. heats of dissociation are 1159 and 2765 g.-cal., respectively.

E. S. H.

Approximate ionisation constant of pantothenic acid as determined by fractional electrolysis. R. J. WILLIAMS and R. MOSER (J. Amer. Chem. Soc., 1934, 56, 169—170).—Fractional electrolysis of pantothenic (I), gallic (II), and salicylic acids and pyrogallol, using the apparatus previously described (A., 1933, 982), shows that (I) is slightly weaker than (II). (I) cannot be an α -OH-acid; it may contain β - or γ -OH groups.

H. B.

Hydrolysis of solutions of stannic chloride. J. GUERON (Compt. rend., 1934, 197, 473—476; cf. A., 1933, 910).—The hydrolysis of aq. SnCl_4 of concn. $> 0.3N$ is complete after 80 days at $20 \pm 5^\circ$. The micelles consist of granules of hydrated SnO_2 , positively charged with Sn^{+4} ions, and surrounded by an atm. of anions, mainly Cl^- , forming the negative charge of the double layer.

C. A. S.

Physico-chemical properties of sulphite-chromic salt solutions. A. L. ZAIDES (Ovlad. Tekhn. Kozhev. Proiz., 1931, No. 2, 24—25).—The electrical conductivity (I) of aq. (violet) Cr^{III} salt in-

creases on addition of increasing amounts of sulphite. In green Cr^{III} solutions containing SO_3'' (I) increases with time. The same holds for light absorption (extinction) in the yellow. The max. of absorbed light moves towards the red with increase in SO_3'' content. The p_{11} curve (glass electrode; quinhydrone and indicator methods unsuitable) of solutions containing green Cr^{III} salt is similar to the acid neutralisation curve with an inflexion at 5 mols. of SO_3'' per atom of Cr at which the viscosity is max. On keeping, the solutions form gels, which later liquefy. The green solution obtained on boiling the violet Cr^{III} solution is considered to contain both positive and negative Cr complexes. On adding 5 mols. of sulphite per atom of Cr to a neutral solution of $\text{Cr}_2(\text{SO}_4)_3$ the mixture has tanning properties. CH. ABS.

Dissociation pressure of silver carbonate. M. WATANABE (Sci. Rep. Tohoku, 1933, 22, 1229—1239).—Dissociation pressures, between 120° and 201° , are given by $\log p$ (atm.) = $-3855.9/T + 7.9040$. Various thermodynamic quantities have been calc.

F. L. U.

Thermal dissociation of normal manganous and cobalt carbonates. J. KRUSTINSONS (Z. Elektrochem., 1933, 39, 936—939).—Dissociation pressures are recorded for MnCO_3 between 367° and 401° and for CoCO_3 between 317° and 341° . The calc. heats of dissociation are 25,030 and 22,940 g.-cal., respectively. Solid solutions appear to be formed in the dissociation of MnCO_3 (cf. A., 1932, 1204) and CoCO_3 seems to decompose in stages.

D. R. D.

Hydrates of nickel sulphate. A. CHRÉTIEN and R. ROHMER (Compt. rend., 1934, 198, 92—94).—The following characteristic points are recorded: ice and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ at -3.15° ; $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ at 29.1° ; β - and $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ at 60.3° ; $\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 5, 4, 3$, and $2\text{H}_2\text{O}$ at 98° , 97.2° , 96.4° , and 90.3° , respectively. The equilibria in the last four cases are metastable, the monohydrate being the only stable solid phase above the transition point of $\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ at 84.3° . The metastable equilibria, especially with the di-, tri-, and tetra-hydrates, are very persistent, and true equilibrium is attained in some cases only after several weeks. The b.p. of saturated solutions of the hydrates with 6, 5, 3, 2, and 1 H_2O are, respectively, 107.7° , 107.2° , 106.6° , 105.9° , 105.1° , and 103.9° .

C. A. S.

Phase diagrams of the systems mercuric sulphate-mercuric iodide, bromide, and chloride. M. PAIÉ (Arh. Hemiju, 1933, 7, 161—169).—Thermal and X-ray data indicate the formation of a 1:1 compound, m.p. 332° (decomp.), in the system $\text{HgSO}_4\text{-HgI}_2$; no compounds appear to be formed in the other two systems. The mutual solubility of the fused salts diminishes in the order HgI_2 , HgBr_2 , HgCl_2 . R. T.

Phase equilibria in the systems TiO_2 , $\text{TiO}_2\text{-SiO}_2$, and $\text{TiO}_2\text{-Al}_2\text{O}_3$. E. N. BUNTING (Bur. Stand. J. Res., 1933, 11, 719—725).—The stable form of TiO_2 above 400° is rutile, m.p. 1825° . It forms no compounds with SiO_2 ; the eutectic, m.p. 1540° , contains 89.5 wt.-% SiO_2 . With Al_2O_3 , TiO_2 forms a compound $\text{TiO}_2 \cdot \text{Al}_2\text{O}_3$, m.p. 1860° . The eutectics, m.p.

1715° and 1850° , contain 15 and 62 wt.-% Al_2O_3 , respectively. J. W. S.

System sodium disilicate-sodium fluoride. H. S. BOOTH, B. A. STARRS, and M. J. BAHNSEN (J. Physical Chem., 1933, 37, 1103—1107).— $\text{Na}_2\text{Si}_2\text{O}_5$ has been prepared by fusing together the calc. amounts of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and SiO_2 . The binary system $\text{Na}_2\text{Si}_2\text{O}_5\text{-NaF}$ gives a simple eutectic curve, the eutectic composition being 39.5 ± 0.1 mol.-% NaF and the temp. $797 \pm 1.0^\circ$. $\text{Na}_2\text{Si}_2\text{O}_5$ has m.p. 874° .

M. S. B.

System cadmium bromide-ethyl alcohol. F. ISHIKAWA, I. MORI, and T. MUROOKA (Sci. Rep. Tohoku, 1933, 22, 1163—1178; cf. A., 1933, 905).—The alcoholate has 2 mols. EtOH, not 1.5 as reported by Lloyd (A., 1928, 479). Solubilities in EtOH between 0° and 60° , and v.p. for the systems $\text{CdBr}_2\text{-CdBr}_2 \cdot 2\text{EtOH}$ and $\text{CdBr}_2 \cdot 2\text{EtOH}$ -saturated solution are recorded. The transition temp. is 37° . Thermodynamic quantities have been calc. from the results of e.m.f. measurements.

F. L. U.

Thermal analysis of binary systems of sulphonal with certain organic compounds. K. HRYNAKOWSKI and F. ADAMANIS [with K. TOKARZOWNA, J. WAWRZYNIAK, S. WESELA, and M. BRONISZOWNA] (Rocz. Chem., 1933, 13, 736—739).—Sulphonal (I) does not form compounds with NHAcPh , phenacetin, resorcinol, salipyrine, or $\text{CO}(\text{NH}_2)_2$. (I) is completely miscible with all the above substances except $\text{CO}(\text{NH}_2)_2$.

R. T.

Thermal equilibrium in the binary systems of phenacetin, carbamide, ethylurethane, anti-pyrine, menthol, salol, and quinine. K. HRYNAKOWSKI and E. ADAMANIS (Bull. Soc. chim., 1933, [iv], 53, 1168—1175).—B.p. data are recorded for all the possible binary systems and represented as a function of mol. composition.

M. S. B.

Effect of pressure on the binary system monomethylaniline-dimethylaniline. J. C. SWALLOW and R. O. GIBSON (J.C.S., 1934, 18—21).—Over the range investigated (0—61.4% NHPhMe , 1 to about 2000 atm.) the m.p. rises linearly with pressure, the effect being greatest (1° per 40 atm.) with pure NPhMe_2 .

D. R. D.

Basic salts. III. Equilibria in system $\text{CuO-CrO}_3\text{-H}_2\text{O}$. E. HAYEK (Z. anorg. Chem., 1934, 216, 315—320; cf. A., 1933, 360).—The system has been studied at 40° . The salts $2\text{CuCrO}_4 \cdot 3\text{Cu}(\text{OH})_2$ (and with 1 H_2O) and $\text{CuCrO}_4 \cdot \text{Cu}(\text{OH})_2$ are described.

F. L. U.

Complex lead halides. (MME.) N. DEMASSIEUX and E. J. GRELLIS (Compt. rend., 1934, 198, 179—180).—Examination of the system $\text{PbBr}_2\text{-NH}_4\text{Br-H}_2\text{O}$ indicates the existence of $2\text{PbBr}_2 \cdot \text{NH}_4\text{Br}$ and $\text{PbBr}_2 \cdot 2\text{NH}_4\text{Br}$ at all temp. (cf. A., 1893, ii, 523; 1898, ii, 512).

C. A. S.

Systems acetone-sodium hydroxide-water and acetone-potassium hydroxide-water at 0° . C. W. GIBBY (J.C.S., 1934, 9—10).—The complete phase diagrams at 0° indicate that COMe_2 can be salted out from any mixture with H_2O by addition of NaOH or KOH, the COMe, layer containing $< 0.5\%$ of alkali.

D. R. D.

Invariant thermodynamics of elastic systems. (MLLE.) Y. DUPONT (Bull. Acad. roy. Belg., 1933, [v], 19, 1167—1179).—Mathematical. J. W. S.

Thermochemistry of aluminium. A. MEICHNER and W. A. ROTH (Z. Elektrochem., 1934, 40, 19—26).—The heats of formation of α - Al_2O_3 and Al_4C_3 at 20° are 393.3 ± 0.3 and 20 ± 3 kg.-cal., respectively (cf. A., 1929, 1389). H. J. E.

Thermochemistry of thallium. W. A. ROTH and A. MEICHNER (Z. Elektrochem., 1934, 40, 19; cf. A., 1932, 341).—A correction. H. J. E.

Heat capacity and entropy of potassium chlorate from 13° to 300° K. Entropy of chlorate ion. W. M. LATIMER, P. W. SCHUTZ, and J. F. G. HICKS, jun. (J. Amer. Chem. Soc., 1934, 56, 88—89).— C_p increases from 0.44 g.-cal. per mol. at 13.95° abs. to 22.84 at 293.35° abs. The entropy of KClO_3 at 298.1° abs. is 34.17 e.u. The entropy and free energy of formation of ClO_3' at 298.1° abs. are 39.3 e.u. and 3700 g.-cal., respectively. E. S. H.

Thermodynamic constants of chlorine monoxide. D. M. YOST and R. C. FELT (J. Amer. Chem. Soc., 1934, 56, 68—69).—Partial v.p. of Cl_2O solutions in CCl_4 have been determined at 0° and 25°. The free energy of the reaction $\text{Cl}_2 + 0.5\text{O}_2 \rightarrow \text{Cl}_2\text{O}$ (all gaseous) at 25° is 21,210 g.-cal. The entropy at 25° and 1 atm. is 67.9 g.-cal. per degree. E. S. H.

Thermochemical measurements with oxides of copper, rhodium, palladium, and iridium. L. WOHLER and N. JOCHUM (Z. physikal. Chem., 1933, 167, 169—179).—The heats of formation are: IrO_2 , 40.14; CuO , 33.02; Cu_2O , 43.00; PdO , 20.40; Rh_2O_3 , 68.30; RhO , 21.72; Rh_2O , 22.70 kg.-cal. The mean mol. heats of these oxides and of Ir have been determined at 16—1000°. The dissociation pressures calc. from these data agree with the observed vals. R. C.

Heats of dissolution and heats of reaction in liquid ammonia. I. C. A. KRAUS and J. A. RIDDERHOF. II. C. A. KRAUS and R. F. PRESCOTT (J. Amer. Chem. Soc., 1934, 56, 79—86, 86—88).—I. A calorimeter, in which the heat effect is determined by the amount of NH_3 vaporised, is described. Heats of dissolution in liquid NH_3 have been determined as follows (g.-cal. per mol.): NaNO_3 3600, NaBr 9500, NaI 17,500, KNO_3 —400, KBr 2900, KI 5900, NH_4Cl 6400, NH_4NO_3 5700, NH_4Br 8100, NH_4I 11,000, LiNO_3 10,800, AgNO_3 22,400, AgI 6700, Na —1450. The heat effects for a no. of reactions have been determined. Heats of formation calc. from these are in agreement with published vals. By direct reaction of S and Te with Na in liquid NH_3 the following heats of reaction have been obtained for the first time: Na_2S , 96,200, Na_2Te 82,500, Na_2Te_2 101,800 g.-cal. per mol.

II. Improvements in technique are described. The following heats of dissolution (g.-cal. per g. mol.) in liquid NH_3 have been determined: AgNO_3 21 400

Heats of dissolution of sugars in water. B. C. HENDRICKS, W. H. STEINBACH, jun., R. H. LE ROY, and G. MOSELEY, jun. (J. Amer. Chem. Soc., 1934, 56, 99—101). The data (in g.-cal. per g.) refer to

dilutions of 0.00035 mol. of sugar per mol. of H_2O : *d*-galactose —21.4, α -methyl-*d*-glucoside —3.13, α -methyl-*d*-mannoside —11.0, *d*-glucose —14.5, β -*d*-glucose —5.65, *d*-glucose hydrate —25.2. Heats of mutarotation of *d*-galactose and *d*-glucose are zero.

E. S. H.

Carbon tetrachloride synthesis. C. G. FINKE and C. F. BONILLA (J. Physical Chem., 1933, 37, 1135—1167).— C_p for CCl_4 vapour at 1 atm. between 0° and 300°, calc. from available data, is $14.0 + 0.02337T$. Two or more of the thermodynamic quantities C_p , ΔF° , and S at 298° have been calc. for C (graphite), Cl_2 , CCl_4 , COCl_2 , CO_2 , SiCl_4 , SnCl_4 , AlCl_3 , SiO_2 (quartz), SnO_2 , and Al_2O_3 . The equilibrium const. for the reaction $2\text{CCl}_4 = \text{C}_2\text{Cl}_4 + 2\text{Cl}_2$ has also been derived from known experimental data. Free energy calculations show that the reaction $\text{COCl}_2 + 2\text{MCl} = \text{CCl}_4 + \text{M}_2\text{O}$, where M is the equiv. of Si, Al, or Sn, cannot be carried out to an appreciable extent. This has been confirmed experimentally. Ordinary animal charcoal is a good catalyst for the reaction $\text{CCl}_4 = \text{C} + 2\text{Cl}_2$, but the reverse reaction could not be observed. Attempts to obtain CCl_4 by the reaction $2\text{COCl}_2 = \text{CO}_2 + \text{CCl}_4$, using different catalysts, were also unsuccessful. A quant. study of the reverse reaction shows that the theoretical equilibrium is not attained. Methods for the volumetric determination of CCl_4 and of the proportions of Cl_2 , COCl_2 , and CO_2 in a mixture are described. M. S. B.

Heat of formation of mixed crystals of potassium chloride and bromide. II. M. M. POPOV and S. F. JAVOROVSKAJA (Z. physikal. Chem., 1933, 167, 180—182; cf. A., 1930, 703).—In order to obtain homogeneous mixed crystals from the molten mixture, crystallisation must occur slowly. The heat of formation, Q , of mixed crystals which have received the same annealing treatment is the same, independent of the duration of cooling. With increasing duration of annealing Q passes through a min. It proved impossible to obtain by grinding mixed crystals for which Q is comparable with that of crystals separated from a molten mixture. R. C.

Electrolytic transport of water in certain bromide and iodide solutions. A. WAGNER (Chem. Listy, 1933, 27, 481—484).—Measurements of the electrolytic transport of H_2O in *N*- and 0.1*N*- NaI and 0.1*N*- KI indicate that I' is associated with 2.55 mols. H_2O . Viktorin's results (A., 1933, 1247) are confirmed for 0.1*N*- KBr and - NaBr . R. T.

Hydration of ions Mg'' , Ca'' , Sr'' , and Ba'' in normal solutions. J. BABOROVSKY and O. VIKTORIN (Coll. Czech. Chem. Comm., 1933, 5, 518—526).—The true transport nos. of the cations in *N*- MgCl_2 , - CaCl_2 , - SrCl_2 , and - BaCl_2 , as measured by Baborovsky's method (A., 1928, 244, 954), are 0.262, 0.299, 0.279, and 0.289, respectively. The mols. of H_2O associated with the respective cations are Mg'' 20, Ca'' 17—16, Sr'' 16, and Ba'' 11. These results are compared with previous data. In all cases H_2O is also transported to the anode. M. S. B.

Conductivity in the transition region between strong and weak electrolytes. R. M. FUOSS (Physikal. Z., 1934, 35, 59—68).—Theoretical.

A. J. M.

Measurement of electrolytic conductivities. W. FINK and P. GROSS (*Monatsh.*, 1933, 63, 271—284).—Data for Na_2SO_4 from 1×10^{-2} to $2 \times 10^{-4} M$, and $o\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ from 2×10^{-2} to $1 \times 10^{-3} M$, are discussed in terms of Onsager's theory. The electrostatic capacity of a cell is shown to be independent of the nature of the solution if the conductivities are equal. D. R. D.

Electrolyte mixtures. II. Measurement of conductivity. V. K. SEMENTSCHENKO, B. V. JEROFEJEV, and V. V. SERPINSKI. **III. Conductivity of mixtures of electrolytes.** V. K. SEMENTSCHENKO and V. V. SERPINSKI (*Z. physikal. Chem.*, 1933, 167, 188—196, 197—208; cf. *A.* 1932, 570).—II. Conductivity measurements with 0.0001—2*N* aq. KCl, using an apparatus similar to that of Shedlowsky (*A.*, 1930, 862), have given results in agreement with the latter's and with the Debye-Onsager equation. The attainable precision with this apparatus is 0.02%.

III. Measurements have been made with aq. solutions of NaN_3 , NaBr, and MgSO_4 , and mixtures of KCl and NaN_3 , of KCl and MgSO_4 , and of KCl, NaBr, and MgSO_4 . The results for the single electrolytes agree with the Debye-Hückel-Onsager theory better than existing data. For the mixed solutions at low concns. the conductivity agrees with the val. calc. by the additive principle, probably owing to mutual compensation of opposing effects. R. C.

Simultaneous conduction by electrolytes in resistance measurements on palladium wires containing hydrogen. C. A. KNORR and E. SCHWARTZ (*Z. Elektrochem.*, 1934, 40, 36—38).—A reply to Smith (*A.*, 1933, 1014). H. J. E.

Absolute determination of the absorption of solutions of electrolytes in glycerol and aqueous glycerol, in high-frequency electric fields. J. HIEGEMANN (*Physikal. Z.*, 1934, 35, 91—93; cf. Whitmore, *A.*, 1933, 1015).—The conductivities of glycerol (I), aq. (I), and solutions of KCl and MgSO_4 in (I) and aq. (I) have been measured for wavelengths 23, 46, and 92 m. A. J. M.

Magnesium electrode in ether solution and free energy of formation of magnesium bromide. G. A. SCHERER and R. F. NEWTON (*J. Amer. Chem. Soc.*, 1934, 56, 18—20).—The e.m.f. of the cell $\text{Mg} | \text{saturated Et}_2\text{O solution of MgBr}_2 \cdot 2\text{Et}_2\text{O} | \text{Hg}_2\text{Br}_2, \text{Hg}$ at 25° is 1.561 ± 0.004 volt. The v.p. of etherates of MgBr_2 at 25° have been determined. The free energy of formation of MgBr_2 at 25° is $-114,000$ g.-cal. per mol. E. S. H.

Standard quinhydrone electrode. F. HOVORKA and W. C. DEARING (*J. Amer. Chem. Soc.*, 1934, 56, 243—244).—The quinhydrone electrode is said to excel the 0.1*N* or saturated calomel electrode in both reproducibility and constancy. E. S. H.

Temperature coefficients of the electromotive force of the cell Cd (metal), CdSO_4 , Cd (satd. amalgam). W. G. PARKES and V. K. LA MER (*J. Amer. Chem. Soc.*, 1934, 56, 90—91).—From e.m.f. measurements at 0—30° the free energy, entropy, and heat content changes for the process $\text{Cd}(\text{metal}) \rightarrow \text{Cd}(\text{s, saturated with Hg})$ are calc. Corresponding data, calc. for the reaction $\text{Cd}(\text{s}) + \text{PbSO}_4(\text{s}) =$

$\text{CdSO}_4(a=1) + \text{Pb}(\text{s})$, are 3153 g.-cal., -45.20 e.u., and 16,536 g.-cal., respectively. E. S. H.

Potential of an electrode in a solution with no common ion. O. ESSIN and M. LOZMANOVA (*Z. physikal. Chem.*, 1933, 167, 209—220).—The potential of a Au electrode, E_1 , in aq. CuSO_4 , $\text{Cu}(\text{NO}_3)_2$, or AgNO_3 is a linear function of the potential, E_2 , of the metal contained in the electrolyte. The vals. of a and b in $E_1 = a + bE_2$ seem to be determined principally by the cation of the electrolyte. It is possible that the establishment of a p.d. between Au and the solution involves a small transfer of charge from the cations of the solution to the Au. R. C.

Dependence of metal-salt equilibria on the nature of the anions. G. TAMMANN and H. O. VON SAMSON-HIMMELSTJERNA (*Z. anorg. Chem.*, 1934, 216, 288—302).—The relation between the electrode potential of metals in contact with their molten salts and the heats of formation of the latter is approx. linear for salts having the same anion. Thus the displacement of one metal by another in a molten salt may be predicted from thermal data. The influence of the anion may be considerable; e.g., K is nobler than Na in the fluorides, baser in the other halides; Pb is almost as noble as Ag in the iodides, and Fe as Cu in the sulphides. F. L. U.

Liquid junction potentials. II. J. B. CHLOUPEK, V. Z. DANES, and B. A. DANESOVA (*Coll. Czech. Chem. Comm.*, 1933, 5, 527—534).—A discussion of the experimental data previously obtained (this vol., 150). The liquid junction potential difference in the cell $\text{Hg} | \text{HgCl}_2, 0.1N\text{-KCl} | \text{junction solution} | 0.1N\text{-HCl} | \text{Hg}$ is a logarithmic function of the concn. of the bridge electrolyte for solutions of a dilution at which the Debye-Hückel theory is valid. In more conc. solutions, 0.1*N* and upwards, the individual character of the electrolyte becomes more marked, but certain regularities appear. Salts with multivalent anions, such as Na_2SO_4 , ZnSO_4 , K_2CrO_4 , $\text{K}_4\text{Fe}(\text{CN})_6$, form a class apart from the salts with univalent anions such as KCl, MgCl_2 , and NaNO_3 , but there is no such distinction between multi- and uni-valent cations. This is attributed to the simpler electronic structure of the multivalent metallic cations as compared with the multivalent anions. M. S. B.

Electrometric titration curves of imino-dibasic acids. A. LITZINGER and L. W. PICKETT (*J. Amer. Chem. Soc.*, 1934, 56, 124—126).—The curves for $\text{NH}(\text{CH}_2\text{CO}_2\text{H})_2$, tyrosine-*N*-acetic and -phenyl-acetic (I), and phenylalanine-*N*-acetic and -phenyl-acetic (II) acids (*A.*, 1933, 166) are all similar; all show the greatest change in $[\text{H}^+]$ with 1 equiv. of KOH. Evidence of a second end-point (2 equivs. of KOH) is found with (I) and (II). The dissociation consts. of the acids are very similar and indicate that they are weak acids. H. B.

Phenanthroline-ferrous ion. II. Oxidation potentials at high acidities and determination of vanadium. G. H. WALDEN, jun., L. P. HAMNETT, and S. M. EDMONDS (*J. Amer. Chem. Soc.*, 1934, 56, 57—60; *A.*, 1933, 924).—Relative oxidation potentials of $\text{Fe}^{III}/\text{Fe}^{II}$, the phenanthroline-ferrous indicator (I), $\text{V}^{V}/\text{V}^{IV}$, and $\text{V}^{IV}/\text{V}^{III}$ have been determined in 1,

3, and 5*M*-H₂SO₄. *V* can be determined in presence of Fe, Cr, and Mo by titrating the solution in 5*M*-H₂SO₄ with dil. FeSO₄ in presence of (I). E. S. H.

Influence of substituents in the nucleus on the energy of reduction of benzaldehyde. G. SEMERANO and A. CHISINI (*Gazzetta*, 1933, **63**, 802—818).—Measurements with the dropping Hg cathode of the reduction potential (I) of PhCHO and various nuclear-substituted derivatives in 0.1*N*-HCl and -NH₄Cl solutions in 50% EtOH are recorded. The influence of the substituents is independent of the nature of the electrolyte present. (I) is increased by a Cl atom in any position and by an *o*-Me group; it is lower for the *p*- and *m*-Me-substituted aldehydes, and for salicylaldehyde, anisaldehyde, etc. The change is greatest when a substituent enters the *o*-position, and least when it enters the *p*-position. The results do not support the theory of induced alternate polarity, but may be qualitatively explained on the basis of Robinson's hypothesis. H. F. G.

Relation of life to electricity. VIII. Mechanism of oxidation-reduction potentials of living tissues.—See this vol., 327.

Thermodynamics of the electrocapillary curve. I. General equations. F. O. KOENIG (*J. Physical Chem.*, 1934, **38**, 111—128).—The theory of electrocapillary curves is re-developed on the single assumption of perfect polarisability, which is defined as the impermeability to electrically-charged particles of the boundary layer between two conducting phases. This corresponds closely with the actual physical conditions in the Lippmann electrometer. The Lippmann-Helmholtz equation holds for all perfectly polarisable systems regardless of composition. M. S. B.

Hydrogen overvoltage and adsorption at the dropping mercury cathode. G. SEMERANO (*Gazzetta*, 1933, **63**, 786—801).—The deposition potential of H at the dropping Hg cathode from 0.002*N* solutions of HCl containing various salts has been determined, together with the diffusion and adsorption currents in similar solutions to which fuchsin has been added. Progressive addition of fuchsin increases the current which flows at potentials < that required for the liberation of H, and, above a certain concn., reduces the quantity of H evolved. The deposition potential is reduced by addition of the dye; pronounced peaks also appear on the polarograph curve, and the diffusion wave is considerably depressed. The results are discussed at some length. H. F. G.

Catalytic activity of palladium and the hydrogen overvoltage. C. A. KNORR and E. SCHWARTZ (*Z. Elektrochem.*, 1934, **40**, 38—43).—Overvoltage data for H on Pd are correlated with its catalytic activity measured by the rate of absorption of H₂ (followed by changes in the electrical resistance of the Pd). At const. c.d. the overvoltage increases with decreasing rate of absorption. A relation between the c.d. and overvoltage is deduced. H. J. E.

Catalytic hydrogen replacement and the nature of overvoltage. J. HORIUTI and M. POLANYI (*Nature*, 1934, **133**, 142).—A reply to criticism (this vol., 150). L. S. T.

Electrolytic oxidation. IV. Anodic polarisation in halide solutions. S. GLASSTONE and A. HICKLING (*J.C.S.*, 1934, 10—18).—In electrolysis of halide solutions at const. c.d. with a Pt anode, two anode potentials are observed: the first is due to reversible discharge of halide ions and the higher one to the formation of H₂O₂, which decomposes causing O₂ evolution when the anode surface is saturated. The presence of catalysts for decomp. of H₂O₂ hastens attainment of this condition, whilst the increased surface of platinised Pt takes far longer to saturate.

D. R. D.

Properties of the layer of oxide formed by anodic polarisation at the surface of oxidisable metals. M. MARINESCU (*Bul. Soc. Romane Fiz.*, 1933, **35**, 135—142).—The anodic resistance of certain oxidisable metals such as Al and Ta is high owing to the adsorption of O by the layer of oxide formed at the anode. A mathematical explanation is advanced of experimental results which have been obtained with a.c. of high and low c.d. H. S. P.

Poisoning of hydrogen electrodes by dichlorochromyl chloride. J. LISIECKI (*Rocz. Chem.*, 1933, **13**, 552—559).—Aq. [CrCl₂(OH₂)₄]Cl (I) depolarises and permanently inactivates H electrodes. The electrode should be freshly platinised before each determination of *p_H* in solutions of (I). R. T.

Passivity of iron and aluminium. W. H. CONE and H. V. TARTAR (*J. Amer. Chem. Soc.*, 1934, **56**, 48—52).—The presence of PO₄^{'''} (excepting small quantities with Al) or SO₄^{''} accelerates the rate of dissolution of Fe or Al in HNO₃ to a degree which is approx. proportional to the concn. Simultaneously the metal becomes more electronegative to the solution. A gradual transition from activity to passivity is obtained, according to the [SO₄^{''}] or [PO₄^{'''}]. The assumption of a film of adsorbed O₂ is preferred to the oxide-film theory. Fe is passive in dil. HNO₃ containing AgNO₃. E. S. H.

Film theory of passivity. W. J. MÜLLER (*Z. Elektrochem.*, 1934, **40**, 18—19).—Schwabe's results (*A.*, 1933, 1248) are discussed in relation to the author's film theory. H. J. E.

Flame temperatures in carbon monoxide and air mixtures. W. T. DAVID and J. JORDAN (*Phil. Mag.*, 1934, [vii], **17**, 172—181; cf. *A.*, 1932, 25).—Temp. was measured with a Pt-Rh thermometer in a spherical explosion vessel. A max. was recorded for equimol. proportions of CO and O₂. The deviation from the calc. temp. was greatest for this mixture. A surface action between the hot wire and the freshly burnt gas is suggested. H. J. E.

Ignition of some explosive mixtures by modified coil discharges. B. W. BRADFORD, G. I. FINCH, and (Miss) A. M. PRIOR (*J.C.S.*, 1934, 75—79).—Previous results are summarised and extended. In a spark, the high-frequency condensed discharge (capacity component) is relatively inefficient as a source of ignition as compared with the inductance component. The igniting power is determined to a greater extent by the discharge duration than by the total energy or its max. rate of dissipation, contrary to the thermal theory of ignition. It is suggested

that ignition is occasioned by the production in the discharge of mols. with the correct excitation energies. R. S.

Decomposition of complex molecules at high pressures. C. C. COFFIN and A. L. GEDDES (J. Chem. Physics, 1934, 2, 47—48; cf. A., 1932, 1094).—The velocity of the thermal decomp. of gaseous paraldehyde to MeCHO slowly diminishes as the initial pressure is increased (e.g., at 254° it is 6×10^{-4} at several mm. and 3×10^{-4} at 18 atm.). It is suggested that at an activating collision the most probable distribution of internal energy is not that most favourable to decomp. The adjustment of internal mol. energy requires a finite time. Hence, the shorter is the time between collisions (e.g., before deactivation), the smaller is the chance of reaction.

H. J. E.

Vapour-phase oxidation of hydrocarbons. I. Amount and rate of oxidation of *n*-heptane as a function of temperature. II. Relative oxidisability of *n*-heptane, Δ^{α} - and Δ^{γ} -heptenes, and mixtures of *n*-heptane and $\beta\beta\delta$ -trimethylpentane. III. Chemiluminescence of *n*-heptane. H. A. BEATTY and G. EDGAR (J. Amer. Chem. Soc., 1934, 56, 102—106, 107—111, 112—114).—I. The effect of temp. on the amount and rate of oxidation of *n*-heptane (I) in "air" [(I) is vaporised in N₂ and mixed with sufficient O₂ for complete combustion; the concn. of (I) is 1.9%] is studied by the method previously described (A., 1929, 906, 1036). Reaction is slow and (probably) heterogeneous at < 250°. At 250—270°, reaction is homogeneous and is accompanied by visible chemiluminescence; so-called "ignition" begins at about 270°, but this does not cause any marked increase in the O₂ consumption. These "ignitions" become continuous at about 305°. The reaction occurring at 250—350° involves 3 mols. of O₂ per mol. of (I) and is termed the primary reaction (A); marked local evolution of heat and a rapid increase in reaction velocity take place. The O₂ consumption increases from 3 to 4.7 mols. at 350—380° and is considered to be due to a subsequent reaction (B). The velocities of (A) and (B) decrease with rise in temp. at 380—470° and the temp. coeff. for 10° is about 0.85. At 470—510°, the velocity of (A) continues to decrease, whilst that of (B) increases. Inflammation, followed by complete combustion, occurs at 500—525°.

II. Under the same experimental conditions, oxidation of (I), Δ^{α} -heptene (II), and Δ^{γ} -heptene (III) begins at 244°, 300°, and 300°, respectively; the relative reaction velocities increase in the order (III), (II), (I), but the general course of reaction and max. O₂ consumption (about 40% of the theoretical) are the same in each case. Oxidation of (II) and (III) does not appear to begin at the double linking. $\beta\beta\delta$ -Trimethylpentane (IV) is oxidised to a slight extent at about 250°; the main reaction begins at 500° (cf. *loc. cit.*) and increases rapidly up to about 550° (at which temp. inflammation occurs). (IV) exerts a slight inhibitory effect on the oxidation of (I), but undergoes induced oxidation; these effects appear to be more pronounced with relatively high concns. of (IV). A marked negative temp. coeff. of

reaction velocity is observed for (I), (II), and (III) at about 400—500°.

III. The chemiluminescence phenomena occurring during the oxidation of (I) and (III) are described.

H. B.

Influence of pressure on the spontaneous inflammation of hydrocarbons. M. NEUMANN and V. ESTROVICH (Nature, 1934, 133, 105—106).—The pressure-temp. curves for the spontaneous inflammation of C₅H₁₂+8O₂ mixtures in an Fe bomb and in a bomb coated internally with Au have sharp breaks near 60 cm. pressure. Oxidation thus proceeds in two different ways each prevailing in a definite region of pressure. Bone's hydroxylation theory explains the facts, and the existence of a sudden lowering of the inflammation temp. at any crit. pressure is considered to be general for the inflammation of complex hydrocarbons. L. S. T.

Free radicals in thermal decompositions and combustion of hydrocarbons. W. A. BONE (Trans. Faraday Soc., 1934, 30, 148—152).—In the pyrolysis of CH₄, C₂H₆, C₂H₄, and C₂H₂ it is necessary to assume the primary formation of free radicals such as CH₂, CH, and possibly CH₃. There is no evidence, other than spectrographic, of their formation in combustion, the primary products being oxygenated.

F. L. U.

Kinetics and mechanism of the thermal decomposition of hydrocarbons. A. I. DINTSES (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 153—157).—The two principal primary reactions in the thermal decomp. of *n*-C₈H₁₄ (I), *n*-C₈H₁₈ (II), and β -dimethylhexane (III) involve the formation of CH₃ and C₂H₅ together with the appropriate olefines which rapidly decompose into lower olefines. The course of the later reactions only are affected by the temp. and time of contact. The velocity coeffs., *K*, are: (I) $\log_{10} K = 14.58 - 14,100/T \pm 0.06$ (525—565°), (II) $\log_{10} K = 14.70 - 14,100/T \pm 0.09$ (495—570°), and (III) $\log_{10} K = 6.553 - 7215/T \pm 0.05$ (490—575°), from which the respective energies of activation of the primary decomp. are 64,500, 64,500, and 33,000 g.-cal. (cf. A., 1933, 1017). Rice's theory of free radicals affords the best explanation of the data, and the difference between the activation energies of *n*- and *iso*-hydrocarbons is emphasised.

J. G. A. G.

Kinetic study of reaction between potassium iodide and hydrogen peroxide in acid solution. (MRE.) P. RUMPF (Compt. rend., 1934, 198, 256—258).—Using a spectrographic method (determination of amount of I₂' by its absorption in solutions buffered by KH₂PO₄-K₂HPO₄, of *p*_H 5—6) and equal concn. of KI and H₂O₂, the velocity of interaction for *C* = 0.004—0.008 and $\propto C^3$, but is greater if *C* is smaller. It varies directly with *p*_H for *p*_H = 5.6—5.9, and *C* = 0.006*N*. The reaction at very low concn. is independent of *p*_H, at higher according to $2\text{I}' + \text{H}_2\text{O}_2 + 2\text{H}^+ = \text{I}_2 + 2\text{H}_2\text{O}$; the latter predominates, the final concn. of I₂' being proportional to *p*_H for *p*_H = 5.25—6.05 (cf. A., 1932, 1212).

C. A. S.

Kinetics of the action of iodine on hydrazine and hydroxylamine hydrochlorides. A. BERTHOUD and D. PORRET (Helv. Chim. Acta, 1934, 17, 32—43).—In each case the velocity of the "dark" reaction

\propto [salt] and [I]. With $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ the velocity $\propto 1/[\text{H}^+]$ and $1/[\text{I}]^n$ ($n < 2$), and is decreased by NaCl , KBr , and KNO_3 . With $\text{NH}_2\text{OH} \cdot \text{HCl}$ it $\propto 1/[\text{H}^+]^2$ and $1/[\text{I}]^2$. The temp. coeffs. for 20–30° are, respectively, 3.4 and 4.0. A mechanism of reaction is suggested. Conclusions of Bhattacharya and Dhar (A., 1930, 1384) are criticised. F. L. U.

Velocity of esterification of alcohols by formic acid. III. A. KAILAN and F. ADLER (Monatsh., 1933, 63, 155–185).—The velocity of esterification (V) of benzyl, β -phenylethyl, γ -phenylpropyl, allyl, *o*-, *m*-, and *p*-nitrobenzyl alcohols and phenyl-methyl-, *o*-ethyl-, and *p*-propyl-carbinols by HCO_2H at 15° under various conditions has been determined cryoscopically and unimol. velocity coeffs. have been calc. therefrom. Dilution with H_2O reduces the val. of V . The increase of V produced by addition of HCl is approx. $\propto [\text{HCl}]$. Neutral salts may have a positive or negative catalytic effect, varying with $[\text{HCO}_2\text{H}]$, $[\text{HCl}]$, and the alcohol and salt employed. Ph groups reduce V the more, the nearer they are to the OH group. The mol. depression of the f.p. of conc. and dil. HCO_2H by its esters is much < the val. calc. from its latent heat. D. R. D.

Velocities of hydrolysis of the methyl esters of the two crotonic acids. A. SKRABAL and W. STOCKMAYER (Monatsh., 1933, 63, 244–254).—The high-boiling Me ester hydrolyses more rapidly than the low-boiling ester under either acid or alkaline conditions. Comparison with related compounds indicates a relation between rate of hydrolysis and constitution. D. R. D.

Stability of fructose in aqueous solutions of varying p_{H} . J. A. MATHEWS and R. F. JACKSON (Bur. Stand. J. Res., 1933, 11, 619–633).—The decomp. of fructose at 4–100° and in solutions of p_{H} 2.6 to 14.2 is unimol. in its earlier stages and approaches an equilibrium, the val. of which is a function of the p_{H} . In acid solutions it is dehydrated to form lævulosans of negative rotation, whilst in alkaline solutions the Lobry de Bruyn-van Ekenstein transformation occurs; at intermediate p_{H} both changes take place. Fructose shows max. stability at p_{H} 3.3, independent of temp. The temp. coeff. of the decomp. at const. p_{H} is high, and is greatest in acid solutions. J. W. S.

Determination of acidity in ethyl alcohol by velocity of acetal formation. A. J. DEYRUP (J. Amer. Chem. Soc., 1934, 56, 60–64).—The rate of formation of Et_2 acetal is suitable as a measure of acidity in abs. EtOH . HCl , HBr , HI , and HClO_4 are completely ionised strong acids, whilst HNO_3 and picric acid are weak acids of about the same strength in EtOH . The effect of change of electrolyte concn. and solvent on the dissociation consts. of weak acids and bases has been determined. The reaction is inhibited by traces of H_2O . Catalysis in presence of CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, and LiCl is due to traces of strong acids. E. S. H.

Optical activity in relation to tautomeric change. II. Comparison between the rate of racemisation of a tautomeric substance and the rate of its tautomeric interconversion. C. K.

INGOLD and C. L. WILSON (J.C.S., 1934, 93–97; cf. this vol., 64).—The velocity and equilibrium consts. of the isomerisation of optically inactive *p*-chlorobenzhydrylidene- α -phenylethylamine (I) have been measured and compared with the rate of racemisation of optically active (I) in the same process. The results agree with the hypothesis that the optical activity of (I) is retained in its ions but destroyed by the subsequent isomerisation, and render the view that racemisation occurs in the preliminary ionisation improbable. R. S.

Reactions between chlorine and solid carbonates. I. Sodium carbonate. F. ISHIKAWA, T. MUROOKA, and H. HAGISAWA. II. Potassium, lithium, and magnesium carbonates. III. Velocity of decomposition of sodium and potassium perchlorates. F. ISHIKAWA and H. HAGISAWA (Sci. Rep. Tôhoku, 1933, 22, 1179–1196, 1197–1206, 1207–1228).—I, II. See A., 1932, 349.

III. NaClO_4 begins to decompose at about 450°, KClO_4 at about 550°. The decomp.-time curves are S-shaped. Admixture of carbonate or of chloride accelerates the decomp. The f.-p. curve of NaClO_4 - NaCl has been determined. The eutectic has m.p. 417°. Expressions representing the isothermal decomp. of NaClO_4 are given. F. L. U.

Corrosion and co-ordination. H. L. RILEY (Proc. Roy. Soc., 1934, A, 143, 399–410).—Measurements have been made of the rates of dissolution of Cu and Ni, respectively, in aq. solutions of the Na salts of the following acids: $\text{H}_2\text{C}_2\text{O}_4$, $\text{CH}_2(\text{CO}_2\text{H})_2$, $(\text{CH}_2\text{CO}_2\text{H})_2$, *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$, H_2CO_3 , AcOH , BzOH , $(\text{OH}\cdot\text{CH}\cdot\text{CO}_2\text{H})_2$, $\text{OH}\cdot\text{C}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})_2$, and *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. The results support an explanation depending on the electrolytic solution pressure of the metal, the tendency which the metal ions possess to form stable complex ions, and the co-ordinating tendency of the anions. L. L. B.

Corrosion of tin-silver amalgams. N. BRECHT (Z. Elektrochem., 1933, 39, 927–935).—Five amalgams in the three-phase field Ag_3Sn Sn-Hg mixed crystal (I)- Ag_3Hg_4 +trace of Sn (II) behaved identically as regards rate of loss of wt. in and potential against 0.1N- HClO_4 , -citric acid, - NaOH , and - NaCl . From such amalgams Sn dissolves anodically in 0.1N- HClO_4 at all c.d. up to 15 ma. per sq. cm., whilst in the other solutions, gas evolution occurs above about 3 ma. per sq. cm. The rate of dissolution at known current shows that the Sn dissolves as Sn^{++} , and examination of the depth of corrosion gives an indication of the degree of porosity. D. R. D.

Corrosion-time relationship of iron.—See B., 1934, 148.

Rate of reduction of carbon dioxide by graphite. M. A. MAYERS (J. Amer. Chem. Soc., 1934, 56, 70–76).—The experimental procedure involves eliminating concn. gradients by increasing the velocity of gas across the reacting surface until the velocity coeff. of the observed rate of reaction disappears. The rate of reduction of CO_2 in terms of c.c. of CO at n.t.p. produced per sec. from CO_2 at 1 atm. in contact with 1 sq. cm. of graphite surface, is given at 950–1300° by $\log A_1 = 5.07 - (38,700/4.575T)$, and at 850–950° by

$\log A_2 = 3.40 - (32,360/4.575T)$. The significance of the two stages is discussed. E. S. H.

Determination of surface activity of wood charcoal. B. G. ŠIMEK and R. KASSLER (Chem. Listy, 1933, 27, 484—487).—The temp. initiating combustion and the flash point of wood C (I) are unaffected by exposing (I) to air during 7 days. The heat of adsorption of H_2O is insufficient to initiate combustion. R. T.

Effect of water vapour on ignition temperatures of methane-air mixtures. G. W. JONES and H. SEAMAN (Ind. Eng. Chem., 1934, 26, 71—72).—The addition of H_2O vapour (aq. v.p. 22.15—26.5 mm. Hg) raises the ignition temp. of CH_4 -air mixtures (CH_4 4—9% on dry basis) 7—11°; smaller quantities of H_2O vapour raise it by smaller amounts. H_2O vapour has no appreciable effect on the lag on ignition. D. K. M.

Mechanism of gaseous reactions. I. Thermal decomposition of methyl ethyl ether. II. Homogeneous catalysis in the decomposition of methyl ethyl ether. W. URE and J. T. YOUNG (J. Physical Chem., 1933, 37, 1169—1182, 1183—1190).—I. The decomp. of $MeOEt$ is a complex process consisting of a unimol. decomp. into $MeCHO$ and CH_4 followed by a bimol. decomp. of $MeCHO$, the first predominating at low temp. (457°) and the second at high temp. (565°). A mathematical treatment for intermediate conditions is given.

II. The decomp. of $MeOEt$ is catalysed by small quantities of EtI , the catalytic process consisting chiefly of the unimol. decomp. of $MeOEt$ followed by the unimol. decomp. of $MeCHO$. By increasing the surface of the reaction vessel by glass-wool packing or Pyrex rods the rate of reaction is decreased. C_2H_6 is also a primary product, and its decomp. to give an equilibrium mixture with C_2H_4 and H_2 is catalysed by EtI . M. S. B.

Stabiliser for hydrogen peroxide. I. R. KONDO and H. HONAMI (Bull. Imp. Hyg. Lab., 1933, 42, 187—189).—Effectiveness is in the order: 0.1% barbituric acid > 0.1% *m*-hydroxybenzoate > 0.1% hippuric acid > uric acid. CH. ABS.

Acid catalysis in non-aqueous solvents. I. Rearrangement of *N*-bromoacetanilide. R. P. BELL (Proc. Roy. Soc., 1934, A, 143, 377—399).—The catalysis by acids of the unimol. transformation of $NBrAcPh$ to p - $C_6H_4BrNHAc$ has been studied in several solvents. The relation between the catalytic coeffs. α_0 , of ten acids in $PhCl$ is expressed by $\alpha_0 = 0.45K_d^{0.30}$, where K_d is the dissociation const. $C_6H_5(NO_2)_3 \cdot OH$ does not obey this relation. The medium has only a small effect on α_0 , and the results in C_6H_6 , although less accurate, also obey the above relationship. Measurements of the temp. coeffs. for catalysis by five acids in $PhCl$ show that the velocity of reaction is $1/10^4$ — 10^5 times the val. calc. from the simple collision formula. L. L. B.

Oxidation of solutions of iodoform. R. DUBRISAY and G. EMSCHWILLER (Compt. rend., 1934, 198, 263—265; cf. A., 1932, 1215).—Addition of I and acid to a solution of CHI_3 in pure C_6H_6 is unnecessary to ensure its oxidation in the cold and dark,

although the velocity is diminished, and independent of the concn. of CHI_3 . There is also a slight delay in starting if the concn. be < 10%. Oxidation is hindered if to the pure C_6H_6 is added 10^{-8} of $PhOH$, NH_2Ph , quinol, pyrrole, or of the C_6H_6 extract of cork; 10^{-5} of vanillin or carbazole; or 10^{-4} of C_5H_5N , azobenzene, or coniferin, but thiophen has no effect. $PhMe$ behaves similarly to C_6H_6 , although the proportions of retarding agents required are different. C. A. S.

Mechanism of the Kolbe reaction. S. GLASTONE and A. HICKLING (Nature, 1934, 133, 177).—Relatively small amounts of Pb^{++} , Mn^{++} , Cu^{++} , Fe^{++} , or Co^{++} ions markedly affect the Kolbe reaction (I) in the electrolysis of acetate solutions. The addition of 0.001*M*- $Pb(OAc)_2$ to a solution containing *N*- $KOAc$ and *N*- $AcOH$ reduces the efficiency for C_2H_6 formation from 70% to approx. zero. The effects of the ions are $Pb^{++} > Mn^{++} > Cu^{++} > Co^{++} - Fe^{++}$. The parallelism with their catalytic influence on the decomp. of H_2O_2 suggests that H_2O_2 is the effective agent in the formation of C_2H_6 by (I). L. S. T.

Optical activity in relation to tautomeric change. III. Constitutional and catalytic influences on the rates of racemisation of prototropic compounds. C. L. WILSON (J.C.S., 1934, 98—99; cf. this vol., 260).—The connexion between racemisation and isomerisation in optically active compounds with coincident centres of asymmetry and prototropy is illustrated by examples from the lit. R. S.

Acetylation of cellulose. D. KRÜGER and W. ROMAN (Angew. Chem., 1934, 47, 58—61).—The widely different catalytic activities of HI , HCl , $HClO_4$, H_2SO_4 , and H_3PO_4 on the acetylation of cellulose by $AcOH$ and Ac_2O are explained on the basis of Brönsted's protolytic theory of catalysis. The greatly increased activity when $NaClO_4$ is added to H_3PO_4 is similarly explained. A. G.

Catalytic effect of ferricyanide in oxygen absorption of oleic acid. B. F. CHOW and S. E. KAMERLING (J. Biol. Chem., 1934, 104, 69—79; cf. A., 1932, 128).— O_2 is necessary for the reduction of $K_3Fe(CN)_6$ (I) by oleic acid in HPO_4^{--} buffer, 5—6 mols. of O_2 being required for the reduction of 2 mols. of (I). With varying $Fe^{+++} : Fe^{++}$ ratios and with $K_3Mo(CN)_6$, Cu -glycine, $Cu-C_5H_5N$ (II), and indophenol the O_2 absorption was proportional to the redox potential. The reaction with (I) as catalyst was inhibited by phenol, (III), $NPhMe_2$ (IV), $OH-C_2H_4NH_2$, and eugenol, and with (II) as catalyst by (III), (IV), and p - C_6H_4BrOH , the inhibition being > could be accounted for by reduction of the catalyst. H. D.

Micro-heterogeneous catalysis of hydrogen peroxide by cholesterol sols. I. REMESOV (Ber., 1934, 67, [B], 134—140).—Mol. disperse cholesterol (I) does not cause decomp. of H_2O_2 , by which it is unaffected under the experimental conditions. Sols of (I) have a catalytic action towards H_2O_2 which is not shared by cholesteryl esters or by lecithin. The change is observed only when the sol is sufficiently conc., and its rate depends on the degree of dispersion of (I). Optimum conditions are given by

about 10% H_2O_2 at p_{H} 6.4–8.04. The catalyst is indifferent towards CN' , but is poisoned by Hg and its salts. Reaction is unimol. and resembles the kinetics of catalases and Pt sols. H. W.

Decomposition of nitric oxide by platinum catalysts. J. ZAWADZKI and G. PERLINSKI (Compt. rend., 1934, 198, 260–262).—The decomp. of NO over Pt between 854° and 1055° is unimol. (cf. A., 1929, 520). The reaction is represented according to the state of the Pt surface by $dx/dt = K_1(a-x)/(1+bx)$ or $-K_2(a-x)/x$, where x is % of NO decomposed, a its initial concn., t time of contact, K_1 , K_2 , and b are const. The results agree with or lie between those calc. according to one or other of these equations. O_2 added previously has only 0.48–0.56 of the effect of the same amount formed by decomp. The apparent heat of activation is 22,000–25,000 g.-cal. C. A. S.

Catalytic activity of zinc oxide.—See B., 1934, 93.

Catalytic polymerisation of ethylene.—See B., 1934, 135.

Catalytic hydrogenation of nitro-compounds.—See B., 1934, 85.

Catalysts for methane conversion.—See B., 1934, 82.

Adsorption of nitrogen by iron synthetic ammonia catalysts. P. H. EMMETT and S. BRUNAUER (J. Amer. Chem. Soc., 1934, 56, 35–41).—Rates of adsorption of N_2 by Fe, Fe- Al_2O_3 , and Fe- Al_2O_3 - K_2O catalysts have been determined at 273–450°. The energy of activation is about 16,000 g.-cal. and the heat of adsorption about 35,000 g.-cal. Adsorption isotherms at –189° are linear with respect to pressure at 100–760 mm. The rate of adsorption is of the right magnitude to be the slow step in the catalytic synthesis of NH_3 . E. S. H.

Heterogeneous combustion of carbonic oxide on quartz: water as a negative catalyst. B. W. BRADFORD (J.C.S., 1934, 73–75).—Whilst H_2O is a positive catalyst on Au surfaces, the reverse is the case on quartz. With dry $2\text{CO} + \text{O}_2$ mixtures up to 600° the activation energy is 20,000 g.-cal. and with $2\text{CO} + \text{O}_2 + 15$ mm. H_2O , 40,000 g.-cal. The absence of a homogeneous reaction in both cases is attributed to long drying of the quartz vessel at 600°. R. S.

Energetics of catalysis. II. Poisoning coefficients and energies of activation of hydrogenation processes. E. B. MAXTED and V. STONE (J.C.S., 1934, 26–29; cf. A., 1933, 680).—The poisoning coeff. is a const. for the hydrogenation of crotonic, oleic, and benzoic acids on a Pt catalyst using Hg^{++} ions as poison, whilst the activation energies increase in the order named. R. S.

Vapour-phase esterification. F. E. DOLIAN and H. T. BRISCOE (Proc. Indiana Acad. Sci., 1933, 42, 101–107).—For $\text{EtOH} + \text{AcOH}$, $\text{Al}_2(\text{SO}_4)_3$ and K alum have little effect on the yield: $\text{Cr}_2(\text{SO}_4)_3$ increases the yield slightly and K Cr alum markedly. MgSO_4 promotes esterification above the dehydration temp. With CaCl_2 esterification activity is a min. at 275°.

The activity of other salts increases in the order: Na_2SO_4 , NaOAc , NaPO_3 , CdSO_4 , ZnSO_4 , MnSO_4 , ZnCl_2 , NiSO_4 . CH. ABS.

Increase in the life-period of β -chloro- β -phenylethylamine by carbon. H. FREUNDLICH and G. SALOMON (Helv. Chim. Acta, 1934, 17, 88–98).—Conversion of $\text{CHPhCl}\cdot\text{CH}_2\cdot\text{NH}_2$ (I) into styreneimine hydrochloride in presence of blood charcoal (II) and carboraffin (III; acid-free) (A., 1933, 1112) has been studied kinetically at temp. between 0° and 38°. With (II) for similar initial concns. of (I) max. retardation (1/60–80 times as fast as in homogeneous solution) at 0°, 25°, 30° and 37° occurs with a proportion of (II) 1, 3, and 10, respectively, and the temp. coeff. of the heterogeneous reaction (IV) is = or slightly > that of the homogeneous reaction (V). With (III) (which gives identical absorption of both cation and anion) the retardation is much smaller and the temp. coeff. of (IV) is much < that of (V). As suggested (*loc. cit.*) with (II) the reaction occurs in the interior of the liquid phase, the acid present in (II) fixing a large proportion of (I) in the form of a salt, but with (III) reaction occurs on the C surface. In agreement with this view the decrease (approx. 5 kg.-cal.) in the heat of activation for the reaction of (I) in presence of (III) compared with that in presence of (II) [which is approx. the same as for (V)] is approx. the same as the decrease for the reaction of $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{NH}_2$ (A., 1930, 551) in homogeneous solution compared with that in presence of (II) (surface reaction). J. W. B.

Electrolytic concentration of heavy hydrogen. H. ERLÉNMEYER and H. GARTNER (Helv. Chim. Acta, 1934, 17, 30–31).—Preliminary. Electrolysis of 0.1N- H_2SO_4 at Pb electrodes is at least as effective as that of aq. KOH at Ni electrodes in concentrating $\text{H}^2\text{H}^2\text{O}$ in the residues. F. L. U.

Swelling of graphite at the anode and the mechanical disruption of carbon anodes. H. THIELE (Z. Elektrochem., 1934, 40, 26–33).—Absorption of O by graphite anodes ("swelling") occurs on electrolysis in presence of H_2SO_4 , HClO_3 , HNO_3 , and HF (or their salts); the amount of combined O increases with the acid concn., and is large (e.g., 0.5 c.c. O_2 per g. of C) only at high concn. (e.g., > approx. 30% for H_2SO_4). A min. c.d. is necessary. The C acquires a steel-blue colour. "Swollen" C contains both O and acid. On adding H_2O or aq. NaOH, O_2 is evolved, but not quantitatively. Amorphous C swells less readily than graphite. Swollen C has the properties of a peroxide. The mechanism of the process is discussed. Surface deterioration of graphite anodes can occur without swelling (e.g., in aq. H_3PO_4), but swelling is much more disruptive. H. J. E.

Electrolytic separation of metallic niobium. II. N. A. ISGARISCHEV and G. E. KAPLAN (Z. Elektrochem., 1934, 40, 33–36; cf. A., 1933, 681).—The optimum concn. of KOH for dissolving the Nb_2O_5 - Ta_2O_5 mixture is 20%. In the alkaline or $\text{H}_2\text{C}_2\text{O}_4$ electrolysis the rate of deposition falls to zero or becomes very small while deposition is still incomplete. This occurs in citric acid solution also,

but the solution recovers on keeping, and deposition may be completed. H. J. E.

Number of centres of crystallisation of copper during electrolysis of cupric sulphate. A. GLAZUNOV and J. JANOUŠEK (Chem. Listy, 1933, 27, 457—461).—The no. of centres (I) of crystallisation of Cu appearing during unit time on the cathode increases with increasing c.d. and with diminishing $[\text{CuSO}_4]$. The velocity of growth of (I) increases rapidly with increasing $[\text{CuSO}_4]$. R. T.

Velocity of crystallisation during electrolysis of aqueous cadmium acetate and nitrate. A. GLAZUNOV and C. B. KOUREL (Chem. Listy, 1933, 27, 489—493).—The velocity of crystallisation of Cd at the cathode increases with the c.d., and diminishes with increasing concn. of $\text{Cd}(\text{OAc})_2$ or $\text{Cd}(\text{NO}_3)_2$. R. T.

Electrolysis of silver acetate in acetic acid and pyridine. (Silver diacetate and the Kolbe reaction.) C. SCHALL and B. M. SCHALL (Z. Elektrochem., 1934, 40, 5—8; cf. A., 1922, i, 87).—In electrolysing AcOH saturated with AgOAc , a brown colour observed near the anode was attributed to $\text{Ag}(\text{OAc})_2$. O_2 produces the same colour. On electrolysing 95% $\text{C}_5\text{H}_5\text{N}$ saturates with AgOAc , the dark red compound $\text{Ag}(\text{OAc})_2 \cdot 2 \cdot 7\text{C}_5\text{H}_5\text{N}$ crystallised, decomp. rapidly when isolated. With aq. NaOH it formed AgO . With I in AcOH it yielded $\text{Ag}(\text{OAc})_2\text{I}$. The mechanism of the Kolbe reaction is discussed. H. J. E.

Electrolytic preparation of isopropyl alcohol. G. A. KIRKHOFF and A. D. STEPANOV (Khim.-Farm. Prom., 1932, No. 1, 21).—A glass cell, 85 sq. cm. in cross-section, and a porous cup diaphragm are used. The anode is Pb in 15% H_2SO_4 , and the cathode Hg in a mixture of 150 c.c. of 15% H_2SO_4 and 37.5 c.c. of COMe_2 . 8 amp. at 6—7 volts is used for 9 hr. The cathode liquid is then neutralised with conc. aq. NaOH and the Pr^iOH distilled (yield 33% of theory). CH. ABS.

Electrolytic reduction of aromatic nitro-compounds. I. Preparation of ethyl *p*-aminobenzoate. G. KAWATA (J. Electrochem. Assoc., Japan, 1933, 1, 51—54).—The optimum temp. is 58—60°. When 7.5% $\text{HCl} + p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ (Sn cathode) and 5% H_2SO_4 (Pb anode) are used, the highest current efficiency (75%) is attained with the best yield (77%). Sb, Cu, and Ni cathodes lower the yield. CH. ABS.

Gaseous combustion in electric discharges. IX. Cathodic water-gas equilibrium. G. I. FINCH, B. W. BRADFORD, and R. J. GREENSHIELDS (Proc. Roy. Soc., 1934, A, 143, 482—486).—An investigation has been made of the cathodic equilibrium between steam and CO. The observed vals. of K_p vary continuously with the pressure throughout the range studied. The results indicate that equilibrium is approached from the CO side in two ways, pressure being favourable to the one but not to the other (cf. A., 1931, 44). L. L. B.

Free radicals and photochemistry of solutions. J. FRANCK and E. RABINOWITSCH (Trans. Faraday Soc., 1934, 30, 120—130).—See A., 1933, 1255.

Photo-oxidation of nitrite to nitrate. N. R. DHAR, S. P. TANDON, N. N. BISWAS, and A. K. BHATTACHARYA (Nature, 1934, 133, 213—214).—Dil. solutions of NaNO_2 or KNO_2 are oxidised to nitrate by exposure to sunlight and air. The photochemical oxidation is accelerated by the presence of TiO_2 , ZnO , and Fe_2O_3 . The equilibrium $2\text{KNO}_3 \rightleftharpoons 2\text{KNO}_2 + \text{O}_2$ is probably obtained and in dil. solutions with excess of O_2 , most of the nitrate (I) is oxidised to nitrate (II) in light. Ammonification, nitrification, and the conversion of (I) into (II) in soil are photochemical rather than bacterial processes. L. S. T.

Photochemistry of phosgene. L. S. KASSEL (J. Amer. Chem. Soc., 1934, 56, 243).—Recent work (A., 1933, 1255) is criticised. E. S. H.

Oxidation of mercury vapour under the action of ultra-violet light. J. M. FRANK (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 146—148).—At $p_{\text{O}_2} < 1$ cm., the formation of HgO initiated by excited Hg is proportional to the intensity of incident light of $\lambda 2537 \text{ \AA}$, and independent of shorter λ . With $p_{\text{O}_2} > 1$ cm., HgO is formed when O_2 mols. alone are excited by $\lambda 1860, 1935$, and 1990 \AA , which produce O_3 , and hence excited Hg is not necessary for HgO synthesis in the presence of O_3 . Consistently with the mechanism (1) $\text{Hg}^* + \text{O}_2 \rightarrow \text{Hg} + \text{O}_2^*$, (2) $\text{O}_2^* + \text{O}_2 \rightarrow \text{O}_3 + \text{O}$, (3) $\text{O}_3 + \text{Hg} \rightarrow \text{HgO} + \text{O}_2$, O_3 is always produced during these reactions (cf. A., 1929, 155, 777). J. G. A. G.

Photographic sensitivity, latent image, and development. S. E. SHEPPARD (Ber. VIII Int. Congr. Phot., Dresden, 1931, 13—28; Sci. Publ. Kodak Res. Labs., 1931—1932, 15, 203—213).—Current theories of latent image formation, sensitisation, and desensitisation are discussed. The theory of the production of photo-Ag and the existence of sensitive Ag_2S nuclei is supported. J. L.

***p*-Aminophenol standard developer for sensitometry.** S. E. SHEPPARD and A. P. H. TRIVELLI (Ber. VIII Int. Congr. Phot., Dresden, 1931, 113—116; Sci. Publ. Kodak Res. Labs., 1931—1932, 15, 200—202).—The "M20" formula [$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{HCl}$ 7.275, Na_2SO_3 (anhyd.) 50, Na_2CO_3 (anhyd.) 50 g., H_2O to 1000 c.c.] is proposed as a standard for sensitometric comparisons. This developer gives the same speed vals. for different emulsions as with pyro-soda, elon, or elon-quinol developers. Nitrobenziminazole ($M/3750$) could be used as an efficient anti-fogging agent to be added when the developer was used for photographic photometry, normalisation of reciprocity failure, etc. J. L.

Spontaneous growth of the latent image between exposure and development. III, IV. E. R. BULLOCK (Sci. Ind. Phot., 1932, [II], 3, 201—206, 241—244; 1933, [II], 4, 6—10, 33—40; Sci. Publ. Kodak Res. Labs., 1931—1932, 15, 45—48; cf. B., 1932, 129).—The growth val. (defined as the max. % density increase of the developable image, corresponding with two different exposure ages) is apparently independent of temp., wave-length of the exposing light, or the effect of a slight general pre-exposure. The max. observed with increasing development time is very marked with process film. The influence of

humidity, intensity of light, and composition of the developer is described. It is suggested that the latent image is formed by stages, one of which is slow in propagation. J. L.

Grainless photographic silver. F. WEIGERT (Naturwiss., 1934, 22, 71—72).—The Ag formed on an exposed and developed photographic plate, after drying, shows dichroism. A portion of the Ag must be grainless. A. J. M.

Solarisation of photographic plates. A. SMAKULA (Z. Physik, 1933, 87, 231—237).—Solarisation of AgBr photographic plates varies rapidly with wave-length, showing a max. near 400 m μ , the region of max. sensitivity for light of normal intensity. It is due to the re-forming of AgBr mols. by excited Br atoms. A. B. D. C.

Law for [photographic] density curves with mixed coloured lights. A. VAN KREVELD (Z. wiss. Phot., 1934, 32, 222—230).—The D curves for red (6500 Å.) and violet (4500 Å.) lights and mixtures of these two on a variety of emulsions have been measured. The energy relation of the coloured lights was: $E_r:E_v=25:1$. For a given const. D , the law $1/I_{r,v}-1/I_r+1/I_v$ (where I_r , I_v , and I_{r+v} are the intensities of red, violet, and mixed light, respectively, required to produce the const. D with const. exposure) is theoretically derived and shown, in practice, to be correct within experimental error. The corollary law $E'_{r+v}/E_r+E_{r+v}/E_v=1$ (E'_{r+v} and E_{r+v} are the red and violet portions of the total energy of the mixed light) is also shown to be experimentally correct. Hence the curve for mixed light can be derived from the curves of the separate lights, and other special relations are deduced. J. L.

Photographic properties of silver sulphide. III.—See B., 1934, 123.

Action of ultra-violet light on glycine. V. HENRI, C. WEIZMANN, and Y. HIRSCHBERG (Compt. rend., 1934, 198, 168—170).—0.1N-Aq. glycine irradiated by Hg light for 15 hr. showed the following changes: conductivity $1.54 \rightarrow 71.20 \times 10^{-3}$, $4.80 \rightarrow 7.45$; % possible NH_3 formed $0 \rightarrow 13.1$. Comparison with non-irradiated aq. glycine and NH_3 showed that the NH_3 formed accounted almost entirely for the changes in conductivity and p_H . The main decomp. is $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{NH}_3$, but the presence of glycollic acid and absence of AcOH were proved. C. A. S.

Ultra-violet radiation in the photochemical oxidation of toluene. A. CASTIGLIONI (Gazzetta, 1933, 63, 818—820).—Experiments with a Hg-vapour lamp screened by ordinary glass and by glass transparent to ultra-violet radiation show that the short wave-lengths accelerate the photochemical oxidation of PhMe to BzOH. H. F. G.

Photochemical reaction between *m*-dinitrobenzene, ethyl alcohol, and ammonia. G. SOLLAZZO (Boll. Chim. farm., 1933, 72, 913—915).—Vessels containing the reactants were exposed to sunlight at an altitude of 2812 m. above sea level. After 13 min. the reaction had commenced, and it was completed within 52 min.; the colour was then stable, and

did not change after 2 months in the dark. Under similar conditions of exposure a mixture of *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$, amyl alcohol, and NH_3 became yellow on the surface within 2 min., and later violet, and subsequently a yellow ppt., becoming red, was formed. The reaction was completed in 60 min., the mixture being then brown; after about 3 hr. the whole of the coloration had vanished. The influence of altitude on photochemical reactions is discussed. H. F. G.

Photochemistry of fluorescein dyes. H. F. BLUM and C. R. SPEALMAN (J. Physical Chem., 1933, 37, 1123—1133).—The peroxide formed when fluorescein dyes are irradiated in H_2O in presence of O_2 is probably H_2O_2 , and the bleaching of the dye is probably due to oxidation by this H_2O_2 after the activation of the dye mol. by light. M. S. B.

Effects of α -particles on aqueous solutions. I. Decomposition of water. II. Oxidation of ferrous sulphate. C. E. NURNBERGER (J. Physical Chem., 1934, 38, 47—69).—A direct and an indirect method of irradiating liquids with α -rays from radon are described and the decomp. of H_2O by α -rays is suggested as a method for the determination of the transmission of α -ray tubes. The gas yields deviate to some extent from the general law of Cameron and Ramsay, owing to recombination of ions in the H_2O . When aq. FeSO_4 is irradiated by either method the gas obtained is nearly 100% H_2 . The ratio M_{FeSO_4}/N , where M is the no. of FeSO_4 mols. transformed and N the no. of ion pairs formed in H_2O by the absorption of the radiant energy employed, increases in solutions of high concn. (up to 0.5000M) without a corresponding increase of M_{H_2}/N , and becomes considerably > 2 , so that reactions other than the simple oxidation of FeSO_4 with the liberation of H_2 must take place. M. S. B.

Ion yield in decomposition of ammonia by α -rays. H. ESSEN and D. FITZGERALD (J. Amer. Chem. Soc., 1934, 56, 65—67).—The ion yield is 1.09 at 22° and 1 atm. E. S. H.

Heavy hydrogen. C. GROENEVELD (Chem. Weekblad, 1934, 31, 54—60, 118—124).—A review.

Chemical separation of diplogen from hydrogen. A. FARKAS and L. FARKAS (Nature, 1934, 133, 139).—The H_2 liberated by the dissolution of Zn in 0.1N- H_2SO_4 containing 25% of H_2 contains only 8% of H_3 , i.e., the rates of production are in the ratio of 4:1 approx. For Al, Na, and Ca the approx. ratios are 2, 1.2, and 1.5, respectively. Reactions of this type may serve as an alternative method for the production of H^2 and its compounds. L. S. T.

Interchange between deuterium gas and hydrogen in compounds. A. J. GOULD and W. BLEAKNEY (J. Amer. Chem. Soc., 1934, 56, 247—248).—The composition of $\text{H}^3\text{-H}^1$ mixtures in contact with H_2O remains const. in absence of preferential solubility, diffusion, and metallic surfaces (cf. this vol., 37). Greased stopcocks may be used without risk of reaction with H_2 . E. S. H.

Formation of alkali-metal hydrides by atomic hydrogen. (MISS) E. FERRELL, T. G. PEARSON, and P. L. ROBINSON (J.C.S., 1934, 7—8; cf. A., 1933,

1257).—At. H from a discharge tube converts mirrors of Li, K, and Na into the white hydrides. R. S.

Dark reaction between sodium formate and iodine. S. S. DOOSAY and W. V. BHAGWAT (Z. anorg. Chem., 1934, **216**, 241—252; cf. A., 1931, 802).—The "dark" reaction between aq. I and HCO_2Na is bimol. both in presence and in absence of KI, but in the latter case the velocity is several hundred times greater. The influence of K halides has been studied. The reaction is retarded by H^+ . The temp. coeff. has been determined. F. L. U.

Action of solutions of alkaline bases on mercuric iodide. (MLLE.) M. L. DELWAULLE (Bull. Soc. chim., 1933, [iv], **53**, 1295—1307).—Dil. solutions of KOH with HgI_2 give yellow HgO and alkaline aq. $\text{HgI}_2 \cdot 2\text{KI}$ with the transitory formation of a wine-coloured oxyiodide $\text{HgI}_2 \cdot \text{HgO}$. More conc. solutions, 2—6*M*, give practically pure red HgO , but as the concn. is gradually increased a white compound, $3\text{HgI}_2 \cdot \text{HgO} \cdot 3\text{KOH}$, is formed in increasing proportion until it alone remains. Very conc. aq. KOH (above 7*M*) gives, according to the amount of HgI_2 present, two oxyiodides, $\text{HgI}_2 \cdot 3\text{HgO}$, and $\text{HgI}_2 \cdot 2\text{HgO}$, containing some KOH. With aq. NaOH on HgI_2 there is a similar formation of $\text{HgI}_2 \cdot \text{HgO}$ at concns. < 6*M*. At concns. < 3*M* yellow HgO is formed and above this concn. red HgO and also a red oxyiodide, if some unchanged HgI_2 is present. Very conc. solutions give a pale yellow oxyiodide, $\text{HgI}_2 \cdot 2\text{HgO}$, containing chemically combined NaOH. The action of LiOH on HgI_2 is not very marked. A small proportion of yellow HgO is formed and HgI_2 dissolves in the aq. LiI produced in the proportion of HgI_2 to 2LiI. M. S. B.

Compounds of hexamethylenetetramine. L. DEBUCQUET and L. VELLUZ (Bull. Soc. chim., 1933, [iv], **53**, 1288—1291).— $(\text{CH}_2)_6\text{N}_4$ (=hex) with K_2CrO_4 and MgSO_4 in H_2O during 24 hr. affords $2\text{MgCrO}_4 \cdot 3\text{hex} \cdot 15\text{H}_2\text{O}$, whereas with $\text{K}_2\text{Cr}_2\text{O}_7$ and MgSO_4 (or CaCl_2), it gives $\text{MgCr}_2\text{O}_7 \cdot 2\text{hex} \cdot 5\text{H}_2\text{O}$ and $\text{CaCr}_2\text{O}_7 \cdot 2\text{hex} \cdot 7\text{H}_2\text{O}$, respectively. Interaction of MgSO_4 with $\text{CaKFe}(\text{CN})_6 \cdot 2\text{hex} \cdot 6\text{H}_2\text{O}$ and $\text{CaK}_2\text{Fe}(\text{CN})_6 \cdot \text{hex} \cdot 6\text{H}_2\text{O}$ in H_2O -hex leads to $\text{Mg}_2\text{Ca}[\text{Fe}(\text{CN})_6]_2 \cdot 4\text{hex} \cdot 24\text{H}_2\text{O}$ and $3\text{MgCaFe}(\text{CN})_6 \cdot 4\text{hex} \cdot 40\text{H}_2\text{O}$, respectively. J. L. D.

Reactions between dry inorganic salts. E. B. THOMAS and L. J. WOOD (J. Amer. Chem. Soc., 1934, **56**, 92—97).—Examination by the X-ray method has established double decomp. of the fused mixtures KCl-NaBr , KCl-NaI , and KCl-NaNO_3 in absence of a solvent. Equimol. mixtures of KF and NaCl give KCl and NaF when melted, whilst equimol. mixtures of AgCl and KBr yield AgBr and KCl. Double decomp. has been observed in KCl-NaBr mixtures at temp. < the m.p. All the reactions go to completion and the final products are insol. in each other in the solid state. E. S. H.

Solubility of copper hydroxide in ammonia. G. ETTISCH, E. HELLRIEGEL, and D. KRUGER (Ber., 1934, **67**, [B], 22—24).—The graph showing the relationship between mol. NH_3 : mol. dissolved Cu and concn. of NH_3 passes through a min. between 4*N*- and 6*N*- NH_3 . H. W.

Constitution of Stromholm's double salts: $2\text{MCl} \cdot \text{M}_2\text{Cr}_2\text{O}_7 \cdot 4\text{HgCl}_2 \cdot 2\text{H}_2\text{O}$. G. SPAOU and C. G. MACAROVICI (Z. anorg. Chem., 1934, **216**, 263—272).—The constitution

$\text{MLHg}[\text{Cl}_5\text{HgH}_2\text{O} \cdot \text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{OHgCl}_5] \cdot \text{HgM}_2$ (Z) is assigned to Stromholm's salts. The following compounds are described: $\text{Z} \cdot 10\text{NH}_3$, $\text{Z} \cdot 8\text{NH}_3\text{Ph}$ ($\text{M} = \text{K}, \text{NH}_4$); $\text{Z} \cdot 6\text{o-C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$, $\text{Z} \cdot 8\text{C}_9\text{H}_7\text{N}$, $\text{Z} \cdot 8\text{C}_5\text{H}_5\text{N}$ ($\text{M} = \text{K}$). F. L. U.

Graphitisation process. V. S. VESSELOVSKI and V. N. PERTZOV (Z. anorg. Chem., 1934, **216**, 228—240).—The course of graphitisation of different varieties of C has been studied. The process is regarded as a thermal recrystallisation of graphite crystallites present in the original material. The latter is classified with respect to its "disperse structure," which determines the character of the resulting graphite. F. L. U.

Oxidation of graphite. V. SIHVONEN (Suomen Kem., 1934, **7**, 75—76b).—A summary of the various reactions described in lit.

Formation of refractory metal carbides by a carbon filament glowing in the vapour of a halogen compound of the metal. W. G. BURGERS and J. C. M. BASART (Z. anorg. Chem., 1934, **216**, 209—222).—C filaments glowed at 1600—2500° in vapours of TiCl_4 and ZrCl_4 are converted into TiC and ZrC, respectively. TaCl_5 vapour with H_2 yields TaC, Ta_2C , or Ta, according to the temp. The products usually contain excess of metal in solid solution, and can be purified by glowing at a high temp. in a vac. The following lattice constns. have been determined: TiC, ZrC, and TaC (face-centred cubic) a 4.320, 4.687, and 4.445 Å., respectively; Ta_2C (hexagonal close-packed) a 3.091, c 4.93 Å. F. L. U.

Action of carbon disulphide on alumina gel. L. A. MUNRO and J. W. MCCUBBIN (Canad. J. Res., 1933, **9**, 424—431; cf. A., 1926, ii, 191).—The yellow coloration produced when CS_2 is adsorbed by Al_2O_3 gel is due to a mixture of Na_2S , NaHS, and NaS_x . CS_2 reacts primarily with H_2O contained in the gel and the products react further with NaOH which is present in small amount, to give the yellow colour. R. S.

Zirconium sulphides. M. PICON (Bull. Soc. chim., 1933, [iv], **58**, 1269—1277; cf. A., 1933, 918).—Cold conc. H_2SO_4 attacks all three sulphides slowly in the order $\text{ZrS}_2 < \text{Zr}_2\text{S}_5 < \text{ZrS}_3$. H_2S is evolved and a sulphate formed. Aq. $\text{H}_2\text{C}_2\text{O}_4$ reacts slowly and incompletely, whether hot or cold, producing H_2S . Neutral H_2O_2 reacts rapidly with ZrS_2 giving H_2S , H_2SO_4 and a basic sulphate. The other sulphides react only slowly. M. S. B.

Quaternary intermetallic compounds. A. S. RUSSELL (Nature, 1934, **133**, 217).—Zn and the simplest ternary compound of Sn and Cu which forms in Hg, viz., SnCu_3Hg_7 , yield quaternary compounds (I) of the following approx. formulæ: $\text{Sn}_4\text{Cu}_{12}\text{Zn}_4\text{Hg}_3$, $\text{Sn}_5\text{Cu}_{15}\text{Zn}_5\text{Hg}_9$, $\text{SnCu}_3\text{ZnHg}_9$, $\text{SnCu}_3\text{ZnHg}_9$, $\text{Sn}_4\text{Cu}_{12}\text{Zn}_4\text{Hg}_{45}$, $\text{Sn}_4\text{Cu}_{15}\text{Zn}_5\text{Hg}_{21}$, and $\text{Sn}_4\text{Cu}_{12}\text{Zn}_4\text{Hg}_{33}$. Sn and ZnCu yield $\text{Zn}_8\text{Cu}_8\text{SnHg}_-$, $\text{Zn}_6\text{Cu}_8\text{SnHg}_9$, $\text{Zn}_{40}\text{Cu}_{40}\text{Sn}_5\text{Hg}_{14}$, and $\text{Zn}_{40}\text{Cu}_{40}\text{Sn}_{12}\text{Hg}_{21}$. Quaternary compounds including Cd could not be prepared. The

derivation of (I), and rules connecting the nos. of valency electrons and atoms, are discussed.

L. S. T.

Reactions of anhydrous thorium tetrabromide with organic liquids. R. C. YOUNG (J. Amer. Chem. Soc., 1934, 56, 29—31).— ThBr_4 reacts with the corresponding org. liquids at temp. up to the b.p., forming $\text{ThBr}_4 \cdot 4\text{EtOH}$, $\text{ThBr}_4 \cdot 2\text{EtOAc}$, $\text{ThBr}_4 \cdot 4\text{MeCN}$, and $\text{ThBr}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$. In other cases mol. compounds are formed at room temp., but hydrated ThOBr_2 org. complexes are formed at the b.p. Such compounds are $\text{ThBr}_4 \cdot 4\text{PhCHO}$, $2\text{ThBr}_4 \cdot 7\text{COPhMe}$, $\text{ThBr}_4 \cdot 4\text{NH}_2\text{Ph}$, $\text{ThOBr}_2 \cdot 2\text{PhCHO} \cdot \text{H}_2\text{O}$, $\text{ThOBr}_2 \cdot 0.5\text{COPhMe} \cdot \text{H}_2\text{O}$, and $\text{ThOBr}_2 \cdot 0.5\text{COPhEt} \cdot \text{H}_2\text{O}$. At room temp. $\text{ThBr}_4 \cdot 3\text{EtOBz}$ is formed, but yields $\text{Th}(\text{OBz})_3$ at the b.p.

E. S. H.

Chemical reactions involving active nitrogen. R. H. EWART and W. H. RODEBUSH (J. Amer. Chem. Soc., 1934, 56, 97—98).—Active N and HBr or HI react to form NH_4Br or NH_4I , accompanied by luminous phenomena. The mechanism is discussed.

E. S. H.

Reactions in liquid ammonia. I. Germanium sulphides. W. C. JOHNSON and A. C. WHEATLEY (Z. anorg. Chem., 1934, 216, 273—287; cf. A., 1932, 1205).—Cryst. and amorphous GeS and GeS_2 have been prepared and their properties are described. Solubilities of GeS , GeS_2 , Na_2S , and $\text{Na}_2\text{S} + \text{NH}_4\text{Br}$ in NH_3 at -33° have been determined. GeS and GeS_2 do not undergo ammonolysis. The solutions are acted on by Na, forming Na_2S and Ge, and ultimately NaGe_x .

F. L. U.

Reaction of nitrous oxide with hydrogen atoms. J. K. DIXON (J. Amer. Chem. Soc., 1934, 56, 101—102).— H_2O is formed by reaction of N_2O and H atoms at 25° under low pressures. No O_2 or H_2 was detected.

E. S. H.

Phosphoric acid and phosphates. V. Hydrolysis of dicalcium and tricalcium phosphates. A. SANFOURCHE and J. HENRY. VI. Superphosphates. A. SANFOURCHE. VII. Decomposition of monocalcium phosphate by water in presence of calcium sulphate. VIII. Action of water on iron and aluminium phosphates. IX. Determination of free phosphoric acid in superphosphate. X. Determination of water-soluble phosphoric acid in superphosphate. A. SANFOURCHE and B. FOCET (Bull. Soc. chim., 1933, [iv], 53, 1210—1217, 1217—1221, 1221—1226, 1226—1232, 1232—1239, 1239—1242).—V. The hydrolysis of CaHPO_4 takes place only in presence of $\text{Ca}_3(\text{PO}_4)_2$, one of the products of hydrolysis. Both substances are then hydrolysed together, giving ultimately $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$. $\text{Ca}_3(\text{PO}_4)_2$ cannot be isolated by a wet method.

VI. A discussion of the possible constitution of superphosphate (I), its physical condition, and the difficulties encountered in attempts to determine its constitution.

VII. The decomp. of $\text{CaH}_4(\text{PO}_4)_2$ by H_2O is abnormal in that the fraction dissociated increases with concn. Addition of CaSO_4 increases the total amount of decomp., but alters its course so that in presence

of 50% CaSO_4 it becomes normal. This behaviour is attributed to the formation of an insol. double salt.

VIII. FePO_4 is hydrolysed in solution forming basic phosphate, the extent depending on the free acid present. The action is generally rather slow and continues during the washing of the phosphate ppt. The effect on the analysis of (I) is to give too high a free acidity and to diminish the amount of P_2O_5 sol. in H_2O . AlPO_4 in solution in H_3PO_4 is not hydrolysed by dilution. When treated directly by H_2O it is attacked similarly to FePO_4 , but the products are sol. and do not affect the (I) analysis.

IX. The most satisfactory liquid for the extraction of free P_2O_5 from (I) is HCO_2Et .

X. Total acidity in (I) is determined volumetrically by NaOH and phosphate by AgNO_3 . The various causes of error and the possibility of correcting some of them are discussed.

M. S. B.

[Explosive] phosphonium perchlorate. F. FIGHTER and H. ARNI (Helv. Chim. Acta, 1934, 17, 222—224).—Direct analysis of phosphonium perchlorate, prepared from PH_3 and 70% HClO_4 at -20° , shows it to have the composition $2\text{PH}_3 \cdot 3\text{HClO}_4$. The compound is dangerously explosive.

F. L. U.

Hydroxo-compounds. H. BRINTZINGER and J. WALLACH (Angew. Chem., 1934, 47, 61—63).—The rate of diffusion through Cellophane indicates the presence of the following anions in complex hydroxides containing KOH: $\text{Sb}(\text{OH})_6^-$, $\text{Sb}(\text{OH})_4^-$, $\text{Ge}(\text{OH})_6^{2-}$, $\text{Al}_2(\text{OH})_9^{3-}$, $\text{Ga}_2(\text{OH})_8^{2-}$, $\text{Zn}_2(\text{OH})_8^{2-}$, $\text{Be}_{10}(\text{OH})_{40}^{10-}$ (?). Plumbites and stannates gave irregular results.

A. G.

Preparation of ductile tantalum by thermal dissociation of tantalum pentachloride. W. G. BURGERS and J. C. M. BASART (Z. anorg. Chem., 1934, 216, 223—227).—The Ta deposited on a Ta filament glowed in TaCl_5 vapour is highly ductile if foreign gases are rigorously excluded. Lattice consts. for Ta and Nb prepared in this way are, respectively, 3.296 ± 0.0005 and $3.294 \pm 0.001 \text{ \AA}$.

F. L. U.

Action of chlorine on chromite in the presence of reducing substances. V. S. JATLOV and A. V. POPOVA (J. Appl. Chem. Russ., 1933, 6, 1049—1053).—The entire metal oxide content of chromite is converted into Fe, Al, and Cr chlorides by passing Cl_2 during 30 min. at 800° ; this process cannot be applied to the separation of these metals. The velocity of formation of chlorides from the metals is $>$ from their oxides, for which reason conversion is obtained at lower temp. in presence of C. Admixture of CO to the Cl_2 retards reaction, owing to dilution of Cl_2 .

R. T.

Class of tartaric acid compounds. J. B. MATHEU (Compt. rend., 1934, 198, 251—253).—The tartrates of the apparently simple formula RT_2 or $2.5\text{H}_2\text{O}$ ($\text{R} = \text{Cr}^{\text{II}}$, Mn^{II} , Fe^{II} , Ni , Co , or Zn ; $\text{T} = \text{C}_4\text{H}_4\text{O}_6^{2-}$) are really complex, $[\text{RT}(\text{OH})_2]_2$ and non-electrolytic. If to a solution of one of them excess of aq. Na_2T is added a true double salt, $\text{R}^{\text{III}}\text{T} \cdot \text{Na}_2\text{T}$ is formed. The reaction $0.4 - 1.7\text{NaOH} + \text{RSO}_4 + \text{Na}_2\text{T}$ (all in aq. solution) gives ppts. of varying composition: $\text{R} = \text{Zn}$, ZnO ; $\text{R} = \text{Mn}^{\text{II}}$, Fe^{II} , or Co , R_2T , and with $\text{R} = \text{Fe}^{\text{II}}$ also $\text{Fe}^{\text{III}}_3\text{T}_2$ (cf. A., 1931, 823); $\text{R} = \text{Ni}$, indefinite and gelatinous. The same compounds are

obtained by digesting $2R(OH)_2$ with tartaric acid. Mixed solutions containing $2NaOH + RSO_4 + Na_2T$ remain clear for some time, but finally give a ppt. of $[R(OH)_2T]Na_2$. The Co and Cu^{II} compounds show circular dichroism, the Ni compound slightly so in the red, the Mn^{II} and Fe^{II} not at all, whilst the Zn compound exhibits normal rotatory dispersion. C. A. S.

Fluorine. I. F. ISHIKAWA and T. MUROOKA (Sci. Rep. Tohoku, 1933, 22, 1155—1162; cf. A., 1933, 1251).—The preservation of F in glass bulbs has been studied. The % of F in a gas mixture needed to cause ignition of some inorg. and org. substances varies from 7.5 (C_6H_6) to 30 (wood C). F. L. U.

Bromine. J. D'ANS and P. HÖFER (Angew. Chem., 1934, 47, 71—74).—The existence of $Br_2 \cdot 8H_2O$ is confirmed; it is converted into Br and H_2O at 5.84° . The v.p. of Br in H_2O and in a solution containing NaCl, KCl, $MgCl_2$, and $MgSO_4$ have been determined at different temp. The iodometric determination of Br' by van der Meulen's method is accurate in presence of a large excess of Cl' . E. S. H.

Formation of carbonyls and related compounds. A. A. BLANCHARD, J. R. RAFTER, and W. B. ADAMS, jun. (J. Amer. Chem. Soc., 1934, 56, 16—17).— $Ni(CO)_4$ and $Co(CO)_4$ are prepared at room temp. by treating alkaline suspensions of the sulphide or cyanide with CO. Using a mixture of CO and NO, $Co(CO)_3NO$ (I) is formed. The v.p. and v.d. of (I) have been determined. E. S. H.

Iridium hydroxopentammines. B. E. DIXON (J.C.S., 1934, 34—36).—The action of Ag_2O on $[Ir(NH_3)_5Cl]Cl_2$ gives the light buff compound $[Ir(NH_3)_5Cl](OH)_2 \cdot H_2O$, which absorbs CO_2 slowly from the atm. and constitutes the most stable of the simple ammine hydroxides. The compounds $[Ir(NH_3)_5(OH)]Cl_2 \cdot H_2O$ and $[Ir(NH_3)_5(OH)](NO_3)_2$ are obtained as colourless crystals by treatment of the corresponding aquo-salts with aq. NH_3 . R. S.

General theory of the contamination of solid systems. D. BALAREV (Z. anal. Chem., 1934, 96, 81—91).—Cryst. ppts. are composed of minute elementary structural units (I) (cf. the Smekal blocks) which must deviate from the stoichiometric composition (II) in proportion to the fineness of the mosaic structure. (II) is attained by a compensating preponderance of one or other ion in the interstitial "cement" (III). Impurities may be included (a) as foreign ions in (III), (b) as adsorbed layers on (I), or (c) as solid solutions within the lattice of (I). J. S. A.

Electrometric methods in physical and analytical chemistry. S. GLASSTONE (Inst. Chem., 1934, 39 pp.).—A lecture.

Methods of "photo-electric titrations." F. MÜLLER (Z. Elektrochem., 1934, 40, 46—51).—A review of the use of photo-electric cells in automatic titrations and colorimetric measurements. H. J. E.

Fluorescence and its use as a method of testing and analysis. J. GRANT (Nature, 1934, 133, 124—126).—A summary. L. S. T.

Standardisation of volumetric solutions. J. GRANT (Chem. and Ind., 1934, 76—77).—A system in

which the normalities of all commonly used volumetric solutions may be determined in relation to a primary standard of 0.5N-HCl is described. D. R. D.

Qualitative analysis of insoluble substances (insoluble residue). A. FOSCHINI (Annali Chim. Appl., 1933, 23, 522—527).—Procedure is described for the qual. examination of inorg. substances not dissolved by boiling conc. HCl. Pptn. of S during the separation of AgCl from AgBr and AgI by means of $Na_2S_2O_3$ may be avoided, and the detection of Sn and Sb is simplified, by treatment with HCl instead of H_2SO_4 . T. H. P.

Spot methods for the determination of p_H . F. R. MCCRUMB (J. Lab. Clin. Med., 1933, 18, 1174—1178).—A discussion of advantages and sources of error. CH. ABS.

Cymyl-orange, a new indicator. A. S. WHEELER and J. H. WATERMAN (J. Elisha Mitchell Sci. Soc., 1933, 49, 36).—Aminocymene sulphate is dehydrated and sulphonated with fuming H_2SO_4 at 165° . The purified sulphonic acid is diazotised and coupled with NMe_2Ph , forming $SO_3H \cdot C_6H_2MePr \cdot N_2 \cdot C_6H_4 \cdot NMe_2$, which, yellow in acid and pink in alkaline solutions, is preferred to Me-orange as an indicator. CH. ABS.

ψ -Cumenesulphonic acid as a standard in alkalimetry. D. TISCHTSCHENKO (J. Appl. Chem. Russ., 1933, 6, 1182—1186).— ψ -Cumene-5-sulphonic acid ($2H_2O$) (I) has m.p. 114.5 — 115° , and may be dried at 40° without loss of H_2O of crystallisation. (I) is a strong acid, behaving as HCl in the titration of alkalis. It is recommended as a standard in alkalimetry. R. T.

New type of antimony electrode for p_H measurements. T. R. BALL, W. B. SCHMIDT, and K. S. BERGSTRESSER (Ind. Eng. Chem. [Anal.], 1934, 6, 60—61).—Sb coated with sulphide instead of oxide may be used as an Sb electrode. Five methods for the prep. of such electrodes are described. When prepared by suspending sticks of Sb in hot 0.30N- HNO_3 for 1 hr., followed by saturation with H_2S , they may be used to determine a p_H range of 2—10 with an agreement within 3 mv. The presence of starch, sugar, or NO_3^- has no effect on the results but OH-acids render them valueless. The electrode may be used to determine the sap. val. of oils, but offers no advantage over the ordinary Sb electrode. M. S. B.

Determination of p_H values with the antimony electrode. J. DI GLERIA (Proc. 2nd Internat. Cong. Soil. Sci., 1933, 2, 17—19).—Results were closely comparable with those obtained with the quinhydrone electrode. A. G. P.

Glass and other electrodes for measuring p_H values of very dilute buffers and of distilled water. J. O. BURTON, H. MATHESON, and S. E. ACREE (Ind. Eng. Chem. [Anal.], 1934, 6, 79, and Bur. Stand. J. Res., 1934, 12, 67—73).—The quinhydrone and H electrodes are not satisfactory for distilled H_2O and dil. buffers. The glass electrode and isohydric indicator methods give approx. the same p_H vals. for clear colourless solutions and are equally satisfactory. For samples which are coloured, turbid, or possess oxidising or reducing properties the glass electrode is preferable. M. S. B.

Volumetric determination of chlorates by induced reduction in presence of osmium tetroxide as catalyst. K. GLEU (Z. anal. Chem., 1933, 95, 385—392).—Oxidation of As_2O_3 by KClO_3 is catalysed by traces of OsO_4 (I), but proceeds only slowly. The powerful induced reducing action accompanying $\text{Ce}(\text{SO}_4)_2$ oxidations in presence of (I), which keeps the $[\text{Fe}(\text{o-phenanthroline})_3]$ indicator (II) in the Fe^{++} state, enables KClO_3 to oxidise As_2O_3 quantitatively, provided ≈ 2 c.c. excess of $0.1N\text{-As}_2\text{O}_3$ are present. Excess As_2O_3 is added to the acid ClO_3^- solution, O_2 expelled by addition of NaHCO_3 , 3 drops each of $0.01M$ - (I) and (II) are added, and the solution is titrated directly with $\text{Ce}(\text{SO}_4)_2$. J. S. A.

Determination of small amounts of bromine in presence of larger amounts of chlorine and iodine. S. H. BERTRAM (Biochem. Z., 1933, 266, 417).—In the author's method (A., 1933, 686) the slight losses of I can be avoided by addition of a few drops of starch solution during distillation. P. W. C.

Potentiometric determination of halogens in mineral water and in saline water.—See B., 1934, 174.

Iodometric micro-determination of IO_3^- and $\text{Cr}_2\text{O}_7^{--}$ in low concentrations. Application of silver catalysis. S. K. HAGEN (Z. anal. Chem., 1933, 95, 414—418).—Suspended AgI catalyses the formation and reaction of the starch-I complex, permitting $\text{Cr}_2\text{O}_7^{--}$ and IO_3^- in very dil. solutions (down to about $2 \times 10^{-4}N$) to be accurately determined iodometrically. 10 c.c. of $0.001N\text{-AgNO}_3$ should be added to each titration. Since the liberation of I by O_2 is also catalysed, and is a photo-reaction, solutions must be freed from dissolved air by passing CO_2 , and titrated in red or orange light. J. S. A.

Application of complex-forming and buffer substances in iodometric determinations. J. D'ANS (Z. anal. Chem., 1934, 96, 1—6).—Examples of the above processes are discussed. PhOH may be determined iodometrically by pptn. as $\text{C}_6\text{H}_5\text{I}_3\text{-OH}$ by excess of I in presence of a NaOAc or NaH_2PO_4 buffer, or of $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$. Salicylic acid may be similarly determined in Na_2CO_3 solution. J. S. A.

Colorimetric determination of fluorine. O. M. SMITH and H. A. DUTCHER (Ind. Eng. Chem. [Anal.], 1934, 6, 61—62).—The determination of F in natural H_2O by the formation of a colour lake, using a Zr-quinalizarin mixture, is described. Al , Fe , SO_4^{--} , and PO_4^{--} may be disturbing factors. They are, however, effective only above certain limits and can be removed. The amount of F present in natural H_2O is usually < 2 p.p.m. M. S. B.

Rapid colorimetric detection and determination of small quantities of oxygen in gases. H. R. AMBLER (Analyst, 1934, 59, 14—15).—The method depends on the brown colour produced by adsorption of the O_2 in alkaline pyrogallol; the depth of colour is matched against standard I-KI solution. An apparatus for making the test is described and illustrated. A P

Volumetric determination of sulphate. V. R. DAMERELL and H. H. STRATER (Ind. Eng. Chem.

[Anal.], 1934, 6, 19—21).—Standard BaCl_2 is added to the SO_4^{--} solution using $\text{Hg}(\text{NO}_3)_2$ as an outside indicator. A yellow basic Hg sulphate is formed. Most of the BaCl_2 can be added rapidly because a preliminary end-point is reached several c.c. before the final end-point. Other salts present as impurities cause appreciable errors, but can be corr. for in standardising the BaCl_2 . NH_4 compounds must not be present, nor any ions which ppt. Hg^{++} or Ba^{++} or give a colour.

M. S. B.

Detection of hyposulphite, ferrous salts, hypochlorites, and dichromates with resorufin. H. EICHLER (Z. anal. Chem., 1934, 96, 98—99; see below).— $\text{Fe}(\text{OH})_2$ or $\text{Na}_2\text{S}_2\text{O}_4$, but not Na_2SO_3 , Na_2AsO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, or CH_2O , reduces resorufin (I) in NaOH solution to non-fluorescent products. OCl^- in the cold, and $\text{Cr}_2\text{O}_7^{--}$ in hot H_2SO_4 solution, oxidise (I).

J. S. A.

Colorimetric determination of nitrogen. R. VON DER HEIDE, jun. (Z. anal. Chem., 1934, 96, 7—16).—The sample, containing 2—7 mg. N, is treated with H_2SO_4 in presence of a known amount of Hg to avoid losses through volatilisation. The Hg is converted into Nessler's reagent *in situ*, and the colour produced, stabilised by addition of gum arabic, matched against standards. The Hg is added as 2 c.c. of standard aq. HgSO_4 to each analysis; after heating, the H_2SO_4 is neutralised against diamond-fuchsin, HCl being added to prevent pptn. of basic Hg salts. The solution is cooled to room temp. and the calc. vol. of standard KI, made alkaline with NaOH , then added. J. S. A.

Use of aeration in Kjeldahl distillations. W. B. MELDRUM, R. MELAMPY, and W. D. MYERS (Ind. Eng. Chem. [Anal.], 1934, 6, 63—64).—With fairly rapid aeration at the b.p. a Kjeldahl distillation may be completed in < 15 min. Bumping is also obviated.

M. S. B.

Nitron as a precipitant for nitrates. J. E. HECK, H. HUNT, and M. G. MELLON (Analyst, 1934, 59, 18—25).—No entrainment of precipitant or metallic cations occurs in the determination of NO_3^- with nitron acetate; the results are accurate and reproducible considering the solubility of the ppt.

A. R. P.

Identification of nitrates, nitrites, and nitrosylsulphuric acid by formation of resorufin, orcinol, and indophenols. H. EICHLER (Z. anal. Chem., 1934, 96, 17—21).—Resorufin (I) (violet-red with strong yellow red fluorescence in alkaline solution, disappearing on acidifying or reducing with $\text{Na}_2\text{S}_2\text{O}_4$) is formed by heating resorcinol (II) in conc. H_2SO_4 with material containing NO_3^- or NO_2^- , and subsequently neutralising with Na_2CO_3 . Orcinol similarly yields orcinol, PhOH and thymol bluish-green, non-fluorescent indophenols. Fe or S^{--} interferes; oxidising agents must be removed by heating with H_2SO_4 before adding (II). NO_3^- , in presence of NO_2^- , may be detected in the residue after evaporating with AcOH . Dissolved NO , or $\text{NO}\cdot\text{SO}_3\text{H}$, gives (I) in the cold. J. S. A.

Colorimetric determination of nitrate in water.—See B., 1934, 174.

Detection of nitrites with Magdala-red. H. EICHLER (Z. anal. Chem., 1934, 96, 99—100).—Magdala-red in dil. acid solution is converted by NO_2' , but not NO_3' , into blue non-fluorescent products. SO_3'' and $\text{S}_2\text{O}_3''$ also destroy the fluorescence.

J. S. A.

Determination of small quantities of arsenic. G. A. QUINCKE and M. SCHNETKA (Z. Unters. Lebensm., 1933, 66, 581—585).—The method combines the electrolytic process of Mai and Hurt (A., 1905, ii, 284) with the colorimetric procedure of Flückiger (cf. A., 1918, ii, 240). Deposition of As with PbO_2 is prevented by enclosing the anode in a porous pot. H_2S is removed with $\text{Pb}(\text{OAc})_2$ or CdCO_3 . Development of the coloration of the Hg halide paper gives incorrect results. Sb and Cu must be removed, since SbH_3 gives a yellow colour and Cu forms Cu_2As_3 which is pptd. in the anode chamber. If when $< 12\%$ aq. H_2SO_4 is used the reaction vessel is cooled, and the gases evolved from the cathode are dried, H_2S does not interfere.

E. C. S.

Separation of arsenic and antimony from tin. P. E. WINKLER (Bull. Soc. chim. Belg., 1933, 42, 503—518).—The separation of Sb from Sn (A., 1932, 591) has been modified for determining As, Sb, and Sn in mixtures. The solution of 0.03—0.3 g. of As, 0.04—0.4 g. of Sb, and 0.04—0.2 g. of Sn containing 10 c.c. of 20% tartaric acid, 10 c.c. in excess of 20% KOH, and 5 c.c. of H_2O_2 is gently boiled until all H_2O_2 is decomposed. Before passing H_2S at the b.p., the solution is neutralised with HCl, 10 g. of $\text{H}_2\text{C}_2\text{O}_4$, H_2O , and 10 c.c. of conc. HCl are added, making the vol. 110 c.c. The pptd. As and Sb sulphides are separated, and in determining Sn in the filtrate, the conversion of Na_2SnS_3 into Na_2SnO_3 by alkaline H_2O_2 is completed by adding KMnO_4 dropwise to the solution acidified with HCl, using Me-orange as indicator. The Sn found is systematically 2—3 mg. low, whilst the As and Sb are generally < 1 mg. in error.

J. G. A. G.

Silver iodide test for hydrocyanic acid. D. L. FOX (Science, 1934, 79, 37).—Air is drawn through the system or culture under test and passed into freshly-prepared alkaline suspension of AgI obtained by mixing 1 drop of 5% KI, 1 of 0.001M-AgNO₃, and 1 c.c. of 5% KOH. When HCN is present the KCN formed clears the solution by dissolving the AgI. H_2S , NH_3 , and HCNS (NaCNS) have no visible effect on the AgI. 1 part of HCN in 2×10^6 can be detected when 0.00025M-AgNO₃ is used under ordinary laboratory conditions, and with special precautions a greater sensitivity should be possible. Roe's method can be used for determination by continuing aeration in the same system after the detection of HCN.

L. S. T.

Platinised silica gel as a catalyst in gas analysis. II. Oxidation of the methane hydrocarbons. K. A. KOBE and E. B. BROOKBANK (Ind. Eng. Chem. [Anal.], 1934, 6, 35—37).—No oxidation over commercial platinised SiO_2 gel occurs with CH_4 at 350°, C_2H_6 at 230°, C_3H_8 at 130°, or C_4H_{10} at 120°. It takes place, however, at temp. 20—25° higher, but is not complete even at 400°. H_2 and CO can be oxidised simultaneously at 300° in presence of CH_4 , but not of higher hydrocarbons. CuO and Pt-SiO₂ gel are

compared, both as regards errors due to catalytic oxidation of hydrocarbons and errors introduced through adsorption of gases.

M. S. B.

Mercurimetric determination of cyanides and thiocyanates. A. IONESCU-MATIU and (MME.) A. POPESCO (J. Pharm. Chim., 1934, [viii], 19, 54—61).—The stoichiometric mixture of Hg and $\text{Hg}(\text{CN})_2$ [or $\text{Hg}(\text{CNS})_2$] obtained by the addition of $\text{Hg}_2(\text{NO}_3)_2$ is dissolved in hot H_2SO_4 - HNO_3 and the Hg determined volumetrically by pptn. with Na nitroprusside followed by titration to a clear end-point with 0.1N-NaCl.

W. S.

Determination of helium and argon in natural gases from their thermal conductivity. E. K. GERLING (J. Appl. Chem. Russ., 1933, 6, 1153—1158).—Apparatus for the rapid analysis (45—60 min.) of He and Ar in natural gases is described. The method, which is based on the difference in thermal conductivity of He and Ar, is as accurate as is that of fractional distillation.

R. T.

Micro-determination of potassium. L. JENDRASSIK and J. SZEL (Biochem. Z., 1933, 267, 124—127).—K is determined with an average error of $\pm 1\%$ by pptn. as $\text{KNa}[\text{Co}(\text{NO}_2)_6]$ (I) with NaNO_2 , $\text{Co}(\text{NO}_3)_2$, and AcOH (added separately), collection on asbestos, dissolution of (I) in H_2SO_4 , oxidation of the liberated HNO_2 with 0.02N- KMnO_4 , addition of 10% aq. KI and titration of the liberated I with 0.02N- $\text{Na}_2\text{S}_2\text{O}_3$. Org. matter in biological matter must first be destroyed.

W. McC.

Colorimetric determination of potassium. S. N. ROSANOV and V. A. KASARINOVA (Z. anal. Chem. 1934, 96, 26—29).— $\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6]$ is pptd. by Kramer and Tisdall's cobaltinitrite reagent (A., 1921, ii, 412) from 1 c.c. of solution containing 0.025—0.10 mg. K_2O . NH_4 salts must first be removed. The ppt. is dissolved in 5 c.c. of 0.1N-NaOH, and 1 c.c. of a solution of sulphanilic acid and PhOH in aq. NH_4Cl added. HCl is added, then the solution made alkaline with aq. NH_3 . The tropæolin formed is matched against that yielded by standard NaNO_2 solution. Large amounts of PO_4''' interfere.

J. S. A.

[Determination of] the alkali content of commercial lime.—See B., 1934, 93.

Determination of potassium as hydrogen tartrate. I. I. TSCHERNJAEVA and R. V. KRASNOVSKAJA (J. Chem. Ind. Russ., 1933, 10, No. 10, 57—59).—10—20 c.c. of 0.33N-Na H tartrate (I) are added to 1—2 c.c. of solution, containing > 0.2 g. of neutral K salt, the solution is filtered after 12 min., and excess of (I) is titrated with 0.1N-NaOH.

R. T.

Triple acetate of uranyl, magnesium, and sodium. E. KAHANE (Bull. Soc. chim., 1933, [iv], 53, 1312).—A correction (cf. A., 1933, 1024).

M. S. B.

Reaction for beryllium in minerals and rocks. H. L. J. ZERMATTEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 899—900).—A fusion bead of the mineral with NaKCO_3 is dissolved in 5N-HCl. Addition of morin and NaOH produces a yellowish-green fluorescence.

C. W. G.

Loss of magnesium in systematic qualitative analysis. L. J. CURTMAN and N. MERMELSTEIN (Rec. trav. chim., 1933, 53, 34—36).—In the conventional scheme of qual. analysis losses of Mg occur in groups III and IV. Some of the Mg may be recovered by repptn.

H. S. P.

Micro-determination of magnesium as the triple ferrocyanide of magnesium, calcium, and hexamethylene tetramine. L. DEBUCQUET and L. VELLUZ (Bull. Soc. chim., 1933, [iv], 53, 1291—1292).—The Mg solution is evaporated to dryness, and the residue treated with a 10% solution of $\text{CaK}_2\text{Fe}(\text{CN})_6 \cdot (\text{CH}_2)_6\text{N}_4 \cdot 6\text{H}_2\text{O}$ in $(\text{CH}_2)_6\text{N}_4$. Pptn. of the Mg compound $[\text{MgCaFe}(\text{CN})_6]_3 \cdot 4(\text{CH}_2)_6\text{N}_4 \cdot 40\text{H}_2\text{O}$ is complete in 1 hr. This is washed with $(\text{CH}_2)_6\text{N}_4$ and COMe_2 , dried, dissolved in H_2O , and determined colorimetrically as Prussian blue by adding aq. FeCl_3 in presence of gum arabic. Quantities of Mg of the order of 0.1 mg. can be determined with an accuracy of always < 5% and often < 3%.

M. S. B.

Micro-determination of magnesium by means of 8-hydroxyquinoline. G. GLOMAUD (J. Pharm. Chim., 1934, [viii], 19, 14—29).—A micro-analytical modification of Berg's volumetric method (A., 1927, 639) serves to determine 1 mg. of Mg to an accuracy of 1%. Procedures are described for its determination in presence of Ca or PO_4''' , and in biological media.

D. R. D.

Detection of cations with resorufin. H. EICHLER (Z. anal. Chem., 1934, 96, 22; cf. this vol., 268).—Resorufin in aq. NH_3 gives with the heavy metal cations violet ppts., readily visible in small quantity against the yellowish-red fluorescent solution.

J. S. A.

Determination of lead as di-lead hydrogen arsenate. C. L. DUNN and H. V. TARTAR (Ind. Eng. Chem. [Anal.], 1934, 6, 64).—Pptn. should take place in a solution of p_H 4.6. The method is not so satisfactory as the PbSO_4 and PbCrO_4 methods.

M. S. B.

Effect of acetic acid on traces of lead chromate. L. T. FAIRHALL and K. AKATSUKA (J. Amer. Chem. Soc., 1934, 56, 14—15).—AcOH induces a good cryst. habit in PbCrO_4 and does not impair its quant. pptn.

E. S. H.

Sensitive drop reaction for copper. A. S. KOMAROVSKY and N. S. POLUEKTOV (Z. anal. Chem., 1934, 96, 23—25).—The $(\text{CN})_2$ liberated by Cu salts + KCN gives with 8-hydroxyquinoline (I) a raspberry-red coloration (II). A solution containing Cu^{++} , added to a spot of (I) on filter paper and moistened with 25% aq. KCN, gives (II), sp. for Cu^{++} in the absence of oxidising agents. Hg^{++} , Cd^{++} , and Pb^{++} do not interfere. Fe and U, which give coloured oxinates, should first be pptd. by NH_3 . The limit is 0.4×10^{-6} g. Cu.

J. S. A.

Quinaldinic acid as an analytical reagent. Determination and separation of copper, zinc, cadmium, and uranium. Colorimetric determination of iron. P. RAY and M. K. BOSE (Z. anal. Chem., 1933, 95, 400—414).—Quinaldinic acid (I) gives insol. salts with Cu, Hg, Pb, Ag, Cd, Zn, Mn, Ni, Co, and Fe^{++} , basic salts with Fe^{++} , Cr, Al, and UO_2^{++} . The Hg, Pb, Ni, and Co salts are readily sol. in acid.

Cu is quantitatively pptd. by aq. (I) from hot acid solution as $(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2\text{Cu} \cdot \text{H}_2\text{O}$ (14.96% Cu); Zn from dil. AcOH solution as $(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2\text{Zn} \cdot \text{H}_2\text{O}$ (15.29% Zn, m.p. 170°); Cd as $(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2\text{Cd}$ (24.63% Cd, m.p. 150°) on neutralisation with aq. NH_3 . Solutions of Fe^{++} give first a silky red ppt., which is transformed rapidly into the bluish-violet $(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2\text{Fe} \cdot 5\text{H}_2\text{O}$; the change is attributed to *cis-trans* isomerism. With very dil. Fe solutions, a pale red colour is produced, much intensified by addition of KCN (limit concn. 1 : 14,500,000), which may be used for colorimetric determination of Fe. Cu and Cd may be separated by pptg. Cu in presence of H_2SO_4 , Cd being pptd. by neutralisation. In presence of Pb, PO_4''' , AsO_4''' , and AsO_3''' , Cu is quantitatively pptd. from AcOH solutions; with Mn, Co, Ni, from H_2SO_4 solution. Zn may be separated from Mn, Mg, Ca, Ba, and PO_4''' by pptn. in AcOH solution. U is pptd. as a basic UO_2 salt, which may be ignited to U_3O_8 .

J. S. A.

Determination of mercury content of the atmosphere. A. STOCK and F. CUCUEL (Ber., 1934, 67, [B], 122—127).—300—500 litres of air, not freed from CO_2 and moisture, are drawn at the rate of about 60 litres per hr. through a U-tube immersed in liquid air, the arms of which are sufficiently long to prevent ingress of volatilised air. Towards the end of the experiment, about 50 c.c. of Cl_2 are drawn into the tube which, after removal of the cooling bath, is allowed to reach room temp. slowly. The U-tube is rinsed with $\text{Cl-H}_2\text{O}$ and Hg is determined electrolytically. The process is applicable to air containing much CO_2 provided that the final evaporation occurs very slowly. If liquid N_2 is available, air is condensed thereby in a glass vessel until the required vol. of liquid is obtained, Cl_2 being allowed to be drawn into the vessel periodically. The liquefied air is allowed to volatilise very slowly and the analysis is completed as described above. Free air has a Hg content lying on the boundary line of analytical detection. The use of Au for determining minute amounts of Hg is not recommended. If liquid air is not available, Moldavski's method (A., 1931, 589), modified by introduction of the micrometric determination of Hg, may be used.

H. W.

Potentiometric determination of mercuric salts. G. SPACU and I. G. MURGULESCU (Z. anal. Chem., 1934, 96, 109—114).— Hg^{++} is converted by excess of KI into HgI_4'' , and pptd. as $[\text{Cu en}_2][\text{HgI}_4]$ by titration with $[\text{Cu en}_2](\text{NO}_3)_2$ solution, using a Hg-coated Pt wire as comparison electrode.

J. S. A.

Volumetric and gravimetric determination of mercury. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 96, 30—34).— $\text{Hg}_2(\text{IO}_3)_2$ is pptd. from a hot neutral or dil. HNO_3 solution of Hg^{II} salts by excess of KIO_3 . After cooling to room temp. the ppt. is washed with EtOH and Et_2O , and dried in vac. By the use of excess of standard KIO_3 solution, the excess of KIO_3 may be determined iodometrically in the filtrate, giving Hg by difference. The solubility of $\text{Hg}_2(\text{IO}_3)_2$ in H_2O is 33.1 mg. per litre.

J. S. A.

Separation and determination of mercury in presence of elements of the hydrogen sulphide

and ammonium sulphide groups. G. SPACU and G. STICIN (Bul. Soc. Ştiinţe Cluj, 1933, 7, 183—189; Chem. Zentr., 1933, ii, 2166).—Hg is pptd. in neutral or slightly ammoniacal solution, in presence of KI and excess of Na K tartrate, as $[\text{HgI}_4][\text{Cu en}_2]$.

A. A. E.

Reactions for distinguishing red and yellow mercuric oxides. I. C. RITSEMA (Pharm. Weekblad, 1934, 71, 58—63).—The reactivities of yellow (I) and red (II) HgO depend both on the method of prep. and subsequent history. The $\text{H}_2\text{C}_2\text{O}_4$ reaction of the Pharmacopœia is not satisfactory but the two forms can be differentiated by the following reagents, which react, under the conditions described, only with (I): $(\text{NH}_4)_2\text{SO}_4$, white ppt.; fresh $\text{K}_4\text{Fe}(\text{CN})_6$, Prussian blue; 10% NH_3 , ppt. of Millon's base; MgCl_2 and phenolphthalein, red colour (III); NH_4CNS , brownish-green basic NH_4Hg salt; CH_2O and Na_2CO_3 , reduction to Hg; NH_4 acetylsalicylate, grey ppt.; $(\text{NH}_4)_2\text{CO}_3$, Millon's base; $\text{K}_2\text{Cr}_2\text{O}_7$, blood-red solution and ppt. containing Cr and Hg; ZnCl_2 , dark green ppt.; MnCl_2 , ppt. of Mn oxides and Hg passes into solution, [(II) gives MnO_2 but no Hg in solution]; HgCl_2 , black oxychloride; 10% CaBr_2 , cryst. ppt. of $\text{Ca}(\text{OH})_2$ (IV) (not given with CaCl_2); NH_4 salicylate, cryst. NH_4Hg salicylate. (II) settles more rapidly than (I). Reactions (III) and (IV) are best for assessing quality.

S. C.

Colorimetric determination of aluminium with eriochrome cyanin. F. ALTEN, H. WEILAND, and E. KNIPPENBERG (Z. anal. Chem., 1934, 96, 91—98; cf. A., 1929, 531).—0.1% eriochrome cyanin is added to the dil. HCl solution, which is made just alkaline, neutralised with AcOH, and brought to p_H 6.0 by addition of a $\text{NaOAc-NH}_4\text{OAc-AcOH}$ buffer. The Al content is evaluated from the extinction coeff. for light of 531 mμ. PO_4^{3-} interferes, and must first be removed as Li_3PO_4 from strongly alkaline solution. KH_2PO_4 is first added to carry down small amounts. Interference due to pptn. of an Fe lake may be avoided by addition of glycerol.

J. S. A.

Electrometric determination of manganese in phosphorite. N. N. SOLOVEVA (Udobr. Uroz., 1931, 1092—1093).—Erich and Muller's method is as accurate as Walters' colorimetric method.

CH. ABS.

Determination of iron and basicity in solutions of ferric salts. A. L. ZAIDES and V. N. SVESHNIKOVA (Ovrad. Tekh. Kozh. Proiz., 1932, No. 4, 45—47).—When 3 NaOH are required for 1 Fe^{3+} (electrometrically with the glass electrode or by titration using bromothymol-blue as indicator) the "basicity" is 100%.

CH. ABS.

Determination of the basicity of ferric salts in presence of ferrous salts. A. A. SOROKINA (Ovrad. Tekh. Kozh. Proiz., 1932, No. 4, 47—48).— Fe^{3+} is converted into Fe^{2+} with H_2O_2 and the hot solution is titrated with 0.1N-NaOH using bromothymol-blue.

CH. ABS.

Volumetric determination of chromium. I. JUMANOV (J. Chem. Ind. Russ., 1933, 10, No. 9, 61).—The substance is fused with 4 parts of 3:1 $\text{Na}_2\text{O}_2\text{-Na}_2\text{CO}_3$, the melt is extracted with boiling H_2O , and H_2SO_4 is added. Standard aq. FeSO_4 (I) is added to

an aliquot part of the solution, and excess of (I) is titrated with 0.5N- KMnO_4 .

R. T.

Determination of molybdenum and copper in special steels.—See B., 1934, 149.

Reaction for tungsten in minerals. J. VERSLUYS and H. L. J. ZERMATTEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 868—870).—A phosphate bead containing W is dipped while still hot into 5N-HCl. On adding Zn powder the liquid turns violet, distinguishing from Ti, Mo, and Nb.

C. W. G.

Rapid determination of titanium in steels.—See B., 1934, 100.

Determination of small amounts of bismuth in copper.—See B., 1934, 150.

Separation of gold from tellurium. V. LENCHER, G. B. L. SMITH, and D. C. KNOWLES, jun. (Ind. Eng. Chem. [Anal.], 1934, 6, 43—45).—Au may be separated from Te by reduction with HNO_2 in a solution of 0.45N-HCl buffered with Rochelle salt to $p_H > 1$ or by reduction with FeSO_4 in 0.3—0.6N-HCl. Au and Te may be determined in presence of each other by pptg. together and separating Au by reduction with HNO_2 .

M. S. B.

Microanalytical determination of palladium with dimethylglyoxime, benzoylmethylglyoxime, and salicylaldoxime. H. HOLZER (Z. anal. Chem., 1933, 95, 392—400).—Hot saturated aq. dimethylglyoxime (I), benzoylmethylglyoxime (II), and salicylaldoxime (III) ppt. Pd quantitatively from dil. acid solution (HCl). The ppts. should be cooled to room temp. before filtering, washed with 30% (not conc.) EtOH, and, with (II) and (III), dried at 110°. With (I), in presence of Pt a few drops of H_2O_2 should be added. The ppt. should be reduced to Pd by covering with HCO_2NH_4 and igniting in H_2 . With (II), the ppt. contains 20.64% Pd. (III) yields $(\text{C}_7\text{H}_6\text{O}_2\text{N})_2\text{Pd}$, containing 28.17% Pd. Pt is not pptd. by these reagents, and may be determined in the filtrate by reduction with N_2H_4 .

J. S. A.

Thermostat for higher temperatures. B. G. ŠMEK and J. ZAMRZLA (Mitt. Kohlenforschungsinstit. Prag., 1933, 1, 485—489).—A thermostat is described in which as heating medium the vapour of a liquid boiling under const. (reduced) pressure is used.

H. A. P.

Eddy-current cryostats. E. JUSTI (Physikal. Z., 1934, 35, 3—6).—The temp. fall in the metal-block cryostat is discussed, and the results show the possibility of constructing such an instrument with eddy-current heating for low-temp. work (60—160° abs.). The quant. theory of the instrument agrees with experiment.

A. J. M.

Use of the Thyatron for temperature control. R. M. ZABEL and R. R. HANCOX (Rev. Sci. Instr., 1934, [ii], 5, 28—29).—A photo-electric cell illuminated by a galvanometer controls the current through a Thyatron in parallel with the furnace windings.

C. W. G.

Cryoscopy of small volumes of liquid. D. THOMAS (Z. ges. exp. Med., 1933, 87, 635—644; Chem. Zentr., 1933, ii, 2164).—The method is applicable to

the determination of f.p. of 0.1—0.15 c.c. and gives results accurate to 0.01—0.02°. A. A. E.

Electrical water heater with thermo-regulating thermometer for refractometry. F. LORENZOLA (*Annali Chim. Appl.*, 1933, 23, 528—529).—The temp. of the H_2O is readily adjustable between 20° and 70° by the arrangement described. T. H. P.

Unit of light. L. S. ORNSTEIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1933, 36, 764—769).—Methods are described for rapid calibration of substandards for total radiation and for radiation in a given direction. By definition of a given energy distribution as a "lumen" and fixation, by definition, of an eye-sensitivity curve, these methods can be applied to the measurement of the lumen value of any lamp. The unit is unsuitable for a lighting practice standard. J. W. S.

Selenium unidirectional layer photo-cells, with special reference to their use in the measurement of meteorological radiations. W. GRUND-MANN and L. KASSNER (*Physikal. Z.*, 1934, 35, 16—20).—The effect of age, duration and intensity of illumination, and temp. on the properties of the Se unidirectional layer cell were investigated. No ageing effect without illumination was found, although such an effect was manifest on long illumination, a limiting current being reached, which is dependent on the light intensity and the characteristics of the cell. Regeneration takes place on keeping in the dark for about 30 min. After this process, each exposure to light results in the recurrence of the ageing process, although the time taken is much shorter, usually < 30 min. By decreasing the light intensity, a partial regeneration can be effected. The photo-current for a given light intensity is independent of variations in temp. < $\pm 10^\circ$. It follows that such cells are unsuitable for meteorological work. A. J. M.

Determination of densities and refractive indices of solutions at higher temperatures. G. PESCE and P. HOLEMANN (*Z. Elektrochem.*, 1934, 40, 1—5).—Pyknetric d determination between 25° and 85° with an accuracy of ± 0.00002 is described. The pyknometer has one end closed and the other sealed with Hg. The Hg expelled at different temp. is weighed. Improvements in the temp. control of the Pulfrich refractometer are described (cf. A., 1931, 1122). H. J. E.

Precision and accuracy of a photo-electric method for comparison of the low light intensities involved in measurements of absorption and fluorescence spectra. F. P. ZSCHEILE, jun., T. R. HOGNESS, and T. E. YOUNG (*J. Physical Chem.*, 1934, 38, 1—11).—By the use of a monochromator, photo-electric cell, electrometer, and high-resistance leak, with a 900-watt Mazda lamp as the source of light, sp. absorption coeffs. and opacities may be determined with errors of < 1.5% and 1.0%, respectively. Photo-electric current sensitivities of 2×10^{-17} amp. per mm. permit the use of slits so narrow that spectral regions varying in width from 3 Å. at λ 4000 Å. to 13 Å. at λ 7000 Å. may be investigated with a small standard monochromator without amplification of the photo-electric current. Spectral measurements of

fluorescent light from strongly fluorescent solutions such as chlorophyll in Et_2O can be made. M. S. B.

Reflexion densitometer. J. W. McFARLANE (*J. Opt. Soc. Amer.*, 1934, 24, 19—24).—An instrument, primarily for investigations on photographic printing papers, is described. N. M. B.

Pfund parallel plate refractometer. M. A. COUNTRYMAN and W. KUNERTH (*J. Opt. Soc. Amer.*, 1934, 24, 25—28).—The construction of the instrument and its use in studying the time rate of change of n for drying oils, varnishes, and lacquers are described. N. M. B.

Cell for absorption measurements at various temperatures. C. SALCEANU (*Bul. Soc. Romane Fiz.*, 1933, 35, 129—131).—The substance is heated electrically in a cell with two quartz windows. H. J. E.

Determination of radiant energy by means of the thermophotometer. M. PLOTNIKOV (*Arh. Hemiju*, 1933, 7, 170—186).—Apparatus is described, consisting of an air chamber containing a non-reflecting screen, which converts incident radiant energy into thermal energy, measured by the expansion of the air in the chamber. R. T.

Electrical instrument for detecting invisible faults in non-magnetic conductors such as tungsten. D. W. DANA (*Rev. Sci. Instr.*, 1934, [ii], 5, 38—41).—The conductor is passed axially through a coil forming part of the tuned circuit of an oscillator. Flaws cause a change in the tuning. C. W. G.

Investigation of electron counters. C. BOSCH (*Ann. Physik*, 1933, [v], 19, 65—98).—In investigating the irregular behaviour of some electron counters, the general occurrence of "counts" in discharge tubes (irregular discharge collisions, separated from each other by periods of no current flow) was studied. The existence of these irregularities is due to impurities in the electrodes, and in the cathode particularly. After purification of the electrodes by heating, the discharge in He, H_2 , N_2 , and, to a certain extent, dry O_2 showed no irregularities. The chief impurity is H_2O . The size of the electrodes is important. A tube with pure Au electrodes of normal size showed no irregularities in the discharge in He, but with point or wire electrodes the effect was noticed. It is due to a positive space-charge. The method of working of normal electron counters can be based on these observations. On the impure cathode there are places where the discharge can easily occur. A. J. M.

Continuous, self-registering gas analysis. H. ULLRICH (*Naturwiss.*, 1934, 22, 11).—Apparatus is described. A. J. M.

Gas absorption apparatus. R. T. DILLON (*Ind. Eng. Chem.*, 1934, 26, 111).—Gas passes down an inner tube (A) sealed at its upper end to an outer tube (B), the lower end of which extends beyond that of A, and upwards through the annular space between A and B, carrying with it a stream of absorbing liquid (C) in which the apparatus is immersed, and out through holes in B just below the seal of A to B which is below the surface of C. D. K. M.

Vacuum distillation apparatus. G. W. ELLIS (*Chem. and Ind.*, 1934, 77—78).—A simple apparatus

in which the vapour is condensed on a cooled surface within a large test-tube in which the material is evaporated is described. The condensate is driven into the receiver through a capillary tube, and a simple device is figured for collecting several fractions separately.
D. R. D.

Inverted fractional distillation. R. A. J. BOSSCHART (Ind. Eng. Chem. [Anal.], 1934, 6, 29—33).—An apparatus for the rapid rectification of gases or liquids at normal pressure between 200° and -170° is described. The analysis can be stopped at any point. This is especially useful in the determination of the fractions of highest b.p. which is chiefly required in the petroleum industry.
M. S. B.

Electrical distillation apparatus and other electrical laboratory apparatus. A. H. W. ATEN (Pharm. Weekblad, 1934, 71, 139—143).—A description of electrical laboratory appliances obtainable on hire from the Municipal Electrical Works, Amsterdam.
S. C.

Vacuum-leak hunting with carbon dioxide. D. L. WEBSTER (Rev. Sci. Instr., 1934, [ii], 5, 42—43).—Advantages over the use of EtOH are discussed.
C. W. G.

Correct construction and handling of the Bunsen burette valve. P. FUCHS (Z. anal. Chem., 1934, 96, 101—103).
J. S. A.

Drying of solids. I, II. S. KAMEI and T. SEDOHARA (J. Soc. Chem. Ind. Japan, 1933, 36, 645—654B).—In the apparatus described the wt. of a solid is continuously recorded while it is being dried by a current of air of controlled temp., humidity, and velocity.
A. G.

Finger-print detection [on coloured objects]. H. L. BROSE (Analyst, 1934, 59, 25—27).—The article to be tested is dusted with phosphorescent ZnS or anthracene powder, the excess of which is blown off, irradiated with ultra-violet light through a sheet of Wood's glass to cut out visible light, and finally photographed through a thick plate of Super-protex Pb glass which eliminates ultra-violet light and allows only the visible light to enter the camera. An exposure of 40 min. is required with Ilford rapid process panchromatic plates.
A. R. P.

Production of collodion thimbles. Apparatus for ultra-filtration. P. KALLÓS and G. HOFFMANN (Biochem. Z., 1933, 266, 128—131).—The thimbles are formed by dipping test-tubes, coated with caramel, in collodion [6% solution in EtOH-Et₂O containing BuⁿOH (3%)]. They may be used for dialysis or for ultrafiltration in the simple apparatus described.
W. McC.

Cleaning platinum wire for flame tests. W. G. LEIGHTON (Ind. Eng. Chem. [Anal.], 1934, 6, 84).—The hot wire is dipped in KHSO₄ which affords a bead of pyrosulphate on heating in the flame.
M. S. B.

Materials for photo-elastic investigations. R. B. CARLETON (Rev. Sci. Instr., 1934, [ii], 5, 30—32).—The synthetic resins Phenolite, Bakelite, and L'Orca are the most suitable.
C. W. G.

Höppler viscosimeter.—See B., 1934, 79.

Apparatus for determining bulk density of powders.—See B., 1934, 127.

Measurement of humidity in closed spaces.—See B., 1934, 127.

Mendeléeff (1834—1907) and the periodic law. ANON. (Nature, 1934, 133, 161).
L. S. T.

Geochemistry.

Cosmic and solar activity. Observations on cosmic rays at Scoresby Sound during the Polar year. A. DAUVILLIER (Compt. rend., 1933, 197, 1741—1744).—Measurements of cosmic rays were made with (a) Wulf and Kolhorster's and (b) Claude's high-pressure (100 atm. A) apparatus. 20% variation was observed during winter storms. μ/p in air = (a) 2.58, (b) 1.66; in Zn (a) 2.1, (b) 2.0×10^{-3} per g. per sq. cm. $I(b) = 2.81$ ion pairs per c.c. of air. Cosmic activity was independent of magnetic-auroral or solar activity. The observations support the author's theory (cf. *ibid.*, 1931, 193, 348), and point to the cosmic rays, like the zodiacal light, being due to the internal equatorial corona.
C. A. S.

Utah Lake water. L. B. DECKER and C. E. MAW (Proc. Utah Acad. Sci., 1933, 10, 35—40).—Dissolved solids vary from 1060.97 to 5089.47 p.p.m. at different points. Na and Ca sulphates, chlorides, and H carbonates predominate.
CH. ABS.

Variations in a hot spring: Les Dames des Plombières. R. DELABY, R. CHARONNAT, and M. JANOT (Compt. rend., 1933, 197, 1739—1741).—The variations in the Rn content (11.4—14.0 μmc in the H₂O, 123.9—150.6 μmc in the gases), the O₂ in the gases

(6—7%), temp. of H₂O (51.6—52°), and amount of solid matter (277.5—294.9 mg. per litre) were determined at intervals during September 1931, 1932, and 1933. No definite connexion *inter se* or with atm. pressure or rainfall was detected; the source is probably deep-seated and from several depths.
C. A. S.

Examination of a water of Bonifica Diamantina, and application of the thermodynamic theory of real solutions. G. BRAGAGNOLO and B. M. FREGNANI (Annali Chim. Appl., 1933, 23, 546—556).—For this H₂O, from a spring in the neighbourhood of borings for petroleum, the activity coeffs. for the separate ions have been determined. The f.-p. depression calc. therefrom agrees well with the experimental val.
T. H. P.

Radioactivity and composition of waters, minerals, and rocks of Lurisia. L. FRANCESCONI and R. BRUNA (Annali Chim. Appl., 1933, 23, 534—546).—Results are given of the examination of ten wells, some of which show marked radioactivity.
T. H. P.

Are there granitic and basaltic shells in the earth? A. N. WINCHELL (Science, 1934, 79, 32—33).—A discussion.
L. S. T.

Weathering of andesite from Mt. Csodi, Hungary. A. VENDL and T. TAKATS (Tsch. Min. Petr. Mitt., 1933, 44, 437—462).—The fresh blue rock contains much glass in the groundmass, and in the weathered yellow rock this has been oxidised and hydrated with devitrification. Analyses are given of the two rocks and of the altered groundmass. Determinations were also made of their porosity and the action of reagents. L. J. S.

Occurrence of gold in King Cassilis ore. F. L. STILLWELL (Proc. Austral. Inst. Min. Met., 1933, No. 90, 227—236).—The Au occurs as minute particles or flakes attached to chalcopyrite or galena veins in arsenopyrite, or disseminated irregularly throughout the pyrite crystals. Characteristic photomicrographs are given to show the Au distribution in various types of ore. A. R. P.

Gold telluride minerals from the Suzaki mine. M. WATANABE (Proc. Imp. Acad. Tokyo, 1933, 9, 621—622).—Au and Te are present, but little Ag. C. W. G.

Auriferous zone of E. Urega (Kivu, Belgian Congo). R. VAN AUBEL (Compt. rend., 1933, 197, 1732—1734).—The Au occurs in quartz veins penetrating schists of the metamorphic series of the lower stage of the Muva-Ankole-Urundi-Kibada system; it is associated with pneumatolytic minerals, tourmaline, etc., mispickel, pyrite, galena, blende, and graphite, with traces of Bi. The occurrences are connected with granitic and diorite-diorite intrusions and radiate out from Mt. Kibukira. C. A. S.

Andradite rich in titanium. O. ZEDLITZ (Zentr. Min. Geol., 1933, A, 225—239; Chem. Zentr., 1933, ii, 1496).—Melanite from Oberrotweil contains 12.10% TiO_2 ; $a = 12.104 \pm 0.008 \text{ \AA}$, which is $>$ for a normal andradite. Livaarite, with an even higher TiO_2 content, has $a = 12.139 \pm 0.008 \text{ \AA}$, whilst melanite from Perlerkopf (Eifel), containing 8.3% TiO_2 , has $a = 12.060 \pm 0.008 \text{ \AA}$. A. A. E.

Sulphide minerals of the Tsumeb mine. H. MORITZ (Neues Jahrb. Min., 1933, A, 67, Bl.-Bd., 118—154; Chem. Zentr., 1933, ii, 1498).—"Green enargite" is Cu As fahl ore. Three new forms of Cu glance are described. Germanite contained Fe 7.80, Cu 42.12, Zn 3.93, Ge 10.19, Ga 1.85, Pb 0.96, As 1.37, S 31.27%; corresponding with $\text{Cu}_8(\text{ZnFeGa})_2(\text{AsGe})_2\text{S}_{11-12}$. A. A. E.

Tektites. E. DITTLER (Zentr. Min., 1933, A, 214—219; Chem. Zentr., 1933, ii, 1496—1497).—Billitonite from Dendang contained SiO_2 70.30, TiO_2 0.50, Al_2O_3 12.77, Fe_2O_3 0.53, FeO 5.43, MnO 0.13, MgO 3.74, CaO 2.37, BaO 0.01, Na_2O 1.73, K_2O 2.48, P_2O_5 0.06, S 0.08, H_2O —0.08, GeO_2 < 0.0005 , Ga_2O_3 0.001, Sc_2O_3 0.0005, Y_2O_3 0.001, C trace; Ni, Ca, Cl, and H_2O were absent; d^p 2.4395. A. A. E.

Radium content of rocks of the Gleinalpe, Styria. H. ROSSNER (Tsch. Min. Petr. Mitt., 1933, 44, 495—504).—Diorite, granite, etc., with SiO_2 60.01—75.36%, contained $1.63\text{--}2.45 \times 10^{-12}$ g. of Ra per g. of rock, the amount increasing with the acidity of the rock and also with the % of alkalis, especially exception to this rule was a tourmaline-pegmatite with SiO_2 72.10% and Ra 2.80×10^{-12} .

These amounts are $<$ those given by other observers on similar rocks from other localities. Results obtained by decomposing the rocks by carbonate fusion or with HF are in agreement. L. J. S.

Abundance of zirconium. G. VON HEVESY and K. WÜRSTLIN (Z. anorg. Chem., 1934, 216, 305—311).—The % of Zr, determined X-radiographically in 1175 rock samples, varies from an average of 0.03 in granites to 0.006 in peridotites. F. L. U.

Abundance of strontium. G. VON HEVESY and K. WÜRSTLIN (Z. anorg. Chem., 1934, 216, 312—314; cf. preceding abstract).—The Sr content of 1046 rock samples varied from an average of 0.011% in volcanic to 0.002% in sedimentary rocks. F. L. U.

Presence of platinum in mineral sulphides. O. E. ZVAGINTSEV, V. V. LEBEDINSKI, and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1933, 4, 165—169).—Existing data and samples of varied origin show that the presence of Pt in sulphides of hydrothermal origin is due to acid intrusions. High content of Pt is found in some of the minerals analysed. J. G. A. G.

X-Ray investigation of clays. I. X-Ray diagrams of minerals occurring in clays. II. Mineral constituents of clay from Malliss. G. NAGELSCHMIDT (Z. Krist., 1934, 87, 120—145).—Powder diagrams of quartz, nacrite, dickite, kaolinite, halloysite, montmorillonite, muscovite, and calcite are critically examined. The method of differentiation based thereon is exemplified by application to four fractions ($< 0.05 \mu$, $0.05\text{--}1$, $1\text{--}5.5$, and $5.5\text{--}30 \mu$) obtained by centrifuging clay from Malliss in Mecklenburg, showing the increase of quartz and decrease of kaolin or halloysite with increasing size of grain (cf. A., 1933, 1030; B., 1930, 832; 1931, 359). C. A. S.

Chemical composition of clays in a vertical profile through layers of different ages. A. SALMINEN (Suomen. Kem., 1933, 6, 71B).—The composition was independent of the depth and age of the layer. E. S. H.

Natural thermoluminescence of minerals and rocks. A. KÖHLER and H. LEITMEIER (Z. Krist., 1934, 87, 146—180).—The thermoluminescence (I) of numerous samples of each of over 100 minerals, and of many rocks was examined. It is comparatively rare, and markedly shown only by (in decreasing order of intensity) fluorite, danburite, calcite, apatite, zircon, topaz, orthoclase, scheelite, anhydrite, harmotome, pectolite, gypsum, strontianite, phenacite, aragonite, witherite, quartz, cryolite, and barytes. The cause is connected with the presence of impurities and probably with that of radioactive material. This view is supported by a comparison between the (I) and U, Ra, and Th content of 50 specimens of granite; high (I) is apparently associated with a mean content of radioactive material. (I) appears to be less intense in very young and in archaic rocks. C. A. S.

Titanaugite of hour-glass structure. J. HOLZNER (Z. Krist., 1934, 87, 1—42; cf. A., 1933, 1030).—In crystals of titanaugite showing hour-glass structure the difference of the growth-cone is in

structure rather than in composition, the structure being looser and the d consequently lower. Relations between replacement of elements by one another (usually in pairs to compensate valency differences) and variations in optical properties are traced.

C. A. S.

Aegirite-augite bearing riebeckite quartz schist from Kamuikotan and some other localities in Hokkaido, Japan. J. SUZUKI (Proc. Imp. Acad. Tokyo, 1933, 9, 617—620).—Analyses are given.

C. W. G.

Orbicular rock from Minedera-yama, Japan. Y. KAWANO (Proc. Imp. Acad. Tokyo, 1933, 9, 613—616).—Analyses are given.

C. W. G.

Orbicular rock from Minedera-yama, Japan. B. YOSHIKITA (Proc. Imp. Acad. Tokyo, 1933, 9, 609—612).—Mineralogical details are given.

C. W. G.

Genesis of lithium pegmatite, S.E. Manitoba. C. H. STOCKWELL (Trans. Roy. Soc. Canada, 1933, [iii], 27, IV, 27—36).—A pegmatite body on the Bear mineral claim consists on the footwall of albite-granite grading into albite-aphite, and on the hanging-wall of quartz and muscovite. The middle is occupied by a spodumene zone with a central zone of lepidolite. After the crystallisation of the albite-granite and the quartz and muscovite on the walls, the remaining magma crystallised in various stages in the middle.

L. J. S.

Genesis of pegmatites, S.E. Manitoba. C. H. STOCKWELL (Trans. Roy. Soc. Canada, 1933, [iii], 27, IV, 37—51).—The pegmatites are believed to be mainly of magmatic origin and later replacements by solutions to be of minor importance.

L. J. S.

Correlation studies of the central and south central Pennsylvanian bentonite occurrences. R. R. ROSENKRANS (Amer. J. Sci., 1934, [v], 27, 113—134).—Analyses and correlations are given.

C. W. G.

Spillite and the average metabasalt. H. W. FAIRBAIRN (Amer. J. Sci., 1934, [v], 27, 92—97).—Spillite is chemically transitional to low-soda metabasalt.

C. W. G.

Nepheline syenite from Solwezi, N. Rhodesia. F. D. ADAMS and F. F. OSBORNE (Amer. J. Sci., 1934, [v], 27, 135—145).—Mineralogical details and analyses are given.

C. W. G.

Weathering of feldspars in relation to soil formation. P. ZEMICHENSKY (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 1, 1—42).—Atm. action on feldspars in N.W. U.S.S.R. and the Murman coast gives rise to a product similar to muscovite (I) in optical properties, but its chemical composition differs from that of (I) in H_2O content, which is much higher.

A. M.

Soil reaction and forest types in the Duke forest [N. Carolina]. T. S. COILE (Ecology, 1933, 14, 323—333).—The litter, fermentation, and humus layers of a large no. of samples show characteristically different ranges of p_H vals. Decomp. and incorporation of the products into the mineral stratum was more rapid in litters of low than of high $[H^+]$. Different types of trees yield litter having fairly characteristic reaction. Differences in soil reaction

between different forest types were insufficient to constitute a factor limiting the distribution of species.

A. G. P.

Microflora of soils of varied structure. N. P. KORNEEVA (Agrophysikal. Lab. Kiev, 1933; Proc. Internat. Soc. Soil Sci., 1933, 8, 202).—Higher proportions of structural units > 3 mm. in soils are associated with larger total nos. of micro-organisms, an increased proportion of *Azotobacter*, and a smaller no. of *Clostridium*.

A. G. P.

Titanium in Moravian soils. II. B. MALAC (Vestník. Českoslov. Akad. Zeměd., 1932, 111—114; Bied. Zentr., 1933, A, 4, 34; cf. B., 1933, 560).—The satisfactory character of the Neumann-Murphy method for determining Ti in 20% HCl extracts of soils, without pre-removal of org. matter, is confirmed.

A. G. P.

Biology and biodynamics of saline, alkali, and solodised soils. F. N. GERMANOV (Pedology, 1933, 28, 203—208).—A general discussion.

A. M.

Alkali soils of Spain: classification, composition, and vegetation. E. H. DEL VILLAR (Mezög. Kutat., [Spec. No.], 1933, 6, 510—521).—Types of vegetation associated with gypsous and saline soils are recorded. Ligneous types predominate in the former and herbaceous in the latter soils.

A. G. P.

Systematic cartography of Sumatra. J. SZEMIAN (Soil Res., 1933, 3, 202—221).—A system of soil classification is described. Relationships between parent material, weathering, and soil formation are discussed.

A. G. P.

Local soil types. A. TILL (Soil Res., 1933, 3, 163—195).—A system of classification of localised soil types in Austria is given.

A. G. P.

Volcanic soils from the province of Tottori, Japan. M. HARADA (Soil Res., 1933, 3, 147—162).—Analyses of the three principal horizons of these soils are given and their formation is discussed.

A. G. P.

Claypan soils. I. C. BROWN, T. D. RICE, and H. G. BYERS (U.S. Dept. Agric. Tech. Bull., 1933, No. 399, 42 pp.).—In nearly all soils examined the ratios SiO_2 :sesquioxide and $SiO_2:Al_2O_3$ and the H_2O of combination of the soil complex show the colloids to be of similar composition in all horizons. The claypan layer has a higher proportion of bases than has the A horizon. Evidence is advanced indicating that the soils were formed by similar processes, the colloid being translocated as a whole from the surface layer downward to a stratum of higher p_H . The original surface probably contained $CaCO_3$ which was transported downward as $Ca(HCO_3)_2$ and redeposited as $CaCO_3$ in the stratum of max. H_2O penetration. Sol. salts immediately above this layer tended to flocculate the clay, forming ultimately a layer of low permeability. Differences in properties of actual claypan layers are attributable to differences in parent material. The composition of the colloids examined conforms to that of salts of pyrophyllic acid (B., 1932, 1002) of the type $MH_5(AlSi_2O_7)_2$.

A. G. P.

Salt domes. R. V. BROWNE (J. Inst. Petroleum Tech., 1934, 20, 73—93).—The geology of salt domes is discussed.

D. K. M.

Oxidation-reduction reactions between natural hydrocarbons and oil-filled waters. C. H. BEHRE, jun., and R. K. SUMMERBELL (*Science*, 1934, 79, 39—40).—Unpublished experiments by other workers show that sulphates can be reduced to sulphides by heating with paraffin-base crude petroleum under pressure at approx. 150°. Sulphate reduction is most pronounced in the presence of FeSO_4 and clay as catalysts.

L. S. T.

Petroleum deposits of Syria and the Lebanon. L. DUBERTRET (*Compt. rend.*, 1934, 198, 379—381).—Throughout the coastal zone there are porous lime-

stones and marls impregnated with bitumen. In the Yarmuk ravine a boring showed 50 m. of asphalt in the lower Meastrichian. A little dark petroleum occurs at Latakia in the Nahr-el-kalb, and a true source (the only one so far known) of a petroleum containing much paraffin at Tchenguene, 17 km. S.W. of Alexandretta. In the E., desert, zone the formation resembles that of Iraq. Bituminous limestone and sandstone occur in W. Jebel Bichri and near Jaffraria. There are indications of domes increasingly evident eastwards, the most promising being in the Karatchok Dag in the extreme N.E.

C. A. S.

Organic Chemistry.

Number of structural isomerides of the more important types of aliphatic compounds. H. R. HENZE and C. M. BLAIR (*J. Amer. Chem. Soc.*, 1934, 56, 157; cf. A., 1932, 495, 597; 1933, 254).—Theoretical. The nos. of isomerides of various types are calc.

H. B.

Thermal decomposition of organic compounds from the viewpoint of free radicals. V. Strength of linkings in organic molecules. F. O. RICE and W. R. JOHNSTON (*J. Amer. Chem. Soc.*, 1934, 56, 214—219).—The extent of decomp. of C_2H_6 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, $n\text{-C}_5\text{H}_{12}$, $n\text{-C}_6\text{H}_{14}$, EtOH , COMe_2 , MeCHO , Me_2CO_3 , Me_2O , Et_2O , $(\text{CH}_2)_2\text{O}$ (I), NHMe_3 , and NMe_3 into free radicals is determined by the method previously described (A., 1932, 1108; 1933, 1270) using Sb mirrors. The activation energies of the decomp. are thus found (cf. *loc. cit.*) and show that the C·O (ether) linking is stronger than C·C. The C·N linking is relatively weak. (I) is the least stable compound examined. There appears to be a definite diminution in stability with ascending members of a homologous series.

H. B.

Kolbe hydrocarbon synthesis in liquid ammonia. R. A. FULTON and F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1934, 56, 167—168).—Electrolysis of $\text{NH}_4\text{CR·NHK}$ (I) ($\text{R}=\text{Me}$, Et , Pr^n , Bu^n) (from R·CN and KNH_2) in conc. solution in liquid NH_3 using a high c.d. gives CH_4 and C_2H_6 (at anode) in each case; N_2 is also formed [probably by decomp. of (I) at the anode] and is practically the sole anodic gas using dil. solutions and low c.d.

H. B.

Determination of ethane by combustion over platinum in the presence of excess oxygen. M. SHEPHERD and J. R. BRANHAM (*Bur. Stand. J. Res.*, 1933, 11, 783—797).—The slow combustion of C_2H_6 over a hot Pt spiral in presence of excess of O_2 does not give theoretical results, the vol. contraction and O_2 consumed being always high and the CO_2 formed low. The best volumetric equation to represent the reaction is $\text{C}_2\text{H}_6 + 3.513\text{O}_2 = 1.994\text{CO}_2 + 2.520 \times \text{contraction}$. Results are explained by losses of C_2H_6 and CO_2 in the distributor, dissolution of CO_2 in the H_2O produced in the reaction and deviations of CO_2 and C_2H_6 from their theoretical mol. vols.

J. W. S.

Vapour-phase oxidation of hydrocarbons. I.—III.—See this vol., 259.

Characterisation of ethylenic linkings by antimony trichloride. R. DELABY, S. SABETAY, and M. JANOT (*Compt. rend.*, 1934, 198, 276—278).—The colours given by SbCl_3 (best in CHCl_3) with ninety-nine compounds of various types are recorded and certain non-reactive compounds named. HgNO_3 , AsCl_3 , and SbBr_3 , but not SbCl_5 , give colours with ethylenic compounds, but are less sensitive.

R. S. C.

Ozonolysis of purely aliphatic olefines. Behaviour of the five simplest *n*-alkyl radicals in the dehydration of *tert*-alcohols. J. M. CHURCH [with F. C. WHITMORE and R. V. MCGREW] (*J. Amer. Chem. Soc.*, 1934, 56, 176—184; cf. A., 1933, 255).—Dehydration of the following *tert*-carbinols by boiling with a little I occurs without rearrangement and more easily with rise in the b.p.; the olefines produced (and % yields) are quoted in parentheses: $\text{CET}_3\text{·OH}$ (γ -ethyl- Δ^2 -pentene; 100); $\text{CPr}^n_3\text{·OH}$ (δ -*n*-propyl- Δ^2 -heptene; 100); $\text{CBu}^n_3\text{·OH}$ (ϵ -*n*-butyl- Δ^2 -nonene; 100); tri-*n*-amylcarbinol (ζ -*n*-amyl- Δ^2 -undecene; 100); $\text{CMe}_2\text{Et·OH}$ (β -methyl- Δ^2 - and - Δ^3 -butene; 22, 78); $\text{CMe}_2\text{Bu}^n\text{·OH}$ (β -methyl- Δ^2 - and - Δ^3 -hexene; 55, 45); dimethyl-*n*-amylcarbinol (β -methyl- Δ^2 - and - Δ^3 -heptene; 40, 60); $\text{CMeEt}_2\text{·OH}$ (mainly γ -methyl- Δ^2 -pentene and trace of β -ethyl- Δ^2 -butene); $\text{CET}_2\text{Pr}^n\text{·OH}$ (γ -ethyl- Δ^2 - and - Δ^3 -hexene; 80, 20); $\text{CET}_2\text{Bu}^n\text{·OH}$ (γ -ethyl- Δ^2 - and - Δ^3 -heptene; 90, 10); diethyl-*n*-amylcarbinol (γ -ethyl- Δ^2 - and - Δ^3 -octene; 85, 15); $\text{CETPr}^n_2\text{·OH}$ (γ -*n*-propyl- Δ^2 -hexene and δ -ethyl- Δ^2 -heptene; 50, 50); di-*n*-propyl-*n*-amylcarbinol (δ -*n*-propyl- Δ^2 - and - Δ^3 -nonene; 60, 40); $\text{CETBu}^n_2\text{·OH}$ (γ -*n*-butyl- Δ^2 -heptene and ϵ -ethyl- Δ^2 -nonene; 40, 60); $\text{CPr}^n_2\text{Bu}^n_2\text{·OH}$ (δ -*n*-butyl- Δ^2 -octene and ϵ -*n*-propyl- Δ^2 -nonene; 25, 75); di-*n*-butyl-*n*-amylcarbinol (ϵ -*n*-butyl- Δ^2 - and - Δ^3 -decene; 60, 40); methyl-di-*n*-amylcarbinol (ζ -methyl- Δ^2 -undecene and β -*n*-amyl- Δ^2 -heptene; 90, 10); *n*-propyldi-*n*-amylcarbinol (ζ -*n*-propyl- Δ^2 -undecene and δ -*n*-amyl- Δ^2 -nonene; 67, 33); $\text{CMeEtBu}^n\text{·OH}$ (β -ethyl- Δ^2 -hexene and γ -methyl- Δ^2 - and - Δ^3 -heptene; 15, 55, 30); methylethyl-*n*-amylcarbinol (β -ethyl- Δ^2 -heptene and γ -methyl- Δ^2 - and - Δ^3 -octene; 20, 50, 30); methyl-*n*-propyl-*n*-amylcarbinol (β -*n*-propyl- Δ^2 -heptene and δ -methyl- Δ^2 - and - Δ^3 -nonene; 20, 50, 30); methyl-*n*-butyl-*n*-amylcarbinol (β -*n*-butyl- Δ^2 -heptene and ϵ -methyl- Δ^2 - and - Δ^3 -decene; 15, 45, 40). The same olefines are also obtained by heating

the corresponding $\text{CR}_3\cdot\text{OMgX}$. The order of decreasing ease with which the groups supply the H for dehydration is Et, Pr^a , Bu^a , n -amyl, Me. The structures and amounts of the olefines are determined by ozonolysis (apparatus described), usually in light petroleum, b.p. $0-30^\circ$, at -10° ; the ozonides (freed from solvent) are best decomposed by H_2O and Zn dust in presence of traces of Ag and quinol (cf. A., 1932, 1109). H. B.

Addition of hydrogen bromide to $\delta\delta$ -dimethyl- Δ^a -pentene. M. S. KHARASCH, C. HANNUM, and M. GLADSTONE (J. Amer. Chem. Soc., 1934, 56, 244).—Addition of HBr to $\delta\delta$ -dimethyl- Δ^a -pentene in presence of air or peroxides gives $\delta\delta$ -dimethyl- n -amyl bromide, b.p. $68.8^\circ/34$ mm. (cf. Whitmore and Homeyer, this vol., 55), which is considered to be the "abnormal" product. The "normal" adduct, formed in presence of good anti-oxidants in a vac., is β -bromo- $\delta\delta$ -dimethylpentane, b.p. $59.4^\circ/34$ mm.; 50% of this is formed when addition is carried out in a vac. H. B.

Catalytic hydrogenation and polymerisation of acetylene under pressure to yield benzene. A. D. PETROV and L. I. ANTUS (J. Appl. Chem. Russ., 1933, 6, 1145—1147).—In presence of Ni 1:5 mixtures of C_2H_2 and H_2 at $170^\circ/18$ atm. yield quantitatively C_2H_6 , whilst under similar conditions 1:1:4 mixtures of C_2H_2 , H_2 , and N_2 yield C_2H_4 5%, C_2H_6 7%, H_2 6%, and liquid hydrocarbons 80%, containing 40% of naphthenes, b.p. $<160^\circ$. R. T.

Reactions of anhydrous thorium tetrabromide with organic liquids.—See this vol., 266.

Dehydration of alcohol. G. A. FESTER, A. ARBATE, and J. MAROSO (Rev. fac. quim. ind. agric., Univ. nac. litoral, 1932, 2, 141—148).—100 c.c. of 84 wt.-% EtOH are shaken with 100 c.c. of gasoline and 5 g. of anhyd. K_2CO_3 . The top layer is mainly gasoline, the middle EtOH and gasoline, and the bottom conc. aq. K_2CO_3 . The EtOH recovered contains 90-7% EtOH. Removal of the K_2CO_3 layer and repetition gives (1) 94.0, (2) 95.5% EtOH.

CH. ABS.

Electrolytic preparation of isopropyl alcohol.—See this vol., 263.

Acetylenic alcohols.—See this vol., 239.

Unsymmetrical tetramethylene glycols. C. F. H. ALLEN, C. V. WILSON, and W. L. BALL (Canad. J. Res., 1933, 9, 432—435).—Reduction ($\text{Na}\cdot\text{ROH}$) of the appropriate arylsuccinic ester affords β -phenyl-, m.p. 70° (Na derivative, —EtOH) (cf. Manske, A., 1931, 619), β -(2:4-dimethoxyphenyl)-, m.p. 89° (affords no solid derivatives), and β -methyl- (I) -butane- $\alpha\delta$ -diol, of which only (I) gives a pure dibromide. With the Ac_2 derivatives of n -butane- $\alpha\gamma$ -diol HBr replaces only 1 Ac group giving a bromo-butyl acetate, b.p. $92-94^\circ/27$ mm. The halogen compounds do not give Grignard reagents, although with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ and Mg an 8% yield of acids is obtained after treatment with CO_2 . J. W. B.

Two constituents of Charon's dipropenyl glycol: isolation of one in a crystalline form. WIEMANN (Compt. rend., 1933, 197, 1654—1656).—When heated with PhNCO and Et_2O at 60° Charon's

dipropenyl glycol (I) affords a mixture of a phenylurethane (II), m.p. 190° , and another of lower m.p. not yet obtained pure. Hydrolysis of (II) with aq. $\text{Ba}(\text{OH})_2$ at 150° gives a cryst. dipropenyl glycol, m.p.

48° , to which the configuration $\text{R}\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}\text{R}$ ($\text{R}=\cdot\text{CH}\cdot\text{CHMe}$) is assigned; it causes further crystallisation of the same form when added to (I) at 0° .

J. W. B.

Syntheses of dulcitol and allodulcitol. R. LESPIEAU and J. WIEMANN (Compt. rend., 1934, 198, 183—184; cf. this vol., 169).—Slightly impure $\alpha\beta\zeta$ -tetrahydroxy- Δ^a -hexinene, m.p. $116-117^\circ$, gives, when hydrogenated, an oily olefinic compound, the Ac_4 derivative, b.p. $190-191^\circ/12$ mm., of which with AgClO_3 and a little OsO_4 gives an oily $\alpha\beta\zeta$ -tetra-acetoxyerithrytol, whence an Ac_6 derivative was obtained which yielded a little dulcitol hexa-acetate.

R. S. C.

Etherification. I. Preparation of some higher aliphatic ethers with sulphuric acid. G. F. HENNION, H. D. HINTON, and J. A. NIEUWLAND (Proc. Indiana Acad. Sci., 1933, 42, 109—111).—The dry alcohol (2 mols.) is treated slowly with conc. H_2SO_4 (15—20 g.) and the mixture is heated for 1 hr. to remove H_2O ; H_2SO_4 (15 g., and after 1 hr. a further similar quantity) is added. When the temp. of the mixture is midway between the b.p. of the alcohol and the ether the mixture is cooled and 150 c.c. of H_2O are added. The separated ether is washed with NaOH, dried, and distilled. CH. ABS.

Reactions of β -halogeno-ethers. I. Action of magnesium on alkyl β -bromoethyl ethers. R. C. TALLMAN (J. Amer. Chem. Soc., 1934, 56, 126—129).— $\text{OR}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, where R is Me, b.p. $111-111.4^\circ/746$ mm., Et, b.p. $127.3-127.7^\circ/743$ mm., Pr^a , b.p. $146.9-147.3^\circ/743$ mm., Pr^s , b.p. $139.9-140.2^\circ/743$ mm., Bu^a , b.p. $67-67.5^\circ/25$ mm., Bu^s , b.p. $56.5-57^\circ/21$ mm., sec.-Bu, b.p. $47-47.5^\circ/15$ mm., and n -amyl, b.p. $75-76^\circ/14$ mm., are prepared from $\text{OR}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ and PBr_3 in $\text{C}_5\text{H}_5\text{N}$. With Mg in Et_2O , these give C_2H_4 , $\text{OR}\cdot\text{MgBr}$, and $(\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OR})_2$ (except when $\text{R}=\text{Me}$; the amount increases with the size of R). $\alpha\delta$ -Diethoxy-, b.p. $59-60^\circ/18$ mm., -di- n -propoxy-, b.p. $94-95^\circ/20$ mm., -diisopropoxy-, b.p. $77-78^\circ/18$ mm., -di- n -, b.p. $117-118^\circ/16$ mm., -iso-, b.p. $107-108^\circ/19$ mm., and -sec-, b.p. $102-103^\circ/16$ mm., -butoxy-, and -di- n -amyloxy-, b.p. $134-135^\circ/12$ mm., -butanes are described. H. B.

Mobility of organic radicals in their bromosulphites. P. CARRÉ (Compt. rend., 1934, 198, 181—182).—The following are the temp. of decomp. of the bromosulphites $\text{OR}\cdot\text{SOBr}$ in $\text{C}_5\text{H}_5\text{N}$ to SO_2 and alkyl bromide: Et $13-14^\circ$, Pr^a $30-31^\circ$, Bu^a $39-40^\circ$, n -heptyl 54° , n -decyl 38° , Pr^s $13-14^\circ$, $\text{CH}_2\text{Cl}\cdot\text{CH}_2$ $39-40^\circ$, and Ph 80° . The compounds are less stable than the corresponding chlorosulphites, but the order of the radicals is the same. R. S. C.

Reaction of substances containing the thiol radical. A. GIROUD and H. BULLIARD (Proto-plasma, 1933, 19, 381—384).—The violet coloration produced by the reduction of Na nitroprusside by $\cdot\text{SH}$

compounds is changed to a stable red colour by the addition of Zn salts.

A. G. P.

Detection and determination of methyl mercaptan and carbon disulphide in air containing hydrogen sulphide. J. F. REITH (Rec. trav. chim., 1934, 53, 18—23).—The gas is bubbled through 0.5N. aq. NaOH, dried with CaCl_2 , and then passed through NaOH in EtOH. The aq. solution is then acidified with HCl, a slow stream of air is passed through, and the evolved gases are dried and passed over cryst. $\text{Pb}(\text{OAc})_2$; this absorbs H_2S , but not MeSH , which is detected by isatin- H_2SO_4 or determined colorimetrically by PdCl_2 . CS_2 is determined by pptn. of $\text{CuO}\cdot\text{CS}\cdot\text{SCu}$ from the alcoholic absorbent with $\text{Cu}(\text{OAc})_2$ and AcOH or, if very small in amount, detected by the yellow coloration given with a little $\text{Cu}(\text{OAc})_2$.

H. A. P.

Production of organo-metalloidal compounds by micro-organisms. II. Dimethyl selenide. F. CHALLENGER and H. E. NORTH (J.C.S., 1934, 68—71).—Strains *A* and *D* (cf. A., 1933, 266) growing on sterile bread-crumbs containing Na_2SeO_3 or Na_2SeO_4 (I) evolve a gas (II) which affords with Biginelli's solution Me_2 selenide mercurichloride, m.p. 153—154° (Et_2 selenide mercurichloride has m.p. 92.5°), with $\text{HgBr}_2\cdot\text{H}_2\text{O}$ the corresponding bromide, m.p. 99—100°, with HNO_3 , Me_2 hydroxyselenonium nitrate, with K_2PtCl_4 , Me_2 selenide platinichloride (A., 1912, i, 71), and with CH_3PhCl , benzyldimethylselenonium chloride (A., 1930, 1302). (II) is free from H_2Se or MeSeH . Strain *D* grown on bread-crumbs containing (I) forms much Se, which is not easily methylated (cf. Proc. C.S., 1902, 138; A., 1902, ii, 629). *A* and *C* grown on bread do not afford Me_2S with many S compounds, but Et_2S is formed when SOEt_2 (but not SO_2Et_2) is added.

J. L. D.

Electrolysis of silver acetate in acetic acid and pyridine.—See this vol., 263.

Modes of addition to conjugated unsaturated systems. VI. Addition of halogens and hydrogen halides to conjugated unsaturated carboxylic acids and esters. C. K. INGOLD, G. J. PRITCHARD, and (in part) H. G. SMITH (J.C.S., 1934, 79—86).—Interaction of β -vinylacrylic acid (I) (A., 1929, 1270) and Cl_2 in H_2O at 50° affords δ -chloro- γ -hydroxy- Δ^{α} -pentenoic acid, m.p. 73—74° (cf. A., 1931, 1148), ozonised to HCl , $\text{H}_2\text{C}_2\text{O}_4$, and AcCHO [2:4-dinitrophenylhydrazones, m.p. 299—300° (decomp.)]. (I) with aq. HOCl (2 mols.) affords a dichlorodihydroxyvaleric acid, m.p. 166° (lit., 143°). Similarly prepared, δ -bromo- γ -hydroxy- Δ^{α} -pentenoic acid has m.p. 92—93° [also obtained from (I) and HOBr]; O_3 affords products similar to the above. Similar conditions, δ -initiation and $\gamma\delta$ -orientation, should hold in all analogous butadiene- α -monocarboxylic acids. Bromination of sorbic acid (II) in CS_2 affords the $\gamma\delta$ -dibromide (cf. A., 1924, i, 8) [which with O_3 gives α -bromocrotonaldehyde (III) and $\text{CHO}\cdot\text{CO}_2\text{H}$] and a liquid (IV) which, contrary to Farmer and Healey (A., 1927, 646), contains the $\alpha\beta$ -dibromide. (IV) with boiling EtOH containing 5% H_2SO_4 during 3 hr. affords sorbic acid tetrabromide and Et sorbate dibromide which with O_3 affords MeCHO , (III), 2,2,4,4 and dibromosuccinic acid. Interaction of

(II) with ICl in AcOH at room temp. affords γ -chloro- δ -iodo- β -ethylacrylic acid, m.p. 88°, which when treated with weak bases affords (II) and γ -chlorosorbic acid (cf. A., 1909, i, 550) (*Et* ester, m.p. 31—32°), the structure of which is confirmed by ozonolysis. Interaction of (II) and H_2O containing Cl_2 at 85° affords δ -chloro- γ -hydroxy- Δ^{α} -hexenoic acid (V), m.p. 97°, also obtained by interaction of (II) in Et_2O with HOCl in H_2O (cf. A., 1932, 930). The structure of (V) is confirmed by (a) ozonolysis, which affords $\text{CHO}\cdot\text{COEt}$ (2:4-dinitrophenylsazone, m.p. 247°), and $\text{H}_2\text{C}_2\text{O}_4$; (b) oxidation with KMnO_4 at room temp. in neutral solutions affords $\text{H}_2\text{C}_2\text{O}_4$ and α -chloropropionic acid; (c) reduction (H_2 -Adams' catalyst) affords δ -chloro- γ -hexolactone. (II) affords with Br in H_2O at 85° mainly α -bromo- γ -hydroxy- Δ^{α} -hexenoic acid (VI), m.p. 110°, and an oil, which after esterification affords *Me* bromohydroxyhexenoate and a product, $\text{C}_7\text{H}_{11}\text{O}_4\text{Br}$, m.p. 154—155°. (II) with HOBr also affords (VI), the structure of which is confirmed by ozonolysis. *Me* sorbate and Br in H_2O afford mainly *Me* $\gamma\delta$ -dibromo- Δ^{α} -hexenoate, ozonised to (III) [2:4-dinitrophenylhydrazones, m.p. 220° (decomp.)]. (II) with Br in EtOH affords γ -bromosorbic acid, m.p. 135° (lit. 140°) (also obtained from $\gamma\delta$ -dibromo- Δ^{α} -hexenoic acid with dil. $\text{EtOH}\cdot\text{KOH}$), ozonised to MeCHO [2:4-dinitrophenylhydrazones, m.p. (less stable form) 146° (cf. A., 1933, 1005)]. The $\alpha\beta$ -addition of 2Br to *Me* cinnamylideneacetate (A., 1904, i, 1012), practically to the exclusion of $\gamma\delta$ -addition, is in support of the present work, as an unsaturated substituent in the δ -position tends to dissipate δ -polarisation, and so inhibit primary halogen attack at this point. Similarly, de-activation of a C_α -polarisation is increased by another $\alpha\text{-CO}_2\text{H}$, so that cinnamylidenemalonate shows mainly $\gamma\delta$ -addition of Br (cf. A., 1904, i, 1012). *Et* muconate (VII) affords a dibromide (cf. J.C.S., 1922, 121, 1306), ozonised to *Et* β -bromo- β -aldehydoacrylate (2:4-dinitrophenylhydrazones, m.p. 193—194°), $\text{H}_2\text{C}_2\text{O}_4$, and *Et* *i*-dibromosuccinate. (VII) with ICl in AcOH at room temp. during 12 hr. affords *Et* β -chloro- α -iodo- Δ^{γ} -dihydromuconate (?), m.p. 68°, converted by dil. Na_2CO_3 into *Et* muconate and by boiling dil. $\text{EtOH}\cdot\text{KOH}$ into muconic acid. (II) with dry HCl during several days at room temp. affords mainly δ -chloro- Δ^{β} -hexenoic acid, an oil, ozonised to AcCHO . The orientation of hydrohalide addition cannot always be predicted, because after α -attack by H_2 the CO_2H is separated from the anionotropic system, which leaves in doubt whether orientation of the halogen atom is determined before or after the prototropic rearrangement.

J. L. D.

Esters of tiglic, angelic, and α -ethylacrylic acids. M. NASTER and A. GAVRILOV (Bull. Soc. chim. Belg., 1933, 43, 519—530).— $\text{OH}\cdot\text{CMeEt}\cdot\text{CN}$ and SOCl_2 give a mixture which with dry HCl at $< 35^\circ$ gives much β - (I), b.p. 62—63°/10 mm., little α -chloro-*dl*-isovaleronitrile, b.p. 33—34°/10.5 mm., and much α -chloromethyl-*n*-butyronitrile (II), b.p. 70—71°/10 mm. With $\text{HCl}\cdot\text{MeOH}$ (I) gives *Me* β -chloro-*dl*-isovalerate (III), cryst., b.p. 54—55°/12 mm. (50% yield), and a little *Me* tiglate (IV), b.p. 37—38°/12 mm. (amide, m.p. 75—76°), a substance, m.p. 170°, *dl*- β -chloro-isovaleric acid, m.p. 63.4—63.8°, and its amide, m.p.

120—120.4°. With quinoline at 125° (I) gives (IV), but no *Me angelate*. *Angelamide* (V) is stable to $\text{NH}_3\text{-C}_6\text{H}_6$. (II) and MeOH-HCl give much *Me α -chloromethylbutyrate*, b.p. 57—58°/12 mm., and acidic products, but no unsaturated ester; with quinoline at 130° it gives *Me α -ethylacrylate* (VI), b.p. 122—123°/761 mm., and (IV). Dry distillation of *dl- α -hydroxyisovaleric acid*, m.p. 71—72°, gives lactide and tiglic acid (separated by distillation) and a mixture, b.p. 74—77°/10 mm., whence by fractionation of the Ca salts were obtained angelic (Ca salt, +2H₂O, more sol. in cold than in hot H₂O) and α -ethylacrylic acid, the K salts of which with MeI in EtOH give *Me angelate*, b.p. 127.6—127.8°/765 mm. [gives (V)] and (VI) [together with (IV)], respectively. (IV) was also obtained from the acid by $\text{MeOH-H}_2\text{SO}_4$. The identity of the amides with authentic specimens confirms the structures of the esters and intermediates. Physical data are recorded for the compounds. R. S. C.

Composition of fatty acid mixtures. II. Further development of Twitchell mixed-m.p. method for determination of individual saturated fatty acids. R. N. WENZEL (Ind. Eng. Chem., [Anal.], 1934, 6, 1—7).—An improved form of electrically heated m.p. apparatus is described. In the analysis of fatty acid mixtures by the Twitchell method palmitic (I) and stearic (II) acids as solvents give normal depression const. ($K_m=1.82, 1.61$), which hold also with glycerides as solute, but myristic acid (III) gives anomalous results with (II) as solute. The m.p. is taken as the point at which the last trace of solid disappears, and is unaffected by previous melting and re-solidification. Results are accurate within a few %. The prep. of pure (I), (II), (III), and oleic acid is described. H. A. P.

Determination of pyruvic acid. G. CARPENI-SEANU (Compt. rend., 1934, 198, 272—274).—Simon's method (A., 1924, i, 632) is modified so as to detect AcCO_2H in concns. of 1 in 50,000 and to determine it within $\pm 5\%$ in 0.002% solution. R. S. C.

α - and β -Cinenic acid. Constitution of β -cinenic acid. H. RUPE and H. HIRSCHMANN (Helv. Chim. Acta, 1934, 17, 98—105).—Ozonolysis of β -cinenic acid (I) in CCl_4 gives α -methylparaconic acid, identical with a synthetic specimen. (I) is therefore α -hydroxy- α -dimethyl- Δ^8 -*n*-heptenoic acid, the isomeric α -acid (II) being 2 : 6 : 6-trimethyltetrahydropyran-6-carboxylic acid. Oxidation of (I) with 4% KMnO_4 at room temp. gives COMe_2 , small yields of HCO_2H , AcOH , and (?) valeric acid, (II), and a mixture of (I) and cinogenic acid (α -dihydroxy- α -dimethyl-*n*-heptonic acid) (separated as its Co salt). J. W. B.

Tartaromanganic salts. G. LEJEUNE (Compt. rend., 1933, 197, 1650—1652).—Dissolution of either hydrated MnO_2 or the green complex manganitartrate of Job (A., 1911, i, 176) in a conc. solution of tartaric acid affords (after pptn. of Na H tartrate in the latter case) a red complex salt $\text{HO-Mn}[\text{C}(\text{OH})\text{-CO}_2\text{H}]_2\text{H}_2\text{O}$, slowly decomposed by H_2O to give MnO_2 , and liberating I from KI. The corresponding brown Na H salt +4H₂O is obtained by dissolving MnO_2 in Na H tartrate solution. J. W. B.

Vitamin-C. VIII. Constitution of vitamin-C. F. MICHEEL and K. KRAFT (Z. physiol. Chem., 1933, 222, 235—249; cf. A., 1933, 1213).—Mainly a review. Catalytic hydrogenation (PtO_2) at 35—40°/60 mm. of ascorbic acid affords a mixture from which was isolated *l*-idonic acid [brucine salt, m.p. 192°, $[\alpha]_D^{20} -16.5^\circ$ in H_2O ; phenylhydrazide, m.p. 115° (sinters at 102°), $[\alpha]_D^{20} +10.5^\circ$ in H_2O ; dibenzylidene compound I, m.p. 225°, II, m.p. 209°, $[\alpha]_D^{20} +57.3^\circ$]. *d*-Idonic acid also gives two dibenzylidene derivatives: I, m.p. 227°, $[\alpha]_D^{20} -57.8^\circ$, II, m.p. 208°, $[\alpha]_D^{20} -57.3^\circ$. With 0.1*N*-NaOH, dimethylascorbic acid neutralises 1 mol.; the Na salt gives the *p*-nitrobenzoyl derivative, m.p. 181°, inactive towards O_3 , $\text{NH}_2\text{OH}\cdot\text{HCl}$, $p\text{-NO-C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, and $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{NH}_2$. J. H. B.

Ascorbic acid and synthetic analogues. D. K. BAIRD, W. N. HAWORTH, R. W. HERBERT, E. L. HIRST, F. SMITH, and M. STACEY (J.C.S., 1934, 62—67).—Glucosascorbic acid (I) [named 3-keto-*d*-glucoheptonofuranolactone in A., 1933, 1275 (improved prep.)] has $[\alpha]_D^{20} -14^\circ$ in H_2O (+1H₂O) (II), m.p. 138° after sintering at 128° (Na salt $[\alpha]_D^{20} -80^\circ$). When heated, (II) gives the anhyd. form, m.p. 191° (decomp.) (cf. loc. cit.), which after treatment with I and $\text{NHPh}\cdot\text{NH}_2$ (III) yields a compound, $\text{C}_{19}\text{H}_{20}\text{O}_5\text{N}_4$, m.p. 222°, which corresponds with an osazone, m.p. 210°, obtained similarly from ascorbic acid (IV). *d*- or *l*-(IV) in H_2O (loc. cit.) affords with (III) (cf. *ibid.*, 1143) after oxidation with I in theoretical amount, a product m.p. 210° (decomp.), identical with that obtained from (IV). A product, $\text{C}_7\text{H}_{11}\text{O}_6\text{N}$, probably $\text{C}(\text{NH})\text{---}\text{C}(\text{OH})\text{:C}(\text{OH})\text{>CH}\cdot[\text{CH}(\text{OH})]_2\cdot\text{CH}_2\cdot\text{OH}$, is an intermediate in the prep. of (I) and is hydrolysed by 20% AcOH at 80° to (I). Arabinosazone in $\text{H}_2\text{O-EtOH-AcOH}$ with PhCHO at 90—95° in N_2 affords $\text{CHPh}\cdot\text{N}\cdot\text{NHPh}$ and arabinosone, which with KCN and CaCl_2 in neutral solution gives ψ -araboascorbic acid, converted by 8% HCl during 48 hr. into *l*-araboascorbic acid, m.p. 168° (decomp.), $[\alpha]_D^{20} +19^\circ$ in H_2O (Na salt $[\alpha]_D^{20} -94^\circ$), oxidised with I and HI to a product with $[\alpha]_D^{20} +12^\circ$ after 90 hr. (cf. *ibid.*, 1143). Maurer and Schiedt's product (cf. *ibid.*, 936) is *d*-araboascorbic acid, for which a furan structure was suggested (cf. *ibid.*, 489). This must now be amended. Similarly prepared, *d*-galactosascorbic acid has m.p. 109° (decomp.), $[\alpha]_D^{20} 0^\circ$ (Na salt, $[\alpha]_D^{20} -77^\circ$). ψ -Lactosascorbic acid when heated with 8% HCl at 50° is hydrolysed to (II), and is used as a source of (II). Maltosone (cf. A., 1902, i, 745) is converted quantitatively into ψ -maltosascorbic acid. In dil. aq. solutions all these substances (except the ψ -compounds) show an intense band at 265 μ . In more conc. solution, the band is at 240—245 μ . J. L. D.

Preparation and properties of aldonic acids and their lactones and basic calcium salts. H. S. ISBELL and H. L. FRUSH (Bur. Stand. J. Res., 1933, 11, 649—664).—The prep. of the commoner aldonic acids and their lactones in the cryst. condition is facilitated by the use of their basic Ca salts, and of dioxan as a solvent. J. L. D.

Micro-method for determination of uronic acids. B. BUCKHART, L. BAUR, and K. P. LINK

(J. Biol. Chem., 1934, 104, 171—181).—The methods of Buston (A., 1932, 602) and Clark (*ibid.*, 867) have been modified to give either a volumetric or a gravimetric determination of uronic acid and its derivatives. The accuracy of the method is of the same order as that of the best micro-modification.

H. G. R.

Polarimetric determination of gluconic acid. T. A. BENNET-CLARK (Biochem. J., 1934, 28, 45—47).— $[\alpha]$ of *d*-gluconic acid (I) is enhanced about 40-fold by formation of complex salts with molybdate (II). The relationship between $[\alpha]$ and (I) is almost linear, but, in presence of carbohydrate, special procedure is necessary owing to oxidation by (II). $[\alpha]$ of complexes of (I) with (II) and with UO_2 salts are in the same direction, in contrast to the behaviour of malates.

H. G. R.

Synthesis of hexuronic acids. III. Synthesis of *dl*-alluronic acid from *allomucic* acid. C. NIEMANN, S. KARJALA, and K. P. LINK. **IV. Synthesis of *d*-galacturonic acid from *d*-galactose.** C. NIEMANN and K. P. LINK (J. Biol. Chem., 1934, 104, 189—194, 195—204; cf. A., 1933, 595).—III. The authors' method (A., 1932, 367) of isolating uronic acids is inferior to that of Fischer (A., 1891, 677). The lactone of *allomucic* acid, m.p. 170—172°, with Na-Hg gives *dl*-alluronic acid, m.p. 145—146°, decomp. 148—149° [lactone; Ba and brucine, $+\text{H}_2\text{O}$, m.p. 172—173°, (anhyd.) 180—181°, $[\alpha]_D^{25} -25 \pm 1^\circ$ in H_2O , salts; Ba salt of *p*-bromophenylosazone, m.p. 209—211° (decomp.); Me ester of methylglucoside, $+\text{H}_2\text{O}$]. The Ba salts of *s*-aldohexuronic acids give osazones, whereas those of *as*-acids give hydrazones.

IV. *d*-Galactose diisopropylidene ether and KMnO_4 give *K* diisopropylidene-*d*-glucuronate (71% yield), $+\text{0.5H}_2\text{O}$, $[\alpha]_D^{25} -66 \pm 2^\circ$ in H_2O (also prepared in 30% yield from *d*-galacturonic acid by COMe_2 and H_2SO_4), whence were obtained successively (a) the free acid, m.p. 157.5—158°, $[\alpha]_D^{25} -84 \pm 2^\circ$ in CHCl_3 , Ba *d*-galacturonate, $[\alpha]_D^{25} +24 \pm 1^\circ$ in H_2O , and the corresponding acid, $+\text{H}_2\text{O}$, m.p. 157—159°, $[\alpha]_D^{25} +51 \pm 1^\circ$ in H_2O , and (b) the Me ester of α -methyl-*d*-galacturonide, $+\text{H}_2\text{O}$, m.p. 137—138°, $[\alpha]_D^{25} +121 \pm 2^\circ$ in H_2O , and α -methyl-*d*-galacturonide (71% yield), $+\text{2H}_2\text{O}$, m.p. 111—111.5°, $[\alpha]_D^{25} +129 \pm 1^\circ$ in H_2O , also obtained in 3.3% yield by electrolytic oxidation of α -methyl-*d*-galactoside (whereby the ring-structure is proved) (cf. A., 1926, 150). α -Methyl-*d*-glucoside does not give α -methyl-*d*-glucuronide by electrolytic oxidation or with NaOBr or H_2O_2 (cf. A., 1924, i, 10).

R. S. C.

Composition of an aldobionic acid from flax-seed mucilage. C. NIEMANN and K. P. LINK (J. Biol. Chem., 1934, 104, 205—206).—The aldobionic acid from flax-seed mucilage with hot 2.5% H_2SO_4 gives *d*-galacturonic acid, m.p. 157—158°, $[\alpha]_D^{25} +54^\circ$ (brucine salt, m.p. 188—189°, $[\alpha]_D^{25} -7.5^\circ$), and *l*-rhamnose (cf. A., 1930, 1408).

R. S. C.

Preparation of calcium lactobionate and δ -lactobionolactone. H. S. ISBELL (Bur. Stand. J. Res., 1933, 11, 713—717).—When Ca lactobionate (cf. A., 1931, 1038) and CaCl_2 in H_2O are evaporated, $\text{Ca}(\text{C}_{12}\text{H}_{21}\text{O}_{12})_2 \cdot \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $[\alpha]_D^{25} +20.0^\circ$ in H_2O separates; this is converted by CaO in hot H_2O into

$\text{Ca}(\text{C}_{12}\text{H}_{21}\text{O}_{12})_2 \cdot 5\text{H}_2\text{O}$, $[\alpha]_D^{25} +23.7^\circ$ in H_2O , which affords, after treatment with $\text{H}_2\text{C}_2\text{O}_4$, δ -lactobionolactone, m.p. 195—196°, $[\alpha]_D^{25} +54^\circ$ to $+22^\circ$ in H_2O .

J. L. D.

Determination of methoxyl in pectin. G. ROMEO (Annali Chim. Appl., 1933, 23, 530—534).—1 g. of the powdered pectin is dissolved on the water-bath in 250 c.c. of H_2O . The cooled solution is made up to the initial vol. and neutralised with 0.5*N*-NaOH. This gives the acid val., which is comparatively high for altered or poor material; 20 c.c. of 0.5*N*-NaOH are then added with vigorous stirring and after 15 min., the liquid is treated with 20 c.c. of 0.5*N*- H_2SO_4 , and titrated with 0.5*N*-NaOH: 1 c.c. of 0.5*N*-NaOH used in the hydrolysis = 0.0155 g. OMe.

T. H. P.

Condensation of chloral and bromal with diamides. F. D. CHATTAWAY and E. J. F. JAMES (J.C.S., 1934, 109—113; cf. A., 1932, 151).—Interaction of $\text{NH}_2 \cdot \text{CO} \cdot \text{NHMe}$ (I) and $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$ (2 mols.) in H_2O affords *N*-methyl-*N'*-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)carbamide, m.p. 140° (decomp.) [Ac_2 derivative, m.p. 90—91° (decomp.)], the Na derivative of which in aq. NaOH with Ac_2O affords *di*-($\beta\beta\beta$ -trichloro- α -*N'*-methylcarbamidoethyl) ether (II), m.p. 230° (decomp.) [Ac_2 derivative, m.p. 131° (decomp.)]. (II) in EtOH containing NaOEt during 24 hr. affords *N*-methyl-*N'*-($\beta\beta\beta$ -trichloro- α -ethoxyethyl)carbamide, m.p. 145° (decomp.). The following are prepared similarly: *N*-ethyl-*N'*-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)carbamide, m.p. 138° (decomp.) [Ac_2 derivative, m.p. 60° (decomp.)], *di*-($\beta\beta\beta$ -trichloro- α -*N'*-ethylcarbamidoethyl) ether, m.p. 226° (decomp.) [Ac_2 derivative, m.p. 145° (decomp.)]; *N*-ethyl-*N'*-($\beta\beta\beta$ -trichloro- α -methoxyethyl)carbamide, m.p. 150° (decomp.) [corresponding *OEt*-, m.p. 135° (decomp.); *OPr*-, m.p. 140° (decomp.)]; *OBu*-derivative, m.p. 95° (decomp.)]. Interaction of $\text{NH}_2 \cdot \text{CO} \cdot \text{NHMe}$ and $\text{CBr}_3 \cdot \text{CHO}$ in H_2O affords similar, though less stable, products. The following are described: *N*-methyl-, m.p. 189° (decomp.) [Ac_2 derivative, m.p. 119° (decomp.)]; *OEt*-compound, m.p. 162° (decomp.)], and *N*-phenyl-*N'*-($\beta\beta\beta$ -tribromo- α -hydroxyethyl)carbamide, m.p. 167° (decomp.) [Ac_2 derivative, m.p. 142° (decomp.)]; *OMe*-, m.p. 158° (decomp.), *OEt*-, m.p. 145° (decomp.), -compound]; *di*-($\beta\beta\beta$ -tribromo- α -*N'*-methyl-, m.p. 200° (decomp.) [Ac_2 derivative, m.p. 180° (decomp.)], and -phenyl-carbamidoethyl) ether, m.p. 185° (decomp.) [Ac_2 derivative, m.p. 163° (decomp.)]. Interaction of $\text{CCl}_3 \cdot \text{CHO}$ with $\text{NH}_2 \cdot \text{CO} \cdot \text{NAlk}$ gives the following, which are unchanged by cold Ac_2O in NaOH: *NN*-dimethyl-, m.p. 157° (decomp.) (lit., 153°); *NN*-diethyl-, m.p. 146° (decomp.) (lit., 142°), and *NN*-diphenyl-*N'*-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)carbamide, m.p. 170° (decomp.) [Ac derivative, m.p. 108° (decomp.)]; *NN*-dimethyl-, m.p. 165° (decomp.) [$+\text{H}_2\text{O}$, m.p. 96° (decomp.)] and *NN*-diphenyl-*N'*-($\beta\beta\beta$ -tribromo- α -hydroxyethyl)carbamide, m.p. 168° (decomp.). ($\cdot \text{CO} \cdot \text{NH}_2$)₂ and $\text{CCl}_3 \cdot \text{CHO}$ (excess) when boiled during 8 hr. afford *NN'*-*di*-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)oxamide (III), decomp. $>190^\circ$ (Ac_2 derivative, m.p. 192°), but no monochloral-oxamide, which also is not formed by interaction of Et *N*-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)oxamate (IV) (A., 1914, i, 666). (IV) with NH_2Ph in EtOH at 100° during 0.5 hr. gives *N*-phenyl-*N'*-($\beta\beta\beta$ -trichloro- α -hydr-

oxyethyl)oxamide, decomp. $> 180^\circ$ into $\text{CCl}_3 \cdot \text{CHO}$ and $\text{CO}_2\text{H} \cdot \text{CO} \cdot \text{NHPh}$ (*Ac* derivative, m.p. 185°). (III) with PCl_5 at 100° during 0.5 hr. affords NN' -di-($\alpha\beta\beta$ -tetrachloroethyl)oxamide, m.p. 170° , converted by boiling EtOH into NN' -di-($\beta\beta\beta$ -trichloro- α -ethoxyethyl)oxamide (V), m.p. 176° . The $(\text{NH}_2)_2$ - and $(\text{NHPh})_2$ -compounds corresponding with (V) have m.p. 213° , and 193° (decomp.), respectively. $\text{CH}_2(\text{CO} \cdot \text{NH}_2)_2$ and $\text{CCl}_3 \cdot \text{CHO}$ (excess) at 100° during 12 hr. afford CNN' -tri-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)malonamide (VI), polymorphic forms m.p. 180° (labile) and 180° (decomp.) (stable) [*Ac*₃ derivative, m.p. 165° (decomp.)]. Reaction between substituted malonamides and $\text{CCl}_3 \cdot \text{CHO}$ occurs only at unsubstituted positions. The following, prepared similarly to (VI), are described: NN' -diphenyl-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)malonamide, m.p. 187° (decomp.); N -phenyl- N' -($\beta\beta\beta$ -trichloro- α -hydroxyethyl)-($\beta\beta\beta$ -trichloro- α -hydroxyethyl)malonamide, m.p. 170° (decomp.) [*Ac*₂ derivative, m.p. 175° (decomp.)]; NN' -di-, m.p. 163° (decomp.) (*Ac*₂ derivative, m.p. 132°), and -phenyl- N' -($\beta\beta\beta$ -trichloro- α -hydroxyethyl)ethylmalonamide, m.p. 164° (decomp.) [*Ac* derivative, m.p. 185° (decomp.)]. Malonanilic acid and $\text{CCl}_3 \cdot \text{CHO}$ afford $\gamma\gamma\gamma$ -trichloro- β -hydroxybutyranilide, m.p. 146° (decomp.) [*Ac* derivative, m.p. 149° (decomp.)]. $\text{CN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ and $\text{CCl}_3 \cdot \text{CHO}$ afford cyanoaceto- $\beta\beta\beta$ -trichloro- α -hydroxyethylamide, m.p. 155° (decomp.) [*Ac* derivative, m.p. 108° (decomp.)]. J. L. D.

Isomerisation of hydroxyaldehydes. V. Oxidation-reduction transformations of α -hydroxyisobutaldehyde. S. DANILOV and E. VENUS-DANILOVA (Ber., 1934, 67, [B], 24—35).—Previously reviewed (A., 1933, 1277). α -Hydroxyisobutaldehyde-semicarbazono and -*p*-nitrophenylhydrazono have m.p. 164 — 165° and m.p. 153 — 159° (decomp.), respectively. H. W.

δ -Hydroxyvaleraldehyde. R. PAUL (Compt. rend., 1933, 197, 1652—1654).— $0.015N$ -HCl converts 2 : 3-dihydropyran (I) (A., 1933, 831) into the cyclic form of δ -hydroxyvaleraldehyde (II), b.p. 80 — $81^\circ/16$ mm., which is tautomeric with the open-chain aldehyde, since it slowly gives a colour with Schiff's reagent, reacts with $\text{NHPh} \cdot \text{NH}_2$, and is oxidised by Ag_2O to Ag δ -hydroxyvalerate. (II) is reconverted into (I) by distillation at 760 mm. with a trace of HCl. The (static) *Me ether* $\text{O} \begin{smallmatrix} \text{CH(OMe)} \cdot \text{CH}_2 \\ \text{CH} \text{---} \text{CH}_2 \end{smallmatrix} > \text{CH}_2$, b.p. 128 — 129° , is obtained by boiling (I) with MeOH-HCl (trace). J. W. B.

Photopyridine reaction. F. FEIGL and V. ANGER (J. pr. Chem., 1934, [ii], 139, 180—182).—Photopyridine is identified by its colour reactions, presence of $\cdot\text{CHO}$, and reversion into $\text{C}_5\text{H}_5\text{N}$ by heat as $\text{CHO} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{ONH}_4$ (cf. this vol., 303). With 2(*m*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$) $_2\text{H}_2\text{SO}_4$ (I) it gives *e*-*m*-nitroanilino- Δ^8 -pentadienal-*m*-nitroanil sulphate, m.p. 116° , also obtained from (I) and $\text{CHO} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{ONa}$. H. A. P.

Condensations of furan compounds. II. Determination of small amounts of acetone. V. V. TSCHELINCEV and E. K. NIKITIN (Bull. Soc. chim., 1933, [iv], 53, 1130—1139; cf. A., 1932, 1140).— COMe_2 is determined in concns. $> 0.0001\%$ by con-

densation with furfuraldehyde and NaOH , acidification with H_2SO_4 , and matching of the violet-red colour produced. The method is valid in presence of aromatic aldehydes, COMeEt , or $\text{CH}_3\text{Ac} \cdot \text{CO}_2\text{H}$, but not in presence of sugars; aliphatic and arylaliphatic aldehydes must be removed previously by KMnO_4 — H_2SO_4 . R. S. C.

Exchange of heavy hydrogen atoms between water and organic compounds. K. F. BONHOEFFER and R. KLAR (Naturwiss., 1934, 22, 45; cf. A., 1933, 1242).—The exchange of heavy H atoms from heavy H_2O with the H of the Me in NaOAc does not take place. If the H atom of a Me is mobile, as in keto-enolic tautomerism, exchange takes place with the H of OH of the enolic form. Pure aq. COMe_2 (keto-form) does not exchange, but after the addition of a small amount of Na exchange takes place. A. J. M.

Action of hydrogen peroxide on acetone. Proof of the existence of a trimeric peroxide of acetone which depolymerises to the monomeride. H. LECOQ (Bull. Soc. chim. Belg., 1933, 43, 531—536).—Mol. wt. determinations show that the peroxide, $(\text{C}_3\text{H}_5\text{O}_2)_x$, obtained from COMe_2 , H_2O_2 (3 parts), and a few drops of H_2SO_4 is trimeric when first dissolved in cold C_6H_6 , but dissociates completely in 2 hr. (cold), or instantly when boiled, into the monomeride (I). The trimeride, m.p. 97 — 98° , gives (I), m.p. 90° , when kept molten for 2—3 min. or when distilled in steam. It liberates I quantitatively from aq. EtOH-HCl-KI . R. S. C.

Stability of fructose in aqueous solutions of varying μ_{H} .—See this vol., 260.

Fructofuranose tetrabenzoate. P. BRIGL and R. SCHINLE (Ber., 1934, 67, [B], 127—130; cf. A., 1933, 378).—Fructofuranose 1 : 3 : 4 : 6-tetrabenzoate (I), m.p. 124 — 125° , $[\alpha]_D^{20}$ -6.1° to -13.7° in CHCl_3 , is readily obtained by successive additions, without cooling, of BzCl (0.5 mol.) to fructose (0.1 mol.) in $\text{C}_5\text{H}_5\text{N}$. The furanoid structure of (I) is confirmed by its formation from the fructose 1 : 6-dibenzoate (II) of Zervas and Sessler (this vol., 58) (improved prep.) by the action of BzCl and $\text{C}_5\text{H}_5\text{N}$ without cooling or of BzCl and $\text{C}_5\text{H}_5\text{N}$ in CHCl_3 at -15° . The cyclic nature of (II) is also established. H. W.

Methylglucosides of naturally occurring hexuronic acids. II. Kinetics of the hydrolysis of α -methyl-*d*-galacturonide. S. MORELL and K. P. LINK (J. Biol. Chem., 1934, 104, 183—188; cf. A., 1933, 595).—In the hydrolysis of α -methyl-*d*-galacturonide (I) ($+2\text{H}_2\text{O}$, m.p. 112° , decomp. 120° , $[\alpha]_D^{25}$ $+127.8^\circ$ in H_2O) and -*d*-galactoside (II) ($+ \text{H}_2\text{O}$, m.p. 114 — 116° , $[\alpha]_D^{25}$ $+199.4^\circ$ in H_2O) in $N\text{-HCl}$ *k* is 1.56 and $2.01 \times 10^{-3} \text{ min.}^{-1}$ at 70° and *E* 29,000 and 35,000 between 60° and 80° , respectively. By analogy with (II), (I) thus has a pyran structure. R. S. C.

Ononin. II. F. WESSELY, F. LECHNER, and K. DINJAŠKI (Monatsh., 1933, 63, 201—209).—Fractional crystallisation of crude ononin (Merck) (I) separates diadzein, (I) being purified as its *Ac*₄ derivative, m.p. 182.5° . Similarly, the specimen of form-ononetin (II) previously used contained impurities partly separated by fractional crystallisation or sub-

limation, but the identity of (II) with the synthetic specimen (A., 1933, 614) is confirmed. With α -acetobromoglucose and NaOH in $\text{H}_2\text{O}-\text{COMe}_2$ at 0° , 2:4-dihydroxyphenyl 4'-methoxybenzyl ketone (A., 1931, 738) affords, after deacetylation, its 4-glucoside, identical with natural onospin, the structure being confirmed by methylation ($\text{MeI}-\text{MeOH}-\text{K}_2\text{CO}_3$) and hydrolysis to 4-hydroxy-2-methoxyphenyl 4'-methoxybenzyl ketone, sinters 171° , m.p. 173° , identical with a specimen synthesised from $m\text{-C}_6\text{H}_4(\text{OH})\cdot\text{OMe}$ and $n\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CN}$ with anhyd. $\text{ZnCl}_2\text{-HCl}$ in Et_2O . J. W. B.

Preparation and enzymic fission of basic glycosides. B. HELFERICH, E. GÜNTHER, and S. WINKLER (Annalen, 1934, 508, 192—205).—*o*-Cresol- β -*d*-glucoside tetra-acetate, m.p. $142\text{--}144^\circ$ (corr.), $[\alpha]_D^{25} -27.5^\circ$ in CHCl_3 , obtained by the method previously described (A., 1933, 379) from *o*-cresol, β -glucose penta-acetate, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ at $120\text{--}130^\circ$, is converted by Br in CHCl_3 in presence of NaHCO_3 and strong irradiation into ω -bromo-*o*-cresol- β -*d*-glucoside tetra-acetate, m.p. $158\text{--}160^\circ$ (corr.), $[\alpha]_D^{25} +35.2^\circ$. Prolonged interaction of this with cold aq. MeOH-NH_3 gives the hydrobromide of *o*-aminomethylphenol- β -*d*-glucoside, m.p. $182\text{--}185^\circ$ $[\alpha]_D^{25} -64.2^\circ$ in aq. AcOH (calc. amount), acetylated ($\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$) to the Ac_5 derivative, m.p. $140\text{--}142^\circ$ (corr.), $[\alpha]_D^{25} -64.5^\circ$ in CHCl_3 , which is hydrolysed (N-NaOH in COMe_2) to the *N*-*Ac* derivative (I), m.p. $195\text{--}196^\circ$, $[\alpha]_D^{25} +33.3^\circ$ in H_2O . *p*-Cresol- β -*d*-glucoside tetra-acetate, m.p. $116\text{--}118^\circ$ (corr.), $[\alpha]_D^{25} -17.6^\circ$ in CHCl_3 , is brominated similarly to the ω -*Br*-derivative (II), m.p. $155\text{--}158^\circ$ (corr.), $[\alpha]_D^{25} -19^\circ$ in CHCl_3 , which is converted (as above) into *p*-aminomethylphenol- β -*d*-glucoside, m.p. about 140° (sinters at 90°), decomp. 147° , $[\alpha]_D^{25} -70.1^\circ$ in aq. AcOH [*N*-*Ac* derivative ($+\text{H}_2\text{O}$), m.p. $130\text{--}132^\circ$ (corr.) (sinters at 119°), $[\alpha]_D^{25} -53.8^\circ$ in H_2O ; Ac_5 derivative, m.p. $123\text{--}125^\circ$ (corr.), $[\alpha]_D^{25} -14.9^\circ$ in CHCl_3]. Successive treatment of (II) with Ag_2CO_3 in aq. COMe_2 and MeOH-NaOMe gives *p*-hydroxymethylphenol- β -*d*-glucoside, dimorphous, m.p. $114\text{--}118^\circ$ (corr.) and $136\text{--}138^\circ$ (corr.), $[\alpha]_D^{25} -65.8^\circ$ in H_2O . *o*-Aminomethylphenol- β -*d*-galactoside, m.p. $218\text{--}220^\circ$ (corr.) (decomp.), $[\alpha]_D^{25} -35^\circ$ in H_2O [*N*-*Ac* derivative (III), m.p. $211\text{--}212^\circ$ (corr.), $[\alpha]_D^{25} -19.7^\circ$ in H_2O]; *p*-cresol- β -*d*-galactoside tetra-acetate, m.p. $105\text{--}107^\circ$, $[\alpha]_D^{25} +3.9^\circ$ in CHCl_3 (ω -*Br*-derivative, m.p. $104\text{--}107^\circ$, $[\alpha]_D^{25} -1.2^\circ$ in CHCl_3), and *p*-aminomethylphenol- β -*d*-galactoside, m.p. $206\text{--}208^\circ$ (corr.) (decomp.), $[\alpha]_D^{25} -45.7^\circ$ in aq. AcOH [*N*-*Ac* derivative, m.p. $166\text{--}168^\circ$ (corr.); Ac_5 derivative, m.p. $131\text{--}132^\circ$], are similarly prepared. Hydrolysis of the above NH_2 - and NHAc -glucosides and -galactosides by emulsin (IV) and acid (V) is studied. (I) and (III) are hydrolysed by (IV) [not by (V)] to a much greater extent than any of the other compounds. In general the -glucosides are hydrolysed more rapidly by (IV) and the -galactosides more readily by (V). In both cases, presence of the NH_2 retards fission. *Acet-p-hydroxybenzylamide* has m.p. $135\text{--}137^\circ$.

H. B.

Lusitanicoside. H. HERISSEY (Compt. rend., 1934, 198, 265—266).—Lusitanicoside, $\text{C}_{21}\text{H}_{30}\text{O}_{10}$, and boiling 2.5% H_2SO_4 give chavicol, *d*-glucose, and

rhamnose. The biose (not isolated) is named *lusitanicoside*. R. S. C.

Glucosides of *Digitalis lanata*. C. MANNICH (Arch. Pharm., 1934, 272, 5—8).—In part polemical against Stoll and Kreis (A., 1933, 1146). Various samples of *lanata* glucoside II (A., 1930, 1561; 1933, 877) contain, respectively, 50—56%, 11—17%, and 31—34% of digiligidin A, B, and C, and are identical with the "total digiligidins" of Stoll and Kreis, whereas lanadigin is mainly digiligidin C (about 45%) contaminated with A (30%) and B (25%). J. W. B.

Preparation and properties of nitric acid esters of starch. I, II. J. HACKEL and T. URBANSKI (Z. ges. Schiess- u. Sprengstoffw., 1933, 28, 306—310, 350—354, 378—382; 1934, 29, 14—16, 16—17).—I. The properties of potato-starch nitrates (I) depend on the conditions of nitration. With 10 parts of HNO_3 (58.08—93.3%) alone for 2 hr. at 20° the yield of (I) and the N content (II) of the product increase with increasing HNO_3 concn., almost no reaction occurring with $< 67\%$ HNO_3 . Viscosity (η) and solubility (s) decrease with increasing (II). Washing the product with cold H_2O and 1% aq. Na_2CO_3 gives products of low stability, and heating with H_2O causes partial hydrolysis, increase in s , and reduction of yield. With 96.26% HNO_3 for 2 hr. at 10° (II) increases, at first rapidly, with increase in the HNO_3 /starch ratio up to 80/1. The decrease in (II) caused by decreasing this ratio is greater the greater is the dilution of the HNO_3 . At first (II) increases rapidly with increasing reaction time, then more slowly to a max., but development of yield-reducing side-reactions is correspondingly favoured. Between 0° and 30° rise in temp. causes diminution in (II) and η , and increase in s . Pptn. of the product with H_2SO_4 instead of H_2O increases (II) consequent on further nitration. The effect of varying concn. of H_2O , HNO_3 , and H_2SO_4 on (II) in mixed acid nitrations is expressed in ternary diagrams, a max. val. for (II) being reached when equimol. proportions of H_2O and H_2SO_4 are used, the results corresponding with those for cellulose nitrate (Saposhnikov), but with mixed acids poor in H_2SO_4 considerable deviations from the latter results occur, due, probably, to the solubility of (I) in the mixed acids. With high H_2SO_4 concn. sulphuric esters are formed giving H_2O -sol. products. With $> 20\%$ H_2O nitration is irregular, and small yields are obtained.

II. Contrary to some statements in the lit., repetition of the above investigations using maize, rice, wheat, tapioca, and sol. starch gives results and products closely similar to those obtained with potato starch. J. W. B.

Highly polymerised compounds. LXXXV. Cellulose. XI. Mol. wt. of methylcellulose. H. STAUDINGER and H. SCHOLZ (Ber., 1934, 67, [B], 48—91).—The deduction of the mol. wt. of cellulose from observation on the tetra- and tri-methylmethylglucosides (Haworth *et al.*) is not valid, since their tri-methylcellulose (I) is derived from a cellulose acetate (II) in the formation of which the cellulose suffers acetylation. Their results, however, give an indirect confirmation of the authors' determinations of the mol. wt. of (II) if it is admitted that further degradation of the mol. does not occur during the transition from

(II) to (I). Evidence on this point is sought in observation of the viscosity of (I) and (II) in *m*-cresol (III). The vals. found for the ethers are almost double those for the esters; the result is attributed to the co-ordinative union of (I) and (III) to oxonium compounds. Suitable, non-combining solvents for (I) and (II) could not be discovered. High vals. for the viscosity of (I) in AcOH and C_5H_5N are recorded. It is considered that the investigations show that the chain-length is not altered during the transformation of polymeric homologous (II) into polymeric analogous (I). The constitution of cellulose and the identity of the colloid particles with the macro-mols. are regarded as established, since it is possible to perform chemical reactions with the macro-mols. of cellulose and its derivatives without alteration of the mean degree of polymerisation just as with the simpler, homogeneous oligosaccharides without change in their degree of polymerisation.

H. W.

Preparation of propyl-, butyl-, and amyl-celluloses by the action of alkyl halides. N. I. NIKITIN and I. M. ORLOVA (J. Appl. Chem. Russ., 1933, 6, 1093—1104).—The reactivity of alkyl halides with alkaline cellulose increases in the order $Cl < I < Br$, and $iso-C_5H_{11} < n-C_5H_{11} < Bu^b < Bu^a < Pr^b < Pr^a < Et$. In the case of *iso*alkyl halides considerable quantities of gas are evolved during the reaction. The no. of alkyl groups introduced increases with increasing temp.

R. T.

Highly polymerised compounds. LXXXVI. Validity of the viscosity law. H. STAUDINGER (Ber., 1937, 67, [B], 92—101).—Reasons are given for considering the viscosity method particularly valuable in the examination of highly polymerised compounds. Objection is raised to the work of Büchner *et al.* (A., 1933, 261), on the ground that technical cellulose acetate was used, whereas trustworthy data can be obtained only by use of as homogeneous material as possible; re-calculation of their results shows them to confirm rather than to refute the law of viscosity. In reply to Kraemer *et al.* (A., 1933, 218) it is pointed out that in the less highly polymerised *t*-hydroxydecoic acids thread mols. of double length are formed by the co-ordinative union of 2 CO_2H . With increasing degree of polymerisation, the co-ordinative forces become weakened, so that normal η vals. are observed. The contention that the polyhydroxydecoic acids are more suitable models than the polystyrenes (Corothers *et al.*, this vol., 56) is disputed for the reason that they do not yield a sufficient range of polymerides.

H. W.

Structure of organic compounds of high mol. wt. H. STAUDINGER (Naturwiss., 1934, 22, 65—71, 84—89).—A review.

Hydrogenation of amides to amines. H. ADKINS and B. WOJCIK (J. Amer. Chem. Soc., 1934, 56, 247).—Reduction of laur-, hepto-, α -phenylbutyr-, furo-, and tetrahydrofuro-amide with H_2 (100—300 atm.) at 175—205° in dioxan using a Cu-Cr oxide catalyst gives 40—70% of the corresponding primary amine (and 25—50% of the *sec.*-amine); $R \cdot CO \cdot NH_2 + H_2 \longrightarrow CH_2R \cdot NH_2 + H_2O$. Substituted amides (*e.g.*, *N*-lauryl- and sebacyl-piperidine; laur-mono- and -di- β -phenylethyl- and -amyl-amides; laur-*cyclohexyl*-

amide and -anilide; hepto- β -phenylethylamide) are similarly reduced to the corresponding *sec.*- and *tert.*-amines in 70—95% yield. High yields of amines are obtained by hydrogenation of NH_4 laurate. H. B.

Preparation of diaminobutanes. II. *dl*- $\alpha\gamma$ -Diamino- β -methylpropane, *dl*- $\alpha\gamma$ -diaminobutane, and $\alpha\delta$ -diaminobutane. E. STRACK and H. SCHWANEBERG (Ber., 1934, 67, [B], 39—45; cf. A., 1933, 1148).— $(\cdot CH_2 \cdot CH_2 \cdot NH_2)_2$ is obtained in 76.4% yield by reduction of succinonitrile (Pd—80% EtOH, 0–125% by vol.) at room temp. Methylmalononitrile (improved prep. from $CHMeBr \cdot CO_2Et$) is hydrogenated (Pd—98—99% MeOH) to *dl*- $\alpha\gamma$ -diamino- β -methylpropane in 92% yield; the hydrochloride, m.p. 201° (corr.), *sulphate*, m.p. $> 300^\circ$, *platinichloride*, decomp. 237° (corr.), *aurichloride*, m.p. 203—205° after softening at 195° or (+2H₂O) m.p. 142° (corr.) after softening at 130°, compound $C_4H_{12}N_2(HgCl_2)_2$, decomp. 196—198° (corr.), *picrate*, decomp. 252° (corr.) after softening at 249°, *picrolonate*, decomp. 269—271° (corr.), Bz_2 derivative, m.p. 145° (corr.), and di-*m*-nitrobenzoyl derivative, m.p. 187° (corr.), are described. β -Iminobutyronitrile (improved prep. from MeCN and Na) is reduced by Na and abs. EtOH or by H_2 (Pd—98% MeOH) to *dl*- $\alpha\gamma$ -diaminobutane in 90% or 93.1% yield, respectively. It yields a hydrochloride, m.p. 117° (corr.), *sulphate*, m.p. $> 300^\circ$, *platinichloride*, decomp. 250°, *aurichloride*, m.p. 210—212° after softening at 200° or (+1 H₂O) m.p. 208—210°, compound $C_4H_{12}N_2(HgCl_2)_2$, m.p. about 200° (corr.), *picrate*, decomp. 251° (corr.) after softening at 248°, *picrolonate*, decomp. about 260° (corr.) after darkening at 245°, Bz_2 derivative, m.p. 170° (corr.) after softening at 168°, and di-*m*-nitrobenzoyl compound, m.p. 201° (corr.).

H. W.

Preparation of isobutylenediamine. H. D. K. DREW and F. S. H. HEAD (J.C.S., 1934, 49—50).— α -Chloroisobutaldoxime, m.p. 104° (lit., 96—97°), in saturated EtOH— NH_3 during 10 min. affords α -aminoisobutaldoxime (I), m.p. 89° [*hydrochloride* (II), m.p. 210° (decomp.)]; *CHPh* derivative, m.p. 110°. Reduction of (I) or (II) in EtOH—AcOH at 30° with Na—Hg affords isobutylenediamine (isolated as the dihydrochloride) and 2:2:5:5-tetramethylpiperazine. Acetylation of (I) affords α -acetamidoisobutyronitrile (cf. A., 1904, i, 563) together with *N*-acetyl- α -aminoisobutaldoxime, m.p. 198—199°.

J. L. D

Compounds of hexamethylenetetramine.—See this vol., 265.

Reaction of aliphatic imino-ethers with hydrazine. W. OBERHUMMER (Monatsh., 1933, 63, 285—300).—Imino-ethers (as their hydrochlorides) react with N_2H_4 to give either amidrazones (new nomenclature suggested) $NH \cdot CR \cdot NH \cdot NH_2 + EtOH$, or hydrazino-ethers $NH_2 \cdot N \cdot CR \cdot OEt + NH_3$, or, probably as a secondary reaction, hydrazidines $NH_2 \cdot N \cdot CR \cdot NH \cdot NH_2 + EtOH + NH_3$, the product depending on reaction conditions, especially on the order of addition of the reactants. Thus addition of acetimido-ether hydrochloride (I) (1 mol.) to N_2H_4 —EtOH at 0° gives a 50% yield of *acetamidrazone hydrochloride* (II) ($R=Me$), m.p. 131—132° (free base stable only in H_2O or EtOH), and with 2 mols. of (I) *acet-*

hydrazidine hydrochloride (III) (*picrate*, decomp. 126—128°; *platinichloride*; *sulphate*, altered at 130°, clear melt at 192—193°; free base stable only in solution), decomp. at 140—150° to give 4-amino-3:5-dimethyl-1:2:4-triazole (IV). Addition of N_2H_4 in EtOH to a solution of (I) in EtOH at 0°, however, gives (IV) and *di-(α -ethoxyethylidene)hydrazine* ($OEt \cdot CMe \cdot N$)₂, sinters 26°, m.p. 28°. With HNO_3 (II) gives only N_3H , NH_4Cl , and $AcOH$, but with $EtO \cdot NO$ in EtOH at 0°, 5-methyltetrazole $\begin{smallmatrix} N \cdot NH \\ | \quad | \\ N - N \end{smallmatrix} \gg CMe$, sinters 144°, m.p. 145—146°, is obtained. With HNO_2 (III) affords only N_3H , N_2H_4 , HCl , and $AcOH$. J. W. B.

Oxidation of organic compounds by potassium permanganate under the conditions of the Kubel-Tiemann method. M. L. COMPERNOLLE (*Natuurwetensch. Tijds.*, 1934, 15, 237—243).—In the oxidation of org. substances with dil. acid $KMnO_4$ solution the ratio of O consumed to the theoretical quantity for complete oxidation is termed the oxidation no. (I). (I) approaches a max. as the dilution is increased. With hydroxybenzoic acids (I) is a max. (equal to unity) at a concn. of 5×10^{-3} and as regards ease of oxidation, $o > m > p$. The following vals. for (I)_{max} are recorded, the optimum concns. being given in parentheses: aminobenzoic acids 0.12 (1×10^{-5}); nitrobenzoic acids 0.12—0.14 (5×10^{-4}); carbamide 0; hippuric acid 0.01 (5×10^{-3}); asparagine 0.11 (5×10^{-4}); aminosuccinic acid 0.4 (1×10^{-3}); glycine 0.55 (1×10^{-2}); phenyldimethylpyrazolone 0.85 (5×10^{-5}); uric acid 0.85 (1×10^{-4}). S. C.

Action of ultra-violet light on glycine.—See this vol., 264.

Action of ammonia and amines on unsaturated esters. III. Action of ammonia, methylamine, and diethylamine on methyl acrylate. K. MORSCH (*Monatsh.*, 1933, 63, 220—235).—Me acrylate (I) with NH_3 -MeOH at room temp. affords successively $NH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Me$ (hydrochloride, m.p. 102.5°; lit. m.p. 95°), *di*-, b.p. 132.5°/10.5 mm. (hydrochloride, m.p. 136.5—137.5°), and its *diamide* (II), m.p. 144.5—145.8° [*platinichloride*, m.p. 200.5° (decomp.)], *tri*-, b.p. 171—174°/9 mm. [hydrochloride, m.p. 172.5° (decomp.)], and its monoamide [as *platinichloride*, m.p. 178—178.5° (decomp.)] and *triamide* (III), m.p. 185.5—186° [*platinichloride*, m.p. 196.5° (decomp.)], $-(\beta\text{-carbomethoxyethyl})\text{amine}$, the proportions (recorded) of these products varying with the concn. and excess of NH_3 , and reaction time. With liquid NH_3 the same products are obtained, prolonged action giving mainly (II) and (III). Similarly with NH_2Me -MeOH, *Me* β -methylaminopropionate, b.p. 50°/11 mm. (acid + H_2O , m.p. 66.5—67.5°, and anhyd., m.p. 144.5—146°), and its *methylamide*, b.p. 131—132°/9 mm. (hydrochloride, m.p. 134.5°), and *methyl-di-(β -carbomethoxyethyl)amine*, b.p. 123—124°/9 mm. (hydrochloride, m.p. 120.5—121.5°), are isolated. With $NHEt_2$ at room temp. (I) gives a quant. yield of *Me* β -diethylaminopropionate, b.p. 66.5°/8 mm., but at 190—200° its *tetraethyl-diamide*, b.p. 123.5—124.5°/10 mm., is obtained. J. W. B.

Tastes of glutamic acid and related compounds. II. Tastes of derivatives of *dl*-glutamic

acid. C. L. TSENG and E. J. H. CHU (*J. Chinese Chem. Soc.*, 1933, 1, 188—198; cf. A., 1932, 503).—*dl*-Glutamic acid is best (71% yield) obtained from the *d*-acid (10 g.), $Ba(OH)_2$ (23.32 g.), and H_2O (100 c.c.) at 160—170° (9 hr.) (cf. A., 1909, i, 368). $NaHCO_3$, Na_2CO_3 , $NaOH$, and $Ca(OH)_2$ do not cause racemisation. The tastes of the following derivatives are recorded: *Na*, *K*, hygroscopic, *Ca*, *Li*, *Ba*, *Mg*, *Sr*, NH_3Me , hygroscopic, m.p. 75° (hydrochloride, m.p. 168.9°), and NH_2Me_2 (hydrochloride, m.p. 178.5°) salts; hydrochloride, m.p. 198.5°; sulphate, m.p. 164.6°; *Et* ester hydrochloride, m.p. 113.1°; *formyl*, m.p. 181.7°, *Ac*, m.p. 187.5°, *propionyl*, m.p. 173.1°, *n-butyl*, m.p. 179°, and *isovaleryl*, m.p. 180.6°, derivatives. M.p. are corr. R. S. C.

Intermediate oxidation product of cystine. T. F. LAVINE, G. TOENNIES, and E. C. WAGNER (*J. Amer. Chem. Soc.*, 1934, 56, 242—243; cf. A., 1933, 598).—A disulphoxide is probably formed when cystine is oxidised with BzO_2H (— rather $> 2 O$).

Triethylsilicyl group. C. A. KRAUS and W. K. NELSON (*J. Amer. Chem. Soc.*, 1934, 56, 195—202).— $SiHET_3$ (I) (from $SiHCl_3$ and $MgEtBr$) and KNH_2 in liquid NH_3 give *K di(triethylsilicyl)amide*, $(SiEt_3)_2NK$, converted by NH_4Br in liquid NH_3 into *di(triethylsilicyl)amine*, b.p. 100°/1 mm., which is readily hydrolysed (H_2O) to $(SiEt_3)_2O$. (I) and *Li* in NH_2Et afford *triethylsilicylethylamine*, $SiEt_3 \cdot NH_2Et$ (II), hydrolysed readily to $SiEt_3 \cdot OH$; the *Li* acts as catalyst. (II) is also obtained from $SiEt_3Br$ (III), NH_2Et , and *Li*. (III) and $NaGePh_3$ in C_6H_6 give *triphenylgermanytriethylsilane*, $GePh_3 \cdot SiEt_3$, m.p. 93.5°, which is converted by *Br* into (III) and $GePh_3Br$; *Li* in NH_2Et gives $LiGePh_3$ and $LiSiEt_3$ [treatment of the mixture with NH_4Br affords (I) and $GeHPh_3$; with $EtBr$, $SiEt_3$, and $GePh_3Et$ result]. *Si benzyl Et*, b.p. 267—269° (corr.), is obtained from $CH_2Ph \cdot SiCl_3$ and $MgEtBr$ or, better, from (III) and $CH_2Ph \cdot MgCl$. $SiPhEt_3$ is prepared from $SiPhCl_3$ and $MgEtBr$ [not from (III) and $MgPhBr$ or $ZnPh_2$], whilst $(SiEt_3)_2$, b.p. 255° (corr.), is readily obtained from (III) and *Na* at 140—145°. H. B.

Structural and stereochemical relationships among the disulphines and diammines of platinum and palladium. H. D. K. DREW and G. H. WYATT (*J.C.S.*, 1934, 56—62).—Interaction of $Pt esCl_2$ [(I); $es = (SEt \cdot CH_2)_2$] and $(\cdot CH_2 \cdot NH_2)_2$ (= en) in H_2O affords some $[Pt en_2]Cl_2$ and (ethylene-diamino)ethylenediethyldisulphineplatinous chloride, $[Pt es en]Cl_2$ [+ H_2O ; *plato-salt*, decomposed by H_2O to give (I) and $Pt enCl_2$ (II); *pallado-salt*, decomposed by hot H_2O into $Pd esCl_2$ and (II); but with boiling 16% HCl gives (I) and $(en H_2)PdCl_2$, converted by warm H_2O into $Pd enCl_2$ (cf. A., 1900, i, 209)] (also formed by interaction of (II) and $es \cdot H_2O$ at 100° during 2 hr.), which is decomposed by dil. HCl to give (I) and en. When $[Pt es en]Cl_2$ is heated with dil. HCl , en, the more stable group, is lost from *cis*-positions to give (I). This, together with the decomp. of the *plato*- and *pallado*-salts, indicates that the cation $[Pt es en]$ has positive charges located on the N atoms (cf. A., 1933, 1040). (I), m.p. 188°, scarcely depresses the m.p. of $Pd esCl_2$, m.p. 182°, which indicates their

structural and stereochemical similarity and, from the foregoing, (I) and (II) are similar, but it is uncertain whether (II) corresponds structurally with Pd esCl_2 and (I). Interaction of $\beta\text{-Pt}(\text{Et}_2\text{S})_2\text{Cl}_2$ and H_2O -en at room temp. during 2 hr. affords a solution of $[\text{Pt}(\text{Et}_2\text{S})_2\text{en}]\text{Cl}_2$ [plato-salt, decomposed by hot H_2O into (II), $\text{Pt}(\text{Et}_2\text{S})\text{Cl}_2$ (III), $\text{Pt}(\text{Et}_2\text{S})_2\text{Cl}_2$ (IV) (α - and β -forms), and (V) (below)], which easily loses Et_2S to give *ethylenediaminomono(diethylsulphine)platinous chloride* (V), $[\text{Pt}(\text{Et}_2\text{S})\text{en}]\text{Cl}_2$ [plato-salt, isolated as the monohydrate, is decomposed by boiling H_2O into (V), (IV), (III), and (II)], and some $[\text{Pt en}_2]\text{Cl}_2$. (V), together with $[\text{Pt en}_2]\text{Cl}_2$ and (II) is formed from (II) and H_2O - Et_2S at 100° during 0.5 hr., whereas $\alpha\text{-Pt}(\text{Et}_2\text{S})_2\text{Cl}_2$ and H_2O -en affords only $[\text{Pt en}_2]\text{Cl}_2$, which is attributed to the difficulty of accommodating the entering chelate grouping; hence the β -platinous disulphines are given a planar *cis*-structure (cf. A., 1933, 1282; A., 1930, 559), which differs stereochemically and structurally from the configuration of the α -isomerides. Because β -(IV) and $\beta\text{-Pt}(\text{Et}_2\text{S})_2\text{Br}_2$ react with Br and Cl_2 , respectively, to give $\text{Pt}(\text{Et}_2\text{S})_2\text{Cl}_2\text{Br}_2$ (VI) (cf. A., 1930, 559), which probably exists in easily interconvertible α - and β -forms, (VI) must have a symmetrical structure with the entering halogens added in the *trans*-positions, a facile migration [similar to that which occurs in the $\beta \rightarrow \alpha$ (IV) change] of one SEt_2 group and one or both halogens accounting for the $\alpha \rightarrow \beta$ -change. The platinous tetrammines are planar (cf. A., 1932, 797; A., 1933, 1040), whence the conclusion that $\alpha\text{-Pt}(\text{NH}_3)_2\text{Cl}_2$ has a *trans*-planar structure; the β -isomeride has a *cis*-structure. Contrary to Werner, the α -disulphines correspond with the α - and not the β -diammines. The m.p. of $\text{Pd}(\text{Et}_2\text{S})_2\text{Cl}_2$ (VII) is depressed on admixture with β -(IV), but not with the isomorphous α -isomeride; hence (VII) has a *trans*-planar formula. The behaviour of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ with en, and the decomp. of $[\text{Pd}(\text{NH}_3)_2\text{en}]\text{Cl}_2$ by HCl, indicate that it has a *trans*-planar structure. The cryst. chelate platinous and palladous disulphines and diammines have (provisionally) halogen attached to the metal (cf. A., 1933, 1282). Interaction of palladous diammines or disulphines in H_2O with a sulphide or amine affords the following results: Et_2S and Pd enCl_2 (VIII) give $[\text{Pd en}_2]\text{Cl}_2$ and (VII) probably through the unstable $[\text{Pd}(\text{Et}_2\text{S})\text{en}]\text{Cl}_2$; es and (VIII) give Pd esCl_2 (IX) and (VIII); es and $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ give (IX) and $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$; es and (VII) give (IX) and (VII); en and (IX) give $[\text{Pd en}_2]\text{Cl}_2$ and (IX). J. L. D.

Slow oxidation of cyclopentanes with one substituent below their b.p. P. DUPONT and G. CHAVANNE (Bull. Soc. chim. Belg., 1933, 43, 537—543).—*cyclopentanone* and MgPhBr give *cyclopentylidenecyclopentanone* (semicarbazone, m.p. 222°), *phenylcyclopentene* (I), and *1-phenylcyclopentanol*, b.p. $121\text{--}121.1^\circ/6\text{ mm.}$, dehydrated by 85% HCO_2H to (I), m.p. 23° , b.p. $109^\circ/14\text{ mm.}$, which is rapidly hydrogenated (Pt-black) in AcOH to *phenylcyclopentane*, b.p. $102\text{--}102.6^\circ/18\text{ mm.}$ This, when oxidised at 130° under the conditions previously described (A., 1930, 1035), gives benzoylbutyric acid, BzOH , and COPhBu . *Ethylcyclopentane* gives similarly HCO_2H ,

AcOH, EtCO_2H , δ -keto-*n*-heptonic acid (also prepared by KMnO_4 from 1-ethylcyclopentene), COEtBu (also prepared by CrO_3 from $\text{CHEtBu}\cdot\text{OH}$) (semicarbazone, m.p. 110°). *Methylcyclopentane* gives BuCO_2H , PrCO_2H , δ -ketononoic acid, b.p. $142^\circ/2\text{ mm.}$, m.p. 40° [semicarbazone, m.p. 133° (block)], and a ketone, $\text{C}_9\text{H}_{18}\text{O}$ [semicarbazone, m.p. 151° (block), $142\text{--}145^\circ$ (capillary)] [not COBu_2 (semicarbazone, m.p. 90°)]. All three cyclopentanes give also CO_2 , H_2 , and a little CO, but no ethylenic or OH-compounds. Oxidation thus ruptures the ring at the *tert.* C. R. S. C.

Determination of constitution by measurement of the mol. depression of the m.p. Constitution of polymerides of cyclopentadiene. J. PIRSCH (Ber., 1934, 67, [B], 101—104; cf. A., 1933, 770).—The argument is based on the observations (*loc. cit.*) that dicyclic compounds of which the mol. structure is almost equally developed in all three spatial directions have very high mol. m.-p. depressions. In this sense the vals. of α -dicyclopentadiene, its H_2 - and H_4 -derivatives confirm the structure assigned to these substances by Alder *et al.* (A., 1933, 941). Tricyclopentadiene and its H_2 - and H_4 -compounds in which the addition of the third cyclopentadiene mol. has caused lengthening in one direction have vals. for E , 8.1—10.4. H. W.

Action of sodium on 1 : 4-dibromocyclohexane. N. D. PRIANTSCHNIKOV and S. I. SCHUJKINA (Ber., 1934, 67, [B], 64—67).—Evidence of the formation of a dicyclic hydrocarbon by the action of Na on 1 : 4-dibromocyclohexane in *disoamyl* ether is not obtained. The product adds Br, is readily oxidised by KMnO_4 to succinic and adipic acids, and is dehydrogenated (Pd-asbestos) to C_8H_8 . These reactions and the physical consts. indicate that it is a mixture of cyclohexadiene (I), cyclohexene, and cyclohexane (II). (I) and (II) form an azeotropic mixture, b.p. 79.2° . H. W.

Carbon rings. XXVII. 26-, 28-, 30-, 32-, and 33-Membered carbon rings and the physical properties of large carbon rings. L. RŮŽICKÁ, M. HŮRBNÍ and M. FUERER (Helv. Chim. Acta, 1934, 17, 78—87).—Revised physical data for further purified samples of *cyclohexacosane*, m.p. $43\text{--}44^\circ$, -octacosane, m.p. $47\text{--}48^\circ$, -triacontane, m.p. $57\text{--}58^\circ$, b.p. $230^\circ/0.2\text{ mm.}$, -triacontanone, m.p. 56° , b.p. $230^\circ/0.25\text{ mm.}$, -triacontane-1 : 16-dione (*dipicrate* of amino-guanidine compound), and -dotriacontane-1 : 17-dione (I), m.p. $77\text{--}78^\circ$, are given. Clemmensen reduction of (I) affords *cyclodotriacontane*, b.p. $230^\circ/\text{high vac.}$, m.p. $59\text{--}60^\circ$. From the boiling EtOH-insol. portion of the semicarbazone from the distillation residue of *cycloheptadecanone* is obtained (as its disemicarbazone) *cyclotetatriacontane-1 : 17-dione* (II), b.p. $260\text{--}280^\circ/0.1\text{ mm.}$, m.p. $83\text{--}84^\circ$, reduced (EtOH-Na) to the -1 : 17-diol, b.p. $250\text{--}260^\circ/0.1\text{ mm.}$, m.p. $110\text{--}111^\circ$. Clemmensen reduction of (II) affords *cyclotetatriacontanone*, b.p. $250^\circ/0.3\text{ mm.}$, m.p. $64\text{--}64.5^\circ$, and *cyclotetatriacontane*, b.p. $230\text{--}240^\circ/0.3\text{ mm.}$, m.p. $66\text{--}67^\circ$. The relationships of d , M_n , and m.p. of large C rings with the no. of C atoms are discussed.

J. W. B.

Ultra-violet radiation in the photochemical oxidation of toluene.—See this vol., 264.

Electrolytic reduction of aromatic-nitro-compounds.—See this vol., 263.

Identification of nitrobenzene and phenol by formation of resorufin. H. EICHLER (Z. anal. Chem., 1934, 96, 21—22; cf. this vol., 268).—PhNO₂ (I), but not other NO₂-compounds, yields resorufin (II) (yellowish-red fluorescence in alkaline solution) when heated with resorcinol in conc. H₂SO₄. PhOH also yields (II) when heated with (I) and H₂SO₄. J. S. A.

Photochemical reaction between *m*-dinitrobenzene, ethyl alcohol, and ammonia.—See this vol., 264.

Nitration of alkylbenzenes. I. Nitration of *p*-ethyltoluene. O. L. BRADY and J. N. E. DAY. **II. Nitro-derivatives of *n*-propylbenzene.** O. L. BRADY and R. N. CUNNINGHAM (J.C.S., 1934, 114—121, 121—124; cf. A., 1933, 1153).—I. 4-Methylacetophenone (I) [2 : 4-dinitrophenylhydrazone, m.p. 256° (decomp.)] is reduced by Zn-Hg in boiling dil. HCl to *p*-C₆H₄MeEt (II), b.p. 160—161°/748 mm. (II) affords with hot HNO₃ (*d* 1.42—1.5) and H₂SO₄ (*d* 1.84) during 2—3 hr. a product which contains *p*-C₆H₄Me·CO₂H (III), (II), (I), 2-nitro-*p*-ethyltoluene (IV), b.p. 248°/760 mm. [oxidised by boiling HNO₃ to 2-nitro-*p*-toluic acid (V) identical with a specimen prepared from (III)], and 3-nitro-*p*-ethyltoluene isolated as 3(?)-benzamido-*p*-ethyltoluene, m.p. 131° (different from the 2-Bz compound), after reduction with Sn-HCl. The amine affords an *Ac* derivative (VI), m.p. 118°, which consists probably of mixed crystals of 2- and 3-acetamido-*p*-ethyltoluene. Dinitration of (VI) affords a compound which only slightly depresses the m.p. of the (NO₂)₂-compound from 2-acetamido-*p*-ethyltoluene; the m.p. of the hydrolytic product of either is 183°. 2 : 4-Dinitrophenylhydrazine also yields *p*-tolylacetaldehyde-dinitrophenylhydrazone, m.p. 206°, when nitration occurs under less severe conditions, but sufficiently severe to mononitrate PhMe completely. (II) with HNO₃ (*d* 1.5) at 20° during 1 hr. affords 2 : 3-dinitro-*p*-ethyltoluene, m.p. 51.5°, oxidised (K₂Cr₂O₇) to 2 : 3-dinitro-*p*-toluic acid (cf. A., 1890, 52). (II) by a three-stage nitration affords 2 : 3 : 6-trinitro-*p*-ethyltoluene (VII), m.p. 93°, and an oil, which affords with N₂H₄·H₂O in EtOH the hydrazine of (V), but not of the 2 : 3 : 5-compound. (VII) with N₂H₄·H₂O in boiling EtOH in 10 min. affords 2 : 6-dinitro-3-hydrazino-*p*-ethyltoluene, m.p. 171° (decomp.), converted by Cu(OAc)₂ in AcOH at 100° during 0.5 hr. into 2 : 6-dinitro-*p*-ethyltoluene (VIII), m.p. 60° [oxidised by K₂Cr₂O₇ to 2 : 6-dinitro-*p*-toluic acid (*Me* ester, m.p. 87—88°), identical with a specimen obtained by nitrating *p*-toluic acid]; with warm EtOH-NH₃ during 3 hr. (VII) affords 2 : 6-dinitro-3-amino-*p*-ethyltoluene, m.p. 143°, converted by NaNO₂ in hot EtOH-oleum into (VIII). (VII) in boiling EtOH with NH₃·Me during 0.5 hr. affords 2 : 6-dinitro-3-methylamino-*p*-ethyltoluene, m.p. 168°, whereas with N₂H₄·H₂O in boiling EtOH in 1.5 hr., it affords 6-nitro-1-hydroxy-7-methyl-4-ethyl-1 : 2 : 3-benzotriazole, m.p. 224° (decomp.). (VIII) with (NH₄)₂S in boiling EtOH during 1 hr. affords 2-nitro-6-amino-*p*-ethyltoluene, m.p. 96° (*Ac* derivative, m.p. 166°). Interaction of (I) and

HNO₃ (*d* 1.5) at 5—10° affords 3-nitro-4-methylacetophenone (IX) (A., 1891, 1020) [*oxime*, m.p. 133°; *semi*-carbazone, m.p. 262° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 232°], oxidised by boiling HNO₃ to (V), and reduced (Fe-HCl) to 3-amino-4-methylacetophenone, m.p. 80° [2 : 4-dinitrophenylhydrazone, m.p. 265° (decomp.); *Ac* derivative, m.p. 142° [*semicarbazone*, m.p. 252° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 280° (decomp.)]], further reduced (Clemmensen) to 2-amino-*p*-ethyltoluene, the *Ac* derivative of which is identical with that from (IV) after reduction. This orients (IV). Reduction of (IX) (Hg-Zn, boiling HCl) during 6 hr. affords a product, b.p. 220—228°/768 mm., acetylated to 2-acetamido-*p*-ethyltoluene (X), m.p. 137°, identical with the product obtained by reduction and acetylation of 2-nitro-*p*-ethyltoluene. 2-Benzamido-*p*-ethyltoluene has m.p. 119°. (X) with HNO₃ (*d* 1.5) at —5° to —10° during 15 min. affords 3 : 5-dinitro-2-acetamido-*p*-ethyltoluene, m.p. 176°, hydrolysed (H₂SO₄-EtOH) to 3 : 5-dinitro-2-amino-*p*-ethyltoluene, m.p. 183°. 2- and 3-Methylacetophenone afford 2 : 4-dinitrophenylhydrazones, m.p. 159° and 207°, respectively.

II. Interaction of PhPr^a (XI) with H₂SO₄ and HNO₃ (*d* 1.42) below 40° affords crude 2 : 4-dinitro-*n*-propylbenzene (XII), reduced by (NH₄)₂S in boiling EtOH during 0.5 hr. to 2-nitro-4-amino-*n*-propylbenzene, m.p. 59° [*Ac* derivative (XIII), m.p. 90°], which with NaNO₂ in H₂SO₄-EtOH at 100° during 15 min. affords *o*-nitro-*n*-propylbenzene, b.p. 133—136°/26 mm. oxidised by KMnO₄ during 2 hr. to *o*-NO₂·C₆H₄·CO₂H. (XII) with SnCl₂ in hot EtOH during 2 hr. affords 4-nitro-2-amino-*n*-propylbenzene, m.p. 73°. Nitration of (XIII) at 0° gives 2 : 3-dinitro-4-acetamido-*n*-propylbenzene, m.p. 130°, hydrolysed by hot 50% H₂SO₄ to 2 : 3-dinitro-4-amino-*n*-propylbenzene, m.p. 124°; removal of NH₂ affords 2 : 3-dinitro-*n*-propylbenzene, m.p. 64° which is oxidised (K₂Cr₂O₇-H₂SO₄) to 2 : 3-(NO₂)₂·C₆H₃·CO₂H. (XI) in H₂SO₄ (*d* 1.8)—HNO₃ (*d* 1.42) containing a little H₂O affords a NO₂-compound. The mixture of amines obtained on reduction (Sn-HCl) is acetylated and the NHAc-compounds (XIV) are nitrated at —5° to give 3 : 5-dinitro-*n*-propylbenzene, m.p. 51°, oxidised (K₂Cr₂O₇-H₂SO₄) to 3 : 5-(NO₂)₂·C₆H₃·CO₂H. Interaction of (XIV) with HNO₃ (*d* 1.5) in AcOH at 0° during 1 hr. gives a product hydrolysed to an amine; the NH₂ is removed with NaNO₂ to give *m*-nitro-*n*-propylbenzene, b.p. 136°/16 mm., oxidised to *m*-NO₂·C₆H₄·CO₂H. Nitration of (XI) gives an impure (NO₂)₂-compound which appears not to be further nitrated, although energetic nitration of (XII) followed by reduction with (NH₄)₂S affords a little 2 : 6-dinitro-4-amino-*n*-propylbenzene, m.p. 162°.

J. L. D.

Catalytic reduction of arylsulphonyl chlorides with palladium. P. DE SMET (Natuurwetensch. Tijds., 1934, 15, 215—226).—The following have been prepared by reducing the corresponding sulphonyl chloride with Pd-H₂ in aq. COMe₂: phenyl- (*Na* salt, +2H₂O), *p*-bromo- (*Na* salt, +2H₂O), and *p*-chlorophenyl-, β-naphthyl-, and *m*-phenylenedi-sulphinic acids. The rapid reaction of zero order is followed by a very slow reduction to the corresponding disulphides. 1 : 3 : 5-C₆H₃(SO₂Cl)₃ is completely decomposed.

Mobility of groups containing a sulphur atom.

III. D. W. COWIE and D. T. GIBSON (J.C.S., 1934, 46—48).—The *p*-directing influence of the SMe group is confirmed (cf. A., 1932, 837). Interaction of cyclohexylsulphonylacetone (I), *d*-camphorylthiolsulphonate (II), and Na₂CO₃ affords anhydrocamphorsulphonylacetone (III) and an oil, which after hydrolysis and oxidation affords cyclohexylsulphonylmethylsulphonylmethane (IV), m.p. 119°, also formed from methylsulphonylacetone (V), m.p. 54° (prepared from MeSO₂Na and CH₂Cl·COMe), cyclohexyl cyclohexanethiolsulphonate, m.p. 38° (lit., b.p. 184°/0.1 mm.), and NaOEt followed by hydrolysis and oxidation. Similarly, ethylsulphonylacetone (VI) and (II) afford *d*-camphorsulphonic acid, (III), and camphorsulphonylmethylsulphonylmethane (VII), m.p. 123°. (I) with Et ethanethiolsulphonate (VIII) affords a product oxidised to MeSO₂Et; also α -ethylsulphonyl- α -ethylthioacetone [converted into bisethylsulphonylmethane (IX)] and α -cyclohexylsulphonyl- α -ethylthioacetone, b.p. 132°/0.2 mm., hydrolysed to cyclohexylsulphonylethylthiomethane, m.p. 38°. Camphordisulphoxide (X), (V), and NaOEt afford (VII), but with (VI) and Na₂CO₃ after hydrolysis and oxidation, (X) gives camphorsulphonylethylsulphonylmethane, m.p. 85°. (V), (VIII) in excess, and Na₂CO₃ after hydrolysis and oxidation give (IX), but with equimol. quantities afford methylsulphonylethylsulphonylmethane, m.p. 95°, different from (IX). Benzyl benzylthiolsulphonate, (V), and Na₂CO₃ give after hydrolysis methylsulphonylbenzylthiolmethane, m.p. 54°, different from (V). (V), *p*-tolyl *p*-toluenethiolsulphonate, and NaOEt afford methylsulphonyl-*p*-tolylthioacetone, m.p. 50°, hydrolysed and then oxidised to *p*-tolylsulphonylmethylsulphonylmethane. CH₃Bz·CN in the theoretical amount of NaOH gives with *m*-*p*-toluenethiolsulphonate (XI) in EtOH, ω -cyano- ω -methylthioacetophenone, m.p. 50°. 4-Chlorophenylsulphonylacetone (1 mol.), (XI) (1 mol.), and KOAc (1 mol.) in EtOH during 5 days afford a 50:50 mixture of the "exchanged" and "normal" material. *m*-Nitrophenylsulphonyl-acetic ester and -acetophenone are not obtained from the Na sulphinate and CH₂Cl·CO₂Et or CPh·CH₂Br (cf. A., 1912, i, 389); Na *o*-nitrophenylsulphonylacetate and PhSNa afford *o*-nitrodiphenyl sulphide, a smoother replacement than those of Levi and Smiles (A., 1932, 735). Interaction of CH₂O and PhSH affords a product which when oxidised gives bisphenylsulphonylmethane, m.p. 121—122°, methylated to bisphenylsulphonylethane (XII), identical with the products of Steinkopf *et al.* (A., 1930, 1566), and $\beta\beta$ -bisphenylsulphonylpropane (A., 1930, 900). (XII) is also obtained from PhSO₂F and MgEtI.

J. L. D.

Action of air in determining the course of bromination. J. HANNON and J. KENNER (J.C.S., 1934, 138).—Bromination of 2:2'-ditolyl is increased by accession of dry air. *o*-Iodocyanobenzene, m.p. 54—55°, with Cu powder gives 2:2'-dicyanodiphenyl, m.p. 176—177°.

F. R. S.

Reaction of potassamide in liquid ammonia with chloroethylenes. G. H. COLEMAN and R. D. MAXWELL (J. Amer. Chem. Soc., 1934, 56, 132—134).—C₂Ar₂·CHCl (I) and CHAr·CHCl₂, prepared by the

methods of Buttenberg (A., 1894, i, 502) and Wicchell (*ibid.*, 507), react rapidly with KNH₂ in liquid NH₃ to give CAr₂:CAr (II). The following are new: β -chloro- α -di-*p*-ethylphenyl-, b.p. 165—166°/1 mm., -di-*p*-*n*-propylphenyl-, b.p. 178—181°/1 mm., -di-*p*-*n*-butylphenyl-, b.p. 190—192°/1 mm., and -di-*m*-4-xyllyl-, b.p. 166—170°/1 mm., -ethylene; $\beta\beta$ -dichloro- α -di-diphenyllethane, m.p. 139—140° [all m.p. (and b.p.) except this are corr.]; 4:4'-diethyl-, m.p. 71.5—72.5°, -di-*n*-propyl-, m.p. 69.5—70.5°, -di-*n*-butyl-, m.p. 41—42°, and -diphenyl-, m.p. 243—244° [oxidised (O₃) to *p*-C₆H₄Ph·CO₂H], and 3:4:3':4'-tetramethyl-, m.p. 143—144°, -tolane. (I) show non-selective absorption in the region 200—280 μ ; (II) show two characteristic absorption bands.

H. B.

Indirect hydrolysis of hexaphenylethane. W. E. BACHMANN (J. Amer. Chem. Soc., 1934, 56, 239—240).—Addition of a solution of CPh₃+MgI₂ in Et₂O-C₆H₆ to H₂O and subsequent aeration gives CPh₃·OH, CHPh₃, and a little (CPh₃·O)₂; I is liberated during the hydrolysis and the following reactions probably occur: (i) CPh₃+I→CPh₃I; (ii) CPh₃I+H₂O→CPh₃·OH+HI; (iii) 2CPh₃+HI→CHPh₃+CPh₃I. In agreement with this view, equiv. amounts of CHPh₃ and CPh₃·OH are obtained when CPh₃ in C₆H₆ is shaken with H₂O containing a little I. Treatment of CPh₃·MgBr with I and subsequent hydrolysis gives CPh₃·OH, CHPh₃, and a little (CPh₃·O)₂; 2CPh₃·MgBr+I₂→2CPh₃+MgI₂+MgBr₂. CPh₃·CO₂H is not obtained from CO₂ and CPh₃+MgI₂ in Et₂O-C₆H₆ unless Mg is present (cf. Gorski, A., 1913, i, 1341). CPh₃ promotes oxidation of MgI₂ by atm. O₂; the active agent is probably the CPh₃O₂ radical (cf. Ziegler and Ewald, A., 1933, 943).

H. B.

Transformation of α - into β -naphthalene derivatives under the influence of catalysts. F. MAYER and R. SCHIFFNER (Ber., 1934, 67, [B], 67—69).—1-Phenyl-3:4-dihydronaphthalene is converted by passage over SiO₂ gel (I) at 350° into 2-C₁₀H₇Ph (II). 1-C₁₀H₇Ph is isomerised to (II) in presence of (I), Co, or Cu silicate at about 350°. 1-C₁₀H₇Me and 1-C₁₀H₇Et are similarly isomerised when passed over (I) at about 420°, whilst 1:6- affords 2:6-C₁₀H₆Me₂. 1-isoPropenylnaphthalene affords essentially C₁₀H₈. 1- passes into 2-C₁₀H₇Br.

H. W.

Synthesis of polynuclear hydrocarbons by cyclodehydration of aromatic alcohols. M. T. BOGERT, D. DAVIDSON, and R. O. ROBLIN, jun. (J. Amer. Chem. Soc., 1934, 56, 248; cf. A., 1933, 153, 599, 601).—1-Ethyl-1:2:3:4-tetrahydronaphthalene is obtained by the action of H₂SO₄ on ϵ -phenyl- α -methylamyl alcohol or ζ -phenyl- Δ^{α} -hexene. γ -Phenyl- α -methyl- α -ethylpropyl alcohol similarly gives 1:2-dimethyl-1:2:3:4-tetrahydronaphthalene and 1-methyl-1-ethylindane.

H. B.

Synthesis of nine chloriodonaphthalenes. R. W. BEATTIE and F. C. WHITMORE (J.C.S., 1934, 50—52).—Interaction of 1:4-C₁₀H₆Cl₂·HgCl (I) (cf. A., 1933, 619), I, and NaI in boiling EtOH affords 1-chloro-4-iodonaphthalene, m.p. 54.5° (90%) (cf. A., 1900, i, 282). The following are prepared similarly: 1-chloro-5-, m.p. 89° (73%), -6-, m.p. 57° (70%), -7-, m.p. 39° (63%), and -8-iodonaphthalene, m.p. 80.5°

(84%); 2-chloro-1-, m.p. 63° (64%), -6-, m.p. 141° (70%), -7-, m.p. 129° (70%), and -8-iodonaphthalene, m.p. 55.5° (71%). (I) and Br in boiling CCl_4 during 2.5 hr. afford 1:4- $\text{C}_{10}\text{H}_6\text{ClBr}$, free from isomerides, and identical with a sample obtained by brominating 1- $\text{C}_{10}\text{H}_7\text{Cl}$. 2- $\text{C}_{10}\text{H}_7\text{HgCl}$ and I afford 2- $\text{C}_{10}\text{H}_7\text{I}$, which demonstrates the validity of the synthetic method. J. L. D.

Dehydrogenation of cholesterol and ergosterol and non-identity of the hydrocarbon $\text{C}_{18}\text{H}_{16}$ with 1:2-cyclopentenophenanthrene. O. DIELS and H. KLARE (Ber., 1934, 67, [B], 113—122).—Ruzicka's assumption (A., 1933, 820) that the hydrocarbons $\text{C}_{25}\text{H}_{24}$ (I) from cholesterol (II) and ergosterol (III) are different is refuted. The dehydrogenation of (III) by Se is described in detail, together with the purification of (I). The supposed identity of 1:2-cyclopentenophenanthrene (IV) (Cook *et al.*, *ibid.*, 1042) with $\text{C}_{18}\text{H}_{16}$ (V) cannot be maintained. (V) and (IV) have m.p. 125—126° and 137—138°, respectively, and differ appreciably in the compounds they form with picric acid and $s\text{-C}_6\text{H}_3(\text{NO}_2)_3$. Further, (IV) does not show the reaction towards N_2O_3 which is particularly typical of (V). The absorption spectra of (I) from (II) or (III) are practically identical, whereas that of (IV) is closely similar, but exhibits divergencies outside the limits of experimental error. Possibly (V) is identical with the 3-methyl-1:2-cyclopentenophenanthrene of Kon (A., *ibid.*, 1153), but differs from the compound thus described by Bergmann (*ibid.*, 1154). H. W.

Polycyclic compounds related to the sterols. II. Diels' hydrocarbon, $\text{C}_{18}\text{H}_{16}$. S. H. HARPER, G. A. R. KON, and F. C. J. RUZICKA (J.C.S., 1934, 124—128).—Interaction of Mg β -(α -naphthyl)ethyl bromide and 2-methylcyclopentanone in warm Et_2O during 0.5 hr. affords 2-methyl-1- β -(α -naphthyl)ethylcyclopentanol (I), b.p. about 190°/3 mm., and $\alpha\delta$ -di-(α -naphthyl)butane, m.p. 102° (*bistrinitrotoluene* compound, m.p. 131°). (I) with P_2O_5 at 140° during 40 min. affords 1-methyl-1:2-cyclopentano-1:2:3:4-tetrahydrophenanthrene (II), b.p. 155°/0.4 mm., dehydrogenated to cyclopentenophenanthrene (III) (cf. A., 1933, 601, 1153). Interaction of 2- β -(α -naphthyl)ethylcyclopentanone and MgMeI in Et_2O affords an undistillable product, dehydrated (P_2O_5) to (II) and then dehydrogenated to (III) (*trinitrotoluene* compound, m.p. 102°) (cf. A., 1933, 820), but no by-product is formed in this reaction. Interaction of 2:5-dimethylcyclopentanone (cf. A., 1924, i, 1203) and MgMeI affords 2:5-dimethyl-1- β -(α -naphthyl)ethylcyclopentanol, b.p. 190—195°/0.2 mm., converted (P_2O_5) into 1:3'-dimethyl-1:2-cyclopentano-1:2:3:4-tetrahydrophenanthrene, b.p. 160°/0.4 mm., and dehydrogenated to a mixture containing a hydrocarbon, m.p. 230°, the *trinitrobenzene* derivative of which, m.p. 145—146°, affords, after treatment with SnCl_2 in boiling HCl (cf. A., 1933, 1042), 3'-methyl-1:2-cyclopentenophenanthrene (IV), m.p. 125—126° [*picric acid* (V), m.p. 118—119°; *trinitrotoluene* compound (VI), m.p. 93°]. (IV), (V), and (VI) are identical (mixed m.p.) with the corresponding compounds prepared from Diels' hydrocarbon (VII). The ultra-violet absorption spectrum and cryst. form of (IV) agree closely

with those of (VII). Bergmann and Hillemann's product (cf., A., 1933, 1154) is prepared according to their directions and shows significant differences in physical properties from (IV). J. L. D.

Isomerisation of the hydrocarbon $\text{C}_{42}\text{H}_{30}$, isomeric with 1:3:1':3'-tetraphenyl-1:1'-dihydorubene. Ninth isomeride. Oxidative scissions. A. WILLEMART (Compt. rend., 1933, 197, 1659—1661).—When heated in xylene with $\text{K}_3\text{Fe}(\text{CN})_6$ (or HgO , PbO , etc.) the colourless hydrocarbon $\text{C}_{42}\text{H}_{30}$ (I), m.p. 179° (this vol., 180), affords another yellow isomeride, m.p. 225°. Repetition of Halley and Marvel's oxidation (A., 1933, 57) of (I) with CrO_3 gives 30—40% of COPH_2 , in addition to BzOH and $o\text{-C}_6\text{H}_4\text{BzCO}_2\text{H}$, so that only partial cyclisation of $\alpha\gamma\delta\delta'$ -hexaphenyl- $\Delta^{\alpha\alpha}$ -hexadiene can occur during rearrangement to (I). Similar oxidation of the yellow isomeride, m.p. 249° (*loc. cit.*), gives the same products and a trace of a substance, m.p. 240°, whereas KMnO_4 affords only a yellow substance, $\text{C}_{42}\text{H}_{30}\text{O}_2$, m.p. 277°. J. W. B.

Compounds of bivalent metallic selenates with aniline. C. H. KAO and T. L. CHANG (J. Chinese Chem. Soc., 1933, 1, 116—119).—Compounds, $\text{MSeO}_4 \cdot 2\text{NH}_2\text{Ph}$, are prepared from the hydrated selenate and NH_2Ph at room temp. or that stated in parentheses, M being Cu, Zn, Ni (100°), Co^{II} (80°), and Cd (in presence of a little H_2O). The Mn compound could not be obtained. R. S. C.

Increase in the life-period of β -chloro- β -phenylethylamine by carbon.—See this vol., 262.

Hydrolysis of substituted benzenesulphonanilides. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1934, 56, 114—117).—*o*- and *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NPhR}$ are decomposed by 80% NaOH at 195—220° to NHPhR , $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, and Na_2SO_3 ; the ease of fission is *o* > *p*. $\text{PhSO}_2 \cdot \text{NHPh}$ is similarly unaffected at 250°. $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NHPh}$ undergoes a small amount of fission at 240°, whilst 2:4-(NO_2) $_2 \cdot \text{C}_6\text{H}_3 \cdot \text{SO}_2 \cdot \text{NPhR}$ are readily cleaved at 125—155°. 2:4-(NO_2) $_2 \cdot \text{C}_6\text{H}_3 \cdot \text{SO}_3\text{H}$ is prepared by oxidation (fuming HNO_3) of 2:4:2':4'-tetranitrodiphenyl disulphide. NH_2Ph and NHPhMe are separable from one another and from NPhMe_2 by *o*-nitrobenzenesulphonylation; the amines are recovered as above. *o*-Nitrobenzenesulphonanilide, m.p. 114—115°, and -methylanilide, m.p. 71—72°, *p*-nitrobenzenesulphonanilide, m.p. 135—136°, and -methylanilide, m.p. 117—118°, and 2:4-dinitrobenzenesulphonanilide, m.p. 112—113°, and -methylanilide, m.p. 148—149°, are described. H. B.

Action of amines on esters of carboxy-carbamides, -thiocarbamides, and -guanidines. III. J. A. MURRAY and F. B. DAINS (J. Amer. Chem. Soc., 1934, 56, 144—146).—Prolonged treatment of Et allophanate (I) with NH_2Me gives α -methylbiuret (II); NH_2Et similarly affords α -ethylbiuret (III). (I) and $\text{CH}_3\text{Ph} \cdot \text{NH}_2$ at 135° give Et γ -benzylallophanate (IV), m.p. 103° (also prepared from $\text{CH}_3\text{Ph} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ and ClCO_2Et); $\alpha\epsilon$ -dibenzylbiuret (V), m.p. 169°, and *s*-dibenzylcarbamide (VI) are formed at 150° and 200°, respectively. (I) and PhNCO at 125° afford some α -carbethoxy- ϵ -phenylbiuret (A., 1919, i, 400), whilst

Et γ -phenylallophanate and $\text{NHPh}\cdot\text{NH}_2$ at 130° give NH_2Ph and 1-phenylurazole (VII) (A., 1921, i, 61). (II) and (III) are obtained from carbonyldiurethane (VIII) and NH_2Me and NH_2Et , respectively. (VIII) and $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ at 115° (or in H_2O) afford (I) and $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$; (I) and (IV) are formed at 135° , (V) at 160° , and (VI) at 200° . N_2H_4 and (VIII) give (I), whilst (VIII) and $\text{NHPh}\cdot\text{NH}_2$ at 115° or 140° afford (VII) [at 160° , *iminodicarboxyphenylhydrazide*, $\text{NH}(\text{CO}\cdot\text{NH}\cdot\text{NHPh})_2$, m.p. 291° , results]. Et thioallophanate is hydrolysed by aq. NH_3 , NH_2Alk , or $\text{EtOH}\cdot\text{KOH}$ to $\text{CS}(\text{NH}_2)_2$; with NH_2Ph and $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ at 160° , $\text{CO}(\text{NHAr})_2$ results.

$\text{CS}(\text{NH}\cdot\text{CO}_2\text{Et})_2$ or $\text{SMe}\cdot\text{C}(\text{N}\cdot\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ (IX) (A., 1930, 1276) and the appropriate NH_2R in EtOH give the γ -substituted $\alpha\beta$ -dicarbethoxyguanidines, $\text{NHR}\cdot\text{C}(\text{N}\cdot\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$; the following are described: $\text{R}=\text{Me}$, m.p. 71° , *Et*, β -hydroxyethyl, m.p. 98° , *benzyl*, *Ph*, m.p. 71° , *o-tolyl*, m.p. 75° , *anilino*, m.p. 192° , *o-hydroxyphenyl*, m.p. 135° , *p-carboxyphenyl*, m.p. 198° , *o-carboxyphenyl* (X), m.p. 174° , *o-carbomethoxyphenyl* (XI), m.p. 67° , *carboxymethyl*, m.p. 210° [hydrolysed (5% $\text{EtOH}\cdot\text{KOH}$) to *carbethoxyguanidinacetic acid*, chars $250\text{--}275^\circ$], and *carbethoxymethyl*, m.p. 56° . (X) and (XI) are hydrolysed ($\text{EtOH}\cdot\text{KOH}$) to 2-carbethoxymino-4-hydroxy-1:2:3:4-tetrahydroquinazoline, m.p. 163° , also formed when (XI) is heated. (IX) and NH_2OH in EtOH give the

compound, $\text{O} \begin{array}{c} \text{NH}\cdot\text{C}\cdot\text{N}\cdot\text{CO}_2\text{Et} \\ \text{CO}\cdot\text{NH} \end{array}$ m.p. 226° ; the compounds, $\text{NH} \begin{array}{c} \text{NH}\cdot\text{C}\cdot\text{N}\cdot\text{CO}_2\text{Et} \\ \text{CO}\cdot\text{NH} \end{array}$ m.p. $> 335^\circ$, and

$\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \text{NH} \end{array} \text{C}\cdot\text{N}\cdot\text{CO}_2\text{Et}$, m.p. 320° (decomp.), are formed from N_2H_4 and $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$, respectively. *s-Di-o-carbomethoxyphenylcarbamide*, m.p. 144° , is obtained from $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ and COCl_2 or (IX) (at 140°). $\alpha\gamma$ -Dicarbethoxyguanidine (A., 1930, 1276) (α -Me derivative, m.p. 85° , from the K salt and Me_2SO_4) and NH_2Ph at 140° give the *triazine*,

$\text{NPh} \begin{array}{c} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{array} \text{C}\cdot\text{NH}$, m.p. $> 335^\circ$; PhNCO affords the ester, $\text{CO}_2\text{Et}\cdot\text{N}\cdot\text{C}(\text{NH}\cdot\text{CO}\cdot\text{NHPh})_2$, m.p. 151° (decomp.), whilst PhNCS gives the *triazine*,

$\text{NPh} \begin{array}{c} \text{CS}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{array} \text{C}\cdot\text{NH}$, m.p. 180° (decomp.) (*S-Me ether*, m.p. 247°). H. B.

Structure of 8-nitro-1-naphthalenesulphonyl-N-phenylglycine. R. E. STEIGER (Bull. Soc. chim., 1933, 53, [iv], 1249—1254).—Interaction of 1-nitro-8-naphthalenesulphonanilide (Na derivative) in EtOH with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ during 2 hr. affords *Et 1-nitro-8-naphthalenesulphonyl-N-phenylglycine* (I), m.p. 150° , hydrolysed by boiling dil. H_2SO_4 to the acid (II), m.p. $182.5\text{--}183^\circ$. The brucine salt of (II) cannot be resolved, which indicates that the NO_2 -group does not impede free rotation about the S-C linking (cf. A., 1928, 748). J. L. D.

Action of nitrous acid on the peri-naphthyl-aminesulphonanilides. R. E. STEIGER (Bull. Soc. chim., 1933, 53, [iv], 1254—1259).—Reduction of 1-nitronaphthalene-8-sulphonanilide with FeSO_4 in NaOH affords the NH_2 -compound, m.p. $143.5\text{--}144.5^\circ$, the diazonium chloride from which is con-

verted by $\text{N}\cdot\text{NaOH}$ at 100° into the *sultam* of 1-o-aminophenylnaphthalene-8-sulphonic acid, m.p. $184\text{--}185^\circ$ (cf. A., 1907, i, 909), which cannot be resolved. Similarly, 1-nitro-5-methylnaphthalene-8-sulphonanilide is converted through the *amine*, m.p. $207.5\text{--}208.5^\circ$, into the *sultam*, m.p. $215.5\text{--}216.5^\circ$, of 1-o-aminophenyl-5-methylnaphthalene-8-sulphonic acid.

J. L. D.

Application of electronic theory to organic compounds. II. Study of the nature of the nitrogen in amine oxides from the viewpoint of the electronic theory. A. M. BERKENHEIM and A. N. TCHIVIKOVA. III. Regrouping of the charges on the carbon ions of the phenyl group during the formation of aromatic amine oxides. A. M. BERKENHEIM, S. I. LURIE, and M. F. ELISEEVA (J. Gen. Chem. Russ., 1933, 3, 411—418, 419—431; cf. this vol., 176).—II. The action of H_2O_2 on *tert.*-amines with the formation of amine oxide was investigated from the viewpoint of the electronic theory, the mechanism being explained as oxidation-reduction. According to this theory, the ion N^{III} should be changed to N^{V} , and the same product, containing S^{IV} and possessing marked reducing properties, should be obtained by the action of SO_3 on the amine oxide as by SO_3 on the *tert.*-amine itself. NPhMe_2 oxide, m.p. $152\text{--}153^\circ$ (decomp.), and SO_2 gave a compound, m.p. $240\text{--}241^\circ$, containing S and showing marked reducing properties, and the same compound was obtained from SO_3 and the amine itself.

III. The theory that oxidation of *tert.*-amines with amine oxides is accompanied by regrouping of the C atom electrons right around the C_6 ring is propounded, and investigated experimentally by introducing groups into the nucleus which might inhibit such a regrouping and so prevent the oxidation. Oxidation of the *tert.*-N in NPhMe_2 alters the charges of the C atom in the *p*-position from $\text{C}^{\text{'''}}$ to $\text{C}^{\text{'''}}$. If, therefore, this atom already carries a group like $\text{SO}_3\text{H}^{\text{'''}}$, $\text{NO}_2^{\text{'''}}$, or $\text{CO}^{\text{'''}}$, such an electronic rearrangement should not occur, and experiments show that *N*-dimethylsulphanilic acid and Michler's ketone cannot be oxidised. Similarly, a group such as OMe in the *m*-position prevents oxidation: *N*-dimethyl-*m*-anisidine cannot be oxidised, whereas the *o*-compound gives the *oxide* (*picrate*, m.p. 151°) which is highly hygroscopic. M. Z.

***p*-Dimethyl- and *p*-diethyl-aminophenylhydrazines.** R. STOLLÉ and K. T. GUNZERT (J. pr. Chem., 1934, [ii], 139, 141—161).—

p- $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{SO}_3\text{H}$, m.p. 179° (decomp.) (cf. A., 1912, i, 920) (*Na salt*), is prepared by reduction of the corresponding diazosulphonate with $\text{Na}_2\text{S}_2\text{O}_4$; it is converted by H_2O at the b.p. into *p*-aminodimethylaniline *p*-dimethylaminobenzenediazosulphonate, m.p. 149° (decomp.), but is hydrolysed by dry HCl in EtOH to *p*-dimethylaminophenylhydrazine dihydrochloride, m.p. 161° (decomp.) {benzylidene, m.p. 138° (decomp.)}; *salicylidene*, m.p. 185° ; $\text{NN}'\cdot\text{Bz}_2$, m.p. 199° (*loc. cit.*) [*hydrochloride*, m.p. 196° (decomp.)]; and *Bz*, m.p. 145° (from the Bz_2 derivative and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH at the b.p.), derivatives of the free base; the last-named is oxidised by $\text{Ca}(\text{OCl})_2$ to *p*-dimethylaminobenzenediazobenzoyl, m.p. 126° (de-

comp. $>200^\circ$). *p*-Diethylaminophenylhydrazine dihydrochloride, decomp. 164° [*p*-tolylidene (hydrochloride, decomp. 165°) and $\text{NN}'\text{-Bz}_2$, m.p. 159° , derivatives of the free base], is similarly prepared. *p*-Diethylamino-benzenediazonium borofluoride, m.p. 113° (decomp.), -benzenediazosulphonic acid [Na (anhyd. and $+6\text{H}_2\text{O}$), K , and NH_4 salts], and -phenylhydrazinesulphonic acid, m.p. 132° (decomp.); Bz , m.p. 209° , and benzylidene, m.p. 145° , derivatives of $4\text{-NH}_2\text{-C}_6\text{H}_4\text{-NPh}_2$; *p*-diphenylaminobenzene-diazonium chloride, m.p. 150° (decomp.), and borofluoride, decomp. 162° , and -diazosulphonic acid (Na salt, decomp. 120°); *p*-aminodiethylaniline *p*-dimethylaminobenzenediazosulphonate, m.p. 158° (decomp.) (by double decomp.); and *p*-dimethylaminobenzenediazonium borofluoride, m.p. 150° (decomp.), are also described. *p*-Dimethylaminobenzenediazosulphonic acid exists in yellow and red (stable) modifications, m.p. 118° (decomp.), of which crystallographic data are given; its Na salt with aq. H_2S gives the (?) diazohydrosulphide ($+ \text{H}_2\text{S}$), decomp. 78° . H. A. P.

4 : 4'-Dihydrazinodiphenylmethane. W. BORSCHE and R. MANTEUFFEL (Ber., 1934, 67, [B], 144; cf. A., 1910, i, 781).—4 : 4'-Dihydrazinodiphenylmethane has m.p. $141\text{--}143^\circ$ (cf. Finger *et al.*, A., 1906, i, 892). Its (CHPh)₂ derivative has m.p. 200° after softening at 196° , whilst ditetramethylenindolylmethane has (air-dried) m.p. 265° (decomp.) and (vac.-dried) m.p. $281\text{--}282^\circ$ when heated slowly. H. W.

Action of acetic acid on 3 : 4-dimethoxybenzenediazonium borofluoride. L. E. SMITH and H. L. HALLER (J. Amer. Chem. Soc., 1934, 56, 237—239).—3 : 4-Dimethoxybenzenediazonium borofluoride, m.p. 123° (decomp.), heated with AcOH gives 2-hydroxy-4 : 5-dimethoxyacetophenone (I) [instead of the expected 3 : 4-dimethoxyphenyl acetate (II) (cf. this vol., 183)] and (probably) a little 1-fluoro-3 : 4-dimethoxybenzene, b.p. $98^\circ/14$ mm. (II) may be first formed and subsequently rearranged to (I) under the influence of BF_3 . 2 : 4 : 5-Trimethoxyacetophenone [semicarbazone, m.p. 206° (softens at 200°) (lit. $186\text{--}188^\circ$)] is oxidised (aq. KMnO_4) to 2 : 4 : 5-trimethoxyphenylglyoxylic acid, m.p. 186° , and thence (alkaline H_2O_2) to asaronic acid. H. B.

Aristol and the preparation of iodophenols. C. V. BORDEIANU (Arch. Pharm., 1934, 272, 8—22).—Thymol 2 : 6-dimercuracetate in dil. aq. NaOH with I-KI-AcOH affords 2 : 6-di-iodothymol (I), m.p. $45\text{--}47^\circ$ (Ac derivative, m.p. $72\text{--}73^\circ$), 6-bromo-2-iodothymol (II), being similarly obtained from the 6-bromo-2-mercuracetate (giving the internal oxide by CO_2 into its NaOH solution). *p*-Xylenol with $\text{Hg}(\text{OAc})_2$ gives its 2 : 6-dimercuracetate, whence 2 : 6-di-iodo-*p*-xylenol (III), m.p. 63° (Ac derivative, m.p. $102\text{--}103^\circ$), is obtained. Iodination of thymol (IV) in alkaline solution gives, successively, the 6-I-compound [prepared in 93% yield by addition of I in MeOH to (IV) in 5% $\text{NH}_3\text{-MeOH}$; oxidised by $\text{CrO}_3\text{-AcOH}$ to iodothymoquinone], (I), and, finally, aristol (V), but (V) is not formed in Na_2CO_3 solutions. Since either (I) or (II) is converted by NaOH (or better with alkaline $\text{K}_2\text{S}_2\text{O}_8$, since oxidation is involved) into (V) thus: $2(\text{I}) + 2\text{NaOH} = \text{C}_{20}\text{H}_{20}\text{O}_2\text{I}_2$ (V) $+ 2\text{NaI} + 2\text{H}_2\text{O}$,

the 6-position must be involved, (V) being the dimeride of 3 : 3'-di-iodo-2 : 2'-dimethyl-5 : 5'-diisopropyl-diphenyl-4 : 4'-quinone. Similarly (III) affords the dimeride of 3 : -di-iodo-2 : 5 : 2' : 5'-tetramethyl-diphenyl-4 : 4'-quinone (xylenolaristol), not melting $< 220^\circ$. J. W. B.

Preparation of *p*-nitrosophenol by nitrosation of phenol. C. L. TSENG and M. HU (J. Chinese Chem. Soc., 1933, 1, 183—187).—A 90% yield of $p\text{-NO-C}_6\text{H}_4\text{-OH}$ is obtained from PhOH , KNO_3 , and AcOH at -10° . R. S. C.

Acyl derivatives of phenetidines. D. M. BIROSEL and H. L. HUANG (Univ. Philippines Nat. Appl. Sci. Bull., 1933, 3, 1—5).—Lauryl chloride and *o*-phenetidine (I) at $120\text{--}130^\circ$ in 6 hr. afford lauryl-*o*-phenetide, m.p. $69\text{--}70^\circ$, in 30% yield. Acid chlorides with (I) in dry COMe_2 in presence of anhyd. Na_2CO_3 gave in 30 min. the following *o*-phenetidides: myristyl-, m.p. 77° (6% yield); palmityl- (II), m.p. $82\text{--}83^\circ$ (18%); stearyl- (III), m.p. $84\text{--}7^\circ$ (30%); chaulmoogryl-, m.p. $280\text{--}3^\circ$ (40%); benzoyl-, m.p. $104\text{--}2^\circ$ (12%); cinnamyl-, m.p. 118° (32%). Mixtures of (II) and (III) melt sharply and behave as individuals. The following *p*-phenetidides were obtained similarly: lauryl-, m.p. $109\text{--}110^\circ$ (17%); myristyl-, m.p. $110\text{--}8\text{--}111^\circ$ (9%); palmityl-, m.p. $117\text{--}5^\circ$ (3%); stearyl-, m.p. $112\text{--}5^\circ$ (30%).

CH. ABS.

Synthesis of chloromethyl derivatives of phenol ethers. R. QUELET (Compt. rend., 1934, 198, 102—105).—Ph alkyl ethers are converted by saturating their mixture with 40% CH_2O in ligroin with gaseous HCl at $0\text{--}5^\circ$ into *p*-(or *o*)- $\text{CH}_2\text{Cl-C}_6\text{H}_4\text{-OR}$ (cf. A., 1933, 707) and thus are obtained: *p*-methoxy- (50% yield), *p*-ethoxy-, unstable, b.p. $123^\circ/15$ mm., 4-methoxy-3-methyl-, b.p. $119^\circ/12$ mm., 4-methoxy-2-methyl-, unstable, b.p. $123^\circ/13$ mm., and 2-methoxy-5-methyl-, b.p. $148^\circ/16$ mm., -benzyl chloride, together with 4 : 4'-dimethoxy-3 : 3'-, m.p. 24° , b.p. $207\text{--}209^\circ$, and -2 : 2'-, m.p. 66° , b.p. $215\text{--}216^\circ/12$ mm., and 2 : 2'-dimethoxy-5 : 5'-, m.p. 55° , b.p. $197\text{--}199^\circ/10$ mm., -dimethyldiphenylmethane, as by-products.

J. W. B.

Influence of the phenyl group on the reactions of thionyl chloride with primary aliphatic alcohols. P. CARRÉ and D. LIBERMANN (Compt. rend., 1934, 198, 274—276).—Unlike $\text{CH}_3\text{Ph-OH}$, $\text{CH}_2\text{Ph-CH}_2\text{-OH}$ and $\text{CH}_2\text{Ph-CH}_2\text{-CH}_2\text{-OH}$ (I) behave as aliphatic alcohols with SOCl_2 . Thus, at room temp. first neutral sulphites (II) and then chlorosulphites (III) are formed, the existence of the latter being proved (a) by hydrolysis to the alcohol and (b) by reaction with an alcohol and $\text{C}_5\text{H}_5\text{N}$ to, e.g., *Bu*⁺ γ -phenylpropyl sulphite, b.p. $191\text{--}193^\circ/24$ mm. $\text{C}_5\text{H}_5\text{N}$ renders formation of (II) almost instantaneous and lowers the temp. of decomp. of (III) by 20° . Thus, (I) in $\text{C}_5\text{H}_5\text{N}$ with SOCl_2 (0.5 mol.) gives γ -phenylpropyl sulphite (IV), b.p. $248\text{--}254^\circ/11$ mm., which decomposes at about $310^\circ/760$ mm. to SO_2 , (I), and CH_3CHPh . The temp. of decomp. of (IV) is lowered by $\text{C}_5\text{H}_5\text{N}$ by about 100° . R. S. C.

Synthesis of phenols with unsaturated side-chains. R. MAJIMA and K. TAMURA (Proc. Imp. Acad. Tokyo, 1933, 9, 606—608).— $\alpha\gamma$ -Dichloro- Δ^{26} .

hexadiene and PhONa in PhMe give *Ph chlorohexadienyl ether* [reduced (catalytically and then Na-EtOH) to the hexyl ether, b.p. 75—77°/1 mm.] and *γ-chloro-Δ⁸-hexadienylphenol*, b.p. 120—140°/1 mm., unstable except in Et₂O, which is a mixture of *o*- and *p*-isomerides, since the *Me ether*, b.p. 108—117°/1 mm., obtained by Me₂SO₄, with KMnO₄ yields anisic and *o*-methoxybenzoic acids; by hydrogenation (Pd-black) is obtained a mixture of *chlorohexylanisoles*, reduced by Na-EtOH to a mixture of *o*- and *p*-hexylanisole, b.p. 85—100°/1 mm. Pyrocatechol gives similarly the *mono*-, b.p. 93—96°/0.8 mm., and possibly the *di-chlorohexadienyl ether* and *γ-chloro-Δ⁸-hexadienylpyrocatechol*, decomp. when distilled, the *Me ether* (obtained by Me₂SO₄) of which gives with KMnO₄ veratric acid, and by reduction *hexylveratrole*, b.p. 100—105°/0.5 mm. R. S. C.

Chloro-derivatives of 4-hydroxydiphenyl. J. C. COLBERT, W. MEIGS, and B. MACKIN (J. Amer. Chem. Soc., 1934, 56, 202—204).—Passage of Cl₂ into a suspension of 4-hydroxydiphenyl (I) in CHCl₃, CCl₄, or CS₂ until dissolution occurs gives the 3-Cl₂-derivative (II), m.p. 76—77.5° (corr.) (*benzoate*, m.p. 95—97°; 2:4-dinitrophenyl ether, m.p. 109—111°); further chlorination affords the 3:5-Cl₂-derivative, m.p. 80.5—82° (corr.) [*benzoate*, m.p. 144—146°; 2:4-dinitrophenyl ether, m.p. 112—113.5° (corr.)]. (I) and Cl₂ in AcOH give a mixture containing some of the 3:5:4'-Cl₃-derivative, m.p. 133.5—137° (corr.) (*benzoate*, m.p. 161°; 2:4-dinitrophenyl ether, m.p. 174—176°). (II) and Br (1 mol.) in CCl₄ afford 3-chloro-5-bromo-4-hydroxydiphenyl, m.p. 84—86° (corr.); with 2 mols. of Br in CS₂, 3-chloro-5:4'-di-bromo-4-hydroxydiphenyl, m.p. 143—146° (corr.), results. H. B.

Action of nascent thiocyanogen on di- and trihydric phenols. G. MACHEK (Monatsh., 1933, 63, 216—219).—Addition of Br in MeOH to pyrocatechol and NH₄SCN (giving nascent SCN) in dry MeOH gives a 48% yield of *thiocyanopyrocatechol*, m.p. 142° (corr.) [*Ac₂* derivative, m.p. 58° (corr.)], but similar treatment of quinol, resorcinol, pyrogallol, and phloroglucinol gives gelatinous products containing polymerised SCN. J. W. B.

Pseudo-quinonoid character of tribromoresorcinol. T. L. DAVIS and V. F. HARRINGTON (J. Amer. Chem. Soc., 1934, 56, 129—132).—I is liberated when tribromoresorcinol (I) is heated with NaI or KI in EtOH; reaction is facilitated by AcOH and retarded by a large excess of HI. (I) is converted by aq. C₂H₅N into an amorphous polynuclear compound, composition C₆H₂O₂Br; a similar compound is formed using aq. NaOH (preferably >2 equivs.). (I) is reduced by aq. or alkaline Na₂SO₃ to 2:4-di-bromo-, m.p. 92.8—93.7°, and thence to 2-bromo- (II), m.p. 101.2—102°, -resorcinol; (I) is also reduced to (II) by SnCl₂ [in solution containing some Sn(OH)₂]. These reactions [and the results previously described (A., 1929, 439)] are readily explained by assuming the intermediate formation, by loss of HBr, of the radical $\text{CO} \langle \text{Br} \cdot \text{C}(\text{OH}) \rangle \text{C} \cdot$. Oxidation (CrO₃, AcOH) of the *Me ether* of (I) gives 3:5:6-tribromo-2-methoxy-*p*-benzoquinone (III), m.p. 168—168.5°; free Br is not

produced and it is suggested that addition of HBr to the 3:5-Br₂-quinone and subsequent oxidation of the resulting quinol occur. (III), which is also obtained from methoxyquinol and excess of Br in CHCl₃, is reduced (H₂SO₃) to 3:5:6-tribromo-2-methoxyquinol, m.p. 175—176°, and with 2N-KOH gives the K salt of *methylbromanilate*, C₇H₄O₄Br₂, m.p. >350°. H. B.

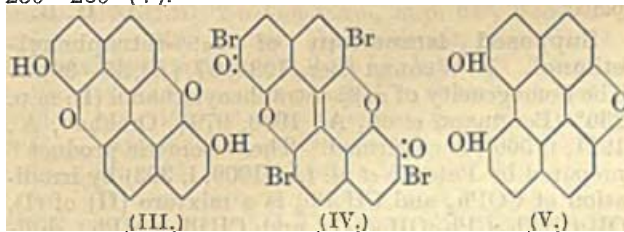
Bromoquinol (adulol). G. A. KIRKHOFF and R. Y. ASTROVA (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 304—305).—HBr is passed into 108 g. of benzoquinone in CHCl₃ containing 1.5 g. of C; bromoquinol, from CHCl₃, has m.p. 106—107°. CH. ABS.

[Preparation of] quinol. G. A. KIRKHOFF and R. Y. ASTROVA (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 303—304).—Benzoquinone is reduced in dil. H₂SO₄ by CaSO₃ at 30—35°. CH. ABS.

Oxidation products of organic developers. A. SEYEWETZ and S. SZYMSON (Bull. Soc. chim., 1933, 53, [iv], 1260—1268).—Quinol (I) with PbO₂ or AgBr in Na₂SO₃ (or K₂SO₃)-alkali in air affords Na quinol-disulphonate (II). (I) with AgBr and Na₂SO₃ in H₂O-COME₂ in air affords the monosulphonate (III). (I) reduces AgBr twice as easily as (II), but (III) has no action. Similarly *o*-C₆H₄(OH)₂ in presence of HgCl₂ affords the monosulphonate, whereas with AgBr or PbO, the disulphonate is formed.

J. L. D.

Diaryls and their derivatives. I, II. Ring-closure of 2:7:2':7'-tetrahydroxy-1:1'-dinaphthyl. J. S. JOFFE and (II) J. V. GRATSCHEV (J. Gen. Chem. Russ., 1933, 3, 453—462, 463—469).—β-Naphthol-7-sulphonic acid on oxidation by boiling with aq. FeCl₃ gives 2:2'-dihydroxy-1:1'-dinaphthyl-7:7'-disulphonic acid (I), which by alkali fusion yields 2:7:2':7'-tetrahydroxy-1:1'-dinaphthyl (II), m.p. (+2H₂O) 114.5°, (anhyd.) 151—152°, also obtained by oxidising 2:7-C₁₀H₆(OH)₂ with FeCl₃. Oxidation of this with FeCl₃ does not give the expected perylene derivative, but a brown substance which could not be further identified. It is considered that this is due to the existence of (II) in the *trans*-form giving rise on further oxidation to dihydroxydinaphthylene dioxide (III) and decomp. products. Bromination of (II) gives the Br₆-derivative, m.p. 250—251°, and ring-closure by removing NH₂ gives a blue dye, probably the *tetrabromodinaphthylene dioxide quinone* (IV), reducible to the (OH)₂-compound. By heating the Pb salt of (II) with AlCl₃, 1:6:7:12-tetrahydroxyperylene is formed, but cannot be isolated, since ring-closure takes place with formation of 6:7-dihydroxy-1:12-furoperylene, m.p. (impure) 250—260° (V).



M. Z.

Synthesis of ψ-ephedrine. R. G. BOSSERT and W. R. BRODE (J. Amer. Chem. Soc., 1934, 56, 165—

166).—Et β -bromo- α -phenylpropyl ether, b.p. 114°/9 mm. (from Et $\alpha\beta$ -dibromopropyl ether and MgPhBr), and MeOH-NH₂Me at 125—130° give Et β -methylamino- α -phenylpropyl ether [*dl*- ψ -ephedrine Et ether], b.p. 116—122°/18 mm., de-ethylated (HBr) to *dl*- ψ -ephedrine. H. B.

Constitution of triarylmethyl salts. P. RUMPF (Compt. rend., 1934, 198, 269—272).—The vals. of the dissociation consts. of the mono- and di-salts of *p*-amino-, *pp'*-diamino-, and *pp'p''*-triamino-triphenylcarbinol, compared with those of the salts of the corresponding derivatives of CHPh₃, support the view that the coloured mono-salts are carbonium salts, not quinonoid. R. S. C.

Synthesis of condensed polynuclear hydrocarbons by cyclodehydration of aromatic alcohols. I. Indanes. M. T. BOGERT and D. DAVIDSON (J. Amer. Chem. Soc., 1934, 56, 185—190).—Alcohols of the types CPhR₂·CR(OH)·CHMe₂ and CPhR₂·CHR·CMe₂·OH, where R is H or Me, are dehydrated by 85% H₂SO₄ to 1:1-dimethylindanes, which are also formed by similar treatment of the olefines, CPhR₂·CR·CMe₂, which are assumed to be formed first. Thus, γ -phenyl- $\alpha\alpha$ -dimethylpropyl alcohol, b.p. 123°/15 mm. (from CH₂Ph·CH₂·MgBr and COMe₂), and α -benzylisobutyl alcohol, b.p. 118—122°/15 mm., both give 1:1-dimethylindane (I), b.p. 191° (SO₃H-derivative, m.p. 67°), which is oxidised (aq. KMnO₄) to $\alpha\alpha$ -dimethylhomophthalic acid, m.p. about 120° (with loss of H₂O). Some (I) is also formed when γ -phenyl- γ -methylbutyl alcohol, b.p. 137—138°/16 mm. [prepared by reduction (Na, EtOH) of CPhMe₂·CH₂·CO₂Et], is dehydrated with H₃PO₄ at 230—240°; admixed olefine is removed with 85% H₂SO₄. Benzylmethylisopropylcarbinol, b.p. 122—124°/18 mm. (from CH₂Ph·MgCl and COMePr²), similarly affords 1:1:2-trimethylindane, b.p. 208° (SO₃H-derivative, m.p. 109°); γ -phenyl- $\alpha\gamma$ -dimethylbutyl alcohol yields 1:1:3-trimethylindane, and γ -phenyl- $\alpha\alpha\gamma$ -trimethylbutyl alcohol, b.p. 133°/17 mm. (from MgMeI and CPhMe₂·CH₂·COMe), gives 1:1:3:3-tetramethylindane, b.p. 206—209° (SO₃H-derivative, m.p. 107—108°). Polymeric material only is obtained from γ -phenylpropyl (using H₃PO₄ at 230—240°), γ -phenyl- α -methylpropyl, and γ -phenyl- $\alpha\beta$ -dimethylpropyl alcohol, b.p. 135—136°/21 mm. [prepared by reduction (Na, EtOH) of CHPh·CMe·COMe], and benzylmethylethylcarbinol. δ -Phenylbutyl alcohol is dehydrated by H₃PO₄ to 1:2:3:4-tetrahydronaphthalene; δ -phenyl- Δ^2 -buteno is not an intermediate since this is polymerised under the same conditions, and in this case direct cyclodehydration must take place. H. B.

Supposed isomerism of $\alpha\alpha\beta\beta$ -tetraphenylethanol. R. WEGLER (Ber., 1934, 67, [B], 35—39).—The homogeneity of $\alpha\alpha\beta\beta$ -tetraphenylethanol (I), m.p. 236° (Bergmann *et al.*, A., 1930, 979; Orckhov, A., 1921, i, 566), is confirmed. The "isomeric product" prepared by Paterno *et al.* (A., 1909, i, 393) by irradiation of CPh₃ and CH₂Ph₂ is a mixture (II) of (I), OH·CHPh₂·CPh₂·OH (III), and CHPh₂·CHPh₂, difficultly separable into its components by crystallisation. (I) is most readily isolated from (II) by C₂H₅N at 135°, whereby (III) is transformed into CPh₃, and

CHPh₂·OH. Analogous observations are made with $\alpha\beta\beta$ -triphenyl- α -*p*-tolylethanol. (I) is transformed by Na into CH₂Ph₃, CPh₃, CHPh₂·OH, BzOH, and, mainly, (·CHPh₂)₂. H. W.

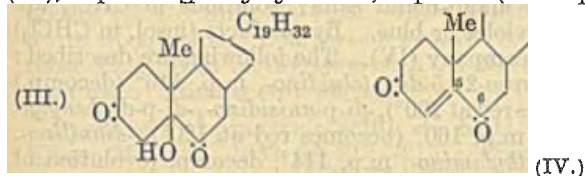
Pinacol-pinacolin rearrangement. V. Rearrangement of unsymmetrical aromatic pinacols. W. E. BACHMANN and H. R. STERNBERGER (J. Amer. Chem. Soc., 1934, 56, 170—173; cf. A., 1932, 737).—*as*-Pinacols, OH·CR₂·CR'₂·OH, prepared from OH·CR₂·CO₂Me and MgR'Br, are rearranged by AcCl in AcOH-C₆H₆ (subsequent treatment with I in AcOH is occasionally necessary) to mixtures of pinacolins, which are analysed by fission with MeOH-KOH to R·CO₂H+R'·CO₂H. The relative migration aptitudes of the groups studied are: *p*-diphenyl 1.18, Ph 1, *m*-tolyl 1, *p*-tolyl 0.96, *p*-C₆H₄Cl 0.75, phenetyl 0.49, anisyl 0.39, *p*-C₆H₄F 0.099; there is no simple relationship between these vals. and those found for the *s*-pinacols (A., 1932, 515). Improved methods of prep. of anisilic (*Me* ester, m.p. 110—110.5°) and 4:4'-diphenylbenzilic acid (*Me* ester, m.p. 130.5—131.5°) are given. 4:4'-Dichloro-, m.p. 143—144.5°, 4:4'-difluoro-, m.p. 166.5—167.5°, 4:4'-diethoxy-, m.p. 162—163°, 4:4'-diphenyl-, m.p. 190.5—191°, 4':4''-dimethoxy-3:3'-dimethyl-, m.p. 153.3—154.5°, 4':4''-dimethoxy-4:4'-dimethyl-, m.p. 159.5—161°, and 4':4''-diphenyl-3:3'-dimethyl-, m.p. 160—161°, -benzpinacols; Ph 4:4'-difluorotriphenylmethyl ketone, m.p. 121.5—122.5°, and 4:4'-difluorotriphenylmethane, m.p. 55—56°, are described. H. B.

Silver-halogen complexes of carboxylic acids. C. PREVOST (Compt. rend., 1933, 197, 1661—1663).—Formation of an I-Ag complex (A., 1933, 711) also occurs with AgOAc, and Br may replace I. Addition (*trans*) to ethylenic derivatives occurs thus: AgI(OAc)₂+CHR:CHR→AcO·CHR·CHRI+AgOAc→AgI+(AcO·CHR)₂; the second stage is slow, causing contamination with halogeno-esters. Various Ac₂ and Bz₂ derivatives are thus prepared, the following being new: Bz₂ derivatives of *n*-pentane- $\alpha\beta$ -diol (I), b.p. 233°/10 mm., phenyl-, m.p. 96° and *as*-diphenyl-, m.p. 108°, ethylene glycol; Ac₂ derivative of (I), b.p. 103°/12 mm.; Bz derivative, m.p. 170°, of CHPhBr·CHPh·OH; Bz₂ derivative, m.p. 152°, of *n*-hexane- $\alpha\beta\zeta$ -tetraol (from diallyl); and (by GIMEL) the Bz₂ derivative of stycerol, and the Bz₂ derivative of Et β -hydroxy- β -phenyl-lactate. J. W. B.

Ring-system of sterols and bile acids. IV. Nomenclature of cholane group. O. ROSENHEIM and H. KING (Chem. and Ind., 1934, 91—92; cf. A., 1933, 1048).—It is suggested that the following substances be re-named as quoted in parentheses: coprosterol (I) (coprostanol), allocholesterol (II) (coprostenol), cholestenone (III) (coprostenone), ψ -cholestane (coprostane), ψ -cholestene (IV) (coprostene); the nomenclature expresses the relationship (which is discussed) between (I), (II), (III), and (IV). The prefix *allo*- is used to denote derivatives (e.g., allocholanolic acid) in which rings I and II are in the *trans*-position. When isomerism is due to steric inversion of the OH group, the prefix *epi*- should be used (e.g., epicholestanol). H. B.

Position of the nuclear double linking in stigmasterol. E. FERNHOLZ (Annalen, 1934, 508,

215—224).—Oxidation (BzO_2H) of stigmasteryl acetate in CHCl_3 at 5° gives (mainly) an α -oxide (I), m.p. 143° , $[\alpha]_D^{25} -36.7^\circ$ in CHCl_3 , and a little of a β -oxide, m.p. 170° , $[\alpha]_D^{25} -32^\circ$ in CHCl_3 ; these are hydrolysed (5% EtOH-KOH) to α -, m.p. 152° , and β -, m.p. 153° , -*stigmasteryl oxides*, respectively. Ozonolysis of (I) affords α -ethylisovaleraldehyde (showing that O adds to the nuclear double linking), whilst hydrolysis (aq. EtOH-HCl) gives about 20% of *stigmastenetriol* (II), m.p. 254° . (II) contains a *tert*-OH since it is oxidised (CrO_3 , AcOH) to *stigmastenedione* (III), m.p. about 260° (with loss of H_2O), which is dehydrated by HCl in CHCl_3 to *stigmastadienedione* (IV), m.p. 155° [*phenylhydrazone*, m.p. 250° (decomp.)].



This is reduced (Zn dust, AcOH) to *stigmastenedione* (III, with $\text{OH}=\text{H}$), m.p. 197° , which with 50% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in EtOH affords an *azine*, decomp. about 260° . Reduction (H_2 , Pt-black , EtOAc) of (I) gives *stigmastenediol monoacetate*, m.p. 206° , which could not be acetylated (Ac_2O) further. The above results are explained by the existence of a double linking in stigmasteryl (V) between C_5 and C_6 (cf. A., 1933, 1290). (V) differs from cholesterol only in the structure of the side-chain. Sitostanoldione, m.p. 256° , is dehydrated (HCl in CHCl_3) to sitostenedione, m.p. 129° (lit. 166°), which is reduced (Zn dust, AcOH) to sitostanedione, m.p. 196° (*azine*, m.p. $197-200^\circ$). γ -Sitosterol may differ from (V) in the arrangement of the asymmetric centres in the side-chain. H. B.

Addition products of halogens and benzene derivatives. I. T. VAN DER LINDEN (Rec. trav. chim., 1934, 53, 45—62).—The work of Matthews (J.C.S., 1900, 77, 1273) is confirmed and extended. PhCN is chlorinated in sunlight at room temp., the α -hexachloride, m.p. $156-157^\circ$ (I), separated by addition of glacial AcOH (cf. *loc. cit.*) after removal of unchanged PhCN , and the residue separated by distillation at $0.06-0.1$ mm., crystallisation of individual fractions, and hydrolysis of residues to amides by hot conc. H_2SO_4 , and of final amide residues to acids by fuming HNO_3 . The following are thus obtained in addition to (I) and known derivatives: β -hexachloro-, m.p. 197° (decomp.) [*amide*, m.p. $246.5-247.5$; free acid, m.p. $219.5-221.5$ (liberates HCl with hot H_2O)], and 1:2:3:4:4:5:6-heptachloro-cyclohexyl cyanide [*amide*, m.p. 309° ; acid (II), m.p. 291° (decomp.)], γ -hexachlorocyclohexanecarboxylic acid (A., 1912, i, 698), 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$, (III) (below), and a little chloranil. The acid, m.p. 195° , corresponding with (I) loses HCl and CO_2 with warm H_2O to give a (?) eutectic mixture from which pentachlorocyclohexene, m.p. $103-104^\circ$ (III), is isolated. This is unaffected by AlCl_3 in C_6H_6 , conc. H_2SO_4 at 100° , and alkaline KMnO_4 , but Cl_2 in sunlight gives enneachlorocyclohexane, m.p. 94° . Reduction of (II) with Zn in EtOH gives $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$, thus proving the structure of the parent nitrile. H. A. P.

cis- and *trans*-Cinnamic acids. Steric hindrance. J. MANTA (Bull. Soc. chim., 1933, 53, [iv], 1277—1286).—The rates of esterification of cinnamic and allocinnamic acid (I) (prep. described) are of the same order (cf. J.C.S., 1909, 95, 315) due to the conversion of (I) into the *trans*-acid, which is also formed when the *cis*-acid is esterified in presence of 2% HCl or H_2SO_4 . Interaction of $\text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H}$ with cyclohexanol and some PhSO_3H affords cyclohexyl phenylpropionate, b.p. $190^\circ/9$ mm., reduced by H_2 -Pd to a mixture from which selective hydrolysis (KOH-EtOH) yields cyclohexyl allocinnamate, b.p. $180^\circ/15$ mm. Similarly prepared, benzyl phenylpropionate has m.p. 35° , and benzyl allocinnamate, m.p. $34-35^\circ$. The rate of hydrolysis (II) in abs. EtOH of several *cis*- and *trans*-esters shows that $K_{\text{trans}}/K_{\text{cis}}=2$, and that (II) for esters of (I) is very small; hence (I) has a *cis*-structure. (II) of the propiolic and hydrocinnamic esters is much greater. (II) in 96% EtOH is increased sixfold (cf. J.C.S., 1921, 119, 970). J. L. D.

Isomerisation of phenylglycide methyl and ethyl ethers. (MLLE.) DARMON (Compt. rend., 1933, 197, 1649—1650).—When heated with a trace of anhyd. ZnCl_2 , phenylglycide Me ether isomerises exclusively to $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OMe}$ (synthesis, this vol., 191), and the corresponding *Et* ether, b.p. $134-135^\circ/13$ mm., similarly affords mainly $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OEt}$ (*loc. cit.*) together with $\text{OEt}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CHO}$ (Beaufour, A., 1913, i, 466). It is concluded that the affinity of $\text{CH}_2\cdot\text{OR}$ is < that of Ph , and the migratory tendency of $\text{CH}_2\cdot\text{OR}$ is < that of H . J. W. B.

Arylamides of 2:3-hydroxynaphthoic acid.—See B., 1934, 88.

Iodo-derivatives of diphenyl ether. I. Mono- and di-iodo-derivatives of diphenyl ether and of 2- and 4-carboxydiphenylethers. R. Q. BREWSTER and F. STRAIN (J. Amer. Chem. Soc., 1934, 56, 117—120).—The following derivatives of Ph_2O are prepared (usually by standard methods): 2-I-, m.p. 56° , 3-I-, b.p. $155^\circ/3$ mm., $194-196^\circ/20$ mm. (from the 3- NH_2 -derivative), 4-I-, m.p. 47° (from Ph_2O and ICl in AcOH), 2-iodo-4'-nitro-, m.p. 104° , 4-iodo-4'-nitro-, m.p. 70° , 2-iodo-4'-amino-, m.p. 69° (*Ac* derivative, m.p. 150°), 2:4'- I_2 -, m.p. 48° , 4-iodo-2'-nitro-, m.p. 86° , 3:4'-(NO_2) $_2$ -, m.p. 123° (from $p\text{-C}_6\text{H}_4\text{F}\cdot\text{NO}_2$ and $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OK}$), 3:4'-(NH_2) $_2$ -, m.p. 72° (*Ac* $_2$ derivative, m.p. 192°), 3:4'- I_2 -, b.p. $200^\circ/3$ mm., 4:4'- I_2 -, m.p. 139° , 4-nitro-2-amino-, m.p. 107° [by reduction (SnCl_2 , HCl) of the 2:4-(NO_2) $_2$ -derivative; the compound is described by Bogert and Evans (B., 1926, 354) as the 2-nitro-4-amino-derivative], 2-iodo-4-nitro-, m.p. 61° , 2-iodo-4-amino-, b.p. $203^\circ/3$ mm. (*hydrochloride*, m.p. 245° ; *Ac* derivative, m.p. 120°), 2:4'- I_2 -, b.p. $198^\circ/3$ mm., 3-nitro-4-acetamido-, m.p. 104° , 3-amino-4-acetamido-, m.p. 126° , 3-nitro-4-amino-, m.p. 82° , 3:4-(NH_2) $_2$ -, m.p. 69° (*Ac* $_2$ derivative, m.p. 188°), 4-iodo-3-nitro-, b.p. $195^\circ/3$ mm., 4-iodo-3-amino-, b.p. $188^\circ/3$ mm. (*Ac* derivative, m.p. 144°), and 3:4'- I_2 -, b.p. $208^\circ/3$ mm. $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$ and ClCO_2Et give *Et* p -phenoxyphenylcarbamate, m.p. 63° , converted by ICl in AcOH into *Et* p - p' -iodophenoxyphenylcarbamate, m.p. 126° , also obtained from 4-iodo-4'-amino-

diphenyl ether (I) and ClCO_2Et . *p-p'*-Iodophenoxyphenylcarbamide, m.p. 201° , is prepared from (I) and KNCO . *o*- $\text{OPh}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (II) (improved prep. given) and HNO_3 (d 1.42) at $40\text{--}45^\circ$ give 2-*p*-nitrophenoxybenzoic acid, m.p. 157° , also prepared by oxidation ($\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4) of 2-*p*-nitrophenoxybenzaldehyde, m.p. 112° (from *p*- $\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{NO}_2$ and *o*- $\text{OK}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$). 2-*p*-Aminophenoxybenzoic acid (*Ac* derivative, m.p. 185°) has m.p. 180° . 2-*p*-Iodophenoxybenzoic acid, m.p. 143° [from (II) and ICl], is converted by conc. H_2SO_4 at 100° into 2-iodoxanthone (III), m.p. 156° . 5-Amino-2-phenoxybenzoic acid, m.p. 164° [*Ac* derivative ($+\text{H}_2\text{O}$), m.p. 111° , m.p. (anhyd.) 165°], is converted into the 5-*I*-derivative, m.p. 148° , and thence into (III). 2-*o*-Nitrophenoxybenzaldehyde, m.p. 77° ; 2-*o*-nitro-(IV), m.p. 153° , -amino-, m.p. 153° (*Ac* derivative, m.p. 179° ; lactam, m.p. 211°), and -iodo-, m.p. 133° , -phenoxybenzoic acids; 4-*p*-iodophenoxybenzoic acid, m.p. 217° ; 5-nitro-, m.p. 178° , -amino-, m.p. 185° , and -iodo-, m.p. 176° , -2-*p*-iodophenoxybenzoic acids, and 5-nitro-2-*p*-nitrophenoxybenzoic acid, two forms, m.p. 158° and $170\text{--}171^\circ$, are also described. 4-Nitroxanthone, m.p. 190° (lit. 127°), is obtained from (IV) and conc. H_2SO_4 . H. B.

Organic solvents and plasticisers [esters of 2-benzoylbenzoic acid].—See B., 1934, 87.

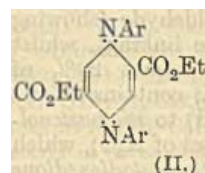
Relation of thyroxine with tyrosine. A. CANZANELLI, C. R. HARRINGTON, and S. S. RANDALL (Biochem. J., 1934, 28, 68—72).—An optically active thyronine, $[\alpha]_{5461} +13.3^\circ$, has been synthesised from natural *l*-tyrosine, and is identical with a sample prepared by catalytic deiodination of *l*-thyroxine which had been shown to be identical with the natural compound (A., 1930, 820). H. G. R.

Action of sulphuryl chloride on unsubstituted amides and imides. Phthalimidodisulphonyl chloride. Sulphondiamide. M. BATTEGAY and L. DENIVELLE (Bull. Soc. chim., 1933, 53, [iv], 1242—1249).—Interaction of SO_2Cl_2 (I) with $\text{ONa}\cdot\text{CMe}\cdot\text{NH}$ (A., 1931, 608) at $0\text{--}5^\circ$ during 1 hr. affords an unstable oil [probably the *N*-sulphonyl chloride (II)] which decomposes into HCl , SO_2 , and MeNCO , whereas the product from (I) and NH_2Bz [probably $\text{NH}_2\text{CPh}\cdot\text{O}\cdot\text{SO}_2\text{Cl}$] affords PhCN . Phthalimidodisulphonyl chloride (III) and dry NH_3 in C_6H_6 afford the sulphonamide (?), easily decomposed to phthalimide and $\text{SO}_2(\text{NH}_2)_2$. (III) with NHPhMe affords a stable product, m.p. 160° , which has no labile H atom and is either the *O*- or *N*-sulphonamide. J. L. D.

Preparation of 3-aminophthalhydrazide for use in demonstration of chemiluminescence. E. H. HUNTRESS, L. N. STANLEY, and A. S. PARKER (J. Amer. Chem. Soc., 1934, 56, 241—242).—Crude 3-nitrophthalhydrazide is obtained when an aq. solution of 3-nitrophthalic acid (1 mol.), N_2H_4 , H_2SO_4 (1 mol.), and NaOAc (2 mols.) is evaporated to dryness and then heated at $160\text{--}10^\circ$; Na_2SO_4 is removed by extraction with H_2O . Reduction ($6N\text{-NH}_4\text{HS}$) gives 3-aminophthalhydrazide ("luminol"), isolated as the Δ salt. H. B.

p-Benzoquinonediarylimine-2 : 5-dicarboxylic acids and esters. H. LIEBERMANN and B. SCHULZE

(Annalen, 1934, 508, 144—153).—Et 2 : 5-diaryliminoterephthalates (I) (A., 1914, i, 658) are converted into the $(\text{NO})_2$ -derivatives, which when heated in PhMe or xylene eliminate NO and give Et *p*-benzoquinonediarylimine-2 : 5-dicarboxylates (II). Reduction (Zn dust, AcOH) of (II) affords (I), whilst



hydrolysis (EtOH-KOH) gives 2 : 5-diaryliminoterephthalic acids (III). *p*-Benzoquinonediarylimine-2 : 5-dicarboxylic acids (IV) are similarly prepared from (III). Solutions of (II) in org. solvents are violet- or blood-red; solutions in conc. H_2SO_4 are emerald-green. (IV) give dark-coloured alkali-metal salts; solutions in CHCl_3 are reddish-violet or blue. By-products (insol. in CHCl_3) often accompany (IV). The following are described : Et dinitroso-2 : 5-di-*p*-toluidino-, m.p. 146° (decomp.) (becomes red at 100°), -di-*p*-anisidino-, -di-*p*-diphenylamino-, m.p. 160° (becomes red at 120°), -dianilino-, and -diethylamino-, m.p. 114° , decomp. (evolution of NO) 170° , -terephthalates; Et *p*-benzoquinone-di-*p*-tolylimine-, m.p. 124° , -dianisylimine-, m.p. 136° , -di-*p*-diphenylimine-, m.p. 185° , -diphenylimine-, m.p. $93\text{--}95^\circ$, and -diethylimine-, m.p. $122\text{--}125^\circ$, -2 : 5-dicarboxylates; dinitroso-2 : 5-di-*o*-, and -*p*-toluidino-, -dianilino-, and -di-*p*-anisidino-terephthalic acids; *p*-benzoquinone-di-*p*-tolylimine-, m.p. $>300^\circ$ (K_2 and Ba salts), -di-*o*-tolylimine-, -diphenylimine-, m.p. 274° (decomp.) (K_2 salt), and -dianisylimine- (K_2 salt), -2 : 5-dicarboxylic acids. The NO -derivative (V), m.p. 283° (darkens from 150°), of 2-anilino-5-hydroxyterephthalic acid (VI) eliminates NO when heated in PhNO_2 ; (VI) only could be isolated from the resultant red solution. The NO -derivative of 2- β -naphthylamino-4-hydroxyterephthalic acid (NO -derivative of Et ester) readily loses NO in xylene; the original acid is again isolable from the reddish-brown solution. *p*-Amino-diphenyl and succinylsuccinic acid in EtOH-AcOH give (cf. *loc. cit.*) Et 2 : 5-di-*p*-diphenylamino- $\Delta^{1:4}$ -dihydroterephthalate, m.p. 235° , oxidised (I in amyl alcohol) to Et 2 : 5-di-*p*-diphenylaminoterephthalate, m.p. 234° . H. B.

α -Phenyl- α' -dimethylsuccinic acid. H. M. CRAWFORD (J. Amer. Chem. Soc., 1934, 56, 139—141).— $\text{CNaMe}(\text{CO}_2\text{Et})_2$ and $\text{CHBrPh}\cdot\text{CO}_2\text{Et}$ give Et α -phenylpropane- $\alpha\beta$ -tricarboxylate (I), b.p. $210\text{--}217^\circ/17\text{ mm.}$, hydrolysed to α -phenyl- α' -methylsuccinic acid. Methylation of (I) could not be effected. α -Phenylpropionitrile [conveniently prepared from $\text{CH}_2\text{Ph}\cdot\text{CN}$ (II), MeI , and NaNH_2 in Et_2O ; unchanged (II) is removed by condensation with PhCHO], $\text{CHBrMe}\cdot\text{CO}_2\text{Et}$, and NaNH_2 in Et_2O afford Et β -cyano- β -phenyl- α -methylbutyrate, b.p. $172\text{--}173^\circ/14\text{ mm.}$, hydrolysed [HBr (const. b.p.)] to α -phenyl- α' -dimethylsuccinic acid, two forms, m.p. $159\text{--}160^\circ$ (*Ag* salt) and $170\text{--}172^\circ$ (III) (*Ag* salt), separable by fractional crystallisation of the Ca salts. (III) is identical with the acid previously obtained (A., 1928, 523) by oxidation of 3-phenyl-2 : 3 : 5 : 6-tetramethyl- Δ^5 -cyclohexene-1 : 4-dione. H. B.

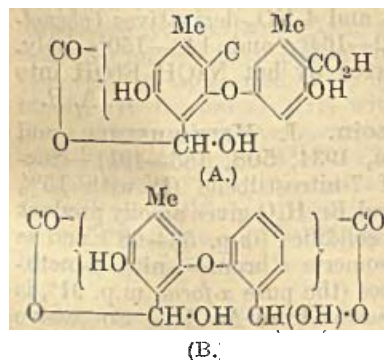
Combination of certain dyes with deoxycholic acid. M. STOCKHOLM and C. L. A. SCHMIDT (Proc. Soc. Exp. Biol. Med., 1933, 30, 877—879).—Com-

pounds of deoxycholic acid with halogenofluoresceins are described. CH. ABS.

Humic acids. I. Determination of carboxylic and phenolic groups. I. UBALDINI and C. SINI-
RAMED (Annali Chim. Appl., 1933, 23, 585—597).—For humic acids separated from lignite and peat (B., 1932, 758), determinations have been made of: (1) total acidity, by boiling with 0.2*N*-KOH-EtOH and determining the residual excess of KOH, and (2) carboxylic acidity, by treating the K humate, suspended in EtOH, with CO₂ and determining the liberated K₂CO₃ by titration: $2\text{OK}\cdot\text{R}\cdot\text{CO}_2\text{K} + \text{CO}_2 + \text{H}_2\text{O} = 2\text{OH}\cdot\text{R}\cdot\text{CO}_2\text{K} + \text{K}_2\text{CO}_3$. The total acidity val. found is 492—500, the carboxyl val. 263—267, and the phenol val. (by diff.) 229—232; these indicate a mol. wt. of about 1700. Comparison of these results with those obtained by methylation with CH₂N₂ shows that such methylation is only partial. T. H. P.

Synthesis of pinastric acid. G. KOLLER and A. KLEIN (Monatsh., 1933, 63, 213—215).—Condensation of equimol. quantities of CH₂Ph·CN and its *p*-OMe-derivative with Et₂C₂O₄ and NaOEt affords *p*-methoxy-pulvinodinitrile, *p*-OMe·C₆H₄·CH(CN)·CO·CO·CHPh·CN, decomp. 255° (in vac.), acid hydrolysis of which gives mixtures, but with KOH-MeOH affords pinastric acid (A., 1933, 508), identical with the natural product. J. W. B.

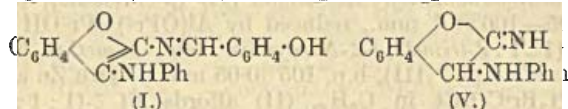
Saxatilis and capraric acid. G. KOLLER, A. KLEIN, and H. POPE (Monatsh., 1933, 63, 301—310).—Protocapraris acid (I) extracted from *Parmelia caperata* and freed from usnic acid has a mol. formula C₁₈H₁₄O₉, confirmed by condensation (—H₂O) with *m*-C₆H₄Br·NH₂ to a bromoanilide C₂₄H₁₈O₈NBr, and by boiling EtOH to an OEt-compound C₂₀H₁₈O₉, decomp. 260°. Since no trace of orcinol is obtained from atranole under the conditions of its fission from (I), both atranole and orcinol nuclei must be present, and



the partial structure (A) is suggested for (I). Fractional extraction of saxatilis acid (II) from *P. saxatilis* gives all fractions of composition C₁₈H₁₄O₁₀ (2 CO₂H), giving a di-*m*-bromoanilide, C₃₀H₂₄O₉N₂Br₂, decomp. 280° (in vac.), and with boiling EtOH a (OEt)₂-derivative C₂₂H₂₀O₁₀, decomp. 172° (in vac.) (*m*-bromoanilide). With Zn-NaOH in H₂O (II) gives traces of atranole (3: 5-dihydroxy-*p*-tolualdehyde) and an unidentified phenol. The partial formula (B) is suggested for (II), the ether linking being assumed. J. W. B.

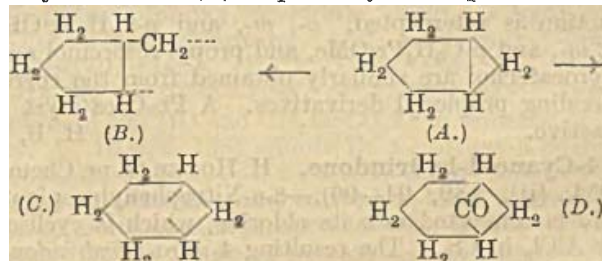
Compounds from salicylidene- and hydrocyanosalicylidene-aniline and related substances. G. ROHDE (J. pr. Chem., 1933, [ii], 139, 17—26, 27—43; cf. A., 1910, i, 775).—The compound (I), m.p. 155—156°, obtained by Schwab (A., 1901, i, 380) by action of KCN on *o*-OH·C₆H₄·CH·NPh (II) is better prepared by interaction of OH·C₆H₄·CH(CN)·NHPh

(III) [from (II) and HCN] with *o*-OH·C₆H₄·CHO (IV) and Na₂CO₃ in boiling MeOH (best in CO₂), and is also obtained from (IV), NH₂Ph, and KCN. The isomeric (V), m.p. 142—143°, of (III) simultaneously formed is produced by the action of KCN alone on (III) in a yield of 84% of theory. Condensation of this with (II) or (IV) in MeOH gives (I), and with PhCHO the corresponding *CHPh* derivative, m.p. 146—146.5°, is formed; similarly, it gives the benzenesulphonyl derivative of (I) with *o*-PhSO₂·O·C₆H₄·CHO. Oxidation of (V) with KMnO₄ gives the nitrile *o*-OH·C₆H₄·C(NPh)·CN, and with air the amide, *o*-OH·C₆H₄·C(NH)·CO·NH₂, m.p. 175—176°, and resinous matter. The oxazone formula for (I) (*loc. cit.*, 1910) is therefore abandoned, and the formulae below are assigned to (I) and (V). A compound, m.p. 175.5—176°,



corresponding with (V) is obtained from the *p*-tolol of (IV), and on acid hydrolysis gives (IV) and the amide, *o*-OH·C₆H₄·CH(NH·C₆H₄Me)·CO·NH₂ (hydrochloride, m.p. 193°). The *N*-Me derivative of (I), m.p. 166—166.5° (*O*-Bz derivative, m.p. 144—144.5°), is similarly obtained from NHPhMe and *o*-OH·C₆H₄·CH(OH)·CN or NHPhMe, (IV), and KCN. H. A. P.

Formation of ketones from cycloparaffins in presence of aluminium chloride. N. D. ZELINSKI and E. M. TARASSOVA (Annalen, 1934, 508, 115—143).—Largely a more detailed account of work previously reviewed (A., 1932, 1120). *cyclo*Hexane (I) is considered to react with AcCl and AlCl₃ in its *cis*- and *trans*-forms. The initial change, especially at lower temp., is dehydrogenation. The *cis*-form is thus readily converted (at 18—35°) into cyclohexene (II), which then affords Δ¹-tetrahydroacetophenone (III) (formed by loss of HCl from the intermediate 1-chloro-2-acetylcyclohexane). Dehydrogenation of the *trans*-form (at 18—70°) gives the dicyclic system (A) which undergoes fission to (B) or (C) [some (C) is also transformed into (II)]; (B) and (C) with AcCl+2H give 2-acetyl-1-methylcyclopentane (IV) and cyclohexyl Me ketone (V), respectively. The production of



2-methylcyclohexanone from (I) and CO (Hopff, A., 1932, 514) is explained by the intermediate formation of (D) and subsequent addition of 2H. Reduction (H₂, Pd-black, MeOH) of (III) gives [according to the method of prep. of (III)] stereoisomeric forms, b.p. 76—76.5°/27 mm. (*semicarbazone*, m.p. 171—172°; *oxime*, m.p. 48°), and b.p. 63°/13 mm. (*semicarbazone*, m.p. 150—151°; *oxime*, b.p. 126—128°/27 mm.), of (V); these differ from the (V) obtained by oxidation (CrO₃) of cyclohexylmethylcarbinol. 2-Acetyl-1-

methyl-Δ¹-cyclopentene (VI), b.p. 82°/17 mm. (*semicarbazone*, m.p. 212—213°), is obtained from methylcyclopentane or -cyclopentene, AcCl , and AlCl_3 ; it is reduced (H_2 , Pd-black, EtOH) to 2-acetyl-1-methylcyclopentane, b.p. 59.8—60°/15 mm. (*semicarbazone*, m.p. 162°), which, contrary to Unger (A., 1932, 514), could not be obtained in different forms. The (VI) described by Unger (*loc. cit.*) is (III). H. B.

Compounds containing the carbon ring of β-ionone and several ethylenic linkings. P. KARRER and R. MORF (Helv. Chim. Acta, 1934, 17, 3—7).—δ-(1 : 1 : 3-Trimethyl-2-Δ²-cyclohexenyl)-β-methylbutadiene-α-carboxylic acid (I) (from the ester, A., 1932, 852) with PCl_3 gives its chloride, converted by ZnMeI into δ-(1 : 1 : 3-trimethyl-2-Δ²-cyclohexenyl)-β-methylbutadienyl *Me ketone* (II) (β-euionone), b.p. 105—106°/0.1 mm., reduced by $\text{Al}(\text{OPr}^i)_3$ - Pr^iOH to ζ-(1 : 1 : 3-trimethyl-2-Δ²-cyclohexenyl)-δ-methyl-Δ⁴-hexadien-β-ol (III), b.p. 105°/0.05 mm. With Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in C_6H_6 , (II) affords *Et* ζ-(1 : 1 : 3-trimethyl-2-Δ²-cyclohexenyl)-βδ-dimethyl-Δ⁴-heptatrienoate (IV), b.p. 142—143°/0.15 mm. Repetition of the syntheses with (IV) was not successful : (II), (III), and (IV) all give colours with SbCl_3 - CHCl_3 , but are inactive *in vivo*. J. W. B.

ω-Nitrophenylglyoxalarylhydrazones. G. D. PARKES and E. H. WILLIAMS (J.C.S., 1934, 67—68).—ω-Nitroacetophenone couples with diazonium salts in solution with NaOAc to give: ω-nitrophenylglyoxal-phenyl-, m.p. 101°, -*p*-chloro-, m.p. 134°, -2 : 4-dichloro-, m.p. 135.5°, -2 : 5-dichloro-, m.p. 137°, -*p*-bromo-, m.p. 137°, -2 : 4-dibromo-, m.p. 139°, -2 : 4 : 6-tribromo-, m.p. 111°, -3 : 4 : 5-tribromo-, m.p. 169°, and -o-nitro-phenyl-hydrazone, m.p. 118°. The action of Br causes replacement of NO_2 by Br. ω-Bromophenylglyoxal-2 : 4-dibromophenylhydrazone with NH_3 gives ω-amino-, m.p. 134°, and with NH_2Ph yields ω-anilino-phenylglyoxal-2 : 4-dibromophenylhydrazone, m.p. 137°. F. R. S.

Palladium catalyst. III. Reduction of ketones. W. H. HARTUNG and F. S. CROSSLEY (J. Amer. Chem. Soc., 1934, 56, 158—159).—COPhEt is reduced (H_2 , Pd-C (A., 1929, 184), EtOH) to PhPr; CHPhEt·OH could not be isolated even when reduction is interrupted. *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Pr}\cdot\text{OH}$, *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Pr}\cdot\text{OMe}$, and propyl-resorcinol and -pyrocatechol are similarly obtained from the corresponding propionyl derivatives. A Pt-C catalyst is inactive. H. B.

4-Cyano-1-hydrindone. H. HOYER (J. pr. Chem., 1934, [ii], 139, 94—96).—β-o-Nitrophenylpropionic acid is converted into its chloride, which is cyclised by AlCl_3 in CS_2 . The resulting 4-nitro-1-hydrindone, m.p. 104—105° (*oxime*, m.p. 212—213°), is reduced by $\text{Fe}(\text{OH})_2$ to 4-amino-, m.p. 122—123° (*Bz* derivative, m.p. 184—185°; *oxime*, m.p. 180—181°), which is converted (Sandmeyer) into 4-cyano-1-hydrindone, m.p. 116—117°. This does not give an aldehyde by Stephen's method and on attempted hydrolysis with aq. AcOH - H_2SO_4 gives (?) truxenetricarboxylic acid. H. A. P.

Ester enolates and keten acetals. XVII. Reactions of ester enolates with acyl halides. H.

SCHEIBLER and H. STEIN (J. pr. Chem., 1934, [ii], 139, 105—112; cf. A., 1930, 1037).—Interaction of $\text{CHPh}\cdot\text{C}(\text{OK})\cdot\text{OEt}$ with BzCl gives, in addition to $\text{CHPh}\cdot\text{C}(\text{OBz})\cdot\text{OEt}$ and $\text{CHPhBz}\cdot\text{CO}_2\text{Et}$, BzOH and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$; similarly, ClCO_2Et gives, in addition to $\text{CHPh}\cdot\text{C}(\text{OEt})\cdot\text{CO}_2\text{Et}$ (I), the *C*-substitution product, $\text{CHPh}(\text{CO}_2\text{Et})_2$. (I) is not affected by NaOEt , but an additive product is formed with KOEt , which regenerates (I) with dry CO_2 , and with EtOH gives $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$. Et isobutyrate does not give a metal derivative with Na, K, NaOEt , KOEt , or NaNH_2 (II); with (II) the main products are $\text{CMe}_2\cdot\text{C}(\text{NH}_2)\cdot\text{ONa}$ and diisobutyramide. A Na derivative is, however, formed with CPh_3Na , but after treating this with BzCl only $\text{CMe}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ was isolated. H. A. P.

Colour and structure of aromatic oximes. (MME.) RAMART-LUCAS (Compt. rend., 1934, 198, 97—99).—The positions of the bands and form of the ultra-violet absorption curves of oximes $\text{ArCR}\cdot\text{NOH}$ are closely similar to those of the corresponding olefines $\text{ArCR}\cdot\text{CHR}'$ ($\text{R}=\text{H}$, alkyl or aryl; $\text{R}'=\text{H}$ or Me), although the absorption coeffs. of the latter are smaller, several examples being given. The structure of the absorbing form of oximes derived from such ketones can thus be determined. J. W. B.

Colour and structure of aromatic oximes. (MME.) RAMART-LUCAS (Compt. rend., 1934, 198, 267—269).—Absorption spectra show that oximes of substances of the types, $\text{CH}_2\text{Ph}\cdot\text{COAr}$, $\text{CHPh}_2\cdot\text{COAr}$, and $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, have the $>\text{C}\cdot\text{NOH}$, and not the $\text{C}\cdot\text{C}\cdot\text{NH}\cdot\text{OH}$, structure, resemblance being to the methylene, rather than to the stilbene, analogues. R. S. C.

Nitration of chalkone. I. TANĂSESCU and A. GEORGESCU (J. pr. Chem., 1934, [ii], 139, 189—192; cf. Le Fevre and collaborators, A., 1933, 611; Goldschmidt, A., 1895, i, 422).—Nitration of chalkone gives a mixture of 2- and 4- NO_2 -derivatives (*phenylhydrazones*, m.p. 162—164°, and 148—150°) only. The former is converted by hot NaOH -EtOH into indigotin. H. A. P.

7-Nitrodeoxybenzoin. J. MEISENHEIMER and E. MAHLER (Annalen, 1934, 508, 185—191).—Successive treatment of 7-nitrostilbene (I) with 15% MeOH - KOH , H_2O , and $\text{Br}\cdot\text{H}_2\text{O}$ gives an oily product (A) which gradually solidifies (m.p. 58—68°) and is a mixture of stereoisomeric α-bromo-α-nitro-β-methoxy-αβ-diphenylethanes (the pure α-form, m.p. 91°, is obtained by crystallisation from AcOH). Successive treatment of (A) with MeOH - KOH and aq. NH_4HCO_3 gives 7-nitrodeoxybenzoin *Me₂ acetal* (α-nitro-ββ-dimethoxy-αβ-diphenylethane) (II), m.p. 117—118° [the compound, m.p. 202—203°, described as this by Wieland and Blümlich (A., 1921, i, 554), is benziloxime *Me₂ acetal*], and some 7-nitro-7'-aminostilbene, m.p. 157°. (II) is hydrolysed by 75% H_2SO_4 at 100—110° to 7-nitrodeoxybenzoin (III), m.p. 73° (*Br*-derivative, m.p. 91—91.5°), which could not be oximated [fission to benzhydroxamic acid and $\text{CH}_2\text{Ph}\cdot\text{NO}_2$ (IV) occurs], is converted by EtOH at 100° into (IV) and EtOBz, and is decomposed by aq. NH_3 to NH_2Bz . Successive treatment of (A) with MeOH - KOH and conc. HCl gives (mainly) 7-nitro-7'-methoxystilbene,

m.p. 87°, and (I). Unsuccessful attempts to prepare (III) by other methods are summarised. $\text{NH}_2\text{OH}\cdot\text{HCl}$ in $\text{C}_6\text{H}_6\text{N}$ is a good oximating reagent; *anthraquinone dioxime*, decomp. 245—250°, is thus prepared.

H. B.

Possible existence of three 2 : 6-dibenzylcyclohexanones. R. CORNUBERT and M. DE DEMO (Compt. rend., 1933, 197, 1656—1658).—Three forms (I), m.p. 122°, (II), m.p. 55°, and (III), m.p. 103° (A., 1931, 161), of 2 : 6-dibenzylcyclohexanone have been isolated in previous work and their interconversions directly or by way of various oximes, semicarbazones, tetrahydropyrones, and reduction products are summarised. Catalytic reduction (H_2 -Pt in Et_2O) of (I) gives a hexahydro-ketone (IV), m.p. 79° [reduced by Na-EtOH to (V)], and the corresponding sec. alcohols, m.p. 72—73° (phenylurethane, m.p. 149°) and m.p. 93—94° (V) (phenylurethane, m.p. 137—138°), whereas (II) gives mainly an alcohol, m.p. 53—56° (phenylurethane, m.p. 102—103°), and 4% of (IV) resulting from slight conversion of (II) into (I) by Pt-black. These results suggest that (I) and (II) are true isomerides. (III) gives a different oxime, m.p. 123°, and no tetrahydropyrone.

J. W. B.

Heteropolarity. XXIII. Tetraphenylcyclopentadienone and its reduction products. W. DILTHEY, W. BRAUN, and O. TROSKEN (J. pr. Chem., 1933, [ii], 139, 1—16; cf. A., 1931, 91).— $\Delta^3\text{-2 : 3 : 4 : 5}$ -Tetraphenylcyclopentenone (I) [(enolic) *Ac* derivative, m.p. 183°] is converted by PCl_5 into its 2-*Cl*-derivative, m.p. 166° (decomp.) (cf. J.C.S., 1901, 79, 1256), which loses HCl at 180—190° to give tetraphenylcyclopentadienone (II), which is also formed directly from (I) by prolonged boiling with KOH in MeOH. (I) is formed by reduction of $\Delta^4\text{-3-hydroxy-2 : 3 : 4 : 5}$ -tetraphenylcyclopentenone (III) or of (II) with HI and P in boiling AcOH, and is converted by further reduction with Zn-Hg and AcOH into $\Delta^4\text{-2 : 3 : 4 : 5}$ -tetraphenylcyclopentenol (IV), m.p. 176°, which is similarly formed from (II) or the derived sec. alcohol (V). (IV) is isomerised to (I) by heating with AcOH in H_2 . Reduction of (III) with Pd-BaSO₄ and H_2 gives $\Delta^2\text{-tetraphenylcyclopentenone}$ (VI), m.p. 163°; with Pt-black (I) and $\Delta^3\text{-2 : 3 : 4 : 5 : 2' : 3' : 4' : 5'}$ -octaphenyl-2 : 2'-biscyclopentenone, m.p. 228°, are formed in addition. Distillation of the last-named with Zn dust gives (VI); (I), (II), (IV), and (V) give tetraphenylcyclopentadiene.

H. A. P.

Dicyclo-[3, 0, 3]-octane-2 : 6-dione. L. RUZICKA, A. BORGES DE ALMEIDA, and A. BRACK (Helv. Chim. Acta, 1934, 17, 183—200).—Cyclisation (Na in C_6H_6) of Et *n*-butane- $\alpha\beta\beta\delta$ -tetracarboxylate affords a mixture, b.p. 145—150°/0.2 mm. of Et cyclopentanone-2 : 3 : 3- and -2 : 4 : 4-tricarboxylate. Similarly, cyclisation of Et *n*-butane- $\alpha\beta\delta$ -tricarboxylate (Kay and Perkin, J.C.S., 1906, 89, 1643, improved) gives a mixture (separated by NaHCO_3 -2*N*-NaOH) of Et cyclopentanone-2 : 3- (I), b.p. 115°/0.1 mm., and -2 : 4- (II), b.p. 115°/0.1 mm., -dicarboxylate. (I) with $\text{CHCl}_3\text{-CH}_2\text{-CO}_2\text{Et}$ gives a mixture of Et cyclopentanone-2 : 3-dicarboxylate-2-propionate, and Et *n*-hexane- $\alpha\gamma\delta\zeta$ -tetracarboxylate, separated by hydrolysis with 20% HCl, trans-*n*-hexane- $\alpha\gamma\delta\zeta$ -tetracarboxylic

acid (V), m.p. 202—203°, crystallising. Re-esterification and fractionation of the residue gives the Et ester (III), b.p. 113—115°/0.05 mm., hydrolysed to cyclopentanone-3-carboxylic-2- β -propionic acid (IV), m.p. 119—120°, and the Et ester, b.p. 162—166°/0.2 mm., hydrolysed to cis-*n*-hexane- $\alpha\gamma\delta\zeta$ -tetracarboxylic acid (VI), m.p. 161.5—162°. Similarly, from (II) are obtained cyclopentanone-4-carboxylic-2- β -propionic acid and *n*-hexane- $\alpha\beta\delta\zeta$ -tetracarboxylic acid (VII), sinters 140°, m.p. 149—150° (probably a mixture of stereoisomerides). Et α -cyanoglutarate (improved prep.) with Et α -bromoglutarate (VIII) gives Et γ -cyano-*n*-hexane- $\alpha\gamma\delta\zeta$ -tetracarboxylate, b.p. 152°/0.03 mm. [also obtained by condensation of $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ with Et α -cyano-*n*-butane- $\alpha\beta\delta$ -tricarboxylate, b.p. 142°/0.18 mm., from $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and (VIII)], hydrolysed by 20% HCl to a separable mixture of the trans- and cis-acids identical with (V) and (VI), respectively : (VI) is converted into (V) by 20% HCl at 185°. Condensation of Et propane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ affords Et *n*-pentane- $\alpha\beta\beta\delta\delta$ -pentacarboxylate, b.p. 158—160°/0.1 mm., which with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ gives Et *n*-hexane- $\alpha\beta\beta\delta\delta\zeta$ -hexacarboxylate, b.p. 173°/0.05 mm., hydrolysed to (VII). Cyclisation of the Et ester of (V) or (VI) with 2.4 atoms of Na gives mainly Et dicyclo-[3, 0, 3]-octane-2 : 6-dione-3 : 7-dicarboxylate, $\text{CHR}\langle\text{CO}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}\rangle\text{CHR}'$ (IX) (A; R=R'=CO₂Et),

m.p. 57.5°, and a little Et cyclopentanone-3 : 5-dicarboxylate-2- β -propionate, b.p. 169—171°/0.15 mm. [hydrolysed to (IV)], which is the main product when 1.2 atoms of Na is used. Hydrolysis of (IX) with 20% HCl in N_2 or in vac. gives dicyclo-[3, 0, 3]-octane-2 : 6-dione (X) (A; R=R'=H), b.p. 83°/0.15 mm., m.p. 45° [dioxime, m.p. 201°; dibenzylidene derivative, m.p. 239—240°; di(hydroxymethylene) derivative, m.p. 110° (decomp.) (giving *n*-butane- $\alpha\beta\gamma\delta$ -tetracarboxylic acid on ozonolysis)]. Hydrolysis of (IX) with KOH-MeOH gives (IV), but with 2*N*-Na₂CO₃ in N_2 Et dicyclo-[3, 0, 3]-octane-2 : 6-dione-3-carboxylate (A; R=H, R'=CO₂Et), b.p. 119°/0.2 mm., and (X) are obtained.

J. W. B.

Preparation of 3-phenyl- β -(β' -hydroxy- β' -phenylpropionyloxy)propionic acid, α -hydroxy- γ -keto- α -phenylpentane, and α -hydroxy- γ -keto- α -phenylheptane. M. E. DITZ (Bull. Soc. chim., 1933, 53, [iv], 1286—1288; cf. A., 1931, 848).—Interaction of PhCHO and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ in presence of Zn (cf. A., 1909, i, 158) affords Et β -hydroxy- β -phenylpropionate, hydrolysed by EtOH-NaOH followed by incomplete acidification to β -phenyl- β -(β' -hydroxy- β' -phenylpropionyloxy)propionic acid (I), m.p. (+2H₂O) 188°. (I) is hydrolysed by cold acid to β -hydroxy- β -phenylpropionic acid (II) (Ag salt). The amide of (II) (0.25 mol.) and MgEtBr (2 mols.) in Et_2O during 24 hr. afford α -hydroxy- γ -keto- α -phenylpentane, b.p. 127—130°/2 mm. (semicarbazone, m.p. 168°). Similarly prepared, α -hydroxy- γ -keto- α -phenylheptane has b.p. about 135°/2 mm. (semicarbazone, m.p. 133°).

J. L. D.

Tautomerism of α -diketones. I. Phenyl benzyl diketone. E. P. KOHLER and R. P. BARNES (J. Amer. Chem. Soc., 1934, 56, 211—214).—Ph benzyl

diketone (I) is prepared by treatment of α -benzoyl- β -phenylethylene oxide with HCl in AcOH and subsequent distillation at 30 mm. in N_2 . The equilibrium mixture obtained when the enolic form, m.p. 89–90° (II), is heated for ≤ 1 hr. in soft glass or in presence of a trace of NaOMe at 100° contains 28.5% of (II) (cf. Moureu, A., 1931, 92) (as determined by indirect titration with Br); the vals. at 125°, 145°, and 165° are 25.5, 23.5, and 21%, respectively. Equilibration by a trace of NaOMe in MeOH, EtOH, $CHCl_3$, and C_6H_6 gives (for 0.1N-solutions) 43, 38, 53, and 39%, respectively, of (II). (II) is oxidised by O_2 in Et_2O to $BzOH$ and $BzCO_2H$. Alkaline solutions of (I) are oxidised rapidly by atm. O_2 , and in such solutions (I) undergoes the benzylic acid rearrangement. (I) and NaOEt in EtOH– Et_2O give a Na salt (+0.5EtOH), which dissolves in Et_2O or MeI and then separates in the “anhyd.” form. Acetylation (various methods) of (I) gives the *O*-acetate, b.p. 195–200°/5 mm.; *C*-acylation does not occur. Methylation (Me_2SO_4 or MeI and alkali under various conditions) of (II) gives a mixture of *O*-Me (III), b.p. 180–185°/0.05 mm., m.p. 32°, and *C*-Me (IV) derivatives; treatment of the mixture with 40% KOH affords α -hydroxy- $\alpha\beta$ -diphenylbutyric acid, m.p. 179–180° [from (IV) by the benzylic acid rearrangement], and unchanged (III) [obtained in max. yield (80.9%) from the Na salt (V) and Me_2SO_4 in $COMe_2$]. (V) and I in Et_2O give the tetraketone, $(COPh\cdot CO\cdot CHPh)_2$, m.p. 198°, oxidised (alkaline H_2O_2) to $BzOH$ and $(\cdot CHPh\cdot CO_2H)_2$. $MgPhBr$ and (I) afford phenylacetyldiphenylcarbinol, m.p. 60°, oxidised (CrO_3 , AcOH) to $COPh_2$, $CH_2Ph\cdot CO_2H$, and a little $BzOH$. The experiments are usually carried out in N_2 .

H. B.

Syntheses of 2-acylresorcinols by the “Nidhon” process. I. 2-Benzoylresorcinol. D. B. LIMAYE (Ber., 1934, 67, [B], 12–15).—4-Methylumbelliferone benzoate or a mixture of 4-methylumbelliferone and $BzCl$ is converted by $AlCl_3$ at 160–170° into 8-benzoyl-4-methylumbelliferone (I), m.p. 210°, and a substance, m.p. 174°, probably the corresponding 6-Bz compound. (I) is transformed by $CH_2Br\cdot CO_2Et$ and NaOEt in boiling EtOH into 7-carbethoxymethoxy-8-benzoyl-4-methylcoumarin, m.p. 130°; the corresponding acid, m.p. 203°, is smoothly transformed by NaOAc and boiling Ac_2O into 3-phenyl-4'-methyl-7':8'-furocoumarin, m.p. 170°, showing that Bz in (I) is *ortho* to OH, and hence occupies position 6 or 8. Treatment of (I) with boiling aq. NaOH leads to 2-benzoylresorcinol (II), m.p. 135°, $COMe_2$, and CO_2 ; the position of Bz follows from the non-identity of (II) with 4-benzoylresorcinol, the possible theoretical alternative. (II) condenses with $CH_3Ac\cdot CO_2Et$ in presence of conc. H_2SO_4 to (I); it yields a Me_2 ether, m.p. 99°, b.p. 345°, and a dibenzoate, m.p. 115°. The above method of preparing 2-acylresorcinols is termed the Nidhon process. H. W.

[Preparation of] benzoquinone. G. A. KIRKHOF, D. F. ALEXEEV, R. Y. ASTROVA, and R. I. GRAYURSKAYA (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 303).—Benzoquinone forms a foam with the gases formed in the $NH_4Ph\cdot K_2Cr_2O_7$ reaction, whilst other reaction products separate at the bottom of the vessel.

CH ABS

Preparation of 2-iodophenanthraquinone. L. McMASTER and R. S. WOBUS (J. Amer. Chem. Soc., 1934, 56, 164–165).—2-Iodophenanthraquinone, m.p. 223–224° (corr.), is prepared by the Sandmeyer method from 2-aminophenanthraquinone [obtained in 91% yield by reduction ($Na_2S_2O_4$, aq. NaOH) of the 2- NO_2 -derivative] (cf. Brass and Ferber, A., 1922, i, 355).

H. B.

Anthraflavone derivatives. H. DE DIESBACH and S. G. QUINZÁ (Helv. Chim. Acta, 1934, 17, 105–113).—With Cl_2 at 50° in conc. H_2SO_4 anthraflavone $CHA:CHA$ ($A=2$ -anthraquinonyl) (I) gives a Cl_1 -derivative, $CHACl\cdot CH_2A$, m.p. 284–286°, whilst with SO_2Cl_2 in $PhNO_2$ the dichloride $(\cdot CHACl)_2$, not melting at 320°, is obtained contaminated with nuclear chlorinated products from which nuclear Cl is eliminated by heating with Cu in $PhNO_2$. Reduction of (I) with either $Al\cdot HCl\cdot AcOH$ or Al -conc. H_2SO_4 gives $(\cdot CH_2A)_2$ (Eckert, A., 1925, i, 413). Nitration of 4:4'-dimethylbenzil (KNO_3 – H_2SO_4 at $<40^\circ$) gives its 3:3'-(NO_2)₂-derivative, m.p. 181–182°, reduced ($SnCl_2$ – HCl) to the $(NH_2)_2$ -derivative, m.p. 159°, which by the Sandmeyer reaction gives the 3:3'-dinitrile, m.p. 207°, hydrolysed to the 3:3'-dicarboxylic acid, m.p. 318–319°, the acid chloride of which condenses with C_6H_6 ($AlCl_3$) to give 3:3'-dibenzoyl-4:4'-dimethylbenzil, m.p. 143°. This with Cl_2 at 180–190° in $C_6H_5Cl_3$ affords di-10:10-dichloro-2-anthrionylglyoxal, m.p. 185° (decomp.), converted by hot H_2SO_4 into di-2-anthraquinonyl glyoxal ($A\cdot CO$)₂, m.p. 280° (quinoxaline, m.p. 326.5°; monohydrazone, decomp. 260°, m.p. 265°), which with NaOEt at 160° gives $\alpha\beta$ -di-2-anthraquinonyl ethyl alcohol. J. W. B.

Chemical properties of puberulic acid $C_8H_6O_6$ and a yellow acid $C_8H_4O_6$. G. BARGER and O. DORRER (Biochem. J., 1934, 28, 11–15; cf. A., 1932, 651).—Puberulic acid (I) is prepared from the Ac_2 compound (II) by hydrolysis with aq. NH_3 . Sublimation of (I) gives a decarboxylated compound. Treatment of tetramethylpuberulic acid (III) with cold NaOH gives trimethylpuberulic acid, m.p. 204°. No CHO group is present, and the Winkler test (A., 1924, i, 72) is negative. (I) is unsaturated. (II) takes up 12 H on catalytic reduction, whilst (III) takes up 10 H. The acid $C_8H_4O_6$ could not be decarboxylated nor acetylated, and no CHO group is present. Colour changes on neutralisation resemble those of a ψ -acid.

H. D.

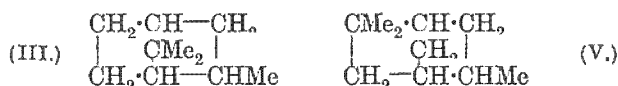
Santonin series. XVIII. Constitution of santoninic acid. E. WEDEKIND and O. ENGEL (J. pr. Chem., 1934, [ii], 139, 115–128; cf. A., 1932, 271).—Santoninic acid, m.p. 170–172°, is not affected by vac. distillation (cf. A., 1877, i, 470) or by H_2 – PtO_2 in AcOH. It is formed from metasantonin and 10% NaOH at 100°. Its H_2 -derivative (modified prep.), m.p. 190–192°, is converted by Ac_2O at the b.p. into the Ac_2 derivative, m.p. 232° (Me ester, m.p. 151°), and a (mono)acetyl-lactone (I), m.p. 204°, from both of which it is regenerated on alkaline hydrolysis. Tetrahydrosantonin (II) is converted by boiling 30% KOH into α -tetrahydrosantoninic acid, which is reconverted into the lactone (II) in warm Et_2O . 30% KOH is without effect on α -santonin oxide, monochlorosantonin, desmotroposantonin, and artemionic

acid. No recognisable products were obtained by dehydrogenation of (I) with Se. H. A. P.

Amber. II. L. SCHMID and F. TADROS (Monatsh., 1933, 63, 210—212).—Direct comparison, after purification through its picrate, of the hydrocarbon $C_{13}H_{14}$ (I) obtained by Se dehydrogenation of suksinin (A., 1933, 831) proves it to be 1:2:5- $C_{10}H_5Me_3$. Oxidation of (I) with $KMnO_4$ and methylation of the acid product with CH_3N_2 affords hemimellitic acid (II) as its Me_3 ester, whereas HNO_3 hydrolysis of the residue gives (II), also converted into its imide-acid.

J. W. B.

Fenchene series. IV. α -Fenchene hydrate (methyl- α -fenchocamphorol) and α - and β -fenchane. G. KOMPPA and S. BECKMANN (Annalen, 1934, 508, 205—214).—*dl*- α -Fenchocamphorone and $MgMeI$ give *dl*-methyl- α -fenchocamphorol (α -fenchene hydrate) (I), b.p. 76—77°/7 mm., 86.5—87°/14 mm., m.p. 46—47° (*phenylcarbamate*, m.p. 117—118°), which when distilled under atm. pressure loses H_2O and affords *dl*- α -fenchene (II), b.p. 154—156°. (I) is also obtained in small yield from *dl*- α -fenchene hydrochloride, m.p. 36—37° [from (II) and HCl in Et_2O], and aq. KOH at 50—60°. Reduction (H_2 , colloidal Pd) of (II) gives α -fenchane (III), b.p. 161—163°/755 mm. *dl*-isoFenchyl alcohol is dehydrated ($KHSO_4$) to *dl*- β -fenchene (IV), b.p. 151—153°, which is simi-



larly reduced to *dl*- β -fenchane (V), b.p. 158—160°/752 mm. (II) is oxidised (alkaline $KMnO_4$) less readily than (IV); the mixture of fenchenes obtained by dehydration ($KHSO_4$) of fenchyl alcohol is thus shown to contain 3—4% of (II). H. B.

5- and --Hydroxycamphor and their derivatives. Y. ASAHINA and M. ISHIDATE [with H. SHIMIZU] (Ber., 1934, 67, [B], 71—77; cf. this vol., 79).—5-Ketocamphor (I) is converted by semicarbazide acetate in dil. $EtOH$ at room temp. into the di-, m.p. 295°, and *mono*-, m.p. 238—240°, -semicarbazone; reduction (Wolff) of the latter affords *d*-borneol, m.p. 203°, $[\alpha]_D^{25} +19.8^\circ$ in abs. $EtOH$. Treatment of (I) in H_2O with $Na-Hg$ in presence of CO_2 leads to 5-hydroxycamphor, m.p. 210°, $[\alpha]_D^{25} +47.4^\circ$ in $EtOH$ [semicarbazone (II), m.p. 222° (decomp.); *Ac* derivative, b.p. 165—167°/22 mm., and its semicarbazone (III), m.p. 237—238° (decomp.)]. (II) or (III) is transformed by $NaOEt$ in $EtOH$ at 170—180° into *epiborneol*, m.p. 188°, $[\alpha]_D^{25} -3.4^\circ$ in $EtOH$, oxidised by $K_2Cr_2O_7$ in $AcOH$ to *d*-epicamphor, m.p. 182°, $[\alpha]_D^{25} +45.4^\circ$ in $EtOH$ (semicarbazone, m.p. 235°). *trans*- π -apoCamphor-7-carboxylic acid is converted by CH_3N_2 into *Me trans*- π -apocamphor-7-carboxylate, m.p. 72—73°, the semicarbazone, m.p. 235—236° (decomp.), of which is transformed by the successive action of Na and $EtOH$ and HCl into *trans*- π -hydroxycamphor (IV), 233°, $[\alpha]_D^{25} +62.20^\circ$ in abs. $EtOH$ [semicarbazone (V), m.p. 224—225° (decomp.)]; *Ac* derivative, b.p. 176°/4 mm., and its semicarbazone, m.p. 234—235° (decomp.)]. Oxidation of (IV) with H_2SO_4 and $Na_2Cr_2O_7$ yields *trans*-7-aldehydo--apocamphor, m.p. 195—196° (disemicarbazone, m.p. $\approx 340^\circ$).

(V) is converted by $NaOEt$ in $EtOH$ at 170—180° into *d*- π -borneol, m.p. 200.5°, $[\alpha]_D^{25} +17.68^\circ$ in $EtOH$, oxidised to π -camphor, m.p. 172—173° [semicarbazone, m.p. 214—215° (decomp.)]. The following compounds are obtained similarly from *Me cis*- π -apocamphor-7-carboxylate, m.p. 74—75° (semicarbazone, m.p. 259—260°); *cis*- π -hydroxycamphor, m.p. 233—234°, $[\alpha]_D^{25} +40.68^\circ$ in abs. $EtOH$ (semicarbazone, m.p. 216—217°; *Ac* derivative, b.p. 160°/22 mm., and its semicarbazone, m.p. 210—211°); *cis*-7-aldehydo- π -apocamphor, m.p. 205° (disemicarbazone, m.p. 256°); *l*- π -borneol, m.p. 200.5°, $[\alpha]_D^{25} -16.77^\circ$ in $EtOH$ (corresponding *r*-compounds, m.p. 200—200.5°); --camphor, m.p. 172—173°, $[\alpha] \pm 0^\circ$ in $EtOH$. H. W.

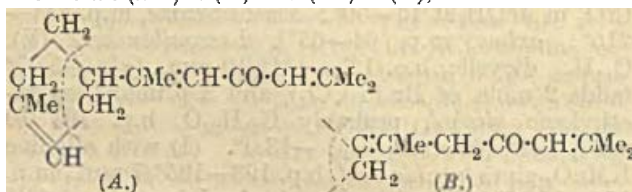
Preparation of camphorquinone. W. C. EVANS, J. M. RIDGION, and J. L. SIMONSEN (J.C.S., 1934, 137).—Camphor is oxidised by SeO_2-Ac_2O to camphorquinone. F. R. S.

Constituents of the volatile oil from the wood of *Chamaecyparis formosensis*, Matsum. K. KAFUKU and N. ICHIKAWA (Bull. Chem. Soc. Japan, 1933, 8, 371—391; cf. B., 1931, 653).—This oil, obtained in 1.1% yield, contains α -pinene, *d*-camphene, α -terpineol, *l*-cadinol, $C_{20}H_{36}O$, b.p. 149—152°/10 mm., $[\alpha]_D^{25} -33^\circ$, allylprocatechol, a phenol, m.p. 127—128°, and a saturated acid, $C_{10}H_{16}O_2$, b.p. 146—147°/7 mm., 263—265°/764 mm. (NH_4 , m.p. about 150°, and *Ag* salts; chloride, b.p. about 100°/10 mm.), a primary, saturated alcohol, *benihiol* (I), $C_{10}H_{18}O$, b.p. 106—108°/10 mm., $[\alpha]_D^{25} +23.15^\circ$ [*H* phthalate, cryst., $[\alpha] +4.55^\circ$ in $EtOH$ (*Ag* salt, decomp. about 165°); formate, b.p. 101—103°/10 mm., $[\alpha]_D^{25} +20.5^\circ$; acetate, b.p. 107—108°/10 mm., $[\alpha]_D^{25} +22.5^\circ$; benzoate, b.p. 161—162°/5 mm., $[\alpha]_D^{25} +15^\circ$; propionate, b.p. 117—120°/10 mm., $[\alpha]_D^{25} +14.24^\circ$; *Me ether*, b.p. 83—84°/11 mm., $[\alpha]_D^{25} +24^\circ$; *benihyl chloride* (II), b.p. 94—97°/10 mm., $[\alpha]_D^{25} +11^\circ$, and *iodide* (III), an oil], *benihinol* (IV), an unsaturated primary alcohol, $C_{10}H_{16}O$, b.p. 96.3—97.7°/10 mm., 216°/766 mm., $[\alpha]_D^{25} +46.8^\circ$ [*H* phthalate, m.p. 107—108° (*Ag* salt, m.p. 88—90°)], *benihinal*, an unsaturated aldehyde, $C_{10}H_{14}O$, b.p. 87°/8 mm. [also obtained from (IV) by CrO_3 in $AcOH$ at 15—50°; semicarbazone, m.p. 214—215°; oxime, m.p. 64—65°], *d*-sesquibenzene (V), $C_{15}H_{24}$, dicyclic, b.p. 127—131°/10 mm., $[\alpha]_D^{25} +35.7^\circ$ (adds 2 mols. of Br in CCl_4), and a primary, monoethylenic alcohol, probably $C_{15}H_{24}O$, b.p. 163°/10 mm., 294°/760 mm., $[\alpha]_D^{25} -13.0^\circ$. (I) with alkaline $KMnO_4$ gives *benihic acid*, b.p. 193—195°/7 mm., m.p. 175—175.5° (*Ag* salt), also obtained by CrO_3-AcOH together with the aldehyde, *benihial*, b.p. 76—77.8°/9.5 mm., $[\alpha]_D^{25} +15^\circ$ (semicarbazone, m.p. 169°, $[\alpha]_D^{25} +151.6^\circ$, in $CHCl_3$; phenylhydrazine, m.p. 122°, $[\alpha]_D^{25} +167.5^\circ$ in $CHCl_3$; oxime, an oil), which is better prepared by Beckmann's reagent. (I) is dehydrated by 50% H_2SO_4 at 80—90°, syrupy H_3PO_4 at 100°, or $ZnCl_2$ at 160—170°, to a hydrocarbon, b.p. about 172—173°, $[\alpha] 0^\circ$, which, when hydrogenated (Pd), gives a hydrocarbon, $C_{10}H_{18}$, b.p. 162°, $[\alpha]_D^{25} +7.5^\circ$, also obtained by hydrogenation (Pd) of (II) or (III) (the latter in 10% $KOH-EtOH$). (V) is stable to Na -amyl alcohol, is racemised by 50% H_2SO_4 , and with Se gives cadinene; it gives a hydrochloride, m.p. 103—104°, hydrobromide, m.p. 112—114°, and unstable hydr-

iodide, m.p. 117—118°, all inactive, whence NaOAc-AcOH yields the *l*-form of (V), $[\alpha]_D^{25} -40.34^\circ$, which regenerates the same inactive halogen derivatives.

R. S. C.

Volatile plant materials. I. Atlantone, the fragrant principle of cedarwood oil. A. S. PFAU and P. PLATTNER (Helv. Chim. Acta, 1934, 17, 129—157).—Fractionation of Atlas cedarwood oil gives a mixture of sesquiterpenes (50%) containing cadinene, and 30% of a complex mixture of di- and tri-cyclic sesquiterpene alcohols (partial separation described), including an alcohol $C_{15}H_{26}O$, m.p. 92—92.5°, $[\alpha]_D^{20} +32.6^\circ$ in EtOH, and ketones $C_{15}H_{22}O$ (I), b.p. 121—123°/1 mm., $n_D +2.48^\circ$, and $C_{15}H_{22}O_2$ (II). The following results show that (I) is a mixture of isomeric α - (III) and γ - (IV) -atlantone. Reduction of (I) with Ni-H₂ at 70° gives hexahydro- α -atlantone, b.p. 147.5—148°/10 mm. (oxime, b.p. 139.5—140°/1 mm.), and tetrahydro- γ -atlantone, whereas Na-EtOH gives a mixture (V), b.p. 158—160°/10 mm., of tetrahydro- α -atlantol, dihydro- γ -atlantol, and [from (II)] a glycol $C_{15}H_{26}O_2$, b.p. 143—145°/1 mm.: (V) is oxidised (KMnO₄-COMe₂) to CH₂Pr⁶-CO₂H (VI) and a diketoid acid $C_{15}H_{26}O_4$, [CH₂Pr⁶-CO-CH₂-CHMe-CH(CH₂-CO₂H)-CH₂-CH₂Ac], isolated as the semicarbazone, m.p. 208—209°, of its Me ester. Reduction (Ni-H₂) of (V) gives a mixture, b.p. 150.5—151°, of hexahydroatlantol and tetrahydro- γ -atlantol, oxidised to (VI) and 4-methylcyclohexanone. With boiling aq. EtOH-NaOH (I) gives COMe₂, *dl*-4-methyl- Δ^3 -cyclohexenyl Me ketone (VII) (hence the presence of this ketone in the steam-distillation products of the original oil), and a trace of mesityl oxide. Under milder hydrolytic conditions (I) affords β -(4-methyl- Δ^3 -cyclohexenyl)- Δ^4 -propenyl Me ketone, b.p. 125.5—126°/10 mm. (semicarbazone, m.p. 152.5—153°) [converted by KOH into COMe₂ and (VII)], from (II), and β -(4-methyl- Δ^3 -cyclohexenylidene)-*n*-propyl Me ketone (as its semicarbazone, m.p. 195—195.5°) from (IV). Ozonolysis of (I) [giving CO(CHO)₂, COMe₂, CH₂O, and HCO₂H] and of various derived products, and the above results, show that (III) is (A) and (IV) is (B), the structures of



the degradation products also being given. In confirmation of this, the (amorphous) semicarbazone from (I) when heated with KOH at 250°/vac. affords α - and γ -bisabolene, identified as the trihydrochloride. (I) is also present in Himalayan, but not in Lebanon, cedarwood oil.

J. W. B.

Orientation in furan nucleus. VII. 2:5-Di-substituted furans. H. GILMAN, N. O. CALLOWAY, and E. W. SMITH (J. Amer. Chem. Soc., 1934, 56, 220—221).—The 4-sulpho-derivative [and not the 3-, as stated by Hill and Palmer (A., 1889, 386)] is obtained by sulphonation of 5-bromo-2-furoic acid, since debromination (Zn) and fusion of the resulting sulphofuroic acid with HCO₂Na give furan-2:4-dicarboxylic

acid. Et 5-methyl-2-furoate, Ac₂O, and SnCl₄ in C₆H₆ afford Et 4-acetyl-5-methyl-2-furoate (I), m.p. 99°; the free acid, m.p. 235° (decomp.), is oxidised (alkaline KMnO₄) to 5-methylfuran-2:4-dicarboxylic acid (II), m.p. 270—272°, decarboxylated to 2-methyl-3-furoic acid. Et 4-bromoacetyl-5-methyl-2-furoate, m.p. 67—68° [from (I) and Br in AcOH-Ac₂O], and C₅H₅N give the pyridinium bromide, converted by aq. 15% KOH into (II). If one of the substituents in a 2:5-disubstituted furan is *op*-directing and the other is *m*-directing, an entering group is directed to the β -position adjacent to the former group. H. B.

Diazotisation of an aminofuran. H. GILMAN and G. F. WRIGHT (Rec. trav. chim., 1934, 53, 13—17).—Et 4-nitro-5-acetamido-2-furoate is reduced by PtO₂-H₂ in abs. EtOH to the 4-NH₂-compound, m.p. 160.5°, which with HNO₂ and HCl gives the diazonium salt [β -naphthol derivative, m.p. 223.5—224.5° (decomp.)]. This with Cu gives Et 5-acetamido-2-furoate, and with Cu and KCN (in dil. H₂SO₄) gives (?) Et 4-hydroxy-5-acetamido-2-furoate, m.p. 143—144°. Et 4-nitro-5-amino-2-furoate (prep. improved) is not extracted from Et₂O by HCl. Neither this nor Et 5-amino-2-furoate could be diazotised, nor could their picrates, although NH₂Ph picrate diazotised smoothly in dil. H₂SO₄. H. A. P.

Preparation and reactions of furylcarbimides. A. T. BLOMQUIST and H. B. STEVENSON (J. Amer. Chem. Soc., 1934, 56, 146—149).—5-Methyl-2-, m.p. 61—62°, 5-bromo-2-, m.p. 135.5—136°, 2:4-dimethyl-3-, m.p. 144—145°, 2-methyl-3-, m.p. 149.5—150°, and 2:5-dimethyl-3-, m.p. 136—136.3°, -furylhydrazides, prepared from the appropriate Et esters and N₂H₄.H₂O at 125—140°, are converted into the corresponding azides, m.p. 35—36°, 66—67°, an oil, 22—23°, and 24—25°, respectively, which when heated in light petroleum (b.p. 90—100°) afford 5-methyl-2-, b.p. 53—54°/35 mm., 5-bromo-2-, b.p. 75°/35 mm., 2:4-dimethyl-3-, b.p. 74—75°/31 mm., 2-methyl-3-, b.p. 42°/15 mm., and 2:5-dimethyl-3-, b.p. 68°/20 mm., -furylcarbimides. The 3-derivatives are more stable to air and light. The following carbamides, carbamates, and benzfurylamides are obtained from the requisite carbimides and H₂O, MeOH, and MgPhBr, respectively: *s*-di-5-methyl-2-, m.p. 182°, -2:4-dimethyl-3-, m.p. 285°, -2-methyl-3-, m.p. 227°, and -2:5-dimethyl-3-, m.p. 247°, -furylcarbimides; Me 5-methyl-2-, m.p. 64—66°, 2:4-dimethyl-3-, m.p. 95—96°, 2-methyl-3-, b.p. 128°/14 mm., and 2:5-dimethyl-3-, b.p. 107°/2.5 mm., -furylcarbimides; benz-5-methyl-2-, m.p. 75—80°, -2:4-dimethyl-3-, m.p. 169—170°, and -2-methyl-3-, m.p. 137.8—138°, -furylamides. H. B.

Bromine derivatives of tetrahydropyran. R. PAUL (Compt. rend., 1934, 198, 375—376).—With Br in CCl₄ at -15° dihydropyran (I) affords 2:3-dibromotetrahydropyran, b.p. 96—98°/9 mm., converted by slow distillation into 3-bromo-5:6-dihydropyran, b.p. 63°/22 mm. (corr.), and by long contact with H₂O into the acetal (CH₂<CH₂-O>CH₂-O), m.p. 110°. With dry HBr at 0° (I) affords 2-bromotetrahydropyran, b.p. 61°/6 mm. J. W. B.

Dihydro-1:4-pyrans. IV. Synthesis of γ -benzoyl- γ -butyrolactone and α -hydroxy- δ -benz-

oylvaleric acid. R. C. FUSON, M. E. DAVIS, B. H. WOJCIK, and J. A. V. TURCK (J. Amer. Chem. Soc., 1934, 56, 235—237).—The NaHSO_3 compound of γ -benzoylbutaldehyde (I) [prepared by oxidation (O_3) of 1-phenyl- Δ^1 -cyclopentene (II)] and aq. NaCN give α -hydroxy- δ -benzoylvaleronitrile, m.p. 151—151.5°, hydrolysed (conc. HCl) to the free acid, m.p. 117.5—118.5° (A., 1932, 279). Oxidation (KMnO_4) of (I) or (II) affords γ -benzoylbutyric acid, m.p. 126°, which with Br in CCl_4 gives the γ -Br-derivative, m.p. 97—98°; this heated with H_2O , aq. NaOH , or AgOBz in Et_2O yields γ -benzoyl- γ -butyrolactone, m.p. 78—79°. H. B.

Cyclic compounds containing a carbonyl group.
Mechanism of the formation of pyrylium salts from 1 : 5-diketones. C. F. H. ALLEN and H. R. SALLANS (Canad. J. Res., 1933, 9, 574—582; cf. A., 1931, 845; 1903, i, 115).—Interaction of cyclohexanone with $\text{COPh}\cdot\text{CH}\cdot\text{CHPh}$ (I) in EtOH — NaOH affords $\text{Ph}\beta$ -2-cyclohexanonyl- β -phenylethyl ketone (II), m.p. 149° [dioxime (III), m.p. 186°; pyrylium ferrichloride, m.p. 161°, perchlorate, m.p. 214° and stannichloride, m.p. 143°], which adds 2 mols. of Grignard reagent (IV), indicating that it is a diketone. In the absence of EtOH — NaOH , a product, $\text{C}_{36}\text{H}_{34}\text{O}_3$, m.p. 167—168° is formed which consumes 3 mols. of (IV). p -Chlorophenyl- β -2-cyclohexanonyl-, m.p. 125—126°, and - β -2-(3-methylcyclohexanonyl)- β -phenylethyl ketone, m.p. 155—156° (pyrylium ferrichloride, m.p. 133°, perchlorate, m.p. 231°, and stannichloride, m.p. 135°), are described. The additive product of (I) with cyclopentanone affords a pyrylium ferrichloride, m.p. 126°, perchlorate, m.p. 240° (decomp.), and stannichloride, m.p. 161°, whereas that with benzylidenediacetophenone (cf. A., 1896, i, 556) gives a pyrylium stannichloride, m.p. 205°, and stibnichloride, m.p. 320° (decomp.). (II) in boiling EtOH with $\text{NH}_2\text{OH}\cdot\text{HCl}$ during 3 hr., followed by cold NaOH , affords the *picrate*, m.p. 196° of 2 : 4-diphenyl-5 : 6 : 7 : 8-tetrahydroquinoline [also formed when (III) is heated with HCl in dry C_6H_6]. (II) with conc. H_2SO_4 in cold EtOH during 24 hr., affords mainly a H_2O -sol. sulphonic acid, some 1 : 3-diphenyl-4 : 8-endocarbonyl- Δ^8 (1)-cyclooctene (?) (V), m.p. 143° (oxime, m.p. 156°), and an oil, b.p. 155—160°/25 mm., from which a solid (VI), m.p. 151°, isomeric with (V), separates; the stereoisomeride of (VI) is not obtained pure. (II) is unchanged by long boiling with AcCl or Ac_2O . (V) reacts with 1 mol. of MeMgI ; hydrolysis of the Grignard compound (VII) affords 1 : 3-diphenyl-4 : 8-endo-(α -hydroxyethyl)- Δ^8 (1)-cyclooctene, m.p. 147°, which re-forms (VII) and does not react with Br . (II) in CHCl_3 — MeOH with HBr at room temp. affords 2-methoxy-2 : 4-diphenylhexahydrobenzopyran (VIII), $\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CHPh}\cdot\text{CH}_2$, m.p. 171° [pyrylium ferrichloride identical with that from (II), which suggests that the pyrylium salts are formed *via* the OH-form of (VIII)] [also obtained from (II) and H_2SO_4], which does not react with (IV), NH_2OH , or KMnO_4 , and is hydrolysed by a trace of H_2SO_4 in EtOH to (II). (I) with anthrone (cf. A., 1919, i, 25) affords an additive product which yields a monoxime, m.p. 144—145°, but adds 2 mols. of (IV).

The menthone analogue affords a monoxime, adds 2 mols. of (IV), and liberates 1 mol. of gas. It is not dehydrated without complete decomp. α -Diketo- $\alpha\beta$ -diphenyl- ε - p -diphenylpentane (A., 1932, 385) affords a pyrylium perchlorate, m.p. 258°, stannichloride, m.p. 206°, and stibnichloride, m.p. 233° (decomp.). J. L. D.

Natural coumarins. VIII. Bergaptol, a new component of Calabrian oil of bergamot. E. SPATH and L. SOCIAS. IX. Heraclin. E. SPATH and S. RASCHKA (Ber., 1934, 67, [B], 59—61, 62—63; cf. A., 1933, 1056).—VIII. Treatment of oil of bergamot with KOH — MeOH at room temp. and of the solution with H_2O —light petroleum gives an aq. portion which on acidification affords bergaptol (I), m.p. 280—282°, transformed by CH_2N_2 in MeOH into bergapten. The possibility that (I) does not exist as such in the oil is excluded by its isolation therefrom by distillation in high vac. and sublimation.

IX. The dried seeds of *Heracleum sphondylium*, L., are extracted with Et_2O and the conc. extract is treated with light petroleum, whereby, after further purification, heraclin (II), m.p. 189—190° (vac.), is isolated. The identity of (II) with bergapten is established by m.p. and mixed m.p. It is proposed to replace the name heraclin by bergapten. H. W.

Plant pigments. LVII. Caricaxanthine, cryptoxanthine, zeaxanthine monopalmitate. P. KARRER and W. SCHLIENTZ (Helv. Chim. Acta, 1934, 17, 55—57).—Caricaxanthine, $\text{C}_{40}\text{H}_{56}\text{O}$, m.p. 169° (cf. Yamamoto *et al.*, A., 1933, 1343), is identical (m.p., absorption spectra, feeding experiments) with cryptoxanthine (Kuhn *et al.*, this vol., 70) and is a monohydroxy- β -carotene. Partial hydrolysis of physalien affords zeaxanthine monopalmitate, m.p. 148°.

J. W. B.

Isomeric 6 : 6'-di-(2 : 4-bistrichloromethyl-1 : 3-benzdioxinyl)sulphones. F. D. CHATTAWAY and A. E. BELL (J.C.S., 1934, 43—45).—6 : 6'-Di-(2 : 4-bistrichloromethyl-1 : 3-benzdioxinyl)sulphone, prepared from 4 : 4'-dihydroxydiphenylsulphone, chloral hydrate, and H_2SO_4 , has been isolated in three out of possible six forms, α -, m.p. 215°, β -, m.p. 240°, and γ -, m.p. 248°. The α - and γ -compounds are converted by dil. EtOH — KOH into α -, m.p. 241°, and γ -6 : 6'-di(trichloromethyl-dichloromethylene-1 : 3-benzdioxinyl)sulphone, m.p. 250°. Each of the isomerides with EtOH — KOH yields 4 : 4'-diethoxy-3 : 3'-dicarboxydiphenylsulphone (I), m.p. 247°. *o*-Cresol is converted by heating with H_2SO_4 into 4 : 4'-dihydroxy-3 : 3'-dimethyldiphenylsulphone, m.p. 268°, which gives the *OEt*-compound, m.p. 134° (4'-OH-4-*OEt*-compound, m.p. 186°), oxidised to 4 : 4'-diethoxy-3-carboxy-3'-methyldiphenylsulphone, m.p. 211°, or the -3 : 3'-dicarboxy-compound, identical with (I). 4 : 4'-Diethoxy-3 : 3'-dicarbomethoxy-, m.p. 162°, and 4 : 4'-dihydroxy-3 : 3'-dicarboxy-diphenylsulphone, m.p. 299°, are described. F. R. S.

Rotenone. XVI. Physiological action of rotenone, deguelin, and rotenone resin. Chemical behaviour of deguelin. S. TAKEI and S. MIYAJIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1933, 12, 62).—Deguelin, $[\alpha]_D^{25}$ —23.22°, which has a physiological action on *Cobitis fossilis* weaker than that of

rotenone, yields on hydrolysis with alcoholic alkali β -tubaic acid, $C_{12}H_{12}O_4$, m.p. 161° , from which on catalytic hydrogenation, dihydro- β -tubaic acid, $C_{12}H_{14}O_4$, m.p. 170° , is obtained identical with the β -dihydrotubaic acid obtained from β -dihydrototenone by hydrolysis.

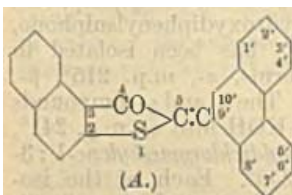
W. O. K.

Constitution of the colouring matter of *Lawsonia alba*, Lam., or Indian mehedi. J. B. LAL and S. DUTT (J. Indian Chem. Soc., 1933, 10, 577—582).—Details are given for the isolation of lawsone (I), $C_{10}H_6O_3$, m.p. 190° (decomp.) [*Ag*, NH_4 , decomp. 150 — 170° , and *Pb* salts; salt, $C_{10}H_5O_3Pb \cdot Ac$; *Ac*, m.p. 128 — 129° , and *Br*-, m.p. 198° , derivatives; *oxime*, m.p. 180° ; *dioxime*, m.p. 200° (decomp.)]; *phenylhydrazone*, m.p. 229° (decomp.); *Et ether*, m.p. 126 — 127°], from the fresh leaves. (I), moist Zn dust, and Ac_2O afford *triacetyldihydrolawsone*, m.p. 134.5° ; with NH_2Ph in $AcOH$, *anilinolawsone*, $C_{16}H_{11}O_2N$, m.p. 190° , results. Distillation of (I) with Zn dust gives $C_{10}H_8$, whilst oxidation ($KMnO_4$, dil. $NaOH$) affords o - $C_6H_4(CO_2H)_2$. (I) is 2-hydroxy-1:4-naphthaquinone. The lawsone, m.p. 192 — 195° (decomp.), described by Tommasi (A., 1920, i, 626) is probably identical with (I).

H. B.

Structure of cubebin. A. S. GINZBERG and M. G. GERCHIKOV (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 214—221).—Rast's method for determining mol. wt. does not give uniform results; b.p. determinations in $CHCl_3$ indicate the val. 316.6 — 323.7 , corresponding with $C_{20}H_{20}O_6$. Primary or *sec.* OH groups, or double linkings in the side chain, could not be detected. The formula $OH \cdot CMe[(CMeR)_2]_2O$, where $R = 3 : 4-C_6H_3 \cdot CH_2O_2$, is proposed. CH. ABS.

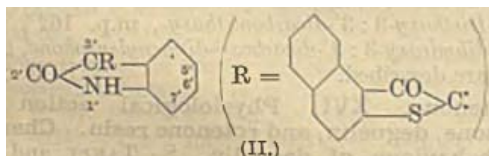
Indigoid dyes. IV. 2:1-Naphthathiophen-anthreneindigotin. V. P. C. DUTTA (Ber., 1934, 67, [B], 5—8, 9—12; cf. A., 1933, 1169).—IV. The condensation of 2:1-naphthoxythiophen (I) with phenanthraquinone by HCl in $AcOH$ leads to dyes which are usually more intensely coloured than the



corresponding 1:2-derivatives (*loc. cit.*). The following substances are described: 2:1-naphthathiophen-9'-phenanthreneindigotin (A) and its 4'- NO_2 -, 2'- NO_2 -, 4:5'-(NO_2)₂-, 4'-*Br*-, 2'- NH_2 -, m.p. $>290^\circ$, 4'- NH_2 -, m.p. $>290^\circ$, and 4'-*OH*-derivatives.

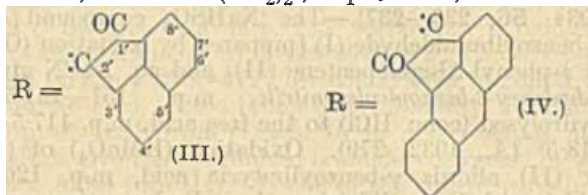
m.p. $>290^\circ$, 2'-*OH*-, m.p. $>290^\circ$, and 4'-*OH*-derivatives.

V. The following substances are prepared by condensation of (I) with the requisite ketonic substance by anhyd. Na_2CO_3 in $EtOH$; the method is applicable also in the 1:2-series (*loc. cit.*): 2:1-naphthathiophen-3'-indoleindigotin (II) and its 5'-*Cl*-, 5'-*Br*-, m.p. $>295^\circ$,



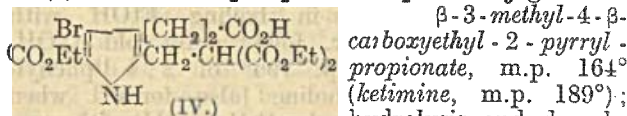
5':7'-*Br*-, m.p. 285 — 287° 5'- NO_2 -, sublimes at 280° , m.p. $>295^\circ$, -derivatives; 2:1-naphthathiophen-2'-acenaphthyleneindigotin (III), m.p. $>295^\circ$, and

its 5'- NO_2 -, m.p. 290 — 292° after evolving red fumes at 260° , and 5':6'-(NO_2)₂-, m.p. $>295^\circ$, -derivatives;



2:1-naphthathiophen-1-acenaphthyleneindigotin (IV), m.p. $>295^\circ$; di-2:1-naphthathiophenethylenindigotin, $R \cdot CH \cdot CH \cdot R$, m.p. $>290^\circ$. H. W.

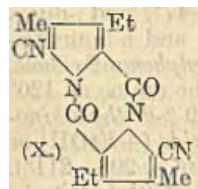
Syntheses of 2-substituted pyrroles and pyrrol sulphides. H. FISCHER and Z. CSUKAS (Annalen, 1934, 508, 167—184).—Opsopyrrolecarboxylic acid (I), $HClN$, and HCl give (cf. A., 1922, i, 758) β -2-aldehydo-3-methyl-4-pyrrolpropionic acid (II), m.p. 151° [*Me* ester (III), m.p. 77°], which with $CH_2(CO_2H)_2$ in $EtOH$ -piperidine affords β -3-methyl-2- β -dicarboxyvinyl-4-pyrrolpropionic acid, m.p. 173° (*Me*₃ ester, m.p. 80°); β -3-methyl-2- β -dicyanovinyl-, decomp. 251° [*Br*-derivative, m.p. 181° (decomp.)], and β -3-methyl-2- β -cyano- β -carbethoxyvinyl-, m.p. 176° , -4-pyrrolpropionic acids are similarly obtained from $CH_2(CN)_2$ and $CN \cdot CH_2 \cdot CO_2Et$, respectively. *Me* β -3-methyl-2- β -dicarbethoxyvinyl-4-pyrrolpropionate, m.p. 89° , is prepared from (III) and $CH_2(CO_2Et)_2$. β -5-Carbethoxy-2:3-dimethyl-4-pyrrolpropionic acid and *Br* in Et_2O - $AcOH$ - HCO_2H give a compound, $C_{12}H_{16}O_9NBr$, decomp. 178° , which when crystallised from aq. C_5H_5N passes into di-(5-carbethoxy-3-methyl-4- β -carboxyethyl-2-pyrrol)methane, m.p. 277° . β -3-Bromo-2-carbethoxy-5-bromomethyl-4-pyrrolpropionic acid and $CHNA(CO_2Et)_2$ in dry C_5H_5N afford the ester (IV), m.p. 127° . Passage of HCl into a mixture of (I) and $CN \cdot CH_2 \cdot CO_2Et$ in Et_2O - $CHCl_3$ gives *Et* β -3-methyl-4- β -carboxyethyl-2-pyrrolpropionate, m.p. 164° (ketimine, m.p. 189°); hydrolysis and decarb-



oxylation of this gives β -2-acetyl-3-methyl-4-pyrrolpropionic acid, m.p. 178° , also prepared from (I), $MeCN$, and HCl . The *oxime* (V), m.p. 185° , of (II) is converted by Ac_2O - $KOAc$ into β -2-cyano-5-acetyl-3-methyl-4-pyrrolpropionic acid, m.p. 144° , whilst (V) and $SOCl_2$ give β -2-chloro-5-cyano-4-methyl-3-pyrrolpropionic acid (VI), m.p. 170° , and di-(5-cyano-4-methyl-3- β -carboxyethyl-2-pyrrol) sulphide, m.p. 249° (decomp.) (*Et*₂ ester, m.p. 120°). The 5-*Cl*-derivative, m.p. 175° (decomp.), of (V) is prepared from (V) and SO_2Cl_2 in Et_2O ; it is dehydrated (Ac_2O - $KOAc$) to (VI). The 5-*Br*-derivative (hydrobromide, m.p. 188°) of (V) has m.p. 158° .

Et 2:4-dimethylpyrrole-4-carboxylate (VII) and $SOCl_2$ in Et_2O give di-(5-carbethoxy-2:4-dimethyl-3-pyrrol) sulphide (VIII), m.p. 252° (free acid, m.p. 193°), in almost quant. yield. (VIII) and *Br* in $AcOH$ afford a compound, $C_8H_{11}O_6NBr_2$, m.p. 152° ; attempted oxidation (H_2O_2 , $AcOH$) gives (VII). Di-(5-carbethoxy-4-methyl-3- β -carboxyethyl-2-pyrrol) sulphide, m.p. 217° [free acid, m.p. 240° (decomp.) (becomes blue at 210°)], and di-(4-acetyl-5-methyl-3-ethyl-2-pyrrol) sulphide, m.p. 219° , are similarly prepared from the appropriate pyrrole. β -5-Cyano-2:4-dimethyl-3-

pyrrolpropionic acid, m.p. 153°, is obtained by dehydration (Ac_2O) of the oxime, m.p. 187° [*Cu* salt, m.p. 256° (decomp.) (darkens at 180°)], of β -5-aldehyde-2:4-dimethyl-3-pyrrolpropionic acid. 5-Cyano-2:4-dimethyl-3-ethylpyrrole (IX) (improved prep. described) and Br in AcOH give a compound,



$\text{C}_9\text{H}_{11}\text{N}_2\text{Br}_3$, m.p. 139° (decomp.), which when heated with AcOH passes into the 2- CH_2Br -derivative. The product from (IX) and excess of SO_2Cl_2 in Et_2O is hydrolysed (H_2O) to 2-cyano-3-methyl-4-ethylpyrrole-5-carboxylic acid, m.p. 228° (decomp.), which when heated at 230—235° affords the compound (X). Hydrolysis of the product from (IX) and 2 mols. of SO_2Cl_2 gives 5-aldehyde-2-cyano-3-methyl-4-ethylpyrrole, m.p. 143°.

H. B.

Acyl derivatives of 6-nitro-2-phenylindoxyl. P. RUGGLI, A. ZIMMERMANN, and O. SCHMID (Helv. Chim. Acta, 1934, 17, 9—22).—The pure 3-O-Ac derivative (I), m.p. 191° [α -compound (A., 1921, i, 812) is a slightly impure form: forms mixed crystals with (II)], of 6-nitro-2-phenylindoxyl (II) is obtained by heating (II) with Ac_2O . With Ac_2O - NaOAc (I) gives its 1-N:3-O-Ac₂ derivative (III), m.p. 178° (probably identical with the β -derivative, *loc. cit.*). Hydrolysis (5% EtOH -piperidine) of (III) gives the 1-N-Ac derivative (IV), m.p. 178—180°, reconverted into (III) by boiling Ac_2O . Similarly, with cold BzCl - $\text{C}_5\text{H}_5\text{N}$, (II) gives its 3-O-Bz derivative (V), m.p. 229°, which with BzCl - $\text{C}_5\text{H}_5\text{N}$ at 45° gives the 1-N:3-O-Bz₂ derivative (VI), m.p. 204°, giving (V) again on hydrolysis ($\text{C}_5\text{H}_5\text{N}$ -piperidine). With Ac_2O -conc. H_2SO_4 at 105° (V) gives the 3-O-Bz-1-N-Ac derivative, m.p. 184°, a very small amount of the isomeric 1-N-Bz-3-O-Ac derivative, m.p. 187—188°, being isolated by the action of BzCl - $\text{C}_5\text{H}_5\text{N}$ on (I) at 45°. With excess of PhNCO (II) affords its 3-phenylurethane, m.p. 214°, and with ClCO_2Et - $\text{C}_5\text{H}_5\text{N}$ at <5°, its 3-carbethoxy-derivative (VII), m.p. 170° [converted by BzCl - $\text{C}_5\text{H}_5\text{N}$ into (VI)], is obtained. With Ac_2O - H_2SO_4 (VII) gives the 1-acetyl-3-carbethoxy-derivative, m.p. 133°, slightly contaminated by (III), but giving (IV) by partial hydrolysis. Reductive acetylation (Zn - Ac_2O) of (I) gives 3-acetyl-6-acetamido-2-phenylindoxyl, m.p. 220° (picrate, m.p. 188°), the 1-N-Ac derivative, amorphous, m.p. indefinite <100°, of which is hydrolysed (piperidine- EtOH) to 1-acetyl-6-acetamido-2-phenylindoxyl, darkens 210°, m.p. 217—219°.

J. W. B.

Action of ultra-violet light on pyridine. V. Reactions [of photopyridine] with further primary aromatic amines, behaviour of pyridine derivatives in ultra-violet light, and nature of photopyridine. H. FREYTAG (J. pr. Chem., 1933, [ii], 139, 44—62; cf. A., 1933, 1304).—The colour reactions of irradiated $\text{C}_5\text{H}_5\text{N}$ with further primary amines are described; they are not sufficiently definite to identify the amine in every case but indicate its class. The colours produced are changed to yellow or orange by alkalis, but the original colour is restored by acids. The homologous methylpyridines are affected by irradiation similarly to $\text{C}_5\text{H}_5\text{N}$, but to a smaller degree, according to the no.

of the groups and their position, and may be identified by the colour given with $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ after irradiation. Other derivatives (NH_2 , NO_2 , SO_3H , CO_2H) also give "photo"-products, that from Et_3C collidinedicarboxylate apparently being the same as from its H_2 -derivative. The photo-products are in most cases destroyed by diffused or direct sunlight. Photopyridine is not formed in absence of O_2 , but is not among the products of reaction of O_3 or H_2O_2 with $\text{C}_5\text{H}_5\text{N}$. The colours it gives with arylamines are similar to those of the arylamine derivatives of glutacondialdehyde (I) and show the same behaviour with alkalis and acids. It has $\cdot\text{CHO}$ reactions (Schiff) and gives NH_3 with alkalis, and is consequently regarded as the NH_4 derivative of the enolic form of (I), viz., $\text{CHO}[\text{CH}:\text{CH}]\cdot\text{ONH}_4$. H. A. P.

Preparation of 2-halogenopyridines from 2-aminopyridine by the diazo-reaction. L. C. CRAIG (J. Amer. Chem. Soc., 1934, 56, 231—232).—Treatment of 2-aminopyridine (I) in 63% HBr (5 mols.) containing Br (3 mols) with aq. NaNO_2 (2.5 mols.) at 0° gives (after addition of aq. NaOH at <25°) an 87% yield of 2-bromopyridine (II), b.p. 91—92°/25 mm. 2-Iodopyridine, b.p. 93°/13 mm., could not be similarly prepared; it is obtained in 65% yield from the Na isodiazotate of (I) and I (1 mol.) in HI (3 mols.) and subsequent basification. (II) warmed with anhyd. CuCN gives 74% of 2-cyanopyridine, b.p. 222.5—223.5° (lit. 212—215°), 118—120°/25 mm.

H. B.

Azopyridines. A. KIRPAL (Ber., 1934, 67, [B], 70—71).—2:2'-Azopyridine (I), obtained by oxidation of 2-aminopyridine (II) with KOC (A., 1932, 622), is contaminated by a small amount of 5-chloro-2:2'-azopyridine (III), m.p. 135°, from which it is separated by crystallisation from H_2O . It is then identical with that prepared by reduction of 2-nitropyridine, so that the supposed isomerism does not exist. (I) yields an octahydrate, m.p. 30°. Oxidation of a mixture of (II) and 5-chloro-2-aminopyridine (IV) by KOC affords (I), (III), and 5:5-dichloro-2:2'-azopyridine, m.p. 248°, which is the sole product of the oxidation of (IV).

H. W.

Complex ferric salts.—See this vol., 241.

Homarine, an animal base. F. A. HOPPE-SEYLER (Z. physiol. Chem., 1933, 222, 105—115).—Homarine (I), $\text{C}_7\text{H}_7\text{O}_2\text{N}$ [hydrochloride (II), decomp. 170—175°; aurichlorides, regular, m.p. 188—190°, irregular, m.p. 138—141°; platinichloride, m.p. 197—198° (decomp.); picrate, m.p. 155—160° (decomp.); Et ester platinichloride, m.p. 199—206° (decomp.)], a base resembling trigonelline and obtained from lobster, *Arca Noe*, and *Arbatia pustulosa* (cf. this vol., 96), is the methylbetaine of picolinic acid (III). With conc. HCl at 200°, (II) gives (III) (aurichloride, m.p. 218°). Methylation of (III) with Me_2SO_4 and aq. Ba(OH)_2 yields (I). Similarly isonicotinic acid gives the methylbetaine [hydrochloride, m.p. 255—260° (decomp.); regular aurichloride, m.p. 233—234° (decomp.); platinichloride, m.p. 222—223° (decomp.); picrate, m.p. 215—217°]. (I) may arise from lysine.

J. H. B.

Quinoline derivatives. XLII. Derivatives of 4'-amino-2-phenylquinoline. H. JOHN [with E.

PIETSCH] (J. pr. Chem., 1934, [ii], 139, 97—104).—4'-Amino-2-phenylquinoline, m.p. 136° [Ac_2 , m.p. 153.5°; Bz , m.p. 234°; *formyl*, m.p. 160°, *carbamido*-, m.p. > 300°; *thiocarbamido*-, m.p. 206°, *selenocarbamido*-, m.p. 217°, $CHPh$, m.p. 153.5°, $p-C_6H_4Me \cdot CH$, m.p. 171°, *p-anisylidene*, m.p. 190°, and CH_2Ph , m.p. 144.5°, derivatives; *s-bis*-(2-phenyl-4'-quinolyl)-methylenediamine, m.p. 172° (CH_2O), and *-thiocarbamide*, m.p. 218° (CS_2), is prepared by heating its 4-carboxylic acid (I), m.p. 273° (Me , m.p. 123°, and Et ester, m.p. 145°), at > its m.p. (I) is prepared from *p*-aminoacetophenone and isatin. H. A. P.

Comparison of the directive powers of elements having consecutive atomic numbers. VI. Examination of further possible comparative cases, and conclusions. (MRS.) C. G. LE FEVRE, R. J. W. LE FEVRE, and J. PEARSON (J.C.S., 1934, 37—43).—Salicylaldehyde (I), $COPhPr$, and $HClO_4$ afford 2-phenyl-3-methylbenzopyrylium perchlorate, m.p. 174—177°, which gives (HNO_3) the 2- NO_2 -derivative, m.p. 248—249°, also obtained from *m*-nitropropionophenone. Isatin, $COPhPr$, and $NaOH$, followed by MeI , yield 2-phenyl-3-methyl-*N*-methoquinolinium methiodide, converted into the *picrate*, m.p. 169—170°. 2-Hydroxy- α -phenylstyryl *Me* ketone, m.p. 180—181°, from $CH_3Ph \cdot COMe$ (II), (I), and $C_5H_{11}N$, could not be caused to undergo ring closure. (I), (II), $HClO_4$, and HCl form 3-phenyl-2-methylbenzopyrylium perchlorate, m.p. 189—191°, which does not give a pure nitration product. β -Naphthol-1-aldehyde (III), $COPhMe$, $HClO_4$, and HCl afford 2-phenyl- α -naphthopyrylium perchlorate, m.p. 216—220°. In a competition experiment of (III) and (I) for a deficiency of $COPhMe$, the former is more reactive. (II) and isatin give 3-phenyl-2-methylquinoline-4-carboxylic acid, m.p. > 250°, which after distillation with $Ca(OH)_2$ yields a methopicate, m.p. 170—175°.

(I), *p*-methylacetophenone (IV), and KOH form salicylidene-4-methylacetophenone, m.p. 158—159°, cyclised by HCl - $AcOH$ to 2-*p*-tolylbenzopyrylium perchlorate, m.p. 148—150°, which is nitrated to 3'-nitro-2-phenyl-4'-methylbenzopyrylium perchlorate, m.p. 199°, also obtained from the appropriate nitromethylacetophenone. Isatin, (IV), and $NaOH$ afford 2-*p*-tolylquinoline-4-carboxylic acid, decarboxylated to 2-*p*-tolylquinoline, m.p. 82—83° (methosulphate, m.p. 158—159°), the methopicate, m.p. 157—158°, of which is nitrated to the *m*- NO_2 -compound, m.p. 192—194°. *o*-Hydroxystyryl *Me* ketone and $HClO_4$ - HCl give 2-methylbenzopyrylium perchlorate, m.p. 153—158°, which cannot be nitrated. 2'-Hydroxy-2-styrylbenzopyrylium perchlorate is dinitrated. Quinaldine methosulphate is nitrated and forms with picric acid 75% of 5-nitro-2-methylquinoline methopicate, m.p. 149—151°, also obtained from 5-nitroquinaldine. 2-*o*-Hydroxy-3-methylbenzopyrylium perchlorate gives a (NO_2)₂-derivative, decomp. > 150°. Benzopyrylium ferrichloride with HNO_3 is nitrated and oxidised to dinitrosalicylic acid. 5-Nitrosalicylaldehyde, $COPhMe$, and $HClO_4$ - HCl give a salt, m.p. 180—185°, whilst the 3- NO_2 -compound yields 3-nitro-2-hydroxychalkone, m.p. 163—164°. The conclusion is reached that experimental comparison of an oxonium salt with an NH_4 salt is impracticable. F. R. S.

Phenanthridine series. III. Meso-substituted derivatives. L. P. WALLS (J.C.S., 1934, 104—109).—9-Bromophenanthridine (I), m.p. 123—124°, is prepared from phenanthridine, $POBr_3$, and PBr_3 . The prep. of aliphatic diamines (Gabriel) is improved by isolating the phthalodialkylaminoethyl-imide: *phthalo*- β -diethyl-, m.p. 46—47°, and *-diisobutylaminoethylimide*, m.p. 52°. (I) and β -aminotriethylamine in $PhOH$ yield *N*-phenylphenanthridone, m.p. 118—119°; (I) and excess of the amine at 120° give on subsequent addition of HCl 9- β -diethylaminophenanthridine dihydrochloride (+ $EtOH$) or (+ $3H_2O$), m.p. 238—243° (*picrate*, m.p. 208—211°). 9- β -Piperidino- (+ $2H_2O$), m.p. 265—270° [*dinitrate*, m.p. 130—135° (decomp.)], and *-diisobutylaminophenanthridine dihydrochloride* (+ $4H_2O$), m.p. 142—144°, are similarly obtained. The dihydrochlorides are inactive therapeutically. 9- $\beta\beta'$ -Dihydroxyisopropylphenanthridine, m.p. 129.5° (Ac_2 derivative, m.p. 93°), prepared from 9-methylphenanthridine, aq. CH_2O , and $EtOH$, is oxidised (Kiliani's dichromate mixture) to *Na* phenanthridine-9-carboxylate (+ $3H_2O$) (*acid*; Et ester, m.p. 57—58°). *o*-Xenylamine and $Et_2C_2O_4$ give *s-di-o-xenyloxamide*, m.p. 233—235°, and Et *o-xenyloxamate*, m.p. 112—113°, whilst the amine and $H_2C_2O_4$ afford *o-xenyloxamic acid* (II), m.p. 155—158° (decomp.). (II) and $POCl_3$ give *s-di-o-xenyloxamide*, a substance, m.p. > 310°, sol. in $AcOH$, and a substance ($C_{13}H_8ON$)₂, m.p. > 310°, insol. in $AcOH$, which with Zn dust affords phenanthridine. *o*-Xenylamine and the appropriate acid chloride form *di*-, m.p. 104—106°, and *tri-chloroacet-o-xenylamide*, m.p. 92—94°, which does not react with $POCl_3$. F. R. S.

Spasmolytics of papaverine type. K. H. SLOTTA and G. HABERLAND (Angew. Chem., 1933, 46, 766—771).—Derivatives of $C_2H_4Ph \cdot NH_2$, prepared by electrolytic reduction of ω -nitrostyrenes in $EtOH$ - $AcOH$ - HCl using Pb electrodes, are condensed with alkoxybenzoyl chlorides, and the resulting amides cyclised by $POCl_3$ to dihydroisquinolines, which are finally dehydrogenated by Pd in boiling xylene. The following are described: 3:4-diethoxyphenylethylamine, b.p. 177°/20 mm. [*hydrochloride*, m.p. 200° (sinters 108°); *picrate*, m.p. 145°]; 3':4':5'-trimethoxybenz- β -3:4-diethoxy-, m.p. 132°, -3:4:5-trimethoxy-, m.p. 179°, and -3:4-dimethoxyphenylethylamide, m.p. 130°; 3':4'-methylenedioxybenz- β -3:4-methylenedioxyphenylethylamide, m.p. 127°; 3':4'-dimethoxybenz- β -3:4-dimethoxy-, m.p. 142°, 3':4'-diethoxybenz- β -3:4-diethoxy-, m.p. 145°, and 3':4':5'-triethoxybenz- β -3:4-diethoxy-phenylethylamide, m.p. 88°; also the following derivatives of 1-phenylisoquinoline (I): 3':4':5'-trimethoxy-6:7-diethoxy- (II), m.p. 212° [*hydrochloride* (+ $1H_2O$); 3:4- H_2 -derivative, m.p. 168° (*hydrochloride*, m.p. 208°)], 6:7:3':4'-bismethylenedioxy- [*hydrochloride*, m.p. 236°; 3:4- H_2 -compound, m.p. 179° (*hydrochloride*, m.p. 236°; *picrate*, m.p. 192°)], 6:7:3':4'-tetramethoxy- [*hydrochloride* (+ $1H_2O$), m.p. 214°; 3:4- H_2 -compound (+ $1H_2O$), m.p. 171° (*hydrochloride*, m.p. 219° {+ $2H_2O$, m.p. 156°})], 6:7:3':4'-tetraethoxy-



[hydrochloride, $(-1\text{H}_2\text{O})$, m.p. 203° ; 3:4- H_2 -compound (hydrochloride, m.p. $140\text{--}145^\circ$, 180°), 6:7:8:3':4':5'-hexamethoxy- [hydrochloride, m.p. 188° ; 3:4- H_2 -compound $(+1\text{H}_2\text{O})$, m.p. 122° (hydrochloride, m.p. 108°), 6:7:3':4':5'-pentamethoxy-, m.p. 160° [hydrochloride, m.p. 218° ; 3:4- H_2 -compound $(+1\text{H}_2\text{O})$, m.p. 160° (hydrochloride, m.p. 215° ; picrate, m.p. 182°), and 6:7:3':4':5'-pentaethoxy-1-phenylisoquinoline {hydrochloride $(+0.5\text{H}_2\text{O})$, m.p. $160\text{--}167^\circ$, 196° ; 3:4- H_2 -compound, m.p. 103° [hydrochloride $(+1.5\text{H}_2\text{O})$, m.p. 218°]. (II) has twice the pharmacological activity of papaverine. The dihydroquinoline bases form H_2O -insol. nitrates.

H. A. P.

Effect of constitution on rearrangement of phenylhydrazones of unsymmetrically substituted distyryl ketones. L. C. RAIFORD and E. L. HILL (J. Amer. Chem. Soc., 1934, **56**, 174—176; cf. A., 1933, 514).—The phenylhydrazone, m.p. $162\text{--}163^\circ$, of styryl *p*-dimethylaminostyryl ketone is rearranged by boiling AcOH to 1-phenyl-5-*p*-dimethylaminophenyl-3-styrylpyrazoline, m.p. $133\text{--}134^\circ$. 1-Phenyl-5-*p*-tolyl-, m.p. $167\text{--}168^\circ$, -5-anisyl-, m.p. 124° , -5-*p*-phenetyl-, m.p. $126\text{--}127^\circ$, -5-*p*-propoxyphenyl-, m.p. $118\text{--}119^\circ$, and -5-3':4'-methylenedioxyphenyl-, m.p. $167\text{--}168^\circ$, -3-styrylpyrazolines are obtained directly from the requisite ketone and $\text{NHPh}\cdot\text{NH}_2$. *p*-Dimethylaminostyryl Me ketone similarly gives 1-phenyl-5-*p*-dimethylaminophenyl-3-methylpyrazoline, m.p. $166\text{--}167^\circ$. 1-Phenyl-5-anisyl-, m.p. $196\text{--}197^\circ$, -5-*p*-phenetyl-, m.p. $163\text{--}164^\circ$, and -5-*p*-dimethylaminophenyl-, m.p. $141\text{--}142^\circ$, -pyrazole-3-carboxylic acids are obtained by oxidation (KMnO_4) of the appropriate pyrazolines. Styryl *p*-methyl-, m.p. $107\text{--}108^\circ$, *p*-ethoxy-, m.p. $77\text{--}78^\circ$, and *p*-propoxy-, m.p. $119\text{--}120^\circ$, -styryl ketones are prepared from $\text{CHPh}\cdot\text{CH}\cdot\text{COMe}$, $\text{C}_6\text{H}_4\text{R}\cdot\text{CHO}$, and aq. $\text{EtOH}\text{--}\text{NaOH}$.

H. B.

Structure and rearrangement of *N*-acylpyrazoles. K. VON AUWERS and K. DIETRICH [with R. NEUMANN] (J. pr. Chem., 1934, [ii], **139**, 65—93).—The *N*-acylpyrazoles formed by cyclisation of the acylhydrazones of β -diketones under mild conditions (POCl_3 at 0°) are converted by heat (at the b.p./vac.) into their more stable *N'*-isomerides, also obtained by direct acylation of the pyrazole. Thus cyclisation of the acetylhydrazone, m.p. $114\text{--}116^\circ$, of CH_2BzAc gives 1-acetyl-5-phenyl-3-methylpyrazole, m.p. $45.5\text{--}46.5^\circ$, converted at its b.p./vac. into 1-acetyl-3-phenyl-5-methylpyrazole, m.p. 41° . The corresponding benzoylhydrazone, m.p. $130\text{--}132^\circ$, also obtained from $\text{CHBz}\cdot\text{CMe}\cdot\text{OMe}$ or $\text{CHBz}\cdot\text{CMe}\cdot\text{OEt}$ and $\text{NH}_2\cdot\text{NHBz}$, is, however, cyclised by POCl_3 to 1-benzoyl-3-phenyl-5-methylpyrazole, m.p. $83\text{--}84^\circ$, but the unstable isomeric 1-benzoyl-5-phenyl-3-methylpyrazole, m.p. $88\text{--}89^\circ$, is obtained in moderate yield from $\text{OMe}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COMe}$ and $\text{NH}_2\cdot\text{NHBz}$ in abs. EtOH at $40\text{--}50^\circ$ in absence of a condensing agent. The following are also described: benzoylaceton-propionyl-, m.p. $87\text{--}88^\circ$, -*n*-butyryl-, m.p. $61\text{--}63^\circ$, -phenylacetyl-, m.p. $94\text{--}96^\circ$, -carbethoxy-, m.p. $104\text{--}105^\circ$, -*o*-, m.p. $113\text{--}114^\circ$, -*m*-, m.p. 111° , and -*p*-toluoyl-, m.p. $148\text{--}150^\circ$; hydroxymethylenacetone-benzoyl-, m.p. $59\text{--}60^\circ$, and -*o*-nitrobenzoyl-, m.p. $137\text{--}139^\circ$; hydroxymethylenacetophenone-benzoyl-, m.p. 148° ,

-*o*-nitrobenzoyl-, m.p. $151\text{--}152^\circ$, and -carbethoxy-, m.p. $117\text{--}118.5^\circ$; and *Et* benzoylpyruvate acetyl- (amorphous), benzoyl-, m.p. 119° , and carbomethoxyhydrazone, m.p. $88\text{--}89^\circ$: 1-propionyl-5-phenyl-3-methyl-, m.p. $33\text{--}34^\circ$; 1-propionyl-3-phenyl-5-methyl-, m.p. $77\text{--}78.5^\circ$; 1-*n*-butyryl-, m.p. $34\text{--}35^\circ$, 1-phenylacetyl-, m.p. $104.5\text{--}105.5^\circ$, 1-carbethoxy-, m.p. $50.5\text{--}51.5^\circ$ (?), $65\text{--}66^\circ$, 1-*o*-, m.p. $63\text{--}65^\circ$, 1-*m*-, m.p. $79\text{--}80^\circ$, and 1-*p*-toluoyl-5-phenyl-3-methylpyrazole, m.p. $78\text{--}79^\circ$ (decomp. $83\text{--}85^\circ$); 1-propionyl-, m.p. $77\text{--}78.5^\circ$; 1-*n*-butyryl-, m.p. $72\text{--}72.5^\circ$, b.p. $150\text{--}152^\circ/10\text{ mm.}$, 1-phenylacetyl-, m.p. $58\text{--}59.5^\circ$, 1-carbethoxy-, m.p. $73.5\text{--}74.5^\circ$, b.p. $193^\circ/10\text{ mm.}$, 1-*o*-, m.p. $36.5\text{--}37.5^\circ$, 1-*p*-, m.p. $68\text{--}70^\circ$, and 1-*m*-toluoyl-3-phenyl-5-methylpyrazole, m.p. $56\text{--}57^\circ$, b.p. $224\text{--}226^\circ/11\text{ mm.}$; 1-*o*-nitrobenzoyl-3-, m.p. $118.5\text{--}119.5^\circ$, and -*o*-methylpyrazole, m.p. 130° , b.p. $199\text{--}201^\circ/13\text{ mm.}$; 1-*o*-nitrobenzoyl-4:5-, m.p. $118\text{--}120^\circ$, and -3:4-dimethylpyrazole, m.p. $149\text{--}150^\circ$; 1-*o*-nitrobenzoyl-*o*-, m.p. $151\text{--}152^\circ$, and -3-phenylpyrazole, m.p. $107.5\text{--}108.5^\circ$, b.p. $208\text{--}210^\circ/15\text{ mm.}$; *Et* 5-, m.p. $37\text{--}39^\circ$ (?), $58\text{--}59^\circ$, and 3-phenylpyrazole-1-carboxylate, b.p. $192^\circ/13\text{ mm.}$; *Et* 5-methylpyrazole-1:3-dicarboxylate, b.p. $178\text{--}179^\circ/13\text{ mm.}$; *Et* 1-*o*-nitrobenzoyl-, m.p. 107° , and 1-carbamyl-5-methylpyrazole-3-carboxylate, m.p. 131° . *Et* 1-acetyl-, m.p. $109\text{--}110^\circ$, and 1-carbomethoxy-3(or 5)-phenylpyrazole-5(or 3)-carboxylate, m.p. $80\text{--}81^\circ$. The structure assigned to many of these acylpyrazoles is confirmed by their optical exaltations. Interaction of 3-phenyl-5-methylpyrazole hydrochloride with KCNO in AcOH gives the known 1-carboxylamide, m.p. $154\text{--}156^\circ$. Attempts at cyclisation of the acetyl- and benzoylhydrazones of $\text{COPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$ and of the acetylhydrazone of $\text{COMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ gave only the corresponding deacylated pyrazoles.

H. A. P.

Action of alkali and ammonia on 2:4-dialkoxypyrimidines. G. E. HILBERT and E. F. JANSEN (J. Amer. Chem. Soc., 1934, **56**, 134—139).—5-Bromouracil (I) (improved prep. given), PCl_5 , and POCl_3 at 125° give 2:4-dichloro-5-bromopyrimidine, b.p. $145\text{--}147^\circ/78\text{ mm.}$, which with $\text{MeOH}\text{--}\text{NaOMe}$ affords 5-bromo-2:4-dimethoxypyrimidine (II), m.p. $63\text{--}64^\circ$, and *Na* α -bromo-3-methylisocarbamidocrylate (III), $\text{NH}_2\cdot\text{C(OMe)}\cdot\text{N}\cdot\text{CH}\cdot\text{CBr}\cdot\text{CO}_2\text{Na}$, m.p. 248° (decomp.). (II) is separable by sublimation. (III) is converted by conc. HCl into (I) and by aq. AcOH into 5-bromo-4-keto-2-methoxy-3:4-dihydropyrimidine, m.p. 190° (decomp.), hydrolysed (conc. HCl) to (I). (III) is also obtained from (II) and aq. $\text{EtOH}\text{--}\text{NaOH}$. (II) and $\text{MeOH}\text{--}\text{NH}_3$ at 80° give 5-bromo-4-amino-2-methoxypyrimidine, m.p. $134\text{--}136^\circ$, hydrolysed (conc. HCl) to 5-bromocytosine (IV), decomp. $245\text{--}255^\circ$ (according to rate of heating). (IV) and 5:5-di-bromo-6-hydroxy-5:6-dihydrocytosine hydrobromide, decomp. $175\text{--}180^\circ$, are obtained from cytosine and Br in H_2O . 5-Bromo-2:4-diethoxypyrimidine, m.p. $72\text{--}74^\circ$, and 5-bromo-4-keto-2-ethoxy-3:4-dihydropyrimidine, m.p. 163° (sinters at 160°), are also prepared. All m.p. are corr.

H. B.

Alkylation of pyrimidines. Attempt to prepare 1-glucosidocytosine. G. E. HILBERT (J. Amer. Chem. Soc., 1934, **56**, 190—195).—4-Amino-2-methoxypyrimidine (I), m.p. 170° (sinters at 168°),

rearranges at 180° to 1-methylcytosine (II), m.p. 303° (decomp.) (lit. 278—279°), which with Br in H₂O gives 5-bromo-1-methyluracil, m.p. 272—274° (decomp.) (lit. 255—260°). (I) and MeI in cold MeOH afford the 1-methiodide (III), m.p. 128° (decomp.), re-solidifying with m.p. 230—235° (sinters at 190°), which is converted by aq. Ag₂SO₄, warm conc. HCl, or boiling EtOH into (II). (III) heated at 130—135° gives (II), a little 1:3-dimethylcytosine (IV), m.p. 147.5°, and (probably) the impure methiodide (V) (below). Prolonged interaction of (II) and MeOH-MeI affords the 3-methiodide (V), m.p. 265—266° (decomp.), which is converted by aq. NaOH into (IV). (IV) and Br in H₂O give 5-bromo-1:3-dimethyluracil. The impure hydrobromides of (I) and (II) are the only cryst. products isolable from (I) and acetobromoglucose in MeNO₂. Improved methods of prep. (cf. A., 1930, 789) of cytosine and isocytosine are given. All m.p. are corr. H. B.

Pyrimidines. CXL. Pyrimidines derived from carbethoxymalonaldehyde. E. DYER and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 222—225).—Et ββ-diethoxypropionate, b.p. 65°/2 mm. (from CHO·CHNa·CO₂Et and EtOH-HCl), HCO₂Et, and Na in Et₂O give carbethoxymalonaldehyde (as Na salt) (I) [Cu salt (+2H₂O)]; K salt, m.p. 264° (decomp.), obtained by hydrolysis (EtOH-KOH) of (II) (below). (I) and NHPh·NH₂ in AcOH give Et 1-phenylpyrazole-4-carboxylate, m.p. 99—100° (all m.p. are corr.) (lit. 96—97°), whilst (I) and SET·C(NH)·NH₂·HBr in H₂O afford an additive compound (II), SET·C(NH)·NH₂·CHO·C(CO₂Et)·CH·OH, m.p. 143.5—144.5° (decomp.), and a little Et 2-ethylthiolpyrimidine-5-carboxylate (III), m.p. 47—48° (free acid, m.p. 182—183°). (II) is dehydrated (Ac₂O at 100°) to (III). Hydrolysis (conc. HCl) of (III) gives 2-ketopyrimidine-5-carboxylic acid (+H₂O), darkens >220°; esterification (EtOH-HCl) of this affords the Et ester (+H₂O) (IV), m.p. 163—164°, and a substance, m.p. 186—187°. (I) and CO(NH₂)₂ in AcOH give Et α-formyl-β-carbamidopropionate, m.p. 175° (decomp.), converted by EtOH-NaOEt into (IV) (poor yield). Et α-formyl-β-thiocarbamidopropionate heated at 150—160°/3 mm. affords Et 2-thiopyrimidine-5-carboxylate, m.p. 214—216° (decomp.) (2·CO₂H·CH₂· derivative, m.p. 175—176.5°).

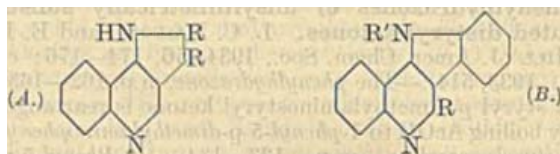
H. B.

Derivatives of piperazine. I. C. B. POLLARD and D. E. ADELSON (J. Amer. Chem. Soc., 1934, 56, 150).—The following are described: 1:4-diphenylacetyl-, m.p. 150—151° (all m.p. are corr.), 1:4-di-β-phenylpropionyl-, m.p. 122.5—123°, and 1:4-dianisoyl-, m.p. 192.5—193.5°, -piperazine; piperazine phenylacetate, m.p. 146.5—147.5°, β-phenylpropionate, m.p. 150.5—151.5°, anisate, m.p. 172—174°, ethylmalonate, m.p. 144°, H malonate, m.p. 180° (decomp.), and H diethylmalonate, m.p. 80—81°. H. B.

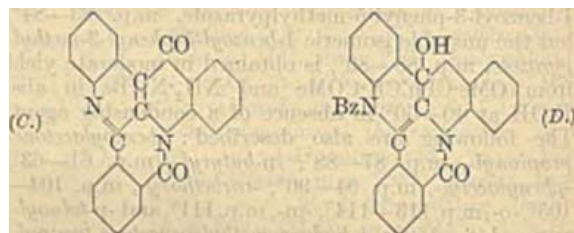
Synthesis of pyrazine by catalytic dehydrogenation of ethanolamine. J. G. ASTON, T. E. PETERSON, and J. HOLOWCHAK (J. Amer. Chem. Soc., 1934, 56, 153—154).—Pyrazine, b.p. 112—114°/730 mm., m.p. 48° (mercurichloride), is obtained in 5.6% yield when NH₂·CH₂·CH₂·OH is passed over finely-divided Cu at 300°: smaller amounts are formed using

Cu-ZnO and ZnO-Na₂CO₃ catalysts. The catalyst rapidly becomes inactive owing to the formation of resin. H. B.

Benzoyl derivatives of indigo. II. H. DE DIESBACH, E. DE BIE, and F. RUBLI (Helv. Chim. Acta, 1934, 17, 113—128).—Correction and extension of results previously published (A., 1933, 285). The base given as C₁₄H₁₀N₂, obtained by NaOH-fusion of Ciba-yellow (I), is actually C₁₅H₁₀N₂ (II), m.p. 332°, giving a compound C₁₅H₉O₂N₃ (not C₁₃H₈O₅N₄) with HNO₃ and oxidised (CrO₃-AcOH) to an acid C₁₃H₈O₄N₂ (not C₁₂H₈O₅N₂), m.p. 325° (decomp.) (probably A; R=CO₂H), decarboxylated at 325°/vac. to a base, C₁₁H₈O₂, m.p. 293—294° (A; R=H), from which oxalylanthranilic acid (III) is obtained by KMnO₄



oxidation, and 4-hydroxyquinoline-3-carboxylic acid, with HNO₃ (d 1.4). (II) is therefore 3:4-indoloquinoline (A; RR= >C₆H₄). The main fusion product, C₁₅H₁₀O₂N₂ (IV), sublimates about 430° (accompanied by a small amount of a tautomeride, m.p. about 400°), with HNO₃ gives C₁₅H₈O₆N₄ (not C₁₃) + 2 mols. quinoline, and solvent-free, and is oxidised (KMnO₄) to (III) and its constituents. With PCl₅ (IV) gives the dichloride C₁₅H₈N₂Cl₂ (V) (B; R=R'=Cl), accompanied by a Cl₂-derivative. Both Cl atoms in (V) are labile, one more readily so. Thus with aq. EtOH-NaOH (IV) is regenerated: with hot NH₂Ph-C₆H₆ a monoanilino-derivative, m.p. 195° (B; R=Cl; R'=NHPh), is obtained, but with boiling NH₂Ph a diamino-compound, m.p. 284° (B; R=R'=NHPh), results. Reduction of (V) (various reagents) gave inconclusive results, but with conc. aq. NH₃-Cu₂Cl₂ a small yield of an amino-hydroxy-derivative, C₁₅H₁₁ON₃, m.p. 285°, is obtained. On the basis of the structure of (II), (IV) is probably B (R=R'=OH), the least labile Cl being that in position 2 in the quinoline nucleus. The results of Hope *et al.* (A., 1933, 75) are explained by reduction occurring with the steel tube used. Fusion of Höchst-yellow R (VI) with NaOH at 245—255° gives BzOH, o-NH₂·C₆H₄·CO₂H (VII), and a base C₁₆H₉O₂N, m.p. 248° (VIII) [oxidised to (VII)], converted by Me₂SO₄-NaOH into the Me ester C₁₇H₁₃O₃N+0.5H₂O and anhyd., m.p. 189°, of the corresponding OH-compound, probably Me 3-hydroxy-2-phenylquinoline-2'-carboxylate, (VIII) being the corresponding lactone.



The different results of Hope (*loc. cit.*) may be explained by the observation that interruption of the

fusion of (VI) at 140° gives a new form of (VI), m.p. 240—242°, in which the OH has migrated from position 4 to 3. Heating (VI) with 10% NaOH in a Cu autoclave at 220° gives BzOH, (VII), and a substance, $C_{16}H_9O_6N$, m.p. 228°. The structures *C* and *D* are proposed for (I) and (VI), respectively, related compounds also being formulated. J. W. B.

6 : 8-Dibromobenzoylenecarbamide [6 : 8-dibromo-2 : 4-diketo-1 : 2 : 3 : 4-tetrahydroquinazoline] and constitution of dinitrobenzoylenecarbamide. F. E. SHEIBLEY and D. P. TURNER (J. Amer. Chem. Soc., 1933, 55, 4918—4923).—The dinitro-2 : 4-diketo-1 : 2 : 3 : 4-tetrahydroquinazoline (I) of Bogert and Scatchard (A., 1916, i, 672; 1920, i, 184) is converted through the $(NH_2)_2$ -derivative into 6 : 8-dibromo-2 : 4-diketo-1 : 2 : 3 : 4-tetrahydroquinazoline (II), m.p. 305—306° (corr.) [$Na (+H_2O)$ and *Li* salts], which is synthesised from $CO(NH_2)_2$ and 3 : 5-dibromoanthranilic acid. (I) is, therefore, the 6 : 8-derivative. The 6-Br-derivative is prepared by fusion of $CO(NH_2)_2$ and 5-bromoanthranilic acid; 2-chloro-3 : 5-dinitrobenzoic acid similarly gives 3 : 5-dinitroanthranilic acid. (II) is ethylated [EtI in aq. EtOH-LiOH or $(CH_2OH)_2$ -KOH] to the 3-Et derivative, m.p. 251° (corr.) (*Na* salt); the 3-Me, m.p. 268° (corr.), and 3-Pr^a, m.p. 225° (corr.), derivatives are prepared similarly. H. B.

Synthesis of heterocyclic compounds by means of isothiocarbamide ethers. J. F. DECK and F. B. DAINS (J. Amer. Chem. Soc., 1933, 55, 4986—4991).—Benzoxazines, quinazolines, benziminazoles, benzoxazoles, and glyoxalones are obtained from $SMe \cdot C(NR) \cdot NHR$ [prepared from $CS(NHR)_2$ and Me_2SO_4 in $COMe_2$ followed by treatment with dil. Na_2CO_3] and $o-OH \cdot C_6H_4 \cdot CO_2R$, $o-NH_2 \cdot C_6H_4 \cdot CO_2H$, $o-C_6H_4(NH_2)_2$, $o-NH_2 \cdot C_6H_4 \cdot OH$, and $NHAr \cdot CH_2 \cdot CO_2H$, respectively. The following are described : *S*-methyl-di-*p*-bromophenyl-, m.p. 129°, -*m*-nitrodiphenyl-, m.p. 87—89°, -di-*m*-tolyl-, m.p. 97·5°, -*p*-bromodiphenyl-, m.p. 79—80°, and -phenylmethyl-, m.p. 58—59° (perchlorate, m.p. 114°), -isothiocarbamides; the *MeHSO_4* salt, m.p. 141—142°, of $SMe \cdot C(NH) \cdot NPh$; 2-anilo-4-keto-3-phenyl-, m.p. 157—158°, 2-*o*-tolylimino-4-keto-3-*o*-tolyl-, m.p. 114° [hydrolysed (EtOH-conc. HCl) to 2 : 4-diketo-3-*o*-tolyl-, m.p. 129—130°], 2-*p*-tolylimino-4-keto-3-*p*-tolyl-, m.p. 163—164°, 2 : 4-diketo-3-*p*-tolyl-, m.p. 221°, 2-anilo-4-keto-3-*p*-bromophenyl-, m.p. 135—136°, 2 : 4-diketo-3-*p*-bromophenyl-, m.p. 214°, and 4-keto-2-phenyl-, m.p. 189°, -benzoxazines; 2-anilo-4-keto-3-phenyl-, m.p. 163°, 2 : 4-diketo-3-phenyl-, m.p. 271°, 2-keto-3-phenyl-1-methyl-, m.p. 224·5°, 2-*p*-tolylimino-4-keto-3-*p*-tolyl-, m.p. 149°, 2 : 4-diketo-3-*p*-tolyl-, m.p. 273°, 2 : 4-diketo-3-*p*-tolyl-1-methyl-, m.p. 190°, 2-*o*-tolylimino-4-keto-3-*o*-tolyl-, m.p. 157—159°, 2 : 4-diketo-3-*o*-tolyl-, m.p. 238—239°, and 2-anilo-4-keto-, m.p. 256°, -1 : 2 : 3 : 4-tetrahydroquinazolines; 2-anilino-, m.p. 188°, 2-*o*-toluidino-, m.p. 182° (hydrochloride, m.p. 89—90°), and 2-*p*-toluidino-, m.p. 207° (hydrochloride, m.p. 174°), -benziminazoles; 1-anilino-, m.p. 170°, 1-*m*-toluidino-, m.p. 146°, 1-*p*-toluidino-, m.p. 178°, 4-chloro-1-anilino-, m.p. 199°, 4-chloro-1-*p*-toluidino-, m.p. 204·5°, 4-nitro-1-anilino-, m.p. 235°, 4-nitro-1-*o*-, -*m*-, and -*p*-tolu-

idino-, m.p. 173—174°, 207°, and 222—224°, respectively, 4-chloro-1-thio-, m.p. 262° (from 4-chloro-*o*-aminophenol and CS_2 in EtOH), and 4-nitro-1-thio-, m.p. 235—238°, -benzoxazoles; 2-anilo-1 : 3-diphenyl-, m.p. 150—151° (4-*m*-nitrobenzylidene derivative, m.p. 170°), 2-keto-1 : 3-diphenyl-, m.p. 138·5°, 2-*p*-tolylimino-1-phenyl-3-*p*-tolyl-, m.p. 158° (4-*m*-nitrobenzylidene derivative, m.p. 156°), 2-keto-1-phenyl-3-*p*-tolyl-, m.p. 153°, 2-*o*-tolylimino-3-phenyl-1-*o*-tolyl-, m.p. 130°, 2-keto-3-phenyl-1-*o*-tolyl-, m.p. 126°, 2-anilo-1-phenyl-3-*p*-tolyl-, m.p. 126° (4-*m*-nitrobenzylidene derivative, m.p. 176°), and 2-keto-1-phenyl-3-*p*-tolyl-, m.p. 155°, -5-glyoxalones. Heterocyclic compounds could not be prepared from $o-C_6H_4(OH)_2$ and $NHPh \cdot CH_2 \cdot OH$. H. B.

Influence of attached rings on formation of heterocyclic compounds. I. T. N. GHOSH (J. Indian Chem. Soc., 1933, 10, 583—589).— $o-NH_2 \cdot C_6H_4 \cdot CO \cdot CO_2K$ and the appropriate ArNCS in EtOH give (after acidification) *o*-phenyl- (I), m.p. 173—174° (decomp.), 2-*o*-tolyl- (II), m.p. 208—210°, and 2-*p*-tolyl-, m.p. 165—166° (decomp.), -thiocarbamidobenzoylformic acid. (I) is converted by boiling with Ac_2O into 6 : 7-diketo-2-thion-1-phenyl-4 : *o*-benz-1 : 3-heptadiazine, $C_6H_4 \begin{smallmatrix} NH \cdot CS \\ CO \cdot CO \end{smallmatrix} NPh$, m.p. 155—157°; the 1-*o*-tolyl derivative, m.p. 205—206°, is similarly formed from (II). *o*-Phenylcarbamidobenzoylformic acid has m.p. 179—180°. *s*-Ethylenedi-phenyl-, -*o*-tolyl-, m.p. 180°, -*p*-tolyl-, m.p. 194—195°, -allyl-, m.p. 103—104°, and -methyl-, m.p. 85—86°, -dithiocarbamides, prepared from $(CH_2 \cdot NH_2)_2$ and RNCS (2 mols.), are unaffected by conc. HCl or 15% KOH. 1 : 2-Naphthylenedi-phenyl-, -*p*-tolyl-, m.p. > 300°, and -*m*-4-xylyl-, m.p. > 300°, -dithiocarbamides are similarly converted into 1 : 2-naphthylenethiocarbamide, $C_{10}H_6 \begin{smallmatrix} NH \\ NH \end{smallmatrix} CS$, m.p. > 300°. 9 : 10-Phenanthrenethiocarbamide, m.p. > 300°, is obtained directly from 9 : 10-diaminophenanthrene and ArNCS in C_5H_5N ; the intermediate 9 : 10-phenanthrenediarlyldithiocarbamides could not be isolated. Benzoylation of *o*-phenylenethiocarbamide (Lellmann, A., 1884, 49) under varying conditions gives only the *Bz* derivative, $o-C_6H_4 \begin{smallmatrix} N \\ NH \end{smallmatrix} C \cdot SBz$, m.p. 186—187°. H. B.

Condensations of toluenesulphonamides with trioxymethylene and formaldehyde. L. McMASTER (J. Amer. Chem. Soc., 1934, 56, 204—206).—*p*- $C_6H_4Me \cdot SO_2 \cdot NH_2$ (I), $(CH_2O)_3$ (II), and AcOH-conc. H_2SO_4 at 100° give tri-*p*-toluenesulphonyltrimethylene-tri-imide [1 : 3 : 5-tri-*p*-toluenesulphonylhexahydro-1 : 3 : 5-triazine], m.p. 169·8—170·5° (all m.p. are corr.), also formed from (I), 40% CH_2O (III), and a little conc. HCl in EtOH. *p*- $C_6H_4Me \cdot SO_2 \cdot NHMe$ and (II) or (III) similarly give methylenedi-(*p*-toluenesulphonmethylethylamide) ($+H_2O$, which could not be removed without some decomp.), m.p. 113—114°. *o*- $C_6H_4Me \cdot SO_2 \cdot NH_2$ and (II) afford 1 : 3 : 5-tri-*o*-toluenesulphonylhexahydro-1 : 3 : 5-triazine (IV), m.p. 245·5—246·5° (slight decomp.), and di-*o*-toluenesulphonyldimethylenedi-imide,

$C_6H_4Me \cdot SO_2 \cdot N \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} N \cdot SO_2 \cdot C_6H_4Me$, m.p. 168·8—

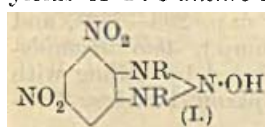
169.9°; with (III), (IV) only is produced. The above triazines form additive compounds with NH_3Ph .

H. B.

Heterocyclic compounds obtained by interaction of benzoin and hydrazine hydrochloride. V. J. VAN ALPHEN (Rec. trav. chim., 1934, 53, 74—76; cf. A., 1933, 838, 964).—1:3:4:6-Tetraphenyl- Δ^2 -trimidine [(+1.5EtOH); hydrochloride, m.p. 260° (decomp.)] is formed in small amount from benzoin and $\text{NH}_2\text{NHMe}\cdot 2\text{HCl}$ in EtOH at 100°, hence is unlikely to contain a N-N linking. It is unaffected by ZnCl_2 at 300° and by HI (d 1.96) and P at the b.p.

H. A. P.

[Reactions of the] 2:4:6-trinitrobenzylidene [derivatives of aromatic bases]. S. SECAREANU (Bull. Soc. chim., 1933, [iv], 53, 1016—1024, 1024—1032).—2:4:6-Trinitrobenzylidene derivatives of aromatic bases or 2:4:6- $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{CHO}$ when warmed with AcOH and excess of the base give good yields of 4:6-dinitro-2-hydroxy-1:3-diarylbenzotriazolines (I), by replacement of



of $\text{CH}\cdot\text{NR}$ and NO_2 by NHR and ring-closure by the HNO_2 liberated. Use of a foreign amine leads to complete or

partial exchange of R. Addition of KI to the reaction mixture lowers the yield of (I) by partial removal of the HNO_2 . The monocyclic NO-formula, alternative to (I), is excluded by the stability of the substances to HCl and the reduction of the NH_2Ph -derivative by $\text{Na}_2\text{S}_2\text{O}_4$ to 4:6-dinitro-1:3-diphenylbenzotriazoline (Bz_2 derivative, m.p. 236—240°). The following are described: derivatives of (I) in which $\text{R}=\text{Ph}$, m.p. 224° [previously (A., 1921, i, 337), described as an isomeride of trinitrobenzylidene-aniline (II)], $\beta\text{-C}_{10}\text{H}_7$, m.p. 262°, $p\text{-C}_6\text{H}_4\text{Me}$, m.p. 272°, $m\text{-bromo-p-tolyl}$, m.p. 298°, and $p\text{-C}_6\text{H}_4\text{Br}$, m.p. 281°; 2:4:6-trinitrobenzylidene- $m\text{-bromo-p-toluidine}$, m.p. 209°, and $p\text{-bromoaniline}$, m.p. 184°. Reduction of 2:4:6-trinitrodiphenylamine and subsequent benzoylation gives 2:4:6-tribenzamidodiphenylamine, m.p. 262°. (II) and hot AcOH give a substance, m.p. 257—258°, and a little $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{CHO}$.

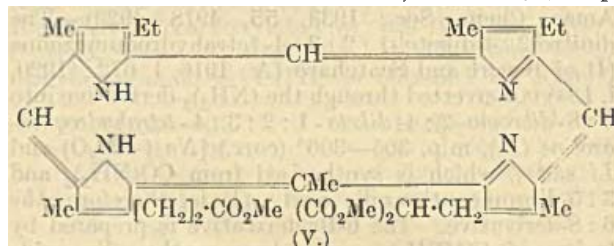
R. S. C.

Action of ozone on porphyrins. I. H. FISCHER and M. DEZELIC (Z. physiol. Chem., 1933, 222, 270—278).—On treatment with 1% O_3 for 6 hr. aetioporphyrin (I) gives a triozone, sinters 150° (decomp.), (+2.5H₂O) m.p. 100° (decomp.), (+H₂O) sinters from 110° (decomp.); after 15 min. a diozone, sinters from 112°, (+2H₂O) sinters from 110°. Aetiohaemin affords an ozonide, no m.p. below 250°, changes from 150°. 6:7-Di-(β -carboxyethyl)-2:3:5:8-tetramethyl-1:4-dipropylporphyrin and its ester and isouroporphyrin ester II show changes in absorption spectra. Methylenevalmaleimide affords a stable ozonide, m.p. 86—87°.

J. H. B.

Chlorophyll. XL. Synthesis of deoxophylloerythrin; derivatives of phylloporphyrin. H. FISCHER, M. SPEITMANN, and H. METH (Annalen, 1934 508, 154—167).—Phyllohaemin (I), $\text{CH}_2\text{Cl}\cdot\text{OMe}$, and SnCl_4 at 40° give hydroxymethylphyllohaemin (?) (II), converted by successive treatment with $\text{HBr}\cdot\text{AcOH}$ and 10% HCl into hydroxymethylphyllopor-

phyrin (III), $\text{C}_{33}\text{H}_{38}\text{O}_3\text{N}_4$. Successive treatment of crude (II) with $\text{HBr}\cdot\text{AcOH}$, MeOH, and 10% $\text{MeOH}\cdot\text{KOH}$ gives methoxymethylphylloporphyrin Me ester (IV), $\text{C}_{35}\text{H}_{42}\text{O}_3\text{N}_4$, m.p. 241° (corr.) (Cu salt, $\text{C}_{34}\text{H}_{37}\text{O}_3\text{N}_4\text{Cu}\cdot\text{Ac}$, m.p. 205—206°). Fusion of (III) or (IV) with methylsuccinic acid at 155° affords deoxophylloerythrin [Me ester, m.p. 261° (Cu salt, m.p. 254°)] (cf. A., 1931, 1431; 1933, 167). (IV) and $\text{HBr}\cdot\text{AcOH}$ at 35—40° give bromomethylphylloporphyrin hydrobromide, $\text{C}_{33}\text{H}_{39}\text{O}_2\text{N}_4\text{Br}_3$, which with $\text{CHK}(\text{CO}_2\text{Et})_2$ affords (after esterification of the intermediate acid with $\text{MeOH}\cdot\text{HCl}$) the ester (V), m.p.



211—212°. (I), Ac_2O , and SnCl_4 at 65—70° give a crude Ac derivative; removal of Fe by $\text{HBr}\cdot\text{AcOH}$ affords acetylphylloporphyrin [Me ester, $\text{C}_{35}\text{H}_{40}\text{O}_3\text{N}_4$, m.p. 286° (Cu salt, m.p. 318°; haemin, m.p. 314°)]. Phylloporphyrin [Et ester Cu salt, m.p. 256° (corr.); Me ester (Fe salt), converted by MgMeI into the corresponding tert-carbinol, $\text{C}_{33}\text{H}_{40}\text{ON}_4$, m.p. 252° (corr.)] and cold conc. HNO_3 give (probably) 6-nitrophylloporphyrin [Fe and Cu salts; Me ester, m.p. 228° (corr.)]. Phylloporphyrin ester can be nitrated with fuming HNO_3 in CHCl_3 .

H. B.

Chlorophyll. VI. Benzoyl derivatives and oximes of methylphæophorbide-a and phæophorbide-a. A. STOLL and E. WIEDEMANN (Helv. Chim. Acta, 1934, 17, 163—182).—The $\text{C}_5\text{H}_5\text{N}$ compound of benzoylphæophorbide-a (I) (improved prep. in 80% yield described) retains its $\text{C}_5\text{H}_5\text{N}$ in vac. and even on dissolution in acid and regeneration by dilution. Methylphæophorbide-a (II) with $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$ also yields a $\text{C}_5\text{H}_5\text{N}$ -compound, m.p. 182°, of its Bz derivative (III), hydrolysed to (II) with 20% $\text{HCl}\cdot\text{Et}_2\text{O}$, and to phæophorbide-a (IV) with 30—35% HCl at room temp. By Willstätter's method (A., 1912, i, 285) (I), (III), (IV), and phæoporphyra- a_5 (V) all retain NH_3 , indicating the presence of a free CO_2H , but (II) and the Me_2 ester of (V) do not. Fischer's view that benzoylation of an enolic OH and not, as previously suggested, a sec. OH, is involved is accepted. With $\text{NH}_4\text{OH}\cdot\text{HCl}$ and $\text{C}_5\text{H}_5\text{N}$ at 100° (II) affords an oxime (VI), not melting < 260° (corr.), hydrolysed by cold Et_2O -saturated 18% HCl to phæophorbide-a oxime [which cannot be prepared directly from (IV)], and by Et_2O -saturated 30% HCl to (IV), identical with the natural product. With $\text{HI}\cdot\text{AcOH}$ (VI) affords the Me ester of phæoporphyra- a_5 oxime. Fischer's view that a CO group is present at C_9 in phase-positive chlorophyll derivatives is thus confirmed. Spectroscopic data for all these derivatives are given.

J. W. B.

Chlorophyll series. XII. Phæopurpurins. E. M. DIETZ and W. F. ROSS (J. Amer. Chem. Soc., 1934, 56, 159—164).—The structure previously

assigned (A., 1931, 368; 1933, 403) to phæopurpurin 7 (I) is supported by its oxidation [$K_3Mo(CN)_8$ in $COMe_2-C_5H_5N$] to CO_2 and chlorin α β - Me_4 ester, which is esterified (CH_2N_2) to the Me_3 ester (II) (Cu, m.p. 235°, and Zn, m.p. 242°, salts), and converted by heating with Ph_2 at 200° into phæopurpurin 18 (III). Mild hydrolysis (0.15N-KOH in C_5H_5N) of the Me ester of (III) gives chlorin α α - Me_1 ester. Hydrolysis (MeOH-KOH) of (II) affords chlorin α Me_2 esters, m.p. 241–242° and 208° (according to conditions used). An unstable chlorin α and a small amount of chlorin α (IV) (A., 1930, 1299) [the chlorin p_6 of Fischer *et al.* (A., 1932, 1263)] are formed by aeration of (III) in 20% HCl; the former gives a Me_3 ester, the m.p. (227–228°) of which is not depressed by (II). The production of (III) from the unstable chlorins (V) obtained by phase-test hydrolysis of methylphæophorbide α , involves oxidation. A C atom is removed as CO_2 and not as HCO_2H (during hydrolysis) (cf. Fischer *et al.*, *loc. cit.*). (III) is most conveniently prepared by oxidation [$K_3Fe(CN)_6$ in dil. aq. NH_3] of (V); (I) is similarly unaffected. (III) and NH_2OH in C_5H_5N give a compound (VI), $C_{33}H_{35}O_5N_5$, whilst methylphæopurpurin 18 similarly affords a compound (VII), $C_{34}H_{37}O_5N_5$. (VI) and (VII) are considered to be analogous to the compounds formed from o - $C_6H_4(CO)_2O$ and NH_2OH ; they are methylated (CH_2N_2) to the Me ether of (VII). Rhodoporphyrin- γ -carboxylic acid anhydride furnishes a similar compound (Me ester Me ether, $C_{35}H_{37}O_5N_5$), which is also obtained [by dehydrogenation (?)] when (VI) is heated. (III) is regarded as the true anhydride of (IV). Rhodin g Me_3 ester oxime has m.p. 212°. H. B.

Derivatives of 5-aminotetrazole. R. STOLLE and O. ROSER (J. pr. Chem., 1933, [ii], 139, 63–64).—Interaction of 5-aminotetrazole with the corresponding chloronitrobenzenes in AcOH and xylene, respectively, at the b.p. gives 5-2': 4': 6'-trinitro-, m.p. 224° (Pb and Ag salts), and 5-2': 4'-dinitro-anilinetetrazole, m.p. 174° (decomp.). H. A. P.

Condensation of the anhydride and esters of diacetyltartaric acid with aniline and phenylhydrazine. A. WRÓBEL (Rocz. Chem., 1933, 13, 588–600).—*Me*, m.p. 102°, *Et* (I), an oil, and *Ph* diacetyltartrate, an oil, yield on heating with NH_2Ph at 135° *N*-phenyl-2:3-dihydro-oxazine-2:3-dicarboxylphenylimide (II), m.p. 264° (dibromide, m.p. 123°; nitrate, m.p. 230–250°), together with the corresponding alcohol, H_2O , and AcOH. (II) decomposes in conc. H_2SO_4 to yield $PhNCO$, CH_2O , and CO. The above esters condense with $NHPh-NH_2$ at 100° to yield 1-anilino-3:4-dihydroxy-2:5-diketopyrrolidine, m.p. 239° (Ac_2 derivative, m.p. 110°), and $NHPh-NHAc$; (I) gives in addition its phenylhydrazone, m.p. 156°. R. T.

Preparation of quinoxazones. H. EICHLER (J. pr. Chem., 1934, [ii], 139, 113–114).—Resorufin is formed in 95–99% yield by addition of $NaNO_2$ (0.8–3 pts.) or KNO_2 (1–3.7 pts.) to m - $C_6H_4(OH)_2$ (2 pts.) in conc. H_2SO_4 (19 pts.) at room temp. H. A. P.

Isomeric 2-tolylimino-3-tolyl-4-*p*-chloro- and -*p*-bromo-phenyl- Δ^4 -thiazolines. R. M. HANN

and E. E. REID (J. Amer. Chem. Soc., 1933, 55, 4998–5000).—*p*-Chloro- and -bromo-phenacyl bromides and $CS(NHPh)_2$ in EtOH give 2-anilo-3-phenyl-4-*p*-chlorophenyl-, m.p. 204° (all m.p. are corr.) (hydrochloride, m.p. 228–229°; picrate, m.p. 206°), and -4-*p*-bromophenyl-, m.p. 206° (picrate, m.p. 203°), Δ^4 -thiazoline, respectively. 2-*o*-Tolylimino-4-*p*-chlorophenyl-, m.p. 132° (picrate, m.p. 187°), and -*p*-bromophenyl-3-*o*-tolyl-, m.p. 123° (picrate, m.p. 196°), and 2-*p*-tolylimino-4-*p*-chlorophenyl-, m.p. 227° (picrate, m.p. 183°), and -*p*-bromophenyl-3-*p*-tolyl-, m.p. 239° (picrate, m.p. 193°), Δ^4 -thiazolines are similarly prepared using di-*o*- and -*p*-tolylthiocarbamides.

H. B.

Bromination of thiazole in gaseous phase at elevated temperatures. J. P. WIBAUT and H. E. JANSSEN (Rec. trav. chim., 1934, 53, 77–80).—Bromination of thiazole (I) over pumice at 250° gives 2-bromothiazole (II), b.p. 69°/15 mm. ($HgCl_2$ compound, m.p. 165.5°), and a dibromothiazole, m.p. 46–47° ($HgCl_2$ compound, m.p. 188.5°); at 400° (II) only is isolated. (I) forms a perbromide with Br in $CHCl_3$.

H. A. P.

Rearrangement of arylbenzthiazoles. M. MEYER, N. MOLOMUT, M. NOWAK, and M. OGUR (Rec. trav. chim., 1934, 53, 37–40).—1-Anilinobenzthiazole is unchanged by 63% H_2SO_4 at 200° or by conc. HCl at its b.p., but at 180–190° the latter converts it into an isomeric primary amine (? 2-*o*-aminophenylbenzthiazole), m.p. 156.4°. The phenyl-, m.p. 206.5°, and *p*-tolyl-thiocarbamido-derivative, m.p. 198.5°, of dehydrothio-*p*-toluidine are described. Phenyl-*p*-tolyl thiocarbamide is converted by the Hugershoff reaction into a 1-anilinomethylbenzthiazole, m.p. 128.5° (cf. A., 1930, 1452). All m.p. are corr. H. A. P.

Interaction of *s*-phenylmethylthiocarbamide and *s*-phenyl-*n*-butylthiocarbamide with bromine. M. R. CHOWDHURY and R. F. HUNTER (Rec. trav. chim., 1934, 53, 1–6).—Interaction of $NHPh-CS-NHMe$ with Br (2 equivs.) in $CHCl_3$ gives 1-methylaminobenzthiazole (I), but excess of Br gives a mixture of hydroperbromides (the “tetrabromide” of A., 1926, 849; cf. A., 1927, 263) reduced by SO_2 to 5-bromo-1-methylaminobenzthiazole (II), m.p. 224–225° (synthesised for comparison from 1-chloro-5-bromobenzthiazole and NH_2Me). Prolonged action of excess of Br gives 3:5-dibromo-1-methylaminobenzthiazole, m.p. 235°, also obtained by further bromination of (II), and synthesised by cyclisation of 5-2:4-dibromophenylmethylthiocarbamide, m.p. 164° (from $NH_2-CS-NH-C_6H_3Br_2$ and NH_2Me) with Br. The hydrotribromide, m.p. 118–126° (sinters 108°), of (II) is obtained by acting with Br on (II) or *s*-*p*-bromophenylmethylthiocarbamide. Bromination of $NHPh-CS-NHBU^a$ similarly gives the hydrodibromide, m.p. 65–75°, of 1-*n*-butylaminobenzthiazole, m.p. 86°, and (with excess of Br) the hydrohexabromide of 5-bromo-1-*n*-butylaminobenzthiazole, m.p. 118° (hydrotribromide, m.p. 100–110°). H. A. P.

Nature of bromo-additive compounds of dehydrothio-*p*-toluidine and its acetyl derivative and synthesis of 4'-acetamido-1-phenyl-5-methylbenzthiazole and 3'-bromo-4'-acetamido-1-phenyl-5-methylbenzthiazole. M. ALI-

passes when heated slowly into the *hydrochloride*, m.p. 304—305°, m.p. 136—138° (softens at 122°) when "drying" is effected at 125°; *aurichloride*, $C_{15}H_{20}ON_2 \cdot 1.5HAuCl_3 \cdot 2.5H_2O$, m.p. 204° (decomp.); *picrate*, m.p. 245—246°, from the air-dried plant. A new system for naming lupin alkaloids is proposed. H. B.

Rotatory dispersion of sparteine.—See this vol., 241.

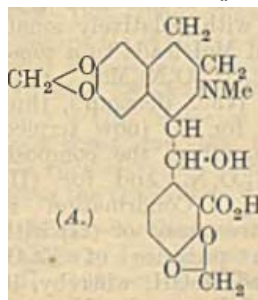
Sophora alkaloids. IV. Alkaloids of the seeds of *S. pachycarpa*. A. OREKHOV and N. PROSKURNINA (Ber., 1934, 67, [B], 77—83; cf. A., 1933, 840).—The dried seeds are percolated with EtOH containing 2% of AcOH; the liquid is neutralised with NH_3 , evaporated, and the residue is treated with 10% H_2SO_4 . After extraction with Et_2O , the acid liquor is saturated with K_2CO_3 and extracted with Et_2O , thereby giving 2.23% of crude alkaloids which do not contain the volatile bases isolated from the foliage (*loc. cit.*). Crystallisation of the hydriodides leads to the isolation of the individual alkaloids. *Sophocarpine*, $C_{15}H_{24}ON_2$, m.p. 54—55° (*monohydrate*, m.p. 81—82°, $[\alpha]_D^{25} -29.44^\circ$ in EtOH), is a strong, monoacid base, stable towards KOH-EtOH, and contains O and the second N in an indifferent, non-reactive form. It yields a *hydrochloride*, m.p. > 300° after darkening at 230—240°, *hydrobromide*, m.p. > 300° after darkening at 230—240°, *hydriodide*, m.p. > 300° after darkening at 240°, *aurichloride*, m.p. 166—170°, *platinichloride*, m.p. 209—212° (decomp.), *picrate*, m.p. 155—157°, and *methiodide*, m.p. 200—202°. *Sophocarpidine* (I), $C_{15}H_{24}ON_2$, m.p. 73—76°, $[\alpha]_D^{25} +38.38^\circ$ in EtOH, is possibly identical with matrine, but does not appear to exist in isomeric forms. It yields a *hydrochloride*, *hydrobromide*, *hydriodide*, *platinichloride*, m.p. 228—230° (also *trihydrate*), and hygroscopic *methiodide* (also +2EtOH). (I) is converted by boiling KOH-EtOH into *sophocarpidic acid* (II), $C_{15}H_{26}O_3N_2$, m.p. 202—204° (*tetrahydrate*, m.p. 170—175°, $[\alpha]_D^{25} +19.16^\circ$ in H_2O ; hygroscopic K salt (III), m.p. 222—226°, and its *mono-* and *tetra-hydrate*; *aurichloride*, m.p. 194—195°; *platinichloride*, m.p. > 250°). (II) is transformed by Ac_2O at 100° into (I). MeI in boiling MeOH transforms (III) into *Me_2 sophocarpidate methiodide*, m.p. 212—214° (also +1 H_2O). H. W.

Sempervirine, an oxygen-free alkaloid of *Gelsemium sempervirens*. V. HASENFRATZ (Bull. Soc. chim., 1933, [iv], 53, 1084—1087).—The rhizomes and roots of *G. sempervirens* contain sempervirine, $C_{19}H_{16}N_2$, + H_2O , m.p. 258—260° (block), $[\alpha]_D^{20}$ 0° in $CHCl_3$, orange-red (intense bluish-violet fluorescence in very dil. solution; *hydrochloride*, +2 H_2O ; *nitrate*, +2 H_2O , pptd. in concns. >1:20,000; *platinichloride*; *picrate*). R. S. C.

Yohimba alkaloids. H. HEINEMANN (Ber., 1934, 67, [B], 15—21).—The following subsidiary alkaloids have been isolated. (I) A base $C_{21}H_{26}O_3N_2 \cdot 3H_2O$, m.p. (hydrated) 104—105°, m.p. (anhyd.) 133—140°, $[\alpha]_D^{25} -73.6^\circ$ in C_5H_5N , identical with *alloyohimbine* of Hahn *et al.* (A., 1927, 471) and the dihydroyohimbine of Wernat (A., 1926, 1263). (II) α -Yohimbine, $C_{21}H_{26}O_3N_2 \cdot MeOH$, m.p. 234—235°, from MeOH or $C_{21}H_{26}O_3N_2 \cdot EtOH \cdot H_2O$ from 95% EtOH (anhyd.) $[\alpha]_D^{25} -28.0^\circ$ in abs. EtOH (*hydrochloride*, $[\alpha]_D^{25} +53.6^\circ$

in EtOH), hydrolysed by KOH-EtOH to α -yohimboic acid, decomp. 276° according to the rate of heating, $[\alpha]_D^{25} +47.5^\circ$ in C_5H_5N , readily purified by treatment with EtOH. Et α -yohimboate, m.p. 236°, $[\alpha]_D^{25} -6.7^\circ$ in C_5H_5N , and its *hydrochloride*, $[\alpha]_D^{25} +64.0^\circ$ in H_2O , are described. The identity of the compound is established by comparison with Merck's α -yohimbine, but unexplained discrepancies remain between the author's work and that of Wernat (*loc. cit.*), and Hahn *et al.* (A., 1930, 1194; 1927, 243). (III) β -Yohimbine, $C_{21}H_{26}O_3N_2 \cdot 2MeOH$, m.p. 235—236°, $[\alpha]_D^{25} -46.8^\circ$ in C_5H_5N , characterised by very sparing solubility in MeOH, not identical with the γ -yohimbine of Hahn *et al.* (A., 1930, 1194). The β -yohimbine described previously is a mixture (cf. Hahn *et al.*, A., 1932, 760); a *monohydrate* and the *hydrochloride*, decomp. 292°, $[\alpha]_D^{25} +27.7^\circ$ in H_2O , are described. Hydrolysis of the base affords β -yohimboic acid, decomp. 257° after softening at 253° (other vals. according to method of purification), $[\alpha]_D^{25} +15.8^\circ$ in C_5H_5N . The base gives a marked depression of the m.p. with *allo-* or α -yohimbine, but not with yohimbine itself. Constancy of m.p. is therefore inadequate evidence of homogeneity. (IV) γ -Yohimbine, $C_{21}H_{26}O_3N_2$, m.p. 254°, $[\alpha]_D^{25} -50.0^\circ$ in C_5H_5N , present only in minor amount and characterised by very sparing solubility in boiling EtOH. The *hydrochloride* (+ H_2O), decomp. 288° (anhyd.), $[\alpha]_D^{25} -18.6^\circ$ in MeOH, and δ -yohimboic acid, m.p. 253°, $[\alpha]_D^{25} +1.5^\circ$ in C_5H_5N , are described. H. W.

Alkaloids of fumaraceous plants. VIII. *Corydalis aurea*, Willd., and the constitution of bicucine. R. H. F. MANSKE (Canad. J. Res., 1933, 9, 436—442).—The dried roots of *C. aurea* contain 1.6% of protopine, whereas only 0.025% is present in the leaves and stem. By the procedure used with *Adlumia fungosa* (A., 1933, 728) are isolated 1-*tetra-hydropalmatine*, m.p. 142°, $[\alpha]_D^{25} -278^\circ$ in 95% EtOH, *capauridine*, $C_{21}H_{27}O_5N$, darkens at 180—190°, m.p. 203—204° [O-Me ether, m.p. 142° (I)], and the isomeric *capaurine*, m.p. 164° [O-Me ether, m.p. 150—151°, probably not identical with (I)] (both containing 1 phenolic OH and 4 OMe groups), *bicuculline* (II), $[\alpha]_D^{25} +130.5^\circ$ in $CHCl_3$, and *bicucine* (III), + H_2O , m.p. 222° (decomp.), $[\alpha]_D^{25} -145^\circ$ to -100° in 24 hr. in $N-HCl$ (both previously obtained from *Dicentra cucullaria*, A., 1933, 617), and at least four others not yet characterised. Oxidation of (III) with $KMnO_4$ -dil. KOH at 0° and treatment of the product with NH_2Et affords *N*-ethyl-3:4-methylenedioxyphthalimide, identical with a specimen prepared from (II). (III) is a free γ -OH-acid of which (II) is the corresponding



lactone, since alkali converts (II) into (III), whereas an equilibrium mixture is produced by boiling (III) with dil. HCl. The structure (A) is suggested for (III). All m.p. are corr. J. W. B.

Cocaine silicotungstate. B. A. KLYACHKINOV, M. K. STRUGATSKI, and V. M. MERLIS (Bull. Nauch.

Issledov. Khim. Farm. Inst., 1931, 268—274).—In the determination of cocaine the amount of reagent required depends on the concn. of electrolyte. The ppt. is at first amorphous, and then becomes cryst.; the ratio is then 4 (alkaloid) : 1. For the determination, either (1) cocaine in 0.5% HCl is treated with 5% aq. silicotungstic acid, diluted to 100 c.c. with 0.5% HCl, warmed 3—4 hr., kept 12—18 hr., and filtered, the ppt. being washed with 0.5% HCl and weighed (factor 0.426), or (2) a known amount of silicotungstic acid is used, an aliquot portion of the filtrate is evaporated, and the residue ignited. CH. ABS.

Strychnos alkaloids. LXXVIII. Isomeride of benzylidenedihydrostrychnine. H. LEUCHS and H. BEYER (Ber., 1934, 67, [B], 108—112).—Repetition of the work of Kotake *et al.* (A., 1933, 1061) shows that the product, m.p. 255°, obtained by the condensation of dihydrostrychnine with PhCHO by NaOEt in EtOH is accompanied by isobenzylidenedihydrostrychnine, m.p. 187—189°, $[\alpha]_D^{25} -325.1^\circ/d$ in EtOH, $[\alpha]_D^{25} -665^\circ/d$ in CHCl₃, which does not give Otto's reaction or a colour with FeCl₃. It gives a methiodide, C₂₈H₂₈O₂N₂MeI, m.p. 278—280° (decomp.), and an Ac derivative, C₃₀H₃₀O₂N₂, m.p. 157—159°, $[\alpha]_D^{25} -295^\circ/d$ in EtOH, but does not react with NH₂OH or NH₂·CO·NH·NH₂. It is moderately stable towards KMnO₄ in COMe₂, does not absorb H (PtO₂) in cold AcOH, but adds 12—14 atoms of H in warm HCl, giving a resinous product. Oxidation of benzylidenedihydrostrychnine by KMnO₄ in AcOH (*loc. cit.*) leads to a product, C₂₈H₃₀O₄N₂ (or C₂₈H₂₈O₄N₂) instead of C₂₈H₂₈O₅N₂, m.p. 268° (lit. 280°), giving a *sulphate*, *hydrochloride*, m.p. 233—236°, *perchlorate*, Ac derivative C₃₂H₃₄O₆N₂, m.p. 242—245°, and its *perchlorate*. Extraction of the pptd. MnO₂ with 2*N*-NH₃ yields the acid, m.p. about 300° (decomp.), $[\alpha]_D^{25} +91.3^\circ/d$ (as Na salt in H₂O). In addition, a neutral compound, (?) C₂₈H₃₀O₄N₂, m.p. 263—264°, $[\alpha]_D^{25} -308^\circ/d$ in 95% HCO₂H, is present in the COMe₂. H. W.

Curare alkaloids. II. Constitution of curine (bebeerine). E. SPATH and F. KUFFNER (Ber., 1934, 67, [B], 55—59; cf. A., 1928, 1264).—Examination of curine Me ether (I) shows that it has no tendency to form basic salts and that it resembles curine (II) (*loc. cit.*) in that its mol. wt. is about 20% > expected. Treatment of (I) with relatively small amounts of MeI leads to a compound (C₁₉H₁₇O₂N₂)MeI, m.p. 257—258° (vac, decomp.), this indicating for (I) (now termed curine Me₂ ether) the composition C₃₈H₄₂O₆N₂, and for (II) C₃₆H₃₈O₆N₂. Confirmation is found by treatment of (II) with CH₃N₂ in presence of Et₂O, COMe₂, and MeOH, whereby, in addition to (I), a curine Me ether, m.p. 206—208°, and a possible mixture of isomeric Me₁ ethers is obtained. The constitution of (I) is therefore modified to A, which explains the production of protocathechuic acid in addition to *p*-OH·C₆H₄·CO₂H

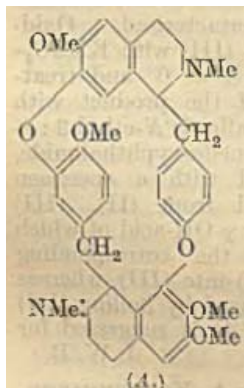
when (II) is fused with KOH and the formation of 5 : 6 : 4'-tricarboxy-2 : 3-dimethoxydiphenyl ether by oxidation of the final product of the Hofmann degradation of (I). H. W.

Molecular condition of the alkaloid silicotungstates. B. A. KLYACHKINA, M. K. STRUGATZKI, and F. D. ZILBERG (Bull. Nauch. Issledov. Khim. Farm. Inst., 1931, 203—208).—Nicotine in quantity too small for acidimetric titration can be titrated with silicotungstic acid (I). For cocaine, methylecgonine, ecgonine, morphine, codeine, thebaine, papaverine, narceine, hydrastine, atropine, piperine, harmine, harmaline, pilocarpine, and aq. strychnine the ratio (I) : alkaloid is 1 : 4. For eserine, quinine, nicotine, emetine, cephadine, anabesine, and strychnine (in 15% HCl) it is 1 : 2. Alkaloids with weakly basic N (dissociation const. < 10⁻¹¹), which do not form salts with acids in aq. solution, react with (I) to form sparingly sol. salts. CH. ABS.

Naphthylarsinic acids. Application of Bechamp reaction to α -naphthylamine. H. P. BROWN and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 151—153).—The acid obtained (a) from α -C₁₀H₇NH₂ and α -C₁₀H₇NH₂ H arsenate (I) at 195°, (b) by fusion of (I), and (c) from α -C₁₀H₇NH₂ and H₃AsO₄ at 165—175°, is 1-amino-2-naphthyl- (II) (A., 1932, 409) and not 4-amino-1-naphthyl- (III) -arsinic acid as stated by Adler and Adler (A., 1908, i, 492; cf. Benda and Kahn, *ibid.*, 591). (III) heated with α -C₁₀H₇NH₂ at > 175° gives (II). The Ac derivatives of (II) and (III) are converted by PCl₅ in CCl₄ into 2-chloro-1-acetamido- and 1-chloro-4-acetamidonaphthalene, respectively. H. B.

Diarsyls. VI. 3 : 3' : 3'' : 3'''-Tetra-nitro-, -amino-, and -acetamido-tetraphenyldiarsyl. F. F. BLICKE, U. O. OAKDALE, and J. F. ONETO (J. Amer. Chem. Soc., 1934, 56, 141—144).—3 : 3'-Dinitrodiphenylhydroxyarsine, H₃PO₂, and a little HI in AcOH give 3 : 3' : 3'' : 3'''-tetranitrotetraphenyldiarsyl, m.p. 203—204° (sealed tube; in N₂) (cf. Michaelis, A., 1902, i, 515). Similar reduction of 3 : 3'-diaminodiphenylarsinic acid, m.p. 235° (decomp.), affords 3 : 3' : 3'' : 3'''-tetra-aminotetraphenyldiarsyl, m.p. 168—169° (sealed tube; in N₂) [*tetrahydrochloride*, m.p. about 283° (decomp.)]; Ac₄ derivative (I), m.p. > 300°, also obtained (a) from 3 : 3'-diaminodiphenylarsine (II) and 3 : 3' : 3'' : 3'''-tetra-aminotetraphenyldiarsyl oxide (III) (Ac₄ derivative, m.p. 236—237°), (b) from AsHPh₂ and (III), and (c) from (II) and (AsPh₂)₂O. (AsPh₂)₂ is also formed in (b) and (c). (I) absorbs O₂ very slowly when suspended in C₂H₄Br₂. H. B.

Evidence for an asymmetrical arsenic atom. C. F. H. ALLEN, F. B. WELLS, and C. V. WILSON (J. Amer. Chem. Soc., 1934, 56, 233—234; cf. A., 1933, 1177).—7-Chloro-7 : 12-dihydrobenzophenarsazine and Ag *d*-bromocamphorsulphonate in Ac₂O give small amounts of two isomeric compounds, C₂₆H₃₅O₄NBrSAs, m.p. 182—183°, $[\alpha]_D^{25} +35.1^\circ$ (all rotations are in 95% EtOH), and m.p. 188—189°, $[\alpha]_D^{25} +59.5^\circ$; solids, m.p. 200° and 211—212°, are also formed. 7-Chloro-9-methyl-7 : 12-dihydrobenzophenarsazine similarly affords a very small amount of a compound,



$C_{27}H_{37}O_4NBrSAs$, m.p. 250° , $[\alpha]_D^{25} + 32.6^\circ$. 12-Chloro-7:12-dihydrobenzophenarsine (?) gives isomeric compounds, $C_{26}H_{35}O_4NBrSAs$, m.p. $218-219^\circ$ and $224-225^\circ$, in addition to two other substances. H. B.

Organic compounds of mercury. VI. Synthesis of organic compounds of mercury with negative substituents by the diazo method. A. N. NESMEJANOV, N. T. GLUSCHNEV, N. T. EPIFANSKI, and P. T. FLEGONTOV (Ber., 1934, 67, [B], 130-134; cf. A., 1933, 292).—Optimum conditions are described for the prep. of compounds, $RN_2Cl, HgCl_2$, in which $R = o\text{-NO}_2\text{-C}_6\text{H}_4\cdot$, $116-117^\circ$, $p\text{-NO}_2\text{-C}_6\text{H}_4\cdot$, $m\text{-NO}_2\text{-C}_6\text{H}_4\cdot$, decomp. 138° , $2:5\text{-C}_6\text{H}_3\text{Cl}_2\cdot$ and $SO_3H\text{-C}_6\text{H}_4\cdot$, m.p. $152-153^\circ$. Slow addition of these compounds to a well-stirred mixture of a suitable solvent (usually $COMe_2$) and Cu powder generally at -20° to -10° , but occasionally at -70° , affords the corresponding $HgCl$ -derivatives in 30% to 70% yield. H. W.

Aryl selenohalides. IV. α -Anthraquinonyl selenohalides and α -anthraquinonylselenenic acid. O. BEHAGEL and W. MÜLLER (Ber., 1934, 67, [B], 105-108; cf. A., 1933, 842).—Di-1-anthraquinonyl diselenide (I) is converted by Br in boiling $CHCl_3$ into *Se* 1-anthraquinonyl bromide (II), m.p. (indef.) 217° . Treatment of (I) in $AcOH$ with Cl_2 or SO_2Cl_2 leads to *Se* 1-anthraquinonyl trichloride, m.p. 203° after darkening, transformed by $COMe_2$ in $CHCl_3$ into *Se* 1-anthraquinonyl chloride (III), m.p. 220° , also obtained from (I) and the calc. amount of Cl_2 . (II) and $NPhMe_2$ in boiling Et_2O afford 4-dimethylaminophenyl 1-anthraquinonyl selenide, m.p. $> 270^\circ$, whilst *Ph* 1-anthraquinonyl selenide, m.p. 178° , results from (II) and $MgPhBr$. (II) or (III) is transformed by $AgOAc$ in boiling $MeOH$ into 1-anthraquinonylselenenic acid, m.p. $> 250^\circ$, which yields a dark blue Na salt. H. W.

Triphenylsilyl ethylamine, $SiPh_3NH_2Et$. C. A. KRAUS and H. EATOUGH (J. Amer. Chem. Soc., 1933, 55, 5008-5014).— $SiPh_3Br$ and Li (1 equiv.) in NH_4Et give triphenylsilyl ethylamine (I), m.p. 45° , which dissociates in boiling Et_2O and affords $(SiPh_3)_2$. (I) can be distilled in a high vac., does not react with Na in liquid NH_3 , but with Li in NH_4Et gives $LiSiPh_3$ (II). (II) and NH_4Br in liquid NH_3 afford $SiHPh_3$; $SiPh_4$ is formed using $PhBr$. (II) and $SnMe_3Cl$ in liquid NH_3 give trimethylstannyltriphenylsilicon (III), $SnMe_3SiPh_3$, which is decomposed by Na in liquid NH_3 to $NaSiPh_3$ and $NaSnMe_3$ (subsequent treatment with MeI gives $SiPh_3Me$ and $SnMe_3$). $SiPh_3Br$ and $SnMe_3Br$ are obtained from (III) and Br in Et_2O . H. B.

Reactions of sodium triphenylstannide with polyhalogenated methanes. C. A. KRAUS and H. EATOUGH (J. Amer. Chem. Soc., 1933, 55, 5014-5016).— $NaSnPh_3$ (I) and CH_2Cl_2 in liquid NH_3 give di(triphenylstannyl)methane, $CH_2(SnPh_3)_2$, m.p. 104.5° (corr.); with $CHCl_3$, tri(triphenylstannyl)methane, m.p. 128° (corr.), and a little $SnPh_3$ (II) result. (I) and CCl_4 afford (II). H. B.

Iodometric determination of protein degradation products. L. UTKIN (Biochem. Z., 1933, 267, 69-73; cf. A., 1930, 1217).—The method of Kober and Sugiura (A., 1917, ii, 398) is improved by pptg. the

$Cu(OH)_2$ in the protein solution which is then buffered with borate and using alkaline KI solution. OH-acids must be absent. The procedure can be applied in following the degradation of proteins and polypeptides, but not in determining the composition of simple peptides or in measuring dipeptidase action.

W. McC.

Nucleoproteins. S. J. PRZYŁECKI (Rocz. Chem., 1933, 13, 681-685).—A classification of nucleoproteins (I) and nucleins is proposed, based on considerations of the nature and no. of the constituent groups. Nucleic acid (II) is combined with protein by its free H_3PO_4 groups; the no. of H_3PO_4 valencies so combined varies with the relative concn. of protein and (II). R. T.

Effect of dilute alkali on cystine content of casein. D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1934, 104, 99-106).—Successive pptn. of very pure casein from $NaOH$ solutions with $AcOH$ produces a loss in the cystine (I) content; after five pptns. 90% of (I) is destroyed. The % arginine, histidine, lysine, tyrosine, and tryptophan are not materially changed. The importance of the losses of (I) in relation to dietary experiments is emphasised. H. D.

Determination of sulphur in organic substances. E. KAHANE and M. KAHANE (Compt. rend., 1934, 198, 372-375).—The substance (0.1-0.2 g.) is heated with 2 c.c. of a 2:1 mixture of $HClO_4$ (d 1.61) and HNO_3 (d 1.39) with a little HIO_3 and the escaping gases are washed with HIO_3 (apparatus described). The HIO_3 is then reduced (NaI , CH_2O , or N_2H_4), the solution neutralised, and SO_4^{2-} pptd. as $BaSO_4$. J. W. B.

Detection of selenium in organic compounds. M. J. HORN (Ind. Eng. Chem. [Anal.], 1934, 6, 34-35).—The sample is completely oxidised with H_2SO_4 containing a little $HgSO_4$ and a few drops of 3% aq. codeine sulphate are added. A green coloration, rapidly changing to blue, is observed if Se is present. Presence of more than a trace of H_2O prevents the development of colour, and V gives a dark greenish-blue coloration. H. A. P.

Determination of active hydrogen. O. SCHMITZ-DUMONT and K. HAMANN (J. pr. Chem., 1934, [ii], 139, 162-166).—The disturbing effects caused by reaction (I) of C_5H_5N with the Grignard reagent when used as solvent in the Zerewitinov determination are obviated by plotting the vol. of gas evolved against time. This increases rapidly at first, but soon falls to a const. rate due to (I) alone. Extrapolation of the corresponding straight line to zero time therefore gives the true vol. H. A. P.

Micro-method for determination of iodine values. J. O. RALLS (J. Amer. Chem. Soc., 1934, 56, 121-123; cf. A., 1933, 709).—The substance (0.75-25 mg.) is treated with I_2 in CCl_4 at 0° ; after addition of KI and titration with $Na_2S_2O_3$, the mixture is treated with KIO_3 to determine $HHal$ produced during the reaction. Results are given for 30 substances. H. B.

Determination of gaseous olefines. V. SOROKIN, A. BELIKOVA, and O. BOGDANOVA (J. Rubber

Ind., U.S.S.R., 1931, 5, No. 4—5, 26—27).—With HBr in glacial AcOH, C_2H_4 is unchanged, C_3H_6 gave $Pr^{\beta}Br$ with some $Pr^{\alpha}Br$, Δ^{β} -butylene gave the bromide, b.p. 90—91°, β -methyl- Δ^{α} -propylene gave the bromide, b.p. 92—93°, butadiene gave the mono-, b.p. 103°, and di-, b.p. 170—172°, -bromides. CH. ABS.

Detection of disubstituted urethanes by colour reactions. F. BECKER and G. A. HUNOLD (Z. ges. Schiess- u. Sprengstoffw., 1933, 28, 372—376).—With HNO_3 , d 1.18 (I), urethanes of the type $NPhR \cdot CO_2Et$ ($R=Me$ or Et) give $(NO_2)_1$ -derivatives, converted by $NaOH-EtOH$ into $p-NO_2C_6H_4 \cdot NHR$, no red colour being produced, but with HNO_3 , d 1.42 (II), $(NO_2)_2$ -derivatives are formed (the R group suffering fission), hydrolysed to $2:4-(NO_2)_2C_6H_3 \cdot NH_2$ with production of a red colour. Similarly centralite $CO(NPhEt)_2$ gives no red with (I)- $NaOH-EtOH$, but does so with (II)- $NaOH-EtOH$. $NPh_2 \cdot CO_2Et$ with (I) gives a $p-NO_2$ -derivative hydrolysed to $p-NO_2C_6H_4 \cdot NHPh$, a red colour being formed, and with (II) the ultimate hydrolysis products are $4:4'$ - and $4:2'$ -dinitrodiphenylamine, also giving a red colour. Similarly akardite ($NPh_2 \cdot CO \cdot NH_2$) gives a red colour with either (I) or (II), the initial products being $2:4:2':4'$ -tetra- and $2:4:6:2':4':6'$ -hexa-nitrodiphenylamine. Thus the usual colour reaction for smokeless powders is not sp. J. W. B.

Reactions of some phenols with (a) antimony pentachloride, and (b) sulphuric-arsenic acid mixture. L. EKKERT (Pharm. Zentr., 1934, 75, 49—50, 50—51).—Colour reactions of (a) 21, (b) 18, phenol derivatives with $SbCl_5-CHCl_3$ and $H_2SO_4-Na_3AsO_4$, respectively, are given. E. H. S.

Detection of *p*-chlorobenzoic acid in the presence of benzoic acid. F. WEISS (Z. Unters. Lebensm., 1934, 67, 84—86).—If, in carrying out Mohler's test by Grossfeld's method (A., 1915, ii, 158), the NH_2OH is added so as to form a distinct upper layer, $p-C_6H_4Cl \cdot CO_2H$ (I) gives a green, $BzOH$

(II) an orange-red, ring. If the solutions are mixed, (I) gives a red colour and cannot be distinguished from (II). E. C. S.

Determination of pyridine in dilute solution. M. V. IONESCU and H. SLUSANSCHI (Bull. Soc. chim., 1933, [iv], 53, 1087—1096).—This is effected by noting the time taken for formation of a ppt. with $N-(CdCl_2+2NaCl)$ or $N-(HgCl_2+2NaCl)$ in concns. of 0.045—0.075 and 0.012—0.006%, respectively. R. S. C.

Aminometry of alkaloids. D. VORLANDER (Ber., 1934, 67, [B], 145; cf. this vol., 198).—Cinchonine and quinine behave quantitatively as diacidic amines, whereas strychnine and brucine are monoacidic. Anhyd. $PhSO_3H$ or other aromatic sulphonic acids can replace HCl . H. W.

Reaction of methylene ether groups in aromatic compounds. J. A. LABAT (Bull. Soc. Chim. biol., 1933, 15, 1344—1345).—With regard to the colour reaction with gallic acid in H_2SO_4 (A., 1909, ii, 771), priority to Sanchez (A., 1932, 866) is claimed. In the event of nornarcotine proving to be related to vitamin-C, the application of the reaction to vitamin-C research is indicated. F. O. H.

Quantitative spectro-photo-electric analytical method applied to solutions of chlorophylls *a* and *b*. F. P. ZSCHEILE, jun. (J. Physical Chem., 1934, 38, 96—102).—Using the apparatus previously described (this vol., 272), quant. light absorption data have been obtained for chlorophylls *a* and *b* and their mixtures, and it is shown that the composition of such mixtures can be determined with an error of < 1%. Measurements at λ 4400 Å. give total concn. and at λ 4100 or 4279 Å. the ratio of *a* to *b*. Beer's law is valid for chlorophyll solutions in 90% $COMe_2$. The method may be applied to all coloured solutions obeying Beer's law and should be especially useful in biochemistry. A supplementary method with an accuracy within 5% is given. M. S. B.

Biochemistry.

Comparison of methods for collection of blood to be used in the determination of gases. J. M. LOONEY and H. M. CHILDS (J. Biol. Chem., 1934, 104, 53—58).—A method of withdrawing and handling blood for gas analysis employing a capped syringe is described. Blood kept in 10-c.c. portions for > 2 hr. under 5 cm. of oil loses < 7.98 vol.-% of CO_2 and gains < 6.44 vol.-% of O_2 . The effect of stasis on the gas content of blood can be avoided by drawing the blood 1 min. after the removal of the tourniquet. A. L.

Van Slyke method of blood-gas analysis. F. RAPPAPORT and K. KOCK-MOLNAR (J. Biol. Chem., 1934, 104, 29—31).—The reagent is modified by the addition of urea (450 g. per litre) to prevent protein pptn. and so permit more exact readings. A. L.

Stimulating action of copper on erythropoiesis. H. B. STEIN and R. C. LEWIS (J. Nutrition, 1933, 6, 465—472).—Feeding of evaporated milk to rats reduces the haemoglobin (I) without the corresponding

reduction in erythrocyte (II) count such as occurs when raw milk is the sole diet. The Cu in evaporated milk causes the temporary maintenance of a high (II) count. Addition of 0.25—0.5 mg. Cu daily to a milk diet has an erythropoietic action without effect on (I). A. G. P.

Spectrophotometric differentiation of the haemoglobins of different species. H. M. WINGARDEN and H. BORSOOK (J. Cell. Comp. Physiol., 1933, 3, 437—448).—It is possible to observe, by spectrophotometric methods, intersp. and (in the case of the rabbit) intrasp. differences in the haemoglobins. Of the erythrocyte-Fe, 4—6% is in a form simpler than haemoglobin. A. G. P.

Crystalline forms of (a) haemin and mesohaemin; (b) esters of haemin, mesohaemin, and protoporphyrin. K. LINDENFELD (Rocz. Chem., 1933, 13, 645—659, 660—680).—(a) The prep. and properties of the polymorphs of X-haemin (I) (A.,

1931, 1079) (X=Cl, Br, I, CNS) are described. "Acetone-(I)," prep. by adding COMe_2 to a solution of Cl-(I) in aq. NH_3 , and acidifying with HCl at 50° , is rapidly converted into the ordinary Teichmann form of Cl-(I) on immersion in boiling 80% AcOH. Cl-, Br-, and CNS-mesohæmin (II) are obtained in hexagonal plates by adding a solution in $\text{CHCl}_3\text{-C}_5\text{H}_5\text{N}$ of the Teichmann crystals (from mesoporphyrin) to 80% AcOH containing NH_4Cl , NH_4Br , or NH_4CNS at 50° ; under analogous conditions I-(II) does not yield a polymorph. These polymorphs are contaminated with impurities adsorbed from solution.

(b) The Me_2 and Et_2 esters of protoporphyrin (III) are prepared by heating (III) in MeOH or EtOH containing 2% of HCl. The Et_2 esters of X-(I), (II), and X-(II) are prepared analogously. The esters exist in two cryst. forms, viz., fusiform obtained by rapid, and octahedral or monoclinic by slow, crystallisation from $\text{CHCl}_3\text{-C}_5\text{H}_5\text{N}$; the formation of the latter crystals, which are the more stable, is favoured by the presence of NH_4X in the solvent.

R. T.

Fluorescence spectrum of the tin complex of blood-protoporphyrin. H. BIERREY and B. GOUZON (Compt. rend., 1934, 198, 615—617).—The Sn complex produced by the action of SnCl_2 on blood in AcOH can be identified with that of protoporphyrin by means of its fluorescence spectrum, which is distinct from that of hæmatoporphyrin.

P. G. M.

Determination of blood-bile acids. II. In serum. K. KUSUI (J. Biochem. Japan, 1933, 18, 345—368; cf. A., 1932, 1053).—Serum (1 c.c.) is treated with EtOH (25 c.c.) and the EtOH-sol. material is separated and extracted with Et_2O . The Et_2O -insol. fraction is extracted with EtOH and the extract treated with sucrose and H_2SO_4 , the resulting colour being compared with suitable standards. The method is applicable to lymph. Human serum contains 6.3—11.6 and dog's serum 6.24—10.5 mg. of bile acid per 100 c.c.

F. O. H.

Determination of indoxyl compounds in blood. H. SHARLIT (J. Biol. Chem., 1934, 104, 115—120; cf. A., 1933, 301).—The method for determining indican (I) in urine is applied to blood; all reactions must be carried out at room temp. In normal fasting individuals the concn. of (I) is negligible; in cases of N retention it may be > 6 mg. per 100 c.c.

H. D.

Extraction of cholesterol from blood. O. MUHLBOCK (Z. physiol. Chem., 1933, 222, 233—234).—Bloor's method is applicable to whole blood (cf. Milbradt, A., 1933, 624). 1 c.c. of oxalated blood is dropped into EtOH- Et_2O (3 : 1). After a few hr. the solution is filtered and dried. The COMe_2 extract of the residue is examined nephelometrically (cf. A., 1932, 666).

J. H. B.

Determination of fructose in blood. R. STÖHR (Z. physiol. Chem., 1933, 222, 261—269).—2 c.c. of the protein-free blood filtrate (from 0.2 c.c. of blood) are treated with 2 c.c. of phosphomolybdic acid reagent. After 25 min. at 100° , the cooled solution is titrated with 0.01N- KMnO_4 to disappearance of the blue colour. AcCHO , $\text{OH}\cdot\text{CH}(\text{COMe})_2$, $\text{CH}_2\text{Ac}\cdot\text{OH}$, glyceraldehyde, and $\text{CO}(\text{CH}_2\text{OH})_2$ interfere, but glucose does not.

J. H. B.

Fluctuations of blood-sugar *in vitro*. I. NEUWIRTH (J. Biol. Chem., 1934, 104, 129—130).—The results of Kleiner (A., 1933, 966) on the fluctuations in the blood-sugar curve of undialysed hyperglycæmic blood could not be repeated.

H. D.

Iron content of the blood. O. H. HELMER and C. P. EMERSON (J. Biol. Chem., 1934, 104, 157—161).—The average Fe content of whole blood is 52.5 and 49.8 mg. per 100 c.c. for men and women, respectively, by Kennedy's method (A., 1927, 987), which gave higher vals. than Wong's method (A., 1928, 785). Hæmoglobin determined by Fe content and O_2 capacity was in good agreement.

H. G. R.

Ultrafiltration of serum and plasma. Content of ultrafiltrates in chlorine, potassium, sodium, calcium, and magnesium. J. LEVY and M. M. PACU (Bull. Soc. Chim. biol., 1933, 15, 1317—1329).—Ultrafiltrations of serum (I) and plasma (II) under 2 atm. pressure indicate the following degrees of ultrafilterability: Cl of (I) and (II), 100%; K of (I) and (II), 95%; Na of (I) and (II), 90%; Ca of (I), 64%, of (II), 72%; Mg of (I) and (II), 60—70%.

F. O. H.

Citration of blood and precipitation of calcium by oxalate. L. BRULL and R. POVERMAN (Bull. Soc. Chim. biol., 1933, 15, 1281—1289).—Addition of up to 1.0% of Na citrate (I) to aq. CaCl_2 (0.01% in Ca) does not influence the pptn. of Ca by $(\text{NH}_4)_2\text{C}_2\text{O}_4$, whilst concns. of (I) of 3.0% or more partly inhibit the pptn. With serum, the concn. of (I) must not be $> 1.0\%$. Addition of 0.3—0.5% of (I) to whole blood influences neither the partition of Ca between serum and fibrin nor the pptn. of Ca from the plasma. That low concns. of (I) cause complex-formation by Ca is therefore refuted (cf. A., 1932, 293).

F. O. H.

Proteinates and cations of blood-serum. J. LEVY and F. GALLAIS (Bull. Soc. Chim. biol., 1933, 15, 1330—1335).—The non-ultrafilterable fraction (I) of Na and K in serum equals that fraction of these cations bound to the proteins (II) isolated by pptn. with EtOH, whilst with Ca, (I) (32%) is $<$ that bound to the pptd. (II) (61%).

F. O. H.

Concentration and distribution of phosphorus in blood of merino sheep on pasture. R. H. WATSON (Austral. J. Exp. Biol., 1933, 11, 253—260).—The total, inorg., exp. acid-sol., and org. acid-insol. blood-P of sheep on natural pasture were 16.5—20.8, 2.8—5.9, 3.4—6.0, and 8.0—11.3 mg. per 100 c.c., respectively.

H. D.

Significance of the iodine content of human blood. G. M. CURTIS, C. B. DAVIS, and F. J. PHILLIPS (J. Amer. Med. Assoc., 1933, 101, 901—905).—Blood-I is normally 0.012 mg. and urinary I 0.025—0.075 mg. per 100 c.c. Vals. are increased in toxic goitre, menstruation, and I medication. Human blood-I is a measure of thyroid function.

CH. ABS.

Analysis of serum with the ultracentrifuge. Serum fractions. P. VON MUTZENBECHER (Biochem. Z., 1933, 267, 460).—A correction of the author's papers (this vol. 93).

P. W. C.

Surface tension of the blood-plasma and -serum in certain marine animals. E. ZUNZ (Bull. Acad. roy. Belg., 1933, [v], 19, 1107—1125).—The dynamic surface tension of the plasma is $>$ that of H_2O in the Selachians examined and $<$ that of H_2O for Teleosteans, Crustaceans, and Cephalopods. Both dynamic and static surface tensions of the sera are always $<$ those of the plasma. J. W. S.

Chemistry of mitogenetic radiation of blood. A. GURVITSCH (Russ. J. Physiol., 1933, 16, 495—500).—The mitogenetic radiation (I) of hæmolyzed blood is due to glycolysis; (I) is in particular associated with dissociation of hexosediphosphoric acid, and with dismutation of phosphoglyceraldehyde. R. T.

Physical chemistry of avian erythrocytes. F. J. BERENSCHTEIN, D. I. LJACH, and N. P. BEDRIKOVSKAJA (Russ. J. Physiol., 1933, 16, 530—540).—Duck erythrocytes (I) suspended in aq. sucrose undergo agglutination (II) at 5.9, goose (I) at p_H 5.3—5.6, and hen (I) at p_H 3.54—5.3; alkali and alkaline-earth salts inhibit (II) in Hofmeister's series. The rate of sedimentation (III) of avian (I) in their homologous plasma (IV) is 1/25 to 1/30 that of horse (I); similar results are obtained for suspensions of horse (I) in avian (IV), and of avian (I) in horse (IV). In all cases (III) is greater for (IV) than for serum suspensions; it increases for avian and diminishes for horse (I) when isotonic solutions of NaCl, $CaCl_2$, Na_2SO_4 , glucose, or sucrose are substituted for (IV). R. T.

Concentration of anti-venom serum. G. C. MATTRA, B. P. B. NAIDU, and M. L. AHUJA (Indian J. Med. Res., 1933, 21, 229—236).—Dil. serum is treated with Na_2SO_4 and pseudoglobulin (I) removed from the pptd. globulin with saturated aq. NaCl. The filtered solution of (I) is treated with AcOH and the ppt. is dialysed in 2% Na_2CO_3 against H_2O until free from SO_4^{--} . The p_H is adjusted to 7.4; 1% NaCl and 0.35% of tricesol are added. CH. ABS.

Microelectrodialysis and its use for the isolation of serum precipitins. T. ASABA (Arb. Med. Fak. Okayama, 1933, 3, 561—568).—Immune bodies were isolated from antigen-antibody complexes in a modified Pauli apparatus. Precipitins with a trace of NaCl were obtained. CH. ABS.

Action of infra-red, visible, and ultra-violet rays on hæmolytic complement and the absorption spectrum of guinea-pig serum. M. PAIC and P. HABER (Compt. rend., 1934, 198, 613—615).—Complete destruction of complement by the light from a Hg-vapour lamp takes place in 10 hr. P. G. M.

Morphology and fine structure of collagen fibres. A. KUNTZEL and F. PRAKKE (Biochem. Z., 1933, 267, 243—295).—Tendon fibres (of Achilles of ox and calf, of rat's tail) are cellular and 10μ in width, and skin-collagen fibres are not in general cellular and 2μ in width. The fibres are composed of fibrils 0.5 μ wide. The fibres are examined under the polarisation microscope and by X-ray analysis, and the changes of form on swelling in H_2O and dil. acid and on contraction are investigated. Swelling of a dry fibre in H_2O leads to thickening and lengthening, the absorption of H_2O being chiefly intramolecular and partly intermicel-

lar. Swelling in acid leads to thickening and shortening with an increase of vol. This effect with rat's tail fibres is reversible. Fibres swollen in H_2O readily decrease in length on drying at 62—90° or on placing in conc. solutions of electrolytes. P. W. C.

Structure of collagen fibres and the point of attack by proteolytic enzymes. D. J. LLOYD and M. E. ROBERTSON (Nature, 1934, 133, 102—103).—Proteolytic enzymes appear to attack collagen fibres with ease at a cut end, but only with difficulty at the undamaged side. L. S. T.

Isolation of a crystalline depressor substance from the brain. C. J. WEBER, J. B. NANNINGA, and R. H. MAJOR (Proc. Soc. Exp. Biol. Med., 1933, 30, 573—515).—0.1 mg. of the substance (prep. described) caused a fall in blood-pressure of 8 mm. in a 12-kg. dog. CH. ABS.

Chemistry of adrenal medulla. S. HUSZAK (Z. physiol. Chem., 1933, 222, 229—232).—The reducing substance in adrenal medulla is ascorbic acid. It fails to produce the reduction of $AgNO_3$ shown by the cortex, owing to the presence of inhibitors, which, however, are removed by Pb acetate. J. H. B.

Chemistry of marine animals. I. Sponge, *Microciona prolifera*. W. BERGMANN and T. B. JOHNSON (Z. physiol. Chem., 1933, 222, 220—226).—From *M. prolifera* there was isolated in yield of 1.25% on dry wt. *microcionasterol*, $C_{27}H_{46}O$, m.p. 126—127°, $[\alpha]_D^{25}$ -19.8° in $CHCl_3$ (acetate, m.p. 125—126°, $[\alpha]_D^{25}$ -24.8° in $CHCl_3$; propionate, m.p. 128°; benzoate, m.p. 143°, clears at 146°, changing through violet and green, $[\alpha]_D^{25}$ -10.7° in $CHCl_3$; chloride (I), m.p. 104—105°; Cl-containing product, m.p. 60—65°). Reduction of (I) with Na in $BuCH_2OH$ gives *microcionastene*, $C_{27}H_{46}$, m.p. 61—62°. The pigment, m.p. 167°, is probably a carotene. J. H. B.

Protein of the chrysalis of the domesticated silkworm. R. INOUE, T. MIWA, and K. KITAZAWA (Bull. Sericult. Japan, 1933, 6, 1—3).— NH_2 -acid composition of the proteins of the pupæ of the domesticated and tussah silkworms are similar. H. G. R.

[Silkworm] pupa-oil emulsion. II. Physical properties. H. KANEKO and K. YAMAMOTO (Bull. Sericult. Japan, 1933, 6, 3—4).—The emulsion (0.93% oil) is very stable. H. G. R.

Hydrogen carbonate content of living muscle. N. BROOKENS (Biochem. Z., 1933, 267, 349—356).—Resting muscle in equilibrium with serum contains 30% less $NaHCO_3$ than serum, whereas in Ringer's solution at lower CO_2 pressure a smaller but similar difference exists which disappears at higher CO_2 pressure. P. W. C.

Distribution of inorganic salts in birds. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1933, 267, 460).—A correction of the authors' paper (A., 1933, 968). P. W. C.

Gastric secretion. V. Composition of gastric juice as a function of its acidity. F. HOLLANDER (J. Biol. Chem., 1934, 104, 33—42).—In the parietal secretion (I), neutral Cl^- , combined acid, inorg. and org. P, and org. solids are absent, and the

sp. gr. is that of aq. HCl of 170 m.-mol. concn. (I) is therefore essentially an isotonic solution of HCl.

A. L.

Gastric mucin. Effect on gastric acidity. D. H. ROSENBERG and L. BLOCH (J. Lab. Clin. Med., 1933, 18, 1041—1052).—Commercial gastric mucin in $\frac{1}{2}$ -oz. doses inhibited secretion of HCl for 40 min. (aver.) after ingestion. The inhibition was due largely to the "peptone ash fraction." Milk and cream had similar inhibitory powers in 3-oz. doses.

NUTR. ABS.

Gastric secretion in a horse with gastric fistula. S. V. EGOROV and V. N. TSCHEREDKOV (Russ. J. Physiol., 1933, 16, 520—529).—A fasting horse secreted 10—30 litres daily of gastric juice (I), during 2.5 days; (I) had a total acidity of 0.22, free HCl 0.14, and a digestive capacity of 3.5 (Mett). Food residues were absent after 1.5 days.

R. T.

Determination of pepsin and rennin activity in gastric juice. B. ANDERSEN (Compt. rend. Lab. Carlsberg, 1933, 19, No. 19, 1—24).—The titratable NH_2 -groups liberated by digesting infants' gastric juice (I) with 3% caseinogen for 2 hr. at 30° and p_H 2.3 were employed to define pepsin activity (II). Rennin activity (III) was measured by Holter's method (A., 1933, 94). Const. vals. for a given (I) could be obtained only by keeping the coagulation mixture at p_H 6.25—6.40. The ratio of (II) to (III) in the (I) of four infants was approx. const.

H. D.

Analysis of pyloric secretion. M. G. NIKOLAEVA (Russ. J. Physiol., 1933, 16, 199—204).—Section of the splanchnic nerves in dogs with isolated pylorus increased the secretion of gastric juice, but did not alter the % increase brought about by HCl. The effect of irrigation of the mucous membranes by solutions of various salts and drugs is recorded.

W. O. K.

Blood composition in relation to milk secretion. S. J. FOLLEY and G. L. PESKETT (Nature, 1934, 133, 142).—Attention is directed to sources of error involved in obtaining samples of blood.

L. S. T.

Dietary requirements for lactation. I. Failure of lactation on an apparently complete synthetic diet. W. NAKAHARA and F. INUKAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 22, 301—307).—A diet of polished rice powder (75 g.), fish-protein (10 g.), butter (10 g.), salt mixture (5 g.), and brewer's yeast (5 g.) was adequate for growth, pregnancy, and parturition of rats but failed to support lactation.

W. O. K.

Lactation in a barren heifer. I. JOHANSSON and M. H. KNUDSEN (J. Dairy Sci., 1933, 16, 523—528).—Milk produced by a barren heifer showed normal chemical composition.

A. G. P.

Fatty acids and glycerides of the milk-fat of Indian camels. D. R. DHINGRA (Biochem. J., 1934, 28, 73—78).—Camel milk-fat has lower Kirschner and Reichert-Meissl vals. than that of other animals. The fatty acids of the mixed saturated-unsaturated glycerides differ little from those of cow and buffalo butters, but more so from those of goat and sheep milk-fats.

H. G. R.

Determination of alcohol in milk. M. SATO and K. MURATA (J. Agric. Chem. Soc. Japan, 1932, 8, 1303—1309).—EtOH is oxidised with $\text{Cr}_2\text{O}_7^{2-}$, the excess being determined iodometrically. Cow's milk contained 1.61—4.95 mg. EtOH per 100 c.c.

CH. ABS.

Precipitation of nitrogenous substances by alkaline mercuric reagents, particularly in urine. M. E. EVERETT, F. SHEPPARD, and E. O. JOHNSON (J. Biol. Chem., 1934, 104, 1—10).—A study of Hg-nitrogenous compounds in alkaline solution indicates that the amount of pptn. is related to the structure, less pptn. occurring with alkylated or acylated N. Whilst glycine and the higher homologues are quantitatively pptd., alanine (I), sarcosine (II), and branched-chain NH_2 -acids, except leucine, are only partly pptd. Cryst. Hg compounds sol. in H_2O of (I), aminoisobutyric, aminomethylbutyric, aspartic, and hippuric acids, isoleucine, methionine, hydroxyproline, proline, and (II), and also Hg compounds of adip-, hexo-, diethylform-, dimethylacet-, hept-, myrist-, phenylacet-, stear-, and valer-amide (no descriptions given) have been prepared. Using the prescribed method of N determination in Hg filtrates from biological fluids, 1.6, 20, and 30% of N remain in the Hg filtrates of urine (III), muscle extract, and liver extract, respectively, hippuric acid being the chief N-constituent of (III).

A. L.

Sugar of normal urine. II. Behaviour of carbohydrates in bromine water and the ketose of normal urine. M. R. EVERETT, B. G. EDWARDS, and F. SHEPPARD (J. Biol. Chem., 1934, 104, 11—28).—The progressive effect of Br oxidation (I) of sugars on the Sumner/Folin-Wu ratio of glucose equivs. assists in identification, particularly in the case of NH_2 -sugars, methylpentoses, and higher oligosaccharides, and indicates the existence of new reducing derivatives of l-fucose, inulin, dextrin oligosaccharides, and d-glucosamine. (I) also indicates that the chief reducing material, designated uroketose (II), of normal urine is a ketose, keturonic acid, or amino-aldose, although a small amount of rapidly hydrolysable sugar more easily oxidised is also present. Some reactions of (II) are described. The major portion of the free sugar of tungstic acid blood-filtrates is oxidised like aldoses, but a second substance is also present.

A. L.

Uroflavin, maltoflavin, and redox potentials of lyochromes. K. G. STERN (Nature, 1934, 133, 178—179).—Uroflavin (I) from normal human urine and maltoflavin (II) from malted barley both show a strong green fluorescence (III) of their yellowish-red solutions; visible blue-violet light and ultra-violet radiation are responsible for (III). Strong irradiation in alkaline solution gives CHCl_3 -sol. "lumiflavins." Colour and (III) are lost on reduction and regained on reoxidation. (I) and (II) have sharp absorption bands at 281 and 255 m μ , respectively, but there is no sp. absorption at longer wave-lengths. The potentiometric measurements recorded show that hepatoflavin, (I), and (II) represent stable oxidation-reduction systems.

L. S. T.

Isolation of phæophorbide α from silkworm faeces. H. FISCHER and A. HENDSCHEL (Z. physiol.

Chem., 1933, 222, 250—260).—In the COMe_2 extract of the faeces phaeophorbide *a* (I) was identified. Cold HI reduction gave isophaeoporphyrin α_6 , hot, α_5 (II). The AcOH extract gave phaeopurpurins 7 (III) and 18. HI reduction of the phaeophorbide fraction afforded mainly (II). (III) arises by secondary oxidation in the prep. of the Na salt. Phyllobombicin is a mol. compound of (I) and (III). The silkworm thus eliminates phytol and Mg from chlorophyll with production of (I). J. H. B.

Anæmia. II. Goat's milk anæmia. C. BOMSKOV and M. AUFFARTH (Z. ges. exp. Med., 1933, 89, 804—808; Chem. Zentr., 1933, ii, 1889).—Anæmia of young rats fed with goat's milk is not due to lack of vitamin-A or -C or to a toxic effect of the volatile unsaturated fatty acids. A. A. E.

Metallised and irradiated milk in the treatment of nutritional anæmia. J. L. MCGHEE and B. FERGUSON (J. Elisha Mitchell Sci. Soc., 1933, 49, 18—19).—Finely divided Cu and Fe suspended in milk fed to anæmic rats causes a rapid rise in hæmoglobin and complete recovery without ill effects due to acid hydrolysis of Cu and Fe salts. CH. ABS.

"Lipoid" extract of spleen that prevents Bartonella muris anæmia in splenectomised albino rats. Protective action of copper and iron against B. muris anæmia. D. PERLA and J. MARMORSTON-GOTTESMAN (Proc. Soc. Exp. Biol. Med., 1932, 29, 987—989, 989—991).—An extract of ox spleen probably contains a sp. hormone. A small amount of Cu was insufficient in absence of splenic hormone (I) but an excess compensated for the deficiency of (I). CH. ABS.

Pigeon as a hæmatopoietic test animal. W. A. PEABODY and R. C. NEALE (J. Amer. Pharm. Assoc., 1933, 22, 1231—1237).—Although the pigeon responds to the active principle of liver-extract, the effects are not parallel with the clinical utility. W. S.

Acute extrarenal azotæmia. M. RACHMILEWITZ (Lancet, 1934, 125, 78—81).—Acute loss of fluids after vomiting and diarrhoea may result in a rise in nitrogenous constituents of the blood. Probably a disturbance in the mineral balance of the body occurs with a consequent disturbance of general metabolism. This is revealed as an abnormal protein breakdown. The administration of chlorides and of glucose lowers the azotæmia. L. S. T.

Vitamin-C and cancer. M. COPISAROW (Chem. and Ind., 1934, 135).—The suggested application of ascorbic acid to cancer (A., 1933, 1252) is criticised. F. O. H.

Growth of transplanted tumours in albino rats maintained on a diet with protein hydrolysates as substitute for protein. U. SUZUKI, W. NAKAHARA, N. HASHIMOTO, and R. IKEDA (Sci. Pap. Inst. Phys. Chem. Res., Tokyo, 1933, 23, 1—8).—The growth of tumours transplanted into albino rats is the same when practically all the protein in the diet is replaced by acid or alkaline hydrolysates of protein. W. O. K.

Influence of alcohol on the growth of transplanted tumours in rats. U. SUZUKI, W. NAKA-

HARA, N. HASHIMOTO, and R. IKEDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, 23, 9—15).—The growth rates (I) of sarcomata transplanted into albino rats as well as that of the animals themselves are low on a carbohydrate-free, fat-rich diet, are slightly improved when fat is partly replaced by MeOH (5%), and much improved when it is replaced by EtOH (10%). The partial replacement of carbohydrate in a balanced diet by EtOH has little effect, but replacement by MeOH decreases (I), both of animals and tumours. W. O. K.

Tumour arginase. IV. Significance of accompanying substances for the activity of arginase in normal and malignant tissue. G. KLEIN and W. ZIESE (Z. physiol. Chem., 1933, 222, 187—202; cf. A., 1933, 315).—Purified arginase (I) is inhibited strongly at every p_H by thiol compounds such as H_2S , cysteine, and glutathione, even in absence of PO_4''' . Crude (I) is activated by the same thiol compounds, especially in alkaline media. The activation occurs also after treatment with O_2 , and is produced by Fe'' and N_2H_4 . It consists in a non-sp. reduction of "carriers." A combination of heavy metal and -SH is possible, but not essential. Purified (I) is not inactivated by O_2 or H_2O_2 in alkaline solution. J. H. B.

Anthelmintic power of some chloro-derivatives of butane in cylicostomosis of horses. MARCENAC (Compt. rend., 1934, 198, 510—512).— β -Dichlorobutane and β -chlorobutylene are very effective. R. S. C.

Intermediate metabolism in puncture diabetes. I. Puncture technique. II. Sugar and blood - amylase. III. Blood - lipins. G. D. OBRAZTSOV, E. T. MINKER-BOGDANOVA, and M. N. KALLINIKOVA (Russ. J. Physiol., 1931, 14, 158—162, 219—230, 231—240).—I. A method for the Claude Bernard puncture (I) is described.

II. The extent of the hyperglycæmia produced by (I) varies in different experiments; liver-glycogen does not entirely disappear. The rise in blood-sugar is accompanied by a reduction in blood-amylase.

III. Neutral fat and cholesterol are but little affected, whilst there is a sudden initial increase in cholesteryl esters, fatty acids, and phosphatides, followed by a decrease. P. G. M.

Bryonia cretica. Action and value in diabetes. M. A. F. SHERIF (Quart. J. Pharm., 1933, 6, 634—642).—The EtOH-sol. material of the powdered root (I) depresses the activity of both cardiac and plain muscle. The min. lethal dose is 0.1 g. [equiv. to 2.5 g. of (I)] per kg. subcutaneously in rabbits and 0.075 g. per kg. intravenously in dogs. The drug reduces diuresis, but has no effect on blood-sugar or glycosuria in the diabetic. F. O. H.

Insulin-resistance in diabetes mellitus. C. M. MACBRYDE (Arch. Int. Med., 1933, 52, 932—944).—Insulin-resistance (I) and -sensitivity (II) are often associated with characteristic responses to alterations in the diet. Thus increase of fat produces a diminution in glucose tolerance with (I), but not with (II), whilst increase of carbohydrate produces immediate glycosuria with (II), but does not affect the sugar excretion

with (I). Whilst (I) is generally due to hyperactivity of the adrenal-sympathetic system, other disorders (*e.g.*, pancreatic, endocrine, hepatic, and infective diseases) are probable factors. F. O. H.

Modified glucose tolerance test. T. L. ALTHAUSEN and H. T. RICKETTS (*Arch. Int. Med.*, 1933, 52, 984—990).—A discussion regarding the merits of the test (see A., 1930, 1470—1933, 971). F. O. H.

Physiological disturbances during experimental diphtheritic intoxication. I. Blood-sugar, -lactic acid, and -non-protein- and -amino-nitrogen. II. Hepatic glycogenesis and glycogen concentration of cardiac and skeletal muscle. H. YANNET and D. C. DARROW. III. Respiratory quotients and metabolic rate. H. YANNET and W. GOLDFARB (*J. Clin. Invest.*, 1933, 12, 767—778, 779—786, 787—791).—I. Rabbits exhibited hypoglycaemia and rise in blood-NH₂- and -non-protein-N.

II. During intoxication liver-glycogen (I) is diminished; muscle- and heart-(I) are unchanged. Hepatic glycogenesis following injection of glucose is diminished.

III. There is no significant change in carbohydrate metabolism or metabolic rate. CH. ABS.

Exophthalmos in thyroidectomised guinea-pigs by thyrotropic substance of the anterior pituitary, and the mechanism involved. D. MARINE and S. H. ROSEN (*Proc. Soc. Exp. Biol. Med.*, 1933, 30, 901—903). CH. ABS.

Is anterior pituitary hormone demonstrable in urine of Graves' disease; in urine of guinea-pigs injected with anterior pituitary extract? M. G. SMITH and E. MOORE (*Proc. Soc. Exp. Biol. Med.*, 1933, 30, 735—739).—Failure to demonstrate the presence of the thyroid-stimulating hormone in urine of Graves' disease is not inconsistent with a possible increase in pituitary function. CH. ABS.

Hypoproteinaemia probably due to deficient formation of plasma-proteins. W. K. MYERS and F. H. L. TAYLOR (*J. Amer. Med. Assoc.*, 1933, 101, 198—200).—Hypoproteinaemia in a case of chronic oedema, low plasma-protein, and reduced colloid osmotic pressure was not influenced by protein feeding. CH. ABS.

Lathyrism in the rat. B. J. GEIGER, H. STEENBOCK, and H. T. PARSONS (*J. Nutrition*, 1933, 6, 427—442).—Lathyrism (produced by eating lathyrus peas) causes red coloration, and abnormal growth and calcification of bones, and is not counteracted by feeding cod-liver oil or dried yeast. Boiling peas for 2½ hr. did not destroy their toxicity, but the toxic factor was extractable by H₂O at b.p. A. G. P.

Cystine content of finger-nails in pellagra. S. A. PAYNE and W. A. PERLZWEIG (*J. Clin. Invest.*, 1933, 12, 899—908).—Low vals. are observed when dermatitis is present. CH. ABS.

Experimental rickets. V. In chicks. F. ROGOZIŃSKI and Z. GŁÓWCZYŃSKI (*Bull. Acad. Polonaise*, 1932, B, 369—384; cf. A., 1932, 1159).—Chicks fed on a diet of corn, butter, NaCl, and Fe^{III} citrate develop leg weakness and die within 30—42

days. This does not occur when the chicks are irradiated by ultra-violet light or when cod-liver oil or CaCO₃ (1%) is added to the diet. F. O. H.

Disappearance of trypan-blue from the blood in experimental scurvy and malnutrition. P. N. VESELKIN (*Russ. J. Physiol.*, 1931, 14, 241—247).—Trypan-blue disappears more rapidly from the blood of scorbutic than of normal guinea-pigs; this is not characteristic of C-avitaminosis, although it always accompanies malnutrition. P. G. M.

Ultra-violet absorption spectra of syphilitic sera. M. PAIC (*Compt. rend.*, 1934, 198, 286—288).—Normal sera do not differ from those of syphilitic patients in ultra-violet absorption spectra.

R. S. C.

Influence of vitamin-A and -D on the humoral reactions in human tuberculosis. J. DONATO, R. JACQUOT, and H. PENAU (*Compt. rend.*, 1934, 198, 397—399).—Intramuscular injection of an oil solution of a mixture of carotene and vitamin-D into tubercular subjects causes an increase in Ca (from 80—90 mg. to approx. 115 mg.), cholesterol (1.44—1.80 g. to 2.5 g. per litre), and P in the blood, a return to normal serum-flocculation (Vernes), and an increase in the proportion of haemoglobin and in body-wt.

J. W. B.

Reaction of the organism to intradermal administration of tuberculin. Changes in the blood-serum. C. LUCCHINI, M. BELLI, and C. GERBI (*Arch. Ist. Biochim. Ital.*, 1933, 5, 485—536).—Intradermal administration of tuberculin to patients suffering from tuberculosis and other diseases produced an allergic reaction and a parallel disturbance in the sedimentation velocity of the erythrocytes, but not in the flocculation reaction of Vernes. In nearly all the cases the total protein content of the serum diminished, whilst the globulin level increased so that the albumin/globulin ratio decreased. A diminution in the serum oncotic pressure also occurred.

F. O. H.

Diazo-substance in typhoid urine. M. MIYAZAKI (*J. Biochem. Japan*, 1933, 18, 379—385).—When antioxyproteic acid (A., 1906, i, 122) from typhoid urine (29 g. of Ba salt were obtained from 80 litres) is injected into rabbits, the greater part does not appear in the excreta, whilst the blood gives a positive Ehrlich diazo-reaction (I) for only a short period. Human faeces give a positive (I) whether the (I) of the urine is positive (due to typhoid) or negative (with healthy persons). F. O. H.

Synthesis of protoplasm. A. L. HERRERA (*Bull. Lab. Plasmogenie*, 1933, 1, 41—42).—Cell-formation is discussed. H. G. R.

Ciliary movement. II. Intracellular oxidation-reduction potential limiting ciliary movement. S. NOMURA (*Protoplasma*, 1933, 20, 85—89).—Ciliary movement (I) probably derives its energy from glycolysis (II). When intracellular redox potential falls below a certain crit. point (*e.g.*, as in anaerobiosis) (II) is suppressed and (I) ceases. A. G. P.

Kinetics of the oxidation processes in fertilised eggs. I. Velocity of oxidation during embryonic development of *Trutta iridea* (Rainbow

trout). W. SCHLENK, jun. (Biochem. Z., 1933, 267, 424—437).—The O_2 utilisation and CO_2 production of unfertilised (I) and fertilised eggs (II) of the rainbow trout are followed continuously from fertilisation to the end of embryonic development (67 days). The respiration of (II) was always much > that of (I), but was different for eggs from different sources. The increase in velocity of oxidation appeared to be logarithmic from the 15th to the 43rd day. P. W. C.

Gaseous metabolism of "natural" and "artificial" nerve impulses. R. W. GERARD and H. K. HARTLINE (Naturwiss., 1933, 21, 882—883).—An increase of 40—50% in the O_2 uptake of the optic nerve of the horseshoe crab *Limulus polyphemus* is observed both when stimulation is electrical and when the eye is illuminated. R. K. C.

Oxygen consumption of stimulated nerve. S. HARASHIMA (J. Cell. Comp. Physiol., 1933, 3, 418—424).—With a const. current applied, the excess O_2 consumption of the nerve is practically the same whether the stimulus is applied to the nerve "inside" or "outside" of the microrespirometer in which the O_2 is determined. A. G. P.

Anoxic recovery of asphyxiated nerve. R. A. COHEN and R. W. GERARD (J. Cell. Comp. Physiol., 1933, 3, 425—436).—Restoration of asphyxiated nerve can be induced by oxidising substances (other than O_2) which yield sufficient energy on reduction. A. G. P.

Gaseous metabolism during muscular work. III. Changes of oxygen saturation of venous blood during the restitution period. J. L. KAHN and M. K. MILOVIDOVA (Russ. J. Physiol., 1933, 16, 155—158).—During the period of recovery from intense muscular work the O_2 capacity of the venous blood gradually falls to the resting level, but the degree of O_2 saturation at first rises, reaches a max. in 3 min., and finally falls, the max. corresponding with the min. val. of the O_2 uptake coeff. W. O. K.

Effect of carbon dioxide and asphyxia on the elimination of phosphoric acid from muscle. V. S. ILJIN and V. V. TICHALSKAJA (Russ. J. Physiol., 1931, 14, 284—288).— CO_2 increases the rate of elimination of PO_4''' from resting frog's gastrocnemius after exercise. Asphyxia by H_2 produces a much smaller increase. P. G. M.

Elimination of phosphoric acid from muscle at rest and after work. V. S. ILJIN and V. V. TICHALSKAJA (Russ. J. Physiol., 1931, 14, 289—295).—The rate of elimination of PO_4''' is increased both by direct electrical stimulation of the muscle and by stimulation by way of the nerve. Resting muscle is permeable to PO_4''' . P. G. M.

Lactic acid in sweat and protein in urine during muscular exercise. A. F. KORIAKINA and A. N. KRESTOVNIKOV (Russ. J. Physiol., 1931, 14, 257—262).—No definite quant. relationship exists between the lactic acid in sweat and the protein in urine, although large amounts of lactic acid are accompanied by small amounts of protein and *vice versa*. P. G. M.

Effect of controlled muscular exercise on the lactic acid and CO_2 capacity of the blood. G. E.

VLADIMIROV, G. A. DMITRIEV, and A. P. URINSON (Russ. J. Physiol., 1934, 16, 139—154).—In man, the blood-lactic acid (I) during rest is not influenced by previous training (II), but after dynamical work (III) the (I) and CO_2 capacity (IV) depend on (II). Increase of duration of (III) did not increase the change of (I) nor of (IV). Statical work did not change (II) or (IV). The O_2 debt cannot be fully attributed to accumulation of (I). During the recovery after (III) hypolactacidemia was often observed. W. O. K.

Influence of glutathione and iodoacetic acid on the production of lactic acid from hexose diphosphate by animal tissues. S. YAMAZOYE (J. Biochem. Japan, 1933, 18, 445—456).—In the decomp. of hexose diphosphate to lactic acid by the enzyme system phosphatase-glycolase-glyoxalase (I) in autolysed liver, glutathione (II) and CH_2I-CO_2H (III) have an accelerating and an inhibitory effect, respectively, due to their action on (I); with (III) the action is probably not on (I) itself, but on the co-enzyme, reduced (II). F. O. H.

Influence of the preceding diet on the rate of glucose absorption and glycogen synthesis. E. M. MACKAY and H. C. BERGMAN (J. Nutrition, 1933, 6, 515—521).—In albino rats, the preceding diet did not appreciably affect, after 24—48 hr. starvation, the rate of absorption of glucose administered by the intestine, or the rate of deposition of glycogen in the liver and skeletal muscle. A. G. P.

Absorption of glucose from chronic jejunal loops. I. S. RAVDIN, C. G. JOHNSTON, and P. J. MORRISON (Amer. J. Physiol., 1933, 105, Proc. 82—83).—The rate of absorption of glucose from 1—65% solutions varied directly as the concn. with const. vol. or as the vol. with const. concn. NUTR. ABS.

Comparison of concentration of glucose in the stomach and intestine after intragastric administration. I. S. RAVDIN, C. G. JOHNSTON, and P. J. MORRISON (Proc. Soc. Exp. Biol. Med., 1933, 30, 955—958). CH. ABS.

Possibility of the conversion of fatty acids into glucose in the animal body. H. H. MITCHELL (J. Nutrition, 1933, 6, 473—491).—A review. A. G. P.

Possibility of gluconeogenesis from fat. II. Effect of high-fat diets on the respiratory metabolism and ketosis in man. E. E. HAWLEY, C. W. JOHNSON, and J. R. MURLIN (J. Nutrition, 1933, 6, 523—557).—Following high-fat diets containing varying proportions of butter-fat the R.Q. in a no. of subjects was < the theoretical level for fat oxidation. The occurrence of low vals. depended more on the tolerance of the subjects than on the amount of fat taken or on the ratio fatty acid: glucose in the diet. The level of the R.Q. was not closely related to the demonstrable ketosis or ketonuria. Depression of the R.Q. is not attributable solely to the production of glycogen from protein or from the glycerol of fats. A. G. P.

Fat metabolism. G. QUAGLIARIELLO (Mem. R. Accad. d'Italia, 1933, 4, 17—32).—Adipose tissue

(I) contains a lipase comparable in activity to the stomach lipase, and also a dehydrogenase, which can act on the free fatty acids, but apparently not on their esters. Both enzymes are active in the isolated (I). Starvation in dogs is accompanied by a gradual rise in the degree of unsaturation of both the (I) and blood-fats; this falls again on feeding. The disappearance of deposited fat is evidently preceded by enzymic lipolysis and sufficient desaturation of the fatty acids to permit diffusion through the cell wall; deposition of fat in normal feeding probably occurs through the same mechanism. R. N. C.

Effect of fat on protein metabolism. G. SANT (Pharm. Weekblad, 1934, 71, 97—98).—Administration of fat produces changes in α of blood-serum after hydrolysis. S. C.

Activation of proteolysis in regenerating tissue. V. N. ORECHOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1933, 27—33).—Following amputation of the axolotl's tail, the regenerating tissue (I) has a much higher content of reduced glutathione (II) than has the normal tissue (averaging 0.0196%), attaining a val. of 0.046% in 5 days, remaining const. for the next 5—6 days (average 0.0456%), and returning to normal vals. after a total period of 15—20 days. The normal tissue in close proximity to (I) also experiences a slight increase in the content of (II). These variations are related to disturbances in normal respiration and to increased proteolytic activity. F. O. H.

Proliferative response of neurones to thiol and sulphoxide in the regenerating ganglion of *Nereis pelagica*. F. S. HAMMETT (Protoplasma, 1933, 19, 117—124).—The neurone increment of regeneration is accelerated by $\cdot\text{SH}$ and retarded by $\cdot\text{SO}$. A. G. P.

Proliferative growth-regulating property of the naturally occurring chemical equilibrium composed of thiol and its partly oxidised derivatives. D. W. HAMMETT and F. S. HAMMETT (Protoplasma, 1933, 19, 161—169).—The retarding effect of $\cdot\text{SO}$ and the accelerating action of $\cdot\text{SH}$ on the proliferation of the regenerating right chela of the hermit crab are demonstrated in the same growth process of individual specimens by alternate exposure to appropriate substances. A. G. P.

Glutathione concentration and hereditary body size. II. Non-nursed young of rabbits differing in genetic constitution for adult size. P. W. GREGORY and H. GOSS (J. Exp. Zool., 1933, 66, 155—173).—Glutathione content is correlated with adult body-size. CH. ABS.

Distribution of the urinary representatives of nitrogen metabolism and its physiological significance. V. Exogenous protein metabolism. E. F. TERROINE and G. BOY (Bull. Soc. Chim. biol., 1933, 15, 1163—1220; cf. A., 1933, 529).—A study of N excretion of rats, pigs, and dogs fed on normal and protein-free diets indicates that the terms endogenous and exogenous N-metabolism are advantageously replaced by "sp. min. N excretion" (I) and "contingent N excretion" (II), respectively. The excretory products (III) may be classified as "differ-

ential" [creatinine and creatine related to (I) and (II), respectively] and "common" [urea, NH_3 , peptides, NH_2 -acids, S compounds, etc.]. The distribution of (III) corresponding with (I) differs with different animals, whilst that of the (III) arising from ingested protein is approx. the same; hence (I) fails as an independent criterion of protein metabolism. The protein and purine oxidation coeffs. (calc. from the excess N excretion on changing from a carbohydrate to a protein diet) during (I) are $>$ those during (II). Such a change in diet also produces an increase in the abs. $\text{NH}_3\text{-N}$, but a fall in the urinary $\text{NH}_3\text{-N}/(\text{NH}_3 + \text{urea} + \text{NH}_2)\text{-N}$ ratio, which is not necessarily accompanied by a change in p_{H} of the urine. No transformation of creatine to creatinine due to protein metabolism is evident. F. O. H.

Constitution of muscle-proteins. I. Total and protein starvation. A. ROCHE (Bull. Soc. Chim. biol., 1933, 15, 1290—1307).—Deprivation of protein (I) in rats produces death in 1—2.5 months, the loss in body-wt. being approx. 48%. With complete starvation the loss at death amounts to 30%. The losses in total N are respectively 23—55% and approx. 15% of the body-N. With (I) starvation, the excreted N originates not only from complete disintegration of body-(I), but also from polypeptide side-chains, so that the (I)-nature of the protoplasm is preserved. F. O. H.

Influence of temperature on protein metabolism. II. Nitrogenous extractives from toad's liver during winter. H. MAKINO (J. Biochem. Japan, 1933, 18, 387—393).—Aq. extraction of the toad's liver during winter yields *l*-leucine (5.0%), *d*-alanine (0.8%), *d*-valine, *l*-proline, *l*-serine, *l*-phenyl-alanine, *d*-glutamic acid, guanine, adenine, xanthine, and hypoxanthine. The contents of these substances in the toad's liver during winter and summer are compared (cf. A., 1932, 299). F. O. H.

Influence of asparagine and betaine on the nitrogen metabolism of pasture cows. P. BRIGL and O. BENEDICT (Bied. Zentr. [Tierernähr.], 1933, B, 5, 532—553).—Replacement of the N of a clover-hay ration for sheep by betaine (I) or asparagine (supplemented with starch) in proportions equiv. to $> 10\%$ of the total N resulted in the breakdown of body-proteins. The amides were excreted as urea. A. G. P.

Creatinephosphoric acid. Influence of denervation on the creatinephosphoric acid content of muscle. A. PALLADIN and R. SIGALOVA (Bull. Soc. Chim. biol., 1933, 15, 1263—1271).—Section of the sciatic nerve in rabbits or guinea-pigs produces within 24 hr. an increase in the creatinephosphoric acid content of the gastrocnemius muscle, whilst the H_2O , total N, and creatine remain unchanged. F. O. H.

Creatinuria in adolescent males. A. B. LIGHT and C. R. WARREN (J. Biol. Chem., 1934, 104, 121—128).—The average creatine excretion (I) of boys aged 14—19 decreases with increasing age. A close relationship exists between (I) and muscular activity; an increase in (I) occurs after exercise following a period of confinement. H. D.

Metabolism of sulphur. XXI. Metabolism of *l*-cystine and *dl*-methionine in the rabbit. R. W. VIRTUE and H. B. LEWIS (J. Biol. Chem., 1934, 104, 59—67).—*dl*-Methionine (I) administered orally and subcutaneously is metabolised, the S occurring in the urine as $\text{SO}_4^{''}$. The urine also contains a substance giving the S-S group and the cyanide-nitroprusside reactions, but not the Sullivan test for cystine. α -Benzoylmethionine is not attacked by the organism, and it is suggested that the course of the reaction with (I) is a demethylation followed by the formation of homocystine. A. L.

Oxidation of stereoisomerides of cystine in the animal body. V. DU VIGNEAUD, H. A. CRAFT, and H. S. LORING (J. Biol. Chem., 1934, 104, 81—89).—Rabbits were fed on *l*- (I), *d*- (II), meso- (III), and *dl*-cystine and the S fractions in their urine determined. After feeding (I), about 80% of the extra S excreted was $\text{SO}_4^{''}$, after (II), 45%. (III) and (IV) produced intermediate results. H. D.

Deamination of amino-acids in the animal organism. Y. KOTAKE, sen., Y. KOTAKE, jun., and I. TANIGUCHI (J. Biochem. Japan, 1933, 18, 395—415).—Hydroxyphenylpyruvic acid (I) in urine is determined by acidification, extraction with Et_2O , and iodometric titration of the residue on evaporation. Oral administration of *dl*- and, to a smaller extent, of *l*-tyrosine to rabbits and dogs produces an excretion of (I), whilst ingestion of (I) yields hydroxyphenyl-lactic acid in the urine. The mechanism is discussed. F. O. H.

Food value of germinating grain. V. V. FAMIANI (Atti R. Accad. Lincei, 1933, [vi], 18, 68—73; cf. A., 1933, 183, 309, 743).—Experiments with rats indicate that this is > that of grain in the resting state. T. H. P.

Digestion and assimilation of soya-bean preparations in the human body. E. S. LONDON, N. I. SHOKHOR, A. G. GAGINA, A. I. KOLOTILOVA, R. M. KUTOX, E. A. MARKARYAN, and L. V. POPEL (Schr. zentr. biochem. Forschungsinst. Nahr. Genussm., U.S.S.R., 1932, 1, 211—234).—The food val. of soya-bean protein is 88% of that of meat and fish; the carbohydrate food val. is 100%. CH. ABS.

Acid-base coefficients and the food-value of meat. I. A. SMORODINCEV (Bull. Soc. Chim. biol., 1932, 15, 1256—1262).—Various parts of meat were extracted with 0.1N-AcOH and with N-NaOAc, and the extracts were titrated with alkali. The two titres gave the acid/base ratio (I), the NaOAc extraction being accompanied by the liberation of free AcOH due to the action of tissue-acids. The val. of (I) for muscle was five times that of connective tissue; hence (I) forms a criterion of the food-val. of meat. F. O. H.

Effect of cranberries on urinary acidity and blood alkali reserve. C. R. FELLERS, B. C. REDMON, and E. M. PARROTT (J. Nutrition, 1933, 6, 455—463).—When fed to normal young men in amounts of 100—300 g. daily cranberries (I) caused an increase in the titratable acidity, total org. acids, hippuric acid, $[\text{H}^+]$, and NH_3 of the urine, and a slight decline in uric acid and urea. The hippuric

acid recovered was approx. proportional to the amount of (I) eaten, and was nearly all voided within the following 24 hr. It is probably derived from the quinic acid (or a glucoside yielding quinic acid) in (I). Large amounts of (I) reduce the CO_2 -combining capacity of the blood. A. G. P.

Acid-base balance of newborn infants. IV. Effect of ingestion of alkali. V. W. LIPPARD and E. MARPLES (Amer. J. Dis. Children, 1933, 46, 495—511).—Ingestion of small quantities of NaHCO_3 or Na citrate decreases serum-Cl, -protein, -acid, and -fixed base. The CO_2 tension diminishes proportionally to the amount of alkali ingested. Older infants require larger amounts to affect the balance. CH. ABS.

Sodium chloride metabolism. I. Influence of injection of bacteria and colloid substances. II. Effect of changing the function of the reticulo-endothelial system by blocking. III. Relationship between the function of the reticulo-endothelial system and retention of sodium chloride in the tissues. H. SAITO (Japan. J. Gastroenterol., 1933, 5, No. 2, 57—66, 67—71, 72—77).—I. Intravenous injection of substances which stimulate the reticulo-endothelial system stimulates NaCl metabolism.

II. Transfer of NaCl from tissues by way of the blood into the urine is no longer observed.

III. Excretion of injected NaCl is diminished by blocking. CH. ABS.

Distribution of water in living tissues. C. I. COX and C. S. HICKS (Austral. J. Exp. Biol., 1933, 11, 269—287).—Rabbits deprived of food and H_2O for 16 hr., and in some of which a diuresis had been induced, were injected with hypertonic saline for 90 min. under paraldehyde anaesthesia. The total urinary output, plasma-alkali reserve, blood dilution, blood-Cl⁷, tissue- H_2O , urinary Cl, and osmotic pressure of the serum-colloids were determined. A direct proportionality between the alkali reserve and the reserve H_2O of the body exists; dehydration of the muscle tissue appears to account for the H_2O loss. H. D.

Effect of body-weight and wool production by merino sheep of adding sulphur to the diet. A. W. PEIRCE (J. Coun. Sci. Ind. Res. Australia, 1933, 6, 294—298).—Addition of 2 g. of S daily to the ration increased neither body-wt. production nor wool yields. A. G. P.

Bromine metabolism. II. Relation between blood-bromine and internal secretions. T. KURANAMI (J. Biochem. Japan, 1933, 18, 417—443; cf. A., 1932, 876).—During pregnancy the blood-Br (I) rises, attains a max. at parturition, and returns to normal after 3 weeks. The (I) of the blood from the umbilical vessels of new-born infants is < that of their circulating blood, but > the normal adult level. (I) is increased during diabetes mellitus and thyroid diseases. The (I) of dogs (normally 0.00055—0.00069%) is increased by subcutaneous injection of thyroxine, adrenaline, or anterior pituitary extract and decreased by that of insulin, posterior pituitary extract, or œstrin; ovariectomy or orchidectomy, however, both produce a rise in (I). Vagus stimulants (pilo-

carpine) decrease, whilst vagus depressants and sympathetic stimulants (atropine and adrenaline) increase, (I). Injection of physiological saline produces a transient decrease in (I), the main controlling factor of which appears to be the anterior pituitary gland.

F. O. H.

Influence of unbalanced mineral constituents in the diet on the growth and composition of rats. (a) Variations in potassium and calcium. (b) Influence of vitamin-A deprivation. L. EME-RIQUE (Bull. Soc. Chim. biol., 1933, 15, 1221—1234, 1235—1238).—(a) Variations in the proportions of Ca or K in the otherwise normal diets of rats do not produce very marked changes in the mineral composition of the body. With high doses of K, the Ca : P and Ca : K ratios decrease, whilst that of Ca : Mg is unchanged, the abs. content of K being increased. With high doses of Ca, the Ca : Mg and Ca : K ratios are increased, whilst that of Ca : P is unchanged, the abs. content of Ca being diminished. The anomaly in the abs. contents of K and Ca is probably due to the different effects on growth.

(b) The subnormal growth of rats on a vitamin-A-free diet (I) is emphasised by a high Ca : K ratio of (I). With either high Ca : K or K : Ca ratios of (I), the abs. contents of the body in P and Ca are increased, that of K is slightly diminished, whilst that of Mg is approx. const. Increases also occur in the P : K, Ca : K, and Ca : Mg ratios of the body.

F. O. H.

Inorganic salts in nutrition. VII. Change in composition of bone of rats on a diet poor in inorganic constituents. R. O. BROOKE, A. H. SMITH, and P. K. SMITH (J. Biol. Chem., 1934, 104, 141—148).—On a low-salt diet, there is a decrease in Ca, P, and CO_3 , and the ratio $\text{Ca}_3(\text{PO}_4)_2$: CaCO_3 is increased. The negative Ca balance is at expense of the CaCO_3 .

H. G. R.

Significance of mineral metabolism [in animals] especially by alkaline earths and phosphoric acid. O. WELLMANN (Biol. generalis [Adametz Festsch.], 387—396; Bied. Zentr., 1933, A, 4, 82).—The Ca and P requirements of various animals and the effects and correction of deficiencies are discussed.

A. G. P.

Calcium and phosphorus in the development of the turkey embryo. W. M. INSKO, jun., and M. LYONS (J. Nutrition, 1933, 6, 507—513).—The increase in wet and dry wts. and ash content of the developing embryo is small until the 12th day, and that of the Ca and P contents until the 17th day. The Ca : P ratio is < 1 until the 19th day and > 1 thereafter. The Ca content of the embryo serves as an index of growth provided the yolk material drawn into the body cavity is removed prior to analysis.

A. G. P.

Metabolism of calcium and phosphorus. I. Influence of carotene and gallosterol. I. ISHIDA (J. Biochem. Japan, 1933, 18, 479—493).—Subcutaneous administration of β -carotene (I) or of gallosterol (II) (vitamin-A-choleic acid) increases the Ca or P balance (III) (i.e., ingested minus excreted Ca or P). On discontinuing the administration of (I) or (II), the P (III) returns almost immediately to its

normal level, whilst the Ca (III) persists for several days. The effect with (II) is $>$ that with bile acids.

F. O. H.

Influence of acid and phosphate on metastatic calcification. D. J. STEPHENS and D. P. BARR (Proc. Soc. Exp. Biol. Med., 1933, 30, 920—924).—Rats fed for 15 days on acid, or alternating acid and alkaline, diets with excess of Ca and P developed calcification (I) in the soft tissues. (I) did not occur in absence of any one of these three factors.

CH. ABS.

Resorption of calcium sulphate in the digestive tract. A. I. VIRTANEN and J. TIKKA (Suomen Kem., 1934, 7, 75B).—100—250 g. per day of CaSO_4 were fed to cows without any harmful effect. The Ca^{++} appeared almost quantitatively in the faeces, whilst the SO_4^{--} appeared mainly in the urine, indicating a resorption process.

P. G. M.

Effect of iodine on the growth and metabolism of thyroid tissue *in vitro*. R. McCARRISON and G. SANKARAN (Indian J. Med. Res., 1933, 21, 183—186).— 12.5×10^{-6} g. I per 100 c.c. of medium had no effect; 25 stimulated tissue growth (I) and rate of metabolism (II), 50 increased (II) without affecting (I), whilst 100 increased (II) but halved the life of the tissue *in vitro*.

CH. ABS.

Determination of the functional activity of the thyroid by means of urine and serum. III. Influence of autonomic nerve on thyroid function. M. KOH (J. Chosen Med. Assoc., 1933, 23, 853—862).

CH. ABS.

Relation between toxicity, resistance, and time of survival. L. REINER (Proc. Soc. Exp. Biol. Med., 1933, 30, 574—576).—An equation is derived showing that asymmetry is to be expected whenever the time which registers the event is a non-linear function of the parameter on which the occurrence of the event depends, even although the variation follows the probability rule.

A. L.

Behaviour of hæmatoporphyrin in the animal body. R. HUTSCHENREUTER (Z. physiol. Chem., 1933, 222, 161—176).—Rats on meatless diet (I) receiving intramuscularly regular moderate doses of hæmatoporphyrin-Nencki (II) increased in wt.; large doses caused a decrease, but oral administration always produced an increase. The orally given (II) in contrast with intramuscular (II) produced no photodynamic action. Hæmateric acid (III) was detected in the faeces of rats on (I). (II) was always detected in the faeces after dosage, but its transformation into (III) was not established. Coproporphyrin was excreted in the urine by rats on (I). After intramuscular, but not oral, doses of (II), (II) was found in the urine and blood.

J. H. B.

Toxicity of urine- and serum-proteic acids. Y. GAMO (J. Biochem. Japan, 1933, 18, 457—478).—Following bilateral nephrectomy in rabbits, the p_{H} and CO_2 capacity of the blood decrease. The toxicity of urea, creatine, or creatinine to such animals is relatively small. The urine contains a toxic substance, the oxyproteic acid fraction (I), the Ba salt of which is insol. in H_2O , but sol. in EtOH, and which is inactivated by acid hydrolysis and is dialys-

able through collodion membranes. A similar substance is also present in the serum. The rôle of (I) in uræmia is discussed. F. O. H.

Relation of interfacial tension to cytolysis of sea-urchin eggs by soaps. I. H. PAGE, H. A. SHONLE, and G. H. A. CLOWES (Protoplasma, 1933, 19, 213—227).—Soaps containing the ricinoleate (I) grouping kill the egg without the corrosive, disintegrating action shown by other soaps. The pigment of the egg is liberated rapidly. The oleate, linoleate, and linolenate class (II) of soaps release the pigment slowly, and the condition of the cytolysed egg is very different from the above. The action of Na laurate is intermediate. In the p_H range 6.0—9.0 soaps of the (I) type show max. catalytic effects towards the acid extreme and those of the (II) type at the alkaline end of the scale. Points of max. cytolysis correspond with points of min. surface tension. A. G. P.

Neuro-muscular action of amides and ammonium salts. R. BONNET (Compt. rend., 1934, 198, 284—285).—Org. NH_4 salts are toxic for both nerve and muscle, amides only for the latter. R. S. C.

Acetylcholine in tissue. III. Oxytocic action of acetylcholine for the induction of labour and in other obstetrical conditions. A. WONG and H. CHANG (Chinese Med. J., 1933, 47, 987—1009).—The acetylcholine (I) content of the placenta varies largely, being > normal in cases of abortion, uterine tetany, premature separation of placenta, foetal death *in utero*, and Caesarean section, and < normal in uterine inertia, prolonged labour, pulmonary tuberculosis, and general debility. The oxytocic action of (I) is studied and its use instead of pituitrin for the induction of labour suggested. A. L.

Influence of acetylcholine on absorption of glucose. E. GELLHORN and D. NORTHUP (Amer. J. Physiol., 1933, 105, 684—686).—Addition of acetylcholine to Ringer's solution perfusing frog intestine influenced the permeability of the gut to glucose in a manner opposite to that of adrenaline; it increased permeability in small concn. and decreased it in greater. Nutr. Abs.

Action of certain ethers of β -alkylcholine derivatives. A. SIMONART (J. Pharm. Exp. Ther., 1934, 50, 1—14).—Of alkyl ethers of β -methyl-, β -ethyl-, and β -propyl-choline the Me and Et ethers have a muscarine-like action, as also has β -butylcholine Me ether (I), whilst the higher alkyl ethers show little or no action. With increase in mol. wt. the nicotine-like action tends to diminish except in the case of (I), in which it is marked. Most of the compounds show a paralyzing action on the sympathetic synapses and on the neuro-muscular junctions of voluntary muscle. W. O. K.

Hypoglycæmic and glycogen-forming action of methylated guanidine. M. TENNENBAUM (Arch. Verdauungskrankh., 1933, 53, 397—401; Chem. Zentr., 1933, ii, 1054).—Administration of decamethylenediguanidine carbonate (I), synthalin (II), and synthalin-B (III) to rabbits diminished the blood-sugar, (I) having an effect > that of (II). The glycogen-forming effect of (I) was also > that of (II)

or (III). The difference between the active and lethal doses of (I) is small. A. A. E.

Santonin and the hyperglycæmia due to glucose ingestion. S. BERTINO (Arch. Farm. speriment., 1933, 56, 601—606).—Intramuscular injection of large doses (0.08—0.15 g. per kg.) of santonin (in glycol) into rabbits increases the hyperglycæmia due to ingestion of glucose, whilst smaller doses (0.01 g. per kg.) have no effect. F. O. H.

Picrotoxin-stramonium antagonism. L. SHUTTER and B. MYERS (Proc. Soc. Exp. Biol. Med., 1933, 30, 935—939).—Picrotoxin convulsions in rats are prevented by subcutaneous administration of dealcoholised tincture of stramonium. CHE. ABS.

(a) Action of cinchophen on nitrogen metabolism. (b) Studies on the denervated kidney. I. Action of cinchophen on the uric acid and allantoin excretion in dogs, and its effect on the nitrogen and sulphur excretion. G. P. GRABFIELD and M. G. GRAY (J. Pharm. Exp. Ther., 1934, 50, 28—31, 123—130).—(a) In dogs on a submaintenance diet, administration of cinchophen (I) increases the rate of excretion (II) of total N, total S, uric acid (III), and allantoin (IV).

(b) Denervation of the kidneys does not influence the action of (I) on the (II) of total N and total S, but its action on (II) of (IV) is slightly increased. (I) at first decreases (II) of (III), but after some time again acts normally probably after regeneration of the renal nerves. W. O. K.

Influence of caffeine on effects of acetanilide. J. A. HIGGINS and H. A. MCGUIGAN (J. Pharm. Exp. Ther., 1933, 49, 466—478).—NHPhAc (I) has little or no effect on the heart. The toxic effects of (I) and EtOH are additive. Citric acid has a variable toxicity in mice. The toxicity of (I) is scarcely affected by caffeine. H. D.

[Pharmacological] action of hydroxyphenylmethylpyrazole. J. W. C. GUNN (Quart. J. Pharm., 1933, 6, 643—649).—The general symptoms and the action on the circulation and smooth muscle of 4-hydroxy-1-phenyl-5-methylpyrazole (I) (A., 1931, 742) are similar to those of antipyrine (II). (I), however, has a toxicity to mice (min. lethal dose 0.55 mg. per g.) and an antipyretic action in pyrexia due to *B. coli* infection in rabbits > those of (II).

F. O. H.

(a) Physiological action of principles isolated from secretion of S. African toad (*Bufo regularis*). (b) Jamaican toad (*B. marinus*). (c) Poisonous secretions of five N. American species of toads. (d) Parotid secretion of *B. bufo garzizans* as source of Ch'an Su. (e) Active groupings in molecules of cino- and marino-bufagins and cino- and vulgato-bufotoxins. (f) Similarity and dissimilarity of bufagins, bufotoxins, and digitaloid glucosides. K. K. CHEN and A. L. CHEN (J. Pharm. Exp. Ther., 1933, 49, 503—513, 514—525, 526—542, 543—547, 548—560, 561—579).—(a) From the parotid secretions (I) of *B. regularis* cholesterol (II), two digitalis-like compounds, bufagin (III) and bufotoxin (IV), an indole derivative, bufotenine (V), which stimulates rabbit's

intestines (VI) and guinea-pigs' uteri and raises arterial blood-pressure, and adrenaline (VII) were isolated.

(b) (II), a (III), and a (IV) with digitaloid properties, and (VII) are found; the (V) found has no pressor action on pithed cats, and has no effect on (VI) or frog's heart tonus.

(c) The (I) of *B. valliceps*, *fowleri*, *alvarius*, *quercicus*, and *americanus* contain characteristic (II), (III), (IV), and (V).

(d) The (I) of the common Chinese toad (*B. bufo gargarizans*) is almost identical with the prep. Ch'an Su (A., 1933, 530) which is evidently prepared from it.

(e) Breaking the lactone ring or saturation with H_2 destroys the activity of cino- and marino-bufagin; acetylation, chlorination, or oxidation of the OH groups modifies their activity; the acid radical attached to OH is almost as important as the lactone ring.

(f) The solubility, colour reactions, chemical composition, structural groupings, crystallisation phenomena, m.p., and physiological properties of 10 (III) and 12 (IV) are compared with those of scillarene A, (VII), ouabain, digitonin, and theretin. (III) and (IV) are generically similar and resemble (VII) most.

H. D.

Rotenone. XVI. Physiological action of rotenone, deguelin, and rotenone resin. Chemical behaviour of deguelin. See this vol., 301.

(a) Comparative assay of standard preparations of *Digitalis* and *Adonis vernalis* originating from different years. (b) Activity and stability of gitalin and adonilin. A. I. MOCHNATSCHIEVA (Russ. J. Physiol., 1933, 16, 541—546, 547—551).—(a) The pharmacodynamic activity of standard preps. of the above plants varies from year to year by > 100%.

(b) The activity of various preps. of gitalin (I) and adonilin (II) varies by > 200%; that of (II) is > that of (I) in all cases. The rate of deterioration of (I) is > that of (II).

R. T.

Potassium and calcium content of frog's blood-serum at different temperatures and resulting from stimulus of the central nervous system (strychnine and curare). O. F. TSCHISTOVITSOV (Russ. J. Physiol., 1931, 14, 320—323).—The Ca content of the serum at 3° (0.0041%) is slightly < that at room temp. (0.0046%); the K content (0.0148%) is appreciably > that at room temp. (0.0125%). Strychnine (0.2 c.c. of 1:5000 solution) and curare (0.4 c.c. of 1:1000 solution) raise the Ca content by 50%, but the K content is unaffected.

P. G. M.

Chronic morphine poisoning in dogs. V. Recovery of morphine from tissues of tolerant and non-tolerant animals. O. H. PLANT and I. H. PIERCE (J. Pharm. Exp. Ther., 1933, 49, 432—449).—Morphine (I) was determined in tissues by pptn. of proteins from the aq. suspension of the ground up tissue with $CCl_3 \cdot CO_2H$; the conc. filtrate was treated as for urine (A., 1932, 1284). Oxalated blood was diluted with 2% aq. AcOH and evaporated to dryness, and the residue extracted with AcOH. The

average total recovery from the liver, muscle, central nervous system (II), heart, lungs, and blood in tolerant dogs (III) was 46.2 and in non-tolerant dogs (IV) 42.8%. In (II), (III) give less (I) than (IV); in the blood the reverse is true. Possibly (I) is stored in the tissues of (III) in a form that is not readily extracted.

H. D.

Toxicity of α - and β -nicotines and nornicotines. Chemopharmacodynamic relationships. D. I. MACHT and M. E. DAVIS (J. Pharm. Exp. Ther., 1934, 50, 93—99).—To a variety of animals and plants, *dl*- β -nicotine (I) and *dl*- β -nornicotine (II) are more toxic than *dl*- α -nicotine (III) and *dl*- α -nornicotine (IV), respectively, but no const. relationship held between the actions of (I) and (II) or between those of (III) and (IV). *l*- β -Nicotine is usually more toxic than (I).

W. O. K.

Pharmacological action of the alkaloids of fumaraceous plants. I. *isocorydine*. R. A. WAUD (J. Pharm. Exp. Ther., 1934, 50, 100—107).—The action of *isocorydine* on frogs and various mammals closely resembles that of *bulbocapnine*.

W. O. K.

Comparison of the pharmacological action of atropine and its optical isomerides, *l*- and *d*-hyoscyamine. W. F. VON OETTINGEN and I. H. MARSHALL (J. Pharm. Exp. Ther., 1934, 50, 15—20).—Atropine, *d*- and *l*-hyoscyamine are destroyed at equal rates when incubated with egg-white, but rabbit's serum destroys the *l*- more rapidly than the *d*-compound, atropine being intermediate. Differential rates of destruction may determine the relative activity of the three isomerides in different animal species and on different organs.

W. O. K.

Absorption of methyl salicylate by the human skin. E. W. BROWN and W. O. SCOTT (J. Pharm. Exp. Ther., 1934, 50, 32—50).—The rate of cutaneous absorption of Me salicylate (measured by the excretion of salicylic acid compound in the urine) was increased by rise of temp., massage, and the use of various solvents of which the most effective was EtOH (50% solution), but the highest rate was found with an 11.8 vol.-% suspension of the ester in H_2O .

W. O. K.

Elimination of barbituric acid derivatives in urine with special reference to sodium amytal and pentobarbital. H. A. SHONLE, A. K. KELTCH, G. F. KEMPF, and E. E. SWANSON (J. Pharm. Exp. Ther., 1933, 49, 393—407).—Barbituric acids (I) are isolated by acidifying the urine with AcOH, extraction with Et_2O , and sublimation. 90% recovery of Na amytal (II) was obtained by this method; owing to the inadequacy of the chemical tests (I) were assayed with mice. Administration of (II) and pentobarbital to men and dogs produces no urinary excretion of (I), whereas barbital and phenobarbital are excreted in amounts up to 53 and 1.5%, respectively, of the dosage.

H. D.

Relative depressant effects of certain barbiturates on heart of elasmobranchs. G. B. ROTH (Proc. Soc. Exp. Biol. Med., 1933, 30, 563—565).—Activities of nembutal, amytal, and luminal were > that of veronal.

CH. ABS.

Narcotic potency of the aliphatic acyclic acetals. P. K. KNOEFEL (J. Pharm. Exp. Ther., 1934, 50, 88—92).—Acetals of various aliphatic aldehydes have definite hypnotic activity, but are inferior to paraldehyde. W. O. K.

Narcosis and mental function. ANON. (Nature, 1934, 133, 110—111).—A summary of Quastel's address to the British Association. L. S. T.

Hyperglycæmic action of certain drugs. D. CAMPBELL and T. N. MORGAN (J. Pharm. Exp. Ther., 1933, 49, 456—465).—2 c.c. of Et₂O given orally to rabbits produce hyperglycæmia (I), whilst with intravenous injection or oral dosage after amytal anaesthesia (II), no (I) is produced. If (II) is induced 20 min. after oral ingestion of Et₂O, (I) continues. Variable effects on the blood-sugar were obtained with pituitrin and ephedrine. H. D.

Influence of liver degeneration and recuperation on the acid-base equilibrium of the blood. W. DE B. MACNIDER (J. Pharm. Exp. Ther., 1934, 50, 108—122).—Dogs intoxicated with EtOH for 12, 18, and 24 hr. develop liver damage demonstrable anatomically and by the phenoltetrachlorophthalein test, whilst kidney function is apparently normal, the elimination of phenolsulphonephthalein being increased. The liver damage is accompanied by a fall in the blood alkali-reserve which returns to normal with recovery of the liver. W. O. K.

Determination of alcohol in blood. J. PELTZER (Chem. Ztg., 1934, 58, 48).—A reply to the criticisms of Heiduschka and Flotow (A., 1933, 744) of the author's method (*ibid.*, 310). Further details are given, and the correction factor of 5.3% is discussed. F. O. H.

Reliability of cerebrospinal fluid analysis in the diagnosis of drunkenness. H. W. NEWMAN and H. G. MEHETENS (Proc. Soc. Exp. Biol. Med., 1933, 30, 725—727).—In man the intravenous injection of 1 c.c. EtOH per kg. gave max. blood-EtOH of 150 mg. per 100 c.c. in 20 min., max. cisternal fluid-EtOH of 120 mg. in 50 min., and max. cerebrospinal fluid-EtOH of 100 mg. in 3 hr. CH. ABS.

Photodynamic action. IV. Photo-stimulation of skeletal muscle. C. R. SPEALMAN and H. F. BLUM (J. Cell. Comp. Physiol., 1933, 3, 397—404).—The production of contraction in skeletal muscle of frogs is independent of the presence of O₂, whereas the photodynamic response occurs only in presence of O₂. A. G. P.

Effect of ultra-violet rays and of methyllithionine chloride and heparin on snake venoms. D. I. MACHT and M. E. DAVIS (Proc. Soc. Exp. Biol. Med., 1933, 30, 990—993).—Ultra-violet rays produced rapid decrease in the potency of snake venoms. Methylene-blue or heparin does not affect the toxicity. CH. ABS.

Toxicity of aluminium and method of administration. G. BERTRAND and P. SERBESCU (Compt. rend., 1934, 198, 517—520).—The m.l.d. of Al [as Al₂(SO₄)₃] in the rabbit is 10 mg. per kg. body-wt. when injected subcutaneously. The salt has only 1/4 of this toxicity when introduced directly into the stomach, but is even more toxic by the peritoneal

route. 20 mg. per kg. by way of the stomach is harmless. P. G. M.

Chronic arsenic poisoning. I. Arsenic content of "mosquito incense." P. L. LI and C. S. YANG (Chinese Med. J., 1933, 47, 979—986).—Mosquito incense made from orpiment and sawdust contains 0.5—1.5% As, 80% of which is liberated on burning. A. L.

Arsenic in tobacco smoke. C. R. GROSS and O. A. NELSON (Amer. J. Publ. Health, 1934, 24, 36—42).—Cigars (I), cigarettes (II), and pipe tobacco (III) contain 8.3—50 p.p.m. of As₂O₃ (cf. A., 1927, 798). The proportions of As volatilised (and partly inhaled) are 15.1—34.7% for (I), 32.2—41.3% for (II), and 32.8% for (III). Data for the As contents of the ash and residues are also given. F. O. H.

Micro-determination of bismuth in animal tissues. G. F. HALL and A. D. POWELL (Quart. J. Pharm., 1933, 6, 628—633; cf. A., 1933, 1264).—The tissue is digested with HNO₃+H₂SO₄, excess H₂SO₄ is removed, and the aq. solution of the residue is boiled to remove NO₂ and diluted with 2.5% H₂SO₄ containing 1% of H₃PO₂ until 1 c.c. contains 0.4—4.0 × 10⁻⁶ g. of Bi. 5 c.c. are then treated with 0.1 g. of KI and 2 c.c. of EtOAc, shaken, and the colour of the EtOAc layer compared with suitable standards. Modifications for tissues containing fat or bone are necessary. F. O. H.

Electromigration of bismuthiodide in colloidal systems. P. J. HANZLIK, F. DE EDS, and J. B. SPAULDING (Proc. Soc. Exp. Biol. Med., 1933, 30, 721—724).—An electrolytic cell is described. Results are correlated with those of absorption and cerebrospinal penetration. CH. ABS.

Toxicology of chromium. K. AKATSUKA and L. T. FAIRHALL (J. Ind. Hygiene, 1934, 16, 1—24).—Cr^{III} salts are harmless to cats either by inhalation or when given orally. H. G. R.

Microchemical detection of lead. R. U. HARWOOD and D. BROPHY (J. Ind. Hygiene, 1934, 16, 25—28).—The Fairhall method (A., 1924, ii, 61) is modified to determine 0.5 × 10⁻⁶ g. of Pb in 5 c.c. of cerebrospinal fluid. H. G. R.

Interaction of magnesium with sodium, potassium, and ammonium ions. S. V. TSIGANOV (Russ. J. Physiol., 1931, 14, 121—128).—Subcutaneous injection of Na⁺ in the rat has no effect on the course of Mg narcosis, whilst K⁺ increases the diastolic action of Mg. In limited doses Mg⁺⁺ is antagonistic to the stimulating effect of NH₄⁺. P. G. M.

Interaction of magnesium with calcium, strontium, and barium ions. S. V. TSIGANOV (Russ. J. Physiol., 1931, 14, 129—136).—Subcutaneous injection of CaCl₂ in rats inhibits MgSO₄ narcosis, which is stimulated by Sr⁺⁺ and Ba⁺⁺. Mg⁺⁺ is antagonistic to the excitatory effect of Ca⁺⁺, Sr⁺⁺, and Ba⁺⁺. P. G. M.

Health aspects of radium dial painting. III. Measurements of radioactivity in workers. J. E. IVES, F. L. KNOWLES, and R. H. BRITTON. **IV. Medical and dental phases.** L. SWARTZ, F. C. MAKEPEACE, and H. T. DEAN (J. Ind. Hygiene, 1933, 15, 433—446, 447—455).—Determinations of γ-radi-

ation from the bodies and in the exhaled air of Ra dial painters indicated that accumulations of radioactive material were present. No bone changes were observed and red cell and hæmoglobin vals. were $>$ normal. Determinations of the radioactivity of the dust in the workrooms suggested that inhalation plays an important part in the poisoning. A. L.

Effect of sulphur on nitrogen metabolism and relation of sulphur and thyroid to the phenomena. S. SHINGU (Folia Endocrinol. Japon., 1932, 8, 7—8).—Intramuscular injection of colloidal S increased urinary N, urea, NH_3 , and creatine increasing in parallel. Creatinine was unchanged. Ingestion of colloidal S decreased total N, urea, and creatine, but increased NH_3 . Increased urinary N following thyroidectomy is reduced by ingestion of colloidal S.

CH. ABS.

Effect of potassium cyanide poisoning on the blood-fat and -lipin, and the effect of various hormones on the action of potassium cyanide. I. Insulin, thyroid substance, and adrenaline. II. Sex organs. III. Injection of extract of adrenal cortex, and thyroidectomy. S. KUBO (Folia Endocrinol. Japon., 1931, 7, 169—170, 170—171, 188—189).—I. After injection of aq. KCN into rabbits, blood-fat and -lipin increase. Adrenaline promotes, whilst insulin or thyroid (oral) retards, this increase.

II. The effect of extracts of testicle and ovary on the above increase has been studied.

III. Thyroidectomy promotes, whilst injection of adrenal cortex extract checks, the increase.

CH. ABS.

Effect of sodium thiosulphate on potassium cyanide poisoning. C. ACHARD and L. BINET (Compt. rend., 1934, 198, 222—224).— $\text{Na}_2\text{S}_2\text{O}_3$ reduces the toxicity of aq. KCN to carp and revives nearly dead fish.

R. S. C.

Alcoholic fermentation of *D*-glucose in deuterium water. E. PACSU (J. Amer. Chem. Soc., 1934, 56, 245—246).—Fermentation occurs about nine times as fast in ordinary distilled H_2O as in 100% H^3O .

H. B.

Pharmacological experiments with deuterium. D. I. MACHT and M. E. DAVIS (J. Amer. Chem. Soc., 1934, 56, 246).—Germination of *Lupinus* seeds is slightly slower in H_2O (concn. 1:2000) than in ordinary distilled H_2O . No differences were found in other experiments (e.g., fermentation; contraction of smooth muscle; assay of digitalis).

B

Harmony [between ionic concentrations]. See this vol., 254.

Relation of life to electricity. VIII. Mechanism of oxidation-reduction potentials of living tissues. R. BEUTNER and J. LOZNER (Protoplasma, 1933, 19, 370—380).—Systems consisting of a non-oxidised and a corresponding oxidised substance, e.g., alcohol-fatty acid, produce a p.d. of kind and magnitude similar to those occurring in living tissues, and with increasing oxidation show a shift of potential towards the positive side. The e.m.f. of these systems

consists of phase boundary potentials and depends on the distribution of ions within the system. A. G. P.

Electromotive force in biological systems. I. Effect of homologous carbamates on the electromotive force of frog skin. E. J. BOELL and A. B. TAYLOR. II. Surface activity of homologous carbamate solutions. A. B. TAYLOR and E. J. BOELL (J. Cell. Comp. Physiol., 1933, 3, 355—383, 385—395).—I. The depression of the e.m.f. of urethanes (I) is a function of the concn. of (I) applied. Traube's rule is applicable to the effects of a homologous series. Absorption of (I) by skin with consequent inhibition of reactions giving rise to the e.m.f. explains the action of these substances.

II. A parallelism exists between the lowered surface tension of (I) solutions and the depressive effect of these solutions on the e.m.f. of frog skin. A. G. P.

Influence of electrolytes on the physico-chemical properties of colloidal systems comparable with cytoplasm. I. Influence of electrolytes on the viscosity of diluted egg-yolk. B. ZAWADZKI (Protoplasma, 1933, 19, 484—509).—With increasing concn. of chlorides, HCl, or NaOH the viscosity of dil. yolk increases to a sub-max. (80—200 millimols. of chloride per litre), declining subsequently to a sub-min. (400—500 millimols. per litre) and finally rising steadily at higher concns. The effect of HCl and NaOH is far $>$ that of salts, the activity of which was in the order $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl} > \text{KCl}$.

A. G. P.

Biological oxido-reduction and the respiration theories of Wieland and Warburg. J. KAUP and A. GROSSE (Z. ges. exp. Med., 1932, 84, 171—223; Chem. Zentr., 1933, ii, 1531—1532).

Direct spectroscopic identification of oxygen-carrying enzyme in *Azotobacter*. E. NEGELEIN and W. GERISCHER (Naturwiss., 1933, 21, 884).—In the living cells the presence of the reduced enzyme is indicated by an absorption band at 632 m μ . The band shifts to 647 m μ on oxidation, or to 637 m μ on reaction with CO, and disappears on reaction of the oxidised enzyme with HCN.

R. K. C.

Decolorisation of methylene-blue by milk and animal tissue. A. BOUTARIC and T. JACQUINOT (Bull. Acad. Méd., 1933, [iii], 109, 114—118; Chem. Zentr., 1933, ii, 1880—1881).—Camphor, S, Me salicylate, PhOH, resorcinol, quinol, guaiacol, HgCN, Na salicylate, and tannin arrest the decolorisation of methylene-blue (I) by milk (containing CH_2O) or liver tissue; Me arsinat, Na_3AsO_4 , and Na_2HPO_4 accelerate the reduction of (I).

A. A. E.

Glyceraldehydphosphoric acid as hydrogen donor. B. GÖZSY (Z. physiol. Chem., 1933, 222, 279—280).—Glyceraldehydphosphoric ester is an active H donor in presence of co-enzyme and compares favourably with fructose diphosphate.

Amylase of mulberry leaves. S. MATSUMURA and T. KASUGA (Bull. Sericult. Japan, 1933, 6, 6).—The physical properties of leaf-amylase are tabulated.

H. G. R.

Amylase system of the liver. L. HOLLANDER (Science, 1934, 79, 17—18).—Comparison of rat-liver

preps., using the Waldschmidt-Leitz and Samec method for observing starch digestion, shows that the amount of maltose (I) formed at the blue-violet I end-point (II) varies markedly in different preps. In a few cases (II) was reached without measurable formation of (I). An amylase prep. can thus be made which in the early stages of starch digestion yields no reducing groups. Incubation of an aq. liver suspension increases its capacity to form (I), whilst the I end-point activity increases only slightly. Two amylases with different characteristic (I) levels at the same (II) and an unstable inhibitor (III) sp. for the component showing more (I) formation appear to exist. (III) can be pptd. at p_H 5.2, and has a quant. inhibiting effect on the formation of (I) from starch by liver preps. The digestion of starch by liver-amylase is performed by two different components.

L. S. T.

Ultrafiltration of malt-amylase solutions. C. T. SNELL (J. Biol. Chem., 1934, 104, 43—51).—Cellulose nitrate membranes made by the method of Pierce (A., 1928, 233) and graded by varying the amount of $(-CH_2OH)_2$ in the collodion have corresponding permeabilities. Using these, malt extract is purified threefold.

A. L.

Enzymic hydrolysis of irisin. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1933, 83, 1042—1044).—Irisin is completely hydrolysed to *d*-fructose by fructosidase at p_H 4.62. For equal enzyme concn., the velocities of hydrolysis of sucrose and irisin are in the ratio $4 \times 10^5 : 1$, although for hydrolysis by acid the velocities are of the same order.

H. F. G.

Enzymic fission of polysaccharides. III. Fission of chitin by emulsin. W. GRASSMANN, L. ZECHMEISTER, R. BENDER, and G. TÓTH (Ber., 1934, 67, [B], 1—5; cf. A., 1933, 55).—Merck's emulsin (*loc. cit.*) hydrolyses oligosaccharides of low mol. wt. from chitin appreciably more slowly than higher members of the series; chito-biose (I) and -triose (II) are scarcely affected. Crude, de-fatted almond powder hydrolyses the two N-containing oligosaccharides only slightly more slowly than the more complex chitodextrins (III). Emulsin purified by pptn. with tannin is appreciably active, whereas samples further purified by fractional pptn. with $AgOAc$ are almost without action. There is no parallelism between the ease of hydrolysis of (III) and (I) or (II). The assumption that chitin is a β -glucoside (*loc. cit.*) is withdrawn. Comparison of the effect of different emulsin preps. on salicin, cellobiose, (III), (I), (II), and cellodextrin shows that the enzyme active towards chitin is not identical with β -glucosidase, from which it also appears to differ in its distribution in the almond kernel.

H. W.

Emulsin of hips (*Rosa canina*). E. HOFMANN (Biochem. Z., 1933, 267, 309—312).—An emulsin prep. obtained from the hips of the wild rose had scarcely any action on β -glucosides, but readily hydrolysed β -galactosides. The extent of hydrolysis of β -phenol-*d*-glucoside and -galactoside at p_H 5 was 3 and 70%, respectively.

P. W. C.

Enzymic behaviour of glycuonides and glycyrrhizic acid. F. BERGMANN (Biochem. Z.,

1933, 267, 296—308).—A simplified method for the prep. of NH_4 glycyrrhizinate is described (cf. A., 1907, i, 545; 1921, i, 259) and the compound shown to be dextrorotatory and unattacked by emulsin, maltase, takadiastase, etc. On hydrolysis with $N-H_2SO_4$ the acid gave glycyrrhetic acid (I), $C_{23}H_{36}O_{37}$, m.p. 303° $[\alpha]_D^{20} + 145.5^\circ$ [Me ester, m.p. 255° , $[\alpha]_D^{20} + 166.7^\circ$; Ac derivative (II), m.p. 317° , $[\alpha]_D^{20} + 144.6^\circ$ (Me ester, m.p. 299° , $[\alpha]_D^{20} + 147.6^\circ$)]. (I) is not reduced by Pd and H_2 and is stable to $KMnO_4$ and $C(NO_2)_4$, whilst (II) is not attacked by CrO_3 .

P. W. C.

Enzymic scission of lecithin. A. CONTARDI (Boll. Chim. farm., 1934, 73, 3—12).—A review.

R. N. C.

Natural activation of plant tissue proteinase. K. MOTHES (Naturwiss., 1933, 21, 883).—Papain preps. can be inactivated by H_2O_2 , by O_3 in presence of Pd, or by O_2 in presence of various plant extracts (plant dehydrases) and then re-activated by H_2 in presence of Pd or plant extracts. Active material contains SH groups, and inactive material S-S groups, and reversible activation and inactivation is regarded as a non-sp. process affecting these groups, which form part either of the prosthetic group of the enzyme or of an adsorbed associated substance.

R. K. C.

Inhibition of cathepsin and activation of papain by α -thiolcarboxylic acids. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, 222, 207—214).—Papain is activated by α - and β -thiolcarboxylic acids, the position of the SH being without effect. Many substances activate only slowly, and show at first slight inhibition. Cathepsin (I) is inhibited by α -thiolcarboxylic acids, most strongly by α -thiolbutyric acid. Cysteine, SH-glutathione, β -thiolpropionic acid [which activates (I)], and ascorbic acid do not, but Fe does, reverse the inhibition by α -SH-acids. The first stage in the inhibition seems to involve removal of Fe

J. H. B.

Catheptic proteinase. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, 222, 215—219).—In preps. of guinea-pig's, hen's, and pig's liver, treated with EtOH to remove sol. SH compounds, the cathepsin present is mostly fully activated. This confirms earlier results (A., 1933, 1081).

J. H. B.

Effect of dehydration on pancreatic and intestinal enzymes. J. R. ROSS and M. M. SHAW (J. Biol. Chem., 1934, 104, 131—139).—Rats maintained discontinuously at 37.5° for several days show diminished production of both intestinal and pancreatic enzymes; individual variations were large.

H. D.

Thiol compounds and crystalline urease. J. B. SUMNER and L. O. POLAND (Proc. Soc. Exp. Biol. Med., 1933, 30, 553—555).—Jack-bean meal contains a substance which reacts similarly to glutathione. Cryst. urease does not contain glutathione, but may contain SH groups. This may account for the readiness with which urease is inactivated by Ag, Hg, and Cu ions and by benzoquinone and other oxidising agents, and whv urease is protected by SH-compounds.

CH. ABS.

Phosphorylated intermediate products and the later phases of alcoholic fermentation. O. MEYERHOF and W. KIESSLING (Biochem. Z., 1933, 267, 313—

348).—Fermentation reactions using yeast maceration extract in presence of NaF and $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$, with sugar and hexose phosphate in presence and absence of MeCHO, are investigated. In the absence of MeCHO and presence of NaF an equimol. mixture of α -glycerophosphoric and phosphoglyceric (I) acids is obtained and in presence of MeCHO exclusively (I), MeCHO being reduced to EtOH. These intermediate compounds are isolated and identified with the corresponding compounds of lactic acid fermentation using muscle extracts. Glyceraldehyde phosphate is also here to be regarded as the intermediate product. A new scheme of intermediate fermentation reactions is given. P. W. C.

Biochemical formation of optically active phosphoglyceric acid from various sugars. T. BABA (Biochem. Z., 1933, 267, 452—455).—Tables show that, using yeast maceration extract or fresh yeast, sucrose, maltose, glucose, and fructose all give phosphoglyceric acid, the yield for maltose being very slightly > for the remaining sugars. P. W. C.

Phosphoglyceric acid from galactose and its degradation by galactose[-fermenting] yeasts. C. CATTANEO (Biochem. Z., 1933, 267, 456—459).—Galactose-fermenting yeasts produce phosphoglyceric acid and convert it into AcCO_2H . P. W. C.

Method for determining sedimentation velocity of yeast. (Agglutination tendency.) N. NIELSEN (Compt. rend. Lab. Carlsberg, 1933, 19, No. 17, 1—11).—The agglutination of a uniform yeast suspension (I) is measured by the change in concn. at the lower end of a column of (I) in a burette. Yeast taken from the bottom of a column of (I) has a sedimentation velocity and N content > those at the top. H. D.

Relation between inorganic salt concentration, hydrogen-ion concentration, and physiological processes in *Amoeba proteus*. I. Rate of locomotion, gel/sol ratio, and $[\text{H}^+]$ in balanced salt solutions. R. F. PITTS and S. O. MAST (J. Cell. Comp. Physiol., 1933, 3, 449—462).—In balanced salt solution the rate of locomotion (I) of *A. proteus* shows a max. at p_{H} 6.2 and decreases (with an intermediate max.) to zero at p_{H} > 8.0. Over the whole range of p_{H} examined locomotion rates vary inversely with salt concn. (II). The gel/sol. ratio varies directly with acidity and with (II), but is not directly correlated with (I). A. G. P.

Oxidation-reduction potential of protozoan cultures. I. Effect of $\cdot\text{SH}$ on *Chilomonas paramecium*. T. L. JAHN (Protoplasma, 1933, 20, 90—104).—Acceleration of cell division by $\cdot\text{SH}$ is antagonised by H_2O_2 . This phenomenon and also the effect of methylene-blue on *C. paramecium* are explained on the basis of changes in oxidation-reduction potential in the medium. A. G. P.

Course of growth of strains of actinomycetes and its quantitative examination on various potato substrates. L. E. KIESSLING (Zentr. Bakt. Par., 1933, II, 89, 177—196).—On nutrient media containing the expressed juice of potatoes, the wts. of mycelium produced by various actinomycetes

showed well-defined differences according to the variety of potato used and the stage of development.

A. G. P.

Composition of fungi. N. V. SABUROV and A. V. VASILIEV (Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm., U.S.S.R., 1931, 1, 77—91).—Ash, protein, fat, mannitol, trehalose, and glucose have been determined in numerous fungi. CH. ABS.

Metabolism and energetics of growth of moulds. H. TAMMIA (Acta Phytochim., 1933, 7, 27—41).—The interpretation of energy data is discussed. F. O. H.

Respiration of moulds. III. Respiration of synthesis and of maintenance. H. TAMMIA and S. YAMAGUTCHI (Acta Phytochim., 1933, 7, 43—64; cf. A., 1932, 1167).—With spores of *Aspergillus melleus* grown in sugar-containing media, the rate of growth (I) increases parallel with the rate of respiration (II) until a max. is attained in 50—60 hr., following which both (I) and (II) decrease, the val. of (I) reaching zero before (II). The R.Q. also rises to a max. and then falls to approx. 1. With 50-hr. cultures, 40% of the total O_2 respiration is utilised for synthesis and the remainder for maintenance. With older cultures less is used for synthesis. The efficiency of energy utilisation decreases from 85% with young moulds to approx. 60% with old moulds. The relation of the rate of (II) to that of (I) can be expressed as an equation of the second degree. F. O. H.

Influence of poisons and of temperature on the utilisation of respiratory energy during growth of moulds. A. YAMAMOTO (Acta Phytochim., 1933, 7, 65—92).—True respiratory poisons, e.g., KCN, act firstly on the respiration (I) of *Aspergillus niger* and secondly on the growth (II), thus producing a preliminary increase in utilisation (III). Other poisons, e.g., phenylurethane, CO, and NaF, primarily decrease (II), resulting in a decrease in (III). Iodoacetate forms a third group which acts on both (I) and (II), so that (III) remains approx. const. The younger is the culture the greater is the val. of (III). (III) has a temp. optimum of 25°, whilst that of (I) or (II) is 35°. F. O. H.

Action of certain alkaloids on the utilisation of carbohydrates by *Aspergillus niger*. G. MEZADROLI and A. AMATI (Atti R. Accad. Lincei, 1933, [vi], 18, 161—165).—The utilisation of glucose or sucrose by *A. niger* in Wehmer's or Raulin's solution at 37° is enhanced by the presence in the solution of 0.05—0.2% of strychnine (nitrate) or 0.05—0.3% of quinine (sulphate), but 0.05—0.3% of caffeine (base) has the opposite effect. These effects are, in general, not dependent on the composition of the nutrient liquid, the nature of the carbohydrate, or the temp. T. H. P.

Electrophoresis of trypanosomes and spirochaetes. F. P. FISCHER and V. FISCHL (Biochem. Z., 1933, 267, 403—404).—Both types of living organism, both in their natural medium and in physiological solutions, and also the dead organisms, always migrate to the cathode. P. W. C.

Dissociation constant of nitrogen-nitrogenase in *Azotobacter*. H. LINEWEAVER, D. BURK, and

W. E. DEMING (J. Amer. Chem. Soc., 1934, **56**, 225—230).—The nature of the dissociation of the complex (N_2E) formed between gaseous N_2 and the enzyme nitrogenase (E) during the fixation of N_2 by *Azotobacter* (I) at ordinary temp. and pressure has been studied (method; A., 1930, 1068). The thermodynamic dissociation const., $K_x = [E][N_2]/[N_2E]$, is 21.5 ± 0.2 vol.-% (0.215 ± 0.002 atm.) (as a function of N_2 pressure) and is independent of wide variations in the concns. of Ca, Sr, Fe, and $C_2O_4^{2-}$, p_H , O_2 pressure, max. velocity of irreversible decomp. of NE_2 (to form protein) at saturating N_2 pressures, and species, age of culture, and concn. of (I). Statistical analysis of the collective data is carried out. The mol. heat and free energy of dissociation of N_2E are 0 (within experimental errors of 1000 and 100 g.-cal., respectively). H. B.

Agar-digesting bacteria. H. E. GORESLINE (J. Bact., 1933, **26**, 435—457).—Three new species are described. A. G. P.

Utilisation of certain sugars and their derivatives by bacteria. S. A. KOSER and F. SAUNDERS (J. Bact., 1933, **26**, 475—488; cf. A., 1933, 639).—The action of a no. of organisms is examined. Organisms utilising glucose rarely acted on α -methyl-*D*-glucoside, and -mannoside; β -methyl-*L*-arabinoside and -*D*-xyloside were not fermented by any organisms which utilise the corresponding pentoses. In most instances *D*-arabinose was much less rapidly attacked than the *L*-form. Rhamnose and fucose were readily decomposed. None of the organisms examined utilised α -gluco-heptose or -heptulose. Glucose-fermenting bacteria in general utilised glucosamine, but more slowly. Many organisms fermented gluconic acid, but none attacked glucose Et mercaptal. A. G. P.

Transformation of optically active phosphoglyceric acid by *B. coli*. C. ANTONIANI (Biochem. Z., 1933, **267**, 376—379).—Fresh cultures and dry preps. of *B. coli* convert phosphoglyceric acid into $AcCO_2H$. P. W. C.

Degradation of *dl*-glyceric acid by *B. coli* and *B. lactis aerogenes*. C. ANTONIANI (Biochem. Z., 1933, **267**, 380—382).—Using loop cultures of *B. coli* and an inorg. medium, glyceric acid gave chiefly $AcOH$, some HCO_2H , and traces of $EtOH$. Lactic acid was not obtained. With *B. lactis aerogenes* similar results were obtained, but the amount of $AcOH$ was greater and acetoin was also present. P. W. C.

Fermentation of pyruvic acid by *B. coli*. J. TIKKA (Suomen Kem., 1934, **7**, 75B).—The action of *B. coli* on $AcCO_2H$ takes the following course: $AcCO_2H + H_2O \longrightarrow AcOH + HCO_2H \longrightarrow AcOH + H_2 + CO_2$. It is possible to detect 57% of the theoretical quantity of HCO_2H . 19% of the original $AcCO_2H$ is reduced to lactic acid by the nascent H . P. G. M.

Respiration and fermentation of lactic acid bacteria. II. J. G. DAVIS (Biochem. Z., 1933, **267**, 357—359).—Two strains of *B. casei* (*Lactobacillus casei*, O. Jensen, and a strain from Reading) differ from other lactic acid bacteria in using practically no O_2 . Methylene-blue does not increase the O_2 -utilisation, but inhibits glycolysis. $COMe_2$ -preps. of *B.*

Delbrücki oxidise lactic acid with the formation of H_2O_2 . P. W. C.

Activator of the metabolism of propionic acid bacteria. C. FROMAGEOT and E. L. TATUM (Biochem. Z., 1933, **267**, 360—375).—Potato extract contains an activator which is indispensable for the metabolism of dissolved glucose and assists in the utilisation of starch, but is unnecessary for the utilisation of lactic acid. The activator probably converts glucose into a labile form. P. W. C.

Prodigiosine, the red pigment of *Bacillus prodigiosus*. V. F. WREDE and A. ROTHHAAS (Z. physiol. Chem., 1933, **222**, 203—206; cf. A., 1933, 1172).—Oxidation of prodigiosine (I) with CrO_3 in $AcOH$ gives maleimide and methoxymaleimide. Oxidation of hydrogenated (I) with $KMnO_4$ affords proline. This affords further evidence of the nature of rings II and III. J. H. B.

Human tubercle bacilli. F. ULZER and H. GRUBER (Wiss. Mitt. österr. Heilmittelstelle, 1933, No. 11, 1—2; Chem. Zentr., 1933, ii, 1882).—The proportions of the dry bacilli dissolved by various solvents are recorded. A. A. E.

Presence of salicylic and phenylacetic acids in the acetone-soluble fat of the tubercle bacillus. N. STENDAL (Compt. rend., 1934, **198**, 400—401).—Isolation and identification of *o*- $OH \cdot C_6H_4 \cdot CO_2H$ and $CH_2Ph \cdot CO_2H$ from the residual aq. liquor after slow steam-distillation of the fatty acids from the $COMe_2$ -sol. fat of the tubercle bacillus (myristic acid in the distillate) are described. It is unlikely that these acids exist in the free state in the fat, since they are not present in the vapour from the unsaponified fat. J. W. B.

Precipitated diphtheria toxoid. L. C. HAVENS and D. M. WELLS (J. Infect. Dis., 1933, **53**, 138—139).—1—2.5% K alum completely ppt. the toxoid with little or no loss of sp. antigen. CH. ABS.

Antibodies in placental extracts. C. F. MCKHANN and F. T. CHU (J. Infect. Dis., 1933, **52**, 268—277).—The protein material contains substances, presumably antibodies, which neutralise diphtheria toxin, blanch scarlet-fever rashes, neutralise poliomyelitic virus, and prevent measles. CH. ABS.

Non-specific precipitins for pneumococcic fraction C in acute infections. R. ASH (J. Infect. Dis., 1933, **53**, 89—97). CH. ABS.

Effect of tyrosine on *C. botulinum* toxin. W. BURROWS (Proc. Soc. Exp. Biol. Med., 1933, **30**, 823—825).—The toxin produced by *C. botulinum* in ox-heart medium was not decreased by addition of tyrosine (I) and/or phenylalanine (40 mg. per 100 c.c.). Incubation with the NH_2 -acids does not affect the toxin, and injection of (I) does not protect the mouse. CH. ABS.

Characteristics of hypertoxic tetanus toxin (hypertoxin). R. LEGROUX and G. RAMON (Compt. rend., 1934, **198**, 620—622).—Tetanus toxin becomes more toxic on acidification of the medium with $PrCO_2H$ to p_H 3—4. To some extent mineral acid produces the same effect, but addition of HCl to p_H 2.0 destroys toxicity. Addition of alkali to a hypertoxic bouillon to p_H 7.0 causes the original toxicity to

return. The acidification also produces loss of flocculating power which is not regained on addition of alkali. Tetanus anatoxin does not acquire any toxic characteristics on acidification. P. G. M.

Fixation of the lytic principle ("bacteriophage"). W. MUTSAARS (Ann. Inst. Pasteur, 1934, 52, 118—135).—Emulsions of staphylococci (I) in contact with media containing bacteriophage (II) absorb a definite amount of (II), the equilibrium attained indicating a physico-chemical process such as adsorption rather than a penetration of (II) into the cells. This is confirmed by the fixation by (I) of (II) inactivated by heating to 65°. The combination of (II) with antilytic serum, however, follows the normal antigen-antibody reaction; a state of equilibrium is attained, but the proportions of the constituents vary. Such a complex is readily dissociated, but becomes more stable with age. Heat-inactivated (II) forms similar, but less stable, complexes.

F. O. H.

Enzymes of the agalactia virus. A. PRIE and B. E. HOLMES (Brit. J. Exp. Path., 1933, 14, 290—296).—The dehydrogenase and oxidative systems are very sensitive to mechanical agitation. Broth has a protective effect. Enzyme activity and viability are greatly reduced by exposure to light in presence of traces of methylene-blue. Growth of a culture is accompanied by a small decrease in lipin-P.

CH. ABS.

Antigenic properties of rabies virus. L. C. HAVENS and C. R. MAYFIELD (J. Infect. Dis., 1933, 52, 364—373).—All strains of rabies virus contain the same antigenic constituents, but in varying quantities. Heterologous strains can be neutralised if large amounts of serum are employed. After passage through the rabbit there is a rearrangement of antigenic structure.

CH. ABS.

Effect of the formalin-vapour-contact method of rearing the silkworm on muscardine and flacherie. Y. NAKAZAWA (Bull. Sericult. Japan, 1933, 6, 5).—The method increases the bactericidal power of the digestive fluid and reduces bacterial growth in the litter.

H. G. R.

Bactericidal power of rivanol. N. P. GOVOROV and V. K. MURSAEV (Russ. J. Physiol., 1931, 14, 175—182).—Storage of a rivanol solution for 15 days has no effect on its bactericidal properties towards *B. paratyphosus* B and *B. pyocyaneus*, whilst it is inactive towards *S. albus* after 5 days. P. G. M.

Carbohydrate-phosphate metabolism and the influence of certain hormones thereon. O. MANOILOVA, N. UTOCHNIKOVA, and A. GORDON (Russ. J. Physiol., 1931, 14, 309—319).—The intimate relation between carbohydrates and P compounds in the organism is emphasised by the fact that hormones such as insulin (I) and adrenaline (II), which influence carbohydrate metabolism, produce a change in the content of inorg. P in the blood parallel with the change in sugar content. (I) lowers the inorg. P by promoting its conversion into the org. P compound, lactacidogen. (II) at first raises the inorg. P content of the blood by furthering the decomp. of lactacidogen. The effects of pituitrin in this direction are negligible.

Diverse results are due to the facts that the change in the blood-P often follows a rhythmic course and that the inorg. P has not always been determined at regular time-intervals after introduction of the hormone. T. H. P.

Effect of the glands of internal secretion on the sulphur content of the various organs.
I. Sulphur, insulin, and thyroid substance.
II. Adrenal capsule. III. Genital glands. S. KUBO (Folia Endocrinol. Japon., 1931, 7, 176—177, 178, 179).—I. Ingestion of S and injection of insulin increase total S (I) and neutral S (II) of most organs, especially of adrenal capsule (III), where SO_4 is also increased. Ingestion of thyroid decreases (I) and (II), and increases SO_4 of (III).

II. Ingestion of (III) and injection of interrenin increase (I) and (II) in (rabbits') organs. (III)- SO_4 is also increased. Injection of adrenaline decreases (I) and (II) in most organs, but increases SO_4 in thyroid, parotid glands, liver, and testicles.

III. Ingestion of testicle powder by male rabbits decreases (I), (II), and SO_4 of most organs; only testicular SO_4 is increased. Ingestion of ovarian tissue decreases, and of corpus luteum increases, the S content of most organs of female rabbits.

CH. ABS.

Is the hormone which initiates movement of intestinal villi specific? E. DE KOKAS and G. DE LUDANY (Compt. rend. Soc. Biol., 1933, 113, 1447—1449).—This hormone ("villikin"), which is prepared from the duodenal mucosa by extraction with HCl, is not sp., preps. from different animals acting on the intestinal villi of the dog. Its activity is greater when prepared from the duodenal mucosa of the cat and fowl than from that of the sheep, pig, or cow.

NUTR. ABS.

Presence in the foetal intestine of a hormone causing movement of intestinal villi. G. DE LUDANY (Compt. rend. Soc. Biol., 1933, 113, 1449—1450).—"Villikin" (I) is not contained in the intestinal mucosa as such, but as a substance which is converted into (I) by acids. When a HCl extract of the intestinal mucosa of embryo dogs was injected intravenously into anaesthetised dogs, stimulation of the villi was observed. (I) was of the same nature when prepared from the duodenal mucosa of the embryo and the adult.

NUTR. ABS.

Influence of the spleen on the excretion of bile and bile acids. T. TANAKA (J. Biochem. Japan, 1933, 18, 369—377).—In dogs with biliary fistulae, splenectomy increases the excretion of bile acids and the secretion of bile. Administration of atropine or of spleen extracts (A., 1933, 308) inhibits this action. Hence the spleen appears to exert a hormonal action on the liver.

F. O. H.

Absorption of insulin from the intestinal tract. D. CAMPBELL and T. N. MORGAN (J. Pharm. Exp. Ther., 1933, 49, 450—455).—Insulin (I) is equally effective in the rabbit when injected in the systemic or portal circulation. An Et_2O extract of a lecithin-(I) hydrochloride was active when intravenously, but not when orally, administered.

H. D.

Colorimetric iodometric determination of adrenaline. G. WELLER (Bull. Soc. Chim. biol., 1933, 15, 1308—1316).—The tissue (1 g.) is extracted with 10% aq. $\text{CCl}_3\text{CO}_2\text{H}$ [in which adrenaline (I) is stable for at least 48 hr.] and the extract (60 c.c.) is treated with KOAc (6 g.). After addition of 0.1 mg. of (I) to one half, both are treated with 10 c.c. of 0.01*N*-I, excess of I is titrated with 0.1*N*- $\text{Na}_2\text{S}_2\text{O}_3$, and the resulting violet solutions are compared colorimetrically. Pyrocatechol, pyrogallol, and gallic and salicylic acids do not interfere. The adrenal glands of female dogs have a content (0.1540%) of (I) > that of males (0.1425%). F. O. H.

Decomposition of adrenaline by isolated organs. B. S. SENTJURIN (Russ. J. Physiol., 1931, 14, 189—194).—Liver tissue destroys adrenaline *in vitro*; all other tissues are inactive in this respect. P. G. M.

Adrenal capsules and metabolism of electrolytes. I. Effect of adrenaline, adrenal capsule extract, and choline on blood-serum-potassium and -calcium. II. Effect of loss of the medullary and cortical portions of adrenal capsules on blood-serum-potassium and -calcium. Liver- and muscle-glycogen of rabbits having adrenal capsules removed. III. Skeletal muscle-potassium and -calcium of rabbits having adrenal capsules removed, and effect of fatigue. S. SUMIMOTO (Folia Endocrinol. Japon., 1932, 8, 2—3, 5—7, 11—12).—I. Adrenaline (injected) decreases -Ca and -K; interrenin or 1% choline slightly increases -K. 2% Choline decreases -K.

II (a). -K increases; -Ca temporarily decreases.

III. After adrenalectomy -K changes; -Ca increases. Fatigue decreases -K and -Ca in normal or adrenalectomised animals. CH. ABS.

Influence of the adrenal-cortex hormone on the chemistry of active muscle. R. INDOVINA (Biochem. Z., 1933, 267, 383—388).—The time required for complete exhaustion of rats in a treadmill under standard conditions is lengthened by 4—6 hr. on injection of the hormone, and the decrease of glycogen and increase of residual N in the fatigued muscles are not so great in the injected as in the uninjected animals. P. W. C.

Dependence of metabolic action of thyroid secretions on the condition of the central nervous system. R. INDOVINA (Biochem. Z., 1933, 267, 389—399).—The increase of basal metabolism in the rat by injection of thyroxine is greatly enhanced under the influence of strychnine, but is unaffected by cocaine. P. W. C.

Production of serum inhibitory to the thyreotropic hormone. J. B. COLLIP and E. M. ANDERSON (Lancet, 1934, 126, 76—78).—Rats (I) and guinea-pigs (II) treated for a long period with anterior pituitary extracts containing the thyreotropic hormone (III) develop an apparent resistance to (III). Blood-serum from animals containing such an inhibitor prevents the usual response of normal (I) and (II) to (III). L. S. T.

Effect of thyroid and pituitary extracts on the composition of the blood and on diuresis. L.

LANGERON, M. PAGET, and J. LEDIEU (Bull. Acad. Méd., 1933, [iii], 109, 843—846; Chem. Zentr., 1933, ii, 1887).—Administration of thyroid increases the ratio plasma vol.: corpuscle vol. when this is low. Plasma-Cl concn. remains unchanged; corpuscle-Cl becomes normal. Plasma-albumin:globulin is unchanged. Diuresis and Cl excretion are slightly decreased. Administration of theobromine with thyroid also increases the blood-plasma. The effect of pituitary extract is opposite to that of thyroid.

A. A. E.

Effect of pituitrin on water balance of rabbits. C. I. COX and C. S. HICKS (Austral. J. Exp. Biol., 1933, 11, 288—294).—Rabbits infused with 5% saline containing 0.4% of pituitrin show inhibited diuresis, blood dilution, and increased excretion of Cl'. The excretions of H_2O and salt by the kidney occur independently. H. D.

Mass excretion of oestrogenic hormone in the urine of the stallion. B. ZONDEK (Nature, 1934, 133, 209—210).—The amount of oestrogenic hormone (II) excreted in the urine of the stallion (I) varies from 10^4 to 4×10^5 mouse units per litre, average val. 1.7×10^5 units per litre, corresponding with an excretion of 1.7×10^6 units a day or 62 g. of (II) per year. This val. is much > that excreted by other mammals, and the higher val. is confined to the male. The castrated or sexually-immature horse excretes only small quantities (0.2—0.5%) of (II). Comparative vals. for other animals are given. The male sex hormone is not excreted in increased quantities in the urine of (I), whilst gonadotropic hormone, prolactin, and corpus luteum hormone are not excreted. An alteration in solubility of (II) occurs in the animal outside the testes, which are the richest (II)-containing tissues known. L. S. T.

Dehydrogenation of the follicular hormone. A. BUTENANDT and H. THOMPSON (Ber., 1934, 67, [B], 140—144; cf. A., 1933, 540).—Distillation of the follicular hormone over electrolytic Zn dust and purification of the distillate by crystallisation from EtOH and light petroleum, and then through the additive compound with 2:7-dinitroanthraquinone, leads to the isolation of chrysene in very small amount.

H. W.

Vitamin content of lichens. N. R. ELLIS, L. J. PALMER, and G. L. BARNUM (J. Nutrition, 1933, 6, 443—454).—Vitamin-A occurs in short but not tall lichens. The vitamin-D potency of tall was > that of short lichens. No appreciable amounts of vitamin-B occurred in any species examined. A. G. P.

Vitamin-A reaction with antimony chloride. II. Spectroscopic investigation of chromogens. III. Placenta and serum. H. GOLDHAMMER and F. M. KUEN (Biochem. Z., 1933, 267, 406—416, 417—423).—II. The colours with SbCl_3 and carotene (I), xanthophyll (II), ergosterol (III), cholesterol (IV), oxysterol (V), and vitamin-A (VI) are investigated and the corresponding absorption spectra determined. The spectra of (I) and (II) are similar and of (III) and (IV) each have four bands, two of which are common to both substances; that of (V) has four bands completely different from those of (IV). Whereas the bands of (IV) gradually disappear on

heating in air and on irradiation, those of (V) intensify. Liver oil gives the (VI) bands at 610 μ , a band at 572 μ , and the four bands of (IV). In alcoholic extracts, the bands are displaced towards the short wave-length. The bands of the unsaponifiable fraction are similarly displaced, but towards the red end of the spectrum. In the unsaponifiable fraction of butter after addition of SbCl_3 , the characteristic bands of (VI), (I), and (IV) are obtained.

III. In human and horse blood-serum a colourless chromogen is present which on treatment with SbCl_3 gives a blue colour and bands at 595 and 541 μ . (I) and (II) are detected, but (VI) only in certain cases. By drying the human placenta in air at 35–40°, lipochrome was destroyed and a colourless chromogen formed which with SbCl_3 gave a blue colour and bands at 595 and 541 μ . The formation of the chromogen depends on the presence of (II).

P. W. C.

Conversion of carotene into vitamin-A in the animal body. B. SKARZYNSKI (Bull. Acad. Polonaise, 1933, B, 31–41).—Ingestion of 0.1 mg. of carotene (I) daily by rats on a vitamin-A (II)-free diet is followed by the appearance of (II) in the liver; (I) and possibly other related substances also appear to be present (cf. A., 1932, 657). (II) is present in the blood in small amount, but not in the spleen. Unchanged (I), but not (II), occurs in the contents of the caecum (cf. A., 1931, 1196; 1932, 309).

F. O. H.

Effect of vitamin-A on the mineral economy [of rats]. C. BOMSKOV and G. SEEMANN (Z. ges. exp. Med., 1933, 89, 771–779; Chem. Zentr., 1933, ii, 1889).—Large doses of vitamin-A (I) lead to brittleness and low mineral content of bones. (I) hinders the curative action of vitamin-D on rickets.

A. A. E.

Effect of vitamin-A on the composition of the blood. C. BOMSKOV and G. SIEVERS (Z. ges. exp. Med., 1933, 89, 780–785; Chem. Zentr., 1933, ii, 1889).—In rabbits only high blood- PO_4 and slightly diminished -Ca, attributed to the vitamin-D content of the prep., were observed.

A. A. E.

Keratoplastic reaction of hoof formation to some physiological factors. V. KLEMOLA (Bied. Zentr. [Tierernahr.], 1933, B, 5, 657–675).—Abnormalities in hoof formation in horses during prolonged feeding of dry rations are ascribed to vitamin-A deficiency.

A. G. P.

Vitamin-A deficiency as related to reproduction in range cattle. G. H. HART and H. G. GUILBERT (Calif. Agric. Exp. Sta. Bull., 1933, No. 560, 30 pp.).—Physiological effects of vitamin-A deficiency are discussed.

A. G. P.

Avitaminosis-A and use of lipins. L. RANDOIN and R. NETTER (Compt. rend., 1934, 198, 395–397).—Growth of rats fed on diets containing vitamin-B and -D, but not -A (I), with addition of either peanut oil or lard, ceases after 50–70 days, death occurring within 3 months. Hence lard contains no (I), and has no effect on the alterations in the tissue-lipins resulting from deficiency of (I).

J. W. B.

Spectroscopic evaluation of solutions of vitamin-D in fatty oils. I. L. FUCHS and Z. BECK

(Pharm. Presse, 1933, 38, Wiss.-prakt. Heft, 81–87; Chem. Zentr., 1933, ii, 1903).—The method employs the ultra-violet absorption spectra of the solutions and their unsaponifiable fractions. The curve relating extinction to λ shows at 265 μ a characteristic max. for vitamin-D. Long preservation in the dark in presence of air causes appearance of a yellow colour.

A. A. E.

Effect of feeding a cod-liver oil concentrate to cows on the vitamin-D content of milk. W. E. KRAUSS, R. M. BETHKE, and W. WILDER (J. Dairy Sci., 1933, 16, 549–555).—Addition of "Vitex" (cod-liver oil concentrate) to cows' rations increased the vitamin-D (I) content of the milk, in proportion to the amount supplied. The decline in the fat content of milk following heavy feeding of fish oils is probably not to be associated with the high intake of unsaturated fatty acids or of (I).

A. G. P.

Comparative antirachitic efficiency of irradiated ergosterol, irradiated yeast, and cod-liver oil for the chicken. R. M. BETHKE, P. R. RECORD, and D. C. KENNARD (J. Nutrition, 1933, 6, 413–425).—Irradiated yeast, and irradiated ergosterol (I) dissolved in linseed, maize, or cod-liver oils were less effective for chicken than the rat-equiv. proportion of cod-liver oil (II). The antirachitic potency of (I) was not reduced by admixture with (II).

A. G. P.

Copper and vitamin-B. J. KARP (Z. ges. exp. Med., 1933, 89, 765–770; Chem. Zentr., 1933, ii, 1890).—Products and organs rich in vitamin-B are relatively rich in Cu. In fruit (poor in -B) the Cu content is particularly low. Fe and vitamin-B content are not parallel. There is no regular relation between Cu and other vitamins.

A. A. E.

Activity of crystalline preparations of vitamin-B₁. A. G. VAN VEEN (Nature, 1934, 133, 137).—A cryst. product, approx. twice as active as the author's former prep. (A., 1932, 782), has been isolated.

L. S. T.

Activity of crystalline preparations of vitamin-B₁. H. W. KINNERSLEY, J. R. O'BRIEN, and R. A. PETERS (Nature, 1934, 133, 177).—A discussion of van Veen's results (preceding abstract).

L. S. T.

Necessary versus optimal intake of vitamin-B₂. H. C. SHERMAN and L. N. ELLIS (J. Biol. Chem., 1934, 104, 91–97).—Increasing the intake of vitamin-B₂ (I) above the actual requirement level results in successive increases in the rate of growth and vitality in rats. The power of the weaned rat to resist the effects of (I) deficiency depends on the diet of its mother.

H. D.

Other factors than vitamin-B₁ and -B₂ in the vitamin-B complex. R. C. LEWIS (J. Nutrition, 1933, 6, 559–570).—A review.

A. G. P.

Vitamin-C distribution in Baldwin and McIntosh apples. C. R. FELLERS, P. D. ISHAM, and G. G. SMITH (Proc. Amer. Soc. Hort. Sci., 1932, 29, 93–97).—The freshly expressed juices are, respectively, rich and poor in vitamin-C. In both cases the epidermis is richer than the flesh.

CH. ABS.

Staining of vitamin-C in adrenal glands. G. BOURNE (Austral. J. Exp. Biol., 1933, 11, 261–267;

cf. A., 1933, 872).—A reducing substance (I) in the fixed tissue from the adrenal glands of mice, rats, cats, and guinea-pigs was demonstrated by the reduction of AgNO_3 , OsO_4 , Fehling's solution, and HAuCl_4 . Differentiation from lipins was obtained by using alcoholic AgNO_3 , fixing the tissue with CH_2O and soaking in Et_2O , and fixing in CHCl_3 . Impregnation with HAuCl_4 confirmed the AgNO_3 findings. (I) may be vitamin-C. H. D.

Reaction of methylene ether groups in aromatic compounds. See this vol., 314.

Electrical charge of the colloid particles of protoplasm. B. SEN (Ann. Bot., 1934, 48, 143—152).—In cataphoretic investigations the protoplasmic particles of the petiole hairs of *Urtica dioica* and of the root hairs of *Azolla pinnata* show a negative charge. If the current applied is not sufficient to injure the protoplasm, the movement of the particles is reversed immediately the current is broken. The rate of migration is independent of the size and shape of the particles. A. G. P.

Hydrogen-ion concentration and the isoelectric reaction of plant protoplasts, especially the cell nucleus and the plastids. G. YAMAHARA and T. ISHII (Protoplasma, 1933, 19, 194—212).—Free surviving nuclei of a no. of plant cells show p_H vals. ranging from 4.0 to 5.0. The p_H of living cell nuclei in the embryonic condition approach the isoelectric point more nearly than those in the actively growing condition. Thixotropy is recorded in free surviving nuclei from *Vicia faba*. Intracellular variations in p_H during karyokinesis in pollen cells are recorded. A. G. P.

Physiologically polarised photosynthetic exchange in submerged water plants. I. K. ARENS (Planta [Z. wiss. Biol.], 1933, 20, 622—658).—Leaves of *Elodea* immersed in $\text{Ca}(\text{HCO}_3)_2$ and exposed to light liberate O_2 and an alkaline material from the upper surface, and take up $\text{Ca}(\text{HCO}_3)_2$ or the corresponding pairs of ions at the under-surface without change of reaction in the surrounding medium. In distilled H_2O the upper-surface changes continue for a time until the reserve Ca in the leaves is exhausted. Normal changes recommence if $\text{Ca}(\text{HCO}_3)_2$ (but not aq. CO_2) is applied to the under-side only. Starch formation occurs mainly near the upper surface of the leaf. The alkaline reaction produced in the vicinity of the upper surface probably results from the elimination of the hydroxide or normal carbonate of the base (Ca, Na, K, etc.) with which the under-side of the leaf is in contact. A. G. P.

Catalase and photosynthesis. E. YAKUSHIJI (Acta Phytochim., 1933, 7, 93—115).—The action of various catalase (I) preps. (from taka-diastrase, yeast, fish liver, *Hydrilla verticillata*, and *Chlorella ellipsoidea*) is inhibited by low concns. of NH_2OH (A., 1905, i, 107) and, to a smaller extent, by HCN. The sensitivity of (I) towards heat varies with the different preps. The dissociation const. of (I)- H_2O_2 is 0.083 for yeast-(I) and 0.094 for fish liver-(I) (cf. A., 1932, 1062). The gaseous metabolism of *C. ellipsoidea* and of *Ulva conglobata* indicates that the evolution of O_2 during photosynthesis is totally due to the (I) of the chloroplasts. The decrease in plant assimilation by NH_2OH or KCN also depends on the inhibition of (I). F. O. H.

ation by NH_2OH or KCN also depends on the inhibition of (I). F. O. H.

Copper in relation to chlorophyll and hæmoglobin formation. O. S. ORTH, G. C. WICKWIRE, and W. E. BURGEE (Science, 1934, 79, 33—34).—The addition of CuSO_4 to soil increased the chlorophyll (I) content of the leaves of orange trees suffering from (I) deficiency. No Cu was found in the leaves. L. S. T.

Chlorophyll content of grain sorghums. J. C. IRELAND and P. A. YEATS (Bot. Gaz., 1933, 95, 300—315).—The chlorophyll content (I) of Kaffir corn increases up to seed maturity and declines as the grain hardens. It varies directly with the amount of evaporation and the temp. A positive relationship is established between yield and (I). A. G. P.

The SH radical and other sources of sulphur affecting growth of isolated root tips of wheat seedlings. P. R. WHITE (Protoplasma, 1933, 19, 132—135).—The elongation of root tips was influenced by S compounds in the following order: $\text{NaSH} > \text{control} > \text{K}_2\text{S} > \text{CS}(\text{NH}_2)_2 > \text{NH}_4\text{CNS}$. A. G. P.

Influence of thiol and its sub-oxidised derivatives on the developmental cycle of hydranths of the genus *Obelia*. F. S. HAMMETT (Protoplasma, 1933, 19, 510—540).—The metaplastic formation of a hydranth on the distal end of a stolon outgrowth is favoured by $\cdot\text{SH}$ and retarded by its suboxidised derivatives. A. G. P.

Significance of growth-substance in the growth and geotropic response of roots of *Vicia faba*. P. BOYSEN-JENSEN (Planta [Z. wiss. Biol.], 1933, 20, 688—698).—Geotropic deviation in roots is associated with the presence of larger proportions of growth substance (I) on the lower than on the upper side of the root tip. (I) retards the elongation of roots. A. G. P.

Catalase activity as a measure of seed viability. C. W. LEGGATT (Canad. J. Res., 1933, 9, 571—573).—Statistical analysis of earlier work shows that the viability of wheat may be ascertained by determination of the total and thermostable catalase activity. A. G. P.

Biological action of metals at a distance. G. A. NADSON and C. A. STERN (Compt. rend., 1934, 198, 282—284).—The rate of germination of seeds of *Sinapis alba* is decreased by Pb, Au, Pt, and Al discs placed at a distance of 2—3 mm., the effect decreasing in the order given (that of decreasing atomic no.) and being greater for a disc 0.6 than for one 0.02 mm. thick. R. S. C.

Physico-chemical properties of seed extracts. C. A. SHULL and J. W. MITCHELL (Bot. Gaz., 1933, 95, 258—278).—Analyses and f.-p. determinations of the cold- H_2O and hot- EtOH extracts of various seeds are recorded. The f.-p. depression is almost entirely accounted for by the proportion of sugars and salts present in the extract, and proteins are a negligible factor in this respect. Autolysis of seeds is indicated at temp. very little above 0° . A. G. P.

Effect of seed formation on the rate of respiration of fruit of the Japanese persimmon or kaki (*Diospyros kaki*, L.). K. MATSUMOTO (Japan.

J. Bot., 1932, 6, 125—137; Bied. Zentr., 1933, A, 4, 37).—Seed-bearing fruits show higher respiratory activity than parthenocarps. No definite relationship is apparent between respiration rates. Treatment with MeCHO increases respiration, especially in unripe fruits, but EtOH is without effect.

A. G. P.

Physiology of apples. XIV. Determination of chemical change and rate of respiration in stored apples. G. LALL (Ann. Bot., 1934, 48, 273—292).—Appropriate technique for the application of the "half-apple" method of examination is described. The cutting of apples results in a temporarily increased rate of respiration which disappears after approx. 7 days' storage at 12°. Considerable variations occur in the ratio of sugars and acid lost to CO₂ produced by individual varieties. Differences in the course of respiratory activity in Bramley's Seedling and Cox's Orange Pippin are probably related to the waxy coating on the skin of the former. Wax accumulation may account for a part of the sugar loss which takes place during respiration. Substances synthesised from CO₂ during respiration include EtOH, MeCHO, and esters but no non-volatile compounds.

A. G. P.

Influence of physico-chemical phenomena in the ripening of corn. M. PIETRE (Compt. rend., 1934, 198, 608—611).—The disappearance of sol. sugars (complete in about 8 days) even at low temp. coincides with the gradual diminution (glutininogenesis) of globulin (0.75—0.34%) and albumin (0.31—0.18%), and with an active evaporation process. At 26° the loss of wt. by evaporation is 35% in 2 days.

P. G. M.

Significance of mannitol in the metabolism of some higher plants. T. ASAI (Japan. J. Bot., 1932, 6, 63—101; Bied. Zentr., 1933, A, 4, 44).—Leaves and bark of stems contain more mannitol (I) than wood or roots. Seasonal variations in (I) content are recorded, but no relationship is apparent between assimilation rates and the distribution of (I) in the plants.

A. G. P.

Transport in the cotton plant. II. Ontogenetic study of concentrations and vertical gradients. T. G. MASON and E. J. MASKELL (Ann. Bot., 1934, 48, 119—141).—During the development of the plants, polysaccharides are stored chiefly in the bark; total N in the bark with little, if any, in the wood; P in the bark and also in wood with depletion from lower zones in the later stages of growth; Ca in the bark and wood. No evidence of accumulation of K was obtained. Vertical concn. gradients of materials stored in the bark are negative and that of K is consistently positive. Stored N in bark occurs principally as asparagine-N and accounts for the negative gradient of crystalloid N. Residual N shows a consistent positive gradient and is probably the mobile component. Gradients of sugar concn. and of total osmotic pressure in the bark become less steep as growth proceeds.

A. G. P.

Nitrogen metabolism of leaves of *Atriplex nummularium*. J. W. WOOD (Austral. J. Exp. Biol., 1933, 11, 237—252).—Below p_H 5.5 NH₂-acids accumulate in the leaves, whilst above this p_H NH₃

and amides accumulate. During wilting the p_H of the leaves changes from 6.5 to 6.2 and thence to 7.8, corresponding with an increase in NH₃- and amide-N and a decrease in NH₂-acid- and protein-N and H₂O content. A rise in temp. of leaves allowed to autolyse at p_H 8.1 appears to favour protein synthesis.

H. D.

Composition of different regions of mounds of *Eutermes exitiosus*, Hill. F. G. HOLDWAY (J. Counc. Sci. Ind. Res. Australia, 1933, 6, 308).—A correction (cf. A., 1933, 1193).

A. G. P.

Composition of Saksaul wood. I. M. ORLOVA (J. Appl. Chem. Russ., 1933, 6, 1120—1121).—The wood of *Haloxylon ammodendron* from Turkestan contains ash 3.4, pentosans 19.0, lignin 29.1, cellulose 36.2, Et₂O-sol. substances 1.6, H₂O-sol. substances 8.0, galactan 9.0, and mannan 0.2%.

R. T.

Spectroscopic study of wood of *Pinus sylvestris*. L. LEMMEL (Compt. rend., 1934, 198, 496—497).—The presence of Ca, Mg, Na, K, Mn, Al, B, Pb, Ag, P, Fe, Si, and (?) Cr and Sn is shown.

C. A. S.

Action of chlorine on lignified tissues. F. M. WOOD (Biochem. J., 1934, 28, 52—61).—The pink colour (I) in lignified tissues produced by the NH₂Cl reaction is associated with the presence of I and lignin. It is concluded that (I) is produced in the presence of I by a vanillylidene derivative formed from vanillin (II) which is in loose association with a form of lignocellulose. (II) predominates in older tissues.

H. G. R.

Composition of common heather (*Calluna vulgaris*). B. THOMAS (J. Agric. Sci., 1934, 24, 151—155).—The crude fibre content of heather declines with age and the highest vals. found were < those of very poor grass. Nearly all of the total N occurs as protein, the small balance consisting of NH₃- and amide-N. The pepsin digestibility of the crude protein is low. The fibre content is similar to that of grass, and shows no regular variation with age. The Et₂O extract increases with age and is always > that of grass.

A. G. P.

Analyses of certain winter pears. J. C. MOORE (Oregon Agric. Exp. Sta. Bull., 1933, No. 316, 10 pp.).—Analytical data show pears to have high total sugars and crude fibre, low fat and protein, and relatively high Cu contents. The fresh tissue has a low buffer val. and the ash a high proportion of bases.

A. G. P.

Determination of pectins in fruits, berries, and vegetables. N. V. SABUROV and S. S. CHERNUSHEVA (Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm., U.S.S.R., 1931, 1, 53—60).—Mehlitz's method gives rather high vals. for fruits and berries. For vegetables Norman and Nanji's method is modified, the extraction being effected by boiling for 1 hr. with 0.5% aq. (NH₄)₂C₂O₄.

CH. ABS.

Mucilage from slippery elm bark. E. ANDERSON (J. Biol. Chem., 1934, 104, 163—170).—The mucilage of *Ulmus fulva* consists of two or more polyuronides, in which the uronic acid is combined with 2 mols. of simple sugars and a coloured non-saccharine substance. The presence of galacturonic acid, l-

rhamnose, and *d*-galactose has been established and there are indications of a pentose, a methylated hexose, and a methylated uronic acid. H. G. R.

Sugar of *Ricaria bullata*. H. COLIN and J. PAYEN (Compt. rend., 1934, 198, 384—386).—The dextrorotation of the residue (sucrose and reducing sugars absent) from the EtOH extract of *R. bullata* is decreased by the action of dil. acids or glucosidase (which produce reducing sugars), and trehalose is isolated. The EtOH-extracted residue with boiling H₂O gives a dextrorotatory, pectin-containing gum, giving, with 2% H₂SO₄ at 120°, a reducing hydrolysate which contains uronic acid and from which the osazones of arabinose and glucose are obtained. J. W. B.

Presence of myrosin in certain plant families and its histochemical detection. P. MARSILI (Boll. Soc. Eustach., 1933, 31, 9—16; Chem. Zentr., 1933, ii, 2032).—The violet coloration given by orcinol and HCl is not sp. for myrosin. A. A. E.

Infra-red absorption spectra of some plant-pigments. See this vol., 238.

Pigment of red cabbage (*Brassica oleracea*). I. I. CHMIELEWSKA (Rocz. Chem., 1933, 13, 725—735).—An anthocyanin (I), C₂₃H₃₃O₁₆Cl, containing 1 OMe and 1 mol. of an unidentified disaccharide, has been isolated from red cabbage. (I) eliminates MeOH and 2 mols. of glucose on acid hydrolysis, yielding cyanidin, and is isomeric but not identical with peonin or mecocyanin. On alkaline hydrolysis (I) yields protocatechuic acid and phloroglucinol; crude (I) yields in addition about 4% of sinapic acid. R. T.

Pigments of the sunflower. II. L. ZECHMEISTER and P. TUZSON (Ber., 1934, 67, [B], 170—173; cf. A., 1931, 402).—Re-examination has confirmed the presence of lutein, C₄₀H₅₆O₂, m.p. 193° (corr., Berl), $[\alpha]_D^{25} +136^\circ$ in EtOAc. Chromatographic adsorption leads to the detection of unimportant amounts of polyenes, possibly including violaxanthin, and to the ready isolation of taraxanthin, C₄₀H₅₆O₄, m.p. 184° (Berl). The small amount of carotene is remarkable. H. W.

Water-soluble organic acids of sunflower seeds. A. GOLDOVSKI and A. BOZHENKO (Maslo-boino-Zhir. Delo, 1933, No. 1, 13—20).—Citric, tartaric, and chlorogenic acids are present. CH. ABS.

Characteristics and composition of Wisconsin-grown tobacco-seed oil. W. L. ROBERTS and H. A. SCHUETTE (J. Amer. Chem. Soc., 1934, 56, 207—209).—The oil expressed from "Havana 142" seed has the same consts. as that obtained by extraction of an unknown strain with light petroleum; the consts. are also similar to those of foreign oils. The oils contain 1.25% of unsaponifiable matter and give palmitic (3.1%), stearic (4.8%), oleic (16.2%), and linoleic acid (I) (70.4%); (I) appears to be present (as glyceride) in two isomeric forms. H. B.

Rye oil. II. Properties as affected by choice of menstruum. A. W. STOUT, H. A. SCHUETTE, G. FISCHER (J. Amer. Chem. Soc., 1934, 56, 0, cf. B, 1932, 899).—Extraction of rye embryos with light petroleum, b.p. 40—60°, Et₂O,

CCl₄, C₂H₄Cl₂, CS₂, C₆H₆, CHCl₃, and COMe₂ gives 11.46, 13.66, 13.84, 14.13, 14.14, 14.45, 15.57, and 17.23%, respectively, of oil. The variations in the vals. of d_4^{25} , n_D^{25} , I val., P content, and unsaponifiable matter are recorded. H. B.

Plants containing oxalates with regard to oxaluræmia. A. GOUDSWAARD (Pharm. Weekblad, 1934, 71, 114—119).—H₂C₂O₄ occurs only in mushrooms, but the Ca (I) and K salts are very widely distributed. (I) is insol. in gastric juice and passes unchanged through the intestine. Of fifty vegetables and fruits examined, amaranth, beetroot, cocoa, spinach, pepper, purslane, rhubarb, tea, figs, sorrel, and species of *Oxalis* contained considerable quantities of C₂O₄". S. C.

Hydrocyanic acid in grasses: *Melica* and *Glycerium*. P. GUÉRIN (Compt. rend., 1934, 198, 383—384).—The leaves of *M. ciliata*, L. (collected in June), contain 0.151—0.306 g. HCN per kg., and those of *M. mutans*, L., or *M. uniflora*, Retz, 0.10—0.15 g. per kg. HCN is also detected in the roots, but not in the fruit. The leaves of *G. argenteum*, Nees, contain 0.23 g. per kg. in June, but the quantity decreases as autumn approaches (0.054—0.068 g. in Sept.), whereas the open inflorescences contain 0.28 g. HCN per kg., but HCN is absent from the fruit. J. W. B.

Proteins of grasses. III. Cystine content of certain grasses and other pasture plant proteins. A. POLLARD and A. C. CHIBNALL (Biochem. J., 1934, 28, 326—336).—The cystine (I) content of several typical grass and pasture plant proteins was determined by Prunty's modification of Sullivan's colorimetric method. Grass proteins contain 0.3—0.95% of (I); lucerne leaf protein contains 1.2% of (I). Vickery and White's gravimetric method always gives a much higher val. for (I)-S than corresponds with the amount known to be present, due to S from an unknown NH₂-acid. Calculation of the (I) content of grasses and pasture plants at various protein levels indicates that pasturage contains ample (I) for the wool-protein requirements of the sheep which it normally carries. C. G. A.

Systematic value of leaf ash. S. SEN (J. Dept. Sci. Calcutta Univ., 1933, 10, 8 pp.).—The mode of deposition of minerals on cell walls is discussed. CH. ABS.

Iodine compounds in seaweed. E. MASUDA (Proc. Imp. Acad. Tokyo, 1933, 9, 599—601).—An EtOH extract of *Ecklonia cava* powder, freed from reducing substances and iodides, with aq. H₂O₂ and C at room temp. gives slowly CH₃I·CO₂H (0.62%), CH₃I·CO₂H (0.02%), m.p. 106° (anilide, m.p. 187°), Cl₂·CH·CO₂H (0.009%), m.p. 133° (anilide, m.p. 134°), (CH₃I)₂CO (0.08%), m.p. 65° [gives (CH₃O)₂CO with AgOBz in ligroin], and (probably) tri-iodoacetaldehyde (0.007%), m.p. 126—127° (decomp.), unstable to light and cold KMnO₄. R. S. C.

Manganese in wheat-grains. P. BRUERE (Compt. rend., 1934, 198, 504—506).—Different parts of wheat-grains have the following Mn content (mg. per 100 g. of dry product): albumen, central 0.2, median 0.28, peripheral 0.21; envelope, external 2.47, internal 10.54; germ 0.285. R. S. C.

Absorption of manganese by wheat seedlings. J. DAVIDSON (Proc. 2nd Internat. Cong. Soil Sci., 1933, 2, 84).—The intake of Mn from MnO_2 by wheat in H_2O cultures was decreased by addition of NaNO_3 and CaCO_3 , but not by NH_4Cl , which increased the $[\text{H}^+]$ of the media. When Mn was supplied as MnCl_2 the inhibitory action of NaNO_3 and CaCO_3 was negligible. Absorption of Mn was reduced by $\text{PO}_4^{'''}$, especially in cultures containing MnCl_2 or MnSO_4 . The intake of Mn by plants is controlled not only by the soil p_{H} , but also by the nature of anions present.

A. G. P.

Physiological importance of mineral elements in plants. V. Distribution of diastase, invertase, and catalase in normal and potassium-starved bean plants. M. CATTLE (New Phytol., 1933, 32, 364—381).—In K-starved plants (I) the diastatic activity of leaves of all ages was < that of normal plants, differences being more pronounced in young and old leaves than in those of intermediate age. The effect of K on the activity of the enzyme is not attributable to a control of the NH_2 -acid content. Both the rates of formation and disappearance of starch from leaves were smaller in (I). In normal plants, invertase activity in upper was > in lower leaves and uniformly low in mature leaves. During K starvation the activity of upper leaves was <, and of lower leaves >, that in normal plants. The distribution of catalase resembled that of diastase in all respects.

A. G. P.

Distribution of potassium in normal and scorched foliage. L. G. G. WARNE (Ann. Bot., 1934, 48, 57—67).—The scorching of leaves resulting from K deficiency is associated with a lowered proportion of K in the dry matter and a steeper K gradient from main veins to margins in the leaves. A negative correlation exists between the dry matter in leaves and the K content of the dry matter. The withdrawal of K from older leaves and its translocation to young growing points is probable.

A. G. P.

Reaction of sphagnum. E. KIVINEN (Bull. Agrol. Inst. Finland, 1932: Proc. Internat. Soc. Soil Sci., 1933, 8, 219).—Differences are recorded in the p_{H} of expressed juices of sphagnum from moor soils of different types.

A. G. P.

Turgidity pressure. W. W. LEPESCHKIN (Ber. Deut. bot. Ges., 1934, 51, 455—469).—A mathematical analysis of the pressure relationships between the cell-contents and cell-wall.

P. G. M.

Inhibitive influence of radium on the growth of the rootlets of *Lens esculenta*, Moench: modification of the minimum preventive dose under the influence of favouring ions. A. SARTORY, R. SARTORY, I. MEYER, and ERNST (Compt. rend., 1934, 198, 386—388).—The inhibitory effect of Ra on the growth of the rootlets of *L. esculenta* is not affected by $\text{Sr}(\text{NO}_3)_2$, but is increased by ZnSO_4 or CuSO_4 , all in isotonic solution. When a mixture of a Ra-sensitising ion (I) (Cu) and one (II) (Mg) which tends to counteract the effect of the Ra is employed, the effect of (I) is much more pronounced than is that of (II).

J. W. B.

Nutrition of various saprophytic and parasitic fungi. M. VOLKONSKY (Ann. Inst. Pasteur, 1934, 52, 76—101).—Of 26 forms of *Saprolegniaceae* of the genera *Saprolegnia*, *Isoachlya*, *Achlya*, *Dictyuchus*, and *Aphanomyces* (I) investigated, none used NO_3^- or $\text{SO}_4^{''}$ as sources of N and S, respectively; all, with the exception of (I), hydrolysed glucose, maltose, dextrin, and sol. starch, but not pentose, galactose, sucrose, etc. Of other fungi (mainly parasitic) studied, a few utilised NO_3^- as a source of N, whilst all assimilated $\text{SO}_4^{''}$. There appeared to be no relation between the mode of S or N utilisation and parasitism.

F. O. H.

Cytosporina, Phomopsis, and Diaporthe. V. Analysis of chemical factors influencing fungal growth in the apple. L. N. SETH (Ann. Bot., 1934, 48, 69—107).—Close relationships are established between concns. of malic acid and sugars in the apple and the rate of penetration of the fungi. In general, increasing concns. of both constituents tend to retard fungal growth, but the various species respond very differently to any one set of conditions. The nature of the sugar and the relative proportions of sugars (if mixed) are also of importance in this respect.

A. G. P.

Physiology of parasitism. XIV. Comparison of enzymic extracts obtained from various parasitic fungi. K. P. V. MENON (Ann. Bot., 1934, 48, 187—210).—Interrelationships between the activity of fungal enzymes and the composition of the medium are examined with special reference to the effect of p_{H} , and the retarding action of certain plant extracts. The effect of the latter is largely associated with the presence of simple org. substances. The secretion of pectinase by fungi is favourably affected by the presence of pectin in the medium.

A. G. P.

Possible chemical nature of tobacco mosaic virus. J. CALDWELL (Nature, 1934, 133, 177).—Barton-Wright and McBain's results (this vol., 230) have been partly confirmed. N-free virus-containing crystals have not been obtained. The virus (I) present after successive recrystallisations has been determined, but there is no evidence that the crystals contain (I) except as an impurity. They have no sp. relation to (I).

L. S. T.

Some dicarboxylic acids as components of fixing fluids. C. ZIRKLE (Protoplasma, 1933, 19, 565—577).—Examination of the fixative action of oxalic, malonic, succinic, glutaric, malic, and tartaric acids used directly and as Cu and Ni salts in conjunction with CH_2O or chromic acid is recorded. The ability of the acids to influence fixation by CH_2O is dependent on the rate of penetration of the specimen. This is directly correlated with the relative fat-solubility.

A. G. P.

Verification of analytical technique for biological media, by the method of added quantities. H. GRIFFON (J. Pharm. Chim., 1934, [viii], 19, 30—36; cf. A., 1933, 1218).—The effect of experimental errors on the calc. systematic error is discussed mathematically.

D. R. D.

Determination of cystine. B. J. KRIJGSMAN and E. F. BONMAN (Arch. neerl. Physiol., 1933, 18,

458—471).—Whilst Folin and Looney's method (A., 1922, ii, 539) for the determination of cystine (I) is unsuitable when applied to blood, that of Sullivan (A., 1925, ii, 1211) (II) determines only total (I). Using (II) the (I) content of the blood of fasting rats (a trace) increases to about 14 mg. per 100 c.c. after feeding. A. L.

Micro-determination of urea in blood and urine. O. DA RIN and C. PASTORINO (Rass. Clin. Terap. Sci. aff., 1932, 31, 306—334; Chem. Zentr., 1933, ii, 2167).—Vals., obtained by Van Slyke and Cullen's modification of Marshall's method, of urea, NH_3 , NH_3^- , and urea-N are tabulated. A. A. E.

Determination of lactic acid. B. J. KRIJGSMAN (Arch. néerl. Physiol., 1933, 18, 503—513).—The methods of Mendel and Goldscheider (A., 1926, 212) and Dische and Laszlo (A., 1927, 985) are modified for the photometric determination of lactic acid in blood with an error of ± 4 , and ± 5 mg. per 100 c.c. respectively. A. L.

Analysis of tissues. J. B. GRAESER, J. E. GINSBERG, and T. E. FRIEDEMANN (J. Biol. Chem., 1934, 104, 149—155).—The tissue is crushed in an apparatus cooled by solid CO_2 , after freezing in liquid air. A method for the determination of glucose and lactic acid is described. H. G. R.

Micro-determination of cholesterol. T. MEUVISSEN and E. NOYONS (Biochem. Z., 1933, 267, 405).—Comments on Monasterio's paper (this vol., 122). P. W. C.

Quantitative spectro-photo-electric analytical method applied to solutions of chlorophyll *a* and *b*.—See this vol., 314.

Titration of betaine in acetone. K. LINDERSTROM-LANG (Biochem. Z., 1933, 267, 45—47).—Despite the statements of Fodor and Kuk (A., 1933, 621) betaine in COMe_2 can be determined by titration with HCl. W. McC.

Enzymic histochemistry. VI. Micro-determination of ammonia. K. LINDERSTROM-LANG and H. HOLTER (Compt. rend. Lab. Carlsberg, 1933, 19, No. 20, 1—8).— NH_3 is determined by allowing the solution to react with a drop of NaOH in a paraffined reaction vessel (A., 1933, 864), the NH_3 formed being collected on a film of H_2O containing HCl and bromocresol-purple. The excess HCl is titrated with NaBO_2 . Amounts of NH_3 between 2 and 0.0135×10^{-6} mol. may be determined with a max. error in the latter case of 10^{-9} mol. H. D.

Method of "chlorine-ashing." J. ERDOS and B. GROAK (Z. anal. Chem., 1933, 95, 327—329).—Org. matter is destroyed by refluxing with HCl, and adding slowly saturated aq. NaClO_3 . The method is applied to the determination of Pb in faeces. J. S. A.

Micro-determination of potassium.—See this vol., 269.

"Elon" and sodium sulphite as reducing agents in the colorimetric determination of phosphorus. G. VAN DER LINGEN (Analyst, 1933, 58, 75b—756).—EtOH-extracted plant materials are ignited with Ca(OAc)_2 , and the colour developed by 10 c.c. of an extract of the residue in 5% HNO_3 , with

1.5 c.c. each of the $\text{H}_2\text{SO}_4\text{--NH}_4$ molybdate reagent, 3.1275% elon (*p*-methylaminophenol sulphate), and of 20% Na_2SO_3 solutions, after dilution to 16.5 c.c. with dil. HNO_3 , is matched after 20 min. at 26° . The accuracy is $>$ when quinol is used, and $\text{CCl}_3\text{CO}_2\text{H}$ from blood-filtrates does not interfere. J. G.

Determination of organic phosphorus. O. H. FULCHER (J. Lab. Clin. Med., 1933, 18, 1053—1057).—The sample (2—6 mg. P) is kept over-night at 100° with 1.4 c.c. of conc. H_2SO_4 ; on continued heating over a small flame $\text{Al}_2(\text{SO}_4)_3$ is used as catalyst, and HNO_3 is added dropwise to clarify. Fiske and Subbarow's colorimetric method is then applied. CH. ABS.

Colorimetric determination of phosphoric acid in presence of arsenate ions. A. E. BRAUNSTEIN (Biochem. Z., 1934, 267, 400—402).—Reply to criticisms of Barrenscheen, Banga, and Braun (A., 1933, 1261). P. W. C.

Determination of iron. Adaptation of the mercaptoacetic acid colorimetric method to milk and blood. G. LEAVELL and N. R. ELLIS (Ind. Eng. Chem. [Anal.], 1934, 6, 46—47).—In the adaptation of this method to the determination of Fe in biochemical products wet-ashing with H_2SO_4 and HClO_4 is preferable to dry-ashing. M. S. B.

Destruction [of tissue] by nitro-sulpho-perchloric acid in the toxicology of gold. E. KAHANE and V. STEFANESCO (Bull. Soc. Chim. biol., 1933, 15, 1239—1246).—During the destruction of Au-containing tissue by $\text{H}_2\text{SO}_4 + \text{HNO}_3 + \text{HClO}_4$ significant amounts of Au are volatilised. Condensation of the vapour followed by a separate re-distillation effects recovery of most of the Au thus lost. F. O. H.

Determination of antimony in viscera and excreta. F. BAMFORD (Analyst, 1934, 59, 101—102).—In the absence of other group II metals, Sb is determined by ashing with MgO and $\text{Mg(NO}_3)_2$. The ash is acidified with HCl, Fe is removed, and Sb is pptd. as colloidal Sb_2S_3 and determined colorimetrically. E. C. S.

Microdetermination of silica in body-fluids and -tissues. W. PARRI and G. SCOTTI (J. Pharm. Chim., 1933, [viii], 18, 513—527; cf. A., 1924, ii, 499; 1928, 1205).—The material (0.2 c.c. of blood or 0.05 g. of dried tissue) is calcined with NaHCO_3 . The ash is treated with HNO_3 and H_2SO_4 , and the SiO_2 pptd. with $(\text{NH}_4)_2\text{MoO}_4$ and EtOH. NH_4 citrate is added to ppt. phosphomolybdate. The silicomolybdate is reduced with NH_2OH , HCl and $\text{Na}_2\text{S}_2\text{O}_4$ and is determined colorimetrically. E. C. S.

Determination of chlorine in biological material. E. KAHANE and M. R. DUMONT (Bull. Soc. Chim. biol., 1933, 15, 1247—1255).—The method of Laudat (A., 1917, ii, 539) for serum is applicable to tissue when sufficient KMnO_4 is used. A modified technique employs HClO_4 in place of KMnO_4 . F. O. H.

Determination of bromine in blood. T. F. DIXON (Biochem. J., 1934, 28, 48—51).—A method is described for the determination of Br in 10 ml. of blood, containing 0.1—100 mg. Br per 100 ml. H. G. R.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1934.

General, Physical, and Inorganic Chemistry.

Continuous spectra of the atom and molecule of hydrogen. D. CHALONGE (*Ann. Physique*, 1934, [xi], 1, 123—214).—Secondary and continuous spectra are excited by an uncondensed discharge, and at spectrum by a condensed discharge in a tube at low pressure. The energy distribution curve as a function of the wave-length consists, in the latter case, of a level beyond the Balmer lines and a level to beyond 9000 Å., corresponding respectively with the Balmer and Paschen continuous series. The influence of the Stark effect is observed. The mol. spectrum energy distribution curve reaches a max. at 2350 Å., falling to the Schumann ultra-violet. Data are obtained for the effect of different discharge conditions.

N. M. B.

Accidental pre-dissociation in band spectra. G. P. ITTMANN (*Naturwiss.*, 1934, 22, 118—119).—Theoretical. The perturbations of the band spectrum of N_2 (3- state) noticed by Coster *et al.* (*A.*, 1933, 991) can be explained assuming accidental pre-dissociation.

A. J. M.

Active nitrogen and the auroral spectrum. J. KAPLAN (*Nature*, 1934, 133, 331; cf. this vol., 125).—The spectrum of the afterglow of N now obtained is like that of the auroral spectrum except for the green auroral line.

L. S. T.

Mean lives of excited neon atoms. J. H. E. GRIFFITHS (*Proc. Roy. Soc.*, 1934, A, 143, 588—604).—A method depending on the measurement of the lag which exists between the excitation and emission of light from atoms in a high-frequency discharge is used to find the average lives (T) of six excited states of Ne. The vals. of T range from 3.9×10^{-8} sec. for the line 5853 to 20×10^{-8} sec. for 6402. Lines originating from the same upper level lead to the same val. of T . The method may be used for any substance of which the spectrum can be obtained from a high-frequency discharge.

L. L. B.

Isotope displacement and hyperfine structure in the arc spectra of chromium, molybdenum, and tungsten. N. S. GRACE and K. R. MORE (*Physical Rev.*, 1934, [ii], 45, 166—169).—Structure is found for several stronger lines of Mo I and W I in the range 4000—6100 Å. The W I lines give three components with 0.1 cm^{-1} overall displacement, attributed to isotope displacement of the even isotopes. Mo I lines give two components with 0.05 cm^{-1} separation, attributed to spin splitting of the odd isotopes, and broad lines of 0.06 cm^{-1} width attributed to a small isotope displacement.

A A

$I=1/2$ is indicated for the odd isotopes of both Mo and W.

N. M. B.

Investigations in the Schumann region. III. Spectra of iron, cobalt, and nickel between 2000 and 1670 Å. R. GRÄFIN ZU DOHNA (*Z. Physik*, 1934, 87, 616—632).

A. B. D. C.

New spectrum of zinc: Zn IV. L. BLOCH and E. BLOCH (*Compt. rend.*, 1934, 198, 645—647).—Using the vac. spark spectrum, 133 lines (4039.34—2589.90) of Zn IV have been measured. This spectrum has no lines between 4900 and 4040, or beyond 2580 Å. (cf. *A.*, 1925, ii, 1100).

C. A. S.

Disruptive discharge produced by selenium. V. BIANU (*Bul. Soc. Fiz. Roman.*, 1933, No. 56, 1—6).

R. T.

Perturbation in the spectrum of Se II. K. R. RAO and S. G. KRISHNAMURTI (*Nature*, 1934, 133, 328).

L. S. T.

Spectra of Br V, Br VI, and Br VII. A. S. RAO and K. R. RAO (*Proc. Physical Soc.*, 1934, 46, 163—168).—Using a Siegbahn spectrograph, the lines of the vac. spark spectra of Br in the region $\lambda\lambda$ 1400—400, under different degrees of excitation, are classified and assigned to the different ionisation stages. Doublet combinations are established by the application of the regular and irregular doublet laws, and principal members involving the low-lying terms are identified.

N. M. B.

Reversibility of red line of cadmium. A. PERARD (*Compt. rend.*, 1934, 198, 727—729).—An improved form of Cd-vapour lamp is described showing more readily the reversal of the Cd red line, and its resolution into two components. The possible error due to this makes the line of doubtful val. as an international standard of length.

C. A. S.

Fluorescence of vapour of iodine excited by circularly polarised light and viewed longitudinally. R. DAURE and A. KASTLER (*Compt. rend.*, 1934, 198, 557—559; cf. *A.*, 1918, ii, 90).

C. A. S.

Nuclear moment of xenon. H. KOPFERMANN and E. RINDAL (*Z. Physik*, 1934, 87, 460—469).— X^{129} has a mechanical moment $1/2$, X^{131} has $3/2$, and the even isotopes showed no splitting. The ratio of the magnetic moments 129 : 131 is 1.1.

A. B. D. C.

Degree of polarisation of fluorescence of mercury vapour. A. KASTLER (*Compt. rend.*, 1934, 198, 723—725; cf. *A.*, 1933, 992).—The degree of

polarisation produced in Hg vapour by light from a Hg arc in various states of polarisation and unpolarised (in the last case with a magnetic field in the direction of the incident beam) has been calc. The calc. result for the unpolarised beam agrees with the experimental, but varies greatly with temp.

C. A. S.

Degree of polarisation of fluorescence of mercury vapour in presence of nitrogen. A. KASTLER (Compt. rend., 1934, 198, 814—816; cf. preceding abstract).—Addition of N_2 (up to a pressure of 1—2 mm. Hg) increases the intensity of fluorescence 10—20 times, the result depending only on the fluorescence of $\lambda 4046 \text{ \AA}$. Previous results and calculations are corr. (cf. A., 1931, 8; 1932, 208; 1933, 760).

C. A. S.

Spark spectra of bismuth, Bi III and Bi II. M. F. CRAWFORD and A. B. McLAY (Proc. Roy. Soc., 1934, A, 143, 540—557; cf. A., 1932, 8).—An extended investigation of the term structures of Bi III and Bi II has been carried out. Term and classified wave-length tables are given, together with information on the hyperfine structures of the lines analysed.

L. L. B.

Arc spectrum of radium. E. RASMUSSEN (Z. Physik, 1934, 87, 607—615).—This spectrum was photographed from 10,000 to 3000 \AA .; the ionisation potential is given as 5.176 volts.

A. B. D. C.

Quenching of atomic thallium fluorescence by foreign gases. N. A. PRILESHAEVA (Compt. rend. Acad. Sci. U.R.S.S., 1933, 282—283).—Measurements of the decrease of the intensity of the fluorescence 5351 \AA . line in the presence of foreign gases at 0—500 mm. pressure indicate the probability of reaction between the excited Tl atom and O_2 and CO_2 , and collisions of the second kind in presence of N_2 , CO, H_2O , and A. No quenching is observed in presence of H_2 .

J. W. S.

Absorption spectrum of thallium vapour in the short-wave ultra-violet. G. S. KVATER, N. V. KREMENEVSKI, and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 111—112).—Measurements have been made using a 70-cm. column of Tl vapour, and lines and bands in the neighbourhood of 2000 \AA . are discussed.

W. R. A.

Nuclear spins and magnetic moments. W. E. CURTIS (Nature, 1934, 133, 256).

L. S. T.

Probe measurements in the positive column of inert gases. K. SOMMERMEYER (Z. Physik, 1934, 87, 741—743).—Measurements of Seeliger and Hirschert (A., 1932, 105) have been repeated and extended, and the variation of the probe characteristic with probe length supports Pupp's theory (Physikal. Z., 1932, 33, 844) rather than that of disturbance of the Maxwell distribution.

A. B. D. C.

Deviations from Paschen's law. S. P. McCALLUM and L. KLATZOW (Phil. Mag., 1934, [vii], 17, 291—297).—For most gases the sparking potential (I) between parallel plates depends on the product of the pressure p and the distance apart S of the electrodes. This applies to He, but with Ne, A, and Kr (I) increases with increase of S for const. vals. of pS . This is due to the diffusion of the electrons

perpendicular to the direction of the electric force, which in Ne and A is $>$ in He.

H. S. P.

Spectrum of the red stars of the *M* and *N* types. G. PICCARDI (Atti R. Accad. Lincei, 1933, [vi], 17, 952—954).—Spectroscopic examination of the different regions of an O_2 - H_2 flame fed with $TiCl_3$ indicates that C_2 and TiO are never present together in any zone of the flame, and this may explain the similar behaviour in the spectra of the *M* and *N* red stars.

O. J. W.

Influence of certain photographic errors on the profiles of absorption lines in stellar spectra. C. T. ELVEY and (Miss) C. WESTGATE (J. Opt. Soc. Amer., 1934, 24, 43—50).—The influence of the Eberhard effect was investigated by the measurement, under various conditions of exposure, density, and development, of the depression of the background at the edge of an image, due to the inhibiting action of the products of development.

N. M. B.

Spectroscopic observations of the variable star RS Ophiuchi (Nova Opchiuchi n. 3). A. COLACHEVICH (Atti R. Accad. Lincei, 1933, [vi], 18, 307—310).—The intensities of the spectral lines of this star have been measured, and many of the lines identified.

O. J. W.

Electrical nature of iron sparks emitted from a grinding wheel. U. NAKAYA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 185—201).—The charge is positive at first, and changes to negative. Both positive and negative ions are emitted, at a rate of 10^{-2} to 10^{-3} e.s.u. per cm.

C. W. G.

Limits of validity of the Klein-Nishina formula. M. BRONSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 273—275).—The formula is more limited in its applicability than is indicated by Bohr (Atti Conv. Fis. Nucl., 1932, 125).

J. W. S.

X-Ray absorption spectra of the Au-Cu alloy. T. HAYASI (Naturwiss., 1934, 22, 90).—The absorption max. of the Au L_{111} spectrum of Au correspond with the Cu K absorption mm. of the Au-Cu alloy. The absorption min. of the first also correspond with the absorption max. of the second. Similarly, relationships are found with the Cu K absorption spectrum of pure Cu and the Au L_{111} spectrum of the alloy.

A. J. M.

Structure of K -rays of light atoms. II. A. HAUTOT (J. Phys. Radium, 1934, [vii], 5, 20—26; cf. A., 1933, 656, 760).—Previous results for O_2 , N_2 , C, B, and Be are amplified with improved apparatus.

N. M. B.

Measurements of the K -absorption edges of carbon, nitrogen, and oxygen, and of the components of carbon $K\alpha$. F. C. CHALKLIN and L. P. CHALKLIN (Phil. Mag., 1934, [vii], 17, 544—553).

H. J. E.

Fine structure of the $K\alpha$ line of beryllium. F. C. CHALKLIN (Nature, 1934, 133, 293—294).

L. S. T.

X-Ray spectra of the L series of silicon and silica. M. SIEGBAHN and T. MAGNUSSON (Nature, 1934, 133, 257; cf. this vol., 125).—Si exhibits a broad band containing max. at $134.3+0.5$ and

138.2±0.5 Å. with a sharp limit towards the shorter wave-lengths. SiO₂ gives a spectrogram of a different character with strong lines at 130.7 and 139.5 Å. and a broader, fainter line at 162 Å. L. S. T.

Extension of X-ray spectrography. Curved crystal focussing spectrograph. X-Ray emission spectra of gases. (MLLE.) Y. CAUCHOIS (Ann. Physique, 1934, [xi], 1, 215—266).—Using a curved-crystal spectrograph previously described (cf. A., 1932, 246) results are obtained for the K spectrum of Kr excited in a separate tube by an electron stream from a high-power Lennard-Coolidge tube. N. M. B.

Ionisation of the K shell by electron collision. D. G. SODEN (Ann. Physik, 1934, [v], 19, 409—433).—Theoretical. A. J. M.

Inner conversion in X-ray spectra. M. N. SAHA and J. B. MUKERJIE (Nature, 1934, 133, 377).—Inner conversion is responsible for many of the intensity anomalies observed in X-ray line spectra. L. S. T.

Ionisation of caesium vapour by ultra-violet light. J. KUNZ (Phil. Mag., 1934, [vii], 17, 483—491).—Measurements have been made at 25°, 75°, and 125° and with wave-lengths 3130, 2800, and 2537 Å. of the coulombs liberated per erg of the incident beam. The at. ionisation coeff. has a max. at the ionisation limit (3184 Å.), and a min. at 2800 Å. H. J. E.

Ionisation by collision in helium. J. S. TOWNSEND and S. P. MACCALLUM (Phil. Mag., 1934, [vii], 17, 678—698).—The coeffs. of ionisation have been measured and compared with vals. for Ne (cf. A., 1928, 567). Traces of impurities give similar effects for Ne and He. H. J. E.

Theory of Dirac's magnetic electron. L. DE BROGLIE (Arch. Sci. phys. nat., 1933, [v], 15, 465—483).

Theory of the positive electron. V. FOCK (Compt. rend. Acad. Sci. U.R.S.S., 1933, 267—271).—Mathematical. J. W. S.

Scattering and absorption of positive electrons traversing matter. J. THIBAUD and F. D. LA TOUR (Compt. rend., 1934, 198, 805—808; cf. this vol., 126).—Application of the method used in the case of Pt to screens of seventeen other elements shows that the range of positrons is generally equiv. to a passage through matter amounting to < 500 mg. per sq. cm., and μ/ρ is approx. const. = 8.5. This val. is also obtained by the same method for negative electrons. Both behave alike until the positrons, after losing most of their kinetic energy, begin to dematerialise. C. A. S.

Dematerialisation of positive electrons. J. THIBAUD (Compt. rend., 1934, 198, 562—564; cf. this vol., 126).—The conclusion as to the dematerialisation of positrons is substantiated by the facts that: (1) photographs show that the well-defined tracks of the positrons end in secondary radiation (photons) spreading in every direction; (2) the yield in photons is < 1, and more probably is 2 per positron, and such yield from a particle that has lost most of its kinetic

energy must be due to dematerialisation; and (3) a modification of the author's magnetic method shows the absorption of positrons of range 1—5×10² cm. (in air at ordinary pressure) to be exponential with $\mu/\rho=8.5$. Joliot's results (cf. *loc. cit.*) are adversely criticised as due to cosmic radiation. C. A. S.

Designation of the positive electron. H. DINGLE (Nature, 1934, 133, 330). L. S. T.

Positron. C. D. ANDERSON (Nature, 1934, 133, 313—316).—An address. L. S. T.

Radiation and ionisation produced by high-energy electrons. A. BRAMLEY (Nature, 1934, 133, 259). L. S. T.

External emission potential W_a . F. ROTHER and H. BOMKE (Z. Physik, 1934, 87, 806—809).—Electron diffraction measurements do not lead to vals. of W_a . This const. is 3.68 volts for Zn, and metals of higher valency have on the average one free electron per atom (cf. this vol., 3). A. B. D. C.

Contrasting properties of ions, zwitterions, and uncharged molecules. E. J. COHN (Science, 1934, 79, 83—84). L. S. T.

Field combinations in velocity- and mass-spectrography. I. W. HENNEBERG (Ann. Physik, 1934, [v], 19, 335—344).—Mathematical. The work of Bartky and Dempster (A., 1929, 863, 972) on the conditions for focussing positive rays is extended. The paths of charged particles in a homogeneous magnetic field and in the electric field of a cylindrical condenser are considered as regards focus, dispersion, and mass-separation. A. J. M.

Theoretical investigation of the mass-spectrometer without magnetic field. R. HERZOG and J. MATTAUCH (Ann. Physik, 1934, [v], 19, 345—386).—The theory of the mass-spectrometer of Smythe and Mattauch (A., 1932, 668) which uses two high-frequency fields instead of the magnetic field of the ordinary spectrograph is discussed. A. J. M.

Deposits of elements by high-frequency discharge. D. BANERJI and D. BHATTACHARYA (Phil. Mag., 1934, [vii], 17, 313—316). H. S. P.

At. wt. of lithium. M. HŁASKO and J. KUSZPECIŃSKA (Rocz. Chem., 1934, 14, 1—9).—Na and K were separated from Li₂CO₃ (I) by extracting the LiCl prepared from (I) with 1:1 EtOH-H₂O saturated with HCl. The LiCl so obtained still contained Fe, from which it was freed by conversion into (I), of which solutions saturated at 0° were heated at 100° in Pt vessels. The at. wt. of Li in LiCl prepared from (I) so pptd. is 6.934±0.001. R. T.

Constitution of dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. F. W. ASTON (Nature, 1934, 133, 327).—Dy (66) consists of 161, 162, 163, and 164 in approx. equal relative abundance; Ho (67) is simple 165; Er gives three strong lines 166, 167, 168, and a weak fourth 170; Tm (69) is simple 169; Yb (70) appears to contain 171, 172, 173, 174, and 176, of which 174 is the strongest; and Lu (71) is simple 175. None of these

elements shows isobares. International vals for the at. wts. of several of the rare earths need revision.

L. S. T.

Designation of heavy hydrogen. N. V. SIDGWICK (Nature, 1934, 133, 256).

L. S. T.

Nomenclature for the isotopes of hydrogen (proto- and deuto-hydrogen) and their compounds. W. D. HARKINS (Science, 1934, 79, 138—140).

L. S. T.

Isotopic nomenclature. J. B. FICKLEN (Science, 1934, 79, 140).

L. S. T.

Artificial disintegration of magnesium by polonium α -rays. H. KLARMANN (Z. Physik, 1934, 87, 411—424).—Four proton groups were observed, at least one of which is a resonance group.

A. B. D. C.

Relative velocities of the α -particles from radon, radium-A, and radium-C'. G. H. BRIGGS (Proc. Roy. Soc., 1934, A, 143, 604—617).—Using the direct deflexion method, the relative velocities of the α -particles from Rn, Ra-A, and Ra-C' have been measured with a probable error of 1 in 8×10^4 . The vals. found for Rn and Ra-A are $>$ those found by other observers.

L. L. B.

Emission of corpuscular rays (β -rays and positrons) and the symmetry between corpuscles and anti-corpuscles. J. L. DESTOUCHES (Compt. rend., 1934, 198, 467—471).—Wave mechanics are applied to demonstrate a theorem whereby the probability of the emission or absorption of a particle by an at. nucleus can be calc. This is applied to Joliot's "new form of radioactivity," and the corpuscle and anti-corpuscle, and also implies that the neutrino and antineutrino are physically indistinguishable (cf. this vol., 127, 234, 236).

C. H. S.

β -Spectrum of Th-B+C+C'. K. C. WANG (Z. Physik, 1934, 87, 633—646).— β -Spectra of Th-B+C+C' and of Th-C+C' were observed to determine the relative intensity of the most intense groups and the end of the primary spectra of Th-B and Th-C'.

A. B. D. C.

Calculation of internal conversion coefficients of γ -rays. J. B. FISK (Proc. Roy. Soc., 1934, A, 143, 674—678).—The internal conversion coeff. of γ -rays has been calc. for the L_1 shell of Ra-C, applying Taylor and Mott's theory (A., 1933, 1224). Previous results for the K shell have been corrected and extended, and limiting vals. for very soft γ -rays for the K and L_1 shells, quadripole and dipole, have been obtained.

L. L. B.

Anomalous absorption of high-energy γ -radiation. II, III. L. H. GRAY and G. T. P. TARRANT (Proc. Roy. Soc., 1934, A, 143, 681—706, 706—724; cf. A., 1932, 791).—II. The results of experiments on the absorption of the secondary γ -radiation emitted by at. nuclei when irradiated with very high-energy γ -radiation are discussed. There is definite experimental ground for rejecting any hypothesis which implies that the major portion of the emission is a "characteristic radiation" of the absorbing system.

III. Experiments are described which show that the whole of the energy of the high-frequency γ -radiation absorbed by a nucleus is re-emitted by it as secondary

radiation. This holds for all elements investigated (C, K, Cu, Fe, Sn, and Pb) with Th-C' radiation. This secondary radiation consists mainly of a radiation of energy $< 0.5 \times 10^6$ ev. The assumption of isotropic emission from which this result follows is justified between 60° and 145° .

L. L. B.

Secondary radiation of hard γ -rays. W. BOTHE and W. HORN (Naturwiss., 1934, 22, 106—107).—The intensity of secondary radiation emitted when hard γ -rays from Th-C' (4.7 X) fell on thin layers of scattering substances has been measured. For the lightest elements pure Compton radiation only was present, but for the higher elements an additional strongly anisotropic radiation was produced. The intensity of this additional radiation at 90° is proportional to the at. no. of the target. At 114° , thin graphite and Pb gave pure Compton radiation, but with greater thicknesses hard secondary radiation was produced, due to multiple scattering of the primary rays in the material of the target. For a 3-cm. thickness of Pb, however, a secondary radiation, of which the hardness approached that of the primary radiation, was produced, which was not due to multiple scattering.

A. J. M.

Equations of motion of a neutron. W. M. ELSASSER (Compt. rend., 1934, 198, 441—443).—Mathematical.

C. A. S.

Experiments with neutrons. L. MEITNER and K. PHILIPP (Z. Physik, 1934, 87, 484—497).—The neutron-proton collision is spherically symmetrical, and the effective cross-section depends on the neutron velocity. Neutron- N_2 collisions were also investigated, and the mass of the neutron is deduced to be 1.0056.

A. B. D. C.

Corpuscular radiation from atomic disintegration of lithium by rapid protons. K. DIEBNER and G. HOFFMANN (Naturwiss., 1934, 22, 119).—A new determination confirms the result of Rutherford and Oliphant that for protons of 70 kv., the ranges of the groups of α -particles emitted are 1.8 and 4.0 cm. Proton groups of ranges between 15 and 21 cm. were also found. The emission of α -rays commences when Li is bombarded with protons of 34 kv.

A. J. M.

Bombardment of the heavy isotope of hydrogen by α -particles. (LORD) RUTHERFORD and A. E. KEMPTON (Proc. Roy. Soc., 1934, A, 143, 724—730).—Experiments to test whether the diplon can be broken up into a neutron and proton by the bombardment of H_2 by the α -particles from Po gave inconclusive results. The no. of neutrons, if any, was < 1 in 10^7 of the no. of α -particles. The stopping power of the α -particles from Po is the same in H_2 as in H_2 . It is deduced that the max. range of recoil in air of the diplon in a head-on collision with an α -particle should be about 7% $>$ that of the proton; this is in agreement with experiment. No difference could be detected between the scattering of α -particles by H_2 and by H_2 , and it is concluded that the fields of force surrounding the diplon and the proton are the same.

L. L. B.

Production of induced radioactivity by high-velocity protons. J. D. COOKCROFT, C. W. GILBERT, and E. T. S. WALTON (Nature, 1934, 133, 328).

—Bombardment of an Acheson graphite target by protons of 600 kv. energy and examination by a Geiger counter for radiations (I) after the bombardment had ceased showed that the no. of counts (II) was increased approx. 40 times the natural effect. (II) decayed exponentially with time and the half-life period (III) is 10.5 ± 0.5 min. (I) consist, in part at least, of positive particles. The results suggest that the unstable isotope N^{13} is produced by the addition of a proton to O^{12} . The difference between the (III) observed and the val. obtained by Curie and Joliot (this vol., 234) may be due to the formation of N^{13} in a different excited state. No marked increase in (II) resulted when a mixed beam of heavy H ions and protons replaced the proton beam. L. S. T.

Disintegration of the separated isotopes of lithium by protons and by heavy hydrogen. M. L. OLIPHANT, E. S. SHIRE, and B. M. CROWTHER (Nature, 1934, 133, 377; cf. A., 1933, 1100).— Li^6 and Li^7 have been separated by two methods depending on the passage of Li ions through electric and magnetic fields. After fixation of the separated isotopes on metal discs by HCl, bombardment by protons (I) and deuterons (II) revealed several hundred disintegration particles per min. from Li^7 and about half this no. from Li^6 . With (I), Li^6 gives α -particles of 11.5 cm. range, and Li^7 α -particles of 8.4 cm. range; with (II), Li^6 gives α -particles of 13.2 cm. range and protons of 30 cm. range, whilst Li^7 gives α -particles up to 8 cm. range and neutrons. L. S. T.

Chemical separation of new positive electron-emitting radioelements. (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1934, 198, 559—561; cf. this vol., 234).—The probable formation of radioactive, positron-emitting N^{13} , Si^{27} , and P^{30} (for which the names *radio-nitrogen*, *-silicon*, and *-phosphorus* are proposed) by capture of α -particles from Po by B, Mg, and Al, respectively, is supported by chemical examination of irradiated BN and Al. The radioelement from B behaved like N, that from Al as P. C. A. S.

Representation of nuclear transformations. G. PETIAU (Compt. rend., 1934, 198, 564—566).—Theoretical (cf. A., 1933, 1224; this vol., 236). C. A. S.

Half-value period of uranium. II. O. A. GRATIAS (Phil. Mag., 1934, [vii], 17, 491—496).—U II, produced by decay of $U-X_1$, is not completely separated by electrolysis (cf. Collie, A., 1931, 891). U II recovered from the solution and separated from $U-X_1$ and Io had a half-val. period of 1.70×10^5 years. H. J. E.

Half-value period of radium-D. E. WALLING (Z. Physik, 1934, 87, 603—606).—This is given as 22.3 years with an error $\pm 2\%$. A. B. D. C.

Diffusion coefficient of radium emanation. N. MORTARA (Atti R. Accad. Lincei, 1933, [vi], 17, 949—951).—The diffusion coeff. is found to be 0.11. O. J. W.

Distribution of radium in crystals of radiferous barium bromide. B. E. MARQUES (Compt. rend., 1934, 198, 819—821; cf. this vol., 22).—There is a marked decrease in the relative amount of Ra from the centre to the periphery of such crystals (cf. A., 1929, 132). C. A. S.

Decomposition of lead atoms. A. SMITS, (FRL.) H. S. V. MEINESZ, (FRL.) J. A. A. KRUGER, and H. G. ROEBERSEN (Z. Elektrochem., 1934, 40, 71—73).—Irradiation of Pb plates by X-rays in air renders them active, but not so Al plates. An air current has no effect on the activity, which seems to exclude the possibility of its being due to radioactive dust. No activation could be obtained in a vac., and later experiments gave none in air. Irradiation with sunlight gave doubtful results. M. S. B.

Steady states produced by radiation with application to the distribution of atmospheric ozone. O. R. WULF (Phil. Mag., 1934, [vii], 17, 251—263).—Theoretical. The equilibrium distribution of O_3 in the earth's atm. due to the absorption of radiation is calc., mechanical transport of the gases being neglected. The O_3 will not occur in a layer, but be spread over a range of altitude. Calculations are also made regarding stellar atm. H. S. P.

Contemporary knowledge of cosmic rays. P. AUGER (J. Phys. Radium, 1934, [vii], 5, 1—5).—A concise summary of available data and explanatory hypotheses. N. M. B.

Three types of cosmic-ray fluctuations and their significance. R. A. MILLIKAN, C. D. ANDERSON, and H. V. NEHER (Physical Rev., 1934, [ii], 45, 141—143).—A theory of cosmic-ray bursts attributes the released energy to the battery which charges the electroscope. Assuming the remainder of the observed ionisation to be due to positrons and "negatrons," fluctuations due to random distribution of these electron shots, and hence the % of cosmic ray "showers," can be computed. N. M. B.

Nature of statistical fluctuations with applications to cosmic rays. R. D. EVANS (Physical Rev., 1934, [ii], 45, 144—151).—Mathematical. The effect of random processes in relation to ionisation chambers and counters is investigated. N. M. B.

Fluctuations of cosmic rays. III. W. MESSERSCHMIDT (Z. Physik, 1934, 87, 800—805).—Daily fluctuations are recorded. A. B. D. C.

Quantum mechanics of photons. Pauli's approximation. A. PROCA (Compt. rend., 1934, 198, 452—454; cf. this vol., 236).—Mathematical. As an interpretation of negative energy of a particle, photon, or electron, it is suggested that its sign must indicate merely the direction of rotation of some component of a field attached to the particle. C. A. S.

Particles which can be associated with propagation of a light wave. A. PROCA (Compt. rend., 1934, 198, 643—645; cf. this vol., 236).—It is shown mathematically that a free particle, of zero mass when in repose, and according to Dirac's equations, can be associated with every group of light waves subject to Maxwell's equations. Such a particle, in a state in which its energy is $h\nu$, corresponds with circularly polarised light of frequency ν , which is dextro if the energy of the particle is positive, laevo if negative. The particle is not a photon, as its spin is $0.5h/2\pi$, but it resembles Pauli's neutrino, which, coupled with an antineutrino, gives a photon. C. A. S.

Waves and photons. I. Schrödinger approximation. A. PROCA (J. Phys. Radium, 1934, [vii], 5, 6—19).—Mathematical. An attempt to establish a theory of photons in configuration space, with a view of eliminating difficulties in radiation theory, leads to three types of approximation analogous to those of Dirac, Pauli, and Schrödinger, of which the last-named, examined here, shows that classical energy density expression is true only to a first approximation and is inapplicable to light.

N. M. B.

Hydrogen molecule ion. G. JAFFE (Z. Physik, 1934, 87, 535—544).—The ξ equation is solved in the form of a convergent power series.

A. B. D. C.

Calculations of atomic wave functions. II. K^+ and Cs^+ . D. R. HARTREE (Proc. Roy. Soc., 1934, A, 143, 506—517).—The results of calculations of at. wave functions by the method of the "self-consistent field" (cf. A., 1933, 1101) are given for K^+ and Cs^+ , together with some additional results for Cu^+ .

L. L. B.

Relation of the H function and entropy according to Fermi statistics. M. SATO (Z. Physik, 1934, 87, 498—499).—The ordinary relation holds.

A. B. D. C.

Elementary indeterminacy, limit of the periodic system, and the mass ratio of the electron and proton. W. GLASER and K. SITTE (Z. Physik, 1934, 87, 674—685).—The limit of ninety-two chemical elements is shown to follow from an elementary indeterminacy in time. Assuming the neutron to be a quantum-mechanical system of proton and electron, the elementary indeterminacy gives the electron-proton mass ratio.

A. B. D. C.

Constitution of heavy nuclei. A. SCHIDLÖF (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 223—227).—Theoretical.

R. S.

Molecular and micellar dissymmetry. C. E. GUYE (Arch. Sci. phys. nat., [v], 15, Suppl., 219—223).

R. S.

Self forces of elementary particles. III. G. WENTZEL (Z. Physik, 1934, 87, 726—733).—Theoretical.

A. B. D. C.

Value of e/m . W. N. BOND (Nature, 1934, 133, 327).

L. S. T.

Gratings as an aid to photographic spectrophotometry. R. LANDWEHR (Z. Physik, 1934, 87, 447—459).—The method of Hertzprung and Merton of using a coarse grating crossed with the normal dispersion apparatus to give a series of lines of varying intensity for each original line has been developed.

A. B. D. C.

Resonance excitation of the thallium spectrum in thallium halide vapour. G. G. NEUJMIN (Compt. rend. Acad. Sci., U.R.S.S., 1933, 213—214).—On illuminating TlX vapours with ultra-violet light, emission lines of the metal were observed which could not be ascribed to photo-dissociation of the TlX. The intensities of these lines were dependent on the intensity of the exciting light; the exciting wavelengths differ for each energy level, and lie near to

an absorption line of Tl. A probable explanation is suggested.

W. R. A.

Spectrum of F_2O . A. GLISSMANN and H. J. SCHUMACHER (Z. physikal. Chem., 1934, B, 24, 328—334).—Absorption starts at about 5400 Å., and is still very strong at 2100 Å. It is continuous, and exhibits several max. It is concluded that the whole absorption region corresponds with primary dissociation into F_2+O or $F+FO$; a max. below 2100 Å. may indicate dissociation into three atoms. Light absorption is accompanied by decomp. with formation of O, much of the F formed yielding, in quartz, SiF_4 and O.

R. C.

Measurements of the intensity and width of predissociation lines of the AlH molecule. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, 1934, 87, 545—546).—Farkas and Levy (A., 1933, 879) have omitted the "apparatus width" in their observations on these lines.

A. B. D. C.

Band spectrum of phosphorus nitride. P. N. GHOSH and A. C. DATTA (Z. Physik, 1934, 87, 500—504).—Observations are given in agreement with Curry, L. Herzberg, and G. Herzberg (cf. this vol., 7).

A. B. D. C.

Spectrum of gadolinium oxide. G. PICCARDI (Gazzetta, 1933, 63, 887—898).—The flame spectrum of GdO between 4462 and 6272 Å. is recorded and the lines are classified. The emission is due to the GdO mol. A new spectrum in the blue (4614—4854 Å.) and several new bands in the red are described. The blue system is relatively sensitive to temp. changes.

H. F. G.

Rotational analysis of the absorption bands of ICl . W. E. CURTIS and J. PATKOWSKI (Phil. Trans., 1934, A, 232, 395—430).—Analyses of twelve bands of the progressions ($v''-0, 1, 2$) and each consisting of P, Q , and R branches are tabulated. The rotation const. B is determined for each state. Band origins are established. A very small A type doubling is found, and its variation with J is examined. Relationships between rotational and vibrational consts. are tested, and vals. of the chief consts. are found.

N. M. B.

Thermo-optical dissociation of sulphur dioxide. K. WIELAND (Trans. Faraday Soc., 1934, 30, 260—265).—The absorption spectrum of SO_2 vapour at $<450^\circ$ has been extended to 1600 Å. Light from the H_2 lamp does not cause decomp. at room temp., but above 300° , parallel with the fading of the SO_2 bands, two systems of bands due to S_2 develop in the ranges 2850—2570 Å. and 1800—1650 Å. (strong). The changes are reversed by fall of temp. Since the reaction $SO_2 \rightarrow 1/2S_2 + O_2$ requires 83 kg.-cal., the net thermo-optical dissociation $SO_2 \rightarrow 1/6S_2 + 4/6SO_3$ (requires 12.6 kg.-cal.) is more probable (cf. A., 1933, 6).

J. G. A. G.

Absolute values of the optical absorption constants of crystals of the alkali halides in the region of their ultra-violet characteristic frequency. G. BAUER (Ann. Physik, 1934, [v], 19, 434—464).—The absorption consts. of vaporised layers of NaBr, KBr, and KI were determined in the neighbourhood of the first ultra-violet absorption

band. The mechanism of the absorption is discussed on the basis of electro-magnetic theory. A. J. M.

Titanium oxide and zirconium oxide bands in stellar spectra. R. S. RICHARDSON (Astrophys. J., 1933, 78, 354—358).—The % of ZrO and TiO mols. dissociated at different temp. and pressures has been calc. L. S. T.

Red titanium oxide system in α_1 Herculis. N. T. BOBROVNIKOFF (Astrophys. J., 1933, 78, 211—218).—66 bands, 11 of which have not been observed in the laboratory, have been measured between 6292 and 8506 Å. in the spectrum of the red system of TiO. L. S. T.

Photographic measurement of the transmission of fluorite in the extreme ultra-violet. E. G. SCHNEIDER (Physical Rev., 1934, [ii], 45, 152—153).—Transmission measurements by photographic methods and by a photo-electric cell are compared for the range 1600—1240 Å. (cf. following abstract). N. M. B.

Photo-electric measurements of the transmission of fluorite in the Schumann region. W. M. POWELL, jun. (Physical Rev., 1934, [ii], 45, 154—157).—Transmission coeffs. and the ratio intensity of light entering cell/current from cell were measured at ten wave-lengths in the range 1600—1235 Å. N. M. B.

Thermo-luminescence spectra of fluorites. IV. Spectra restored by X-rays. E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 212—223; cf. this vol., 130).—Fluorites can be classified as those which, after heating, (a) are restored by X-rays to their original condition, (b) give the same bands, but of different relative intensities, (c) give new bands. C. W. G.

Cathodo-luminescence spectra of fluorites, calcites, and certain synthesised phosphors containing samarium. J. YOSHIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 224—247).—Green fluorites generally contain more rare earths than those of other colours. C. W. G.

Polyatomic molecules. Structure and activation of benzaldehyde. III. Optical properties of the benzaldehyde molecule. F. ALMÄSY (J. Chim. phys., 1933, 30, 713—725; cf. A., 1929, 409).—The absorption spectra of the vapour and solutions in n -C₆H₁₄ are very similar, and consist of three regions. The frequencies of the vibrational terms correspond with those of the Raman and infra-red spectra. As the temp. is raised to 270° the narrow bands change over to a continuous spectrum and photo-dissociation occurs. At 270°, radiation below λ 3200 produces dissociation, but that $< \lambda$ 2438 gives photochemical decomp. into CO and C₆H₆ at room temp. J. G. A. G.

Ultra-violet absorption spectra of some aromatic substances. I. A. HILLMER and P. SCHORNING (Z. physikal. Chem., 1934, 167, 407—420). The effect on the absorption spectrum of the introduction into C₆H₆, PhPr^a, allyl- and propenyl-benzene of one or two phenolic OH or alkoxyl groups into the α -positions has been studied. R. C.

Determination of the light transmission of anisotropic melts of p -azoxyanisole in magnetic

fields. Swarm theory of liquid crystals. W. KAST and L. S. ORNSTEIN (Z. Physik, 1934, 87, 763—767).—Determination of this light transmission immediately a magnetic field is removed shows that orientation imposed by the field is destroyed in accordance with the swarm theory. A. B. D. C.

Infra-red absorption spectra of nitrogen dioxide and tetroxide. L. HARRIS and G. W. KING (J. Chem. Physics, 1934, 2, 51—57).—Data are given for new bands in the region 1.9—4 μ for NO₂, analysed as combinations of two fundamentals, and for N₂O₄, interpreted as combinations and harmonics of reported fundamentals. The spectrum demands models in which the NO₂ groups are joined by the N atoms, and there is evidence for non-planar arrangement of the NO₂ groups in the mol. N. M. B.

Infra-red absorption spectra, and the structure of polyatomic molecules. R. TITEICA (Bul. Soc. Fiz. Roman., 1933, No. 57, 31—38).—Data are given for the infra-red absorption spectra of MeOH, EtOH (cf. A., 1933, 337), and COMe₃, in the low-pressure gaseous condition, and the results have been compared with the Raman spectra, and with those calc. from Mecke's formula (Leipzig Vortrage, 1931). The distances C—C=1.50 Å., and the angle of C—C—C=127°. R. T.

Infra-red absorption of stereoisomeric 1:2-dimethylcyclohexanes. O. MILLER and J. LECOMTE (Compt. rend., 1934, 198, 812—813; cf. A., 1933, 815, 990).—The infra-red absorption spectra (333—1455 Å.) of the *cis*- and *trans*-isomerides differ markedly *inter se*, and from their Raman spectra. C. A. S.

Reflexion spectrum of quartz in the region of 9 μ . S. SILVERMAN (Physical Rev., 1934, [ii], 45, 158—160; cf. A., 1931, 408).—Previous work is extended, using polarised light and a crystal cut parallel to the optic axis. Complex fine structure was found. N. M. B.

Rotational Raman effect in liquids. S. BHAGAVANTAM (Indian J. Physics, 1933, 8, 197—207).—The intensity distribution in the rotational Raman spectra of C₆H₆, HCO₂H, and molten salol are not in accord with any existing theory. Regarding the liquid state as consisting partly of gas mols. and partly of solid mols., and applying Pauling's theory (A., 1930, 1357) for determining the state of motion of mols. in a solid, it is concluded that liquids are of two types. In the first type (H₂, HCl, O₂, N₂, etc.) the intensity distribution should accord with the gas laws; in the second type neither the intensity nor its distribution can be predicted from the gas laws, the patterns being due to internal oscillations in the liquid similar to those existing in a solid. J. W. S.

Molecular scattering of light in liquids. E. CANALS, (Mlle.) G. CAUQUIL, and P. PEYROT (Compt. rend., 1934, 198, 471—473; cf. A., 1926, 559).—The depolarisation factor, ρ , for Hg light filtered through quinine sulphate and scattered at 90° to the incident beam, has been determined for twelve cyclanes, twelve cyclenes, ten alkyl halides or esters, and three other compounds. Few generalisations are possible:

ρ for the cyclanes (0.077—0.222) is definitely $<$ for the cyclenes (0.222—0.375), and the variations point to a non-planar configuration for both. Introduction of an alkyl group generally increases ρ . C. A. S.

Raman effect. XXXI. Raman spectrum of organic substances. (Multi-substituted benzenes. III.) K. W. F. KOHLRAUSCH (Monatsh., 1933, 63, 427—444).—Data are given for *o*-, *m*-, *p*-compounds of the type C_6H_4MeX , where X is Me, NH_2 , OH, CN, F, Cl, Br, I, CO_2Me , or CO_2Et . E. S. H.

Raman effect in nitrobenzene. H. F. HERTLEIN (Z. Physik, 1934, 87, 744—748).—The sharp change in dielectric const. observed by Wolfke and Mazur (A., 1932, 329) just above the m.p. of $PhNO_2$ is not reflected in the Raman spectrum, and the two phases cannot therefore differ in at. structure. A. B. D. C.

Raman effect. XXIX. Raman spectra of halogen acetic esters. H. C. CHENG (Z. physikal. Chem., 1934, B, 24, 293—312; cf. A., 1933, 1228).—From a study of the esters of chloro- and bromo-acetic acids frequencies have been assigned to various groups. If in $X\cdot CO_2R$ ($X=H$ or Me) X is replaced by Cl, the frequency of the CO group is increased considerably, but if the Cl is separated from the CO by CH_2 , the increase is slight, and the introduction of two or three Cl atoms is required to produce a notable increase. With progressive substitution of CO_2Et for H in $EtOAc$ the frequency of the CO group rises steadily, whereas substitution by Me causes a continual fall. The CO frequencies of all the Pr^s esters lie below the average val. for normal ester chains. The results in general justify the assumption that the spectrum of $X\cdot CO_2R$ consists of the superimposed partial spectra of \bar{X} , CO, and OR. R. C.

Molecular scattering of light in fluorescent liquids. [Determination of quinine.] E. CANALS and P. PEYROT (Compt. rend., 1934, 198, 746—749).—With dil. H_2SO_4 solutions of quinine sulphate of const. p_H (2), but varying concn. in quinine, at 18° , and a quartz-Hg lamp (cf. A., 1927, 932) the depolarisation factor, ρ , is const., whilst the intensity of fluorescence is proportional to c and obeys Vavilov's law (cf. A., 1925, ii, 474). The proportionality is such that the method may be used for the determination of small amounts of quinine. C. A. S.

Circular polarisation of Raman lines of pinene illuminated by circularly polarised light and observed longitudinally. P. DAURE (Compt. rend., 1934, 198, 725—727; cf. A., 1930, 1498; 1932, 212).—The ratio of the intensities of the light polarised in the reverse and same directions as that of the incident beam has been determined visually for forty-four lines ($\Delta\nu=139$ —1659 cm^{-1}). It varies for the different lines, but is independent of the direction of rotation of the incident beam. C. A. S.

Scattering of light and molecular polymorphism. R. LUCAS (Compt. rend., 1934, 198, 721—722).—It is suggested that, as in the case of rotatory power etc., polymorphism will affect scattering by a liquid, and in the case of Raman spectra will increase the no. and modify the relative intensities

of the lines, and that this explains the anomalies observed in the case of C_6H_6 (cf. A., 1927, 295; 1933, 889; this vol., 132). C. A. S.

Fine structure of the Rayleigh radiation. W. RAMM (Physikal. Z., 1934, 35, 111—113; cf. A., 1932, 445).—The fine structure of the radiation emitted when monochromatic light is scattered by $PhMo$ and CS_2 has been studied. Lines displaced towards the red and blue, respectively, have been found, as required by theory. Their distance from the principal line is given by Brillouin's equation (Ann. Physique, 1922, [ix], 17, 88). Further lines of higher orders were not obtained even with the above strongly anisotropic substances (cf. A., 1930, 1237, 1345, 1498; 1932, 676); anisotropic substances show a continuous ground. A. J. M.

Polarisation of Rayleigh radiation in crystals. F. MATOSI (Physikal. Z., 1934, 35, 148—149).—The polarisation of the Rayleigh scattered radiation in quartz and calcite has been investigated, and the presence of an anisotropic effect, different from that of Lorentz, demonstrated. A. J. M.

Continuous spectrum in the light scattered by glycerol and other liquids. O. H. HOWDEN and W. H. MARTIN (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 91—96).—Repeated recrystallisation of glycerol (I) diminishes the continuous spectrum (II) in the Raman effect. (II) reappears if purified (I) is irradiated with the whole Hg spectrum, owing to light scattered by a fluorescent impurity produced by the photochemical decomp. of (I) by light of short wave-lengths. Hg line 4358 Å. is best for the investigation of Raman spectra to avoid decomp. of liquids by light < 4100 Å. H. S. P.

Influence of solvent on variation of fluorescent power of dyes as function of concentration of solution. J. BOUCHARD (Compt. rend., 1934, 198, 649—651).—The linear relation between $\log \Phi$ and c required by $\Phi = \Phi_0 e^{-kc}$ (cf. A., 1924, ii, 713) was verified for many fluorescent dyes in various solvents, with const. p_H . If the viscosity, η , of the solvent is approx. that of H_2O , k varies with the dielectric const., but if η is markedly $>$ than that of H_2O , k decreases more rapidly. The equation giving Φ in presence of an inhibitor (cf. A., 1933, 337) is valid only when neither η or ϵ is affected thereby. C. A. S.

Polarisation of fluorescence. I. Solutions of some dyes. S. M. MITRA (Indian J. Physics, 1933, 8, 171—188).—The degree of polarisation of the fluorescence of solutions of fluorescein, eosin, Magdalar, red, aesculin, rhodamine B, and erythrosin in H_2O -glycerol mixtures varies with the wave-length of the exciting radiation, temp., concn., and the H_2O :glycerol ratio. J. W. S.

[Fluorescence of substances in] filtered ultra-violet light. N. D. COSTEANU and A. S. COCOSINSCHI (Bul. Fac. Stiinte Cernauti, 1931, 5, 169—175; Chem. Zentr., 1933, ii, 1150).—All uranyl compounds show a group of lines between 4850 and 5700 Å., and a red line, in the fluorescence spectrograms. Na H sulphosalicylate gives a faded field in the red, Na salicylate between 4100 and 4950 Å., Hg_2Cl_2 a weak faded field in the red, $N_2H_4\cdot H_2O$ between 4250 and

4900 Å. Ignited ZnCO_3 gives brown to dirty yellow fluorescence. L. S. T.

Excitation of alkali halide crystals. M. V. SAVOST'YANOVA (Compt. rend. Acad. Sci., U.R.S.S., 1934, 115—118).—KCl, KBr, and KI were illuminated and the phosphorescence was examined. W. R. A.

Fluorescence of a marine diatom and the fluorescence spectrum of its chlorophyll-like colouring matter. E. BACHRACH and C. DHÉRE (Compt. rend. Soc. Biol., 1933, 108, 385—387; Chem. Zentr., 1933, ii, 1195). L. S. T.

Influence of intensity of light on photovoltaic phenomena. R. AUDUBERT and (Mlle.) G. LEBRUN (Compt. rend., 1934, 198, 729—731; cf. A., 1933, 662).—The relation $E = (RT/nF) \log(1 + aI)$, where a is a const. depending on the nature of the photo-sensitive substance, the liquid in contact therewith, and the temp., I the intensity of the light, and R , T , n , and F have their usual meanings, is valid for Cu/CuO, Cu/Cu₂O and several other electrodes, if $n=1$. It is concluded that the photolysis of H_2O is $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$. C. A. S.

Autoxidation and ionisation potentials of molecules. N. A. MILAS (J. Amer. Chem. Soc., 1934, 56, 486—487).—The ionisation potentials (I) of the hydrides of elements in each of the fifth, sixth, and seventh groups of the periodic table decrease with rise in the at. wt. The regular diminution of (I) denotes an increased looseness of the reactive unshared electrons, and, hence, a relative increase in the tendency towards autoxidation. H. B.

Rectifying layer of lead sulphide. F. HEINECK (Physikal. Z., 1934, 35, 113—118).—The effect of various gases (H_2 , O_2 , N_2 , CO_2 , H_2S) and vapours (H_2O , C_6H_6 , COMe_2 , MeOH) on the rectifying action of sublimed PbS was investigated. H_2 , O_2 , N_2 , and CO_2 caused inactive PbS to become a weak rectifier, but the effect disappeared on removing the gas in vac. H_2S has no effect. The vapours caused a considerable increase in rectifying power, which was removed in vac. in the case of H_2O , but remained with the others. Pure PbS does not rectify, the presence of foreign substances on the surface of the semi-conductor being necessary. There is no relationship between rectifying power and contact potential. A. J. M.

Ionisation potential and heat of formation of non-polar molecules. J. SAVARD (Compt. rend., 1934, 198, 751—753; cf. this vol., 11).— D calc. from the relation previously deduced agrees with the val. determined thermochemically or spectrographically for H_2 , N_2 , C_2 , CO , CO_2 , CH_4 , HCl , Cl_2 , SO_2 , HCN , C_2N_2 , and O_2 ; the results for the four last point, respectively, to mols. S_8 and S_8 in S vapour; HCN as $\text{H}^+\cdot\text{C}^-\cdot\text{N}$; C_2N_2 as $\text{N}^+\cdot\text{C}^-\cdot\text{C}^-\cdot\text{N}$; and O_2 as $\text{O}^+\cdot\text{O}$. C. A. S.

Inner potential of semi-conductors. K. R. DIXIT (Phil. Mag., 1934, [vii], 17, 732—733).—The val. for ZnS is $+2.6 \pm 1$ volts (not -4.8 ; cf. A., 1933, 1230).

Electronic conduction in crystals. R. W. POHL (Physikal. Z., 1934, 35, 107—111).—The presence of electrons capable of wandering under an applied e.m.f. in transparent crystals is shown by the color-

ation produced in KBr in the neighbourhood of a point electrode. The absorption spectrum of this coloration is very simple, and alteration of temp. affects both the position of the absorption max. and the width of the band. Wandering of the electrons is accompanied by an electrolytic compensating charge effect. The photochemical production of colour centres is also due to freedom of motion of electrons. A. J. M.

Electrical conductivity in thin metal layers. A. JAGERSBERGER (Z. Physik, 1934, 87, 513—517).—Theoretical. Variation of the density of free electrons with thickness cannot be obtained from variation of the sp. resistance. A. B. D. C.

Bloch's theory of electrical conductivity. E. KRETSCHMANN (Z. Physik, 1934, 87, 518—534).—This theory is criticised. A. B. D. C.

Electrical conductivity of thin layers of hydrocarbons. A. E. VAN ARKEL and W. KOOPMAN (Physica, 1933, 13, 189—192; Chem. Zentr., 1933, ii, 1152—1153).—Thin layers of C_6H_6 , C_6H_{14} , PhNO_2 , $\text{C}_6\text{H}_4\text{Cl}_2$, and hexachloropropylene like those of paraffin oil conduct an electric current. Conduction (I) is due to conducting C particles formed by decomp. (I) does not occur in liquid N_2 . The distance between the electrodes varies with the nature of the electrode material. With Fe electrodes microscopic glowing points presumably of Fe_2O_3 are visible. L. S. T.

High-frequency loss, and molecular structure. P. DEBYE (Physikal. Z., 1934, 35, 101—106).—Pure solvents with non-polar mols. show no loss. Loss occurs only with polar mols. and increases with increase of dipole moment. With substances with the same dipole moment, it increases with the size of the mol. The connexion between the relaxation time and the viscosity of the solvent is discussed. The calculation of the loss in a mixture is given. A. J. M.

Anisotropic liquids (liquid crystals) in electric fields. III. Measurements of dielectric loss of liquid-crystalline *p*-azoxyanisole. W. KAST and P. J. BOUMA (Z. Physik, 1934, 87, 753—762).—Observations of the variation of energy loss with frequency and temp. for the liquid and solid cryst. states, distinguish loss max. peculiar to the liquid state from those due to dipole mols. A. B. D. C.

Dispersion in short waves. R. LUTHI (Helv. phys. Acta, 1933, 6, 139—159; Chem. Zentr., 1933, ii, 1151).—The anomalous dispersion of the dielectric const. of dil. solutions of PhNO_2 , BuOH , and $\text{C}_5\text{H}_{11}\cdot\text{OH}$ in a mineral oil of high has been investigated for temp. from 0° to 35° . L. S. T.

Dielectric coefficients of gases. II. Lower hydrides of carbon and silicon, oxygen, nitrogen, oxides of nitrogen and carbon, and fluorides of silicon and sulphur. H. E. WATSON, G. G. RAO, and K. L. RAMASWAMY (Proc. Roy. Soc., 1934, A, 143, 558—588).—The dielectric coeffs. of CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , C_2H_2 , SiH_4 , Si_2H_6 , CO , CO_2 , O_2 , N_2 , air, N_2O , NO , SiF_4 , and SF_6 have been measured by the "series" method previously employed (A., 1931, 1113) and also by the "parallel" method, using a condenser specially constructed for measuring very small capacity changes. The results given by the two methods are in satisfactory agreement, and also agree

in most cases with the vals. given by previous observers. Compressibilities have been determined by making measurements at different pressures. Of the gases studied, only C_2H_6 , CO, N_2O , and NO have a measurable electric moment. The existence of such a moment for N_2O is considered in connexion with the structure of the mol., and the possibility of a slightly bent N-O-N mol. is discussed. L. L. B.

Electric dipole moments of nitrosomesitylene and of the bimolecular forms of nitrosomesitylene and β -nitroso- β -dimethylhexane. D. L. HAMMICK, R. G. A. NEW, and R. B. WILLIAMS (J.C.S., 1934, 29—32).—The moment of bimol. nitrosomesitylene is 1.37 at 8° and 1.63 at 25°, and that of β -nitroso- β -dimethylhexane is 0.99. This supports the formula $R-N \rightarrow N-R$. W. R. A.



Dipole induction effect for molecular compounds. G. BRIEGLER and J. KAMBEITZ (Naturwiss., 1934, 22, 105—106; cf. A., 1933, 25).—Direct experimental proof of the existence of moments induced in non-polar mols. by polar mols. in mol. compounds is difficult. The induced moments in the case of $m-C_6H_4(NO_2)_2$, $C_{10}H_8$, and $PhNO_2$, $C_{10}H_8$ should be small, but demonstrable. $PhNO_2$ should be $> \mu_{ind. m-C_6H_4(NO_2)_2}$. The dipole moments of $s-C_6H_3(NO_2)_3$, $m-C_6H_4(NO_2)_2$, $PhNO_2$, and $PhCl$ in $C_{10}H_8$ and in C_6H_6 are given. All but $PhCl$ form mol. compounds with $C_{10}H_8$. The moments in $C_{10}H_8$ are $<$ in C_6H_6 , but the difference is small in the case of $PhCl$. The greatest effect is with $PhNO_2$. This decrease in the moment in $C_{10}H_8$ is ascribed to the induced moment. A. J. M.

Relation between dipole moment and cohesive forces. VI. A. E. VAN ARKEL (Rec. trav. chim., 1934, 53, 246—256; cf. A., 1933, 8).—The distribution of substituted groups in various saturated, unsaturated, and halogenated hydrocarbon series is correlated with variations of b.p. H. J. E.

Dispersion in nitrogen. C. E. BENNETT (Physical Rev., 1934, [ii], 45, 200—207).—High-precision measurements with improved apparatus were made at four wave-lengths corresponding with pressure runs up to 14 atm. Results at n.t.p. are, for the Cauchy dispersion consts. A and B , $A_0 - 1 = 0.0002932$, $B_0 = 1.637 \times 10^{-14}$, and calc. dielectric const. 1.0005864. N. M. B.

Refractive index of H^2H^2O ; refractive index and density of solutions of H^2H^2O in H^1H^1O . D. B. LUTEN, jun. (Physical Rev., 1934, [ii], 45, 161—165).—Data are tabulated for a range of concns., temp., and wave-lengths. The dispersion of H^2O is $<$ that of H^1O . Typical vals. for mol. refraction at 20° for D line are 3.7121 for H^2O and 3.687 for H^1O . N. M. B.

Refraction and dispersion of gases and vapours. I. General introduction. K. FAJANS. II. Refraction and dispersion of air, hydrogen sulphide, and water vapour in the visible region. J. WÜST and H. REINDEL. III. Refraction and dispersion of mercury halide vapours in the visible region. M. A. BREDIG, T. VON HIRSCH,

and J. WÜST. IV. Refraction and dispersion of aluminium chloride and bromide vapours in the visible region. M. A. BREDIG and F. K. V. KOCH. V. Refraction and dispersion of aluminium iodide vapour in the visible region. F. K. V. KOCH and H. KOHNER. VI. Refraction and dispersion of vapours of some halides of elements in the fourth group of the periodic system in the visible region. P. HÖLEMANN and H. GOLDSCHMIDT. VII. Refraction and dispersion of vapours of stannous halides in the visible region. H. GOLDSCHMIDT and P. HÖLEMANN (Z. physikal. Chem., 1934, B, 24, 103—154, 155—176, 177—186, 187—193, 194—198, 199—209, 210—214).—I. In deriving vals. for the refractivity, R , of free gaseous ions from data for compounds or solutions, account must be taken of the effect on R of the fields of force of adjacent particles. Fajans and Joos's data for R for gaseous ions of the inert gas type and for the apparent refraction of ions in aq. solution (A., 1924, ii, 372) have been revised. For Na^+ in aq. solution the most probable val. of R_0 is 0.25 ± 0.05 c.c. The methods used by other authors for calculating R for ions are reviewed. The vals. calc. by Pauling (A., 1927, 394) and Hasse (A., 1931, 14) for gaseous ions of the He type are more trustworthy than Fajans and Joos' vals. For many ions the latter closely agree with Mayer's vals. (A., 1933, 550). The relative change, Q , in the refraction, R^I , of a halogen ion caused by addition of H^+ increases with R^I from zero when R^I is zero to a limiting val., 0.28 , $Q = 0.2859(1 - e^{-0.2848R^I})$. This relation can be utilised to derive R^I from the R of the product, and also gives acceptable results when used to calculate R^I for other single-charged gaseous ions, such as SH^+ and OH^+ . The relation is applicable to the addition of H^+ to neutral mols., but for the addition to a doubly-charged anion Q is $>$ for addition to a singly-charged anion. The refractometric relations of halides with cations not of the inert gas type (heavy-metal halides) differ from those of halides with cations of the inert gas type, probably because the former class of compounds constitute a transitional type between ideal ionic linking and non-polar linking. The wave-mechanical resonance energy must be responsible for a considerable proportion of the total energy of linking in compounds of this type.

II. The use of a Zehnder interferometer for the measurement of n for gases and vapours over a wide temp. range is described. Measurement of n and dispersion, D , for H_2S at room temp. and D for H_2O vapour at 130—150° gave results agreeing with those of Cuthbertson (A., 1913, ii, 358).

III. n and D of $HgCl_2$, $HgBr_2$, and HgI_2 vapours at 340° have been measured. n for $HgBr_2$ at 440° shows that the effect of temp. on n is $<$ 0.003% per degree. The mol. refractions of the Hg^{II} halides are not additively constituted of the R of the free gaseous ions, and the deviations from additivity do not accord with the relations observed by Fajans and Joos with the H and alkali halides. The same is true of the mol. dispersions. That Hg^{II} is not of the inert gas type is the probable explanation.

IV. The n and D of Al_2Cl_6 and Al_2Br_6 in the vapour state have been measured at 230° and 300°.

respectively. The fall in R on formation of the salt from the free gaseous ions, ΔR , is greater for Al_2Br_6 than for Al_2Cl_6 , and the vals. fit in with those for the corresponding effect with other cations of the He type.

V. The n and D of Al_2I_6 vapour have been measured at 380° . ΔR is $<$ would be anticipated from the vals. for Al_2Cl_6 and Al_2Br_6 and the regularities observed by Fajans with alkali and H halides, perhaps owing to the relatively complex structure of the double mol.

VI. D and n have been measured for the vapours of CCl_4 , SiCl_4 , SnCl_4 , SnBr_4 , and SnI_4 . The vals. of $R_{\text{MX}_4} - R_{\text{X}}$ for the Na D line become increasingly negative in the order $\text{SnCl}_4 < \text{SiCl}_4 < \text{CCl}_4$, and the vals. for infinite wave-length in the order $\text{SnCl}_4 < \text{SnBr}_4 < \text{SnI}_4$.

VII. D and n have been measured for SnCl_2 , SnBr_2 , and SnI_2 vapours at 700° . ΔR becomes increasingly positive in the order $\text{SnCl}_2 < \text{SnBr}_2 < \text{SnI}_2$. With the transition from Sn^{IV} to Sn^{II} the equiv. refractivity of the halide rises considerably by an amount which increases with the size of the anion. R. C.

Polarisability and molecular refraction of alkali ions. R. SCHOPPE (Z. physikal. Chem., 1934, B, 24, 259—262).—The mol. refractions and polarisabilities of the alkali ions have been recalcd. by Herzfeld and Wolf's method (A., 1926, 11). The polarisabilities are $<$ Mayer's vals. (A., 1933, 550) and those of Fajans and Joos (A., 1924, ii, 372). The mol. refractions of alkali halides have been recalcd. R. C.

Refractive dispersion of organic compounds. IV. *cyclohexene* and 1 : 3-*cyclohexadiene*. C. B. ALLSOPP (Proc. Roy. Soc., 1934, A, 143, 618—630; cf. A., 1931, 1214).—Vals. are given for n at 20° of *cyclohexene* (I) at 67 wave-lengths from 6708 to 2420 Å., and of $\Delta^{1:3}$ -*cyclohexadiene* (II) at 48 wave-lengths from 6708 to 2940 Å. Mol. extinction coeffs. are recorded for both compounds in solution in *cyclohexane* (III). The following dispersion equations represent the data for (I) and (II) from 6708 to 3034 Å., and from 6708 to 3700 Å., respectively: (I) $n^2 = 0.97487 + [1.07441\lambda^2/(\lambda^2 - 0.012226)] + [0.00327\lambda^2/(\lambda^2 - 0.056406)]$; (II) $n^2 = 1.06977 + [0.973295\lambda^2/(\lambda^2 - 0.012226)] + [0.0779625\lambda^2/(\lambda^2 - 0.072900)]$. Each equation contains a high-frequency term corresponding with the partial refraction of a hypothetical band in the Schumann region, at the same wave-length as that deduced for (III), and a low-frequency term which is the partial refraction of the absorption bands observed in the ultra-violet. The refractive dispersion is correlated with the absorption spectrum of the two compounds. L. L. B.

Influence of solvents and of other factors on the rotation of optically active compounds. XXXII. Rotation dispersion of esters of dibenzoyl-*d*-tartaric acid in various solvents. T. S. PATTERSON and D. MCCREATH (J.C.S., 1934, 100—103).—Rotations of Bz_2 derivatives of Me, Et, Pr^a , and Bu^a *d*-tartrates in quinoline, $\text{C}_5\text{H}_5\text{N}$, and ethylene bromide (Me ester also in MeNO_2) are tabulated. No definite region of anomalous dispersion was observed. W. R. A.

Configuration and optical rotation in inorganic complex compounds. W. KUHN and K. BEIN (Z. anorg. Chem., 1934, 216, 321—348).—Compounds of the type $[\text{M}(\text{en})_2\text{AB}]\text{X}_n$ and $[\text{M}(\text{C}_2\text{O}_4)_3]\text{K}_3$, where en is $(\text{CH}_2\text{NH}_2)_2$ or some other base, M is Co, Cr, Rh, or Ir, and A and B are two like or unlike co-ordinate univalent substituents or one bivalent substituent, bear a resemblance in optically active behaviour, i.e., Cotton effect and rotation for the longer waves. The optically active behaviour of a compound is not characterised by a statement of the mol. rotation for a definite wave-length, the same for all compounds, but by the sign of the rotation which analogous absorption bands contribute to the total rotatory power. The long-wave absorption bands of all these substances can be considered as of analogous origin. Measurements of the optical rotation in the long wave, circular dichroism, and absorption of $[\text{Co}(\text{C}_2\text{O}_4)_3]\text{K}_3$ have been made in the spectral region 2600—8000 Å. Agreement with calc. vals. is good. M. S. B.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. VII. Magneto-optical dispersion of isobutyl formate, methyl butyrate, and ethyl malonate. R. H. LAVERY and E. J. EVANS (Phil. Mag., 1934, [vii], 17, 351—369; cf. A., 1931, 24).—Data for the dispersion and magneto-optical dispersion between 3000 and 7000 Å. are tabulated, and represented by equations. Verdet's const. and vals. of e/m are calc. H. J. E.

Magnetic rotation of fused organic substances, in connexion with Malleman's molecular theory. C. SALCEANU (Bul. Soc. Fiz. Roman., 1933, No. 53, 1—4).—See A., 1932, 215, 561. Deviations from de Malleman's theory are observed for $1\text{-C}_{10}\text{H-Me}$ and phenanthrene. R. T.

Valency angle of sulphur. G. M. BENNETT and S. GLASSTONE (J.C.S., 1934, 128—129).—Thi-anthrene has a dipole moment of 1.50×10^{-18} e.s.u. in CS_2 or CCl_4 solution. Hence it must have a non-planar configuration; this is discussed, and it is shown that S has valency angle $< 120^\circ$. W. R. A.

Polar molecules and amphoteric ions. G. DEVOTO (Gazzetta, 1933, 63, 845—848).—Of amphoteric substances, some are polar and others non-polar. A formula which satisfactorily represents the chemical behaviour of a substance does not, therefore, necessarily correspond with the actual structure. H. F. G.

Chemical and physico-chemical properties of polonium. I. Chemical study of certain compounds of polonium. M. SERVIGNE (J. Chim. phys., 1934, 31, 47—64).—By co-crystallisation of Po compounds with known compounds, confirmation has been obtained that Po has valencies 3 and 4. Po is tervalent in the oxalate, whilst with CH_2Ac_2 it forms stable complexes in which it may be ter- or quadri-valent. H. S. P.

Magnetic susceptibilities at high temperatures. R. A. FEREDAY (Proc. Physical Soc., 1934, 46, 214—230).—An electromagnet is designed for measurements of small susceptibilities by a method previously described (cf. A., 1932, 678), modified for

use in conjunction with a special furnace up to 450°. Results are given for anhyd. NiSO_4 and $\text{Ni}(\text{CN})_2$.

N. M. B.

Paramagnetism. W. J. DE HAAS and E. C. WIERSMA (Rapp. Comm. VI Congr. Int. Froid; Comm. K. Onnes Lab. Univ. Leiden Suppl., 1932, No. 74, 36—70).—At 292—113° abs. van Vleck's formula for the magnetic moment of NO as a function of temp. gives results in accord with experimental vals. to a few tenths of 1%. At 292·10° abs. $\chi = 49\cdot07 \times 10^{-6}$; at 112·77° abs. $\chi = 87\cdot32 \times 10^{-6}$. Vals. for O_2 at 293—155° abs. are summarised. Gaseous O_2 does not follow the same law as liquid O_2 . To a first approximation $\chi(T+1\cdot7)=C$. Tabulated results for 290—14° abs. are given for K_2SO_4 , $\text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, CeF_3 , CeCl_3 , $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, and $\text{Pr}_2(\text{SO}_4)_3$. Experimental vals. for the moments of V^{II} , V^{III} , V^{IV} , Cr^{III} , Cr^{II} , Mn^{II} , Fe^{III} , Fe^{II} , Co^{II} , Ni^{II} , and Cu^{II} agree in general with the Bose-Stoner predictions. Cryomagnetic anomalies exhibited by CuCl_2 , CuSO_4 , and FeCl_2 are discussed. CH. ABS.

Paramagnetism. I. Mechanism of quenching of orbital magnetic moment in paramagnetic ions of the iron group. S. DATTA (Phil. Mag., 1934, [vii], 17, 585—602).—The magnetic moment of Co^{II} and Ni^{II} in co-ordinated compounds (mostly containing N_2H_4) is lower than in powdered crystals of hydrated and anhyd. salts. Measurements on CoCl_2 and NiCl_2 in EtOH and HCl solution from 90° to 390° abs. show a break in the $1/\chi-T$ diagram, which is correlated with colour changes. At lower temp. the ions exist as hydrated or alcoholated complexes, and at higher temp. as homopolar chlorides. The interpretation is discussed. H. J. E.

Influence of light on paramagnetic susceptibility. D. M. BOSE and P. K. RAHA (Nature, 1934, 133, 258—259).—A criticism (cf. A., 1933, 664).

L. S. T.

Magnetic investigations on insoluble amorphous substances. I. Magnetic susceptibility of different iron salts. L. N. BHARGAVA and S. PRAKASH (Z. anorg. Chem., 1934, 217, 27—32).—The susceptibilities of amorphous Fe^{II} and Fe^{III} arsenates, phosphates, molybdates, borates, tungstates, oxalates, and benzoates have been measured. On calcination the susceptibility increases to a greater extent than corresponds with the loss in wt. The oxide obtained by calcining FeC_2O_4 is strongly paramagnetic, whilst those from $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ and $\text{Fe}(\text{OBz})_3$ are ferromagnetic. FePO_4 is readily sol. in $\text{H}_2\text{C}_2\text{O}_4$, and the solution has a much higher paramagnetic val., relatively, than the corresponding solutions in HCl and H_2SO_4 , although, for these in turn, the vals. are much > is to be expected from Wiedemann's law. M. S. B.

Covalent radii of atoms and interatomic distances in crystals containing electron-pair linkings. L. PAULING and M. L. HUGGINS (Z. Krist., 87, 205—238).—The possibility of formation of various sets of covalent linkings (tetrahedral, octahedral, square, etc.) is deduced from quantum-mechanical considerations, and the characteristics distinguishing crystals of covalent from those of ionic or metallic character are described. From

these and measured inter-at. distances sets of radii are deduced corresponding with the different types (tetrahedral etc.) of linkings, and satisfactory agreement with results otherwise obtained is demonstrated, save in the case of Mn, the measured radius of which is much > the calc. The reported structures of several crystals (niccolite, eulytite, AsI_3 , BiI_3 , etc.) are shown to be doubtful (cf. A., 1927, 399; 1931, 670; 1932, 1191).

C. A. S.

Energetics of oxides of nitrogen, and the structure of nitrous oxide. L. V. PISARSHEVSKI (Bull. Acad. Sci. U.R.S.S., 1933, 7, 971—974).—A comparison of the heats of formation and decomp. of N_2O , NO, NO_2 , and N_2O_3 leads to the conclusion that N_2O is produced from the ions $\text{N}^{\text{+}}$ and $\text{O}^{\text{-}}$.

R. T.

Quantised Brownian motion. M. SATO (Z. Physik, 1934, 87, 669—673).—Numerical calculations for H_2 and He show that quantised Brownian motion should be observable in a highly quantised gas.

A. B. D. C.

Brownian motion in gases. R. FURTH (Z. Physik, 1934, 87, 810—814).—Sato's deductions (A., 1933, 460, 1115) are erroneous. A. B. D. C.

Space-charge in ice. G. OPLATKA (Helv. phys. Acta, 1933, 6, 198—209; Chem. Zentr., 1933, ii, 1152).—Pure ice exhibits no space-charge when outgassed, but does so when not completely outgassed.

L. S. T.

Surface tension of mercury in a vacuum and in the presence of hydrogen. R. S. BRADLEY (J. Physical Chem., 1934, 38, 231—241).—An apparatus for the determination of the surface tension (γ) of Hg by the flat-drop method is described. A mean val. of 500·3 dynes per cm. at 16·5° was obtained. The fall of σ with time in H_2 at pressures 0—100 mm. has been studied and interpreted theoretically. On illumination of the surface of Hg by a Hg-vapour lamp no immediate effect was observed, but γ fell more rapidly than normally.

M. S. B.

Surface tension of carbon tetrachloride at low temperatures. T. ALTY and G. F. CLARK (Canad. J. Res., 1934, 10, 129—133).—Measurements by the drop-wt. method at temp. of -10° to 12° give $m = 0\cdot022161 - 9\cdot2557 \times 10^{-5}t - 4\cdot896 \times 10^{-8}t^2$. The calc. vals. of γ are tabulated. A. G.

Atomic parachors of carbon and hydrogen. C. H. CHEESMAN (Chem. and Ind., 1934, 135).—The anomaly reported (Vogel, this vol., 243) is due to an abnormality of the dibasic acids and does not extend to alkyl groups attached thereto. E. S. H.

Parachors of some substituted methanes. D. L. HAMMICK and H. F. WILMUT (J.C.S., 1934, 32—34).—The following have been determined: $\text{C}(\text{NO}_2)_4$ 280·8 (anomaly -20·4), CH_2Ph_2 419·6, $\text{CH}(\text{NO}_2)_3$ 247·0, as molten substances; and the following solutions: CBr_4 in CCl_4 260·1 (-16·7), $\text{C}(\text{NO}_2)_4$ in C_6H_6 280·0 (-21·2). The parachor of CHPh_3 evaluated from Przyłuska's data is 578 (-13·9). The size of the substituent group may explain the anomalies. Mumford and Phillips' consts. do not give better agreement. W. R. A.

X-Ray method of distinguishing certain space-groups in the hexagonal system. W. H. BARNES and A. V. WENDLING (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 133—140).—There is difficulty in determining to which of two space-groups certain classes of hexagonal crystals belong. This applies to the D_{3h} class of the hexagonal division and to the C_{3v} , D_3 , and D_{3h} classes of the rhombohedral division, the structures of which are based on a T_h lattice. By examination of Laue pictures taken along the a , b , and c axes of the crystal, it is possible to discriminate in the case of seven pairs out of a total of nine. The method has been tested on α -quartz, and also used to show that $K_2S_2O_8$ belongs to space-group D_{3h}^2 .

H. S. P.

Space-group of tourmaline. W. H. BARNES and A. V. WENDLING (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 169—175).—The method described in the preceding abstract shows that of the two possible space-groups, C_{3v}^1 and C_{3v}^2 , tourmaline belongs to C_{3v}^1 .

H. S. P.

Scattering of homogeneous X-rays of 0.25—0.4 Å. I. BACKHURST (Phil. Mag., 1934, [vii], 17, 321—351).—Scattering by Be, C, Al, S, Fe, Cu, Mo, W, Pb, paraffin wax, H_2O , turpentine, C_6H_6 , EtOH, and $COPh_2$ has been measured with a homogeneous incident beam with reference to the angular intensity distribution, the proportion of modified and unmodified scattered radiation, and the abs. vals. of the scattering coeffs. Results agree in general with wave-mechanics equations for scattering from gases.

H. J. E.

Effect of the divergence of primary X-rays on the valuation of diagrams from reflexion processes. F. LIHL (Ann. Physik, 1934, [v], 19, 305—334; cf. A., 1932, 1078).—Exact formulæ are derived for calculating the interference angle from the outer and inner edges of the interference lines. A. J. M.

Barker's determinative method of systematic crystallography. P. TERPSTRA, J. D. H. DONNAY, J. MÉLON, and W. J. VAN WEERDEN (Z. Krist., 1934, 87, 281—305).—The conclusions of the Conference held at Groningen in August, 1933, to remedy deficiencies in the system are given.

C. A. S.

Cohesion. V. Cleavage measurements of anhydrite. H. TERTSCH (Z. Krist., 1934, 87, 326—341; cf. A., 1933, 452).—Cleavability (parallel to crystal faces) increases in the order (100), (010), (001).

C. A. S.

Madelung constant of cuprite. J. SHERMAN (Z. Krist., 1934, 87, 342; cf. A., 1933, 12).—The correct val. of the Madelung const. of cuprite is 5.12972; and those of the crystal energies of Cu_2O and Ag_2O are 736 and 631 kg.-cal., respectively.

C. A. S.

Crystal structure of lanthanum, cerium, and praseodymium hydrides. A. ROSSI (Nature, 1934, 133, 174).—La annealed in a vac. at 350° for several days gives powder photographs of the β -phase, but after removal of a thin outer layer, characteristic photographs of the α -phase are obtained. The same thermal treatment does not affect Pr. The difficulty of H_2 absorption increases in the order Ce, La, Pr.

The hydrides all have face-centred cubic lattices with sizes $>$ those of the real or possible β -phases of the pure elements. La has a_0 5.62—5.63 Å., Ce 5.61 Å., and Pr a lattice only slightly $>$ that of metallic Ce. In one case La gave simultaneously two face-centred cubic phases with a_0' 5.62 Å. and a_0'' 5.70 Å.

L. S. T.

X-Ray investigation of the nature of change of structure in a metal resulting from deformation at high temperatures. E. F. BAKHMETEV, M. D. VOZDVIZHENSKI, S. I. GUBKIN, G. F. KOSOLAPOV, and B. M. ROVINSKI (Mitt. Forschungsinst. Luftfahrtmaterialprüf., U.S.S.R., 1933, No. 1, 131 pp.).—A study of duralumin. When deformation has reached 60—70%, anisotropy is observed. Samples deformed at 450° and at room temp. are similar in structure.

CH. ABS.

Structure of oxide films on nickel. G. D. PRESTON (Phil. Mag., 1934, [vii], 17, 466—470).—The thin oxide films on heated Ni have been shown by electron diffraction to have a NaCl type lattice (approx. parameter 4.10 Å.), identical with that of massive NiO.

H. J. E.

Debye-Scherrer photograph. G. GREENWOOD (Indian J. Physics, 1933, 8, 269—273).—Kettman's graphical method of evaluation of lattice consts. (A., 1929, 629) yields consistent results with specimens of CdO of different origin using both Cu $K\alpha$ and Fe $K\alpha$ radiation.

J. W. S.

Crystal structures and expansion anomalies of MnO, MnS, FeO, Fe_3O_4 , between 100° and 200° abs. B. S. ELLERSON and N. W. TAYLOR (J. Chem. Physics, 1934, 2, 58—64).—All structures are cubic, and no major structure changes were apparent in the X-ray patterns. Lattice const. data indicate similarity in the abnormal expansion behaviour of MnS and FeO, and of MnO and Fe_3O_4 . The sp. heat and expansion anomalies are probably due to electron transitions within certain atoms in the crystal lattice.

N. M. B.

Silver ferrite. IX. Structure of the orthoferric hydroxide from ferrous carbonate. A. KRAUSE and L. SKORUPSKA (Z. anorg. Chem., 1934, 216, 377—385).—By pptg. aq. $FeSO_4$ with an equiv. quantity of Na_2CO_3 and adding dil. H_2O_2 in excess, a voluminous, gelatinous, light brown ppt. of ortho- Fe^{III} hydroxide is obtained. Examination by the Ag ferrite method (A., 1932, 481) gives a ratio $Ag_2O : Fe_2O_3 = 1 : 1.9$, which indicates a chain mol. containing 6 Fe, or a mixture of higher and lower polymerised mols. The Debye-Scherrer diagram shows no interference. Ageing under aq. NaOH causes the formation of larger polymerides.

M. S. B.

Crystal structure of ferric oxychloride. S. GOLDSZTAUB (Compt. rend., 1934, 198, 667—669).— Fe^{III} oxychloride (cf. A., 1890, 1063) has a 3.75, b 7.95, c 3.3 Å., with 2 mols. in the unit cell, space-group V_1^a-mnm . The structure consists of layers, each made up of two (subordinate) layers of Cl atoms with two each of alternate Fe and O atoms between them, Cl-Cl in the same (principal) layer being 3.3, in different layers 3.75 Å.; the perfect cleavage parallel to (010) is thus explained.

C. A. S.

Crystal structure of hydrargillite. (Miss) H. D. MEGAW (Z. Krist., 1934, 87, 185—204; cf. A., 1930, 732).—Hydrargillite, $\text{Al}(\text{OH})_3$, is monoclinic with a 8.6236, b 5.0602, c 9.699 Å., β 85° 26', and 8 mols. in the unit cell, space-group C_{2h}^{2b} — $P2_1/n$. It is neither pyro- nor piezo-electric. The structure is pseudo-hexagonal, and is made up of layers each consisting of two planes of approx. close-packed OH with a plane of Al atoms between; 3 OH in one plane and 3 OH of the other form a distorted octahedron with an Al in the centre, in which Al—O=1.89 Å., and O—O=2.49 and 2.78, whilst O—O in different layers =2.79 Å. The structure explains the thermal expansion (cf. A., 1933, 1237). C. A. S.

Accurate measurements of rhombohedral lattices: NaNO_3 . J. WEIGLE (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 228—229).—An improved method of calculation gives a =6.3108 Å. and α =47° 15' 59" at 18° within 1/50,000. R. S.

Crystal structure of BPO_4 and BaSO_4 . G. E. R. SCHULZE (Z. physikal. Chem., 1934, B, 24, 215—240).—Both compounds have the same structure and 2 mols. in the unit cell. BPO_4 has a 4.332±0.006, c 6.640±0.008, and BaSO_4 a 4.458±0.006, c 6.796±0.008 Å. The space-group is S_6^2 — $I4$. Both P(As) and B are tetrahedrally surrounded by O. R. C.

Crystal structure of silver sulphate tetramoniate. R. B. COREY and R. W. G. WYCKOFF (Z. Krist., 1934, 87, 264—274).— $\text{Ag}_2\text{SO}_4 \cdot 4\text{NH}_3$ is tetragonal with a 8.44, c 6.35 Å., and 2 mols. in the unit cell, space-group V_4^1 . The SO_4 form tetrahedral groups, the $[\text{Ag}(\text{NH}_3)_2]^+$ are linear; S—O=1.65, Ag—N=1.90 Å. C. A. S.

X-Ray spectroscopic studies of problems of structure of complex compounds. IV. O. STELLING (Z. physikal. Chem., 1934, B, 24, 282—292; cf. this vol., 133).—The λ -absorption spectra of Cl in complex compounds of chlorides of bi-, ter-, and quadri-valent metals with org. bases have been studied. MnCl_2 may combine with up to four mols., e.g., of $\text{CS}(\text{NH}_2)_2$, without the Cl being displaced from the complex. ZnCl_2 additive compounds exhibit only a single absorption edge, possibly consisting, however, of two edges very close together. SbCl_3 and BiCl_3 exhibit double edges, and are therefore not ionic compounds. ZrCl_4 exhibits two edges, and the co-ordination no. of Zr is at least 6, and probably 8. $(\text{C}_5\text{H}_5\text{N})_2\text{ZrCl}_6$ and $(\text{C}_5\text{H}_5\text{N})_2\text{CeCl}_6$ each give three absorption edges. R. C.

Crystal structure of carotenoids. G. MACKINNEY (J. Amer. Chem. Soc., 1934, 56, 488).—X-Ray powder patterns of carotene (from carrot roots and spinach, cauliflower, and sunflower leaves), leaf xanthophyll, lutein, and lycopene are given; no spacings > 7.53 Å. were observed. H. B.

X-Ray studies of the structure of hair, wool, and related fibres. II. Molecular structure and elastic properties of hair keratin. W. T. ASTBURY and H. J. WOODS (Phil. Trans., 1933, A, 232, 333—394; cf. A., 1931, 897).—The X-ray fibre photograph of stretched hair [β -keratin (I)] is analogous to that of natural silk; the former is built of extended, and unstretched hair [α -keratin (II)] of

folded, polypeptide chains. Intramol. folds of the nature of linked pseudo-diketopiperazine rings which open on extension to produce the normal zigzag protein chain are assigned to (II). The side-chains of (I) unite neighbouring main chains by cross-linkings, including covalent and electrovalent linkings. The (I) structure is of flat polypeptide grids adhering by attraction between CO and NH groups of the main chains of neighbouring grids. Elastic properties may be referred to three phases of the keratin theme associated with intercellular, cell-wall, and intracellular keratin. The side-chain differences of the three phases may be successively eliminated by progressive action of H_2O at rising temp., or by dil. NaOH. Decay of tension, leading to "set" of hair stretched in H_2O , is due to side-chain disturbances arising from hydrolytic modification of (I). Intermediate between side-chain breakdown and recombination is a new phenomenon, "supercontraction," defined by closest approach of acidic and basic side-chains. Irradiation of unstretched keratin by ultra-violet light or X-rays causes intramol. changes analogous to those due to H_2O on stretched keratin. N. M. B.

Electron diffraction experiments with graphite and carbon surfaces. R. O. JENKINS (Phil. Mag., 1934, [vii], 17, 457—466).—Polishing a graphite (I) surface reduces the crystal size, and orients them with the main cleavage plane (001) in the plane of the specimen. For "amorphous" C polishing first disintegrates the aggregates of small graphite crystals and then orients them. Fe or Ni, which have been lubricated with oil containing colloidal (I) and then washed with C_6H_6 , retains a film of adsorbed (I), the crystals of which are reduced in size and oriented by friction. The inner potential of natural (I) is 10.7 volts. H. J. E.

Surface lattice interference with electron beams at thin silver layers. H. LASSEN (Physikal. Z., 1934, 35, 172—175).—The apparatus is described. In some cases the usual Debye-Scherrer rings were obtained, but frequently point interference photographs were produced. Various types of surface lattice interference photographs were obtained. The Ag produced in the manner described is composed of a single crystal with a cube face parallel to the plane of the foil. A. J. M.

Crystal structure and orientation in zinc oxide films. G. I. FINCH and A. G. QUARRELL (Proc. Physical Soc., 1934, 46, 148—162).—Using a new type of high-precision electron-diffraction camera, partly and completely oxidised Zn films were examined by transmission. The normal type of ZnO is formed by oxidation by way of a ZnO which is basally pseudo-morphic with the Zn, and forms a corrosion-resisting coating. N. M. B.

Electron reflexion of glasses. K. R. DIXIT (Physikal. Z., 1934, 35, 141).—Seven glasses used all gave a diffuse Debye-Scherrer ring corresponding with a period of 1.5 Å., and inside this, a point, corresponding with 1.55 Å. The 1.55 Å. period is the Si—O separation. A. J. M.

Investigation of thin films of organic substances by electron diffraction. C. A. MURISON

(Phil. Mag., 1934, [vii], 17, 201—225).—The investigation of thin films of grease-like mixtures by electron diffraction shows that the mols. are oriented normal to the surface of the film. The orientation is greater with impure substances (e.g., grease), as the mols., being of different lengths, are less likely to crystallise and so form crystals arranged at random. This is probably the cause of the better lubrication by grease than pure substances. H. S. P.

Determination of size of particles by electronic radiation. R. BRILL (Z. Krist., 1934, 87, 275—280).—A relation between the width of the electron diffraction ring and the magnitude of the diffracting particle is deduced (cf. A., 1919, ii, 274). C. A. S.

Intensity of cathode rays scattered by potassium chloride. S. SHIRAI (Proc. Phys.-Math. Soc. Japan, 1933, 15, 420—427).—The intensities of the Debye-Scherrer diagrams are uniform in all directions. With KCl there is fair quant. agreement between the experimental and the theoretical results. CH. ABS.

Spreading of waves in crystal lattices. K. FÖRSTERLING (Ann. Physik, 1934, [v], 19, 261—289).—Mathematical. In the theory of the anomalous dispersion shown by Lippmann colour plates, analogous results are obtained if the Schrödinger equations for electron waves are substituted for the Maxwell equations. A. J. M.

Crystal structure and electrical properties. VI. **Conductivity surfaces in bismuth crystals.** I. O. STIERSTADT (Z. Physik, 1934, 87, 687—699).—Conductivity distribution for a metal crystal in a magnetic field is shown to give a picture of the lattice symmetry. The conductivity surfaces of a Bi crystal without magnetic field are rotation ellipsoids; with a magnetic field these depend in a complicated way on the angle between the field and the crystal axis. A. B. D. C.

Ferromagnetism of $\gamma\text{-Fe}_2\text{O}_3$. J. G. KOENIGSBERGER (Naturwiss., 1934, 22, 90).—The magnetic properties of several natural and artificial specimens of Fe_2O_3 , pure, and mixed with magnetite, were investigated. A ferromagnetic trigonal $\gamma\text{-Fe}_2\text{O}_3$, differing from magnetite in its crit. temp., can be formed under conditions prevailing in nature (temp. $< 200^\circ$; pressure < 40 atm.). A. J. M.

Magnetic anisotropy of graphite. K. S. KRISHNAN (Nature, 1934, 133, 174—175).—The principal susceptibilities of crystals of Ceylon graphite are $\chi_1 = 0.4 \times 10^{-6}$ and $\chi_2 = 22.8 \times 10^{-6}$. L. S. T.

Magnetic variations in iron and steel as a function of temperature. J. SEIGLE (J. Phys. Radium, 1934, [vii], 5, 37—48).—The effect of temp. on magnetic and expansion anomalies is considered from an examination of curves for various types of Fe and steel. Curie points and paramagnetism are discussed. The β form of Fe is regarded as a combination of α and γ forms, in the temp. range $720\text{--}910^\circ$, for pure Fe. N. M. B.

Crystal diamagnetism of bismuth crystals. A. GOETZ and A. B. FOCKE (Physical Rev., 1934, [ii], 45, 170—199).—The effect on electron configuration in the single crystal lattice of the presence of small

concns. of foreign atoms is investigated. Magnetic anisotropy and susceptibility data for various field strengths are tabulated for several hundred crystals of Bi with small admixtures of Ag, Sn, Pb, Te, Se, and Sb, grown by a modified Goetz method at eight temp. between -185° and 245° . The problem of crystal diamagnetism (I), a property of cryst. matter depending on the presence of large nos. of atoms in the cryst. array, is examined, and the influence on anisotropy, susceptibility, and (I) of concn., type of admixture, and temp. is discussed in detail. N. M. B.

Magnetostriction and ferromagnetic ellipsoids. I. Theory. R. BECKER. II. Measurements with iron and cobalt. M. KORNETZKI (Z. Physik, 1934, 87, 547—559, 560—579).—I. Dependence of the magnetostriction of an ellipsoid on the ratio of its axes is determined for regions below, at, and above saturation.

II. Longitudinal and vol. magnetostriction were observed in ellipsoids of Fe and Co for fields up to 7000 and 10,000 gauss, respectively; the results agree with Becker's theory. A. B. D. C.

Magnetic quenching of tellurium (Te_2). J. GENARD (Compt. rend., 1934, 198, 816—819; cf. this vol., 1, 2).—With similar methods, but using a more powerful field, Smoluchowski's results are confirmed and amplified (cf. A., 1933, 1095). C. A. S.

Supposed allotropy of liquid nitrobenzene. E. COHEN and L. C. J. TE BOEKHORST (Z. physikal. Chem., 1934, B, 24, 241—258; cf. A., 1933, 12).—No criterion for existence of allotropy is found with pure PhNO_2 in the density and viscosity data. R. C.

Structure and gas content of nickel layers formed by cathodic sputtering. W. BUSSEM and F. GROS (Z. Physik, 1934, 87, 778—799).—Ni films sputtered in H_2 are hexagonal I, in N_2 tetragonal and hexagonal II, and the hexagonal I may be transformed into the cubic, the tetragonal into hexagonal II, and then into the cubic structure. A. B. D. C.

Damping power as an essential property of mica. E. OROWAN (Z. Physik, 1934, 87, 749—752).—Mica, cut so that it is not flaked, rings like a piece of steel. A. B. D. C.

Critical field in superconductivity. D. R. INGLIS (J. Franklin Inst., 1934, 217, 227—228).—A brief discussion.

Metallic photo-resistance. Q. MAJORANA (Atti R. Accad. Lincei, 1933, [vi], 18, 184—188; cf. A., 1932, 898).—Practically no variation in resistance of thin films of Al or Na is obtained when they are exposed to intermittent light from a Hg or incandescence lamp. O. J. W.

Magneto-thermo-electric effects in nickel and iron: A. PERRIER and (Mlle.) T. KOUSMINE (Compt. rend., 1934, 198, 810—812).—The differences, ΔE , between the thermoelectric power of couples consisting of a non-magnetic metal and Ni or Fe unmagnetised, and of couples consisting of the same metal and Ni or Fe magnetised parallel, \parallel , or perpendicular, \perp , to the direction of the temp. gradient are plotted against the strength of magnetic field ($H=55.5\text{--}1300$ gauss). ΔE is positive, i.e., indic-

ates increase in thermo-electric power, or negative according as H is \parallel or \perp , and much greater when it is \parallel . C. A. S.

Hall, Nernst, Ettingshausen, and Righi-Leduc effects. N. AKULOV (Z. Physik, 1934, 87, 768—777).—Change of thermo-electric forces of ferromagnetic metals with magnetisation and deformation is shown to be due to anisotropy of the crystals and change in orientation of resultant spin of individual crystal regions. A. B. D. C.

Reflexion of ultrasonic waves. E. HIEDEMANN and H. R. ASBACH (Z. Physik, 1934, 87, 442—446).—Diffraction of light by ultrasonic waves was used to photograph reflexion from concave and convex cylindrical mirrors. A. B. D. C.

Propagation of supersonic waves through an electrolyte. S. OKA (Proc. Phys.-Math. Soc. Japan, 1933, 15, 413—419).—Relaxation and electrophoretic forces are taken into account in an extension of Debye's theory. CH. ABS.

Absorption of supersonic waves in mixtures of air and carbon dioxide at different relative humidities. H. H. ROGERS (Physical Rev., 1934, [ii], 45, 208—211).—The absorption of waves of frequency 409.6 kc. per sec. from a quartz crystal oscillator was measured for the R.H. range 10—75%. The absorption const. is a linear function of the % CO_2 , and is a max. at 45% R.H., then falling rapidly. N. M. B.

Rendering visible standing ultrasonic waves in liquids: determination of ultrasonic wave velocity. C. BACHEM, E. HIEDEMANN, and H. R. ASBACH (Z. Physik, 1934, 87, 734—737).—The waves are followed by the variation of light transparency along the direction of the wave, and the wave-lengths thus observed give an accurate measure of the velocity. A. B. D. C.

Rendering visible progressive ultrasonic waves in liquids by means of a high-frequency stroboscope; determination of ultrasonic velocities in liquids. C. BACHEM (Z. Physik, 1934, 87, 738—740; cf. preceding abstract). A. B. D. C.

Attainment of low temperatures. F. SIMON (Z. Physik, 1934, 87, 815—818).—A reply to Justi (this vol., 246). A. B. D. C.

Specific heats of real gases. E. J. HONIGMANN (Z. Physik, 1934, 87, 659—673).—A theoretical deduction of the sp. heats of gases obeying relations of the type: $d(PV) = (n-1)dU$, U being the internal energy; n is a term of proportionality of real gases. A. B. D. C.

Specific heats of liquids by a cooling method. R. W. B. STEPHENS (Phil. Mag., 1934, [vii], 17, 297—312).—The sp. heat in g.-cal. of C_6H_6 is 0.399 at 12.5° and 0.402 at 8°, and that of PhMe 0.390 at 12.5° and 0.386 at 7.5°. The accuracy is limited by that for the calibrating liquids, and a method of eliminating this possible source of error is suggested. For bakelite the following data have been determined: thermal conductivity 7.47 and 7.62×10^{-4} cal./cm./sec./° C., at 7.5 and 12.5°, respectively, d^{15} 1.335, linear coeff. of expansion 2.5×10^{-5} per ° C., sp. heat 0.383 g.-cal. ° C. H. S. P.

Heat capacities at low temperatures of the alkaline-earth carbonates. C. T. ANDERSON (J. Amer. Chem. Soc., 1934, 56, 340—342).—Heat capacities have been determined between 55° and 300° abs. The following entropies at 298.1° abs. (in e.u.) have been calc.: calcite (coarse) 22.24 ± 0.4 , calcite (fine) 22.40 , aragonite 21.18 ± 0.3 , strontianite 23.21 ± 0.4 , witherite 26.75 ± 0.5 . E. S. H.

Law of the additivity of specific heats in heteropolar compounds. F. M. JAEGER (Chem. Weekblad, 1934, 31, 60—61).—The apparent sp. heat (C_p) of the O in metallic oxides, calc. additively from recent data, varies from (approx.) 3700 (IrO_2) to 5400 (Cu_2O) at 0°, and from 5800 (Rh_2O_3) to 7500 (IrO_2) at 530°. At all temp. the val. in Cu_2O is $>$ in CuO , and falls in RhO , Rh_2O , and Rh_2O_3 in the order given. H. F. G.

Heat-capacity curves of the simpler gases. IV. Extension of the "free energy" formula of Giauque and Overstreet to yield reliable approximation formulæ for calculation of entropy and heat capacity from spectroscopic data. Entropy and heat capacity of carbon monoxide and nitrogen from near 0° K. to 5000° K. H. L. JOHNSTON and C. O. DAVIS (J. Amer. Chem. Soc., 1934, 56, 271—276; cf. A., 1933, 229, 1005).—The calc. vals. of entropy and heat capacity are tabulated for the temp. range indicated. E. S. H.

Discontinuity in thermal behaviour of methane at 20.4° abs. as a phase change of the second order. K. CLUSIUS and A. PERLICK (Z. physikal. Chem., 1934, B, 24, 313—327).—Ehrenfest's theory (A., 1933, 569) is applied. Phase changes of the second order probably occur in many solidified gases and NH_4 salts. The transformation of CH_4 at 20.4° abs. has been studied. CH_4 crystals become doubly refracting on cooling with liquid H_2 owing to strain. The sp. heat of the solid has been measured at 15—25°. At the change point there is no heat effect, but the mol. heat changes abruptly from 81 to 13 g.-cal. The val. of $\Delta(cv/\partial T)$ calc. by Ehrenfest's theory from observations of the effect of pressure on the change point agrees with the val. derived from the variation of the mol. vol. with temp., showing that the transformation is a phase change of the second order. The probable reason for the change is that above 20.4°, but not below, the mols. rotate freely in the lattice. R. C.

Heat of dissociation of Bi_2 determined by the method of molecular beams. C. C. KO (J. Franklin Inst., 1934, 217, 173—199).—By a modified technique (cf. A., 1931, 542) the ratio of Bi_2 to Bi in mol. beams has been determined to within 1%. The Bi deposits are stabilised by heating to 60°. The v.p., $P_{(\text{mm.})}$, of the metal between 1100° and 1220° abs. by the Knudsen method is given by $\log_{10} P = -52.23 \times 195.26/T + 8.56$, and the heat of dissociation of Bi_2 is $77,100 \pm 1200$ g.-cal. The beam at 827° contains approx. 2% of Bi_8 mols. in addition to Bi and Bi_2 , but Bi_3 , Bi_4 , and Bi_6 are absent. J. G. A. G.

Calculation from optical and thermal data of heats of dissociation into atoms of gaseous lithium iodide, and sodium and potassium

chlorides, bromides, and iodides. Heats of vaporisation of potassium and lithium. H. BEUTLER and H. LEVI (Z. physikal. Chem., 1934, B, 24, 263—281).—By means of a cycle combining thermochemical, physical, and optical measurements, heats of dissociation have been calc. with a precision equal to that attainable by direct calculation from data for band spectra. The heats of sublimation of K and Li are calc. from the chemical consts. to be 21.42 ± 0.2 and 33.3 ± 0.8 kg.-cal., respectively, at 0° abs. R. C.

M.p. of NF_3 . O. RUFF and W. MENZEL (Z. anorg. Chem., 1934, 217, 93—94).—Of the three halts in the heating curve of NF_3 previously observed (A., 1930, 986) two have been confirmed. The m.p. is -208.8° and there is a transition point at -219° . Below this temp. NF_3 is snow-white and opaque; above, it forms transparent crystals. M. S. B.

Volume of the meniscus at the surface of a liquid. III. A. W. PORTER (Phil. Mag., 1934, [vii], 17, 511—518; cf. *ibid.*, 1932, [vii], 14, 694).—Data are tabulated. H. J. E.

Determination of the thermal conductivity of air between 0° and 100° C. S. W. MILVERTON (Phil. Mag., 1934, [vii], 17, 397—422).—The method, based on the measurement of heat losses from a hot Pt wire, is described, and data are tabulated. H. J. E.

Effect of accommodation on heat conduction through gases. B. G. DICKINS (Proc. Roy. Soc., 1934, A, 143, 517—540).—By means of a modification of the "hot-wire" method, the thermal conductivities and accommodation coeffs. have been determined for He, A, H_2 , CO, O_2 , air, N_2 , N_2O , CO_2 , NH_3 , and SO_2 . Experimental errors have been reduced to a min. The vals. obtained are > those of previous investigators. L. L. B.

Volume coefficients of expansion of several gases at pressures below one metre. J. B. M. COPPOCK and R. WHYTLOW-GRAY (Proc. Roy. Soc., 1934, A, 143, 487—505).—Using a modified Callendar const.-pressure air thermometer and reservoirs of both glass and SiO_2 , determinations of the vol. coeffs. of expansion of C_2H_4 , CO_2 , N_2O , NO, CO, Me_2O , and SF_6 have been made at several pressures over two temp. ranges, 25—50° and 11—48°. The limiting val. for the coeff. at zero pressure, obtained by extrapolation, is > the accepted val. 3661×10^{-6} for CO_2 , N_2O , and C_2H_4 in glass vessels, but in SiO_2 vessels it is in close agreement. This discrepancy is due to the greater adsorption on glass than on SiO_2 surfaces. L. L. B.

Preparation, [vapour] pressures, and densities of pure hydrogen sulphide. (Atomic weight of sulphur.) A. KLEMENC and O. BANKOWSKI (Z. anorg. Chem., 1934, 217, 62—64).—The criticism by Batuecas (A., 1933, 1006) gives no ground for changing the data previously given for H_2S gas (A., 1933, 16). S

Isotherms of nitrogen between 0° and 150°, and at pressures up to 400 atmospheres. J. OTTO, A. MICHELS, and H. WOUTERS (Physikal. Z., 1934, 35, 97—100).—Data for the N_2 isotherms at temp. between 0° and 150°, by 25°, and pressures of

45—400 atm. are given. Empirical formulæ are given connecting p_v with density and with pressure.

A. J. M.

Calculation of thermodynamic quantities from spectroscopic data for polyatomic molecules; free energy, entropy, and heat capacity of steam. A. R. GORDON (J. Chem. Physics, 1934, 2, 65—72; cf. this vol., 31).—Mathematical. Data for steam in the temp. range 298.1—1500° abs. are tabulated, and revised vals., in agreement with experiment, for the equilibrium const. of the water-gas reaction are calc. N. M. B.

V.p. of liquid and solid deutochloric acid. G. N. LEWIS, R. T. MACDONALD, and P. W. SCHUTZ (J. Amer. Chem. Soc., 1934, 56, 494—495).— H^1Cl is prepared by reaction of H_2O with MgCl_2 at 600°. V.p. have been measured at 152.6—200.9° abs. Comparing the v.p. of H^2Cl , p_2 , with those of H^1Cl , p_1 , the expression $\log_{10}(p_1/p_2) = 15.4/T - 0.075$ holds accurately for the liquid state and $\log_{10}(p_1/p_2) = -57.7/T + 0.387$ holds approx. for the solid state. E. S. H.

Relation between van der Waals' constant b and the dimensions of molecules and atoms. III. K. JABECZYNSKI (Rocz. Chem., 1934, 14, 10—13).—The radii R of mols. and atoms of gases, calc. from a formula based on van der Waals' theoretical equation $b = 4R$, are in good agreement with experimental vals. for a no. of gases, and for their constituent atoms in cryst. compounds. R. T.

Temperature variation of the orthobaric density of unassociated liquids. A. FERGUSON and J. T. MILLER (Proc. Physical Soc., 1934, 46, 140—147).—A formula is obtained, and tested for thirty org. liquids, connecting orthobaric density and temp. It is applied to the evaluation of expansion coeffs., and to show the variation with temp. of free and total mol. surface energies. N. M. B.

Mercury crystals. E. GRUNEISEN and O. SCKELL (Ann. Physik, 1934, [v], 19, 387—408).—Hg has $d_{-191} 14.46(9)$. The sp. resistances parallel and perpendicular to the trigonal axis are 0.0557×10^{-4} and 0.0737×10^{-4} , respectively, at -187.5° . The mean coeffs. of thermal expansion parallel and perpendicular to the trigonal axis between -188° and -79° are 47.0×10^{-6} and 37.5×10^{-6} , respectively; the vol. coeff. of expansion is 122×10^{-6} . There is considerable elastic anisotropy compared with the weak thermal anisotropy. A. J. M.

Thermal expansion of silver measured by X-rays. H. SAINI (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 229).— $a = 4.07725 \text{ \AA.}$ at 18° and the coeff. of expansion measured between 20° and 300° is $(19.1 \pm 0.2) \times 10^{-6} \text{ degree}^{-1}$. R. S.

Shift of transformation interval of glass by pressure. E. JENCKEL (Z. anorg. Chem., 1934, 216, 349—352).—On heating a glass, there is a narrow temp. range through which the expansion coeff. dv/dt and sp. heat c increase very rapidly. The curves of dv/dt and c against T have the same inflexion point at T_w , which is also the point at which the two branches of the curve of v against T and heat content against T intersect. By modifying the Clausius-Clapeyron expression for the dependence of the m.p. of

a crystal on pressure, the shift of the transformation interval with temp. is: $dp/dt = (c_1 - c_2)/T_w[(dv/dt)_1 - (dv/dt)_2]$, where indices 1 and 2 indicate conditions for the highly viscous liquid and the glass, respectively. Calc. vals. of dp/dt agree satisfactorily with known experimental data for Se, salicin, B_2O_3 , and colophony.

M. S. B.

Determination of the temperature interval of transformation of glasses by change of viscosity with temperature. E. JENCKEL (Z. anorg. Chem., 1934, 216, 367—375).—Two methods of determining η by the extension of loaded glass filaments, isothermally at different temp. or as the temp. slowly rises, are described, and data given for B_2O_3 and some silicate glasses. This provides a simple method for determining T_w with nearly the same degree of accuracy as by determination of dv/dt or c (cf. preceding abstract).

M. S. B.

Compressibility of certain gases at low pressures. T. BATUECAS (J. Chim. phys., 1934, 31, 65—75; cf. A., 1933, 770).—A criticism of the data used by Cawood and Patterson in deducing mol. wts. from their compressibility measurements. Vals. of the coeffs. of expansion for C_2H_4 , CO_2 , N_2O , SO_2 , Me_2O , and MeF calc. from their measurements agree satisfactorily with the theoretical vals. deduced by Leduc.

H. S. P.

Heavy water inert, due to low association. E. C. BINGHAM and W. H. STEVENS, jun. (J. Chem. Physics, 1934, 2, 107—108).—Fluidity data indicate that the associations of H_2O and D_2O are in the ratio 1.34 : 2.50. This and other evidence is in agreement with the observed inertness of H_2O .

N. M. B.

Viscosity of liquids. I, II. E. N. DA C. ANDRADE (Phil. Mag., 1934, [vii], 17, 497—511, 698—732).—I. A theoretical expression has been derived for the viscosity near the f.p., in approx. agreement with experimental vals. for Hg, Pb, Sn, Cu, Sb, Bi, Cl., Br, I, O_2 , and H_2 .

II. Theoretical. The temp. variation of viscosity (η) is expressed by $\eta v^{1/3} = Ae^{c/T}$ (A , c are consts., v = sp. vol.), in agreement with experimental vals. for associated and non-associated liquids. H_2O and certain *tert.* alcohols are exceptions. c shows gradual changes in homologous series of liquids, and for many liquids is proportional to the total internal energy. An expression for the variation of η with p is derived, agreeing with experimental vals. for Et_2O , $COMe_2$, $EtBr$, and EtI .

H. J. E.

Solubility of vapours in gases. W. MACFARLANE and R. WRIGHT (J.C.S., 1934, 207—210).—The pressure decreases when a gas is mixed with the vapour of a liquid in which the gas is very sol. Data at 25° are recorded for binary mixtures of CO_2 , air, SO_2 , NH_3 , and HCl with Et_2O , $MeOH$, $COMe_2$, and $CHCl_3$ vapours.

J. G. A. G.

X-Ray study of aluminium-zinc alloys. E. A. OWEN and J. IBALL (Phil. Mag., 1934, [vii], 17, 433—457).—Alloys quenched from 250° consist of (1) an α -phase (close-packed hexagonal; < 2 wt.-% Al), (2) an $\alpha + \gamma$ region (2—80% Al), (3) a γ -phase (face-centred cubic; > 80% Al). The parameter of the γ -phase changes from 4.0406 Å. (100% Al) to 4.0345 Å.

(80% Al). Photographs at 290—450° show a transformation temp. at 300—310°. The β -phase is a solid solution (face-centred cubic; 19—45% Al at 375°). The corresponding parameters are 4.016, 4.058 Å. In the $\beta + \gamma$ region the two face-centred cubic lattices of different parameter co-exist. The solubility range of Zn in Al at higher temp. is < previous vals. indicate.

H. J. E.

Lattice structure of lithium-cadmium alloys. Z. ZINTL and A. SCHNEIDER (Z. Elektrochem., 1934, 40, 107).—A criticism of Baroni's results (this vol., 137).

M. S. B.

Solid phase in the system antimony-bismuth. W. F. EHRET and M. B. ABRAMSON (J. Amer. Chem. Soc., 1934, 56, 385—388).—X-Ray and microscopical examination reveal the presence of only one phase, indicating a continuous series of solid solutions.

E. S. H.

Platinum-chromium alloys. V. A. NEMILOV (Ann. Inst. Platine, 1933, No. 11, 125—134).—The existence of PtCr is suggested by hardness, conductivity, and microcrystallographic data. The thermal diagram, on the other hand, is of the type which corresponds with the formation of solid solutions.

R. T.

Resistances of copper-palladium alloys. D. STOCKDALE (Trans. Faraday Soc., 1934, 30, 310—314).—The sp. resistance and temp. coeff., α , of annealed alloys with 53.4—60.8 at.-% Pd have been determined over the range 0—148°. α decreases with rise of temp. and passes through a min. at 56—58 at.-% Pd.

J. G. A. G.

Electrical conductivity and phase diagram of binary alloys. IX. System magnesium-thallium. G. GRUBE and J. HILLE (Z. Elektrochem., 1934, 40, 101—106).—The diagram is constructed from electrical conductivity measurements at different temp. and thermal analysis. The existence of $TiMg_2$ and $TiMg$ is confirmed, and Tl_2Mg_5 is also shown to be formed. The effect of Mg on the transformation α -Tl β -Tl is indicated.

M. S. B.

Effect of nickel on transformation point of β -brass and heterogeneous equilibria of the ternary system Cu-Zn-Ni. K. YAMAGUCHI and K. NAKAMURA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 89—109).—The transformation point of β -brass near 460° is raised by the addition of Ni.

C. W. G.

Equilibria in the iron-carbon system. A. STANSFIELD (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 177—178).—Fe-C equilibria may be investigated by passing a mixture of CO and CO_2 of known composition over fine turnings of the Fe-C alloy contained in a quartz tube in an electric furnace at known temp., and finding the change in the CO_2 content of the gas.

H. S. P.

Influence of cathodic hydrogen on the stability of steel. D. ALEXEEV, P. AFANASIEV, and V. OSTROUMOV (Z. Elektrochem., 1934, 40, 92—98).—The fragility which results when steel is polarised in H_2SO_4 in presence of H_2S , SO_2 , or As_2O_3 is apparently due to the entry of H_2 into the inter-cryst. spaces. Neither metallographic nor X-ray examination indicates any structural change in the steel thus satur-

ated with H_2 . The gas is probably present in two forms, a loosely bound form which is easily removed by mechanical working or rise of temp., and a solid solution. The added substances probably act as H_2 carriers. The effect of variation of c.d., loading of steel wire, H_2S concn., time of polarisation, and temp. has been studied. M. S. B.

Crystal structure and ferromagnetism of Mn-Al-Cu alloys. O. HEUSLER (Z. Metallk., 1933, 25, 274—277).—Debye-Scherrer photographs of quenched β -Mn-Al-Cu alloys show threefold superstructure lines corresponding with a lattice made up of two face-centred cubic lattices making up a lattice of the NaCl type (I) and a body-centred cubic lattice (II) symmetrically disposed in (I). When the composition of the β -phase corresponds with Cu_2MnAl , the Al and Mn atoms occupy the points of (I) and the Cu atoms the points of (II); with other compositions the element in excess of that necessary to fill one lattice fills the points in the other lattice left vacant by the absence of sufficient of its appropriate atoms. On ageing the quenched alloys no new lines appear in the photographs, but the intensities of the superstructure lines change. This, taken in conjunction with measurements of the electrical conductivity, affords evidence in support of the assumption that completely regular orientation of the lattice structure occurs only on prolonged annealing, the lattice of the quenched alloys containing 20—30% of its atoms in random orientation. Magnetisation experiments lead to the conclusion that the magnetic properties of these alloys are adversely affected by the introduction of foreign atoms into the regularly oriented lattice structure, whether these are introduced by variation of the composition from Cu_2AlMn or by heat-treatment of the alloy with stoichiometric composition. A. R. P.

M.p., b.p., refractive indices, and densities of the system water-1:4-dioxan. J. GILLIS and A. DELAUNOIS (Rec. trav. chim., 1934, 53, 186—190).—The m.-p. data show a eutectic at -14.82° . Formation of a hydrate is indicated. H. J. E.

Constancy of viscosity of concentrated lithium chloride solutions at low-velocity gradients. G. W. S. BLAIR and R. K. SCHOFIELD (Phil. Mag., 1934, [vii], 17, 225—229).—Observations made with a rotating cylinder show that the viscosity remains const., even when the max. velocity gradient is only 0.003 sec.^{-1} . Previously reported anomalies are explained. H. S. P.

Diffusion in molecular dispersions. R. O. HERZOG, R. ILLIG, and H. KUDAR (Z. physikal. Chem., 1934, 167, 329—342).—The Einstein-Sutherland diffusion equation may be deduced from Riecke's diffusion theory by the methods of hydrodynamics without using the concept of driving force due to osmotic pressure gradient. Equations are derived for the diffusion coeff., D , for diffusing mols. having the form of ellipsoids of revolution. D has been measured for numerous solutions of org. substances in org. solvents, the solute usually being a halogen derivative of the solvent. The val. of the mol. radius deduced from the observed val. of D is usually $<$ the val. deduced from space-filling data. This divergence is

ascribed to a reduction in the rotational component of the viscosity (A., 1933, 770) due to attractive forces between the solvent and solute mols., which are probably mainly of a dipole character. It is inferred that the Einstein-Sutherland formula will be valid for the diffusion of spherical dipole-free mols. (saturated hydrocarbon) in a dipole-free solvent (saturated hydrocarbon). R. C.

A law of corresponding states for solutions of dipole substances. A. E. VAN ARKEL and J. L. SNOEK (Physikal. Z., 1934, 35, 187—196).—The examination of twenty-three non-associating dipole liquids shows that the dependence of mol. polarisation on concn., temp., and pressure can be expressed by an equation in which the only parameters are the moment per unit vol. and the temp. Hence for corresponding states the same behaviour is found. A formula is also given for mixtures of two dipole substances. The behaviour of liquids with groups capable of free rotation and of strongly associated substances is described with reference to the dependence of mol. polarisation on concn., temp., and pressure. A. J. M.

Internal equilibria and partial vapour pressures of mixtures of primary normal alcohols with normal paraffin hydrocarbons. G. VON ELBE (J. Chem. Physics, 1934, 2, 73—81).—For mixtures of MeOH, EtOH, PrOH, and BuOH with hexane and heptane the heat of mixing at $10\text{--}45^\circ$ is always negative, and heat absorption per mol. of alcohol increases with dilution to a limit of 5800 g.-cal. per mol. The curves of mol. heat absorption-mol. alcohol concn. are identical. It is inferred that the pure liquid primary n -alcohols are completely associated to double mols., and dissociate to single mols. on mixing with a hydrocarbon. The equilibria between single and double mols. at the same mol. concn. are identical for all primary n -alcohols in all n -hydrocarbons. This theory leads to an equation for the partial v.p. of n -alcohols in n -hydrocarbons, and for the degree of dissociation and heat of mixing at any temp. and concn. N. M. B.

Differences and similarities between azeotropic and heteroazeotropic phenomena, and the relation between composition of heteroazeotrope and temperature. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1934, 14, 19—23).—The phenomena of azeotropy are due to changes in the degree of association of the components, whilst those of heteroazeotropy follow from summation of the v.p. of the components according to Dalton's law. R. T.

Stability of heterogeneous liquids. J. L. SYNGE (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 1—18).—Mathematical. Investigations have been made of the stability of rotating heterogeneous liquids and of the horizontal streaming of such a liquid under gravity. H. S. P.

Critical miscibility of liquids. P. BRUN (J. Chim. phys., 1934, 31, 76—78; cf. A., 1932, 1091).—A reply to the criticisms of Mondain-Monval.

H. S. P.

Critical solution phenomena. M. FREED (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 179—181).—The crit. solution temp. of the system $MeOH-n-C_6H_{11}$ is

34.6° using synthetic C_6H_{14} and 29.3° using purified C_6H_{14} from petroleum. Hand's observation relative to the influence of pressure on the system $AcOH-C_6H_6-H_2O$ (A., 1930, 1512) is not confirmed. H. S. P.

Solutions of methyl alcohol in cyclohexane, in water, and in cyclohexane and water. E. R. WASHBURN and H. C. SPENCER (J. Amer. Chem. Soc., 1934, 56, 361—364).—Equilibrium data are given for the ternary system at 25°. The f.p. curve for solutions of MeOH in cyclohexane has been determined. E. S. H.

System carbon tetrachloride-water-methyl alcohol at 30°. H. A. SHOWALTER (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 183—185).—Bonner's observation that the plait point at 0° is near the CCl_4 end of the binodal curve has been confirmed. The binodal curve and tie lines at 30° have been measured. H. S. P.

Solubility of iodine in the vapour of its solvents. W. BRULL (Z. anorg. Chem., 1934, 216, 353—366).—By a streaming method the saturation concn. at 35° and 46° approx. of pure I in air, N_2 , O_2 , CH_4 , CO_2 , and the vapours of CS_2 , $CHCl_3$, CCl_4 , and C_6H_{14} has been determined. In these liquid solvents I gives violet solutions. In all cases the saturation concns. at the same temp. are equal. In Et_2O , however, the saturation concn. is higher, but the max. is reached only slowly. The results are in good agreement with the supposition that a compound $I_2 \cdot Et_2O$ is formed with a heat evolution of 3.3 kg.-cal. At a higher concn. of Et_2O vapour a brown product containing I and Et_2O separates from the gaseous phase saturated with I. A similar effect is observed in the vapour of other solvents forming brown solutions with I. M. S. B.

Vapour-liquid equilibria in the system nitrogen-water. A. W. SADDINGTON and N. W. KRASE (J. Amer. Chem. Soc., 1934, 56, 353—361).—Data are given for the range 50—250° and pressures up to 300 atm. N_2 has a min. solubility in H_2O at 70—80°; the effect of pressure is not quantitatively in accordance with Henry's law. The concn. of H_2O vapour in a given vol. of the compressed gases is considerably > that calc. by the usual methods, especially at higher temp. and pressures. At temp. > 150° an additive rule for the calculation of the compressibility coeff. of the mixture does not hold. E. S. H.

Heptane and its solutions. VII. Solubility of methylamine in heptane. G. O. DOAK (J. Amer. Pharm. Assoc., 1934, 23, 20—21).—The recorded data extend from -13° to 40°. Max. solubility (0.00137 g. per c.c.) is shown at -7°. C. G. A.

Solubility of potassium acid tartrate. I. Tartaric acid and dipotassium tartrate solutions. D. C. CARPENTER and G. L. MACK (J. Amer. Chem. Soc., 1934, 56, 311—313).—Data are given for the range 0—25°. The solubility of K H tartrate is decreased by tartaric acid or K_2 tartrate. Equations have been derived to express the results. E. S. H.

Solubility of potassium acid tartrate. II. Sugar solutions. D. C. CARPENTER and J. J. KUCERA (J. Amer. Chem. Soc., 1934, 56, 324—327).—The solubility of K H tartrate (C_1) in solutions of

d-glucose, *d*-fructose, invert sugar, or sucrose at 0—20° is given by $C_1 = C_0 - kC_2^a$, where C_0 is the solubility of K H tartrate in H_2O , C_2 the concn. of sugar, and k and a are consts. E. S. H.

Solubility of potassium hydrogen tartrate in solutions of equi-ionic salts. A. WRÓBEL (Rocz. Chem., 1934, 14, 45—52).—The solubility L of K H tartrate (I) in presence of KCl, KBr, KI, and Na H tartrate is given by $L = -x/2\gamma + \sqrt{[(L_0\gamma/\gamma_0)^2 + x^2/4\gamma^2]}$, where L_0 is the solubility of (I) in H_2O , γ_0 and γ are the dissociation consts. in the saturated aq. solution, and in presence of a concn. x of K^+ or $C_4H_5O_6^-$. L increases in presence of K malonate (II), probably owing to association of mols. of (I) and (II). R. T.

Solubility of cupric oxide in salt solutions. J. M. RIGION and H. L. RILEY (J.C.S., 1934, 186—187).—The rate of dissolution and the solubility of CuO in aq. Na citrate and oxalate are increased by CO_2 , but are diminished by OH^- . The enhanced solubility is attributed to the co-ordinating tendencies of the anions coupled with the neutralisation by CO_2 of the OH^- produced by the dissolution. J. G. A. G.

Solubility in mixtures of solvents, which separately do not dissolve given solutes. A. A. GRUNBERG and V. M. SCHULMAN (Ann. Inst. Platine, 1933, No. 11, 111—123).—The solubility of $[Pd(NH_3)_4][Pt(SCN)_4]$ is at a max. at 0° and 25° in 60% $COMe_2$, and at 25° in 60% MeOH. Solvent action is ascribed to the affinity of $[Pd(NH_3)_4]^{++}$ for H_2O , and of $[Pt(SCN)_4]^{--}$ for $COMe_2$ or MeOH. R. T.

Distribution of small amounts of substances between liquid and solid crystalline phases. I. Distribution of barium nitrate between saturated aqueous solution and crystals of lead nitrate. A. POLESSITSKY (Z. physikal. Chem., 1934, 167, 394—398).—The distribution between saturated $Pb(NO_3)_2$ solution and $Pb(NO_3)_2$ crystals of small amounts of $Ba(NO_3)_2$ at 0°, 25°, and the b.p. is independent of the concn. The distribution ratio increases in favour of the liquid phase as the temp. rises. R. C.

Diffusion with absorption. S. BERNSTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 230—234).—Mathematical. H. J. E.

Sorption of hydrogen by reduced nickel. III. Heat-treatment of reduced nickel and its relation to the sorption velocity and to the quantity of hydrogen sorbed. S. IJIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 164—172).—Heat-treatment at 300—500° shortens the time required for equilibrium to be established in the adsorption of H_2 by reduced Ni at 0° and 20.30 cm. pressure, but diminishes the quantity adsorbed. The velocity of diffusion of H_2 in reduced Ni is unaffected by previous heat-treatment at temp. up to 500°. J. W. S.

Vapour-binding power of active charcoal. I. Dependence of vapour-binding power on the magnitude of the vapour charge of the charcoal. F. KRCZL [with H. WEJROCH] (Kolloid-Z., 1934, 66, 155—163).—The binding power is determined by saturating different kinds of active C with C_6H_6 vapour and measuring the amount of C_6H_6 which can

be subsequently removed in vac. or by the passage of a stream of air. The amount of C_6H_6 thus recovered depends at first on the C_6H_6 content of the C, but later becomes independent at a val. which is characteristic of the kind of C. No relation between adsorptive power and binding power was observed. E. S. H.

Adsorption of carbon dioxide by activated charcoals in the presence of carbon tetrachloride and hydrogen cyanide. R. CHAPLIN (Trans. Faraday Soc., 1934, 30, 249—260).—The isothermals at 25° and < 0.12 mm. obtained with air-, steam-, and chemically-activated charcoals show that CO_2 adsorption, A , is diminished by adsorbed CCl_4 or HCN, but the nature of the process is unchanged; when CCl_4 and HCN are adsorbed together, the irreversible A is suppressed, and only the reversible A persists. HCN displaces more bound CO_2 than CCl_4 , but a second displacement of CO_2 always occurs when the second vapour is added, suggesting that neither vapour, when adsorbed singly, can occupy all the active points on the C. J. G. A. G.

Sorption of gases by minerals. IV. Zeolites and bentonite. J. SAMESHIMA and H. HEMMI (Bull. Chem. Soc. Japan, 1934, 9, 27—41; cf. A., 1929, 757; 1931, 34, 1120).—The velocity of absorption of NH_3 , CO_2 , SO_2 , C_2H_2 , O_2 , and H_2 by laumontite (I), stilbite (II), mordenite (III), natrolite (IV), apophyllite (V), analcite (VI), inesite (VII), and bentonite (VIII) has been measured. All except (VI) absorb a large vol. of NH_3 , which combines chemically with (I), (II), (IV), (V), and (VII). (III) absorbs NH_3 , CO_2 , SO_2 , C_2H_2 , and O_2 , and belongs to the chabazite class of sorbent. (VIII) absorbs NH_3 , CO_2 , and SO_2 , and belongs to the SiO_2 gel class. D. R. D.

Adsorption of electrolytes on crystalline surfaces. Influence of sign of charge on adsorbent. L. DE BROUCKERE (Compt. rend., 1934, 198, 822—824; cf. A., 1933, 457).— $BaSO_4$ formed by pouring aq. H_2SO_4 rapidly into aq. $BaCl_2$ is positive, whilst that formed by slowly adding aq. $BaCl_2$ to aq. K_2SO_4 is negative. The log x -log C curves (x = electrolyte adsorbed, C = concn. of solution) for the negative $BaSO_4$ resemble those previously obtained with the positive, and are consistent with the hypothesis of a unimol. layer. The differences at low concn. are due to the fact that the cations are in contact with the (negative) $BaSO_4$. In both cases the adsorption appears to be wholly or partly due to electrostatic action. C. A. S.

Adsorption of organic substances on crystal surfaces. II. Influence of electrolytes on the adsorption of octyl alcohol on silver sulphide, mercuric sulphide, and barium sulphate, and of nonoic acid on silver sulphide. N. A. HELD and K. N. SAMOCHVALOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 263—266).—Ions common to the liquid phase and the lattice generally reduce adsorption on the crystal. Adsorption on $BaSO_4$ is influenced only to a small extent by a common ion. H. J. E.

Colouring of marble in iodine vapour and the nature of the polish layer. E. BEUTEL, H. HABERLANDT, and A. KUTZELNIGG (Monatsh., 1934, 64, 53—60).—I is taken up from a dry atm. by marble at room

temp., especially at a surface which has been sawn. The coloration is less when the surface has been etched or sand-blasted, and is much less in the coarsely cryst. material prepared by heating at 350—500°. Adsorption is greater at a polished surface, which is said to consist of crystallites of colloidal dimensions.

E. S. H.

Influence of salts on the adsorption of cupric ions by ferric hydroxide. J. H. HAMENCE (Trans. Faraday Soc., 1934, 30, 299—303).—Equilibrium is reached rapidly, but the adsorption is diminished by rise of temp., and by the presence of NH_3 , NH_4 and Pb salts, whereas K and Na salts have no effect. The rate of coagulation of $Fe(OH)_3$ decreases with increasing $[NH_3]$. J. G. A. G.

Adsorption of hydrogen sulphide by activated alumina. C. H. BAYLEY (Canad. J. Res., 1934, 10, 19—23).—Measurements by static and dynamic methods of the adsorption of H_2S by activated Al_2O_3 show that this is a max. when the temp. of preheating is 550°. A. G.

Adsorption and catalysis on alumina. GUICHARD (Compt. rend., 1934, 198, 573—575; cf. A., 1926, 475).—The adsorption of H_2O , EtOH, and Et_2O by Al_2O_3 has been determined at various temp. and pressures. At 240° (the usual temp. for dehydrating EtOH by catalysis with Al_2O_3) the adsorption of H_2O and Et_2O is practically nil, whilst that of EtOH is still appreciable. C. A. S.

Adsorption and amount of adsorbent. II. Adsorption of dyes by hydrophilic adsorbents. T. P. PĀPKOVA-KVITZEL (Kolloid-Z., 1934, 66, 148—155; cf. A., 1933, 346).—The variation of total and sp. adsorption, x , with the amount of adsorbent, m , has been studied in the systems acid-violet- $Al(OH)_3$ (positive and negative), acid-violet- SiO_2 , Me-violet- SiO_2 . The expression $x = km^{1/n}$ is valid only in presence of sufficiently great amounts of adsorbent. Anomalies when m is small are traced to the effects of dispersion, dehydration, and coagulation of the adsorbent. E. S. H.

Absorption of dyes by cellulose. II. Influence of temperature. W. M. GARVIE, L. H. GRIFFITHS, and S. M. NEALE (Trans. Faraday Soc., 1934, 30, 271—278; cf. A., 1933, 1241).—At const. temp. in the range 25—100°, the rate of diffusion, D , of heliotrope 2B and fast-red K into sheet viscose (I) passes through a max. with increasing concn. of NaCl, but the absorption equilibria rise continuously. With fixed NaCl concn. D is approx. doubled by each rise of 20°, but the wt. of dye absorbed at equilibrium is approx. halved for every 30° rise. (I) usually absorbs more dye than cotton, but the difference decreases and is ultimately reversed when the absorption is diminished either by raising the temp. or decreasing $[NaCl]$. J. G. A. G.

Sorption of iodine vapour by fibrous materials. I. Plant fibres. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1934, 64, 41—52).—Plant fibres take up more I from a wet than from a dry atm. The influence of moisture is due to some non-cellulose material. The sorptive power of cotton is not altered by extracting with EtOH or Et_2O ($COMe_2$ produces a

slight effect), but is strongly affected by degreasing with alkali. Flax, ramie, jute, and kapok take up I rapidly when heated with it in a sealed tube at 120°. The resulting material is grey, appearing brown in transmitted light, and has a reduced strength. Under similar conditions cotton becomes brown and its mechanical properties are not impaired. Brown colours are due to thin layers of I, and indicate general adsorption, whilst a chemical change is involved in the production of the blue colours. E. S. H.

Relation between ascent of colloidal particles in porous substances and their adsorption by such. A. BOUTARIC and M. PEYRAUD (Compt. rend., 1934, 198, 651—652; cf. this vol., 24).—The velocity, v , of ascension in vertical strips of filter-paper, and the adsorption-concn. in the paper, σ , have been determined for As_2S_3 sols diluted with H_2O or aq. NaCl, and $Fe(OH)_3$ sols diluted with H_2O or aq. $FeCl_3$. For As_2S_3 and H_2O σ is zero, but increases with NaCl concn., whilst v decreases. In $Fe(OH)_3$ and $FeCl_3$ v increases to a max. and then decreases, whilst σ changes in reverse fashion. Colloidal dyes with negative particles behave like As_2S_3 , whilst those with positive particles behave like $Fe(OH)_3$ in that v always varies oppositely to σ . C. A. S.

Adsorption and capillary condensation. A. A. SCHUCHOVITZKI (Kolloid-Z., 1934, 66, 139—147).—Theoretical. E. S. H.

Relation between activated and van der Waals adsorption. J. HOWARD (Trans. Faraday Soc., 1934, 30, 278—287; cf. A., 1933, 1112).—The activated adsorption (I) of H_2 by Cr oxide gel (II) is not due either to impurities (cf. A., 1933, 898) or to diffusion of dissolved gas. The influence of (II) on the velocity of the para- H_2 conversion (III) shows a min. in the temp. range where van der Waals adsorption is small and (I) is very slow. This suggests that (III) occurs with mols. which are adsorbed at low temp. by van der Waals forces and at high temp. by (I) (cf. A., 1933, 680). J. G. A. G.

Theory of adsorption. I. Negative adsorption of solute of dilute electrolytic solution at the free surface. K. SHIBA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 109—115).—The connexion between adsorption and the changes of surface tension is discussed. C. W. G.

Diffusion of hydrogen through metals: fractionating the hydrogen isotopes. C. G. FINK, H. C. UREY, and D. B. LAKE (J. Chem. Physics, 1934, 2, 105—106).—When electrolysis is carried out with Fe, Ni, or Pd tube cathodes, fractionation results from diffusion through the metal, H^1 diffusing more rapidly than H^2 . Pd gave the best results, and the mixture, on burning, gave H_2O of d 1.00020. N. M. B.

Influence of hydrogen-ion concentration on the velocity of diffusion of the chlorine ion through collodion membranes. K. HRYNAKOW (Rocz. Chem., 1934, 14, 53—59).—The velocity of diffusion of Cl^- through collodion diminishes with increasing p_H and $[Ca^{++}]$. R. T.

Shape of the profile of a liquid film draining on a vertical, clean, wetted glass plate and the

combined effects of gravity, viscosity, surface tension, and evaporation on the same. J. SATERBY and H. GIVENS (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 145—159).—A theoretical and experimental attempt has been made to ascertain the influence of evaporation and surface tension (I) on the thickness of the film. The influence of (I) is exceedingly small. H. S. P.

Thin films on a water surface. B. G. WHITMORE, R. RICHMOND, and H. A. McTAGGART (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 113—123).—Films of triolein and oleic acid on compression form droplets showing Brownian motion (I). The droplets are probably lens-shaped with a vol. equal to that of a sphere of 0.5 μ diameter. Films of palmitic and stearic acid show (I) at low, but not at high, pressures. (I) also occurs when a solid film of tripalmitin is heated to its m.p. CH_2PhOBz spreads in an unusual way and the film on compression shows (I). H. S. P.

Unimolecular films of fatty acids on glass. K. B. BLODGETT (J. Amer. Chem. Soc., 1934, 56, 495).—The films are formed by withdrawing a glass slide from 0.001N-NaOH covered with a film of stearic acid under slight surface pressure. Orientation phenomena are described. E. S. H.

Physical chemistry of wetting phenomena and flotation processes. XI. Wettability of aqueous solutions of surface-active substances on paraffin. P. REHBINDER, M. LIPETZ, and M. RIMSKAJA (Kolloid-Z., 1934, 66, 212—219; cf. this vol., 141).—The influence of several fatty acids, alcohols, phenols, amines, xanthates, and soaps on the boundary paraffin-aq. solution-air has been studied. The increase of wetting power due to the reagent is greater the higher is the surface activity and the greater is the mol. wt. in a homologous series. The wetting effect is determined by the undissociated mols. and not by the ions. E. S. H.

Phase boundary potential of monolayers of fatty acids on metals. L. JACOBS (Trans. Faraday Soc., 1934, 30, 303—310; cf. A., 1933, 775).— n -Octoic (I) and myristic (II) acids spread uniformly from light petroleum solutions on clean dry Au, Ag, and Pt surfaces. Max. vals. of the phase boundary potential indicate saturation max., and the accessible areas, which depend on the pretreatment of the surfaces, are shown to be 2.7—7.8 times the apparent area. The potential due to (I) increases continuously with concn., but that due to (II) exhibits a discontinuity suggesting a two-dimensional phase change at approx. 39 \AA^2 per mol. The variation of the optical properties of the surface indicates changes of this character at 40—45 and 20—26 \AA^2 per mol. J. G. A. G.

Lyotropic series and the spreading of proteins. E. GORTER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 20—22; cf. A., 1933, 21).—The influence of univalent ions on the spreading of ovalbumin on solutions of p_H 3 increases in the order Cl^- , Br^- , I^- , CNS^- . The influence of cations on the spreading of pepsin on solutions of p_H 6 increases in the order NH_4^+ , Li^+ , K^+ , Na^+ . J. W. S.

Selectivity as exhibited by osmotic diaphragms. L. L. BURGESS (J. Amer. Chem. Soc.,

1934, 56, 414—419).—Diaphragms have been made by impregnating canvas with (a) Na alginate, (b) soap solution, and (c) casein in aq. Na_2CO_3 and subsequent treatment with (a) a solution containing NaCl, NaBr, KCl, CaCl_2 , MgCl_2 , and MgSO_4 , or (b, c) one containing Ca and Mg salts. Diaphragms (a) and (b) retard Na^+ and favour the passage of K^+ (or the corresponding salt mols.); (a) favours Br^- (at the expense of Cl^-) and to a much smaller extent SO_4^{2-} (against Cl^-) and Ca^{2+} (against Na^+ and Mg^{2+}). With (c), the selective action with respect to Na^+ and K^+ is reversed. Much greater adsorption of certain ions or salt mols. may occur at the surface of the diaphragm. H. B.

Accumulation of electrolytes. VI. Factors affecting penetration. VII. Molecular versus ionic transport. W. J. V. OSTERHOUT, S. E. KAMERLING, and W. M. STANLEY (J. Gen. Physiol., 1934, 17, 445—467, 469—480).—VI. The relative proportions of the Na and K salts (obtained by shaking aq. KOH and NaOH with a mixture of 70% guaiacol and 30% *p*-cresol) show a change when the salts from one aq. phase are allowed to pass through a non-aq. phase (I) into a second (acid) aq. phase (cf. A., 1932, 977). The observed change depends chiefly on the partition coeffs. (II) and the diffusion consts. in (I). Other factors affecting the ratio are temp., viscosity, rate of stirring, shape and surface of (I), surface forces in (I), outward diffusion from acid aq. layer, movement of H_2O into (I), and the variation of (II) with concn. and p_{H} . The observed range of variation in the ratio of K to Na in the above system approximates to that found in *Valonia*.

VII. The order of penetration $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ corresponds with that of the ionic mobilities in H_2O , but is due to the fact that (II) are in the same order, the movement taking place in (I) in the mol. form. NH_4^+ penetrates more quickly than its (II) would indicate, this being probably due to rapid penetration of NH_3 . Both observation and calculation indicate that the rate of penetration is not directly proportional to (II), but increases less rapidly. A. L.

Compressibility of aqueous solutions. E. H. LANMAN and B. J. MAIR (J. Amer. Chem. Soc., 1934, 56, 390—393).—The compressibility coeffs. for aq. LiCl, NaCl, KCl, LiOH, NaOH, KOH, HCl, AcOH, and KOAc (1 mol. of solute to 25, 50, and 100 mols. of H_2O) have been determined at 25° and 100—300 megabars. The compressibility of anhyd. AcOH has also been determined at 25°. The data confirm the linear relation between the apparent mol. compressibility and the sq. root of the concn. E. S. H.

Cryoscopic determination of hydration of ions of nickel chloride. (MLLE.) O. HUN (Compt. rend., 1934, 198, 740—742; cf. this vol., 252).—The hydration in 0.5*M*- and 0.25*M*- NiCl_2 corresponds with $\text{NiCl}_2 \cdot 28.5\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 33.1\text{H}_2\text{O}$, respectively. C. A. S.

Cryoscopic determination of hydration of ions of barium chloride. E. ROUYER (Compt. rend., 1934, 198, 742—744; cf. preceding abstract).—The hydration in 0.5*M*- and 0.25*M*- BaCl_2 corresponds with $\text{BaCl}_2 \cdot 26.1\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 29.1\text{H}_2\text{O}$, respectively. C. A. S.

Observation of Brownian movement with the unaided eye. N. ANDREEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 62).—The light reflected from a point source by a ground or oxidised metal plate shows a flickering in its interference colours as observed by the unaided eye when a thin layer of dil. milk or similar substance is smeared over the surface of the plate. This is attributed to Brownian motion of the fat particles in the milk. J. W. S.

Influence of concentration on the velocity of sedimentation of suspensions. T. PIECHOWICZ (Przemysł Chem., 1934, 18, 4—9).—The measured velocities v of sedimentation of 0.038—0.38% suspensions of SiO_2 in H_2O are in good agreement with those calc. from the theoretical formula $v = kr^2(d_s - d_l)(1 - c) \times \{1 - c^{1/3}(r + \alpha)/1.61r\}/\eta$, where r is the radius of the particles, d_s and d_l the d of the solid and liquid phases, respectively, c the concn. of SiO_2 , and k and α are consts. The above equation does not apply to suspensions of SiO_2 in PhMe, CS_2 , or CCl_4 . R. T.

Highly polymerised compounds. LXXXVII. Behaviour of polystyrenes in Svedberg's sedimentation-velocity centrifuge. R. SIGNER and R. GROSS (Helv. Chim. Acta, 1934, 17, 59—77).—Approx. homogeneous fractions of polystyrenes (I) dispersed in org. liquids have been studied in the ultracentrifuge. At the lowest concns. employed the sedimentation const. (s) bears a similar relation to mol. complexity as it does to particle size in suspensions of spherical particles. This relationship becomes progressively obscured as the concn. (c) is increased, and at 2.75 g. per litre different fractions give almost the same s . The partial sp. vol. of the dispersed material is independent of c and of the degree of polymerisation, whence it is inferred that the effect is not due to change of solvation with c . That it is not caused by elastic forces is clear from the observation that the sedimentation velocity is everywhere \propto the centrifugal field, and that s exhibits no drift during sedimentation. The frictional resistance of the mols. in a given fraction of (I) is \propto the viscosity of the dispersion medium in CHCl_3 , $\text{C}_2\text{H}_4\text{Br}_2$, PhBr, xylene, and cyclohexanone, indicating that the mols. have the same form in each of the liquids. For five different fractions examined the mol. friction coeff. is $\propto c$, and its val. at $c=0$ (i.e., when there is no mutual interference between the mols.) is a fundamental characteristic of the fraction. The results support Staudinger's view of the mols. of (I) as extended mol. threads. F. L. U.

Mechanical properties of disperse systems. II. Deformation of soils under tension. G. I. POKROWSKI and V. G. BULYTSHEV (Kolloid-Z., 1934, 66, 137—139; cf. A., 1933, 901).—A mathematical relation, expressing the influence of pressure and tension on highly conc. disperse systems, is confirmed by experiments on clays. E. S. H.

Diffusion of rod-shaped colloids. (Determination of molecular dimensions from diffusion.) R. O. HERZOG and H. KUDAR (with R. ILLIG and W. HERZ) (Z. physikal. Chem., 1934, 167, 343—353).—The equation $D = kT[\log_e(c/a) - 0.69]/6 - \eta c$ is derived, where D is the diffusion coeff. of a rod-shaped mol. of

length $2c$ and radius a , η the viscosity, and k the Boltzmann const. This agrees with experimental data for solutes of low mol. wt. provided that account is taken of slip, and for hemicolloids, for which there is no slip. For eucolloids, where D is a function of the concn., agreement is also reached by using a mean D calc. from data afforded by experiments in which diffusion has already progressed for some time. The above equation thus affords a means of determining c if a is known.

R. C.

Dialysis of colloids. II. Colloidal thorium hydroxide. B. N. DESAI and A. K. DESAI (Trans. Faraday Soc., 1934, 30, 265—271; cf. this vol., 142).—With progressive dialysis of ThO_2 sols, the stability decreases continuously and the cataphoretic velocity, V , passes through a max. Although the initial increase of V with addition of electrolyte occurs only with univalent coagulating ions, coagulation in the presence of other electrolytes begins at about the same V , in accord with the view that a crit. pptn. potential exists. With progressive dilution, V passes through a max., and in all cases the viscosity increases with dialysis and increasing concn. of colloid.

J. G. A. G.

Aggregation of colloidal electrolytes from transport number and conductivity measurements: some benzidine dyes. C. ROBINSON and J. L. MOILLIET (Proc. Roy. Soc., 1934, A, 143, 630—653).—The transport nos. of benzopurpurin 4B, its isomeride prepared from *m*-tolidine, and Bordeaux-extra have been determined in the moving-boundary apparatus of MacInnes and Brighton (A., 1925, ii, 542) over a range of concns. From these data and concurrent conductivity measurements conclusions are reached as to the micellar constitution of the dyes.

L. L. B.

Structure of soil colloids. I. Structure of colloidal ferric hydroxide. A. I. RABINERSON and G. E. FUCHS (Proc. Leningrad Dept. Gedroiz Inst. Fert., 1933, 22, 1—56).—A classification of soil colloids is suggested which depends on (a) slow coagulation with a local lowering of the ζ potential [$\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$], or (b) expansion of the sheath of hydration (bentonite, solonetz).

A. M.

Preparation of colloidal ferric oxide and the properties of its hydrosols. A. VON BUZAGH (Kolloid-Z., 1934, 66, 129—137).—By heating pptd., washed $\text{Fe}(\text{OH})_3$ in an autoclave with H_2O and filtering, pure Fe_2O_3 is obtained, and may be readily dispersed to a brick-red sol by washing with H_2O . The ability to be peptised is retained after drying at low temp. or with EtOH or Et_2O . The peptisation of Fe_2O_3 is related to the electrophoretic migration velocity and follows the solid-phase rule. The sols are typically hydrophobic; the particles are positively charged, about 20—70 μ in diameter, and approx. spherical. In sols stabilised by FeCl_3 a part of Cl^- is replaceable by other anions, especially with increasing dilution. Gels are not formed on coagulation.

E. S. H.

Nature of radiocolloids. Colloidal solutions produced from bismuth nitrate. M. HAISINSKY (Compt. rend., 1934, 198, 580—583).—The coagulation of the colloidal solutions is its relation to

the p_H of the solution has been examined in some detail.

C. A. S.

Cooling curves of sodium stearate solutions in presence of electrolytes. E. ANGELESCU and M. POPESCU (Kolloid-Z., 1934, 66, 175—183).—Cooling curves have been determined for aq. Na stearate in presence of NaCl , NaBr , NaI , NaNO_3 , NaOAc , EtCO_2Na , Na palmitate, NaCNS , and the corresponding K salts. Equiv. amounts of the Na salts (excepting palmitate) raise the gelation temp. to the same extent. K salts have a similar, but smaller, effect. The presence of electrolytes also increases the heat of gelation and the thermal conductivity.

E. S. H.

Influence of unipolar charged air, X-rays, and ultra-violet light on the properties of sols of Congo-rubin and albumin. B. S. PUTSCHKOVSKY and V. N. NEKLUDOV (Kolloid-Z., 1934, 66, 191—197).—Positively- and negatively-charged air currents have no influence on the colour of Congo-rubin (I) or on the protective properties of albumin (II) sols. X-Rays do not affect the (I) sol, but reduce the protective power of (II). Ultra-violet light discharges the colour of (I), and at first increases, but later decreases, the protective power of (II). The changes are attributed to alterations in dispersity.

E. S. H.

Variation of the cataphoretic speeds of colloidal particles. VI. Variation with dilution of the colloidal solution and in presence of electrolytes. J. MUKHERJEE, S. ROYCHOUHDURY, and S. PALIT (J. Indian Chem. Soc., 1934, 10, 713—725; cf. A., 1928, 15).—The electrophoretic velocity (I) of As_2S_3 sols varies with dilution according to an S-shaped curve. With sols of SiO_2 and $\text{Al}(\text{OH})_3$ (I) increases with dilution. Addition of KCl ($< 0.001N$) to $\text{Al}(\text{OH})_3$ sols increases (I); at higher concns. (I) is decreased, coagulation occurring at 0.1N-KCl. K_2SO_4 causes (I) to decrease continuously. Addition of progressively increasing concns. of KCl , K_2SO_4 , or NaCl to $\text{Fe}(\text{OH})_3$ sols leads to a continuous fall in (I). The observations are not consistent with a crit. coagulation potential.

E. S. H.

Electro-osmosis. II. Influence of concentration of electrolyte on electrokinetic potential. H. ISOBE and S. IMAI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 3).—Mathematical.

P. G. M.

Adsorption and swelling of cellulose in electrolyte solutions of varying concentration. K. KANAMARU (Kolloid-Z., 1934, 66, 163—175).—When cellulose is placed in aq. HCl , H_2SO_4 , NaOH , AlCl_3 , or KCl , the p_H of the acid solutions increases, whilst in the alkaline region the p_H decreases. Measurements of swelling indicate max. in the acid and alkaline regions. The swelling min., which does not correspond with the isoelectric point (excepting AlCl_3), is termed the point of hylotropic adsorption. Swelling phenomena are symbatic with the ζ potential of cellulose.

E. S. H.

Complex relationships in lyophilic colloidal systems. I. General introduction. H. G. B. DE JONG. II. Complex and autocomplex gels. H. G. B. DE JONG and H. J. C. SENGERS (Rec. trav. chim., 1934, 53, 163—170, 171—185).—I. The classification into complex and autocomplex colloidal

systems and the effect of neutral salts on these are discussed.

II. Gels obtained by cooling a mixture of gelatin sol and gum-arabic sol become turbid in dil. AcOH, and have a decreased tendency to swell. They form a complex gel. The turbidity has a max. for a given concn. of acid. Neutral salts restore the swelling tendency, their efficiencies depending on the valencies of anion and cation. $\text{Fe}(\text{CN})_6'''$ and $\text{Fe}(\text{CN})_6''''$ are adsorbed and behave abnormally. Gelatin forms complex gels with nucleic acid or agar. Isoelectric gelatin gel, and agar gel+hexol nitrate, are autocomplex gels. H. J. E.

Paradoxical salt polarity in presence of colloids. R. KELLER (Kolloid-Z., 1934, 66, 205—211).—Discussion of published work leads to the view that ion antagonism is due to the opposite electric charges acquired by the respective ion-colloid complexes. Thus, in presence of excess of colloid, Li^+ , Na^+ , Ca^{++} , SO_4'' , and PO_4''' retain their usual sign of charge, whilst Rb, Cs, K, NH_4 , Cl, and Br form part of complexes having a sign opposite to that of the free ion. E. S. H.

Dielectric constant and conductivity of aqueous solutions of gelatin. A. PIEKARA and B. PIEKARA (Compt. rend., 1934, 198, 803—805; cf. A., 1929, 646; 1931, 424).—The dielectric const., ϵ , and conductivity, κ , have been determined for 0.81—1.2% gelatin solutions. For these, ϵ is $>$ for H_2O , and the difference increases with concn. and with rise of temp. Vals. of ϵ and κ for the sol are $>$ those for the gel under the same conditions. Both show thermal hysteresis. C. A. S.

Dielectric constant studies. III. Aqueous gelatin solutions. A. L. FERGUSON, J. G. MALONE, and L. O. CASE (J. Chem. Physics, 1934, 2, 94—98; cf. this vol., 163).—The variation of the dielectric const. with the gelatin concn. and with p_{H} supports the Bjerrum theory of ampholytes. The amount of H_2O fixed by the gelatin and the mol. wt. have been calc. from dielectric absorption data. N. M. B.

Regularity for periodic reactions in gels. P. MICHALEV, V. NIKIFOROV, and F. M. SCHEMJAKIN (Kolloid-Z., 1934, 66, 197—200).—In five periodic structures of the Liesegang ring type the product of the distance between successive bands and the velocity of diffusion was found to be const. E. S. H.

Formation of Liesegang rings by electrolysis. E. BANDERET (Compt. rend., 1934, 198, 821—822; cf. A., 1933, 786).—The rings produced by the author's electrolytic method obey Veil's law, i.e., $\sqrt{\delta} = an + b$, where δ is the distance between the n th and $(n+1)$ st rings, and a , b are consts. The effect of continued application of electrolysis is illustrated. C. A. S.

Magnetic study of sols and gels. I. S. PRAKASH (Indian J. Physics, 1933, 8, 243—258).—The paramagnetic susceptibility (I) of FeCl_3 and CrCl_3 solutions is greater at low concns. than at high concns., owing to formation of colloidal $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ by hydrolysis. Addition of NaOAc to FeCl_3 and CrCl_3 decreases (I); in the latter case the reaction is slow, and is accompanied by continuous decrease in

(I). Addition of KH_2AsO_4 , K_2HPO_4 , Na_2WO_4 , or K_2MoO_4 to excess FeCl_3 yields the corresponding colloidal Fe^{III} salts, for which (I) is slightly $>$ for the powdered compounds. No marked change in (I) accompanies the sol-gel change for $\text{Fe}_2(\text{HPO}_4)_3$, but the diamagnetic susceptibilities of $\text{Al}(\text{OH})_3$ and $\text{Zr}(\text{OH})_4$ sols increase on ageing. J. W. S.

Cryotropic behaviour of some inorganic jellies. S. PRAKASH (Indian J. Physics, 1933, 8, 231—242).—Sols of $\text{Fe}_2(\text{HPO}_4)_3$, $\text{Fe}_2(\text{HAsO}_4)_3$, $\text{Al}(\text{OH})_3$, $\text{Zr}(\text{OH})_4$, Th molybdate, and Th phosphate are formed when the corresponding gels are cooled in liquid air and allowed to return to room temp. The sols pass into the gel form on keeping. The process can be repeated even with aged gels. The phenomenon is called cryotropy; gels which have developed marked agglomeration tendency are non-cryotropic. Conditions favouring cryotropy and its relation to thixotropy are discussed. J. W. S.

Emulsions. I. Proteins and allied substances as emulsifiers for phenolic liquids. R. M. WOODMAN (J.S.C.I., 1934, 53, 57—60t).—In many instances, proteins, protein-containing substances, and their degradation products yield dual types of emulsions with phenolic liquids; the oil-in- H_2O type only is formed with a hydrocarbon such as PhMe. Explanatory hypotheses are briefly summarised. Gels are formed in certain systems, rendering verification of type difficult and often impossible. The formation of these gels is discussed, and the notion put forward that some measure of swelling in H_2O is necessary before emulsoid colloids can emulsify; the presence of H_2O may, therefore, be essential to emulsification in such cases.

Electrokinetic properties of proteins. II. Adsorption of gliadin at a glass-liquid interface as influenced by hydrogen-ion concentration. W. McK. MARTIN (J. Physical Chem., 1934, 38, 213—229).—A streaming-potential apparatus for measuring the rate of adsorption at a glass-liquid interface is described. The fritted glass diaphragms used were negatively charged in both acids and alkalis, the magnitude of the charge being a function of the total ionic concn. rather than of p_{H} . The electrostatic charge of the double layer at the glass-liquid interface is reversed on adding protein to the streaming liquid if its p_{H} is on the acid side of the isoelectric point of the protein. The negatively-charged glass surface apparently adsorbs a layer of positively-charged protein and assumes its electrokinetic properties, the system becoming protein-liquid instead of glass-liquid. The rate of adsorption of gliadin was determined by the sign and magnitude of the difference in the charge of the glass and the protein micelles. In alkaline solutions there should be no adsorption, since both glass and gliadin are negatively charged. The disturbance of the adsorption equilibrium at the isoelectric point of gliadin by changes in p_{H} indicates, therefore, either structural transformation of the adsorbed protein micelles or displacement by micelles or fragments with different isoelectric points. M. S. B.

Surface tension of proteins, a peptone, and amino-acids. J. ERRERA and E. MILLIAT (J. Chim. phys., 1933, 30, 726—732).—The stalagmometrically

determined surface tension of aq. ovalbumin, serum albumin, and gelatin is min. at the isoelectric point, and for a given change of p_H the effect of univalent is $>$ of bivalent acids and bases. Unpurified Witte peptone affords analogous results, but the effect of varying the constitution of the anion of the added org. acid sometimes exceeds that due to changing the valency. Solutions of NH_2 -acids show the same behaviour as that obtained with H_2O . J. G. A. G.

Kinetic interpretation of the activity coefficients of non-electrolytes. J. W. BELTON (Proc. Leeds Phil. Soc., 1934, 2, 499—501).—An expression is deduced kinetically for the activity coeff. in which account is taken of adsorption (I). The agreement with experiment is good at high concns., but poor at low concns., due probably to increase in the index of the (I) isotherm. H. S. P.

Equilibrium between ammonium thiocyanate and thiocarbamide in solution. W. URE and F. A. DE LISLE (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 105—111).—The system NH_4CNS $CS(NH_2)_2$ has been investigated in glycol solution and vals. of the equilibrium const. have been obtained at 184.4°, 178.3°, and 162.2°. Decomp. of the materials at the higher temp. is considered to explain earlier discrepancies. H. S. P.

Statistical basis of the theory of electrolytes. O. HALPERN (J. Chem. Physics, 1934, 2, 85—93).—Mathematical. N. M. B.

Entropies of aqueous ions. W. M. LATIMER, P. W. SCHUTZ, and J. F. G. HICKS, jun. (J. Chem. Physics, 1934, 2, 82—84).—A crit. summary of existing thermodynamic data for aq. ions leads to consistent vals. for ionic entropies; vals. for twenty positive and twelve negative ions are tabulated. N. M. B.

Dissociation constants of organic acids. VIII. Phenylacetic acid. G. H. JEFFERY and A. I. VOGEL (J.C.S., 1934, 166—168).—According to the conductivities at 25° of 0.0002—0.01N- $CH_2Ph\cdot CO_2H$ and its Na salt in H_2O , the limiting mobility of the anion is 34.7 and the thermodynamic dissociation const. of the acid is 4.884×10^{-5} . The classical dissociation const. increases with rise of concn., and for 0.003—0.01N solutions the mean val. is 5.068×10^{-5} . Earlier data are corr. (cf. this vol., 146) J. G. A. G.

Chemical constitution and dissociation constants of monocarboxylic acids. I. Substituted phenylacetic acids. J. F. J. DIPPY and F. R. WILLIAMS (J.C.S., 1934, 161—166).—From the conductivities of 0.03—0.0001N-acids and their Na salts in H_2O at 25°, the classical dissociation consts. and the following thermodynamic dissociation consts. of the acids are evaluated: phenylacetic 4.88×10^{-5} , diphenylacetic 11.5×10^{-5} , *p*-chloro- 6.45×10^{-5} , *p*-bromo- 6.49×10^{-5} , *p*-iodo- 6.64×10^{-5} , and *p*-nitrophenylacetic acid 14.1×10^{-5} . J. G. A. G.

Dissociation constant of chloroacetic acid from D. D. WRIGHT (J. Amer. Chem. Soc., 1934, 56, 314—317).—The vals. are derived from e.m.f. data for cells without liquid junctions, using the quinhydrone electrode. Equations are deduced which express the influence of temp. on $\log K$, the

heat of dissociation, and the difference in the mol. heat capacities of the ions and undissociated acid.

E. S. H.

Acidity and reducing power of ascorbic acid. P. KARRER and G. SCHWARZENBACH (Helv. Chim. Acta, 1934, 17, 58—59).—Redetermination of the dissociation const. gives K_1 3.25×10^{-4} and K_2 7×10^{-12} . The reduction potential found by Green (A., 1933, 1015) is too negative. F. L. U.

Hydrogen-ion concentration of solutions of hydrazine and hydroxylamine hydrochlorides. A. BERTHOUD and W. EICHENBERGER (Helv. Chim. Acta, 1934, 17, 23—24).—The $[H^+]$ of aq. $N_2H_4 \cdot 2HCl$ between 0.05 and 0.0125M, measured with a H electrode at 21°, indicates that the dissociation $N_2H_4 \cdot 2HCl \rightarrow N_2H_4 \cdot HCl + HCl$ is practically complete. The $[H^+]$ of aq. $NH_2OH \cdot HCl$ cannot be determined potentiometrically, but colorimetric measurements indicate that $[H^+] \propto [NH_2OH \cdot HCl]^{1/2}$. F. L. U.

Halide-iodine equilibria in neutral salt solvents. V. K. LAMER and M. H. LEWINSOHN (J. Physical Chem., 1934, 38, 171—195).—The solubility of I in H_2O (at p_H 5 to prevent hydrolysis) is $0.001321 \pm 2 \times 10^{-6}M$. The vals. for the mass-action expressions for the equilibria: $XI'_2 = I_2 + X'$, where $X = Cl, Br, \text{ or } I$, are a little greater for H_2O than for 2M- KNO_3 and more nearly const. in the presence of the latter. KNO_3 does not appear to combine chemically with I and is used to maintain const. ionic environment. Vals. of K_c for the tri-iodide equilibrium deviate considerably from K_a in aq. KCl , which maintains const. ionic environment, but reacts with I. This contradicts Carter and Hoskin's assumption (A., 1929, 501). The probable influence of the salting-out effect of the different ions on one another is discussed. M. S. B.

Constitution of hydrobromic acid solutions of cobalt and copper salts. P. JOB (Compt. rend., 1934, 198, 827—828; cf. A., 1933, 228).—It is found that the respective HBr solutions contain the ions $CoBr^+$, $CoBr_3^-$, $CuBr^+$, and $CuBr_3^-$. The equilibrium consts. are respectively 5×10^{-3} , 1.1×10^{-5} , 6.3×10^{-2} , and 6×10^{-4} ; those for $CoCl^-$ and $CoCl_3^+$ are 4.5×10^{-3} and 2.9×10^{-4} . C. A. S.

Activity coefficient of silver acetate and silver monochloroacetate in presence of electrolytes. F. H. MACDOUGALL and J. REHNER, jun. (J. Amer. Chem. Soc., 1934, 56, 368—372).—Solubilities of $AgOAc$ (I) and of $CH_2Cl \cdot CO_2Ag$ (II) have been measured at 25° in aq. $LiNO_3$, $NaNO_3$, KNO_3 , $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, and $La(NO_3)_3$. For (I) in presence of $NaNO_3$ and $Sr(NO_3)_2$ and for (II) in presence of $NaNO_3$ and $LiNO_3$ the activity coeffs. pass through a min. E. S. H.

Hydrols. W. D. BANCROFT and L. P. GOULD (J. Physical Chem., 1934, 38, 197—211).—On the assumptions that liquid H_2O is a mixture of tri-, di-, and mono-hydrol, co-existing in reversible equilibrium, that this equilibrium is differently influenced by different anions, and that the electrolytic solution pressure of H_2 and O_2 is different in the different polymerides, an attempt is made to explain the many phenomena associated with aq. solutions. B.-p. data

have been determined for conc. aq. solutions of NaCl, NaBr, NaI, NaNO₃, NaSCN, and Na₂SO₄. The adsorption by gelatin of NaSCN, NaI, NaCl, and NaNO₃ in EtOH-H₂O solution has been measured. E.m.f. measurements of the cells H₂[HX|KCl|Hg₂Cl₂]Hg, where X=Cl, Br, or I, have been made for different concns. of acid, and it is found that the vals. are not the same for the same concn. of different acids.

M. S. B.

Piezochemical studies. XXX. Effect of pressure on chemical equilibrium in condensed systems. E. COHEN and K. PIEPENBROEK (Z. physikal. Chem., 1934, 167, 365—393).—Planck's equation $(\partial \log_e K / \partial p)_T = -\Delta V / RT$ for the effect of change in external pressure, p , on the equilibrium const., K , has been verified by a study of the equilibrium $\text{TiCl}_3(\text{solid}) + \text{CNS}' \rightleftharpoons \text{TiCNS}(\text{solid}) + \text{Cl}'$. The vals. of K at high pressures were derived from measurements with the cell $\text{Ti-Hg}|\text{TiCNS-KCNS}|\text{KCl-TiCl}|\text{Ti-Hg}$ and were checked by measurements of the heat effect and application of the van 't Hoff isochore.

R. C.

Binary system of flavone and primetin. T. ASAHINA (Acta Phytochim., 1933, 7, 187—190).—Softening-point and m.p. curves for mixtures of flavone and primetin (I) (dihydroxyflavone) show that these substances form solid solutions. The natural plant secretion, m.p. 175—180°, contains about 1 mol. of each. Two kinds of crystals exist at 20° when the mixture contains from 40 to 90% of (I). J. H. B.

Thermodynamics of solid solutions. I. Perfect solutions. H. SELTZ (J. Amer. Chem. Soc., 1934, 56, 307—311).—Theoretical. The liquidus and solidus curves for binary systems forming solid solutions are deduced from the fugacities or activities of the components. Equations are derived for calculating the liquidus and solidus from the temp. and heats of fusion of two pure solids, assuming that both solutions are perfect.

E. S. H.

Hydrazine: dissociation pressures of hydrazinium dichloride and dibromide. B. E. CHRISTENSEN and E. C. GILBERT (J. Amer. Chem. Soc., 1934, 56, 393—395).—Dissociation pressures determined by the dynamic isotenoscope method show dissociation of N₂H₄·2HCl to be practically complete at 197.8° at 1 atm. N₂H₄·2HBr decomposes below its m.p., and satisfactory dissociation pressures are obtained only at lower temp.

E. S. H.

Dynamic comparison between physico-chemical systems. H. DAMIANOVICH (Anal. Inst. invest. cient. tecn., 1931, 2, 5—14).—Existing data show that the approx. val. of Q/T , where Q is the heat of reaction and T the temp. of the isobar corresponding with a dissociation pressure of 1 atm., is 32 for the systems $\text{MCl}_2 \cdot y\text{NH}_3$, and 38.5 for homogeneous gaseous systems and for the carbonates of Ag, Pb, Mn, Ca, etc. Divergencies from constancy of Q/T (which is a min. for simple and non-associated systems) serve to indicate the degree of association or polymerisation in a system, or the degree of complexity of the reaction involved.

H. F. G.

Polyhalides. II. Thermal decomposition of KICl₄, and the stability of compounds of the

type MICl₄ and MICl₂. V. CAGLIOTI and G. CENTOLA (Gazzetta, 1933, 63, 907—916).—At 20° KICl₄ decomposes continuously, yielding KCl and ICl₃; its dissociation pressure is appreciable (0.1 mm.) at 14°. The heat of formation from KCl, ICl (gas), and Cl₂ is —29.5 kg.-cal. CsICl₄ decomposes in two stages; at 28° CsICl₂ is formed, and at 116° this yields CsCl and ICl. The theoretical aspects of the stability of compounds of this type are considered.

H. F. G.

Compound formation between sodium iodate and sodium iodide. J. E. RICCI (J. Amer. Chem. Soc., 1934, 56, 295—299).—The double salts 2NaIO₃·3NaI·20H₂O, 2NaIO₃·3NaI·15H₂O, and 2NaIO₃·3NaI·10H₂O exist in the range 20—55°.

E. S. H.

Ternary systems KIO₃-KBr-H₂O and NaIO₃-NaBr-H₂O. J. E. RICCI (J. Amer. Chem. Soc., 1934, 56, 290—295).—Equilibrium data are given for temp. between 5° and 50°. No double salt occurs in the K-salt system. 2NaIO₃·3NaBr·15H₂O occurs below 40°, and 2NaIO₃·3NaBr·10H₂O at higher temp.

E. S. H.

Ternary systems involving alkali bromates. J. E. RICCI (J. Amer. Chem. Soc., 1934, 56, 299—303).—Systems containing H₂O and the following salt pairs have been studied at 25°: NaBrO₃-NaCl, NaBrO₃-NaI, NaBrO₃-NaNO₃, NaBrO₃-Na₂SO₄, KBrO₃-KCl, KBrO₃-KBr, KBrO₃-KI, KBrO₃-KNO₃, KBrO₃-K₂SO₄. There is no evidence of the formation of double salts.

E. S. H.

Liquidus and solidus studies. IV. [Nitrates.] K. LAYBOURN, W. M. MADGIN, and [in part] D. FREEMAN (J.C.S., 1934, 139—146; cf. A., 1933, 465).—The binary systems are of the simple eutectic type; the characteristic eutectic data (% alkali nitrate and temp.) are: Na-Ba, 82.7, 284.0°; Na-Sr, 84.2, 294.9°; Na-Ca, 50.8, 211.3°; K-Ba, 73.0, 285.7°; and K and Sr, 33.8, 274.8°. The graphical thermodynamic treatment is extended to ternary nitrate systems: (1) Na-Pb-Sr, mixture of lowest m.p. M , is the binary eutectic Na-Pb, (2) Na-Ca-Sr, M is the binary eutectic Na-Ca, (3) Na-Ca-Pb, M (202°) contains 51.8% Na and 3.0% Pb, (4) Na-Ba-Pb, M (269°) contains 61.5% Na and 36% Pb, and (5) K-Sr-Ba, M (260°) contains 73.5% K and 3% Ba. M.p. and f.p. data are given for (1) and (5).

J. G. A. G.

Crystallisation of mixtures of acetic acid and normal liquids. The ternary mixture acetic acid-benzene-ethylene dibromide. L. GAY and P. CARCASSÈS (J. Chim. phys., 1933, 30, 709—712).—The data cover the entire range of concn. The ternary eutectic is —29.3° with 50.89 mol.-% C₆H₆ and 44.53 mol.-% C₂H₄Br₂.

J. G. A. G.

Dependence of the equilibrium FeO+Ni NiO+Fe in the melt on added SiO₂. III. **Equilibrium between metals, oxides, and silicates in the melt.** W. JANDER and H. SENE (Z. anorg. Chem., 1934, 217, 48—52).—In presence of SiO₂, up to 12% the val. of $K=[\text{Fe}][\text{NiO}]/[\text{Ni}][\text{FeO}]$ at 1600° (cf. A., 1933, 352) diminishes, if no distinction is made between combined and uncombined oxide; this indicates that FeO·SiO₂ undergoes less dissociation than NiO·SiO₂, or, alternatively, that the solvent

has changed the activity of the mols. The dependence of K on temp., in presence of SiO_2 , is represented by $\log K = -6300/T + 1.29$. M. S. B.

Formula for reducing experimental heat of combustion to the corresponding isothermic value. L. J. P. KEFFLER (J. Chim. phys., 1934, 31, 1—8).—The formula applies to most substances containing C, H, O, and N or certain of these elements, but $\text{H}_2\text{C}_2\text{O}_4$ is an exception. H. S. P.

Heat of ionisation of some metals. W. A. ROTH and A. BUCHNER (Z. Elektrochem., 1934, 40, 87—89).—The heats of dissolution in kg.-cal. of the anhyd. salts AlCl_3 , GaCl_3 , InCl_3 , ZnCl_2 , CuCl_2 , and AgCl are, respectively, 78.09, 45.1 ± 0.2 , 23.2 ± 0.1 , 16.6 ± 0.01 , 11.9 ± 0.02 , and 31.2 ± 0.1 . The heats of ionisation calc. from these are Ga 51, In 32.7, Zn 37.0, Cu —16.6, and Ag —24.5. M. S. B.

Composition and heat of formation of the carbon fluoride mixtures formed from norit and silicon carbide. (Heat of formation of CF_4 and SiC .) O. RUFF and O. BRETSCHNEIDER (Z. anorg. Chem., 1934, 217, 19—21).—With CF_4 norit forms about 14% of the higher fluorides, whilst SiC gives 43%. On the assumption that the heat evolved by 1 g.-atom of noritic C on forming this mixture is 162 kg.-cal., the heat of formation of CF_4 is 183.5 kg.-cal., but this assumption cannot be regarded as valid. The combustion in F of C in the form of SiC gives 134 kg.-cal. It is not possible to determine the heat of formation of SiC from these data. M. S. B.

Electrolytic transport of water in barium chloride solutions. J. BABOROVSKÝ and O. VIKTORIN (Chem. Listy, 1934, 28, 2—6).— H_2O is transported to the anode in $0.2\text{--}2N\text{-BaCl}_2$, and to the cathode in $0.1N\text{-BaCl}_2$; the amount of H_2O transported $\propto [\text{BaCl}_2]$. The Ba^{++} is associated with 11 mols. of H_2O in N , and with 97 mols. of H_2O in $0.1N$ solutions. R. T.

Revised figures for the electrical conductivity of aqueous solutions of sodium and potassium hydroxides, and the limiting mobility of the hydroxyl ion at 25° . G. H. JEFFERY and A. I. VOGEL (Phil. Mag., 1934, [vii], 17, 582—584; cf. A., 1933, 353).—Results are recalcd. The limiting mobility of OH^- at 25° is 210.78. H. J. E.

Conductivity of aluminium bromide in non-aqueous solutions. E. WERTYPOROCH and B. ADAMUS (Z. physikal. Chem., 1934, 168, 31—44).— C_6H_6 , PhMe , and $\text{C}_6\text{H}_4\text{Me}$, dissolve AlBr_3 readily, forming non-conducting solutions, from which HCl or HBr ppts. a highly conducting oil containing all three components. PhF and PhI , but not PhCl and PhBr , give conducting solutions, for which the mol. conductivity, λ , falls with increasing dilution owing to break-up of the solvates. Addition of EtBr to solutions of AlBr_3 in various halogenated benzenes (I) greatly increases the sp. conductance. It is concluded that the pseudo-salt solvates of EtBr and AlBr_3 can add (I) as a whole. In solutions in (I) the H atom is loosened by AlBr_3 so slightly that ethylation according to the Friedel-Crafts reaction cannot occur. With chloro- and bromo-toluenes as solvents the highest λ is attained with the *m*-isomeride, which agrees with the

general rules for the loosening of nuclear H by substituents. PhNO_2 and the nitrotoluenes give with AlBr_3 very stable additive products in which the catalytic action of the AlBr_3 has disappeared. PhCN and MeCN behave similarly to the NO_2 -compounds. MeCN dissolves ZnCl_2 when HCl is passed in, giving highly-conducting solutions containing such acids as H_2ZnCl_3 and H_2ZnCl_4 ; C_6H_6 is added and ketone formed by hydrolysis. R. C.

Conductivities of titanium, tin, and silicon tetrachlorides in non-aqueous solutions. E. WERTYPOROCH and B. ALTMANN (Z. physikal. Chem., 1934, 168, 1—30).—The mol. conductivity, λ , of these salts in MeOH and EtOH solution shows that the complexes formed by solvation have a salt-like structure. With $\text{CH}_3\text{Ph-OH}$ colorations appear, suggesting conjugated double linkings in the solvates. In Et_2O the solvates are salt-like, but only weakly dissociated, and dioxan forms complexes, but gives non-conducting solutions. With alkyl and acyl chlorides there are formed weakly conducting salt-like complexes, which are saturated, and therefore incapable of adding hydrocarbons and loosening H atoms. These metal chlorides do not, therefore, bring about the Friedel-Crafts reaction. MeCHO is decomposed by all three chlorides. With other aldehydes (A) salt-like solvates are formed, and at higher concns. compounds, $\text{MCl}_4 \cdot 2\text{A}$ separate. For COME_2 solutions of TiCl_4 and SnCl_4 λ does not vary appreciably with the concn., whereas solutions of SiCl_4 behave as solutions of true salts. For solutions of TiCl_4 in MeCN λ is large, whilst SiCl_4 solutions have the same conductivity as the solvent and SnCl_4 gives a salt-like complex. Solutions in PhCN are coloured and λ is small. In general, the presence of the Ph radical in the solvent involves small λ . R. C.

Conductivity of solutions of certain substances in fused antimony chloride. Z. KLEMENSIEWICZ and A. ŻEBROWSKA (Rocz. Chem., 1934, 14, 14—18).—The equiv. conductivity, κ , of HCl and HBr in fused SbCl_3 (I) is at a max. in $0.25N$ solutions; that of SbOCl is given by $\log \kappa = kC^{1/3}$, where C is the concn. The results obtained for solutions of H_2O in (I) are untrustworthy, owing to hydrolysis. The vals. of κ are considerably < for the corresponding aq. solutions. R. T.

Conductivity and solubility relations in the ternary systems sodium-potassium-ammonia and sodium-lithium-ammonia between -40° and -70° . F. GRIENGL, F. STEYSKAL, and K. STEYSKAL (Monatsh., 1933, 63, 394—426).—The electrical conductivity of K-Na and Li-Na alloys dissolved in liquid NH_3 is an additive property, giving no indication of compound formation. The solubility relations show the presence of Na_2K . The limits of the miscibility gaps in the ternary systems have been determined. E. S. H.

Conductivity of dipyriddy ethylenediamino-tetrachloroplatinum. S. I. CHORUNSHENKOV (Ann. Inst. Platine, 1933, No. 11, 73—75).—Conductivity measurements confirm the structure $[\text{enCl}_4\text{Pt}](\text{C}_5\text{H}_5\text{N})$. R. T.

Conductivity titrations in heterogeneous systems. O. SCHWARZKOPF and J. WEISS (Cellulose-

chem., 1934, 15, 29—31).—When a heterogeneous system consisting of the insol. Na salt of an insol. acid and aq. NaOH is titrated conductometrically with HCl, three types of curve are possible, according to whether $[\text{OH}^-]$ in equilibrium with the Na salt is $>$, $=$, or $<$ $[\text{OH}^-]$ for H_2O . The titration of Na cellulose in aq. NaOH is discussed. A. G.

Electrical conductivity of compressed graphite powder. J. BRUNNER and H. HAMMERSCHMID (Z. Elektrochem., 1934, 40, 60—67).—Measurements have been made on six different graphites for a pressure range of 31—300 atm. by Ryschkewitsch's differential method, and the linear dependence of sp. resistance on $1/\sqrt{p}$ has been confirmed. The influence of mechanical working on the resistance, on d , and on compressibility varied very much in 20 graphite powders examined. M. S. B.

Determination of normal potentials. (MLLE.) M. QUINTIN (Compt. rend., 1934, 198, 718—720; cf. A., 1933, 781).—The heat of reaction, ΔH , derived from e.m.f. data for the cell Cu (amalgam two phases) $[\text{CuSO}_4(c)]\text{HgSO}_4[\text{Hg}]$, is a linear function of c . For $c=0$, $\Delta H=18,640$ g.-cal. per. mol. The normal potential, E_0 , is $0.4042-0.00050T$. C. A. S.

Potential of the cobalt electrode. M. M. HARING and B. B. WESTFALL (Trans. Electrochem. Soc., 1934, 65, 61—72).—Cells of the type $\text{Co}|\text{CoSO}_4$ solution, $\text{Hg}_2\text{SO}_4|\text{Hg}$ have been constructed with very finely-divided Co (electrodeposited on a Pt wire at 75—85° and 16 amp. per sq. cm.), and the e.m.f. measured in the absence of O_2 which has a very considerable influence on the Co potential. From data at 25° the standard electrode potential is -0.278 ± 0.002 . H. J. T. E.

Potentials of the lead oxide electrodes in alkaline solution. L. V. ANDREWS and D. J. BROWN (J. Amer. Chem. Soc., 1934, 56, 388—390).—The following vals. have been obtained: $\text{PbO}-\text{Pb}_2\text{O}_3|\text{OH}^- + 0.2488 \pm 0.0005$, $\text{Pb}_2\text{O}_3-\text{PbO}_2|\text{OH}^- + 0.1295 \pm 0.001$, $\text{PbO}-\text{PbO}_2|\text{OH}^- + 0.280 \pm 0.001$ volt. The calc. free energies of formation of the oxides at 298° abs. are: $\text{Pb} + 0.5\text{O}_2 = \text{PbO} - 45,100$, $3\text{Pb} + 2\text{O}_2 = \text{Pb}_3\text{O}_4 - 142,210$, $\text{Pb} + \text{O}_2 = \text{PbO}_2 - 50,600$ g.-cal. E. S. H.

Electrochemistry of non-aqueous solutions. IX. Determination of e.m.f. of silver-silver nitrate concentration cells in nine organic solvents and comparison with the values calculated from conductivity measurements. R. MULLER, H. KUMPFILLER, E. PINTER, and B. VON SEEBACH (Monatsh., 1933, 63, 317—328).—Determinations of e.m.f. in EtOH, MeCN, PhCN, NH_2Ph , $\text{C}_6\text{H}_5\text{N}$, and quinoline agree with vals. calc. from electrical conductivity data. Agreement was not obtained in MeOH, isoamyl alcohol, or COMe_2 . It is inferred that Nernst's theory of concn. cells is applicable to non-aq. systems. E. S. H.

Influence of an electric field on the potential at a metal-solution interface. H. K. McCLAIN and H. V. TARTAR (J. Physical Chem., 1933, 38, 161—170).—The potential of Au or Pt against a solution is only slightly affected by an electric field of moderate strength. The changes of potential

may be due to a current between the electrodes caused by the field, or to a longitudinal movement of the ions through the diffuse double layer at the metal-solution interface. The change has its source at the interface, since addition of a small amount of a substance highly absorbed at the interface, such as tannic acid or gelatin, reduces the change of potential. As the effect diminishes with the size of the electrodes, the potential of an electrode of colloid particle size will probably not be affected, which supports the assumption in cataphoretic measurements that the charge distribution in the double layer is unaffected by the applied field. The electrolytes used were H_3BO_3 , KH_2PO_4 , Na_2HPO_4 , and $\text{Al}_2(\text{SO}_4)_3(+\text{HCl})$. M. S. B.

Electrokinetic (ζ) potential of thin metal films. G. W. SMITH and L. H. REYERSON (J. Physical Chem., 1934, 38, 133—151).—Metallised SiO_2 gels have been used in streaming potential measurements and a direct comparison of the electrokinetic potential (ζ) with the Nernst thermodynamic potential (e) is thus obtained. Gels covered with Ni or Ag have been prepared by adsorption of $\text{Ni}(\text{NH}_3)_4$ and $\text{Ag}(\text{NH}_3)_2$, respectively, from solution, and reduction by heating in a current of H_2 . ζ is negative for both Ni and Ag, whereas e_{Au} would normally be positive. ζ in the Ni-Ni(NO_3)₂ system reaches zero at $N/2000$. This is characteristic of the effect of bivalent ions on. The behaviour of Ag is different from that of other univalent ions. There is an initial sharp decrease followed by a rise and then the usual gradual decrease. The causes of this behaviour are discussed. Variations in ζ depend on changes in thickness of the double layer which varies with the concn. of the solution, adsorption of anions, and adsorption of cations. e depends only on the osmotic pressure of the ions supplied by the metal. The other factor, the electrolytic solution pressure, is a const. for each metal. M. S. B.

Decomposition voltages of fused salts. II. Magnesium chloride and sulphate. Y. KONISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 44—45B).—The decomp. voltages measured at 548—908° (MgCl_2) and 856—968° (MgSO_4) lead to 3.257 and 4.543 volts, respectively, at 15°; the temp. coeffs. are -0.000646 and -0.00171 volt per °C. The decomp. voltages are in accord with the thermal data. A. G.

Reversibility of oxidation-reduction systems derived from carbohydrates. R. WURMSER and J. A. DE LOUREIRO (Compt. rend., 1934, 198, 738—740).—The reversibility of such systems consisting of reduced carbohydrates in neutral or alkaline solution, or of ascorbic acid is shown by the agreement between the normal potentials derived, on the one hand, electrometrically, and on the other, by a colorimetric method in which the oxidation of a leuco-compound, e.g., methylene-blue, is determined. The result previously obtained with ascorbic acid appears to have been due to the use of acid which has not been freshly recryst. C. A. S.

Oxidation-reduction potential of system xanthine uric acid. (MLLE.) S. FILITTI (Compt. rend., 1934, 198, 930—932; cf. this vol.,

32).—Determined by a similar method the normal potential of the reaction $C_5H_4O_3N_4 + H_2O$ $C_5H_4O_3N_4 + H_2$ is $+0.113 \pm 0.0015$ volt, and $\Delta F = 5220$ g.-cal. The heat of reaction at const. pressure is $-12,000$ g.-cal. If the (acid) dissociation of hypoxanthine ($K_H = 2.12 \times 10^{-12}$) be taken into consideration, ΔF for the reaction $C_5H_4ON_2 + 2H_2O$ $C_5H_4O_3N_4 + 2H_2$ is 5720 g.-cal. C. A. S.

Optical method for investigation of concentration polarisation during electrolysis. A. G. SAMARCEV (Z. physikal. Chem., 1934, 168, 45—58).—The changes in concn. at the electrodes were deduced from the change in n of the solution in the diffusion layer and the thickness and structure of the latter studied by means of photographs of the interference images under varying conditions of electrolysis. The electrolyte was mixed by causing it to flow between the electrodes, and the cells $Cu|CuSO_4, aq.|Cu$ and $Ag|AgNO_3, aq.|Ag$ were examined. In the immediate vicinity of the electrode the concn. gradient is proportional to the c.d., and increases on approaching the electrode surface. In the above cells the total polarisation is $>$ the concn. polarisation.

R. C.

Hydrogen overvoltages of iron-chromium alloys in potassium hydroxide solution. M. DE K. THOMPSON and D. M. FLEMING (Trans. Electrochem. Soc., 1934, 65, 73—77).—H overvoltages for c.d. from 10^{-4} to 1 amp. per sq. cm. in $M-KOH$ have been determined at polished Fe-Cr surfaces of varying composition. The composition of each surface was determined by X-ray analysis. With increasing proportion of Cr the overvoltage remains close to the val. for pure Fe until Cr exceeds 60%, and then rises gradually to that for Cr. An 89.5% Cr alloy prepared by fusion gave results in good agreement.

H. J. T. E.

Theory of passivity. XXIII. Passivity of lead. W. J. MULLER and W. MACHU (Monatsh., 1933, 63, 347—367).—Current-time curves, obtained for the anodic polarisation of Pb in H_2SO_4 , are examined in the light of Muller's theory. It is inferred that the normal anodic process consists in $Pb \rightarrow Pb^{++}$ at -0.3 volt, the p.d. rising to 1.8 volts through film polarisation. At higher p.d. the process $Pb \rightarrow Pb^{+++}$ occurs, followed by $Pb^{+++} + 2H_2O \rightarrow PbO_2 + 4H^+$.

E. S. H.

Unimolecular decomposition at high pressures. L. S. KASSEL (J. Chem. Physics, 1934, 2, 106).—A criticism of Coffin and Geddes' explanation of the decomp. of paraldehyde (cf. this vol., 259).

N. M. B.

Homogeneous first-order gas reactions. IV. Decomposition of para-*n*-butaldehyde and para-isobutaldehyde. C. C. COFFIN (Canad. J. Res., 1933, 9, 603—609).—The thermal depolymerisations of $(Pr^iCHO)_2$ and $(Pr^eCHO)_2$ at pressures between 13 and 550 mm. in the range $215-261^\circ$ are homogeneous first-order reactions of which the velocity coeffs., k , are given by $\log_e k = 33.12 - 42,000/RT$ and $\log k = 34.06 - 42,800/RT$, respectively. From these data and those for $(MeCHO)_2$ (A., 1932, 1094) it is inferred that for a series of reactions with the same energy of activation, an increase in the no. of contributory

internal degrees of freedom of a mol. increases the probability of reaction. J. G. A. G.

Dynamics and mechanism of aliphatic substitution. E. A. MOELWYN-HUGHES (Nature, 1934, 133, 294).—A discussion. L. S. T.

Rates of formation of quaternary phosphonium salts. W. C. DAVIES and S. U. EVANS.—See this vol., 397.

Temperature gradient in flames. O. C. DE C. ELLIS and E. MORGAN (Trans. Faraday Soc., 1934, 30, 287—298).—A technique and a mathematical analysis for determining the sign of the temp. gradient from point to point in spherical flames are given. Only in entire absence of "after-burning" does the gradient fall inwards from the surface throughout the flame period. The experimentally investigated mixtures, $NH_3 + 3O_2$, and $2CO + 2H_2 + xO_2 + 10A$, conform, in general, to one or the other of two types: the temp. rises inwards from the flame surface (1) throughout the flame period when the reactions lead to equilibria that shift exothermically under conditions of rising temp. and pressure, the gradient becoming steeper as combustion proceeds, or (2) for a considerable portion of the flame period even when the reactions lead to equilibria that shift endothermically under conditions of rising temp. and pressure. The method affords a new and independent demonstration of "after-burning." J. G. A. G.

Speed of "uniform movement" of flame in mixtures of carbon monoxide and oxygen. (A) W. PAYMAN and R. V. WHEELER. (B) W. A. BONE (Nature, 1934, 133, 257, 257—258).—(A) The max. speed (I) of "uniform movement" of flame in moist mixtures of CO and O_2 is obtained with a mixture $2CO + O_2$.

(B) (I) is attained with a mixture $3CO + O_2$.

L. S. T.

Explosive and non-explosive reactions between oxides of nitrogen and inflammable gases. M. J. VAN DER WAL (Rec. trav. chim., 1934, 53, 97—117).—Explosion limits have been determined in the systems CH_4-N_2O , CH_4-N_2O , CH_4-N_2O-NO , $CO-N_2O$, CH_4-CO-N_2O , $CO-N_2O-NO$, H_2-N_2O , H_2-NO-N_2O , H_2-CO-N_2O , and H_2-CO-N_2O-NO . H. J. E.

Kinetics of the methane-oxygen reaction. G. L. FREAR (J. Amer. Chem. Soc., 1934, 56, 305—307).—In absence of SiO_2 packing, a chain mechanism predominates in the reaction of $76:22$ CH_4-O_2 mixtures in a SiO_2 tube at 600° , the apparent reaction order being 3.5 at 450—575 mm. and increasing rapidly with increasing pressure. In a tube packed with SiO_2 the reaction is approx. unimol., and its rate exceeds that of the reaction in the unpacked tube at < 300 mm.

E. S. H.

Action of condensed spark on mixtures of carbon monoxide and hydrogen. H. LEFEBVRE and M. VAN OVERBEKE (Compt. rend., 1934, 198, 736—738; cf. A., 1932, 580).—With the same method the condensed spark shows very little change in mixtures of CO and H_2 containing 20—80% of either, at pressures > 9 mm. Hg, unless the products of reaction are immediately removed, e.g., by connecting the reaction tube with one cooled by liquid O_2 . Pressure then

decreases, and ultimately only CO or H₂ remains, the two having interacted as far as possible with formation of H₂O, CO₂, and C₂H₂, the ratio CO : C₂H₂ increasing with the initial % of CO. C. A. S.

Thermal reaction between chlorine trioxide and ozone. G. K. ROLLEFSON and A. C. BYRNS (J. Amer. Chem. Soc., 1934, 56, 364—367).—The kinetics of the reaction of ClO₃, formed during the decomp. of O₃ sensitised with Cl₂, with O₃ have been interpreted in terms of a chain mechanism. The relative efficiencies of Cl₂, N₂, and O₂ in breaking these chains are of the same order of magnitude. The temp. coeff. of the reaction corresponds with a heat of activation of 10.9 kg.-cal. E. S. H.

Autoxidation of sodium hypophosphite. W. BOCKEMULLER and T. GÖTZ (Annalen, 1934, 508, 268—297).—Aq. NaH₂PO₂ is not normally autoxidised in the absence of heavy metals, but in presence of F₂O or O₃ it readily absorbs O₂. Velocity of autoxidation in a buffered solution depends not only on the *p*_H of the solution, velocity being greater and autoxidation more complete with lower *p*_H, but also on the concn. of the buffer. Phosphate buffer was used. The dependence on NaH₂PO₂ concn., temp., and partial pressure of O₂ has been studied. An unstable intermediate product, *monoperphosphorous acid*, is formed. CuSO₄ and FeCl₃ are strong stabilisers of this compound and O₂ to a smaller extent. The part played by O₃ or F₂O is still in doubt. The results are explained by a chain mechanism. The rôle of the heavy-metal ions in bringing about autoxidation (cf. Wieland and Franke, A., 1929, 1309) is discussed. The behaviour of Cu⁺⁺ is peculiar, since small quantities increase the velocity of autoxidation, but larger quantities stabilise the per-acid and break the reaction chain. VCl₃ increases the velocity, but brings the reaction to an end at an earlier stage, and very little per-acid is present. Autoxidation of the hypophosphite leads to phosphate, and does not stop at the phosphite. The latter also is autoxidised to phosphate, and in absence of heavy-metal ions requires the presence of O₃ or F₂O to initiate the reaction. Monoperphosphoric acid is formed. The course of the chain reaction in this case also is discussed. Very little autoxidation of arsenite takes place.

M. S. B.

Kinetics of ethylene polymerisation. H. H. STORCH (J. Amer. Chem. Soc., 1934, 56, 374—378).—The primary product of polymerisation at 377° and 1415 mm. is butylene, giving propylene as a secondary product. Small amounts of O₂ accelerate the reaction. At 350—400° the heat of activation is about 42,000 g.-cal. E. S. H.

Kinetics of the thermal isomerisation of cyclopropane. T. S. CHAMBERS and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1934, 56, 399—405).—The thermal reaction cyclopropane → propylene is homogeneous and unimol. The rate coeffs. depend on the pressure; at high pressure log *K*_∞ = 15.17—65,000/2.3RT. E. S. H.

Thermal decomposition of *tert*-butyl and *tert*-amyl alcohols. Homogeneous unimolecular reactions. R. F. SCHULTZ and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1934, 56, 395—398).—

The thermal decomp. at 487—555° are homogeneous and unimol., with the activation energies: Bu^oOH 65,500 g.-cal., *tert*-amyl alcohol 60,000 g.-cal. The corresponding rate coeffs. are given by $4.8 \times 10^{14} e^{-65,500/RT}$ and $3.3 \times 10^{13} e^{-60,000/RT}$ E. S. H.

Velocity of decomposition of diazo-compounds in water. XIII. E. YAMAMOTO, R. GOSHIMA, and J. HASHIMA (J. Soc. Chem. Ind. Japan, 1934, 37, 29—33B).—Decomp. velocity coeffs. at various temps. are given for 1 : 2-, 2 : 1-, and 7 : 2-SO₃H·C₁₆H₅·N₂Cl. A. G.

Hydration of unsaturated compounds. I. Rate of hydration of isobutene in dilute nitric acid. H. J. LUCAS and W. F. EBERZ (J. Amer. Chem. Soc., 1934, 56, 460—464).—Hydration of isobutene (I) (to Bu^oOH) is catalysed by dil. HNO₃ (II) at 25°. At const. ionic strength the rate of hydration is unimol. with respect to both the concn. of (I) and the concn. of (II). For a fixed concn. of (II), the rate is increased by addition of KNO₃; this increase is > the increase in the activity of (I) as determined by distribution experiments between CCl₄ and aq. KNO₃. The sp. rate of hydration of (I) in 0.2*N*-HNO₃ at 25° is practically unchanged by addition of various metal salts [e.g., CuSO₄, NiSO₄, Pb(NO₃)₂, Hg(NO₃)₂, Th(NO₃)₄]. The ratio *k*_{35°}/*k*_{25°} is about 3.6 [for three concns. of (II)]; the heat of activation is 23.39 kg.-cal. Mixtures of Δ^α- and Δ^β-butenes are not hydrated in *N*-HNO₃ at 25°.

H. B.

Unimolecular reaction velocities and intramolecular energy exchange. C. C. COFFIN (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 161—168).—A theoretical discussion is given of results obtained from the preliminary study of the thermal decomp. in the gaseous state of ethylidene diesters and of paraldehydes.

H. S. P.

Raman effect in the study of chemical reactions. S. PARTHASARATHY (Phil. Mag., 1934, [vii], 17, 471—476).—The reactions between EtOH and AcOH, EtOH and Ac₂O, and Ac₂O and H₂O have been followed by observing the intensity variation of characteristic Raman frequencies. Some new frequencies for chloral, solid chloral hydrate, CH₂Cl·CO₂H, and CCl₃·CO₂H are recorded.

H. J. E.

Thermal decomposition of organic compounds from the viewpoint of radicals. VI. Mechanism of some chain reactions. F. O. RICE and K. F. HERZFELD (J. Amer. Chem. Soc., 1934, 56, 284—289).—Theoretical. The observations that (a) the decomp. of C₂H₆, COMe₂, and Me₂O are unimol. reactions, (b) the decomp. of MeCHO is of the order 1.5, (c) the formation of C₂H₆ from C₂H₄ and H₂ is bimol., are consequences of the theory of free radicals (A., 1931, 819; 1933, 930). E. S. H.

Kinetics of reaction of the thiosulphate ion with the ions of brominated malonic and succinic acids. M. H. BEDFORD, R. B. MASON, and C. E. MORRELL (J. Amer. Chem. Soc., 1934, 56, 280—283).—Velocity determinations at different concns. cannot be explained by Bronsted's theory, but are explicable in terms of the theory of La Mer and Kamner (A., 1931, 1132). E. S. H.

Autoxidation of stannous chloride. IV. Effect of some non-aqueous solvents. R. C. HARING and J. H. WALTON (J. Physical Chem., 1934, 38, 153—160).—The formation of a complex between SnCl_2 and HCl has been indicated by f.-p. measurements in dioxan. An equimol. compound of SnCl_2 and dioxan has been identified. The autoxidation of SnCl_2 in dioxan and BzOH increases nearly linearly with HCl concn. until the latter approaches the concn. of SnCl_2 , when the rate becomes practically const. At const. HCl concn. the rate also approaches a const val. with increasing concn. of SnCl_2 . The results confirm the assumption that SnCl_2 is autoxidised in the form of its complex HSnCl_3 or H_2SnCl_4 (cf. A., 1933, 472). Induced oxidation of the solvents dioxan and BzOH also takes place. Several positive and negative catalysts are found to have, qualitatively, the same effect as in aq. solutions (*loc. cit.*). M. S. B.

Kinetics of reaction and adsorption in the system silver-oxygen. A. F. BENTON and L. C. DRAKE (J. Amer. Chem. Soc., 1934, 56, 255—263).—Finely-divided Ag reacts with O_2 at $160^\circ/1$ atm. The no. of c.c. of O_2 reacting per hr. per mm. pressure is given by $7.2 \times 10^7 e^{-22,000/RT}$; the rate is proportional to the pressure, but independent of the extent of oxidation over the range 0.3—10%. In absence of oxide the initial rate is about four times as great. The rate of decomp. is given by $1.9 \times 10^{17} e^{-35,600/RT}$. The difference between the energies of activation of the forward and reverse reactions is equal to the heat of reaction. Two types of adsorption occur below the dissociation pressure of Ag_2O : (a) physical adsorption, which is great at -183° , but small at -78.5° , (b) activated adsorption, which is slow at 0° , but increases rapidly at higher temp. The energy of activation for (b) is 12.7 kg.-cal., and for desorption 28.4 kg.-cal. Solubility is not an appreciable factor. Calculation shows that the rate at which O_2 mols. collide with the surface with energy in excess of the required activation energy is approx. equal to the initial rate of adsorption.

E. S. H.

Rate of dissolution of electrolytic zinc in acids. M. CENTNERSZWER and M. STRAUMANTIS (Z. physikal. Chem., 1934, 167, 421—430).—The rate of dissolution, v , in $N\text{-HCl}$ rises as reaction proceeds, and ultimately reaches a steady val., v' ; the period of induction is longer than with any other form of pure Zn . If the Zn is first treated for 3 min. with $4N\text{-HCl}$, v is a max. at the start and slowly falls towards a limiting val. Rubbing the Zn with emery-paper also eliminates the period of induction, and v ultimately approaches v' . This mechanical treatment possibly establishes local elements between points deformed to different extents. v' varies with the acid concn., C , according to $v' = K(C - C_0)$, where C_0 is the acid concn. for which $v' = 0$, and K is a const. Stirring does not affect v' , which indicates that the rate of dissolution is determined by the rate the chemical process. Electrolytic Zn dissolves far more slowly than in HCl of the same $[\text{H}^+]$, rubbing with emery-paper increases v initially.

R. C.

Velocity of dissolution of copper in cupric salt solutions. A. BASINSKI (Rocz. Chem., 1934, 14, 31—44).—The velocity v of dissolution of Cu in aq. CuCl_2 and CuBr_2 varies with temp. and rate of stirring in a way characteristic of diffusion processes, and is unaffected by the presence of NH_4Cl , or by variations in the concn. of CuCl_2 ; the val. of v for various solutions increases in the order: $\text{Fe alum} < \text{CuCl}_2 < \text{CuBr}_2$. Saturating the solutions with CO_2 slightly increases v . R. T.

Rate of decomposition of cathode deposits formed on platinum electrodes in presence of helium, nitrogen, and oxygen at low pressure. J. PIAZZA (Anal. Inst. invest. cient. tecn., 1931, 2, 33—49).—Isotherms showing the rate of evolution of He , N_2 , or O_2 from the deposits at temp. between 87° and 143° have been determined. At low temp. the reaction is partly reversible, but above a certain temp. it becomes completely irreversible; in all cases the decomp. begins at a definite temp. The rate of decomp. varies with the composition. The isotherms indicate the occurrence of autocatalysis. Several compounds appear to be formed in each case between the Pt and the gas. H. F. G.

Rate of oxidation of quinol with atmospheric oxygen. I. II. Influence of sodium sulphite. W. REINDERS and P. DINGEMANS (Rec. trav. chim., 1934, 53, 209—230, 231—238).—I. At p_{H} 6.9—7.9 the rate is proportional to $[\text{C}_6\text{H}_4(\text{OH})_2]$, to the pressure of O_2 (p_{O_2}) and to $[\text{OH}]^2$. No H_2O_2 is formed. The reactions are (1) $\text{C}_6\text{H}_4(\text{OH})_2 + \text{O}_2 = \text{C}_6\text{H}_3(\text{OH})\text{O}_2 + \text{H}_2\text{O}$ (this reaction determines the measured rate), (2) $\text{C}_6\text{H}_3(\text{OH})\text{O}_2 + \text{C}_6\text{H}_4(\text{OH})_2 = 2\text{C}_6\text{H}_4\text{O}_2 + \text{H}_2\text{O}$ or $n\text{C}_6\text{H}_3(\text{OH})\text{O}_2 \rightarrow \text{polymerides}$. The reaction is catalysed by CuSO_4 in proportion to its concn. The catalysed rate is proportional to $[\text{C}_6\text{H}_4(\text{OH})_2]^{1.05 \text{ or } 0.6}$, to $[\text{OH}]$, and to p_{O_2} ; MnSO_4 is a weak catalyst. The catalytic action of CuSO_4 is due to a colloidal complex of Cu with $\text{C}_6\text{H}_4(\text{OH})_2$.

II. The rate has been measured with additions of Na_2SO_3 up to 100%, at p_{H} 7.35—8.18. Each substance hinders the oxidation of the other. The Na_2SO_3 in a mixture is oxidised before the $\text{C}_6\text{H}_4(\text{OH})_2$. The mechanism of inhibition is discussed. An explanation on the chain theory is unsatisfactory.

H. J. E.

Rate of oxidation of metol with atmospheric oxygen and the influence of sodium sulphite. W. REINDERS and P. DINGEMANS (Rec. trav. chim., 1934, 53, 239—245).—At p_{H} 6.0—6.6 the rate is proportional to the concn. of metol, to p_{O_2} , and to $[\text{OH}]$. CuSO_4 is a weak catalyst. Na_2SO_3 has the same effect as on $\text{C}_6\text{H}_4(\text{OH})_2$ (cf. preceding abstract). The rate is controlled by the reaction $\text{NHMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}' + \text{O}_2 = \text{NHMe}\cdot\text{C}_6\text{H}_4\text{O}_3'$. This is followed by the rapid reaction $\text{NHMe}\cdot\text{C}_6\text{H}_4\text{O}_3' + \text{H}^+ = \text{NMe}\cdot\text{C}_6\text{H}_4\text{O}_2 + \text{H}_2\text{O}$.

H. J. E.

Mechanism of oxidation processes. XXXVIII. [Dehydrogenation] with ethyl peroxide catalysed by iron. H. WIELAND and K. BOSSERT (Annalen, 1934, 509, 1—18; cf. A., 1930, 890).—The reaction $\text{RH}_2 + \text{Et}_2\text{O}_2 \text{ (I)} \rightarrow \text{R} + 2\text{EtOH}$ is catalysed by Fe^{2+} ; the catalysis is not retarded by KCN . Thus HCO_2H is dehydrogenated by (I) in presence of a little FeSO_4 .

to CO_2 (max. amount at $p_{\text{H}} 6$). Lactic acid (II) affords CO_2 (best at $p_{\text{H}} 7$), but with high concns. of (II), AcCO_2H (which is oxidised to CO_2) is detected as an intermediate. The following compounds are also dehydrogenated (the products formed are given in parentheses): tartaric acid at $p_{\text{H}} 5-7$ (CO_2); dihydroxymaleic acid; mandelic acid (CO_2 and PhCHO); *o*- and *m*- $\text{C}_6\text{H}_4(\text{OH})_2$; *p*- $\text{C}_6\text{H}_4(\text{OH})_2$ (*p*-benzoquinone); pyrogallol (purpurogallin in dil. solution; cf. Willstätter and Stoll, A., 1918, i, 555); guaiacol; hydrazobenzene; benzidino. Glycine, alanine (III), and phenylalanine react with (I) only in presence of Fe^{++} to give CO_2 ; β -amino- γ -hydroxybutane [*H* oxalate, m.p. 164—165° (decomp.); oxalate, m.p. 208° (decomp.); platinichloride, m.p. 190° (lit. 185°)], and CH_2O , MeCHO , and $\text{CH}_2\text{Ph}\cdot\text{CHO}$, respectively: $\text{NH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H} + 2\text{Et}_2\text{O}_2 \longrightarrow \text{RCHO} + \text{CO}_2 + 2\text{EtOH} + \text{NH}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{OH}$. (III) is dehydrogenated more readily in presence of MeCHO probably owing to the suppression of the reaction $\text{Et}_2\text{O}_2 \longrightarrow \text{MeCHO} + \text{EtOH}$, which is also catalysed by Fe^{++} and occurs during the above dehydrogenations. All the reactions are carried out at 20° or 37° in N_2 .

H. B.

Effect of methyl substitution on catalysed dehydrogenation of cyclic hydrocarbons with six-membered rings. A. A. BALANDIN and A. M. RUBINSTEIN (Z. physikal. Chem., 1934, 167, 431—440).—The rates of dehydrogenation of cyclohexane (I), methylcyclohexane (II), and mixtures of the two on Ni supported on Al_2O_3 have been determined at 200—270°. At all temp. (II) is dehydrogenated approx. 20% more rapidly than (I). The energy of activation, Q , is practically the same for (I), (II), and their mixtures, viz., 13,590 g.-cal. The relation previously reported (A., 1933, 234) between Q and k_0 in Arrhenius' equation $K = k_0 e^{-Q/RT}$ is confirmed.

R. C.

Neutral salt action in ion reactions in concentrated salt solutions. A. VON KISS [with R. KUKAR] (Z. physikal. Chem., 1934, 167, 354—364).—Polemical against Parts (cf. A., 1933, 789) with reference to the effect of neutral salts on the reactions $\text{CO}\cdot\text{Me}\cdot\text{CH}_2\cdot\text{CO}_2' + \text{OH}' = \text{OH}\cdot\text{CH}\cdot\text{CO}_2' + \text{CO}_2\cdot\text{Me}'$ and $\text{CO}\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2' + \text{OH}' = \text{CO}_2\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}_2' + \text{Br}' + \text{H}_2\text{O}$ at 25°. $\log k$, where k is the velocity coeff., increases linearly with the neutral salt concn., c , from N upwards. Assuming that $k = h_r h_m F$ (A., 1925, ii, 681) experimental data show that $\log F$, or at least the logarithm of the correspondingly constructed quotients, and $\log h_m F$ are both linear functions of c . The applicability of Grube and Schmid's rule (A., 1926, 474) to ion reactions is thus demonstrated. R. C.

Metallic corrosion. Topochemistry of magnesium. A. VYSKOČIL (Coll. Czech. Chem. Comm., 1934, 6, 1—16).—Relative adsorbability on the Mg limits the catalysis of corrosion by a mixture of anions. Although Cl' alone is more active catalytically than SO_4'' , the latter is more strongly adsorbed from a mixture and controls the velocity. The adsorbability of $\text{I}' > \text{Br}' > \text{Cl}'$, and thus I' and Br' depress the effect of Cl' except in the final stages of corrosion. The catalysis is explained as the formation of complexes between Mg atoms and hydrated anions at discon-

tinuities of the metal surface, the H_2O liberated during complex formation being decomposed by neighbouring Mg atoms. If the exchange of electric charges is especially favoured, a black, unstable substance ("suboxide"), probably a mixture of disintegrated Mg and $\text{Mg}(\text{OH})_2$, is formed.

J. G. A. G.

Active oxides. LXXII. Course of reactions in the solid state. G. F. HÜTTIG [with E. ROSENKRANZ, B. STEINER, and H. KITTEL] (Z. anorg. Chem., 1934, 217, 22—26).—The changes in the catalytic activity of an equimol. mixture of MgO and Fe_2O_3 , as it is transformed by rising temp. into MgFe_2O_4 , have been investigated by its effect on the velocity of oxidation of CO to CO_2 . The max. activity is reached at 625°. The ferromagnetic behaviour and X-ray diagram indicate that at this point the formation of cryst. aggregates of spinel is beginning, but that most of the mixture is still in the stage preceding this formation. Pure MgO , formed by the thermal decomp. of MgCO_3 or MgC_2O_4 , also catalyses CO oxidation. If the freshly prepared MgO be heated at 700°, the activity falls as the time of heating increases. If the MgO is prepared from magnesite containing Fe, there is a subsequent rise in activity to a max. which is the same as the activity max. for MgFe_2O_4 .

M. S. B.

Two types of activated adsorption of hydrogen on the surface of a promoted iron synthetic ammonia catalyst. R. W. HARKNESS and P. H. EMMETT (J. Amer. Chem. Soc., 1934, 56, 490—491).—Evidence of two distinct types of activated adsorption and one type of physical adsorption at a catalyst of Fe promoted with 1.3% Al_2O_3 and 1.59% K_2O is adduced. The characteristics of the types are described.

E. S. H.

Catalysts for oxidation of ammonia. I. Chromium catalysts.—See B., 1934, 236.

Formation of ammonia on highly-dispersed metals. D. P. DOBYTSCHIN and A. V. FROST (Z. Elektrochem., 1934, 40, 89—91).—A mixture of finely-divided Fe and NaCl, formed by vaporising the two together at a pressure of 0.06 mm. in N_2 and H_2 , adsorbs these gases when cooled in liquid air. Even at 20° the pressure returns to 0.03 mm. only, but, contrary to the observations of Müller and Schwabe (A., 1933, 36), there is no evidence of the production of NH_3 . The $\text{N}_2\text{--H}_2$ complex on the Fe is very stable, and cannot be readily destroyed below 100°. The production of NH_3 by vaporised Pt (cf. Bastow, A., 1931, 1120) has been confirmed.

M. S. B.

[Formation of ammonia on highly dispersed metals.] E. MÜLLER and K. SCHWABE (Z. Elektrochem., 1934, 40, 91—92; cf. preceding abstract).—The temp. 175—355° at which the Fe adsorption complex is heated is sufficient to cause the decomp. of any NH_3 formed.

M. S. B.

Kinetic measurements with concentrated strong acids. B. BLASER (Z. physikal. Chem., 1934, 167, 441—457).—The reaction $\text{H}_4\text{P}_2\text{O}_6 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_4$, which is catalysed by acids (A., 1933, 1130), has been used to assess the strength of conc. acids. Similar results have been obtained from kinetic measurements on the hydrolysis of HSO_3F and Frey and Elöd's indicator method (A., 1931, 1401). With

the acids studied, except HNO_3 , the activity rises rapidly with the concn. up to about 70 wt.-%. The strength of HNO_3 above about 6*N* rises much more slowly than that of other acids; probably the acid begins to change into a weaker tautomeric form. The hydrolysis of $\text{MeO}\cdot\text{SO}_3\text{H}$ and $\text{NHPh}\cdot\text{SO}_3\text{H}$ cannot be used to determine the strength of acids owing to intermediate and side reactions. R. C.

Influence of surface-active substances on the velocity of evaporation of carbon dioxide from supersaturated solutions. N. A. HELD and A. D. TRATSCHKEV (Compt. rend. Acad. Sci. U.R.S.S., 1933, 299—302).—Surface films of *iso*amyl, *n*-butyl, and *n*-heptyl alcohols and *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ each produce a retardation of the evaporation of CO_2 from its supersaturated solution, the effect being greatest with concns. corresponding with < a unimol. surface layer. The effect is greatest with *iso*amyl alcohol. With higher concn. the evaporation is less retarded, and may even be accelerated by the film. The phenomena are explained on the basis of the resistance of the film itself, and the effect on the stirring of the surface layer of the aq. solution by the motions in the film.

J. W. S.
Electrolytic concentration of the heavy hydrogen isotope. B. TOPLEY and H. EYRING (Nature, 1934, 133, 292; cf. this vol., 154).—The electrolytic separation coeff., α , defined by the equation $d \log H^1 = \alpha d \log H^2$, of the metals examined lies between 7.9 and 2.8, the order being: smooth $\text{Pt} > \text{Pb} > \text{Fe} > \text{Cu} > \text{Ag} > \text{Ni} > \text{W} > \text{Pt-black} > \text{Ga}_{\text{liq.}} > \text{Hg}$. α is slightly lower in acid than in alkaline solution, and moderate changes in c.d. have little effect. The over-voltage mechanism proposed by Gurney presents serious difficulties for its acceptance. L. S. T.

Preparation of heavy hydrogen. P. HARTECK (Proc. Physical Soc., 1934, 46, 277—280).—Details of a method by the electrolysis of an alkaline solution with Ni electrodes are described. N. M. B.

Enrichment of the heavy hydrogen isotope [in water]. W. UHLMANN (Naturwiss., 1934, 22, 119—120).—The acid in an old battery of accumulators, which had been in use for 6—10 years and to which only H_2O had been added, afforded H_2O of d 1.000033 (i.e., $\text{H}^2 : \text{H}^1 = 1 : 3000$). A. J. M.

Alkaline accumulator. I. Electrolysis of alkali zincate solution. S. TANAKA. II. S. TANAKA and K. IWASA. III. Alkali zincate accumulator with nickel-mesh cathode. S. TANAKA and T. TOMINAGA (J. Electrochem. Assoc. Japan, 1933, 1, 143—149, 149—153, 220—225).—I. Relative vals. of the current at a Ni electrode and the cathode p.d. were determined in aq. NaOH , or preferably KOH , containing ZnO of various concns. An amalgamated Ni cathode is most effective for prolonged Zn deposition.

II. The solubility of the deposited Zn is low in 7*N*- KOH with $\text{KOH} : \text{ZnO} = 12$. Amalgamation of the cathode increases the rate of deposition of the Zn and lowers its solubility.

III. Ni-mesh cathodes give the most compact Zn deposit, the cryst. particles become coarser on repeated charge and discharge. CH. ABS.

Electrolysis of molten silicates and preparation of silicon and silicides. L. ANDRIEUX and M. DODERO (Compt. rend., 1934, 198, 753—755; cf. A., 1930, 405).—With a C crucible as anode, an Fe rod as cathode, and a mixture of $2\text{SiO}_2 + \text{Li}_2\text{O} + 6\text{LiF}$, at 950° a current of about 25 amp. at 10 volts gave a product containing Si 24.1—46.8%, Si combined with Li 30.7—55.5, Si with Fe 0.7—2.6, Li 17.0—17.8, and Fe 0.7—2.6; with H_2O -cooled cathode and a mixture of $\text{SiO}_2 + \text{Li}_2\text{O} + 2-4\text{LiF}$ (or $6\text{LiF} + \text{LiCl}$) at $800-920^\circ$ the corresponding figures were 0—6.4, 48.6—61.8, 0.5—2.5, 26.3—36.4, and 0.5—2.6. In the latter case the product was spontaneously inflammable in air, as also was the gas evolved on contact with H_2O . The Li silicide is violet-coloured, and approx. Si_3Li_8 (cf. A., 1902, ii, 452). C. A. S.

Electrolysis of metals, studied with a scraped electrode. J. HOEKSTRA (Coll. Czech. Chem. Comm., 1934, 6, 17—36).—Whereas the unscraped Ag electrode (I) in *M*- AgNO_3 gave irregular current-voltage curves, the scraped electrode afforded a rectilinear relationship. The resistance is independent of the pressure on the scraper, is increased by adding gelatin, and has a min. val. for a particular rate of scraping. The resistance decreased with increase of a.c. Cu behaved, qualitatively, like Ag, whilst Hg deposition from HgNO_3 in HNO_3 afforded a linear relationship. Scraping eliminated slight irregularities from the curves for the unscraped Pb electrode (II) and had a very large effect on the Zn electrode (III). A close parallelism was found between the polarographic resistances observed with (I), (II), and (III), and the corresponding sp. resistances recorded by Kohlrausch and Holborn. The scraped Ni electrode had no permanent polarisation, and hence the polarograms coincided in both directions, but without scraping coincidence was absent although all of the curves were logarithmic. Photomicrographs of growing deposits of Ag, Cu, Pb, Sn, and Tl are given and rates of spreading are recorded. The c.d. attains high vals. at the many step-edges of the surface, and from the data for scraped electrodes it was inferred that only about 1 in 10^5 atoms of the Ag surface was activated during electrolysis. Without scraping, the no. of such active points does not remain const. Existing data are interpreted in terms of activation and adsorption.

J. G. A. G.
Polarographic studies with the dropping mercury cathode. XXXVII. Electrodeposition of gold. J. HERMAN (Coll. Czech. Chem. Comm., 1934, 6, 37—53).—Current-voltage curves, *C*, have been obtained for the deposition, at the dropping Hg cathode, of Au from Au^{I} and Au^{III} complexes in O_2 -free alkali hydroxide and cyanide solutions. Au^{III} complexes slowly decompose into, and are always accompanied by, Au^{I} complexes; this change is catalysed by KCN , OH^- , and rise of temp. The deposition from AuCl_3 in 2*N*- KOH at zero voltage decreases with age of the solution owing to slow transformation into more stable complexes, but no mobile equilibrium exists between Au^{III} and Au^{I} . Au is deposited from Au^{III} and Au^{I} at -0.4 and -1.1 volts, respectively, referred to the *N*- Hg_2Cl_2 electrode. The limiting currents at < 1.4 volts in the complex Au-CN solutions have vals.

characteristic of Au^{I} and Au^{III} , respectively, and are directly proportional to concn. This affords the basis of a polarographic determination of Au in ores and alloys, since in large $[\text{KCN}]$, Zn, Cu, Fe, Ag, As, Sb, Pb, and Bi do not interfere. The form of C indicates that KCN produces with the $\text{Au}^{\text{III}}\text{-OH}$ complex a $\text{Au}^{\text{III}}\text{-OH-CN}$ complex (I) which is unaltered by excess of KCN, whilst the addition of KOH does not change the $\text{Au}^{\text{III}}\text{-CN}$ complex (II). C for a mixture of (I) and (II) is the sum of the effects of (I) and (II). (II) only is produced by adding AuCl_3 to a mixture of KOH and KCN, and the $\text{Au}^{\text{I}}\text{-OH}$ complex is transformed into the $\text{Au}^{\text{I}}\text{-CN}$ complex by KCN. The general stability of these complexes and their slow response to conditions in solution are emphasised. J. G. A. G.

Electrolysis of sodium bismuthiodide solutions. A. E. JURIST and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 15—17).—Electrolysis of Na_2BiI_5 in $(\text{CH}_2\text{OH})_2$ solution causes migration of most of the Bi to the anode, where I is also liberated. About 6% of the Bi is deposited on the cathode.

C. G. A.

Comparison between cathode deposits of silver and colloidal silver. J. PIAZZA (Anal. Inst. invest. cient. tecn., 1931, 2, 50—52).—Colloidal Ag is produced when a suspension of pptd. Ag_2O in alcoholic Na tauroglycocholate solution is heated at 50—60°, particularly in presence of H_2 . The product obtained by filtering and evaporating the solution is readily sol. in H_2O or abs. EtOH, but not in aq. EtOH. If, however, the Ag_2O is projected cathodically (at 860 volts) on to a film of the same salts formed on the walls of the discharge tube, in presence of O_2 at 0.75 mm. or air at 0.2 mm., it does not possess colloidal properties, even after being warmed with EtOH.

H. F. G.

Electrolytic manufacture of magnesium.—See B., 1934, 203.

Theory of chromium plating. E. LIEBREICH (Z. Elektrochem., 1934, 40, 73—87).—The current-voltage curve of H_2CrO_4 has two branches. Metallic Cr separates when the Cr^{++} stage is reached. Four-branched curves are obtained with a Au cathode when an additional acid, e.g., HCl, HF, H_2SiF_6 , HClO_3 , or HClO_4 , is present. The position of the curves is practically independent of the nature of the acid. With a Pt cathode there is a further branch showing H_2 evolution without Cr deposition at zero ϵ_{aq} . A Cr oxide film is formed on the Au cathode, but not to an appreciable extent on Pt. As a result there is a considerable H_2 overvoltage in the former case, but not in the latter. The temporary occurrence of a negative potential is due to a saturation of the cathode with H_2 and not to a transition resistance as a result of the formation of an oxide film. The nature of the Cr deposit at 20° and 40° for different concns. of a no. of acids and mixed acids has been studied.

M. S. B.

Rare earths. XLI. Electrolytic preparation of rare-earth amalgams. 3. Amalgams of lanthanum, neodymium, cerium, samarium, and yttrium. Metallic lanthanum, neodymium, and cerium by thermal decomposition of their amalgams. E. E. JUUKOLA [with L. F. AUDRIETH

and B. S. HOPKINS] (J. Amer. Chem. Soc., 1934, 56, 303—304; cf. A., 1931, 805).—Dil. amalgams of La, Nd, Ce, Sm, and Yt are prepared by electrolyzing conc. solutions of the anhyd. chlorides in EtOH, using a Hg cathode. By distilling in vac. a concn. of 15% has been reached. La, Nd, and Ce have been prepared by thermal decomp. of the amalgams.

E. S. H.

Texture of cathodic deposits. A. GLAZUNOV (Z. physikal. Chem., 1934, 167, 399—406).—The deposition of metal in electrolysis is essentially a process of crystallisation (I), but the no. of centres of (I), Z , and the linear rate of (I), G , are functions of more factors than in ordinary (I). G is much greater in the direction of the current lines than perpendicular to this direction. In the deposition of Ag, Pb, Cu, and Cd at 20° G and Z increase with the c.d., whilst with increasing concn. Z and G in the direction of the current lines fall and G perpendicular to the current lines rises.

R. C.

Anodic oxidation of lactic to pyruvic ion. G. CARPENISEANU (Compt. rend., 1934, 198, 460—462; cf. A., 1923, ii, 298).—This is effected when pure aq. Na lactate is electrolysed with p.d. 1.5—3.5 volts, at low c.d. (about 1 milliamp.). The yield is low, much of the AcCO_2H formed being oxidised to CO_2 and MeCHO . Electrolysis under identical conditions of 0.01M-Na lactate, and of 0.01M- AcCO_2Na shows that the anodic oxidation potentials are almost the same. The reactions are: $\text{OH}\cdot\text{CHMe}\cdot\text{COO}' + 0.5\text{O}_2 = \text{AcCOO}' + \text{H}_2\text{O}$, and $2\text{OH}\cdot\text{CHMe}\cdot\text{COO}' + 2\oplus = \text{MeCHO} + \text{CO} + \text{H}_2\text{O} + \text{AcCO}_2\text{H}$, the former predominating. Presence of diastase has no effect.

C. A. S.

Electrolytic reduction of camphoric acid imide. B. SAKURAI and Y. TAMURA (J. Electrochem. Assoc. Japan, 1933, 1, 139—143).—Reduction does not occur in 80% H_2SO_4 , or at < 30° whatever the H_2SO_4 concn.; it occurs readily at > 80° in 15—30% H_2SO_4 . β -Camphidone (I) is formed at high, and α -camphidone (II) at low, H_2SO_4 concn. The yields of both decrease, and of camphidine (III) increases, at high temp. Reduction of (I) to (III) is difficult, and of (II) to (III) easy. The different reducibilities are due to a difference in the properties of the two CO_2H groups in camphoric acid imide.

CH. ABS.

Electrolytic oxidation of piperidine. K. YAMAMOTO and M. YOKOYAMA (J. Electrochem. Assoc. Japan, 1933, 1, 160—162).—Piperidine (5.15 g.) in 2N- H_2SO_4 electrolysed with PbO_2 -Pb anode and Pt cathode at 0.05 amp. per sq. cm. and 8 faradays per mol. gives δ -aminovaleraldehyde, δ -aminovaleric acid (0.95 g.), glutaric acid (0.5 g.), NH_3 (1.9 g. as NH_4Cl), succinic acid (2.0 g.), and HCO_2H (1.8 g.).

CH. ABS.

Synthesis of cuprous nitride by cathodic dispersion of copper in nitrogen at low pressure. G. BERRAZ (Anal. Inst. invest. cient. tecn., 1931, 2, 70—78).—When Cu is dispersed cathodically at 800—1500 volts in an atm. of N_2 at 0.5—1 mm. pressure, the tube being maintained at room temp., a dark iridescent deposit containing 75% of Cu_3N and 25% of Cu_2N is formed on the walls. The X-ray diagram of the deposit indicates the presence of cryst. Cu_3N , and the absence of free Cu.

H. F. G.

Preparation of sputtered metal films. E. O. HULBERT (Rev. Sci. Instr., 1934, [ii], 5, 85—88).—In a cathode sputtering chamber containing residual air, opaque films of Sb, Bi, Cd, Au, Pb, Pt, Ag, and Sn were obtained in about 1 hr., films of Co, Cu, Ir, Fe, Ni, Se, and Te in about 2 hr., whilst Mo, Ta, and W required several hr. Al, Be, C, Cr, Mg, and Si sputter very slowly under these conditions, but films of Al, Cr, and Si were obtained after a few hr. in residual atm. of Hg, He, or A. Most sputtered particles are of mol. or at. dimensions. Films of Pt, Ta, and Cr have a nearly const. transmission for wave-lengths 0.5—2.2 μ ; films of Si and C are relatively transparent from 1.0 to 2.2 μ . E. S. H.

Cathodic sputtering of metals. R. K. COWSIK (Indian J. Physics, 1933, 8, 209—229).—The relative rates of cathodic sputtering of a no. of metals, when plotted against their respective total heats of vaporisation, yield a smooth curve, which is not quite a rectangular hyperbola. The results are in accord with the thermal theory of Waran (A., 1931, 405).

J. W. S.

Role of oxygen as an inhibitor for the photo-synthesis of hydrogen chloride. K. B. KRAUSKOPF and G. K. ROLLESON (J. Amer. Chem. Soc., 1934, 56, 327—333).—Kinetic measurements at high concns. of O_2 show that as the ratio $O_2 : Cl_2$ increases the ratio $H_2O : KCl$ approaches a limit between 1 and 2. The rate of approach to the limit increases slightly with increasing concns. of H_2 and HCl , and depends slightly on the temp., indicating that the activation energy for the reactions yielding HCl is $>$ that for those yielding H_2O . The existence of the limit shows that the Nernst chains must be ended by a reaction $H + O_2 = HO_2$ rather than $Cl + O_2 = ClO_2$.

E. S. H.

Photochemical union of hydrogen and chlorine.
III. Effect of wave-length on quantum efficiency. Experiments with dispersed light. J. B. BATEMAN and A. J. ALLMAND (J.C.S., 1934, 157—161).—The quantum efficiency, γ , is independent of λ between 400 and 490 $m\mu$ and falls slowly on either side of this region, being still appreciable at 550 $m\mu$. Allmand's earlier statement (A., 1931, 1136), that γ falls considerably in the ultra-violet, was due to the accidental use of a glass window in place of SiO_2 . The results obtained at 492 $m\mu$ (just beyond the convergence limit of the banded spectrum of Cl_2) are anomalous, since $\gamma_{492}/\gamma_{405}$ rises on prolonged irradiation from an initial val. of about 0.6 to a const. val. of about 8. The rate of reaction is proportional to the intensity of illumination at 313 $m\mu$.

D. R. D.

Photodecomposition of chlorine dioxide. J. W. T. SPINKS and J. M. PORTER (J. Amer. Chem. Soc., 1934, 56, 264—270).—In presence of H_2O dark reactions are avoided and 1 mol. disappears from the gaseous phase for each mol. of ClO_2 decomposed by light. The quantum efficiency, γ , is independent of concn. and light intensity for low concns. of ClO_2 . At 3650 Å., γ is > 3 ; the ratio of γ at 4360 and 3650 Å. is 0.86 : 1. The sensitised reaction in presence of Br at 5460 Å. gives γ equal to that at 3650 Å. With dry gases the reaction is sensitive to temp. changes.

At 15° the pressure decreases during the reaction, and Cl_2O_6 is formed; at 30° the pressure increases and Cl_2 and O_2 are formed. The photolysis of dry ClO_2 is a chain reaction.

E. S. H.

Photodecomposition of gaseous ammonia. R. A. OGG, jun., P. A. LEIGHTON, and F. W. BERGSTROM (J. Amer. Chem. Soc., 1934, 56, 318—323).—Using ultra-violet light of wave-lengths 2194, 2144, and 2099 Å., NH_3 is decomposed into N_2 and H_2 stoichiometrically, with a quantum efficiency (γ) of 0.14 at 20°. γ increases with rise of temp., but is practically independent of pressure of NH_3 or wave-length of light. When N_2H_4 is added the reaction consists in decomp. of N_2H_4 photo-sensitised by NH_3 . A mechanism of the reaction is suggested.

E. S. H.

Photochemical reaction of ammonia with oxygen. H. E. BACON and A. B. F. DUNCAN (J. Amer. Chem. Soc., 1934, 56, 336—340).—Using the radiation from a Zn spark, the reaction can be represented approx. by $8NH_3 + 7O_2 \rightarrow 2N_2 + 2NH_4NO_3 + 8H_2O$. The reaction takes place in several steps, mechanisms for which are discussed. The quantum yield is variable.

E. S. H.

Photographic blackening law for ultra-soft X-rays. H. BRIOLI and H. KIESSIG (Z. Physik, 1934, 87, 425—431).—At 1.5 Å. the blackening varied almost linearly with time, but at 45 Å. no such relation was observed. Various emulsions were used.

A. B. D. C.

Density surface of [a solid diagram representing] the Villard effect. II. H. ARENS (Z. wiss. Phot., 1934, 32, 233—238; cf. A., 1931, 1378).—The density surfaces obtained with Agfa-Laue film without and with small and large pre-exposures to X-rays are of similar form. The Villard effect can also be produced by pre-exposure with white light. The differences which occur with increasing pre-exposure are discussed.

J. L.

Photochemical reaction between bromine vapour and platinum. J. URMSTON and R. M. BADGER (J. Amer. Chem. Soc., 1934, 56, 343—347).—The initial rate of reaction of finely-divided Pt with Br at low pressures, using blue or yellow light, is reduced by 18% when the temp. is lowered by 25°. The acceleration due to illumination is proportional to the light intensity for both colours. A mechanism is not proposed, but it is inferred that the initial step is the same with blue or yellow light, and that a considerable proportion of Br_2 mols. dissociate without collision with other mols.

E. S. H.

Separation of photochemical and thermal action in the photo-bromination of cinnamic acid. W. H. BAUER and F. DANIELS (J. Amer. Chem. Soc., 1934, 56, 378—385).—The reaction in CCl_4 was followed by means of a monochromator. A chain reaction is involved. The quantum yield, ϕ , is 1—15 or more, varying with the concn. of Br and the temp. over the ranges $2-8 \times 10^{-3}$ mol. Br_2 per litre and 0—30°. The photochemical reaction consists of (a) a primary photo-reaction of 1 mol. per quantum and (b) a photo-excited thermal reaction measured by $\phi - 1 = \theta$, which is suppressed

at low Br concn. or low temp. Log 0 is nearly a linear function of $1/T$.
E. S. H.

Action of light on vinyl iodide. G. EMSCHWILLER (Compt. rend., 1934, 198, 464—466; cf. A., 1931, 694; 1933, 706).—When exposed to ultra-violet (Hg) light vinyl iodide decomposes according to: $C_2H_3I \rightarrow CH_2\cdot C + (H\cdot I) \rightarrow C_2H_2 + (H\cdot I)$ and $C_2H_3I + (H\cdot I) \rightarrow C_2H_4 + I_2$, the solitary H attached to the C to which the I is attached being removed. There is always a relative deficiency of C_2H_4 and a smaller one of C_2H_2 due to I combining therewith. In presence of O_2 in a SiO_2 vessel in ultra-violet light vinyl iodide decomposes with evolution of I and formation (mols. per mol. of C_2H_3I) of 0.6—0.65 HCO_2H , 0.2 CH_2O , 0.09 glycolaldehyde, 0.6—0.65 CO, 0.085 C_2H_2 , and a little CO_2 . (In glass the reaction is slower with relatively more glycolaldehyde and less CH_2O , less C_2H_2 , and no CO_2 .) The reactions are: $2C_2H_3I + 7O \rightarrow 2HCO_2H + 2CO + H_2O + I_2$; $2C_2H_3I + 3O + H_2O \rightarrow 2OH\cdot CH_2\cdot CHO$ (or $4CH_2O$) + I_2 (the CH_2O may result from photolysis of the $OH\cdot CH_2\cdot CHO$); and $2C_2H_3I + O \rightarrow 2C_2H_2 + H_2O + I_2$.
C. A. S.

Piperidine metavanadate, a new light-sensitive compound. O. BAUDISCH and F. L. GATES (J. Amer. Chem. Soc., 1934, 56, 373—374).—The prep. of $C_5H_{11}N\cdot HVO_3$ (I) is described. (I) is sensitive to ultra-violet light, but not to visible light. The darkening under ultra-violet light is a reversible reduction; oxidising agents regenerate (I). The ultra-violet absorption spectrum of (I) has been determined; the absorption is much > that due to $C_5H_{11}N$.
E. S. H.

Influence of light on nitrification in soil. N. R. DHAR, A. K. BHATTACHARYA, and N. N. BISWAS (J. Indian Chem. Soc., 1934, 10, 699—712).—The amount of NO_2 formed from NH_4 salts mixed with sterilised or unsterilised soils in presence of air and sunlight is much > in the dark. A similar observation was made for the amounts of NH_3 and NO_2 formed on exposing solutions of $CO(NH_2)_2$ or egg-yolk mixed with soil. Evidence is adduced to support the view that ammonification and nitrification in soil occur actively under the influence of light even in absence of micro-organisms.
E. S. H.

Influence of sensitisers on chemical reactions produced by γ -radiation. G. HARKER (Nature, 1934, 133, 378—379).—Radiation from Ra decomposes $CHCl_3$, liberating Cl_2 , which then slowly disappears with the formation of HCl as a secondary product. The apparent rate of decomp. is markedly affected by the presence of the reaction products. γ -Radiation (I) oxidises solutions of ferrous salts, but Berthelot's solution of $FeCl_3$ and $H_2C_2O_4$ is not reduced. The Fe in the reduced solution, however, is oxidised, and the addition of small amounts of different org. and inorg. substances modifies the rate of oxidation. The oxidation of $K_2S_2O_5$ in air is accelerated by (I). The addition of I, KI, or $KHSO_4$ further increases the rate of oxidation of the irradiated H sulphite solution. The oxidation of glutathione is also accelerated, but the addition of I, KI, or KIO_3 has no further effect in this case. L. S. T.

Heavy hydrogen. (Sir) J. J. THOMSON (Nature, 1934, 133, 281).—A lecture on early work concerning H_3 .
L. S. T.

Isotopic fractionation of hydrogen. H. HUNT (J. Chem. Physics, 1934, 2, 106).—The H_2 from electrolysis of H_2O containing H^2 : H^1 , 1:200 passed successively over CuO at 200° and 600° gave H_2O of which 10 ml. in the first case weighed 6.6 mg. < 10 ml. in the second case. The difference fell to 5.0 mg. on doubling the rate of H_2 flow.
N. M. B.

Chemical separation of the isotopes of hydrogen. E. D. HUGHES, C. K. INGOLD, and C. L. WILSON (Nature, 1934, 133, 291—292).—The figures given by A. and L. Farkas (this vol., 264) for the ratio of the sp. rates at which H^1 and H^2 are discharged by the dissolution of metals in H_2O must not be regarded as characteristic consts. of the metals. The vals. obtained for a given metal appear to depend in an unknown way on the experimental conditions. The authors' val. for Na is 2.9 (2.8—3.0 for media varying from strongly alkaline to strongly acidic), for Ca 1.3—1.6, and Al 4.0—4.9, the higher vals. in these two cases relating to reaction in alkaline solution. Zn containing a trace of C gives 5.6, commercial Zn 6.8, and Zn—Cu couples vals. up to 8.0.
L. S. T.

Reaction of heavy water with metallic sodium. J. HORUTI and A. L. SZABO (Nature, 1934, 133, 327—328; cf. following abstract).—When heavy H_2O containing 1.81 parts of H^2 (I) to 100 parts of H^1 reacts with Na the percentages of (I) in the $H_2 + HH^2$ formed are as follow: H_2O in excess, at room temp. 0.96, Na in excess at room temp. 0.99, Na in excess at -10° 1.01, H_2O in excess at room temp. [?] 1.03. Decomp. of HH^2O by Na apparently can lead to the formation of $NaOH$ or $NaOH^2$ alternatively, the latter being preferred, or when HH^2O comes in contact with Na, the H atom escapes with greater ease to combine with a H atom released by a neighbouring pair of reacting particles $Na + H_2O$ than does the H^2 atom.
L. S. T.

Fractionation of the hydrogen isotopes by addition of sodium to water. C. O. DAVIS and H. L. JOHNSTON (J. Amer. Chem. Soc., 1934, 56, 492—493).—Differences in d have been observed in the original H_2O , the H_2O formed by burning the H_2 liberated by Na, and H_2O obtained by distillation of the aq. $NaOH$ formed.
E. S. H.

Thermal decomposition of deuterium iodide. D. RITTENBERG and H. C. UREY (J. Chem. Physics, 1934, 2, 106—107).—The difference in the fraction decomposed at equilibrium of pure H^1I and a sample rich in H^2I showed that thermal decomp. depends on the concn. of H^2 in the HI .
N. M. B.

Introduction of deuterium atoms into acetone. J. O. HALFORD, L. C. ANDERSON, and J. R. BATES.—See this vol., 394.

Existence of ammoniates of double salts. II. G. SPACU and P. SPACU (Z. anorg. Chem., 1934, 217, 80—84; cf. A., 1933, 1128).—Ammoniates of more complex double salts have been prepared at -79° and

investigated tensimetrically. The existence of the following has been indicated :

$2M^I Cl, M^I_2 Cr_2 O_7, 4HgCl_2, 2H_2O, 10NH_3$ ($M^I = K$ or NH_4) ; $HgCl_2, HgC_2O_4, 4KCl, 11$ and $2NH_3$. The constitution of the salts is discussed. M. S. B.

Modification of form of crystals grown in solution containing foreign material. L. ROYER (Compt. rend., 1934, 198, 585—587; cf. this vol., 249).—Examples of such modifications are [figures in parentheses show the interionic distances in Å. in the (111) plane, in which in all cases the ions in one plane are alternately all metal or all halogen] : the production of octahedral crystals of NaCl (3·97) by addition to its solution of $CdCl_2$ (3·85), $ZnCl_2$ (3·77), or $MnCl_2$ (3·70), whilst these have no effect on KCl (4·43); and of octahedral faces on crystals of both salts by addition of $NaNO_3$ (5·07) to aq. NH_4I (5·09), and to a smaller extent if added to aq. KI (4·97), or KBr (4·70), but not if added to NaCl. C. A. S.

Hydrolysis of some alkali metallotartrates. J. P. MATHIEU (Compt. rend., 1934, 198, 576—578; cf. this vol., 266).—Solutions of $[TM(OH)_2]$ ($M = Mn, Fe, Co, Ni, Zn$; $T = C_4H_2O_6$) are simply hydrolysed by NaOH. Solutions of $Na_2[TM(OH)_2]$ are unstable if dil., giving if $M = Zn$ a ppt. of $Zn(OH)_2$, but if $M = Fe, Mn$, or Co , hydrolysis is according to (a) $Na_2[TM(OH)_2] + 2H_2O \rightleftharpoons H_2[TM(OH)_2] + 2NaOH$; and (b) $2Na_2[TM(OH)_2] + 2H_2O \rightleftharpoons M[TM(OH)_2] + Na_2T + 2NaOH$. (b) is proved, when $M = Co$, by the diminution in the circular dichroism caused by addition of NaOH or Na_2T , and also by the equilibrium const. of the reaction. C. A. S.

Interaction of aqueous cupric sulphate and cupric hydroxide. O. BINDER (Compt. rend., 1934, 198, 653—655).—Mixtures of 5 g. of $Cu(OH)_2$ and 100 c.c. of aq. $CuSO_4$ of varying concn. were agitated at 22° until equilibrium was attained. The ratios CuO/SO_3 and H_2O/SO_3 were both invariably 4, and no basic salt other than $(Cu_4O_3)SO_4 \cdot 4H_2O$ was found. If the relative proportions of $Cu(OH)_2$ and $CuSO_4$ were incorrect, one or other of $Cu(OH)_2$ or $CuSO_4 \cdot 5H_2O$ accompanied the basic salt. X-Ray investigation confirmed this result (cf. A., 1897, ii, 491; 1926, 246; 1932, 238). C. A. S.

Prevention of the tarnishing of silver. F. MARKHOFF (Sprechsaal, 1933, 66, 370—371; Chem. Zentr., 1933, ii, 1245).—The tarnishing of Ag in air can be prevented by varnishing. The action of alkali on Ag passivates the surface. Examples of this process are given. L. S. T.

Allotropic modifications of calcium. P. BASTIEN (Compt. rend., 1934, 198, 831—833; cf. A., 1931, 416).—When sublimed Ca is heated and allowed to cool in A, breaks occur in the cooling, thermo-electric power, and dilatation curves, and sudden changes in hardness at 240—265° (with hysteresis) and 430—440°. C. A. S.

Hydrated calcium aluminates. J. LEFOL (Ciment, 1933, 38, 322).—In the dehydration by heating of the hydrates of tetra- (I), tri- (II), and di- (III) -Ca aluminates, hydrates with lower H_2O contents are formed. The mols. of H_2O in the compounds are : (I) 10·5 11 at 95°, 6 at 175°; (II) 8—8·5 at 135° (from

the needle form), 6 up to 260°, and 1·5 from 260° to 310° (from the cubic form); (III) 5 at 150°.

T. W. P.

Composition of the black precipitate formed by the action of ammonia on mercurous chloride. S. AUGUSTI (Gazzetta, 1933, 63, 859—861).—The ppt. consists of Hg with Hg_2NCl , $Hg_2NCl \cdot NH_4Cl$, or $HgNCl \cdot 3NH_4Cl$, according to the quantity of NH_3 present. H. F. G.

Preparation of mercurous ammonium compounds from mercurous ammonium nitrate. I. Halides. S. AUGUSTI (Gazzetta, 1933, 63, 849—859).—Pptn. of an ammoniacal solution of $HgNO_3$ with NH_4Br yields Hg_2NBr ; if washing is not prolonged the product contains $Hg_2NBr \cdot NH_4Br$. NH_4Cl , KCl, and KI yield, respectively, $Hg_2NCl \cdot 3NH_4Cl$, $Hg_2NCl \cdot H_2O$, and $Hg_2NI \cdot H_2O$. With NH_4F no ppt. is formed, but KF yields Hg_2NF . The properties of the ppts. are described and photomicrographs are reproduced. H. F. G.

Microscope as aid to study of detonation. A. MICHEL-LEVY and H. MURAOUR (Compt. rend., 1934, 198, 825—826).—Microscopical examination of the result of detonating a minute particle of PbN_6 shows a central space covered with globules of Pb; this is surrounded by an almost continuous ring of Pb, and this again by pulverised Pb arranged radially. A second similar particle placed at a distance of 2—4 mm. is detonated almost simultaneously, i.e., by the explosion wave, and one further off, e.g., 15 mm., after a longer interval, i.e., by the hot gases (cf. A., 1931, 689). C. A. S.

Concentration of gallium by means of adsorption on hydrated aluminium and iron oxides. E. WAINER (J. Amer. Chem. Soc., 1934, 56, 348—350).—Hydrated Ga_2O_3 is co-pptd. with $Al(OH)_3$ and especially with $Fe(OH)_3$. The method affords a means of extracting Ga from low-grade ores. E. S. H.

Carbide hydrolysis. N. G. SCHMAHL (Z. Elektrochem., 1934, 40, 68—70).—The nature of the reaction products of the hydrolysis of the carbides of the rare earths, Th, and U is discussed from the thermochemical point of view. M. S. B.

Oxidation of hydrazine by potassium ferricyanide. I. Influence of gaseous supersaturation on the measurement of reaction velocity. II. Reaction in presence of acetone. T. N. RICHARDSON and K. C. BAILEY (Sci. Proc. Roy. Dublin Soc., 1934, 21, 43—49, 49—56).—I. Oxidation of N_2H_4 by aq. alkaline $K_3Fe(CN)_6$ is very rapid, but the rate of evolution of N_2 is governed almost entirely by the rate of stirring.

II. The reaction is retarded and eventually inhibited by large amounts of $COMe_2$ owing to formation of $(CMe_2 \cdot N)_2$. R. S. C.

Interaction of phosphorus bromide and chloride. IV. A. RENC (Rocz. Chem., 1934, 14, 69—77; cf. this vol., 158).—The products obtained by mixing CS_2 solutions of PCl_5 and PBr_5 in various proportions are the same as those obtained in the absence of a solvent. The Cl content of the products of recrystallisation of $PClBr_4$ and $PCl_{0.5}Br_{4.5}$ from CS_2 is <, and that of PCl_4Br is >, that of the original crystals.

Crystals containing > 3 atoms of Cl per atom of P lose Br under reduced pressure, yielding products of limiting composition PCl_4Br , whilst those of composition $\text{PCl}_{0.5-2.55}\text{Br}_{5.6-8.5}$ yield $\text{PCl}_{0.19-0.31}\text{Br}_{4.7-4.8}$. The d of PCl_2Br and PClBr_2 is $<$ that of mixtures of PCl_3 and PBr_3 in corresponding proportions.

R. T.

Amphoteric hydrated oxides, their higher molecular compounds, and their solutions. XXII. Iso- and hetero-polyvanadic acids, purpureo- and luteo-phosphovanadates; explanation of the structure and constitution of heteropoly-compounds. G. JANDER, K. F. JAHR, and H. WITZMANN (Z. anorg. Chem., 1934, 217, 65—79; cf. this vol., 146, and earlier abstracts).—In alkaline or slightly acid vanadate solutions the presence of H_3PO_4 has no influence on the aggregation process. Di-, tetra-, penta-, and the unstable octa-vanadic acids are formed. With increase of acidity, H_3PO_4 stabilises octavanadic acid. Isopolyvanadates and the double salts, purpureophosphovanadates, are formed. The following compounds have been isolated as reddish-brown crystals: $3\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 8\text{V}_2\text{O}_5 \cdot \text{aq.}$, $10\text{SrO} \cdot \text{P}_2\text{O}_5 \cdot 8\text{V}_2\text{O}_5 \cdot \text{aq.}$, $4(\text{NH}_4)_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot \text{aq.}$, $5(\text{NH}_4)_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot \text{aq.}$, $11\text{K}_2\text{O} \cdot 2\text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot \text{aq.}$, $10\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot \text{aq.}$, $10\text{BaO} \cdot \text{P}_2\text{O}_5 \cdot 24\text{V}_2\text{O}_5 \cdot \text{aq.}$ From still more strongly acid solutions, rich in H_3PO_4 , $p_H < 1$, greenish-yellow crystals of luteophosphovanadates are formed. These are double salts of alkali and $(\text{VO})^{\text{III}}$ or $(\text{VO}_2)^{\text{I}}$ phosphates, and not salts of true heteropolyacids. Are of the general composition $\text{M}^{\text{I}}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot \text{aq.}$ or $\text{M}^{\text{I}}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot \text{aq.}$, V being actually present as the phosphate $(\text{VO})\text{PO}_4$. From strongly acid solutions poor in H_3PO_4 a double octavanadate of Na and $(\text{VO}_2)^{\text{I}}$ is obtained of the probable composition $\text{Na}_2(\text{VO}_2)[\text{H}_7\text{V}_8\text{O}_{25} \cdot \text{aq.}]$. These results do not support the view that the existence of the heteropoly-acids is to be explained on the basis of Werner's co-ordination hypothesis. M. S. B.

Ammonium arsenates. C. MATIGNON and A. DE PASSILLE (Compt. rend., 1934, 198, 777—779).— $\text{NH}_4\text{H}_2\text{AsO}_4$, prepared from aq. NH_3 and As_2O_5 in correct proportions, forms non-deliquescent prisms, d_4^{20} 2.340. It loses NH_3 above 300° to form an almost insol. acid meta-arsenate, $\text{NH}_4\text{H}(\text{AsO}_3)_2$, which is unchanged at 425° ; no trace of As_4O_6 or As is formed. When boiled with H_2O the meta-arsenate re-forms orthoarsenate. $(\text{NH}_4)_2\text{HASO}_4$ is pptd. by EtOH from solution of its constituents. The aq. solution loses NH_3 to form $\text{NH}_4\text{H}_2\text{AsO}_4$, as also does the dry salt on gentle heating, although it is stable in dry air in the cold. $(\text{NH}_4)_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ is pptd. on saturating a solution of As_2O_5 or of either acid salt with NH_3 ; it rapidly loses NH_3 . The anhyd. salt is formed when either acid salt absorbs NH_3 under 8 atm. pressure; it also rapidly loses NH_3 . Q_0 (in $\log p = -Q_0/4.57T + 1.75 \log T + 3.3$) for the $(\text{NH}_4)_2$ and $(\text{NH}_4)_3$ salts is, respectively, 15,500 and 13,070. C. A. S.

Alkali bismuthiodides. D. MOTARD (Compt. rend., 1934, 198, 655—657).—Varying amounts of alcoholic or aq. MI were added to a mixture of freshly powdered Bi and conc. EtOH-I. After agitation and ceeping the cryst. mass was extracted with COMe_2 , whence the bismuthiodide crystallised out. The only

compounds obtained were, with EtOH-KI, $\text{KI} \cdot 2\text{BiI}_3$ and $4\text{KI} \cdot 2\text{BiI}_3$; with aq. KI, $2\text{KI} \cdot 2\text{BiI}_3 \cdot 2\text{H}_2\text{O}$ and $3\text{KI} \cdot 2\text{BiI}_3 \cdot 2\text{H}_2\text{O}$. The methods described by Arppe and Linau (Pogg. Ann., 1845, 64, 237; 1860, 111, 242) yielded no others; the $6\text{KI} \cdot 2\text{BiI}_3$ claimed by Astruc (cf. A., 1890, 1067) seems to have contained BiOI. In similar fashion $\text{NaI} \cdot \text{BiI}_3 \cdot n\text{H}_2\text{O}$ ($n=0, 1$, and 2) were prepared. C. A. S.

Reaction of bismuth [nitrate] with thiocarbamide. J. V. DUBSKY, A. OKAČ, and B. OKAČ (Z. anorg. Chem., 1934, 216, 386—390).—Addition of $\text{CS}(\text{NH}_2)_2$ to aq. $\text{Bi}(\text{NO}_3)_3$ acidified with HNO_3 gives an intense yellow solution, from which can be obtained crystals of varying shades of yellow according to the proportions in which the constituents are mixed. $1\text{Bi} : 1\text{CS}(\text{NH}_2)_2$ gives pale brownish-yellow needles, m.p. 149° (I), $1\text{Bi} : 2\text{CS}(\text{NH}_2)_2$ gives light yellow prisms, m.p. 153° (II), but (I) and (II) appear, on analysis, to have practically the same composition. In (I) $\text{Bi} : \text{N} = 1 : 8.68$ and in (II) $1 : 8.38$. The proportions $1\text{Bi} : 3\text{CS}(\text{NH}_2)_2$ give bright brownish-yellow needles, m.p. 151° . Analysis gives the composition $\text{Bi}(\text{NO}_3)_2 \cdot \text{CS}(\text{NH}_2)(\text{NH}) \cdot 2\text{CS}(\text{NH}_2)_2$. Acid BiCl_3 and $\text{CS}(\text{NH}_2)_2$ give $\text{BiCl}_3 \cdot 3\text{CS}(\text{NH}_2)_2$ in a yellow, cryst., rather labile modification and an orange-red, more stable variety. Possible formulæ are discussed.

M. S. B.

Preparation of sources of radium-E. M. HAISINSKY (J. Chim. phys., 1934, 31, 43—46).—The Ra-E in dil. HNO_3 solution is pptd. in presence of Sb by means of pyrogallol. The ppt. is dissolved in HNO_3 , NH_4 tartrate and tartaric acid are added, and the solution is electrolysed between Pt electrodes. The Ra-E is deposited at the cathode and the Sb remains in solution. H. S. P.

Isotope enrichment in technical oxygen fractions. R. KLAR and A. KRAUSS (Naturwiss., 1934, 22, 119).—A concn. of O^{18} in fractions of liquid O_2 was found ($\text{O}^{18} : \text{O}^{16} = 1 : 510$). The proportion of O^{18} in liquid and vapour of the fraction, and the v.p. of the $\text{O}^{16}\text{O}^{18}$ were derived. The v.p. of $\text{O}^{16}\text{O}^{18}$ in the neighbourhood of the b.p. is $5\% <$ that of $\text{O}^{16}\text{O}^{16}$.

A. J. M.

Potentiometric examination of the formation of thiosulphate from alkali sulphide and sulphurous acid. E. MULLER and K. MEHLHORN (Angew. Chem., 1934, 47, 134—139).—Potentiometric titration of Na_2S with aq. H_2SO_3 shows the changes $12\text{Na}_2\text{S} + 12\text{H}_2\text{SO}_3 = 6\text{NaHS} + 9\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O}$ and $6\text{NaHS} + 6\text{H}_2\text{SO}_3 = 3\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O} + 6\text{S}$ to occur successively. Passage of 100% and 7% SO_2 , respectively, through aq. Na_2S causes the respective reactions, $6\text{Na}_2\text{S} + 9\text{H}_2\text{SO}_3 = 6\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O} + 3\text{S}$ and $6\text{Na}_2\text{S} + 7\text{H}_2\text{SO}_3 = 3\text{Na}_2\text{SO}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O} + 4\text{H}_2\text{S}$ which, in presence of NaOH, become $6\text{Na}_2\text{S} + 6\text{NaOH} + 12\text{H}_2\text{SO}_3 = 9\text{Na}_2\text{S}_2\text{O}_3 + 15\text{H}_2\text{O}$ and $6\text{Na}_2\text{S} + 6\text{NaOH} + 10\text{H}_2\text{SO}_3 = 6\text{Na}_2\text{SO}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 + 9\text{H}_2\text{O} + 4\text{H}_2\text{S}$. The technical prep. of $\text{Na}_2\text{S}_2\text{O}_3$ from Na_2S and dil. SO_2 is discussed in the light of these results.

H. W.

Reactions of chromous acetate. M. CHATELET and (MME.) P. M. CHATELET (Compt. rend., 1934, 198, 833—834).—Moist $\text{Cr}(\text{OAc})_2$ (I) in C_6H_6 suspension in N_2 is converted by dry HCl (O_2 -free) into a

green compound $\text{Cr}_2\text{OCl}_4 \cdot 5\text{H}_2\text{O}$, but with $\text{HCl}-\text{O}_2$ mixtures of composition between Cr_2OCl_4 and CrCl_3 are obtained. Pptn. of a solution of dry (I) in $\text{C}_6\text{H}_5\text{N}$ with Et_2O gives the compound $[\text{Cr}(\text{OAc})_2]_2 \cdot \text{C}_6\text{H}_5\text{N}$, and passage of NH_3 into a dry C_6H_6 suspension of (I) gives the compound $[\text{Cr}(\text{OAc})_2]_2 \cdot \text{NH}_3$. J. W. B.

Sodium permolybdate. K. GLEU (Z. anorg. Chem., 1934, 216, 376; cf. A., 1933, 1258).—In presence of molybdic acid H_2O_3 should be titrated iodometrically, and not with KMnO_4 . The latter method introduces an error of varying size according to conditions (cf. A., 1932, 484). M. S. B.

X-Ray confirmation of a new type of combination. I. Tungsten oxides W_4O_{11} and W_8O_{23} . F. EBERT and H. FLASCH (Z. anorg. Chem., 1934, 217, 95—104).—By the action of active H, obtained by the glow discharge in H_2 , W_8O_{24} (or 8WO_3) is reduced to a readily oxidisable compound W_8O_{23} and a more stable oxide W_4O_{11} . It is shown by X-ray analysis that these are not mixtures of WO_3 and WO_2 , but have a definite cryst. structure in which W^{VI} and W^{IV} exist together as structural units. The removal of O in stages results in a deformation of the lattice indicated in the Debye-Scherrer diagram. M. S. B.

Oxygen fluorides, O_2F_2 and OF. O. RUFF and W. MENZEL (Z. anorg. Chem., 1934, 217, 85—92).—The fluorides were prepared as previously described (A., 1933, 476). V.p. for O_2F_2 has been determined for the temp. range -132° to -57° . Decomp. into OF begins above -100° ; b.p. (extrapolated) -57° , m.p. -163.5° , $d = 2.074 - 0.002917$. The vol. of the mol. sphere, as determined from the mol. vol. at b.p., is 41.75 \AA^3 and radius 2.15 \AA . OF is distinguished from an equimol. mixture of O_2 and F_2 by the fact that it is completely absorbed by HI. Data for v.p. are given for the temp. range -201.1° to -185.4° and are represented by $\log p = 6.897 - 352.7/T$; b.p. -185.4° , m.p. -223° . There are also two transition temp., -235° and -226° . $d \text{ } 1.82_3 - 0.00567$ between -198.0° and -190.7° ; $d_{\text{solid}} \text{ } 1.625$ at -225° . OF is nearly as chemically reactive as F_2 , but is fairly stable in a quartz vessel at room temp. The vol. of the mol. sphere is 22.7 \AA^3 and radius 1.76 \AA . M. S. B.

Reaction products of different forms of carbon with fluorine. II. Carbon monofluoride. O. RUFF and O. BRETSCHNEIDER [with F. EBERT] (Z. anorg. Chem., 1934, 217, 1—18; cf. A., 1930, 1387).—F combines with C either in the form of norit (I) at approx. $280^\circ/25 \text{ mm.}$ or of graphite (II) at $420^\circ/760 \text{ mm.}$ to form CF. This is a grey solid, $d \text{ } 2.39$, insol. in ordinary solvents, not wetted by H_2O and aq. solutions, but wetted by org. solvents, e.g., C_6H_6 , COMe_2 , EtOH , etc., and unattacked by H_2 at 400° and by aq. HI. Zn dust and AcOH reduce it to its original C form, whether (I) or (II). The sp. electrical resistance is $> 3000 \text{ ohms}$, whilst that of (II) is 0.03 ohm . CF does not adsorb HCl or methylene-blue from EtOH solution, but it adsorbs NaOH and PhOH giving, with the former, a brown colloidal solution. X-Ray investigation indicates that F is inserted between the base planes of (II), two F atoms being connected to two C atoms. At higher pressure

and temp. volatile fluorides are formed, the amount and composition varying with conditions. Graphitic CF may decompose explosively. M. S. B.

Manganese oxides. M. LE BLANC and G. WEHNER (Z. physikal. Chem., 1934, 168, 59—78).— MnO , prepared by heating MnCO_3 in a vac. at $420-450^\circ$, is able to take up O_2 even at room temp., the sorbed O being active. Up to $\text{MnO}_{1.13}$ the product is homogeneous, and has the MnO lattice, but from $\text{MnO}_{1.13}$ to Mn_3O_4 the X-ray diagram shows the product to be a mixture of MnO and Mn_3O_4 . Mn_3O_4 can take up O_2 up to $\text{MnO}_{1.42}$ without change in lattice or appearance of a second solid phase, but with further absorption of O_2 a new phase, an unstable modification of Mn_2O_3 , probably having a tetragonal body-centred lattice, starts to be present. This form, which changes into the ordinary form with the bixbyite structure on tempering, is apparently able to take up O_2 without change in lattice. The max. amount of O_2 which can be absorbed by active MnO corresponds with $\text{MnO}_{1.58}$. No O_2 can be withdrawn from MnO_2 without the immediate appearance of the lattice of the stable form of Mn_2O_3 , but it seems impossible to achieve complete reversal of evolution or absorption of O_2 . No evidence of formation of mixed crystals by the various oxides in the course of withdrawal of O from MnO , could be obtained; the systems seem always to be two-phase. The lattice structures of the naturally occurring Mn oxides have been checked. R. C.

Iodates. I. Iodates of Al^{III} , Cr^{III} , and Fe^{III} . A. VON ENDRÉDY (Z. anorg. Chem., 1934, 217, 53—61).—The following iodates have been prepared: $\text{Al}(\text{IO}_3)_3 \cdot \text{NO}_3 \cdot 6\text{H}_2\text{O}$, monoclinic; $\text{Al}(\text{IO}_3)_3 \cdot 6\text{H}_2\text{O}$; $\text{Cr}(\text{IO}_3)_3 \cdot 2\text{H}_2\text{O}$, dark green; $\text{Cr}(\text{IO}_3)_3 \cdot 4.5\text{H}_2\text{O}$, dark green; $\text{Cr}(\text{IO}_3)_3 \cdot 5\text{H}_2\text{O}$, green, amorphous; $\text{Fe}(\text{IO}_3)_3$, α -form, light green, amorphous, $d_{20}^{25} \text{ } 4.85$, and β -form, intense yellow, $d_{20}^{25} \text{ } 4.76$. With increasing ionic radius and falling electroaffinity the stability and solubility of the hydrates diminish. M. S. B.

Rhenium oxybromides. A. BRUKL and K. ZIEGLER (Monatsh., 1933, 63, 329—334).—The prep. and properties of ReO_3Br (m.p. 39.5° , b.p. 163°) and ReO_2Br (decomp. $60-70^\circ$) are described. E. S. H.

Rhenium. III. Reduction of perrhenates with stannous chloride and a potentiometric method of determination for septavalent rhenium. H. HOLEMANN (Z. anorg. Chem., 1934, 217, 105—112).—The reduction of HCl solutions of perrhenates by SnCl_2 can be followed potentiometrically, and the method can be used for the potentiometric titration of perrhenates at about 80° . Re^{VII} is reduced to Re^{V} . The end-point is still more definite in presence of Re^{IV} as in a chlororhenate. In presence of CNS' in the cold Re^{VII} is reduced to Re^{IV} , with the establishment of a const. potential. A reddish-brown coloration is observed. M. S. B.

Structure and ferromagnetism of ferrous ferrites, and the autooxidation of ferrous hydroxide. A. KRAUSE and J. TUŁECKI (Rocz. Chem., 1934, 14, 60—68).—Dry $\text{Fe}(\text{FeO}_2)_2$ (I) containing $\text{Fe}^{\text{II}} : \text{Fe}^{\text{III}} < 1 : 1.13$ cannot be prepared from $\gamma\text{-FeO}_2\text{H}$ (II) and $\text{Fe}(\text{OH})_2$ (III) by varying the proportions of (II) and

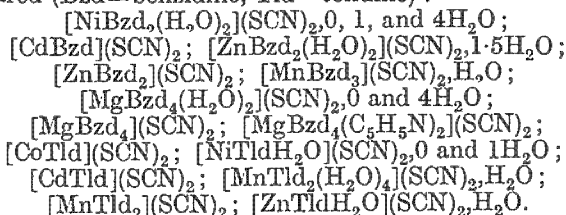
(III), or by excluding atm. O_2 from the reaction mixture; this result is ascribed to adsorption of (III) by (I), with subsequent oxidation to $Fe(OH)_3$ during drying. The ferromagnetism of (I) is ascribed to the

presence of $\cdot Fe \langle \overset{O}{\underset{O}{\parallel}} \rangle Fe \cdot$ groups in the mol. H_2O_2 is produced during the autoxidation of (III), which is catalysed by $BaSO_4$. A structural formula of the spinel type is proposed for (I). R. T.

Alkoxides of tervalent iron in internal complex union. B. EMMERT and E. JACOB (Ber., 1934, 67, [B], 286—289; cf. A., 1931, 825).—Passage of O_2 through $FeR_2 \cdot 2C_6H_5N$ (I) ($R = COMe \cdot CH \cdot CO \cdot Me$) in EtOH at 35—40° affords the substance $R_3Fe \cdot OEt$, m.p. 159.5°, whereas in MeOH at 40—45° the compound, $RFe(OMe)_2$, is obtained. With PhOH in C_6H_6 (I) is oxidised to $R_3Fe \cdot PhOH$, m.p. 109°, also obtained from its components in C_6H_6 . Oxidation of $FeR'_2 \cdot 2C_6H_5N$ ($R' = COMe \cdot CH \cdot CO \cdot Ph$) leads uniformly to the compounds R'_2FeOX in which $X = Me$, m.p. 209.5°, $= Et$, m.p. 222—223.5°, $= Bu^c$, m.p. 200—201°, $= Ph$, m.p. 219°, $= CH_2 \cdot CH_2 \cdot OH$, m.p. 212—213°. The substance, $R_3Fe \langle \overset{OH \cdot CH}{\underset{OH \cdot CH}{\parallel}} \rangle$ is described.

H. W.

Thiocyanammines of benzidine and tolidine. IV. G. SPACU and C. C. MACAROVICI (Bul. Soc. Stiinte Cluj, 1933, 7, 227—247; Chem. Zentr., 1933, ii, 2225).—The following compounds have been prepared (Bzd=benzidine, Tld=tolidine):—



A. A. E.

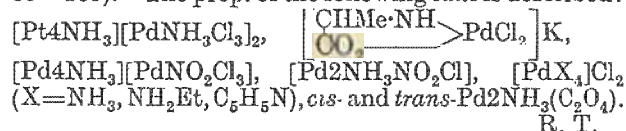
Complex salts with 2 : 2'-dipyridyl. Complex salts of bivalent nickel. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 10—15).—On mixing 2.5 g. $NiSO_4 \cdot 7H_2O$ in aq. solution with an EtOH solution of 4.7 g. dipyridyl (dipy; I) the solution turns deep red and on evaporation on the H_2O -bath red monoclinic crystals of $[Ni(dipy)_3]SO_4 \cdot 7H_2O$ (II) are obtained. If a solution of 2 equivs. of $NiSO_4 \cdot 7H_2O$ is added to a solution of (II), the solution turns blue and on evaporation yields triclinic blue crystals of $[Ni(dipy)(H_2O)_2]SO_4 \cdot 4H_2O$ (III), which loses 4 mols. of H_2O at 100°. Addition of powdered $NiSO_4 \cdot 7H_2O$ (2 mols.) to a conc. solution of (II) (1 mol.) followed by heating on the H_2O -bath, and cooling, yields long hair-like pale blue crystals of a second modification of (III). Details are given of the crystal structures of (I), (II), and (III). The cation of (III) is very stable and is decomposed only by powerful reagents. No di-(I) compound could be obtained.

New series of rhodammines. V. V. LEBEDINSKI (Ann. Inst. Platine, 1933, No. 11, 5—12). $(NH_4)_2[RhNH_3Cl_5]$ (I) is prepared by adding aq. NH_4OAc to a saturated solution of Na_3RhCl_6 and

NH_4Cl . (I) undergoes hydrolysis in H_2O to yield $(NH_4)_2[RhNH_3Cl(OH)_4]$. Crystallographic and other data are given for (I), and for the corresponding K_2 and $[Pt_4NH_3]$ salts. R. T.

Isomeric pallado-diammines. A. A. GRUNBERG and V. M. SCHULMAN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 218—220).—The following isomeric palladodiammines have been prepared: $Pd_2NH_3Cl_2$, $Pd_2NH_3Br_2$, $Pd_2(C_6H_5N)Cl_2$, and $Pd_2(C_6H_5N)Br_2$ by the action of NH_4OAc (or pyridinium acetate) on $K_2[PdCl_4]$ or $K_2[PdBr_4]$. These compounds give only $AgCl$ or $AgBr$ when treated with $AgNO_3$ and none of the brownish ppt. obtained by the action of $AgNO_3$ on compounds $[Pd_4X_4][PdX_4]$. They are analogues of the cis-platinum diammines, and have the formula $[(NH_3)_2PdCl_2]$. Solubility in H_2O is greater for cis- than for trans-diammines of both Pt and Pd. cis- $[Pd_2NH_3Br_2]$ in $COMe_2$ gives an intense red colour with KI , whereas the trans-isomeride does not. All the cis-compounds give a red colour with KI . W. R. A.

Complex compounds of bivalent palladium. A. A. GRUNBERG (Ann. Inst. Platine, 1933, No. 11, 95—109).—The prep. of the following salts is described:



R. T.

Complex chloronitrites of iridium. I. K. PSCHENITSIN and S. E. KRASKOV (Ann. Inst. Platine, 1933, No. 11, 13—19).— HCl and $Na_3[Ir(NO_2)_6]$ yield, amongst other products, the acid $H_3[IrCl_5NO_2]$ (I), which with aq. $K_2C_2O_4$ forms $K_3[IrC_2O_4Cl_3NO_2] \cdot 2H_2O$. The Ag , K , and Cs salts of (I), and the compound $[Ir_5NH_3Cl]_3[IrCl_5NO_2]$ are described. R. T.

Action of ammonia on Gros' salt. I. I. TSCHERNIAEV (Ann. Inst. Platine, 1933, No. 11, 55—59).—Gros' salt yields with aq. NH_3 the pentammine $(NH_3)_5ClPtCl_3$, which is readily converted into $(NH_3)_5(OH)PtCl_3$ (I) by excess of NH_3 ; a hexammine is not formed in the above reaction. The sulphate of (I) exists in two forms: $(NH_3)_5(H_2O)Pt(SO_4)_2$ and $(NH_3)_5(OH)Pt(HSO_4)_2SO_4$. R. T.

Asymmetrical chloride of the type of Clève's salt. I. I. TSCHERNIAEV and A. S. SAMSONOVA (Ann. Inst. Platine, 1933, No. 11, 39—43).—The salt $[NH_3RNH_3ClPt]_2PtCl_4$ ($R = NH_2OH$) is obtained by adding K_2PtCl_4 to aq. $NH_3RNH_3ClPtCl$. C_6H_5N and the complex NH_3RCl_2Pt yield chiefly $NH_3R(C_6H_5N)ClPt$, together with $NH_3R(C_6H_5N)_2PtCl_2$. R. T.

Chemical inertia and activity of the rare gases. IV. Differences between platinum and the platinum-helium compound. V. X-Ray diagrams. H. DAMIANOVICH (Anal. Inst. invest. cient. tecn., 1931, 2, 15—23, 24—32).—IV. The rate of dissolution (I) in $HCl-HNO_3$ of Pt containing He is approx. proportional to the He content. If the Pt is heated to remove the He, (I) diminishes. The solubility of Pt deposited in presence of He, O_2 , and N_2 diminishes in the order given. Photomicrographs reveal con-

siderable differences between the structures of electro-deposited Pt containing He and Pt deposited by condensation from the vapour phase. The results afford evidence of the existence of a Pt-He compound.

V. The X-ray diagrams, obtained with a specimen of the Pt-He compound mounted in a manner which obviates the diffuse halo due to the support, exhibit haloes similar to those observed in the case of colloidal Pt and Bi sulphides but not with pure Pt. This fact is regarded as proof of the existence of a Pt-He compound. H. F. G.

Nitro-compounds of platinum. XI. Ethylamine compounds. I. I. TSCHERNIAEV and N. V. VALDENBERG. **XII. Diethylamine compounds.** I. I. TSCHERNIAEV and T. B. PEIZNER. **XIII. Reaction of nitration.** I. I. TSCHERNIAEV and L. J. GENNING. **XIV. Determination of nitrogen.** I. I. TSCHERNIAEV (Compt. rend. Acad. Sci. U.R.S.S., 1933, No. 11, 21—32, 33—38, 45—53, 61—62).—XI. The NH_2Et derivatives of enPtNO_2Cl (I) behave in every way analogously to the previously described NH_2Me derivatives (A., 1932, 240).

XII. NH_2Et , and aq. (I) yield $[\text{enNO}_2\text{NHEt}_2\text{Pt}]\text{Cl}$, which with Cl_2 gives $[\text{enNO}_2\text{NHEt}_2\text{Cl}_2\text{Pt}]\text{Cl}$ (II), from which the azo-diammine could not be prepared by the usual methods. (II) yields $[\text{enNO}_2\text{NHEt}_2\text{NH}_3\text{ClPt}]\text{Cl}$, with NH_3 , and $[\text{enClNHEt}_2\text{Cl}_2\text{Pt}]\text{Cl}$ (III) with excess of HCl ; re-introduction of the NO_2 group into (III) was not possible.

XIII. The reaction of nitration of platinichlorides, nitroplatinichlorides, and tetrammines of Pt^{II} is more complex than in the case of non-electrolytic *cis*- Pt^{IV} derivatives (A., 1932, 240). Two stereoisomeric forms of the compound $[(\text{NH}_3)_4\text{Pt}(\text{NO}_2)_2](\text{NO}_3)_2$ have been prepared. The NO_2 groups of a no. of Pt, Ir, and Rh derivatives are quantitatively eliminated as N_2 by heating with saturated aq. NH_4Cl , as follows: $\text{R}\cdot\text{NO}_2 + \text{NH}_4\text{Cl} \rightarrow \text{RCl} + \text{N}_2 + 2\text{H}_2\text{O}$. This reaction affords a convenient and exact method for determining the NO_2 content of such compounds.

XIV. The N content of a no. of previously described Pt compounds is given. R. T.

Chemical evidence for planar configuration of platotetrammines. H. D. K. DREW and F. S. H. HEAD.—See this vol., 397.

Kinematic method of quantitative spectral analysis. A. BETIM (Compt. rend., 1934, 198, 566—569).—A suitable spectral line of the substance to be determined is photographed at fixed intervals, whilst the mineral in which it occurs is steadily heated electrically. The quantity is deduced from the length and rate of diminution in breadth and intensity of the line. C. A. S.

Quantitative micro-mineral analysis. F. HECHT (Mikrochem., 1934, 14, 283—285, 286—288). A. A. BENEDETTI-PICHLER (*ibid.*, 285—286, 288).—Polemical. J. S. A.

New method of preparative microchemistry. J. WINCKELMANN (Mikrochem., 1934, 14, 171—180).—The prep. of permanent characteristic specimens of microchemical ppts., using a permeable collodion film (I), is described. The undisturbed ppt. is washed

free of precipitant through (I), or may be actually pptd. beneath it. J. S. A.

Scheme for dilutions in the laboratory. C. J. LYON (Science, 1934, 79, 60).—A scheme for calculating the amounts of solution and solvent to be used in making up a series of solutions of various concns. from a given stock solution is described. L. S. T.

Effect of sulphated fatty alcohols in the colorimetric determination of p_{H} . J. E. SMITH and H. L. JONES (J. Physical Chem., 1934, 38, 243—244).—Data are given showing the extent of the errors obtained in the colorimetric determination of the p_{H} of buffered solutions containing 0.5% Na lauryl or oleyl sulphate, using a no. of different indicators. M. S. B.

Volumetric standardisation. R. H. CURTIS (Chem. and Ind., 1934, 135).—Iceland spar is recommended for standardising HCl . The CaCl_2 solution thus obtained can be pptd. as CaC_2O_4 and used to standardise KMnO_4 . E. S. H.

Determination of dissolved oxygen in water.—See B., 1934, 254.

Nephelometry. I. Analysis of potable waters.—See B., 1934, 254.

Silver halides and the potentiometric titration curve. I. E. ORLOV (Khim. Farm. Prom., 1933, 213—218).—The presence of electrolytes eliminates the retardation of the potential jump. CH. Abs.

Synthesis in the homoneurine series. III. Homoneurine derivatives of the cinchona alkaloids as qualitative reagents for iodide ions. E. MACOVSKI, A. SILBERG, E. RAMONTIANU, and (FRL.) E. CRĂCIUNESCU (J. pr. Chem., 1934, [ii], 139, 254—260).—Owing to the insolubility of the iodides the dihomoneurine bromides (A., 1933, 169) are qual. reagents for I^- , 5—10% aq. solutions of the quinine and cinchonine bromides detecting 0.05*N*- and 0.025*N*- I^- , respectively. Sensitivity is increased if the Bz derivatives are used, 3% benzoylcinchonine dihomoneurine bromide detecting 0.0025*N*- I^- . J. W. B.

Colorimetric determination of traces of fluorine. L. SZEGOE and B. CASSONI (Giorn. Chim. Ind. Appl., 1933, 15, 599—602).—The sample is treated with $\text{Ca}(\text{OH})_2$ solution, ignited at $> 550^\circ$, and fused with Na K carbonate and SiO_2 . The extract, after removal of SiO_2 , is treated with HCl and BaCl_2 , and the ppt. dried, mixed with SiO_2 , and distilled with H_2SO_4 . The SiF_4 is passed into H_2O , 0.025*M*- $\text{Ti}(\text{SO}_4)_2$ and H_2O_2 are added, and the coloration is compared with a standard. In an alternative method, the F is separated by distillation of the sample with HClO_4 at (initially) $100\text{--}110^\circ$. H. F. G.

Rapid accurate determination of minute quantities of nitrite. G. G. RAO and K. M. PANDALAI (Analyst, 1934, 59, 99—100).— HNO_2 is determined by treating it with HI and titrating the I liberated: $2\text{HNO}_2 + 2\text{HI} = 2\text{H}_2\text{O} + \text{I}_2 + 2\text{NO}$. O_2 is excluded by bubbling CO_2 through the solution for 10 min. NO is expelled as it is formed by adding NaHCO_3 and acidifying. 5.6×10^{-4} — 5.6×10^{-5} g. of NO_2' -N are determined to within $\pm 0.7\%$. E. C. S.

Sensitivity of diphenylamine as a reagent for nitric acid. R. KRAUER, jun. (*Chimica*, 1933, 1, 122—123; *Chem. Zentr.*, 1933, ii, 2297).—0.0002% HNO_3 in H_2SO_4 is detected only after addition of a little H_2O ; 0.00084% HNO_3 slowly affords a blue coloration without H_2O . A. A. E.

Oxidation of white phosphorus by iodine. Course of the reaction in the determination by the D.A.B. VI method. F. VIEBOCK (*Arch. Pharm.*, 1934, 272, 88—100).—The amount of I (as I—KI or in org. solvents) reduced by P in mineral oil varies with the rate of mixing. According to the conditions and amount of MeOH or EtOH used, varying proportions of H_3PO_4 , HPO_3 , H_3PO_3 , and their esters are formed. The PIH_2 compounds, being normally stable to I, are considered to be produced in labile forms. R. S. C.

Colorimetric determination of phosphoric acid.—See this vol., 338.

Reactions of the cyanide ion with tetrathionate and pentathionate ions. B. FORESTI (*Z. anorg. Chem.*, 1934, 217, 33—47).—It is shown theoretically that the reaction between HCN and $\text{S}_4\text{O}_6^{2-}$ or $\text{S}_5\text{O}_6^{2-}$, giving HCNS, ceases when one third of the reaction is completed, unless a continuous supply of OH^- is available. The velocity coeffs. $K_{s_4o_6}$ and $K_{s_5o_6}$ have, therefore, been determined at p_H 7.23 and 7.46 at 37° (temp. of human blood; or 7.31 and 7.54 at 18°). Under these conditions the reactions are complete. Assuming constancy of OH^- , both reactions are bimol., the decomp. of $\text{S}_5\text{O}_6^{2-}$ taking place in two stages, the first being the formation of $\text{S}_4\text{O}_6^{2-}$. In each case the increase in K doubles K , and $K_{s_5o_6}$ is approx. five times $K_{s_4o_6}$. $\text{S}_5\text{O}_6^{2-}$ should therefore be a valuable antidote to HCN poisoning, provided it exercises no unforeseen harmful effect. M. S. B.

Spot reaction for potassium. N. S. POLUEKTOV (*Mikrochem.*, 1934, 14, 265—266).—The insol. K salt of hexanitrodiphenylamine is pptd. from slightly alkaline solutions as an orange spot, reddened by addition of HCl. Rb, Cs, and large amounts of NH_4^+ interfere. J. S. A.

Microchemical identification of sodium ions by means of picric acid. G. DENIGES (*Bull. Soc. Pharm. Bordeaux*, 1933, 71, 191—195; *Chem. Zentr.*, 1933, ii, 2427).—Na picrate forms characteristic yellow needles, distinguishable from other alkali picrates. H. J. E.

[Detection of sodium with uranyl acetate.] L. ROSENTHALER (*Mikrochem.*, 1934, 14, 267; cf. A., 1933, 583).—A correction. J. S. A.

Detection and microdetermination of silver, mercury, and iodides. I. M. KORENMAN (*Mikrochem.*, 1934, 14, 181—188).—The formation of the blue starch—I colour (I) requires the presence of I^- , and is hindered by Hg^+ , Hg^{2+} , and Ag, which form insol. iodides. By the non-formation of (I), using 0.02% aq. I, limiting concns. of 1 in 2×10^4 of Ag, 1 in 7×10^6 of Hg^+ , and 1 in 4×10^6 of Hg^{2+} may be detected. Large excesses of Pb, Cu, and Cd do not interfere. The amount of I^- necessary to produce (I) is proportional to the amount of Ag or Hg present. I^- may be determined by titration with 0.01N- HgCl_2

until (I) disappears. By use of 0.01N-KI, Ag and Hg may be similarly determined. Large amounts of Cl^- , also Br^- and CNS^- , interfere. J. S. A.

Reaction differentiating the hydrated calcium aluminates. A. TRAVERS and P. LEDUC (*Compt. rend.*, 1934, 198, 828—831).—Cubic $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (I) (cf. A., 1930, 436) scarcely reacts with boiling $\text{NH}_4\text{Cl-EtOH}$, whereas all other hydrated Ca aluminates do so more or less readily, indicating that in (I) the CaO is more firmly combined. It is therefore suggested that (I) is derived from the acid H_3AlO_3 , the other Ca aluminates being basic salts of HAlO_2 , i.e., $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{CaO} \cdot aq.$, convertible into the former by heat. C. A. S.

Microchemical contributions. X. L. ROSENTHALER (*Mikrochem.*, 1934, 14, 268—270; cf. A., 1933, 1262).—The crystal forms of Ba, Sr, and Ca sulphates, under different conditions of pptn., are described. J. S. A.

Qualitative reaction of radium. B. A. NIKITIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 1, 19—21).—10 c.c. of 0.1% Ra solution, when heated to boiling and treated with 0.3 c.c. of 50% aq. $\text{CCl}_3\text{CO}_2\text{H}$ and 0.5 c.c. of 10% aq. K_2CrO_4 gives a compact cryst. ppt. on cooling to 0° . Ba gives no ppt. under similar conditions. The solution, however, retains 0.01—0.015% Ra, so the method cannot be applied to the determination of Ra. J. W. S.

Analysis of magnesium alloys. L. C. NICKOLLS. —See B., 1934, 240.

Volumetric determination of lead. M. N. LU (*J. Chinese Chem. Soc.*, 1933, 1, 139—142).— Pb^{2+} is pptd. as PbO_2 by adding excess of NaOCl and NaOH, the ppt. is dissolved in HCl in presence of KI, and the liberated I titrated with $\text{Na}_2\text{S}_2\text{O}_3$ and starch. The procedure is applicable in presence of any metal that does not ppt. a peroxide when treated with NaOCl. E. S. H.

Determination of lead dioxide in red lead.—See B., 1934, 193.

Colorimetric determination of lead and copper with "dithizon" [dithiocarbazon]. H. FISCHER and (FRL.) G. LEOPOLDI (*Angew. Chem.*, 1934, 47, 90—92).—The use of dithizon (I) as a qual. reagent for metals (A., 1929, 1412) is extended as a quant. method. (I) is purified by extraction from CCl_4 solution with dil. aq. NH_3 (1:200), and repptn. into fresh CCl_4 with dil. H_2SO_4 . This resultant solution should contain about 20 mg. of (I) per 100 c.c., and is diluted to contain 6 mg. per 100 c.c. for use; it is stored in the dark under a layer of aq. SO_2 . In determination of Pb, a solution containing 0.006—0.120 mg. of Pb is made alkaline with dil. aq. NH_3 , holding up other metals with Na K tartrate, and shaken with several successive portions of the reagent until no further red colour is produced. The separated reagent is then shaken with 5 c.c. of 1% aq. KCN to remove excess (I), washed with H_2O , and then shaken with dil. HCl, giving a green colour which is compared with standards made up from known amounts of Pb. Many metals interfere. For Cu, the metal content must lie between 0.004 and 0.050 mg., and it is extracted similarly to Pb from a dil. H_2SO_4 solu-

tion, giving a violet colour, excess of (I) being removed by dil. NH_3 , and the resultant solution compared with standards. Only Hg, Ag, and Au interfere, but excess of Fe^{+++} oxidises the reagent. D. R. D.

Detection of copper by means of *p*-phenylenediamine. R. J. McILROY (Analyst, 1934, 59, 103).—When KCNS and $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ are added to a solution of a Cu salt, a black ppt. of Cu thiocyanate-phenylenediamine is formed in the presence of aq. NH_3 or in neutral solutions. The ppt. is sol. in acid, giving a black solution. No other of the common metals except Ag, which gives a white ppt., is pptd. in aq. NH_3 . 1 part of Cu in 100,000 can be detected. E. C. S.

Determination of copper by means of 5:7-dibromo-8-hydroxyquinoline. J. V. DUBSKY and J. CHYTIL (Chem. Listy, 1934, 28, 6—7).—Haase's method (A., 1929, 1159) is preferred. R. T.

Colorimetric determination of copper by precipitation with mercuric thiocyanate. J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1933, 71, 16—24; Chem. Zentr., 1933, ii, 2427—2428).—Pptn. of Cu in presence of Zn by $\text{K}_2[\text{Hg}(\text{CNS})_4]$ as violet $\text{CuZn}[\text{Hg}(\text{CNS})_4]_2$ will detect 0.001 mg. Cu. The Zn salt, $\text{Zn}[\text{Hg}(\text{CNS})_4]$, pptd. simultaneously, is colourless. H. J. E.

Magneto-optic Nicol rotation method for the quantitative analysis of copper. E. R. BISHOP, I. G. OTTO, and L. BAISDEN (J. Amer. Chem. Soc., 1934, 56, 408).—Preliminary observations indicate that the method should be useful for solutions containing 5×10^{-12} to 1×10^{-4} g. Cu per c.c. E. S. H.

Spectroscopic determination of secondary constituents in copper.—See B., 1934, 202.

Determination of very small amounts of copper by measurement of their catalytic action. F. L. HAHN (Mikrochem., 1934, 14, 280—282; cf. B., 1933, 1062).—The time for decolorisation (I) of $\text{Fe}(\text{CNS})_3$ by $\text{Na}_2\text{S}_2\text{O}_3$ varies considerably with minor factors. The ratio (I) in absence of Cu/(I) for given Cu concn. is less affected and reproducible with different solutions. Instead of (I), the time to reach a matched shade is advocated. J. S. A.

Iodometry. I. Micro-determination of iron. F. RAPPAPORT and E. HOHENBERG (Mikrochem., 1934, 14, 119—128).—The solution containing Fe^{+++} is treated with acid KI in a micro-Kjeldahl apparatus, the liberated I being distilled into 2 c.c. of $\text{NaOH} + \text{Na}_2\text{SO}_3$. Decomp. of the KI in the hot acid solution is avoided by use of $\text{KI} + \text{CdSO}_4$ (K_2CdI_4). The NaOH is neutralised, and 3% Br in AcOH added, oxidising the I to IO_3^- , which is determined iodometrically. Excess of Br is removed by HCO_2H . Fe^{++} must first be oxidised by HNO_3 , with subsequent addition of $\text{CO}(\text{NH}_2)_2$, PO_4^{---} and other metals do not interfere. Org. substances are ashed with H_2SO_4 and H_2O_2 in presence of Ti, which serves as catalyst and indicator of excess H_2O_2 . Difficultly ashed substances may be treated with HNO_3 . J. S. A.

Micro-iodometric determination of iron. (Iron content of thyroid glands.) J. STRAUB (Mikrochem., 1934, 14, 251—255).—The solution, con-

taining 0.01—0.5 mg. Fe in 10 c.c. is treated with $\text{KI} + \text{HCl}$, and titrated with 0.002N- $\text{Na}_2\text{S}_2\text{O}_3$ within 2 min. J. S. A.

Phenanthroline-ferrous ion. III. Silver reducing agent. Direct determination of iron in presence of vanadium. G. H. WALDEN, jun., L. P. HAMMETT, and S. M. EDMONDS (J. Amer. Chem. Soc., 1934, 56, 350—353; cf. this vol., 257).—The solution is reduced with finely-divided Ag, H_2SO_4 is added to give a concn. of 5M, and Fe is determined by titration with 0.1M- $\text{Ce}(\text{SO}_4)_2$, using the phenanthroline-ferrous ion as indicator. E. S. H.

Determination of tin in copper-zinc alloys.—See B., 1934, 202.

Potentiometric study of the quinhydrone electrode in the determination of nickel. B. K. CHATTERJEA and J. B. JHA (J. Indian Chem. Soc., 1934, 10, 727—733).—Ni salt solutions, containing 0.34—0.09 g. Ni in 25 c.c., may be titrated with KCN solution, using the quinhydrone electrode. The change of e.m.f. occurs at the point corresponding with the formation of $\text{Ni}(\text{CN})_2$. E. S. H.

Colorimetric determination of nickel.—See this vol., 396.

Reaction of hydrogen peroxide with potassium iodide and its use for the determination of chromium. E. RUPP [with G. HAMANN and R. MULLER] (Arch. Pharm., 1934, 272, 57—60).—Neutral aq. H_2O_2 is rapidly decomposed by a little KI, the reaction proceeding by formation and decomp. of HOI, and being accelerated by heat and hindered by alkali. In the determination of aq. H_2O_2 by HI it is thus necessary to add the acid before the KI. In the determination of Cr^{+++} by oxidation to CrO_4^{--} with alkaline H_2O_2 , excess of H_2O_2 is readily removed in presence of KI, before titration of the liberated I. R. S. C.

Potentiometric determination of chromium in steel.—See B., 1934, 240.

Determination of chromium and vanadium in steel.—See B., 1934, 240.

Determination of antimony. R. I. SHREIDER (Khim. Farm. Prom., 1933, 151—152).—The substance (0.2—0.3 g.) is heated in a Kjeldahl flask with K_2SO_4 (2 g.) and conc. H_2SO_4 (3 c.c.); after 30 min. the cooled liquid is diluted with H_2O (25 c.c.), SO_2 is boiled off, 4 c.c. of aq. HCl are added, and Sb is determined by the BrO_3^- method. CH. ABS.

Volumetric determination of metals of the platinum group. A. A. GRUNBERG and B. V. PRITSYN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 286—290, and Ann. Inst. Platine, 1933, No. 11, 77—94).— Pt^{II} compounds can be oxidised by KMnO_4 in presence of H_2SO_4 : $\text{R} \cdot \text{Pt}^{II} + \text{H}_2\text{O} + \text{O} \rightarrow \text{R} \cdot \text{Pt}^{IV}(\text{OH})_2$, the ease of oxidation varying with the groups co-ordinated to the Pt atom. This reaction is applied to the determination of Pt^{II} by potentiometric titration (I) and by visual titration. (I) methods for the determination of Ir^{III} with KMnO_4 , of Ir^{IV} with $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, of Pt^{IV} by reduction with Cu_2Cl_2 in HCl followed by differential titration with KMnO_4 , and of Pt^{II} and Ir^{III} simultaneously

with KMnO_4 have also been developed. Other methods of volumetric determination of the Pt metals are discussed critically. J. W. S.

Separation of iridium from rhodium. B. G. KARPOV and A. N. FEDOROVA (Ann. Inst. Platine, 1933, No. 11, 135—139).—The solution of Ir and Rh chlorides is diluted to 600—800 c.c., and 40 c.c. of conc. H_2SO_4 , 3—5 c.c. of saturated aq. HgCl_2 , and excess of aq. VCl_2 are added. The solution is filtered through porcelain 2 hr. later, and the ppt. of Rh is dissolved in aqua regia; the solution is evaporated to dryness, and the residue is dissolved in 40 c.c. of conc. HCl . The above pptn. is repeated, and the ppt. is ignited, treated with HF to remove traces of SiO_2 , reduced, and weighed. R. T.

Inexpensive and economical warm room. G. GRINLING (Analyst, 1933, 59, 103—104). E. C. S.

Mercury-in-glass thermo-regulator. C. C. COFFIN (Proc. Nova Scotian Inst. Sci., 1932—1933, 18, 213—214).—A Hg-in-glass thermo-regulator giving control within 0.001° is described. Its advantage lies in various details of construction and in the fact that rapid heat exchange is more important for control than a large coeff. of expansion. R. S. C.

Improved m.-p. apparatus and comparative study of types of apparatus for m.-p. determinations. C. L. TSENG (J. Chinese Chem. Soc., 1933, 1, 143—182).—A modification of Mulliken's apparatus is described, and results obtained therewith are compared with those obtained by other methods. Numerous sources of error in m.-p. determinations are discussed, and it is maintained that none of the commonly used types of apparatus based on the capillary tube method can give results trustworthy to $\pm 1^\circ$, even under the best conditions. As a rule the initial fusion point, determined by a capillary tube method, is higher than the true m.p. E. S. H.

Application of the ether calorimeter to measurements of the heat of radiation of feebly radioactive substances. A. DORABIALSKA (Rocz. Chem., 1934, 14, 24—30).—The results obtained for monazite, Sb_2O_3 , Sb_2S_5 , and As_2S_3 using an Et₂O calorimeter (I) are of the same order of magnitude as those previously obtained using an adiabatic (I). R. T.

X-Ray spectroscopy and photography with bent crystal reflectors. II. Description of a focussing spectrograph with point-scattered slit images. L. VON HAMOS (Ann. Physik, 1934, [v], 19, 252—260).—A new focussing X-ray spectrograph, using a rock-salt crystal bent into a cylinder as a reflector, is described. A. J. M.

Photo-electric measurement of absorption and colour change. R. SEWIG and F. MÜLLER (Chem. Fabr., 1934, 7, 25—27).—The use of metal-vapour discharge lamps, in conjunction with suitable filters, is recommended. The spectral line chosen should correspond approx. with the absorption max. of the indicator used. Thus a Na lamp is satisfactory with bromophenol-blue (absorption max. 5920 Å.) and bromocresol-purple (5910 Å.); a Ti lamp with Me-red (5300 Å.); a Hg lamp with cresol-red (5720

Å.), thymol-blue (5440 Å.), and phenolphthalein (5530 Å.); and a Cd lamp with α -naphtholphthalein. H. F. G.

Simple photo-electric colorimeter. G. A. MILLIKAN (J. Physiol., 1933, 79, 152—157).—A photo-electric colorimeter, especially suitable for measuring the degree of O_2 saturation of dil. haemoglobin solutions, is described. Use is made of a differential Cu—Cu₂O photo-electric cell (I) and colour filters. The source of light is a Hg arc lamp, and readings are made by means of a galvanometer attached to (I). NUTR. ABS. (m)

Turbidity and colour measurements. I. Photo-electric cell arrangement for measuring small quantities of certain impurities in reagent chemicals. R. A. OSBORN (J. Assoc. Off. Agric. Chem., 1934, 17, 135—141).—Appropriate apparatus is described and its use in determining small amounts of Pb, Fe, Cl, and SO_4 recorded. A. G. P.

Automatic photo-electric photometer. E. B. MOSS (Proc. Physical Soc., 1934, 46, 205—213). N. M. B.

Application of photo-electric cell to nephelometry. E. CANALS and A. HORTALA (Bull. Soc. Chim. biol., 1933, 15, 1535—1551).—Cheneveau and Audubert's relation between the concn. of suspended particles and light absorption (A., 1920, ii, 327) is confirmed and may be used to determine the concns. of suspensions of mastic, argyrol, and AgCl. The optimum λ for the last is 4100 Å., giving a max. error of 4% depending on the mode of prep. of the AgCl. H. D.

Preparation of uniform nephelometric suspensions. A. F. SCOTT and F. H. HURLEY (J. Amer. Chem. Soc., 1934, 56, 333—335).—A device for effecting the uniform addition of a pptg. agent is described, thus enabling uniform turbidities to be obtained. In suspensions of AgCl the $[\text{Ag}^+]$ before pptn. has no influence on the turbidity at the concns. generally used. Turbidity tests are not vitiated by the presence of $< 0.6M\text{-KNO}_3$. E. S. H.

Vacuum [photo-electric] cells for measurement of weak luminous fluxes. L. CARDECOMME (Compt. rend., 1934, 198, 462—464).—To examine the optical properties of opaque minerals a cell is required of great sensitiveness, stability, and strict proportionality to the light flux. For this purpose the best is a vac. Cs cell, but working at p.d. < 150 volts. As the sensitiveness varies with time and previous history, to be strictly comparable measurements must be made immediately after one another, and on the same part of the cathode. C. A. S.

Photo-electric densitometer for use with suspensions. T. J. B. STIER, W. ARNOLD, and J. N. STANNARD (J. Gen. Physiol., 1934, 17, 383—392).—The apparatus consists of two photo-electric cells, a light source of high intensity, and a Wheatstone bridge. The suspension of micro-organisms is placed in the path of a beam of light entering one cell whilst another beam falls on the second. The ratio of the magnitude of the two currents set up is then determined. The accuracy obtainable is 1% for

cultures of the same age and comparable optical characteristics. A. L.

Characteristics of the sodium lamp as influenced by vapour pressure. G. R. FONDA and A. H. YOUNG (*J. Opt. Soc. Amer.*, 1934, 24, 31—34).—Graphs are given for luminous variation with temp. for various c.d., and variation of voltage characteristics with temp. for a Na lamp containing 1.5 mm. pressure of Ne. Results are explained qualitatively on the energy changes of a Na atom in collision with an electron. Efficiency increases at const. temp. as c.d. is decreased, and max. light output for all c.d. is at a v.p. corresponding with 200°.

N. M. B.

Yellow-blue ratio and personal errors in heterochromatic photometry. W. S. STILES (*Phil. Mag.*, 1934, [vii], 17, 660—668).—An approx. formula gives the personal error in matching brightnesses of different colour temp., in terms of the yellow-blue ratio of the observer.

H. J. E.

Rapid electro-dialyser. H. BRINTZINGER [with A. ROTHHAAR and H. G. BEIER] (*Kolloid-Z.*, 1934, 66, 183—188).—The apparatus is described and its performance is compared with that of others.

E. S. H.

Measurement of specific resistance by eddy current shielding. W. B. KOUWENHOVEN and G. P. DAIGER (*Rev. Sci. Instr.*, 1934, [ii], 5, 94—101).—The method is based on the change in inductance of a solenoid, which occurs when conducting material is brought into the field of the solenoid, owing to eddy currents which are set up in the material by the alternating magnetic field. Experimental results for Cu and some Cu alloys show satisfactory agreement with those obtained by d.c. measurements.

E. S. H.

Combined apparatus for measurement of corrosion and of p_H and for potentiometric titration for process control and testing of materials. ANON. (*Chem.-Ztg.*, 1934, 58, 197—198).—The measurement of p_H and potentiometric titrations are simplified by the use of the twin-tube potentiometer; the galvanometer scale reads directly in p_H units. A similar apparatus can be used in the determination of corrosion by the direct measurement of current.

A. G.

Conrady system of weighing as an aid to the chemist. W. H. J. VERNON (*Chem. and Ind.*, 1934, 211—214).—A description is given of the Conrady system of weighing as adapted for routine work. The method can be applied to a balance of robust design carrying loads of 100 or 200 g., with only slight structural modifications; it is capable of yielding an accuracy of 1×10^{-6} of the load on the pan, or 0.001 mg. in 100 g. The underlying principle is an extension of the Gaussian method of exchange, and aims at eliminating, by a process of cancellation, errors that are introduced in a simple double weighing.

Glass micro-balance. H. DAMIANOVICH (*Anal. Inst. invest. cient. teen.*, 1931, 2, 85—90).—The beam is of glass, 0.02 mm. in diam. and 12 cm. long, and carries a mirror at the centre of oscillation. The balance is more sensitive and less difficult to

construct than the usual quartz type. Up to 3 mg. may be weighed to within 0.001 mg.

H. F. G.

Vacuum absorption pipette; its use in the examination and determination of gases and vapours. R. GROS (*J. Pharm. Chim.*, 1934, [viii], 19, 156—162).—Apparatus and technique are described.

E. S. H.

Horizontal micro-burette. E. J. CONWAY (*Biochem. J.*, 1934, 28, 283—287).—A simple micro-burette (to deliver 0.1 ml.), easily assembled from Pyrex thermometer and graduated tubing, is described. It may be used for micro-titrations, for the accurate delivery of small vols. if a large vol. of liquid is available, and as an accurate wash-out pipette for very small vols. of blood or serum.

A. E. O.

Gas analysis with modified Orsat apparatus.—See B., 1934, 175.

Unitised gas analysis apparatus.—See B., 1934, 223.

Micro-Kjeldahl still. T. P. NASH, jun. (*J. Lab. Clin. Med.*, 1933, 18, 1285—1287).

CH. ABS.

Extraction apparatus. K. PETERS (*Chem. Fabr.*, 1934, 7, 21—25).—Many forms of apparatus are crit. reviewed; none fulfils satisfactorily the requirements for coal extraction. An apparatus is described which is suitable for extractions with exclusion of air, under reduced pressure, and with solvents of low b.p., together with a condenser operating in any desired atm. In a modification of the apparatus only part of the extract at a time falls into the lower flask, the sudden bursts of vapour occurring when a mixed solvent is used being thus avoided. A further modification renders the apparatus suitable for extraction with liquid SO_2 at 2—3 atm. pressure. A device for ensuring that the whole of the condensate falls on to the material to be extracted (of importance in the extraction of coal) is described.

H. F. G.

Improved equilibrium distillation still and the equilibrium distillation test. M. MIZUTA (*J. Soc. Chem. Ind. Japan*, 1934, 37, 11B).—The temp. difference between the inside and outside of the glass wall of the upper part of the still is kept const. by electric heating, and condensation prevented. With this still correct vals. were obtained for the b.p. of mixtures of C_6H_6 and PhMe.

A. G.

Apparatus for rectifying small quantities of gas, and the purification of krypton. H. VAN DIJK, J. MAZUR, and W. H. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1933, 36, 822—825).—Small quantities of Kr are more easily purified by rectification than by fractional evaporation. The rectifier incorporates Claude's principle of "retour en arrière" and consists of a small heater below a uniform Cu screw fitting snugly in an unsilvered Dewar vessel surrounded by a cooling bath.

J. G. A. G.

Improved vacuum fractionation apparatus. H. F. J. LORANG and J. KLUIZENAR (*Chem. Fabr.*, 1934, 7, 66—67).—A single specially constructed tap (illustrated) enables successive fractions to be collected and run out without risk of destroying the vac. accidentally.

D. R. D.

Rapid evaporation of frothing liquids. E. JANTZEN and H. SCHMALFUSZ (Chem. Fabr., 1934, 7, 61—62).—A simple apparatus for vac. distillation of liquids which foam badly is described. The foam is broken up and thrown back into the evaporator (capacity 1—5 litres) by rapidly rotating vanes.

D. R. D.

Nickel vessel for storing standard alkali hydroxide solutions. E. C. RIGHELLATO (Analyst, 1934, 59, 104).

E. C. S.

Silvering of mirror surfaces by cathodic sputtering. M. ROMANOVA, A. RUBTSOV, and G. POKROVSKI (Compt. rend. Acad. Sci., U.R.S.S., 1934, 1, 15—18).—Surfaces prepared by cathodic sputtering in H_2 at 0.04—0.05 mm. pressure, using an applied voltage of 1200—1400 volts d.c., and a current of 15—20 milliamp., are very suitable for use in interference gratings.

J. W. S.

New accessories for a microscope for micro-chemical work (capillary holder, microchemical manipulator), with some notes on qualitative microelectrolysis. H. ALBER (Mikrochem., 1934, 14, 219—244).—A description of the apparatus. A refinement of the Brenneis electrode (A., 1931, 924), using Pt wires 0.05 mm. diam., sealed through a glass capillary and ground off flush, enables amounts of metal of the order of 0.01×10^{-6} g. to be deposited out of 5—10 c.c. of solution, identification under the microscope following.

J. S. A.

Modification of Chamberland's autoclave permitting the desiccation of dressings in the same autoclave. G. HIRT (J. Pharm. Chim., 1934, [viii], 19, 162—168).—After sterilisation at 134° for 45 min., the H_2O in the autoclave is withdrawn through a tube leading to the bottom, and the contents are dried by a current of hot air.

E. S. H.

Automatic elementary analysis. H. REIHLEN and E. WEINBRENNER (Chem. Fabr., 1934, 7, 63—66).—Org. combustions are made automatic by arranging a clock to control the heating by drawing a burner along on rails and turning off the gas.

D. R. D.

Use of charcoal in maintaining high vacua. C. H. COLLIE (Proc. Physical Soc., 1934, 46, 252—255).—Measurements were made of the limiting pressures reached by charcoals and SiO_2 gels cooled with liquid air or liquid H_2 when a small const. stream of gas is admitted into the apparatus.

N. M. B.

High-vacuum leak device. G. A. WHIPPLE (Proc. Physical Soc., 1934, 46, 281—282).—The device operates on a diffusion principle, and allows continuous variation of pressures in the discharge tube of cold-cathode-ray oscillographs.

N. M. B.

Valve for the regulation of the rate of gas flow. K. HAUSCHILD (Chem. Fabr., 1934, 7, 27).—The needle of a needle valve is raised or lowered by a screw operating through a ball and socket joint. Pressures of 30—40 mm. and 5 mm. on either side of the valve may be maintained const. to within 2%.

H. F. G.

Probable error of sampling sediments for mechanical analysis. W. C. KRUMBEIN (Amer. J.

Sci., 1934, [v], 27, 204—214).—In beach sands the error varied between 0.75 and 4.51%.

C. W. G.

Apparatus for determination of size distribution of particles in fine powders.—See B., 1934, 223.

Hydroclassifier employing motionless liquid. E. JOUKOWSKY and L. CHARREY (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 209—211).—An instrument for the determination of the granular structure of ppts. is described. The ppt. is allowed to fall through a column of H_2O in a thermostat and samples are removed from the bottom at definite intervals.

R. S.

Correction nomograph for pressure changes supplementary to humidity chart of gases. S. HATTA (J. Soc. Chem. Ind. Japan, 1934, 37, 38—43B; cf. B., 1933, 735).—A nomograph and the calculations for its construction are given for finding the saturated humidity at any temp. and pressure. The change of heat capacity with pressure may be ignored. Adiabatic cooling lines at different pressures are nearly parallel and the distance between them is equal to the difference in saturated humidity.

A. G.

Viscosity of basalt glass at high temperatures. I. K. KANI (Proc. Imp. Acad. Tokyo, 1934, 10, 29—32).—Rice-jelly is employed as standard in a method involving measurement of the relation between load and velocity of revolution of an immersed cylinder.

C. W. G.

Electromagnetic rotating [cylinder] viscosimeter. G. BERRAZ (Anal. Inst. invest. cient. tecn., 1931, 2, 79—84).—The force exerted on the inner cylinder by the rotating mass of liquid is balanced by adjusting the current in two bobbins mounted astatically. The balancing current is directly proportional to the viscosity of the liquid. The results obtained are slightly < those given by the Ostwald viscosimeter. The sensitivity is high, but the apparatus is somewhat expensive and requires expert handling.

H. F. G.

Measurement of abnormal viscosity by the falling-sphere method. F. HIRATA and K. KUBO (J. Soc. Chem. Ind. Japan, 1934, 37, 11—14B).—The velocities of steel balls falling through 3.83% and 11.88% solutions of caoutchouc in $C_6H_4Me_2$ are $v = kr^{2.35}$.

A. G.

Increasing the sensitivity of chemical reactions. E. W. BLANK (J. Chem. Educ., 1933, 10, 746—747).—The collection of a ppt. at the interface between an aq. solution and an org. solvent, and centrifuging of an opalescent liquid followed by microscopical examination of the point of the centrifuge tube, are aids in the detection of pptn.

CH. ABS.

"Exergic" and "endergic reactions." W. BLUM (Science, 1934, 79, 84).—"Exergic" reactions occur with a decrease, and "endergic" reactions with an increase, in free energy.

L. S. T.

Practical exercises in colloid chemistry. A. LOTTERMOSER (Kolloid-Z., 1934, 66, 188—191).

E. S. H.

Geochemistry.

Composition of air in the stratosphere. A. F. KAPUSTENSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 109).—The observation that the composition of the air is the same on the earth's surface and at a height of 19 km. can probably be explained either by the enrichment of the stratosphere with N_2 by means of gravitational forces or by O_2 enrichment due to thermal diffusion. W. R. A.

Atmospheric ozone at the Pic du Midi. J. GAUZIT (Compt. rend., 1934, 198, 492—494).—Measurements of O_3 with the author's spectrophotometer (cf. A., 1933, 45) at the Pic du Midi during August, 1933, are explicable on the supposition that the O_3 is partly (70—92%) collected in a thin layer at heights of 18—45 km. (above the Pic) and partly (8—30%) uniformly diffused throughout the atm. The amount so diffused is equiv. (at normal pressure) to a layer $35—85 \times 10^{-4}$ cm. thick per km. (cf. A., 1931, 458). C. A. S.

Radioactivity of air in the Observatory at the Pic du Midi. H. GARRIGUE (Compt. rend., 1934, 198, 494—496).—Conductivity observations show that the spontaneous ionisation due to radioactivity of the Rn type is approx. 1000 times as great when the Pic is under snow as in summer. C. A. S.

Soft radiation on the Pic du Midi. H. GARRIGUE (Compt. rend., 1934, 198, 764—765; cf. preceding abstract).—Determinations with the author's apparatus of the soft radiation of terrestrial radioactive origin in July—Aug., and Nov.—Dec. 1933, show that this is about 4.5 times as strong in winter as in summer. C. A. S.

Radioactivity of the thermal springs of Mangalia. T. DONESCU (Bul. Soc. Fiz. Român., 1933, No. 56, 6—8).—The radioactivity of the H_2O varies from 9 to 144 m μ c. R. T.

Variations in the chemical composition of natural waters in relation to atmospheric precipitation. E. PODA (Annali Chim. Appl., 1933, 23, 581—584).—The electrical resistance of the H_2O of the Adige runs parallel to the piezometric height of the river. Atm. pptn. produces a proportional and almost immediate effect on the resistance, but with spring H_2O the effect is delayed and less marked. T. H. P.

Gold content of the streams of the canton of Geneva. J. J. PITTARD (Arch. Sci. phys. nat., 1933, [v], 15, Suppl., 232—234).

Content of dissolved oxygen in water of maritime Seine. P. CHAUCHARD (Compt. rend., 1934, 198, 594—596; cf. A., 1932, 1227).—The content of O_2 in the H_2O of the Seine estuary increases on passing from fresh to brackish, to fall slightly in the salt H_2O of the open sea. It is reduced by the bore and incoming tide which stir up a reducing mud, but is increased by insolation. C. A. S.

Isotopic composition of sea-water. E. S. GIL—(J. Amer. Chem. Soc., 1934, 56, 406)— H_2O obtained by distillation of sea- H_2O had d 1.0000023 \pm 0.0000002 at 0° compared with that

obtained by distillation of Cambridge (U.S.A.) tap-water. A method of determining small differences of d is described. E. S. H.

Law of variation of the coefficient of carbonation in the world's oceans. P. T. DANILT-SCHENKO and N. S. SPIRO (Bull. Acad. Sci. U.R.S.S., 1933, 1439—1458).—The available data show that the carbonation coeff., $100HCO_3/Cl$ ($-K$), varies from 1259 for river- H_2O to 0.79—0.15 for ocean and salt-lake H_2O . For ocean H_2O KS —const., S being the % of total salts present. In general the H_2O of seas, oceans, rivers, stagnant and salt lakes is saturated with $CaCO_3$, the content of which is independent of the salinity and approx. the same in the different parts of the hydrosphere. In certain cases (Black and Caspian Seas) the H_2O is super-saturated, and in others (Baltic) unsaturated, with $CaCO_3$. T. H. P.

Pink mineral in a serpentine from Bou Oufroh (Morocco). R. FREY and J. BURGHELLE (Ann. Chim. Analyt., 1934, [ii], 16, 61—62).—Pink veins in a yellowish-green serpentine were round grains of pleochroic, monoclinic plates, showing strong birefringence, hardness 1, d 2.1—2.2. Analysis gave $2Fe_2O_3, Cr_2O_3, 27MgO, 6CO_2, 54H_2O$, corresponding with a mixed basic carbonate of Fe, Cr, and Mg or with a mixture of $Mg(OH)_2$ with a basic carbonate of Fe and Cr. J. G.

Ægirine-augite hyalo-rhyolite from Tokachi, Hokkaido. T. NEMOTO (Proc. Imp. Acad. Tokyo, 1934, 10, 21—24).—Analyses are given. The mineral is similar to an average rhyolite. C. W. G.

Thermal expansion of basaltic hornblende. S. KÔZU and J. UEDA (Proc. Imp. Acad. Tokyo, 1934, 10, 25—28).—The linear expansions along the three crystal axes have been determined. C. W. G.

Nickel ore from Petsamontunturit and its examination. H. VAYRYNEN (Suomen. Kem., 1934, 7, A, 11—16).—Ores containing 1.6—2.8% Ni and 1.3—1.6% Cu are recorded among intrusive rocks. The Co content is unusually low. A. G. P.

Rocks of Kenya. (Mlle.) E. JEREMINE (Compt. rend., 1934, 198, 838—840).—Analyses of the following are given: oceanite from an island in lake Naivasha; a banded spherulitic phonolite containing poikilitic agyrite and æigmatite, from lake Narasha; a phonolite containing large crystals of nepheline and sphene, with agyritic augite, hedenbergite, and æigmatite, from between Timboroa and Eldoret; and a similar phonolite with kataforite and soda amphibole in place of hedenbergite, from south of Eldoret. C. A. S.

Emery [rock] of Samos. J. DE LAPPARENT (Compt. rend., 1934, 198, 760—761; cf. A., 1933, 928).—The vein of emery rock consists of 4.5 m. of homogeneous steel-blue diaspore with traces of pisolitic structure, and containing white mica and Fe oxides but no corundum; above this is 1.5 m. of ferruginous nodules in an Fe-free matrix, pisolitic and mainly diaspore, but containing mica, chloritoid,

and a little kaolin. It becomes more kaolinic at the top, where there is an argillaceous layer, followed by one of spathic limestone containing mica and kaolin. The emery contains 3.5% TiO_2 and 24% Fe_2O_3 , and is a metamorphosed ferruginous siliceous bauxite. The Naxos emery is similar, but metamorphism has proceeded further with formation of corundum. C. A. S.

Boracite. M. MEHMEL (Z. Krist., 1934, 87, 239—264).—Boracite at Stassfurt (I) occurs in nodules associated with pure carnallite, at Luneberg (II) in single crystals in gypsum or anhydrite. The composition of (I) averages $\text{MgCl}_2 \cdot 5.2(\text{MgFe})\text{O} \cdot 6.7\text{B}_2\text{O}_3$; that of (II) $\text{MgCl}_2 \cdot 5.0(\text{MgFe})\text{O} \cdot 6.8\text{B}_2\text{O}_3$; it is suggested that the crystals are mixed, $\text{Mg}_6\text{B}_{14}\text{O}_{26}\text{Cl}_2$ and $\text{Mg}_7\text{B}_{16}\text{O}_{30}\text{Cl}_2$. They are rhombic, pseudocubic by reason of polysynthetic twinning (cf. A., 1929, 749). The process of twinning in connexion with the transformation on heating is detailed (cf. A., 1901, ii, 111). C. A. S.

Role of water in basaltic magma. I. T. C. PHEMISTER (Tsch. Min. Petr. Mitt., 1934, 45, 19—77).—From a consideration of crystallisation in the system $\text{K}_2\text{SiO}_3\text{--SiO}_2\text{--H}_2\text{O}$ an attempt is made to deduce the probable influence of dissolved H_2O in a basaltic magma on its crystallisation. L. J. S.

Liparite and obsidian dykes in the Kolymsk district [East Siberia]. W. A. WAKER (Tsch. Min. Petr. Mitt., 1934, 45, 1—18).—Dykes 2—3 m. wide of liparite have a selvage of obsidian. These rocks are ultra-acid, the liparite with 76.87% and the obsidian 72.12% SiO_2 . L. J. S.

Minerals of the Niari basin [French Equatorial Africa]. V. LEBEDEFF and G. CHOUVERT (Compt. rend., 1934, 198, 484—486).—Deposits of compact or cryst. calamine with smithsonite occur in almost vertically inclined beds of limestone at Mt. Fouati. These minerals are accompanied by willemite, galena, cerussite, Cu glance, malachite, diopside, and other Zn, Pb, or Cu minerals. There also occur well-developed crystals of desclozite (usually growing on vanadinite, which is often covered with a thin crust of pyromorphite), phosgenite, and wulfenite. The earth of rock around these deposits is largely impregnated with vanadates.

Volcanic rocks west of Lake Rudolph. (MME.) E. JEREMINE (Compt. rend., 1934, 198, 673—675).—The volcanic rocks west of Lake Rudolph (Kenya) consist of: rhyolites, including comendites and pantellerites (a); phonolites with phenocrysts of sanidine and much aegyrine (a); nepheline microsyenites containing solvsbergites and some tinguaita; and basaltic rocks often rich in analcite (a), and including ankaramites (a) and doleritic basalts, whilst some flows contain large (5—6 cm.) phenocrysts of plagioclase (a). A basanitoid basalt resembling ordanichite (a) occurs at Lodwar. Holocryst. rocks are found only in dykes or as rounded blocks; they include essexite resembling berondrite, and shonkinite rich in aegyrine and arfvedsonite (a). Chalcodony, calcite, analcite, stilbite, heulandite, and mesotype are found in cavities. Eight complete analyses are given of the rocks marked (a). C. A. S.

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Constitution and origin of leverrierite. J. DE LAPPARENT (Compt. rend., 1934, 198, 669—671).—Leverrierite (cf. A., 1900, ii, 86) is an association of muscovite and kaolin in varying relative amounts, probably resulting from decomp. of biotite under humid conditions. The crystals of the two minerals appear to be in definite orientation (epitaxy) (cf. A., 1930, 569). C. A. S.

Minerals from the Tschetscha deposit (Caucasus). A. SHAPOVALOV (Min. J., Moscow, 1931, 107, 58—60).—Crude saltpetre contained KNO_3 10.9, NaNO_3 41.1%. CH. ABS.

Chemical and mineralogical composition of the lavas of the Timok basin. J. TOMIC (Ann. géol. pénins. balkan, 1931, 10, 128—138).—Four analyses of andesites are given. CH. ABS.

Genetic relations between the crystalline limestones, dolomites, and amphibolites in the rock series at Chynov. A. ORLOV (Vestn. Král. Ces. Spol. Nauk, 1931, II, 36 pp.).—Analyses are given. CH. ABS.

Salt layers of the Solikamsk deposit. E. RAZUMOVSKAYA (Trans. Geol. Prospect. Serv., U.S.S.R., 1931, 54, 1—40).—Halite, sylvite, carnallite, anhydrite, gypsum, haematite, clay, and quartz are present. CH. ABS.

Silicate nickel ores of the Tiulenevsk deposits in the Urals. E. KUZNETSOVA (Bull. Geol. Prospect. Serv., U.S.S.R., 1931, 50, 265—285).—Analyses are given. CH. ABS.

Organic minerals. II. Occurrence of chlorophyll derivatives in an oil-shale from the upper Trias. A. TREIBS (Annalen, 1934, 509, 103—114).—The powdered shale (from Wallgau in the upper Isar) is repeatedly extracted with AcOH at 100° , the extract is evaporated to dryness in a vac., the residue washed with H_2O to remove salts, and then extracted with CHCl_3 . The mixture of oil and porphyrin complex (from the CHCl_3 extract) is then treated with AcOH-HBr at 50° for 4 days. Subsequent washing of the Et_2O extract with 2.5% HCl removes the major part of the porphyrin mixture; deoxophylloerythrin, deoxophylloerythrochlorophyllin, $\text{C}_{32}\text{H}_{36}\text{N}_4$, m.p. 235° (block), and a porphyrin resembling (spectrum) pyrroporphyrin were isolated in small amounts. The nature of the metal in the original complex was not determined. H. B.

Thermal history of the earth. J. H. J. POOLE (Sci. Proc. Roy. Dublin Soc., 1934, 21, 9—22).—Some difficulties in the current views relating to a convective layer beneath the earth's crust and the generation of heat due to radioactivity are discussed.

L. J. S.

Actinium-uranium bifurcation ratio. M. FRANCIS and CHENG DA-CHANG (Compt. rend., 1934, 198, 733—735; cf. A., 1932, 919).—The U and Pa were separated from three samples of Belgian Congo pitchblende and one of Colorado carnotite. The thin layers were prepared by crushing in the ordinary way; by ultrasonic pulverisation; and (for U only) by electrolysis and conversion into U_3O_8 at 700° . The ratio of the ionisation currents averaged (with good

agreement) 0.023, giving the bifurcation ratio of 4% (cf. Grosse, A., 1933, 110). C. A. S.

Radioactive minerals from Shimden, Gifu Prefecture. S. IIMORI, J. YOSHIMURA, and S. HATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 209—211).—Analyses and mineralogical descriptions of an allanite and a U-bearing gadolinite are given. C. W. G.

Working formula for the age determination of a radioactive mineral. A. F. KOVARIK (Amer. J. Sci., 1934, [v], 27, 193—203).—Successive approximations introducing the Ac series are used. C. W. G.

Soils of the Pechora Region. G. A. LIVEROVSKY (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 7, 1—47). A. M.

Geology and soils of the Koltushi Region. I. N. IVANOVA, O. P. DOSMANOVA, and N. A. ARCHANGELSKAYA (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 6, 1—107). A. M.

Soil-climatic facies of the plains of the U.S.S.R. and neighbouring countries. I. P. GERASIMOV (Trans. Dokuchaiev Soil Inst., 1933, 8, No. 5, 1—38). A. M.

Soils of Abyssinia and Erythrea. L. I. PRASSOLOV (Pedology, 1933, 28, 359—373).—Two types, black earths (I) and red earths (II), are distinguished. (I) seems to be most closely related to Indian regur, whilst (II) resembles Mediterranean terra rossa. A. M.

Soils of the Crimean National Forest. I. N. ANTIPOV-KARATAIEV and L. I. PRASSOLOV (Trans. Dokuchaiev Soil Inst., 1933, 7, 1—280). A. M.

Takyr soils and their formation. I. P. GERASIMOV (Pedology, 1933, 28, 401—403).—A discussion (cf. Sushko, B., 1933, 401). A. M.

Qualitative composition of organic matter in soils of U.S.S.R. N. P. REMEZOV (Pedology, 1933, 28, 374—394; cf. A., 1933, 929).—C:N ratio is not const. for all soils, but a characteristic average val. is found for each soil zone. The ratio increases from the serozem zone (1:4.5) northwards to the Siberian chernozem (1:14) and then decreases. In the northern peats it is again wider. Cellulose and hemicellulose are absent from serozem and proteins predominate over ligno-humus complex. In chestnut soils hemicelluloses are present and ligno-humus complex exceeds proteins. In chernozem there is a large increase in ligno-humus. In podzols the ligno-humus complex is again small. A. M.

Saline and alkaline soils. F. HARDY (Trop. Agric. [Trinidad], 1933, 10, 35—40).—The classific-

ation and reclamation of these soils and their influence on the mineral intake of plants are discussed. A. G. P.

Podzols and brown forest soils. I. K. LUND-BLAD (Soil Sci., 1934, 37, 137—155).—Profile descriptions and characteristics are recorded. The acid-oxalate extraction method (Tamm) for characterising the sesquioxide and SiO_2 of soil colloids differentiates podzols from brown earths. A. G. P.

Pedology of the soils of France. V. AGAFONOFF (Ann. Agron., 1933, 3, 587—650).—Classification, chemical composition, and mineral constituents are described (cf. A., 1933, 1269). A. G. P.

Fossil spores and pollen grains as a thermometer for the process of coal formation. F. KIRCHHEIMER (Brennstoff-Chem., 1934, 15, 21—25).—Spores and pollen grains show characteristic changes when heated at $> 130^\circ$. Similar changes have been observed in spores and pollen in samples of coal taken from the neighbourhood of igneous intrusions. The pollen grains in soft brown coals have undergone no thermal change; those of many bright brown coals show changes which indicate a max. temp. of $130\text{--}200^\circ$. Similarly it has been shown that low-rank bituminous coals cannot have been subjected to a temp. $> 200^\circ$. The data relating to high-rank bituminous coals are at present insufficient to decide the max. temp. reached during their formation. A. B. M.

Temperatures reached during the formation of coal. B. NEUMANN (Brennstoff-Chem., 1934, 15, 25—27).—The appearance of the resin inclusions in a Chinese bright brown coal shows that they have been softened by heat, but have undergone no marked thermal decomp. By comparison with the behaviour of a sample of the resin on being heated it is concluded that the temp. of the coal during its formation must have reached $\leq 265^\circ$, but cannot have been $> 320^\circ$. It has similarly been shown that the max. temp. reached by a German brown coal and a German bituminous coal must lie within the ranges $150\text{--}180^\circ$ and $230\text{--}300^\circ$, respectively. The significance of these conclusions is briefly discussed. A. B. M.

Salt domes, gases, and petroleum. V. I. LUCHITZKI (Min. Suir., 1933, 8, No. 7, 1—2).—Test borings in the Pomen and Isachek regions, N. Poltava, disclosed deposits of rock salt and gases. Doming and the presence of petroleum deposits are indicated. CH. ABS.

Relationship between porosity and mechanical composition of sands in the Old Grozni area. S. M. ILINSKI (Neft. Choz., 1933, 24, 24—27).—Sands affording the lowest production have the lowest degree of porosity. CH. ABS.

Organic Chemistry.

Catalytic methods in organic chemistry. J. P. WIBAUT (Chem. Weekblad, 1934, 31, 142—147).—A review.

Dynamics and mechanism of aliphatic substitution.—See this vol., 368.

Elementary organic reactions. F. O. RICE (J. Amer. Chem. Soc., 1934, 56, 488—490).—The nos. quoted after the following reactions are the activation energies assigned (the evidence is discussed briefly): $\text{H} + \text{CH}_4 \longrightarrow \text{H}_2 + \text{Me} > 20$; $\text{H} + \text{C}_2\text{H}_6 \longrightarrow \text{H}_2 + \text{Et} 17$; $\text{Me} + \text{H}_2 \longrightarrow \text{CH}_4 + \text{H} 23$; $\text{Et} + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6 +$

H 25; $\text{Me} + \text{C}_6\text{H}_6 \rightarrow \text{CH}_4 + \text{Et}$ 20; $\text{Me} + \text{COMe}_3 \rightarrow \text{CH}_4 + \text{CH}_2 \cdot \text{COMe}$ 15; $\text{Me} + \text{Me}_2\text{O} \rightarrow \text{CH}_4 + \text{CH}_2 \cdot \text{OMe}$ 15; $\text{CH}_4 \rightarrow \text{Me} + \text{H}$ 100; $\text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2$ 100; $\text{Me} \rightarrow \text{CH}_2 + \text{H}$ 100; $\text{C}_6\text{H}_6 \rightarrow 2\text{Me}$ 79.5; $\text{Et} \rightarrow \text{C}_2\text{H}_4 + \text{H}$ 49; $\text{CH}_3 \cdot \text{COMe} \rightarrow \text{CH}_2 \cdot \text{CO} + \text{Me}$ 48; $\text{CH}_2 \cdot \text{OMe} \rightarrow \text{CH}_2\text{O} + \text{Me}$ 38; $\text{Ac} \rightarrow \text{CO} + \text{Me}$ 10. H. B.

Suitability of alloy skeletons as catalysts for the synthesis of benzene from carbon monoxide and hydrogen. F. FISCHER and K. MEYER (Ber., 1934, 67, [B], 253—261).—The vol. of the Ni-Mn-Al contacts containing SiO_2 can be reduced to $\frac{1}{3}$ by protracted grinding without loss of catalytic activity. Alloy skeletons (I) are obtained by fusing Ni and Al together, crushing the cold mass, and removing Al therefrom by aq. NaOH followed by washing with hot H_2O . Similar (I) are prepared by adding Si to molten Ni or Co and treating the products with NaOH, after which 5—10% of the Si remains. The behaviour of Ni-Al, Ni-Si, Co-Al, Co-Si, and Ni-Co-Si alloys is fully described. Presence of Fe is disadvantageous. The yields of liquid hydrocarbons from CO and H_2 with pptd. contacts (II) are usually 10—20% > with (I). (I) are advantageous in that they operate without additions, whereas an efficient (II) contains a variety of components. (I) are very readily prepared, whilst the prep. of (II) is very tedious. Advantages claimed for (I) are enhanced conductivity for heat, unusually small vol., and ready regeneration by fusion with Si. The theoretical aspects are discussed. H. W.

Ethane from acetic acid. H. E. ARMSTRONG (Nature, 1934, 133, 379).—A note on the Kolbe synthesis. L. S. T.

Rate of hydration of isobutene in dilute nitric acid.—See this vol., 369.

Acetylene-mercury complex salt. E. FERBER and E. ROMER (J. pr. Chem., 1934, [ii], 139, 277—283).—Contrary to Bilz *et al.* (A., 1905, i, 2) HgCl_2 in abs. EtOH absorbs C_2H_2 at room temp. to form an amorphous substance $\text{HgC}_2\text{H}_2 \cdot \text{HgCl}_2 \cdot \text{HgCl}$ (I), decomp. 230° (insol. in EtOH), decomposed by dil. HCl to give C_2H_2 and traces of MeCHO, thus confirming Manchot's views (A., 1913, i, 1009). Addition of H_2O to the filtrate from (I) gives (with fission of MeCHO) a cryst. complex $\text{C}_2\text{H}_2 \cdot \text{HgCl}_2 \cdot \text{H}_2\text{O}$, m.p. $93\text{—}95^\circ$, losing H_2O by crystallisation from C_6H_6 to give the Biginelli complex. Saturated $\text{Hg}(\text{OAc})_2$ in AcOH with C_2H_2 gives an explosive substance $2\text{HgC}_2\text{H}_2 \cdot \text{C}_2\text{H}_2 \cdot \text{H}_2\text{O}$ which loses its explosive character on keeping. J. W. B.

Action of light on vinyl iodide.—See this vol., 375.

aci-Trinitromethane. L. W. ANDREW and D. L. HAMMICK (J.C.S., 1934, 244).—Addition of damp $(\text{NO}_2)_2\text{C} \cdot \text{NO}_2\text{K}$ to conc. H_2SO_4 gives (?) aci-trinitromethane, m.p. 50° [with conversion into $\text{CH}(\text{NO}_2)_3$, m.p. 14°]. H. A. P.

Tertiary alcohols derived from mesityl oxide. R. JACQUEMAIN (Compt. rend., 1934, 198, 482—484).—Mesityl oxide and the appropriate Grignard reagent give δ -hydroxy- $\beta\delta$ -dimethyl- Δ^8 -hexene, b.p. $48\text{—}50^\circ/3\text{—}6$ mm., -heptene, b.p. $66\text{—}68^\circ/5\text{—}6$ mm., and

-octene, b.p. $78.5\text{—}80^\circ/3\text{—}5.4$ mm. The alcohols are dehydrated by cold PhNCO [forming $\text{CO}(\text{NHPh})_2$] or by short heating at > 6 mm. The pure products are stable at room temp. for 6 months, but, if impure, slowly lose H_2O . R. S. C.

Catalytic decomposition of complex alcohols. M. URION (Ann. Chim., 1934, [xi], 1, 5—87).—Erythrol ($\gamma\delta$ -dihydroxy- Δ^4 -butene), b.p. $94\text{—}95^\circ/12$ mm. (formate, b.p. $86\text{—}88^\circ/12$ mm.; modified prep., giving a 35% yield), is stable alone at 320° , but with Al_2O_3 at $310\text{—}320^\circ$ gives a little EtCHO and H_2O and much crotonaldehyde (I) and its dimeride (Ia), and with Cu at 280° gives a little EtCHO, divinyl, CO, and saturated hydrocarbons, and much α -hydroxy- β -ketobutane (oxime, m.p. 62° ; with $\text{NHPh} \cdot \text{NH}_2$ in boiling EtOH gives glyoxalosazone), $\gamma\delta$ -diketohexane (II), (I), H_2O , and CO_2 . Divinyl glycol (III) at 300° gives acetaldehyde (IV), EtCHO, cyclopentene-1-aldehyde (V), b.p. $48^\circ/11$ mm., m.p. -32° (semicarbazone, m.p. 209° ; oxime, an oil; phenylhydrazone, cryst., resinifies readily; NaHSO_3 compound; dibromide, an oil; p-nitrophenylhydrazone, m.p. 198°), formed from adipaldehyde, a little of which is also obtained; with Al_2O_3 at 280° the same products, including 62% of (V), are formed; with Cu at 300° (III) yields EtCHO, (IV), H_2O , (II) (25%), (V), and γ -hydroxy- δ -ketohexane (VI), b.p. $57\text{—}58^\circ/10$ mm. [with $\text{NHPh} \cdot \text{NH}_2$ in hot EtOH gives slowly NH_2Ph and the bisphenylhydrazone of (II)], whereas at 280° (II), (V), (VI), EtCHO, (IV), and 3-methylcyclopentane-1:2-dione (VII) (20%) are obtained. Hydrogenation (Pd-black) of (V) gives a little alcohol and a 60% yield of cyclopentane-aldehyde, b.p. $34^\circ/10$ mm., $136^\circ/758$ mm. (semicarbazone, m.p. 124°), stable to $\text{Br} \cdot \text{CHCl}_3$ at -5° , but at 20° giving the 1-Br-derivative. (V) and Ag_2O give cyclopentene-1-carboxylic acid, m.p. 121° , b.p. 210° (dibromide, m.p. 133°), oxidised by KMnO_4 to CO_2 and $\text{CO}_2\text{H} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$. With the appropriate Grignard reagent (V) gives 85—90% yields of α -hydroxy- α - Δ^1 -cyclopentenyl-ethyl, b.p. $165\text{—}166^\circ/749$ mm., $67\text{—}68^\circ/10$ mm., -n-propyl, b.p. $179\text{—}180^\circ/749$ mm., $78\text{—}79^\circ/10$ mm., and -n-butyl alcohol, b.p. $197\text{—}198^\circ/760$ mm., $92\text{—}94^\circ/10$ mm., dehydrated in 80% yield by Al_2O_3 at 320° to Δ^1 -cyclopentenyl-ethylene (VIII), b.p. $114\text{—}115^\circ/754$ mm., - Δ^4 -propene, b.p. $142\text{—}144^\circ/754$ mm., and - Δ^4 -butene, b.p. $59\text{—}62^\circ/14$ mm., respectively. (VIII) is shown by Raman spectra to contain 1% of 1-ethylcyclopentene and ethylenecyclopentane. (II), b.p. $130^\circ/760$ mm., m.p. about -10° [dioxime, m.p. 185° ; bisphenylhydrazone, m.p. 161° ; (? bis)semicarbazone, m.p. about 270° (decomp.)], with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives the diethylquinoxaline, m.p. 50.5° , and with H_2O_2 EtCO $_2\text{H}$. (VII), m.p. 104.5° , sublimes at $97^\circ/10$ mm., $+2\text{H}_2\text{O}$ (lost at the m.p.), m.p. $78\text{—}79^\circ$ [dioxime, m.p. (from H_2O) $148\text{—}149^\circ$ (decomp.), (from EtOH) 175° (decomp.); bisphenylhydrazone, m.p. 143° ; disemicarbazone (formed slowly), m.p. about 280° (block); quinoxaline derivative, m.p. $73\text{—}73.5^\circ$], is identical with the compound of Dupont *et al.* (Ann. Off. Combust. Liq., 1929, 3, 467), but not with that of Riley *et al.* (A., 1932, 833), which has now been crystallised and has m.p. $38\text{—}40^\circ$; it exists in the

enolic form, since it instantly gives a violet-red colour with FeCl_3 , gives salts, $\text{C}_6\text{H}_5\text{O}_2\text{Na}_2 \cdot 2\text{C}_6\text{H}_5\text{O}_2$ and $\text{C}_6\text{H}_7\text{O}_2\text{Na} \cdot 2\text{C}_6\text{H}_5\text{O}_2$, a *phenylurethane*, m.p. 137—138°, and a liquid *dibromide*, which at 20—30° passes into an *isomeride*, m.p. 153—154°; this last gives a violet colour with FeCl_3 , loses HBr with NHPH-NH_2 , and with Zn in hot EtOH regenerates (VII). (VII) reduces Fehling's solution and ammoniacal AgNO_3 , is stable to H_2SO_4 (d 1.84), distillation over Zn , fusion with S , H_2 -Ni at 300°, and H_2 -PtO₂; with alkaline KMnO_4 it gives $\text{H}_2\text{C}_2\text{O}_4$ and CO_2 , with CrO_3 or H_2O_2 and FeSO_4 (not without Fe^{++}) CO_2 only. $\delta\epsilon$ -Dihydroxy- Δ^8 -octadiene (IX), b.p. 103°/3 mm., with Al_2O_3 at 320° gives H_2O , (I), (Ia), and a mixture of *cis*- and *trans*-forms of 1:2-dimethyl- Δ^3 -cyclopentene-3-aldehyde (X), b.p. 64—72°/12 mm. [semicarbazone, m.p. 185—186° (block)], oxidised by Ag_2O to a little PrCO_2H [formed from a little $\delta\epsilon$ -diketo-octane (XI), present as impurity] and much 1:2-dimethyl- Δ^3 -cyclopentene-3-carboxylic acid, b.p. 105—107°/3 mm., which gives some of the *trans*-form, m.p. 42° (Ba salt; *dibromide*, m.p. 160—161°). (IX) with Cu at 280° gives (I), (XI), a little (X), b.p. 57—58°/10 mm. [oxime, m.p. 186—187° (block)], 1:2-diketo-4-methyl-3-ethylcyclopentane (XII) (20%), b.p. 106—108°, m.p. 24°, and a mixture of $\Delta^{8,9}$ -n-octatrienes (XIII), b.p. 137—148°. (XII) shows keto-enolic tautomerism [*dioxime*, m.p. 150—152° (decomp.) (block); *bisphenylhydrazine*, m.p. 132°; sol. in dil. aq. KOH ; the 2:5-dibromide, m.p. 142°, can be titrated with KOH (phenolphthalein), loses HBr to NHPH-NH_2 , and regenerates (XII) with Zn dust]. (XIII) is separable by distillation into fractions, b.p. 137—143°/764 mm. and 144—148°/764 mm.; the latter yields a *trans-trans*-form, m.p. 52.5°, b.p. 147—148°/764 mm., 43°/10 mm. (exaltation of $[M]_D$ 2.76) (*hexabromide*, m.p. 122°, also obtained from the first fraction), which in air gives (I).

The above results are explained by ionisation, rupture of the linking between CO and CH-OH , and relinking of the radicals and H atoms thus formed; this is supported by the following evidence. (VI), prepared in 80% yield from EtCO_2Et and Na in Et_2O , and Al_2O_3 at 320° give EtCHO , H_2O , and (II) (> 45%). $\text{CH}_3\text{Ac-OH}$, b.p. 47—49°/15 mm. (Ac derivative, b.p. 64—65°/11 mm.), with Al_2O_3 at 325° gives MeCHO , Ac_2 , and CO_2 , and with Cu at 290° also AcCHO . Glycide is stable in H_2O vapour at 300°, but with Al_2O_3 at 320° gives MeCHO (a little), (IV), Ac_2 , $\text{CH}_3\text{Ac-OH}$, glycerol, CO_2 , and a little CO ; with Cu at 280° it gives H_2O and (II). AcCO_2H with Cu at 300° gives MeCHO , Ac_2 , AcCHO , H_2O , and a 70% yield of methylsuccinic acid, m.p. 112.5° (Ba salt, $+2\text{H}_2\text{O}$, hygroscopic) [formed by elimination of CO_2 from $\text{CO}_2\text{H-CMe(OH)-CH}_2\text{-CO-CO}_2\text{H}$].

R. S. C.

Determination of glycerol. E. KATAOKA (J. Biochem. Japan, 1934, 19, 15—20).—The sample (of glycerol or of neutral glyceride) is heated with KHSO_4 in CO_2 , the $\text{CH}_2\text{:CH-CHO}$ evolved is absorbed in Bertrand's Cu solution (A., 1907, ii, 136), and the pptd. Cu_2O determined by FeSO_4 and KMnO_4 .

F. O. H.

Compounds of bivalent carbon. VII. Action of carbon monoxide on sodium ethoxide. H. SCHEIBLER and G. FRIKELL (Ber., 1934, 67, [B], 312—314; cf. A., 1932, 143).—Freshly prepared, EtOH -free NaOEt is treated with CO at 15—20°/80 atm. during 120 hr. Determination of total Na , free alkali, and HCO_2H (sole volatile acid) shows the product to be a mixture of NaOEt , HCO_2Na , and OEt-C-ONa (I). Preserved specimens evolve CO_2 when treated with acid, arising probably from NaEtCO_3 formed by autoxidation of (I).

H. W.

Glycerophosphoric acid. I. Recognition and separation of α - and β -glycerophosphates. J. J. RAE, H. D. KAY, and E. J. KING (Biochem. J., 1934, 28, 143—151).—Methods are described for determining the relative amounts of α - and β -glycerophosphates, including an enzymic method for small amounts of the β -form in the reputed α -variety and purification of the α -form. Attempts to resolve the α -salt were not successful and the addition of molybdates and tungstates does not increase the rotation to a point where it can be read.

H. G. R.

Synthesis of ribose-5-phosphoric acid. P. A. LEVENE and E. T. STILLER (J. Biol. Chem., 1934, 104, 299—306; cf. A., 1933, 1145).—*d*-Ribose, COMe_2 , and MeOH give with CuSO_4 and H_2SO_4 *isopropylidene-methylribofuranoside* (I), b.p. 83—86°/0.05 mm., which is converted by Purdie's reagent into a Me_1 ether (II) identical with that described (*loc. cit.*). Since (II) is hydrolysed (0.04*N*- HCl) to a methylribofuranose identical with 5-methylribofuranose (*loc. cit.*) (*p*-bromophenylosazone, m.p. 175°, $[\alpha]_D^{25}$ -55.2° in $\text{EtOH-C}_5\text{H}_5\text{N}$, not 161—162° and -48°, respectively, as reported), phosphorylation of (I) with POCl_3 in $\text{C}_5\text{H}_5\text{N}$ at -40° is assumed to proceed in the 5-position. The product in the form of its Ba salt is hydrolysed (0.5*N*- H_2SO_4) to ribose-5-phosphoric acid, $[\alpha]_D^{25}$ +16.54° in aq. BaCl_2 , which was isolated in the form of an amorphous Ba salt, $\text{C}_5\text{H}_9\text{O}_8\text{PBA} \cdot 5\text{H}_2\text{O}$, $[\alpha]_D^{25}$ +5.99° anhyd. in H_2O , and was identical with the natural substance, $[\alpha]_D^{25}$ +16.09° (A., 1911, i, 408). The correctness of the 5-structure is supported by a comparative study of the hydrolysis of the acid by 0.01*N*- HCl in sealed tubes at 100°.

W. S.

Hexosephosphoric acid obtained by hydrolysis of potato starch. T. POSTERNAK (Compt. rend., 1934, 198, 506—507).—Potato starch and boiling 2% H_2SO_4 give glucose-6-phosphoric acid.

R. S. C.

Polymerisation of unsaturated mercaptans. J. VON BRAUN and T. PLATE (Ber., 1934, 67, [B], 281—285).— Δ^8 -Butenyl bromide is converted by $\text{NH}_2\text{-CS-SNH}_2$ in EtOH into the non-cryst. *dithiourethane*, $\text{NH}_2\text{-CS-S-CH}_2\text{-CH:CHMe}$, transformed by KOH into Δ^8 -butenyl mercaptan, b.p. 99—101°, which rapidly polymerises. Similarly, γ -methyl- Δ^8 -butenyl bromide, from isoprene alcohol by dehydration by anhyd. MgSO_4 at 250° and treatment of the distillate with AcOH-HBr , yields γ -methyl- Δ^8 -butenyl mercaptan, b.p. 125—127°, which polymerises less readily (*Bz* derivative, b.p. 122°/0.2 mm.). Δ^7 -Butenyl mercaptan, b.p. 98—103°, becomes rapidly polymerised at room temp. Δ^5 -Pentenyl mercaptan (I), b.p. 135—137°, does not change rapidly at room temp. and relatively

slowly at 100°. Δ -cyclopentenyl mercaptan, b.p. 116°, closely resembles (I) in its tendency towards polymerisation. cyclopentenyl sulphide, b.p. 112°/16 mm., from cyclopentenyl chloride in PhMe and Na₂S in EtOH, yields a sulphinium iodide, decomp. 204°.

H. W.

Formation of acids from aldehydes and water vapour. S. GOLDSCHMIDT, P. ASKENASY, and H. GRIMM (Ber., 1934, 67, [B], 202—213).—Catalytic oxidation of EtOH in presence of Ag leads to MeCHO and a small amount of AcOH which is not increased by a large excess of O₂. The possibility that acid arises from MeCHO and H₂O vapour in absence of O₂ is established for many contacts, the most suitable of which is a slightly sintered mixture of CuO and Cr₂O₃ (7:1) at 280—320°. The only products of the action are AcOH, H₂, and a little EtOH. PrCHO and PhCHO are similarly converted into acids. The equilibrium is investigated. Owing to side changes, equilibrium from the direction AcOH+H cannot be reached, but the hydrogenation of AcOH to EtOH and MeCHO in presence of the catalyst is established.

H. W.

Preparation of acid chlorides. R. H. CLARK and A. BELL (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 97—104).—Interaction of many acids (I) (1 mol.) with PCl₅ (1 mol.) affords acid chlorides (II), the yield being decreased by ZnCl₂ (0.2 mol.), whereas (I) with PCl₃ gives improved yields with ZnCl₂. (I) (1 mol.) and SOCl₂ (1.5 mols.) gives the best yields of (II).

J. L. D.

Dehydrogenation with ethyl peroxide catalysed by iron.—See this vol., 370.

Compounds of bivalent carbon. VIII. Action of ethyl formate on sodium triphenylmethyl. H. SCHLEIBLER and H. COBLER (Ber., 1934, 67, [B], 314—317; cf. this vol., 390).—HCO₂Et behaves as an enolisable ester towards CPh₃Na in Et₂O giving CHPh₃ and a colourless cryst. ppt. hydrolysed by H₂O to NaOH, HCO₂Na, and NaHCO₃. The mechanism of the change is discussed.

H. W.

Acid iodides. III. Addition of acetyl iodide to unsaturated hydrocarbons. P. G. STEVENS (J. Amer. Chem. Soc., 1934, 56, 450—452).—Prolonged interaction of CMe₂:CHMe (I) and AcI at 25° in the dark gives a product, b.p. 25°/1 mm., containing 40.4% I, which with Et₂O-NPhMe₂ affords a little $\beta\gamma$ -dimethyl- Δ^2 -penten- δ -one [semicarbazone, m.p. 184—185° (sinters at 183°)]. This is also obtained from (I), AcCl, and SnCl₄ in CS₂ and from COMe₂, COMeEt, and HCl; in both cases the initial product is treated with NPhMe₂. cycloHexene and AcI similarly give tetrahydroacetophenone, whilst thiophen at -15° to 0° affords much I, tarry material, and a little 2-acetothienone. C₆H₆, stilbene, and Δ^2 - and iso-butenes react with AcI at 25°, but the products could not be identified; cyclohexane and CHCl:CHCl do not react.

H. B.

Reactions of chromous acetate.—See this vol., 377.

Properties of pure deuteriacetic acid. G. N. LEWIS and P. W. SCHUTZ (J. Amer. Chem. Soc., 1934, 56, 493—494).—AcOH², prepared by reaction of H²Cl

and AcOAg, has m.p. 13.3° and *d* 1.096. The v.p. at 50° is 7.5% > for AcOH, and 3% higher at 90°. No H² is attached to the C.

E. S. H.

Constitution of coccerin. A. C. CHIBNALL, A. L. LATNER, E. F. WILLIAMS, and C. A. AYRE (Biochem. J., 1934, 28, 313—325).—Coccerin (Liebermann, A., 1885, 1045) is a mixture of waxes. Extraction of the wax with EtOH-C₆H₆ gives a least sol. fraction, m.p. 106—106.5° (corr.), which on successive hydrolysis with EtOH-KOH in C₆H₆ and EtOH-NaOEt in C₆H₆ (the fatty acids must be removed after each treatment as Ca salts) affords cocceryl alcohol, which, contrary to Liebermann and Bergami (A., 1887, 650) and Becker (A., 1931, 1321), is *o*-keto-*n*-tetraatriacontanol (I), m.p. 100.5—100.7° (corr.) [acetate, m.p. 80.9—81.3° (corr.); oxime, m.p. 74.5—75°]. (I) is reduced (Clemmensen) to *n*-tetraatriacontanol, m.p. 91.9—92.2° (corr.), and thence (through the iodide) to *n*-tetraatriacontane. Oxidation (CrO₃, AcOH) of (I) gives ξ -keto-*n*-tetraatriacontanoic acid, m.p. 106.5—107° (corr.), the oxime, m.p. 62.5—63°, of which is converted by conc. H₂SO₄ at 100° and subsequent hydrolysis (conc. HCl at 180°) into *n*-nonadecylamine (II) (hydrochloride; benzoate, m.p. 88°), and *n*-eicosanoic (III), ν -amino-tetradecoic, m.p. 181—182° (hydrochloride, m.p. 168°), and tridecamethylene- $\alpha\omega$ -dicarboxylic acids. (I) is reduced (Na, amyl alcohol) to *n*-tetraatriacontane- $\alpha\omega$ -diol, m.p. 98.9—99.1° (corr.) [diacetate, molten at 49°, clear at 50—51° (corr.)]. Coccerin acid (*loc. cit.*) is a mixture of *n*-triacontanoic, m.p. 93.6° (corr.), and μ -keto-*n*-dotriacontanoic acid (IV), m.p. 104.5—105° (corr.), separable by oximation and fractionation with COMe₂. The oxime, m.p. 56—57°, of (IV) is converted (as above) into (II), (III), and undecane- $\alpha\lambda$ -dicarboxylic and λ -aminododecoic acid, m.p. 183° (hydrochloride, m.p. 163°). (IV) is synthesised by Robinson's method (A., 1930, 742) from Et sodio- α -ketoundecane- $\alpha\lambda$ -dicarboxylate and *n*-eicosanoyl chloride. The generic relationship between (I), (IV), and *n*-nonacosan- α -ol (A., 1932, 250) is discussed briefly. The conclusions of Schulz and Becker (A., 1931, 975) regarding the acid and alcohol [probably identical with (I)] from the wax of *Pemphigus xylostei* are criticised.

H. B.

Oxidation of some α -hydroxy-acids with lead tetra-acetate. H. OEDA (Bull. Chem. Soc. Japan, 1934, 9, 8—14).—The following α -OH-acids are oxidised to the aldehyde: lactic acid to MeCHO, leucic acid to isovaleraldehyde, mandelic acid to PhCHO, α -hydroxy- β -phenyl- and - β -*p*-hydroxyphenyl-propionic acid to CH₂Ph-CHO and *p*-hydroxyphenylacetaldehyde (*p*-nitrophenylhydrazones, m.p. 165°). F. R. S.

Micro-determination of acetyl and hydroxyl in fatty acids. O. FÜRTH, H. KAUNITZ, and M. STEIN (Biochem. Z., 1934, 268, 189—201).—OAc or OH in about 0.1 g. of material (*e.g.*, OH-acids separated from fats by hydrolysis with conc. HCl) is determined by a modification of the method of Friedrich *et al.* (A., 1932, 1051), the process being carried out in N₂. The vals. for cod-liver oil, dog fat, and human fat are, respectively, 32—33, 9.5—12.3, 25—27.

W. McC.

Anodic oxidation of lactic to pyruvic ion.—See this vol., 373.

Polymerisation and ring formation. XXIII. ϵ -Hexolactone and its polymerides. F. J. VAN NATTA, J. W. HILL, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1934, **56**, 455—457).—Crude ϵ -hydroxyhexoic acid (I) (obtained as a by-product in the reduction of Et adipate) is converted into ϵ -acetoxyhexoic acid, which is hydrolysed to a mixture (A) of (I) (80%) and ϵ -hexolactone (II) (20%), b.p. 98—99°/2 mm., m.p. about -5°. When (A) is heated to 150—210°, (I) and a little of the dimeric lactone (III), m.p. 112—113°, are produced; (III) contains a 14-membered ring. (II) polymerises at 150° (sealed tube) to a linear polyester (IV), $\text{OH}\cdot([\text{CH}_2]_5\text{CO}\cdot\text{O})_n\cdot\text{H}$, m.p. 53—55°, M 3660, 4300, which is depolymerised to a slight extent at 250°/1—2 mm. (mol. still). ϵ -Bromohexoic acid and EtOH-NaOEt (1 equiv.) give (cf. Marvel and Birkheimer, A., 1929, 295) Et ϵ -hydroxyhexoate (V), b.p. 104—106°/4 mm., (III), and a polyester (VI), m.p. 51—53°, M 1660, 1980, which resembles (IV). (II)—(VI) are all converted by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ into ϵ -hydroxyhexohydrazide, m.p. 114—115°. H. B.

Synthesis of succinic acid. M. S. ROSHDESTVENSKI, E. A. SLASTENINA, and N. O. VALTER (Khim. Farm. Prom., 1933, 117—120).—Technical tartaric acid (960 g.), red P (240 g.), I (144 g.), and 96% AcOH (960 c.c.) are heated slowly, with agitation, to 100—105°. The temp. is then raised to 140°, the mixture refluxed for 3 hr., most of the AcOH distilled off, the mixture dissolved in H_2O , and filtered with active C. Succinic acid which separates on cooling the filtrate is washed with H_2O at 4°. CH. ABS.

Ready rupture of the carbon chain of a succinic acid derivative. K. VON AUWERS and O. UNGEMACH (Ber., 1934, **67**, [B], 249—252).— α -Acetoxy- $\alpha\beta$ -trimethylsuccino-*p*-tolil (I), m.p. 131°, is converted by NaOH into isobutyro-*p*-toluidide, m.p. 108°, and hydroxytrimethylsuccino-*p*-toluidic acid (II), m.p. 155—156°, showing the structure of the latter to be $\text{CO}_2\text{H}\cdot\text{CMe}(\text{OH})\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$. The Ac group of (I) appears very labile, since it is partly removed by the action of 1 mol. of KOH at 0° and (II) results when acetoxytrimethylsuccinic anhydride is treated with excess of *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ in C_6H_6 . H. W.

Citrate derivatives and their properties. W. E. DONALDSON and R. F. McCLEARY [with E. F. DEGERING] (J. Amer. Chem. Soc., 1934, **56**, 459—460).— Me_3 citrate, b.p. 98°/0.2 mm. (0.1 mol.), Bu^nOH (0.15 mol.), and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ (I) (0.1 g.) boiled for 24 hr. give about 86% of Me_3Bu^n citrate, b.p. 111°/0.08 mm.; the Me_2 *Pr*, b.p. 106°/0.05 mm., and Me_2 *amyl*, b.p. 121°/0.2 mm., esters are similarly prepared. The catalytic effect of (I), PhSO_3H , and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ decreases in the order quoted; α -naphthol-4-sulphonic acid is inactive. H. B.

Pyrophosphate of citric acid. E. WERTPOROCH and H. KICKENBERG (Biochem. Z., 1934, **268**, 8—16).— Et_2O reacts with P_2O_5 to give the anhydride of diethylpyrophosphoric acid ($\text{OEt}_2\text{PO}\cdot\text{O}\cdot\text{PO}(\text{OH})_2$) (I) [*Ca*, *Na*, and *brucine*, m.p. 215° (decomp.), salts], and a small amount of EtOPO_2 . (I) heated with citric acid yields an oily citrate (II) (*Ca*, *Ba*, and *brucine*, m.p. 142—143°, salts), H being eliminated from the

OH of (II) and OH from (I). Acid hydrolysis of (II) yields aconitic acid. Tartaric and malic acids appear to yield similar pyrophosphates. W. McC.

Glucosonic (α -ketogluconic) acid. III. Constitution of compounds of sugars with *o*-phenylenediamine. H. OHLE (Ber., 1934, **67**, [B], 155—162; cf. A., 1930, 744).—The compound described (*loc. cit.*) as Na α -ketogluconate (I) is Na glucosaccharonate. (I) crystallises with $1\text{H}_2\text{O}$, $[\alpha]_D^{20}$ -83.0° to -75.24° in H_2O . Me α -ketogluconate has m.p. 187°, $[\alpha]_D^{20}$ -80.36° to -70.93° in $\text{MeOH}\cdot\text{H}_2\text{O}$ (1 : 3). Pure α -ketogluconates do not immediately reduce cold Fehling's solution and do not decolorise I in acid solution or react with cold KOI. α -Ketogluconic acid and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in H_2O at 15—20° afford 2-hydroxy-3-*d*-arabotetrahydroxybutylquinoxaline (II),

$$\begin{array}{c} \text{N}:\text{C}(\text{OH}) \\ | \\ \text{C}_6\text{H}_4-\text{N} \end{array} \geq \text{C}[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\cdot\text{OH}$$
, m.p. 199—200° (decomp.), $[\alpha]_D^{20}$ -87.5° in *N*-NaOH (tetra-acetate, m.p. 170.5—171.5°, $[\alpha]_D^{20}$ -17.38° in CHCl_3), oxidised by KMnO_4 to dihydroxyquinoxaline. The reducing action of (II) is due to fission of the mol. since treatment with $\text{NHPh}\cdot\text{NH}_2$ in boiling H_2O leads to 2-hydroxyquinoxaline-3-aldehydephenylhydrazone (III), m.p. 278—279°, and glycerol contaminated with the phenylsazone of methylglyoxal or glyceraldehyde. (III) is obtained by condensing dibromopyruvic acid with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in EtOH or H_2O at room temp. to 2-hydroxy-3-dibromomethylquinoxaline, m.p. 250° (decomp.), which is treated with $\text{NHPh}\cdot\text{NH}_2$ in boiling 50% EtOH. Fructose and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ yield 3-*d*-arabotetrahydroxybutylquinoxaline, m.p. 187—188° (decomp.), $[\alpha]_D^{20}$ -75.2° in 5*N*-HCl, identical with that derived from glucose and behaving qualitatively like (II); the tetra-acetate has m.p. 120°, $[\alpha]_D^{20}$ -30.32° in CHCl_3 . On the other hand, the product from *l*-arabinose and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ is *l*-arabotetrahydroxybutylbenziminazole, $\text{C}_6\text{H}_4\text{--}\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array}\text{C}[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\cdot\text{OH}$, m.p. 234° (decomp.), $[\alpha]_D^{20}$ -51.96° in 5*N*-HCl, since it is stable towards Fehling's solution, KOI, and $\text{NHPh}\cdot\text{NH}_2$; the tetra-acetate has m.p. 141—142°. H. W.

***d*-Glucosaccharosonic acid, an isomeride of ascorbic acid. I. Preparation and properties.** H. OHLE, H. ERLBACH, and H. CARLS (Ber., 1934, **67**, [B], 324—332; cf. A., 1930, 744).—Hydrolysis of Me α -ketogluconate (I) to *d*-glucosaccharosonic acid (II), $\text{C}_6\text{H}_5\text{O}_6$, is effected at 60—70° by alkali if added so that the solution is neutral to neutral-red, by alkali carbonate or phosphate, by $\text{C}_5\text{H}_5\text{N}\cdot\text{H}_2\text{O}$ (not by $\text{C}_5\text{H}_5\text{N}$ or $\text{C}_5\text{H}_5\text{N}\cdot\text{EtOH}$), or best by NaHCO_3 . Reaction is confined to (I) and the lactone; (II) is not obtained from α -ketogluconates and alkali or from α -ketogluconic acid and H_2O or by hydrolysis of triacetyl- α -ketogluconolactone (III). (II) is obtained in 50% yield from (III) and NaOMe. Na *d*-glucosaccharosonate has $[\alpha]_D^{20}$ +94° to +100° in H_2O , variations being caused by differences in p_H of the solution. (II) (cf. Maurer *et al.*, A., 1933, 936) has m.p. 166°, $[\alpha]_D^{20}$ -18.5° in H_2O , $[\alpha]_D^{20}$ +7.66° in COMe_2 ; the *brucine* salt (?+ H_2O), m.p. 220° (decomp.), $[\alpha]_D^{20}$ +6.25° in H_2O , *cinchonine* salt, m.p. 221—222° (decomp.), and amorphous *Pb* salt are described.

(II) has antiscorbutic action. It gives non-cryst. products when acetylated, and is not esterified by MeOH or EtOH. The oily product with CH_2N_2 does not give a cryst. acetate or react with COMe_2 . (II) does not afford a $\cdot\text{CPh}_3$ or $\cdot\text{CMe}_2$ derivative. 5-OH therefore appears to be replaced by cyclic O. (II) is very stable towards acid, but boiling 5*N*-HCl or H_2SO_4 causes loss of CO_2 and production of furfuraldehyde. Reducing power of the Na salt in H_2O towards I at 20° gradually diminishes and ultimately disappears. (II) in H_2O or AcOH or the Na salt in H_2O is not reduced (Pd-BaSO₄). Oxidation by H_2O_2 or KMnO_4 is not sp. According to Willstätter and Schudel, (II) reduces 2NaOI and then has no action on Fehling's solution. At higher concn. less NaOI is consumed and $\text{H}_2\text{C}_2\text{O}_4$ is produced. Oxidation with Ag_2O is vigorous, yielding CO_2 , $\text{H}_2\text{C}_2\text{O}_4$, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, AcOH, and small amounts of a non-reducing, optically active material. H. W.

Optically active β -thiodipropionic acid. A. FREDGA (Svensk Kem. Tidskr., 1934, 46, 10—15).—Resolution of β -thiodipropionic acid, $\text{S}(\text{CHMe}\cdot\text{CO}_2\text{H})_2$, is effected by fractional crystallisation of its quinine salt to give the quinine salt, +1.25 H_2O and anhyd. (35%), of the *d*-acid, $[\alpha]_D^{25} +200.5^\circ$, and the quinine salt, + H_2O and anhyd. (49%), of the *l*-acid, $[\alpha]_D^{25} -204.3^\circ$. J. W. B.

Amido- and imido-chlorides of non-aromatic acids. VIII. Preparation of $\alpha\beta$ -unsaturated aldehydes. J. VON BRAUN and W. RUDOLPH [with H. KROPER and W. PINKERLE (Ber., 1934, 67, [B], 269—281; cf. A., 1932, 371)].—The unsuitability of imidochlorides of aliphatic acids for further transformations is attributed to the readiness of the change $\cdot\text{CH}\cdot\text{CCl}\cdot\text{NR} \rightarrow \cdot\text{C}\cdot\text{CCl}\cdot\text{NHR}$ followed by condensations due to NH. With compounds $\cdot\text{CH}\cdot\text{CCl}\cdot\text{NR}$ such change is impeded by the general difficulty of producing the type $\cdot\text{C}\cdot\text{C}\cdot\text{CCl}\cdot\text{NHR}$, and these substances are reduced to $\alpha\beta$ -unsaturated aldehydes by CrCl_2 , but not by Dimroth's reagent. $\text{Cr}(\text{OAc})_2$ washed with MeOH and Et_2O is turbined with 2—3*N*-HCl- Et_2O , whereby CrCl_2 is pptd.; the imidochloride in Et_2O or C_6H_6 is gradually added to the well-stirred mixture, which is finally treated with dil. H_2SO_4 and distilled. Benzanilide- and cinnamylanilide-imidochloride yield PhCHO and $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ in >80% yield. BzCl and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COCl}$ are unattacked. β -Phenylpropionanilide and -*o*-toluidide, m.p. 123°, are converted by very cautious treatment with PCl_5 in C_6H_6 into the corresponding cryst. imidochlorides [amidine $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{NPh})\cdot\text{NHPH}$, m.p. 212°], which are not appreciably reduced. Campholyl chloride, campholyl-*N*-ethylimidochloride, b.p. 125°/12 mm. (from campholethylamide, m.p. 88°, and PCl_5), and the phenylimidochloride, b.p. 163°/10 mm., are resistant. Δ^a -Hexenoanilide, m.p. 109°, yields a very unstable imidochloride. The imidochloride, b.p. 120°/0.07 mm., of Δ^a -hexeno-*o*-toluidide, m.p. 125°, is reduced by CrCl_2 to Δ^a -hexenaldehyde, b.p. 43°/12 mm., in 50% yield (*p*-nitrophenylhydrazone, m.p. 137°; semicarbazone, m.p. 173°). Δ^a -Nonenoic acid [from heptaldehyde and $\text{CH}_2(\text{CO}_2\text{H})_2$] yields successively the corresponding chloride, b.p. 70—72°/0.4 mm.,

anilide, b.p. 182—184°/1 mm., m.p. 50—51°, non-cryst. imidochloride, and Δ^a -nonenaldehyde, b.p. 92°/12 mm. (*p*-nitrophenylhydrazone, m.p. 109°; semicarbazone, m.p. 163°). Δ^a -Nonenoamide is transformed by POCl_3 in C_6H_6 into Δ^a -nonenonitrile, b.p. 100—102°/12 mm. (yield 85%), which is indifferent towards $\text{SnCl}_2 + \text{HCl}$ and CrCl_2 . α -Phenylacrylyl chloride, b.p. 87—88°/0.35 mm., is prepared in 75% yield from the acid and SOCl_2 (2 mols.) or in 40% yield from tropic acid and SOCl_2 followed by distillation. The corresponding anilide, m.p. 134°, yields the unstable imidochloride, reduced by SnCl_2 and CrCl_2 to α -phenylacetaldehyde (semicarbazone, m.p. 148°) in 5% and 25—30% yield, respectively. Me 3-methylamyl ketone, obtained by reduction of methylheptenone, is converted by Zn and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ into *Et* β -hydroxy- $\beta\gamma$ -dimethyloctate, b.p. 131°/11 mm. (80% yield); the corresponding OH-acid, b.p. 172°/11 mm., is transformed by NaOAc and boiling Ac_2O into $\beta\gamma$ -dimethyl- Δ^a -octenoic (dihydrogeronic) acid, b.p. 145—147°/11 mm. $\beta\gamma$ -Dimethyl- Δ^a -octenoyl chloride yields the (sterically non-homogeneous) anilide, b.p. 190—192°/0.3 mm., m.p. 36—54°, and *o*-toluidide, b.p. 165—166°/0.1 mm., m.p. 60—74°, the cryst. imidochloride of the former being reduced (CrCl_2) to $\beta\gamma$ -dimethyl- Δ^a -octenaldehyde, b.p. 96—98°/12 mm. (semicarbazone, m.p. 141—145°; *p*-nitrophenylhydrazone, m.p. 104—109°).

Chloro- Δ^2 -cyclopentene (from cyclopentadiene and 30% HCl-PhMe) is converted into *Et* Δ^2 -cyclopentenylacetate, b.p. 130°/16 mm., transformed by 10% KOH- H_2O into cyclopentenylacetone (I), b.p. 67°/12 mm. (semicarbazone, m.p. 150°; oxime, m.p. 86—87°). (I), Zn, and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ yield *Et* β -hydroxy- γ - Δ^2 -cyclopentenyl- β -methylbutyrate, b.p. 151°/19 mm. β -Hydroxy- γ - Δ^2 -cyclopentenyl- β -methylbutyric acid, b.p. 170°/0.6 mm., NaOAc, and boiling Ac_2O afford (sterically non-homogeneous) γ -cyclopentenyl- β -methylcrotonic acid (II), b.p. 160—161°/13 mm., from which are prepared the corresponding chloride, b.p. 82—85°/0.5 mm., *Et* ester, b.p. 123°/13 mm., amide, b.p. 157°/0.1 mm., m.p. 34—41°, anilide (III), b.p. 193—195°/0.35 mm., and γ -cyclopentyl- β -methylbutyric acid, b.p. 150°/13 mm. (II) is unaffected by 70% H_2SO_4 , but transformed by conc.

H_2SO_4 into the lactone  m.p.

39° (*H*₂-derivative, b.p. 144°/13 mm.). (III) is transformed into the imidochloride, reduced (CrCl_2) to γ - Δ^2 -cyclopentenyl- β -methyl- Δ^a -butenal, b.p. 108—110°/12 mm. [semicarbazone, m.p. (indef.) 139—145°; *p*-nitrophenylhydrazone, m.p. about 140°]. 80-Dimethyl- $\Delta^{a\gamma\gamma}$ -decatrienoic acid is converted successively into the chloride, anilide, b.p. 210°/0.1 mm., imidochloride, and 80-dimethyl- $\Delta^{a\gamma\gamma}$ -decatrienal (semicarbazone, m.p. 125—150°). The odours of the aldehydes are described. H. W.

Acidic nature of aqueous formaldehyde solutions. M. WADANO (Ber., 1934, 67, [B], 191—197).—Potentiometric titration with 0.02*N*-NaOH of solutions of CH_2O obtained by subliming paraformaldehyde or α -polyoxymethylene into conductivity H_2O at 0° shows the presence of HCO_2H in small amount. After making the requisite allowance

for this, the acid dissociation const. of CH_2O is 1.62×10^{-13} at 23° . The basic properties of CH_2O are insufficiently marked to permit potentiometric measurement. H. W.

Determination of acetone. R. GROS (J. Pharm. Chim., 1934, [viii], 19, 214—220).— COMe_2 (I) is determined in aq. solution by distilling the vapour into a modified Nessler solution contained in an absorption pipette; the yellow ppt. is collected in a sintered-glass crucible and weighed. The method is satisfactory for the determination of (I) in urine and blood. C. G. A.

Introduction of deuterium atoms into acetone. J. O. HALFORD, L. C. ANDERSON, and J. R. BATES (J. Amer. Chem. Soc., 1934, 56, 491—492).— H^1 in COMe_2 is replaced by H^2 when COMe_2 is warmed with H_2O containing H_2O and a small amount of K_2CO_3 . The change has been followed by determining the decrease in d of H_2O and the increase in d of COMe_2 . E. S. H.

Aliphatic ketyls of metals. II. I. N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 123—126).—Di- and tri-ethylpinacolin are converted by Na into $\text{CMe}_3\text{-C(ONa)-CHEt}_2$ and $\text{CMe}_3\text{-C(ONa)-CET}_3$ (I), which slowly associate to yield the corresponding pinacone salts. (I) is comparatively very stable, not being completely associated after 3 months. R. T.

Preparation of diethoxyacetone and β -substituted glycerol $\alpha\gamma$ -diethers. G. DARZENS and M. MEYER (Compt. rend., 1934, 198, 478—480).— $\text{OEt-CH}_2\text{-CO}_2\text{Et}$ and NaOEt in PhMe give a 75% yield of $\text{OEt-CH}_2\text{-CO-CH(OEt)-CO}_2\text{Et}$, which with hot aq. K_2CO_3 gives an 85% yield of diethoxyacetone, b.p. $195^\circ/760$ mm., $94\text{--}95^\circ/15$ mm. (semicarbazone, m.p. 91°), whence by Grignard reagents are obtained good yields of the following β -substituted glycerol $\alpha\gamma$ - Et_2 ethers: Me , b.p. $73\text{--}74^\circ/20$ mm., Bu^n , b.p. $110^\circ/25$ mm., CH_2Ph , b.p. $154^\circ/5$ mm., $p\text{-OEt-C}_6\text{H}_4$, b.p. $149^\circ/2$ mm., and *evclohexyl*, b.p. $160^\circ/15$ mm. R. S. C.

Micro-method for detection of monoses in presence of reducing bioses. H. TAUBER (Mikrochem., 1934, 14, 167—169).—The Barfoed Cu(OAc)_2 reagent is modified by substitution of lactic acid for AcOH . The Cu_2O produced by monoses is treated with Na_2MoO_4 , giving a blue coloration proportional to the amount of reducing sugar. J. S. A.

Inhibition of oxidation of phenylhydrazine [in the preparation of glucosazone]. R. H. HAMILTON, jun. (J. Amer. Chem. Soc., 1934, 56, 487).—Glucosazone, unaccompanied by tarry material, is obtained from glucose (1 mg.), 50% AcOH saturated with NaOAc (1 c.c.), 50% NaHSO_3 (1 c.c.), NHPh-NH_2 (0.1 c.c.), and H_2O (8 c.c.); in absence of NaHSO_3 , the reaction must be carried out in evacuated sealed tubes. H. B.

Crystallisation of osazones and hydrazones as a means of identifying different sugars. M. WAGENAAR (Pharm. Weekblad, 1934, 71, 229—242).—Using a solution of NHPh-NH_2 in glycerol- AcOH (1) containing a trace of NaHSO_3 , crystals suitable for microscopical identification are obtained with

pentoses (I) and hexoses but not with bioses and trioses. NPhMe-NH_2 gives a glucosazone with fructose (II) and not with glucose, and cryst. hydrazones with (I), mannose (III), and galactose. $\text{NPh}_2\text{-NH}_2$ gives hydrazones with (I) and an osazone with rhamnose, but fails with other sugars.

$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH-NH}_2$ and $p\text{-C}_6\text{H}_4\text{Br-NH-NH}_2$ react only with (III). Less satisfactory results are obtained if citric or oleic acid is used instead of AcOH , but with lactic acid, maltose, cellobiose, melibiose, and raffinose also give phenylosazones. Only (II) and (III) react in the absence of acid. S. C.

Nucleic acids. III. Ring structure of ribose in yeast-nucleic acid. H. BREDERECK (Z. physiol. Chem., 1934, 223, 61—65; cf. A., 1933, 261).—With CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$, eytidine (I), adenosine (II), and inosine (III) afford *triphenylmethyl-cytidine* (IV), m.p. $255\text{--}257^\circ$ (corr.) (+ EtOH), $[\alpha]_D^{25} -0.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$, -adenosine (V), m.p. $255\text{--}258^\circ$ (corr.), $[\alpha]_D^{25} -8.7^\circ$ in CHCl_3 , and -inosine, m.p. $231\text{--}232^\circ$ (corr.). (IV) and (V) are not hydrolysed by KOH in EtOH , indicating that the CPh_3 radical is not attached to N. Hence the ribose in (I), (II), and (III) has the furanose structure. J. H. B.

Isolation of a crystalline dimethylanhydro-methylhexoside. Characterisation of 3:4:6-trimethylglucose. W. N. HAWORTH, E. L. HIRST, and L. PANIZZON (J.C.S., 1934, 154—157).—2-*p*-Toluenesulphonyl- β -methylglucoside (I) is converted by MeI and Ag_2O in MeOH into the 3:4:6- Me_3 derivative, m.p. 67° , $[\alpha]_D -16^\circ$ in CHCl_3 , hydrolysed by 4% NaOMe at the b.p. to 3:4:6-trimethyl- β -methylglucoside, m.p. 51° , b.p. $95^\circ/0.04$ mm., $[\alpha]_D^{25} -20^\circ$ in CHCl_3 , and further hydrolysed by 5% aq. HCl to 3:4:6-trimethylglucose, $[\alpha]_D^{25} +71^\circ$ in H_2O . This is oxidised by $\text{Br-H}_2\text{O}$ at 35° to (8-)3:4:6-trimethylgluconolactone, b.p. $140^\circ/0.1$ mm. (phenylhydrazide of the acid, m.p. 126°). The corresponding acid amide gives a positive Weerman reaction and with NaOCl gives 2:3:5-trimethyl-*d*-arabofuranose, identified by oxidation to 2:3:5-trimethyl-*d*-arabonolactone. De-acetylation of the Ac_3 derivative of (I) with NaOMe in CHCl_3 at 0° gives an anhydro- β -methylhexoside, $[\alpha]_D^{25} -25^\circ$ in H_2O [Me_2 ether, m.p. 69° , $[\alpha]_D^{25} +24^\circ$ in H_2O ; this is non-reducing, but with hot 5% HCl gives the strongly reducing (?) dimethylanhydrohexose], which with 5% HCl at 95° gives a strongly reducing product, $[\alpha]_D^{25} -77^\circ$. H. A. P.

Action of pyridine-acetic anhydride on aldose oximes. Production of hexa-acetylaldomannoseoxime. V. DEULOFEU, P. CATTANEO, and G. MENDIVELZUA (J.C.S., 1934, 147—148).—With $\text{Ac}_2\text{O-C}_5\text{H}_5\text{N}$ arabinose-, xylose-, and rhamnose-oximes give only the Ac_4 derivatives of the corresponding nitriles even at 0° ; glucose- and mannose-oximes at 0° give the Ac_6 derivatives and at $>70^\circ$ and $>30^\circ$, respectively, only the corresponding penta-acetylnitriles. Hexa-acetylaldomannoseoxime has m.p. 94° , $[\alpha]_D^{25} -8.3^\circ$ in CHCl_3 . H. A. P.

Sulphonation of sucrose. T. SODA (Bull. Chem. Soc. Japan, 1934, 9, 1—8).—Sulphonation of sucrose with ClSO_3H in $\text{C}_5\text{H}_5\text{N}$ gives a disaccharidesulphonic acid, which examination of the Ba and brucine salts

shows to be a variable mixture of mono-, di-, tri-, and tetra-derivatives. Fermentation of the acid affords a salt, $C_6H_{11}O_6 \cdot SO_3K$, $[\alpha]_D +26.5^\circ$, with no mutarotation. The glucose end of the mol. is probably chiefly glucose-6-monosulphonic acid. F. R. S.

Constitution of picrocrocin and its relationship to the carotene pigments of saffron. R. KUHN and A. WINTERSTEIN (Ber., 1934, 67, [B], 344—357; cf. Kayser, A., 1885, 59; Winterstein *et al.*, A., 1922, i, 563).—Picrocrocin (I), m.p. 156° , $[\alpha]_D^{20} -58^\circ$ in H_2O (corr.; Berl; decomp.), obtained from *Safran electus* in which lycopene, β - and γ -carotene, zeaxanthin, and hentriacontane are also identified, is $C_{16}H_{26}O_7$. Its hydrolysis by acid or alkali occurs without addition of H_2O , giving exclusively *d*-glucose (identified as the penta-acetate and through its sp. rotation) and *safraanal* (II). The reactions of fructose (*loc. cit.*) are attributed to accompanying glucosides. (I) reddens fuchsin- H_2SO_4 and reduces $Ag-NH_3$ solution. Hence it is an aldehyde, and as (II) is also aldehydic, CHO is not involved in the union of the glucose. (I) is transformed by $Ac_2O-C_5H_5N$ into *picrocrocin tetra-acetate*, m.p. $142-143^\circ$ (corr.; Berl), $[\alpha]_D^{20} -31.8^\circ$ in $CHCl_3$ [*semicarbazone*, $C_{25}H_{37}O_{11}N_3$, m.p. 106° (corr.; Berl)], which absorbs $2H_2$ (Pt- SiO_2 in $EtOH-AcOH$), giving a compound from which glucose is not removed by alkaline hydrolysis. (I) is therefore a derivative of a hydroxycarbonyl compound, $C_{10}H_{16}O_2$, in which glucose is involved with OH; it cannot, however, be obtained by acid or alkaline hydrolysis. (II), b.p. $93^\circ/14$ mm., $[\alpha] \pm 0^\circ$ [*semicarbazone*, m.p. 175° (corr.; Berl)], is best obtained from (I) by treatment with boiling 3% $Ba(OH)_2$ in a current of steam. It closely resembles eucarvone (III) and the absorption spectra indicate the presence of the system $C:C:C:C:C:O$. Oxidation of (II) with $KMnO_4$ affords *as*-dimethylsuccinic acid and $AcOH$, also obtained from (III). With CrO_3 , (II) and (III) give 1 $AcOH$. With $PhCHO$, (III) affords a $CHPh$ derivative, whereas (II) gives the additive compound $C_{17}H_{20}O_2$, m.p. $135-136^\circ$, indicating that CH_2 is not vicinal to CO . Partial catalytic hydrogenation of (II) affords β -cyclocitral (IV) (*semicarbazone*, m.p. $163-165^\circ$), oxidised by air to β -cyclogeranic acid, m.p. 91° . Consideration of the results of oxidative degradation, of mol. refraction, and absorption spectrum proves the double linking saturated by partial hydrogenation to be in conjugation with those of (IV). (II) is therefore 2:2:6-trimethyl- $\Delta^{4:6}$ -cyclohexadiene-1-aldehyde. Since the absorption spectrum of (I) shows the $C:C$ double linking to be in conjugation with $C:O$, the 4:5-double linking of (II) is solely responsible for the addition of glucose. (I) is therefore $CHO \cdot C \begin{smallmatrix} \text{CMe} \cdot CH_2 \\ \text{CMe} \cdot CH \end{smallmatrix} > CH \cdot OGluc$. The glucose residue has the pyran form, since (I) does not yield CH_2O under the influence of $Pb(OAc)_4$. The val. of $[\alpha]_D$ indicates (I) to be a β -glucoside. It is considered that the parent substance is a symmetrical dicyclic carotene pigment with 40 C and that this hypothetical "protocrocin" undergoes oxidative degradation into 1 mol. of crocin (V) and 2 mols. of (I). The pigment therefore is derived from the intermediate polyene chain, the bitter substance from the terminal ring systems. In fresh saffron the mol. ratio

of (V):(I)=1.4:1. The sensitiveness of (I) is such that it cannot be obtained cryst. from the preserved material. H. W.

β -cycloGeraniol and β -cyclogeraniol- β -*d*-glucoside. R. KUHN and M. HOFFER (Ber., 1934, 67, [B], 357—361).—Reduction of *cyclocitral* (mixture of α - and β -forms) with $Al(OPr^i)_3$ and Pr^iOH affords a mixture of much β - (I) and less α -cyclogeraniol, from which (I) separates in crystals, b.p. $101-102^\circ/11$ mm., m.p. $43-44^\circ$. Treatment of (I) with PBr_3 in C_5H_5N at 0° affords β -cyclogeranyl bromide (II), b.p. $96-99^\circ/11$ mm., which with Mg in Et_2O gives *di*- β -cyclogeranyl, m.p. 116° (corr.), but no Grignard reagent. (II) and KI in boiling $COMe_2$ give probably 1:1:3-trimethyl-2-methylene- Δ^3 -cyclohexene, b.p. $48.5-49^\circ/11$ mm., which does not add maleic anhydride and yields CH_2O when ozonised. (I), acetobromoglucose, and Ag_2O in anhyd. Et_2O yield β -cyclogeraniol- β -*d*-glucoside tetra-acetate, m.p. 104° , $[\alpha]_D^{20} -37.7^\circ$ in 96% $EtOH$, hydrolysed by aq. $Ba(OH)_2$ to β -cyclogeraniol- β -*d*-glucoside, m.p. $74-75^\circ$, $[\alpha]_D^{20} -35.9^\circ$ in 96% $EtOH$, which does not reduce Fehling's solution and is not hydrolysed by alkali. H. W.

Criteria of purity of crystalline digitalin (digitoxoside). R. CHARONNET (Compt. rend., 1934, 198, 476—478).—Commercial cryst. digitoxin (I) gives by fractionation a product, m.p. 276° (block), $[\alpha]_D^{20} +17.2^\circ$, $[\alpha]_D^{18} +28^\circ$ in $CHCl_3$, $[\alpha]_D^{17} -5.7^\circ$ in C_5H_5N , $[\alpha]_D^{16} +22.5^\circ$ in $EtOH-HCl$, a less sol., less dextro-rotatory (m.p. 277°), and a more sol. fraction (II), m.p. about 170° . (I) and (II) have similar physiological action. Digitoxigenin has $[\alpha]_D^{18} +18.1^\circ$ in $MeOH$ and -22.7° in C_5H_5N , inversion being thus a function of the lactone group. Commercial residues from (I) gave an inactive oil and flavone and three sapogenins having $[\alpha]_D -64^\circ$ to -68° and giving a violet-red colour with 85% H_3PO_4 and a little vanillin, with which (I) gives a brown colour. R. S. C.

Molecular complexity of amylose in potato starch. J. REILLY, P. P. O'DONOVAN, and (Miss) H. MURPHY (Sci. Proc. Roy. Dublin Soc., 1934, 31, 37—42).—Depression of the f.p. of NH_2Ac by dry amylose (containing 1% of ash) indicates a formula $C_{12}H_{20}O_{10}$. R. S. C.

Constitution of inulin. Synthesis of 3:4:6- and 1:4:6-trimethyl- γ -fructose. T. N. MONTGOMERY (J. Amer. Chem. Soc., 1934, 56, 419—423).— β -Diisopropylidene-fructose is benzoylated ($BzCl$, C_5H_5N) to the 1-benzoate, m.p. 82° , which is hydrolysed (aq. $EtOH-H_2C_2O_4$) to fructose 1-benzoate. This is converted by $MeOH-HCl$ into γ -methylfructoside 1-benzoate, which is methylated (MeI , Ag_2O) to 3:4:6-trimethyl- γ -methylfructoside 1-benzoate. Successive hydrolysis of this with aq. $EtOH-NaOH$ and 0.01*N*- HCl gives 3:4:6-trimethylfructose (I), $[\alpha]_D +20.4^\circ$ in $CHCl_3$, identical with that obtained by hydrolysis of trimethylinulin (A., 1933, 700). Condensation of (I) with $COMe_2$ gives (according to time of reaction) products with $[\alpha]_D +58^\circ$ to $+80^\circ$; partial hydrolysis of the isopropylidene derivative (which is probably a mixture of isomerides) leaves unchanged material of $[\alpha]_D +32^\circ$. Complete hydrolysis of all the specimens regenerates (I). α -Diso-

propyridene-fructose and N_2O_5 in cold CHCl_3 give the 3-nitrate, m.p. 61—62°, hydrolysed (0.1*N*-HCl in COMe_2) to 1 : 2-isopropylidene-fructose 3-nitrate, m.p. 151—152°. This is hydrolysed (aq. $\text{H}_2\text{C}_2\text{O}_4$) to crude fructose 3-nitrate, which when treated successively with MeOH-HCl , $\text{MeI-Ag}_2\text{O}$, Na-Hg and 50% EtOH , and 0.01*N*-HCl gives 1 : 4 : 6-trimethylfructose, $[\alpha]_D^{20} +29.7^\circ$ in CHCl_3 , when regenerated from its isopropylidene derivative, b.p. 100° (bath)/0.2 mm., $[\alpha]_D^{20} +17.8^\circ$ in COMe_2 . H. B.

Phosphorus- and nitrogen-free glycogen. M. SOMOGYI (J. Biol. Chem., 1934, 104, 245—253).—The solubility of glycogen (I) at 22° and 0° in various concn. of EtOH and NaCl has been studied. A method for prep. of N- and P-free (I) is described. H. G. R.

Highly polymerised compounds. LXXXVIII. Constitution of cellulose. H. STAUDINGER (Chem.-Ztg., 1934, 58, 145—148).—A summary. A. G.

Action of anhydrous hydrogen chloride under pressure on organic compounds. H. H. SCHLUBACH, H. ELSNER, and H. KNOOP (Angew. Chem., 1934, 47, 130—131).—Saturated aliphatic hydrocarbons (dicetyl) are not attacked by HCl under pressure. Pure aliphatic alcohols (Bu^OH ; glycerol) are not at all or only slightly attacked, whereas impure materials react; $(\text{CH}_2\text{OH})_2$ appears to yield $(\text{CH}_2)_2\text{O}$ and thence Cl-compounds. Acids (AcOH , palmitic acid, BzOH) and ethers (Et_2O PhOMe) are not attacked. Esters (EtOAc , fats) are slowly, glucosides (α - and β -methylglucoside) more rapidly, attacked. Ac_2O is quantitatively converted into AcOH and AcCl . Cellulose occupies a position between ester and anhydride. H. W.

Mechanism of the degradation of cellulose by hydrogen chloride under pressure. H. H. SCHLUBACH and V. PROCHOWNICK (Angew. Chem., 1934, 47, 132—133).—With increasing dryness of material reaction occurs with increasing smoothness; augmented H_2O content causes increase in carbonisation. The intermediate production of 1-chloroglucose (I) during the action of HCl on cellulose is established by treating the product with Ag_2CO_3 and $\text{H}_2\text{O-COMe}_2$ or Ag_2CO_3 and MeOH , whereby glucose (II) and methylglucoside, respectively, are produced. If addition of H_2O precedes the after-treatment, only (II) results. The yield of (I) is 50—60%, the deficit being attributed to formation of polyglucosans by direct loss of HCl. The intermediate formation of 2 : 3 : 6-trimethyl- α -chloroglucose by the action of HCl on trimethylcellulose is established by the isolation of 2 : 3 : 6-trimethyl- β -methylglucoside. H. W.

Use of ethyl sulphone diacetate in identification of aliphatic amines. J. P. ALDEN and B. HOUSTON (J. Amer. Chem. Soc., 1934, 56, 413—414).— $\text{SO}_2(\text{CH}_2\text{CO}_2\text{Et})_2$, b.p. 164—167°/2 mm. [improved prep. of acid described (cf. Lovén, A., 1885, 241)]; reacts rapidly with NH_2Alk (4—5 mols.) to give $\text{SO}_2(\text{CH}_2\text{CO}\cdot\text{NHalk})_2$. The following are described: $\text{Alk}=\text{Me}$, m.p. 186°, Et , m.p. 178°, Pr^a , m.p. 184°, Pr^s , m.p. 148°, Bu^a , m.p. 192°, Bu^s , m.p. 155°, n -amyl, m.p. 174°, isoamyl, m.p. 152°, n -heptyl, m.p. , and cyclohexyl, m.p. 170°. Reaction does

not occur with $\text{NH}_2\cdot\text{CHMeEt}$, NHMe_2 , NHEt_2 , or NHP^a . H. B.

Reduction of aliphatic cyanides and oximes with sodium and *n*-butyl alcohol. C. M. SUTER and E. W. MOFFETT (J. Amer. Chem. Soc., 1934, 56, 487).—The cyanide or oxime (1 mol.) in boiling Bu^OH (2300 c.c.) is treated with Na (161 g.) during 10—15 min. The yields of amine from Bu^CN , n -hexonitrile, heptaldoxime, and a series of Me alkyl ketoximes are 69—86%. H. B.

Detection of tri(hydroxyethyl)amine and colorimetric determination of nickel and of tri(hydroxyethyl)amine. E. JAFFE (L'Ind. Chimica, 1934, 9, 151—153).—When a few drops each of 20% aq. $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ (I) solution, conc. NH_3 , and 30% KOH solution are added to 1 c.c. of a solution containing 0.02% of Ni and the vol. is made up to 6 c.c. (cf. A., 1933, 246), a green colour forms; about 1 Ni in 30,000 is thus detectable. To detect (I) in cosmetics etc., the substance is acidified and treated with Et_2O , light petroleum, or C_6H_6 to remove fatty acids often present, the aq. solution being made alkaline with 30% KOH solution and treated with a few drops of a reagent containing 10 g. NiSO_4 and 25 c.c. conc. NH_3 per 100 c.c. This colour reaction serves for the determination of both Ni and (I). T. H. P.

Conversion of 2-*p*-toluenesulphonyl- β -methylglucoside into methylepiglucosamine. E. W. BODYCOTE, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1934, 151—154).—2-*p*-Toluenesulphonyl- β -methylglucoside or its triacetate is converted by NH_3 in MeOH at 100° into methylepiglucosamine (cf. A., 1920, i, 420), identified by isolation of its hydrochloride (I) and anhydro-base, and hydrolysis of the former by 0.5% HCl at the b.p. to epiglucosamine [*phenylosazone*, m.p. 225—227° (decomp.)]. Deamination of (I) with AgNO_2 gives a methylhexoside, $[\alpha]_D^{20} -52^\circ$ in H_2O (Ac_4 , $[\alpha]_D^{20} -22^\circ$ in CHCl_3 , and Me_4 , b.p. 105°/0.2 mm., $[\alpha]_D^{20} -47^\circ$ in CHCl_3 , derivatives), believed to be β -methylaltroside. H. A. P.

Dehydrogenation of α -*N*-methylaminoisobutyric acid. F. BERGEL [with K. BOLZ and R. WAGNER] (Z. physiol. Chem., 1934, 223, 66—70).—*N*-Methylaminoisobutyric acid is slowly oxidised by animal C and O_2 and unattacked by glucose (cf. Akabori, A., 1933, 263) and *p*-benzoquinone. Apparently for the oxidative degradation of NH_2 -acids paired H atoms must be present at C and N or at N alone. J. H. B.

New class of hypnotics. E. FOURNEAU, J. R. BILLETTER, and D. BOVET (J. Pharm. Chim., 1934, [viii], 19, 49—54).— NH_3 in aq. EtOH at 4—6° gives with glycidic esters $\text{CRR}'\text{CH}\cdot\text{CO}_2\text{Et}$ quant. yields of the amides $\text{CRR}'\text{CH}\cdot\text{CO}\cdot\text{NR}''\text{R}'''$ (II) ($\text{R}''=\text{R}'''=\text{H}$) (cf. Claisen, A., 1905, i, 286), also obtainable by condensing $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ with ketones CORR in presence of NaOEt (cf. Darzens, A., 1905, i, 116).

NH_2Me (first method) gives the methylamides (II) ($\text{R}''=\text{Me}$, $\text{R}'''=\text{H}$) (poor yields); it does not react with cyclohexylideneglycidic ester. NHMe_2 only reacts with two of the esters (I), viz., $\text{R}=\text{Ph}$, $\text{R}'=\text{Me}$,

and $R=Ph$, $R'=H$, with the former normally, but with the latter giving *NN*-dimethylisoserine (Fourneau, A., 1907, i, 622). NH_2Et_2 and $C_5H_{11}NH_2$ do not react with (I). The following eight *amides* (II) exercise on mice, rabbits, and fish a feeble narcotic action which presents certain novel features: $R=R'=Me$, $R''=R'''=H$, m.p. $85-87^\circ$, b.p. $127^\circ/15$ mm.; $R=R'=Et$, $R''=R'''=H$, m.p. 104° (148° given elsewhere in paper); $R=R'=Et$, $R''=Me$, $R'''=H$, m.p. 48° ; $R=Ph$, $R'=R''=R'''=H$, m.p. 148° ; $R=Ph$, $R'=R''=R'''=Me$, m.p. 132° ; $R=CH_2Ph$, $R'=Me$, $R''=R'''=H$, m.p. 133° ; $(RR')=CH_2<\underset{2}{CH_2\cdot CH_2}>\underset{H}{C}$, $R''=R'''=H$, m.p. 139° . $OPh\cdot CH_2$, $R'=Me$, $R''=R'''=H$, m.p. 139° .

W. S.

Ammonolytic reactions.—See this vol., 182.

Reaction of bismuth [nitrate] with thiocarbamide.—See this vol., 377.

Rates of formation of quaternary phosphonium salts. W. C. DAVIES and S. U. EVANS (J.C.S., 1934, 244).—The rate of formation of quaternary salts from PPr_3 and PBu_3 and a series of *n*-alkyl bromides in dil. $COMe_2$ solution at 25° diminishes as the series is ascended and is less with PBu_3 than with PPr_3 . PPr_3 is much more reactive than NPr_3 .

H. A. P.

Preparation of organo-magnesium compounds by catalysis. V. GRIGNARD (Compt. rend., 1934, 198, 625–628).—Formation of $MgRX$ is facilitated in many cases by the addition of $EtBr$, which acts by keeping the Mg surface clean and by the formation of a sol. $MgRX-MgEtBr$ complex, rather than insol. $(MgRX)_2$.

J. L. D.

Chemical evidence for planar configuration of platotetrammines. H. D. K. DREW and F. S. H. HEAD (J.C.S., 1934, 221–226).—Synthesis of the tetrammines $[Pt am ae ib]Cl_2$ and $[Pt ib_2]Cl_2$ [$am=NH_3$, $ae=NH_2Et$, and $ib=NH_2\cdot CMe_2\cdot CH_2\cdot NH_2$ (I)] from the β -diammines gives well-defined *cis*- and *trans*-isomerides; this isomerism is destroyed by use of a chelate *s*-diamine $[C_2H_4(NH_2)_2]$ (II) or by use of NH_2Et in place of NH_3 . Both forms of the tetrammines are therefore considered to have a planar structure. The following complex salts are described: α - $Pt am ae Cl_2$ (from β - $[Pt am ae_2]Cl_2$ and conc. HCl); β - $Pt am ae Cl_2$ (III) (from $K[Pt am Cl_3]$ and NH_2Et); α - $Pt am ae Cl_4$ [from (III), H_2O_2 , and HCl]; β - $Pt am py Cl_2$ (IV) (from aq. C_5H_5N and $Pt am Cl_2$ or, better, $K[Pt am Cl_3]$); $[Pt am py en]Cl_2$, H_2O [from (II) and (IV) in H_2O] (+ $PtCl_2$; anhyd. and + $1H_2O$); $[Pt am py_3]Cl_2$, H_2O (+ $PtCl_2$, H_2O); and $Pt ib Cl_2$ [from (I) and K_2PtCl_4]. Interaction of (I) and (III) in H_2O gives the isomeric salts α (+ $PtCl_2$) and β - $[Pt am ae ib]Cl_2$ (+ $PtCl_2$), but (II) and (III) give only a single $[Pt am ae en]Cl_2$ (+ $PtCl_2$). The isomeric salts α - (anhyd. and + $2H_2O$: + $PtCl_2$) and β - $[Pt ib_2]Cl_2$ (anhyd., + $1H_2O$, + $2H_2O$: + $PtCl_2$) are similarly formed from (I) and α - $Pt am_2 Cl_2$, $Pt ib Cl_2$, or K_2PtCl_4 in H_2O .

H. A. P.

Structure of the thio-ether compounds of platinum and palladium chlorides. E. G. COX, H. SAENGER, and W. WARDLAW (J.C.S., 1934, 182–186).— α - (I) and β -Bisdimethylsulphineplatinum chloride (II) are interconvertible, (I) \rightarrow (II) being

complete in hot H_2O , and an equilibrium mixture being formed in (hot) $CHCl_3$ or on melting. With Cl_2 *tetrachlorides*, m.p. $219-229^\circ$ (decomp.), and $215-226^\circ$ (decomp.), are formed. With Ag_2O (II) immediately gives $AgCl$ and a yellowish-brown base, reconverted into (II) by HCl , but (I) reacts slowly to give Me_2S , $AgCl$, and PtO, xH_2O ; similarly, (II) gives a ppt. of $AgCl$ with HNO_3 and $AgNO_3$ but (I) does not. Crystallographic agree with X-ray data in assigning a planar structure to the isomerides, (I) being the *trans* and (II) the *cis* form; this is supported by the difference in d , and by formation of the complex salt $[Pt en (Me_2S)_2]PtCl_4$ from (II), $s-C_2H_4(NH_2)_2$, and K_2PtCl_4 under conditions that with (I) lead only to Me_2S and $[Pt en]PtCl_4$.

H. A. P.

Complex compounds of bivalent palladium.—See this vol., 379.

Formation of cyclic compounds. I. Relative ease of formation and relative stability of simple carbon rings. S. SAKO (Bull. Chem. Soc. Japan, 1934, 9, 41–54).—Theoretical. Evidence is brought forward to show that free rotation of the atoms inhibits ring formation.

F. R. S.

Catalysed dehydrogenation of cyclic hydrocarbons.—See this vol., 371.

Stereoisomeric 1-methyl-2-propylcyclopentanes. G. CHURDOGLU (Bull. Soc. chim. Belg., 1934, 43, 35–48).— Et cyclopentanone-2-carboxylate, Pr^iI , and Na give Et 2-*n*-propylcyclopentanone-2-carboxylate, b.p. $126.0-126.2^\circ/13$ mm., m.p. -37.6° (semicarbazone, decomp. 160.2°), hydrolysed in 85% yield to 2-*n*-propylcyclopentanone, b.p. $183.1-183.2^\circ/760$ mm., $70.2^\circ/15$ mm., m.p. -68.25° (semicarbazone, decomp. 214°), which with $MgMeI$ gives a 90% yield of *trans*- (I), b.p. $84.5-85.0^\circ/18.1$ mm., and *cis*- (II), b.p. $91.5-92.0^\circ/18.1$ mm., -1-methyl-2-*n*-propylcyclopentan-1-ol, and a small amount of an unstable substance, b.p. $173-177^\circ/15$ mm. (I) at 300° gives H_2O , cyclopentene derivative, and up to 20% of *trans*-1-methyl-2-propylcyclopentane (III). (I) and (II) with HCO_2H give 1-methyl-2-*n*-propylcyclopentene, b.p. $150.15-150.25^\circ$, which is hydrogenated (Pt-black) in $AcOH$ to a mixture of *trans* and *cis* forms of (III), b.p. $146.37-146.38^\circ$ and 152.58° , sets to a glass and m.p. -104.9° , respectively.

R. S. C.

Action of hypochlorous acid on [optically] active 1-methyl- Δ^3 -cyclohexene. M. GODCHOT, M. MOUSSERON, and R. GRANGER (Compt. rend., 1934, 198, 480–482).—3-Methylcyclohexanol and 2% H_2SO_4 give 1-methyl- Δ^2 - (5%), b.p. $104^\circ/743$ mm., 80.44° , and - Δ^3 -cyclohexene (I) (95%), b.p. $102.5^\circ/743$ mm., 106.19° (oxidised to β -methyladipic acid, $[\alpha]_D +8.5^\circ$). (I) with $HOCl$ gives a mixture, separable by careful fractionation into four forms of 2-chloro-5-methylcyclohexan-1-ol, b.p. $79^\circ/16$ mm., $91^\circ/16$ mm., $93^\circ/15$ mm., and $95^\circ/15$ mm., $[\alpha]_{5461} +20.14^\circ$, -6.32° , $+4.21^\circ$, and $+11.15^\circ$, respectively (cf. A., 1905, i, 141). The 5-Cl-2-Me structure is considered improbable. The forms differ widely in γ .

R. S. C.

Side-chain reactions of benzene derivatives. W. S. NATHAN and H. B. WATSON (Nature, 1934, 133, 379–380).—Theoretical (cf. A., 1933, 1124).

L. S. T.

Side-chain chlorination of toluene. H. S. KING and W. B. BEAZLEY (Proc. Nova Scotian Inst. Sci., 1932—1933, **18**, 204—212).—The course of the chlorination of boiling PhMe is best followed by the temp. of the boiling liquid. When this is 145° and 155°, the liquid contains 21 and 12% of PhMe, 70% of CH₂PhCl, and 9 and 13% of CHPhCl, respectively. The relation between n and composition is linear.

R. S. C.

Allyltoluenes. C. D. HURD and H. T. BOLLMAN (J. Amer. Chem. Soc., 1934, **56**, 447—449).—*o*-Allyltoluene (I), b.p. 88—90°/25 mm., 181—181.6°/750 mm. (dibromide, b.p. 166—168°/15 mm.), and *p*-allyltoluene (II), b.p. 58—60°/1.65 mm., 180—181°/750 mm. (dibromide, b.p. 110—112°/0.7—0.9 mm., 186°/34 mm.), are prepared from allyl bromide and *o*- and *p*-C₆H₄Me·MgBr, respectively. (I) is not formed by prolonged heating of δ -phenyl- Δ^a -butene (III) at 400°. Pyrolysis of (I) and (II) in quartz (method: A., 1933, 371) gives H₂, CH₄, C₂H₄, and C₃H₆, showing that fission occurs at all the C·C linkings in the side-chain; aromatic hydrocarbons (PhMe, C₆H₄Me₂) are also formed. (I) and (II) are more stable than (III).

H. B.

Action of aluminium chloride on isopropyl and butyl chloride in the presence of benzene. T. FIRLA (Rocz. Chem., 1934, **14**, 87—92).—18% yields of C₆H₅Pr^{*s*} (I) are obtained from Pr^{*s*}Cl, C₆H₆, and AlCl₃ at 0°, when the duration of reaction is > 5 min. (I) undergoes decomp. to C₆H₅Pr^{*s*}, C₆H₄Pr^{*s*}, and PhPr^{*s*} on leaving at room temp. with AlCl₃ during 2 hr. C₆H₄Bu₂ (II) is obtained from BuCl, C₆H₆, and AlCl₃ at 0° after 90 sec.; (II) is converted into C₆H₅Bu₃, PhBu, and an unidentified product if the reaction mixture is left at room temp.

R. T.

Reaction of *o*- and *p*-dichlorobenzene with cuprous oxide and water. N. N. VOROSHCHEV and P. S. KARLASCH (Compt. rend. Acad. Sci. U.R.S.S., 1933, 223).—On warming *o*- or *p*-C₆H₄Cl₂ with Cu₂O and H₂O at 275°/80 atm. only PhOH is obtained. The reaction proceeds through *p*-C₆H₄Cl·OH. Cu₂O is a sp. reagent for this reaction.

W. R. A.

Aromatic sulphonates of elements of the second group of the periodic table. V. ČUPR and J. ŠIRŮČEK (J. pr. Chem., 1934, [ii], **139**, 245—253).—The following are described: Mg (+6H₂O), Zn (+6H₂O), Cd (+6H₂O), and Sr (+H₂O) *p*-ethyl-; Mg (+6H₂O), Zn (+6H₂O), Cd (+2H₂O), Ca, and Sr (+H₂O) *p*-chloro-; Mg (+6H₂O), Cd (+3H₂O and +2H₂O), and Sr (+2H₂O) *p*-bromo-; Mg (+6H₂O), Zn (+6H₂O), Cd (+6H₂O), and Sr (+H₂O) *p*-iodo-; and Cd (+4H₂O) and Sr (+5H₂O) *p*-hydroxy-benzene-sulphonate; Mg (+6H₂O), Zn (+2H₂O), Cd (+2H₂O), Ca (+3H₂O), and Sr (+3.5H₂O) sulphanilates; Be (+9H₂O), Mg (+8H₂O), Zn (+8H₂O), Cd (+9H₂O and +5H₂O), Ca (+6H₂O), Sr (+2H₂O), and Ba (+H₂O) 2-nitro-*p*-toluenesulphonates; Be (+8H₂O), Mg (+8H₂O), Zn (+9H₂O), Cd (+9H₂O), and Sr (+H₂O) 6-chloro-3-nitrobenzenesulphonates; Be (+4H₂O and anhyd.) and Ba (+1.5H₂O) 1- and Be (+6H₂O and anhyd.) 2-naphthalenesulphonate. The relative proportions of H₂O of crystallisation (I) are discussed, (I) being greater the greater is the mol. vol. of the anion.

J W

Reduction by magnesium+magnesium iodide.
XII. Reduction of phenyl triphenylmethyl ketone. W. E. BACHMANN (J. Amer. Chem. Soc., 1934, **56**, 449—450).—CPh₂·CPh₂ is obtained in 92% yield from CPh₃·COPh, Mg, and MgI₂ in C₆H₆—Et₂O at 80°; about 8% of a viscous product (formed in 70—80% yield at room temp.) is also produced. Small amounts of MgI₂ can effect (slowly) complete reduction: CPh₃·COPh + Mg + MgI₂ → CPh₂·CPh₂ + MgO + MgI₂.

H. B.

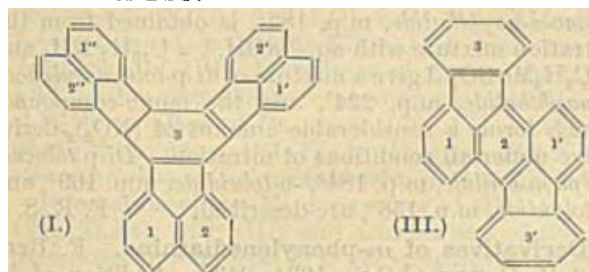
Derivatives of 1:6-dimethylnaphthalene. F. FEIST (J. pr. Chem., 1934, [ii], **139**, 261—268).—1:6-C₁₀H₆Me₂ (I) with Br at 0° gives a Br₂-derivative, m.p. 134.5°, and an isomeric Br₂-derivative, m.p. 62—64° (probably the 4:5- and 4:8-derivatives); with Br in CHCl₃ and Fe powder a Br₃-derivative (II), m.p. 115—116° (also by Br—H₂O on the mother-liquor from the Br₂-derivative), is obtained, the mother-liquor giving a Br₃-derivative, b.p. 227°/10 mm., m.p. 107—108°, which on further bromination gives a Br₄-derivative (III), m.p. 180—181°. Neither (II) nor (III) condenses with AcCl—AlCl₃ in CS₂ or PhNO₂, but (I) is thus converted into a 1:6-dimethylnaphthyl Me ketone (IV), m.p. 43° (Br₄-derivative, m.p. 183—184°), converted by Cl₂ (Hg lamp) into an amorphous Cl₉-derivative C₁₀H₅(CCl₃)₂·CO·CCl₃, b.p. 244—250°/5 mm., which gives only amorphous acids with conc. H₂SO₄ at 140° and (?) trimellitic acid with KOH at 170°. Oxidation of (IV) with CrO₃—AcOH gives the corresponding quinone, m.p. 150°.

J. W. B.

Polyterpenes and polyterpenoids. LXXXVI.
Dehydrogenation of cholesterol, ergosterol, cholic acid, and phytosterols. L. RUZICKA, G. THOMANN, E. BRANDENBERGER, M. FURTER, and M. W. GOLDBERG (Helv. Chim. Acta, 1934, **17**, 200—221).—In part a reply to Diels (A., 1933, 1047; this vol., 288). Dehydrogenation of cholic or cholatrienic acid with Se at 360° affords picene (I), m.p. 354—355° (corr.) [compound with 2:7-dinitroanthraquinone (II), m.p. 292—293°], identical with that from tar, a hydrocarbon C₂₁H₁₆ (III), m.p. 272—274° (corr.), and a small amount of chrysene (IV), identical with that from tar. Dehydrogenation at 420° affords less (I), more (IV), and no (III). Hence the production of (IV) (Diels) results from the higher dehydrogenation temp. employed, at which (III) is either not formed or is destroyed. Absorption and Röntgen spectra show the identity of (I) and (IV) with the specimens from tar, and differentiate them from (III), from the hydrocarbon, m.p. 214—215°, obtained by Se dehydrogenation of ergosterol (C₂₈), and from the hydrocarbon C₂₇H₂₈ (V), m.p. 202—203° [compound with (I), m.p. 246—247°] (crystallographic data), obtained by dehydrogenation of phytosterol (from soya bean) with Se at 320°. Contrary to Diels, but in agreement with suggested mechanisms for the production of these hydrocarbons from sterol skeletons, the identity of the hydrocarbons obtained by dehydrogenation of C₂₇, C₂₈, and C₂₉ sterols is disproved.

Catalytic hydrogenation of decacyclene and rubicene under pressure. J. VON BRAUN [with G. MANZ and W. KELLER] (Ber., 1934, **67**, [B], 214—218).—Addition of H to pure decacyclene (I) in deca-

hydronaphthalene in presence of Ni occurs very slowly at moderate temp. and pressure. Reaction occurs suddenly at about 230°/200 atm., leading immediately to *trisdecahydrodecacyclene* (II), m.p. 215°, not affected by conc. H_2SO_4 at 50–60° and oxidised by HNO_3 to mellitic acid. (II) is stable towards heat and is very extensively degraded when distilled over PbO .



Cautious treatment with S at 200°/20 mm. in N_2 leads to the substance, $\text{C}_{36}\text{H}_{38}$, m.p. (indef.) 245°, arising from complete dehydrogenation of one of the decahydronaphthalene nuclei. Hydrogenation of (I) containing about 1% of S can be controlled to yield *dodecahydrodecacyclene*, m.p. 303–306°, with tetrahydronaphthalene rings arranged symmetrically around the C_{10}H_8 nucleus. Rubicene (III) is readily reduced to *perhydrorubicene*, $\text{C}_{30}\text{H}_{40}$, m.p. 55–65°, readily dehydrogenated in hot EtOAc at 3 and 3' to the substance, $\text{C}_{26}\text{H}_{28}$, m.p. 246–248°. Hydrogenation (Ni) of (III) at about 250°/200 atm. gives a substance, m.p. 145–160°, approximating closely to $\text{C}_{26}\text{H}_{34}$. Analogies with the behaviour of fluoranthrene (A., 1930, 1570) are discussed.

H. W.

Internal molecular compounds. L. DEDE and A. ROSENBERG (Ber., 1934, 67, [B], 147–153).—The optical properties of the nitroanilines (I) are attributed to the mutual action of the two substituents resulting in the formation of "internal mol. compounds." PhNO_2 and NH_2Ph yield a coloured mol. compound in solution. Addition of HClO_4 to (I) causes their absorption spectra to become nearly identical with that of PhNO_2 , the smallest concn. of acid to produce the effect being observed with the *m*-derivative. Similarly, acetylation by involving NH_2 hinders the formation of an internal complex, with the expected effect on the absorption band. The optical behaviour of the nitrophenols in presence and absence of acid or alkali or in various media is in harmony with an internal union between NO_2 and O by OH. The inability of *o*- in contrast to *m*- and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ to yield mol. compounds with NH_2Ph , *o*-, *m*-, or *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, or α - or β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$ is attributed to the firmness of the union of NO_2 and OH within the mol. The aminobenzoic acids show the band characteristic of internal mol. compounds, and addition of HClO_4 causes their spectra to become identical with that of BzOH . Where little affinity between the radicals exists, the bands are not observed. Thus the nitrotoluenes do not differ markedly from PhNO_2 and $p\text{-C}_6\text{H}_4\cdot\text{Cl}\cdot\text{NH}_2$ and the toluidines closely resemble NH_2Ph .

H. W.

Nitration of *m*-chloro- and *m*-bromo-aniline derivatives. M. M. DE MONCHY (Rec. trav. chim., 1934, 53, 141–162).—Interaction of abs. HNO_3 at 0°

with *N*-*m*-chlorophenyl-*N'*-ethylcarbamide (I), m.p. 120° (from $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ and EtNCO), gives the $\text{N} : 4 : 6\text{-(NO}_2)_3$, m.p. 95°, $\text{N} : 2 : 6\text{-(NO}_2)_3$, m.p. 85°, and $\text{N} : 2 : 4\text{-(NO}_2)_3$ (not isolated) -derivatives. The crude nitration mixture when boiled with MeOH gives *Me* 3-chloro-4 : 6-dinitro-, m.p. 67°, and *Me* 3-chloro-2 : 6-dinitro-phenylcarbamate, m.p. 188°; with EtOH the corresponding *Et* esters, m.p. 70° and 155°, respectively, and (?) *Et* 3-chloro-2 : 4-dinitrophenylcarbamate, m.p. 163° (3-chloro-2 : 4-dinitroaniline, m.p. 100°), are formed. Nitration of (I) with $\text{HNO}_3\text{-H}_2\text{SO}_4$ gives the $\text{N} : 2 : 4 : 6\text{-(NO}_2)_4$ -derivative, converted by MeOH into *Me* 3-chloro-2 : 4 : 6-trinitrophenylcarbamate, m.p. 196°, but attempted further nitration of the trinitrocarbamides or dinitrourethanes gave only 1 : 3 : 2 : 4 : 6- $\text{NH}_2\cdot\text{C}_6\text{HCl(NO}_2)_3$. The identity of the above NO_2 -compounds is determined by hydrolysis to amine. Nitration of *Me* *m*-chlorophenylcarbamate, m.p. 81° (from $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ and ClCO_2Me), gives the 2 : 4- and 2 : 6- $\text{-(NO}_2)_2$ -derivatives. Similar products are obtained by nitration of derivatives of $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, but whilst the carbamide gives only a trace of nuclear $\text{-(NO}_2)_3$ -compound, the urethanes readily yield such derivatives. The following are described: *N*-*m*-bromophenyl-*N'*-ethylcarbamide, m.p. 129° (products of nitration not separated, but converted direct into urethanes); *Me* 3-bromophenylcarbamate [4 : 6- $\text{-(NO}_2)_2$, m.p. 81°, 2 : 6- $\text{-(NO}_2)_2$, m.p. 193°, and 2 : 4 : 6- $\text{-(NO}_2)_3$, m.p. 176°, -derivatives]; *Et* 3-bromophenylcarbamate [4 : 6- $\text{-(NO}_2)_2$, m.p. 110°, 2 : 6- $\text{-(NO}_2)_2$, m.p. 173°, and 2 : 4 : 6- $\text{-(NO}_2)_3$, m.p. 230°, -derivatives]; and 3-bromo-2 : 6-dinitro-, m.p. 136°, and -2 : 4 : 6-trinitroaniline, m.p. 213°. 3-Chloro-2 : 6-dinitroaniline is dimorphic, m.p. 112°, 136° [*Ac* derivative, m.p. 175° (by nitration of $m\text{-C}_6\text{H}_4\text{Br}\cdot\text{NHAc}$)]. With NaOMe it gives 2 : 4-dinitro-5-aminoanisole, m.p. 207°, as also does the corresponding *Br*-compound. Both 3-chloro- and 3-bromo-2 : 6-dinitroaniline give 2 : 4-dinitro-3-aminodiphenylamine, m.p. 200°, with NH_2Ph .

H. A. P.

Colour reactions of organic compounds. I. Colour reactions of arylthiocarbamides. G. M. DYSON (J.C.S., 1934, 174–177).—The colour developed by thiocarbamides, $\text{A}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHB}$, in warm conc. H_2SO_4 is dependent on group B, which must be aromatic and contain no NO_2 group, and the presence of NO_2 in the aryl residue A. It is due to formation of the corresponding amine, which is oxidised by a trace of HNO_3 produced from the NO_2 group. The following are described: *o*-nitrophenylthiocarbamide, m.p. 74°; *N*-*o*-nitrophenyl-*N'*-propyl-, m.p. 168°; *o*-nitro-, m.p. 188°, 2-nitro-2', m.p. 192°, -3', m.p. 150°, and -4'-methyl-, m.p. 207°, and 4'-bromo-2-nitro-*s*-diphenyl-, m.p. 210°; *N*-*o*-nitrophenyl-*N'*- α -, m.p. 145°, and - β -naphthyl-, m.p. 176°; *s*-*di*-*o*-nitrophenyl-, m.p. 160°; 2 : 3', m.p. 116°, and 2 : 4'-dinitro-*s*-diphenyl-, m.p. 153°; *N*-*m*-nitrophenyl-*N'*-propyl-, m.p. 119°; 3-nitro-, m.p. 156°, 3-nitro-2', m.p. 154°, -3', m.p. 158°, and -4'-methyl-, m.p. 157°, 3 : 3'-dinitro-, m.p. 168°, 4'-bromo-3-nitro-, m.p. 173°, 2 : 4'-dichloro-3-nitro-, m.p. 151°, and 3 : 2'-dinitro-6-methyl-*s*-diphenyl-, m.p. 160°; *N*-*m*-nitrophenyl-*N'*- α -, m.p. 156°, and - β -naphthyl-, m.p. 164°; 3 : 3', m.p. 136°, and 3 : 4'-dinitro-6'-methyl-, m.p. 158°, 3 : 4'-dinitro-, m.p. 172°, 3 : 3', m.p. 115°,

and 3:2'-dinitro-4'-methyl-s-diphenyl-, m.p. 188°; 4-nitro-, m.p. 175°, 4-nitro-2'-, m.p. 132°, -3'-, m.p. 135°, and -4'-methyl-, m.p. 165°; 4:4'-dinitro-, m.p. 175°, 4'-bromo-, m.p. 164°, and 4'-chloro-4-nitro-, m.p. 179°, and 4-nitro-4'-methoxy-s-diphenyl-, m.p. 155°; N-p-nitrophenyl-N'-α-, m.p. 187°, and -β-naphthyl-, m.p. 157°; 4:3'-, m.p. 175°, and 4:4'-nitro-6'-, m.p. 181°, and 4:3'-, m.p. 176°, and 4:2'-dinitro-4'-methyl-s-diphenyl-, m.p. 176°; 4-nitro-o-tolyl-, m.p. 140°; N-4-nitro-o-tolyl-N'-propyl-, m.p. 173°; 5-nitro-, m.p. 171°, and 4'-bromo-5-nitro-2-methyl-, m.p. 183°, o-nitro-2:2'-, m.p. 149°, 2:3'-, m.p. 156°, and 2:4'-dimethyl-s-diphenyl-, m.p. 161°; N-4-nitro-o-tolyl-N'-α-, m.p. 191°, and -β-naphthyl-, m.p. 154°; 3:3'-dinitro-6:6'-dimethyl-s-diphenyl-, m.p. 162°; N-5-nitro-o-tolyl-N'-propyl-, m.p. 157°; 4-nitro-2:2'-, m.p. 154°, -2:3'-, m.p. 152°, and 2:4'-dimethyl-s-diphenyl-, m.p. 150°; N-5-nitro-o-tolyl-N'-α-, m.p. 166°, and -β-naphthyl-, m.p. 165°; 2-nitro-p-tolyl-, m.p. 122°; N-2-nitro-p-N'-propyl-, m.p. 147°; 3-nitro-, m.p. 152°, and 4'-bromo-3-nitro-4-methyl-, m.p. 173°, 3-nitro-2':4-, m.p. 147°, -3':4-, m.p. 152°, and -4:4'-dimethyl-s-diphenyl-, m.p. 176°; N-2-nitro-p-tolyl-N'-α-, m.p. 165°, and -β-naphthyl-, m.p. 212°; 3-nitro-p-tolyl-, m.p. 138°; N-3-nitro-p-tolyl-N'-propyl-, m.p. 144°; 2-nitro-, m.p. 125°, and 4'-bromo-2-nitro-4-methyl-, m.p. 156°, 2-nitro-2':4-, m.p. 164°, -3':4-, m.p. 156°, and -4:4'-dimethyl-s-diphenyl-, m.p. 162°; N-3-nitro-4-p-tolyl-N'-α-, m.p. 168°, and -β-naphthyl-, m.p. 159°; o-nitro-2-methoxyphenyl-, N-5-nitro-2-methoxyphenyl-N'-propyl-, m.p. 171°; 5-nitro-, m.p. 173°, and 4'-bromo-5-nitro-2-methoxy-, m.p. 180°, 5-nitro-2-methoxy-2'-, m.p. 162°, -3'-, m.p. 168°, and -4'-methyl-, m.p. 162°, 3':5-, m.p. 164°, and 4':5-dinitro-2-methoxy-s-diphenyl-, m.p. 162°; N-5-nitro-2-methoxy-N'-α-, m.p. 178°, and -β-naphthyl-, m.p. 175°; 5:5'-dinitro-2:2'-dimethoxy-s-diphenyl-, m.p. 175°; 3-nitro-o-tolyl-, m.p. 171°; 4'-bromo-2-nitro-6-methyl-s-diphenyl-, m.p. 164°; N-3-nitro-o-tolyl-N'-α-naphthyl-, m.p. 171°; 2-nitro-4':6-dimethyl-, m.p. 160°, 4-nitro-, m.p. 158°, 4'-fluoro-, m.p. 154°, and 4'-bromo-4-nitro-3-methyl-s-diphenyl-, m.p. 147°; N-6-nitro-m-tolyl-N'-α-, m.p. 142°, and -β-naphthyl-, m.p. 172°; and 4-nitro-3:4'-dimethyl-s-diphenyl-thiocarbamide, m.p. 110°; 3-, m.p. 84°, 4-, m.p. 74°, and 5-nitro-o-, m.p. 92°, 2-, m.p. 68°, and 3-p-, m.p. 67°, and 6-nitro-m-tolyl-, m.p. 77°, and o-nitro-2-methoxyphenyl-thiocarbimide, m.p. 83°.

F. R. S.

Inhibitory effect of substituents in chemical reactions. III. Reactivity of the thiocarbimide group in substituted arylthiocarbimides. D. W. BROWNE and G. M. DYSON (J.C.S., 1934, 178—179).—The rate of reaction between arylthiocarbimides and EtOH has been measured (cf. A., 1932, 154) and indicates that the addition of EtOH is a side-chain reaction favoured by "electron-recession." *m*- and *p*-NH₂·C₆H₄·CO₂H and CCl₄ afford respectively 3-, m.p. 163° (decomp.), and 4-carboxyphenylthiocarbimide, m.p. 220° (decomp.). 4-Carbo-propoxy-, m.p. 32°, -*n*-butoxy-, b.p. 180°/5 mm., and -*n*-amyl-oxy-phenylthiocarbimide, b.p. 205°/5 mm., have been prepared from the corresponding *p*-aminobenzoate, and *Et* phenylacetate-, m.p. 58°, *Et* cinnamate-, m.p. 62°, and *Et* β-phenylpropionate-4-thiocarbimide, b.p. 296°, have been similarly obtained. o-Nitro-1:2:3-trimethoxy-

benzene on reduction and treatment with CCl₄ yields 3:4:5-trimethoxyphenylthiocarbimide, m.p. 65°.

F. R. S.

Nitration of some α-naphthalides. H. H. HODGSON and J. WALKER (J.C.S., 1934, 180—181).—*o*-*p*-Ratios for nitration of formo-, benzo-, and *o*-carboxybenzo-α-naphthalide (cf. A., 1933, 1155) are respectively 0.4—0.6, 1.1—1.3, and 1.1—1.3. 4-Nitroformo-α-naphthalide, m.p. 182°, is obtained from the nitration mixture with aq. NaOH. α-C₁₀H₇·NH₂ and *p*-C₆H₄Me·SO₂Cl give a mixture of di-*p*-toluenesulphon-α-naphthalide, m.p. 224°, and the mono-compound, which forms a considerable amount of (NO₂)₂-derivative under all conditions of nitration. Di-*p*-toluenesulphon-anilide, m.p. 184°, -*o*-toluidide, m.p. 169°, and *p*-toluidide, m.p. 158°, are described.

F. R. S.

Derivatives of *m*-phenylenediamine. F. BELL and R. COHEN (J.C.S., 1934, 243).—Addition of Br to the C₆H₅N "salt" of 1:3-di-*p*-toluenesulphonamidobenzene (I) gives the 4:6-Br₂-, m.p. 209° [free base, m.p. 134° (Ac. derivative, m.p. 257—260°)], and with more Br the 2:4:6-Br₃-derivative, m.p. 233° (identified by hydrolysis). Fuming HNO₃ in AcOH converts 1:3-di-*m*-nitrobenzenesulphonamidobenzene, m.p. 195°, into 4:6-(NO₂)₂-, m.p. 235°, and 2:4:6-(NO₂)₃-, m.p. 218°, -derivatives. Nitration of (I) gives 4:6-(NO₂)₂-, m.p. 208—210°, and 2:4:6-(NO₂)₃-, m.p. 223°, -derivatives.

H. A. P.

***p*-Cymene.** II. Preparation of an azo-dye [from 2-amino-*p*-cymene] and 5-amino-*p*-cymene. S. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 4b).—The red dye *p*-NH₂·C₆H₄·SO₃H → 2-amino-*p*-cymene, reducible to 2:5-diamino-*p*-cymene, which is converted by oxidation into thymoquinone, is described. When diazotised and reduced it gives 5-amino-*p*-cymene.

H. A. P.

Alleged colour and dyeing properties of some derivatives of tetra-arylmethanes. A. WEISSBERGER and J. THIELE (J.C.S., 1934, 148—151).—Condensation of pararosiline (I) with NH₂Ph, NMe₂Ph, and some phenolic derivatives (cf. Sen and Banerjee, A., 1931, 840) gives mixtures, the dyeing properties of which are due to the presence of unchanged (I). From PhOH, pp'p''-tri-amino-p'''-hydr-oxytetraphenylmethane, colourless, m.p. 247° (decomp.), has been isolated. The dyeing properties of the compounds obtained by condensing resorcinol (II) with ketones (cf. Sen *et al.*, A., 1930, 778) are probably due to substances produced by the action of dehydrating agents on (II).

F. R. S.

Extension of Michael's reaction. III. T. N. GHOSH and P. C. GUHA (J. Indian Inst. Sci., 1933, 16, A, 103—112).—The Michael condensation takes place with NPh·N·CO₂Et (I), (N·CO₂Et)₂ (II), and NHPh·N·C(CO₂Et)₂ (III), the yields from (I) and derivatives being poor, and the products from (III) unstable. It does not occur with CHPh·NPh or NPh·CH·CO₂Et, but addition of Na enolates readily occurs to the ·CN· group of CO₂Et·NCS. Interaction of (I) in Et₂O with the Na derivatives of CH₃Ac·CO₂Et (IV), CN·CH₂·CO₂Et (V), CH₃Ac₂, and NH₂·CO₂Et (VI), respectively, gives *Et* β-N-carbethoxyacetylmethyl m.p. 103—104°, *Et* β-N-carbethoxycyanomethyl-, m.p.

69—70°, *Et* β -*N*-diacetylmethyl-, m.p. 130—131°, and *Et* β -*N*-hydroxy-phenylcarbazinate (VII), m.p. 178—179° (decomp.). Hydrolysis of (VII) with *N*-KOH gives a *K* salt, m.p. 135—136°, to which the formula $\text{NPh} \langle \text{N} \rangle \text{C} \cdot \text{OK}$ is assigned as it cannot be esterified,

but with MeI and EtI gives the *Me*, m.p. 128—129°, and *Et*, m.p. 130—131°, derivatives; the free OH-compound (VIII) (+1H₂O) has m.p. 214—216°. Interaction of *p*-C₆H₄Me·N·N·CO₂Et with the Na derivative of (VI), hydrolysis of the product, and acidification gives the corresponding compound [(VIII), C₆H₄Me in place of Ph], m.p. 168—170°. Addition of the Na compound of (IV) to (II) gives *Et* β -*N*-carbethoxyacetylmethylhydrazinedicarboxylate, m.p. 74—75°.

Interaction of the Na derivatives of (IV), (V), and CH₂(CO₂Et)₂ with (III) and acidification of the product gives in every case *Et* *H* phenylhydrazinomalonate, m.p. 110—111° (NHPH·NH₂ salt, m.p. 124—125°); this is hydrolysed by KOH in EtOH to NHPH·NH·CH₂·CO₂H, m.p. 153°, and oxidised by aq. FeCl₃ to *Et* *H* benzeneazomalonate, m.p. 174—176°. Similarly, from carbethoxythiocarbimide (IX) and ONa·CMe·CH·CO₂Et (X) acetylcarbethoxythioacetocarbamic acid, CO₂Et·CHAc·CS·NH·CO₂H, is obtained; the corresponding *Et*₂ ester does not appear to be cyclised by NaOEt. From (IX) and CHNa(CO₂Et)₂ is obtained dicarbethoxythioacetocarbamic acid, CH(CO₂Et)₂·CS·NH·CO₂H, m.p. 70—72°, and a compound, m.p. 164—165°; similarly with (X) diacetylthioacetocarbamic acid, CHAc₂·CS·NH·CO₂H, m.p. 121—122° (decomp.), and with CN·CHNa·CO₂Et *Et* carbethoxycyanothioacetocarbamate, CN·CH(CO₂Et)·CS·NH·CO₂Et, m.p. 152—153° (decomp.), hydrolysed by cold 0.1*N*-NaOH to the *Et* *H* ester, m.p. 158—160° (decomp.), is formed. H. A. P.

Arylazoforamidoximes. G. LONGO (Gazzetta, 1933, 63, 923—926).—PhN₂Cl is converted by KCN into the cyanide, and this treated with NH₂OH, whereby benzeneazoforamidoxime, NPh·N·C(NOH)·NH₂, m.p. 125—126° [*Ac* and *Bz* derivatives, m.p. 168° and 191—192° (decomp.)], is formed. The *p*-toluene compound has m.p. 164—165° (decomp.) [*Ac* and *Bz* derivatives, m.p. 193—194° and 192—193° (decomp.)]. E. W. W.

Carbonitrosohydrazines. II. Hydrazo- and azo-hydroxamic acids. A. QUILICO and R. JUSTONI (Gazzetta, 1933, 63, 862—870; cf. A., 1933, 59).—Carbonitrosohydrazines react with NH₂OH in EtOH to form compounds of type NHR·NH·C(OH)·NOH, e.g., phenyl-, m.p. 164° (decomp.), *p*-tolyl-, decomp. 165°, *p*-anisyl-, decomp. 162°, and *p*-chlorophenyl-, decomp. 155°, hydrazinoformhydroxamic acids. These all give a strong reddish-violet FeCl₃ reaction; the last is oxidised by H₂O₂ in AcOH to *p*-chlorobenzene-azoformhydroxamic acid, m.p. 165° (decomp.). *p*-Anisylcarbonitrosohydrazine has m.p. 136°.

E. W. W.

***o*-Quinonephenylhydrazones.** A. BURAWOY (Annalen, 1934, 509, 60—73; cf. A., 1933, 828, 946).—A reply to von Auwers (A., 1933, 1156). The *o*-quinonephenylhydrazone structure for *o*-hydroxyazobenzenes is supported by the results of bromination and nitration and from refractometric measurements.

The conclusions of von Auwers and Heimke (A., 1928, 688) are criticised. H. B.

Action of bromine on 2- and 6-chloro- and 2- and 6-iodo-3-bromophenols. H. H. HODGSON and J. NIXON (J.C.S., 1934, 137—138).—2-Chloro-3-bromophenol, m.p. 60° [from 3-bromo-2-aminophenol (I)], with Br in CHCl₃ gives 2-chloro-3 : 4 : 6-tribromophenol, m.p. 96°. 2-Chloro-*o*-bromophenol, m.p. 60° [from 5-bromo-2-aminophenol (II)], similarly gives 6-chloro-2 : 3 : 4-tribromophenol, m.p. 98°, also obtained by chlorination of the tribromophenol obtained from *m*-C₆H₄Br·OH (A., 1933, 1045). 3-Bromo-2-, m.p. 85°, and -6-iodophenol, m.p. 55° [from (I) and (II)], with Br in AcOH give 2 : 3 : 4 : 6-tetrabromophenol, the former by less prolonged action also giving 3 : 4 : 6-tribromo-2-iodophenol, m.p. 125°, also obtained through the 2-NH₂-compound from 3 : 4 : 6-tribromo-2-nitrophenol (*loc. cit.*). A. A. L.

Anomalous introduction of nitro-groups into the benzene nucleus through a diazo-compound. A. CONTARDI and B. CROCCA (Gazzetta, 1933, 63, 878—884).—Action of nitrous fumes on 2 : 6-dibromoaniline-4-sulphonic acid in H₂O gives an internal diazonium salt, which when treated with aq. NaNO₂ yields 4-bromo-2 : 6-dinitrophenol; 2 : 6-dinitrophenol-4-sulphonic acid is presumably an intermediate product. 2 : 6-Dibromophenol-4-sulphonic acid and aq. NaNO₂ form 2 : 6-dibromo-4-nitrophenol and 2-bromo-6-nitrophenol-4-sulphonic acid. E. W. W.

Halogenation of phenolic ethers and anilides. IV. Chlorination of some *p*-substituted anilides. B. JONES (J.C.S., 1934, 210—213).—The velocity coeffs. of the chlorination at 20° of 13 *p*-substituted anilides in AcOH containing 1% of H₂O have been determined at different concns. With one exception the results show that an increase in the proportion of HCl to anilide decreases the velocity coeff., the relative directive powers varying with the initial concns. of the reactants. In spite of hydrochloride formation the results confirm the previous conclusions (cf. A., 1932, 26). A comparison of the relative directive influences of Br, Cl, CO₂H, and NO₂ in *p*-substituted phenolic ethers and anilides is made.

F. R. S.

Displacement of *tert*-butyl by the nitro-group. G. TIERIE (Rec. trav. chim., 1934, 53, 126—127).—Nitration of *p*-*tert*- ("p-iso-")butylphenol (cf. Schaaf, A., 1932, 378) displaces the Bu^{*t*} group and gives *s*-C₆H₄(NO₂)₃·OH, which is similarly obtained by nitration of tyrosine.

H. A. P.

Substitution in the methyl-4'-nitro- and -4'-acetamido-diphenyl ethers. H. A. SCARBOROUGH and J. L. SWEETEN (J.C.S., 1934, 52—56).—*p*-C₆H₄Cl·NO₂ (I) and *o*-C₆H₄Me·OK (II) give 4'-nitro-2-methyldiphenyl ether (III), m.p. 35°, b.p. 225—230°/14 mm., which with HNO₃, *d* 1.4, gives nitrophenols and 4 : 4'-dinitro-2-methyldiphenyl ether, m.p. 132° [also obtained from K 5-nitro-*o*-tolyl oxide and (I)], and on reduction gives 4'-amino-2-methyldiphenyl ether, isolated as the *Ac* derivative (IV), m.p. 110°. (III) with SO₂Cl₂ in AcOH gives 4-chloro-4'-nitro-2-methyldiphenyl ether, m.p. 65°, b.p. 235—240°/12 mm., reduced and acetylated to the 4'-NHAc-derivative,

m.p. 122°, which on nitration gives 4-chloro-3'-nitro-4'-acetamido-2-methyldiphenyl ether (V), m.p. 128°, changing above 124° to a form, m.p. 133°, also obtained by chlorinating 3'-nitro-4'-acetamido-2-methyldiphenyl ether (VI), m.p. 83°, which results from the nitration of (IV). The 4'-NH₂-derivative, m.p. 104°, from (V) on deamination gives 4-chloro-3'-nitro-2-methyldiphenyl ether, m.p. 52°, also obtained from *m*-C₆H₄·NO₂ (VII) and K 5-chloro-*o*-tolyl oxide. (VI) similarly gives 3'-nitro-4'-amino-2-methyl-, m.p. 94°, and 3'-nitro-2-methyl-diphenyl ether, b.p. 235°/14 mm., also obtained from (VII) and (II), and converted by Br into the 4-Br-derivative (VIII), m.p. 50°. (III) with Br in AcOH gives 4-bromo-4'-nitro-2-methyldiphenyl ether, m.p. 73° [also obtained from (I) and K 5-bromo-*o*-tolyl oxide], which is converted as above into the 4'-NHAc-derivative, m.p. 144°, also obtained by the bromination of (IV), and nitrated to 4-bromo-3'-nitro-4'-acetamido-2-methyldiphenyl ether, m.p. 147°, which also results from the bromination of (VI), and is converted through the 4'-NH₂-compound, m.p. 92°, into (VIII). Nitration of (IV) gives 3':4-dinitro-4'-acetamido-2-methyldiphenyl ether, m.p. 137°, hydrolysed to the 4'-NH₂-compound, m.p. 170°, which is converted into 3':4-dinitro-2-methyldiphenyl ether, m.p. 110°, also obtained from 2-bromo-5-nitrotoluene and *m*-NO₂·C₆H₄·OK. 4'-Nitro-3-methyldiphenyl ether (IX) with HNO₃, *d* 1·4, gives nitrophenols and 4:4'-dinitro-3-methyldiphenyl ether, m.p. 120° [also obtained from (I) and K 6-nitro-*m*-tolyl oxide, and oxidised to the 3-CO₂H-compound, m.p. 185°], whilst reduction gives 4'-amino-3-methyldiphenyl ether, m.p. 82° [purified through the sulphate; *Ac* derivative (X), m.p. 140°]. Nitration of (X) yields 3'-nitro- (XI), m.p. 81°, or 3':4-dinitro-4'-acetamido-3-methyldiphenyl ether, m.p. 144° [also obtained from (XI)], which gives 3':4-dinitro-3-methyldiphenyl ether, m.p. 87° [also obtained from *m*-NO₂·C₆H₄·OK and 5-bromo-2-nitrotoluene], after hydrolysis to the 4'-NH₂-compound, m.p. 140°. (XI) similarly gives a 4'-NH₂-compound, m.p. 52°, yielding 3'-nitro-3-methyldiphenyl ether (XII), m.p. 47°, also obtained from *m*-C₆H₄Me·OK and (VII). Chlorination of (IX) gives 4-chloro-4'-nitro-3-methyldiphenyl ether, m.p. 114° [also obtained from (I) and 6-chloro-*m*-tolyl oxide], from which the 4'-NH₂-compound is obtained as the hydrochloride, m.p. 200° (decomp.), through the *Ac* derivative, m.p. 115°. The last-named is also obtained from (X) (together with a little Cl₂-compound), and on nitration gives 4-chloro-3'-nitro-4'-acetamido-3-methyldiphenyl ether, m.p. 101°, also obtained from (XI) and yielding 4-chloro-3'-nitro-3-methyldiphenyl ether, m.p. 57°, through deamination of the 4'-NH₂-compound, m.p. 95°. (I) with K 6-bromo-*m*-tolyl oxide gives 4-bromo-4'-nitro-3-methyldiphenyl ether (XIII), m.p. 96°, also obtained by bromination of (IX), and reduced and acetylated to the 4'-NHAc-compound, m.p. 130° [also obtained by bromination of (X)]. This on nitration gives 4-bromo-3'-nitro-4'-acetamido-3-methyldiphenyl ether, m.p. 102° [also obtained by bromination of (XI)], the 4'-NH₂-compound, m.p. 111°, from which gives 4-bromo-3'-nitro-3-methyldiphenyl ether, m.p. 59°, also obtained by bromination of (XII). 4'-Nitro-4-methyldiphenyl (XIV), m.p. 68° [from (I) and *p*-C₆H₄Me·OK (XV)], on nitration gives 2:4'-dinitro-4-methyldiphenyl

ether, m.p. 104° [also obtained from 4-chloro-5-nitrotoluene and *p*-NO₂·C₆H₄·OK], and on reduction gives 4'-amino-4-methyldiphenyl ether, m.p. 125° [*Ac* derivative (XVI), m.p. 135°]. (XVI) on nitration gives 3'-nitro-, m.p. 95° [yielding as above 3'-nitro-4'-amino-4-methyl-, m.p. 91°, and 3'-nitro-4-methyl-diphenyl ether, isolated as a (NO₂)₂-derivative, m.p. 86°, similarly obtained from the condensation product of (VII) and (XV)], and 2:3'-dinitro-4'-acetamido-4-methyldiphenyl ether, m.p. 134°, which gives the 4'-NH₂-compound, m.p. 119°, and 2:3'-dinitro-4-methyldiphenyl ether, m.p. 87°, also obtained from *m*-NO₂·C₆H₄·OK and 4-chloro-3-nitrotoluene. (XIV) gives a 2-Br-derivative, m.p. 82° [also obtained from (I) and K 5-bromo-*p*-tolyl oxide], which is reduced and acetylated to give 2-bromo-4'-acetamido-4-methyldiphenyl ether, m.p. 142°, yielding a 3'-NO₂-derivative, m.p. 98°. This gives 2-bromo-3'-nitro-4'-amino-4-methyldiphenyl ether, m.p. 101°, yielding 2-bromo-3'-nitro-4-methyldiphenyl ether, m.p. 47°, which is also obtained from *m*-C₆H₄Cl·NO₂ and K 3-bromo-*p*-tolyl oxide. (VII) and K 2-bromo-*p*-tolyl oxide give 3-bromo-3'-nitro-4-methyldiphenyl ether, m.p. 68°. (III) is unattacked by oxidising agents, whilst (IX) with CrO₃ in AcOH gives 3-carboxy-4'-nitrodiphenyl ether, m.p. 183° (small yield). Similarly are obtained 3-carboxy-4-bromo-4'-nitro-, m.p. 157° (*Et* ester, m.p. 76°), 4'-nitro-4-carboxy-, m.p. 245° (*Et* ester, m.p. 78°), and 2-bromo-4'-nitro-4-carboxydiphenyl ether, m.p. 168° (*Et* ester, m.p. 119°). (IX) with AcCl and AlCl₃ in CS₂ gives 4'-nitro-4-acetyl-3-methyldiphenyl ether, m.p. 88°, oxidised to the 4-CO₂H-compound, m.p. 204°. The position taken on substitution in these compounds is determined by the ethereal O, except in the nitration of the NHAc derivatives.

A. A. L.

Reaction of chlorobenzene with sodium sulphide and hydrosulphide. N. N. VOROSHCHEV, jun., and S. P. MITSCHENGLER (Compt. rend. Acad. Sci. U.R.S.S., 1933, 291—295).—The primary product of reaction of PhCl with NaSH or Na₂S at 350—360° is Ph₂S, which reacts with excess of Na₂S, NaSH, or NaOH to yield PhSNa and PhONa; the yield of secondary products increases with increasing temp., duration of reaction, and relative concn. of Na₂S or NaSH.

R. T.

Action of sodium on 9-methoxy-10-phenylphenanthrene and 3-phenyl-1-diphenyleneindene. C. F. KOELSCH (J. Amer. Chem. Soc., 1934, 56, 480—484).—Mg *o*-diphenyl iodide (I) and PhCHO give *o*-phenylbenzhydrol, m.p. 69—70°, the *Me* ether, m.p. 72—73°, of which is converted by successive treatment with Na (in Et₂O and N₂) and CO₂ into phenyl-*o*-diphenylacetic acid (II), m.p. 171—173°. (I) and BzCO₂Et afford (after hydrolysis) *o*-phenylbenzilic acid, m.p. 189—191° (decomp.), oxidised (CrO₃, AcOH) to *o*-phenylbenzophenone and reduced (I, red P, AcOH) to (II). Successive treatment of (II) with PCl₅ and AlCl₃ in C₆H₆ gives 9-phenyl-10-phenanthrol, m.p. 142—143° (acetate, m.p. 153—155°; benzoate, m.p. 179—180°; picrate, m.p. 135°), methylated (Me₂SO₄, aq. MeOH-NaOH) to 9-methoxy-10-phenylphenanthrene (III), m.p. 189—190°. Treatment of a suspension of (III) in Et₂O and N₂ with 40% Na-Hg until dissolution occurs affords 10-sodio-9-

phenylphenanthrene, which with EtOH, CO₂, and PhCHO gives 9-phenylphenanthrene (IV), m.p. 105—106° (*picrate*, m.p. 115°; 10-*Br*-derivative, m.p. 108—110°), 9-phenylphenanthrene-10-carboxylic acid (V), m.p. 185—187° [together with (IV)], and 9-phenyl-10- α -hydroxybenzylphenanthrene (VI), respectively. More prolonged action of (III) and Na-Hg affords the violet 9:10-disodio-9-phenyl-9:10-dihydrophenanthrene, which is hydrolysed to (IV) and 9-phenyl-9:10-dihydrophenanthrene; treatment with CO₂, ClCO₂Me, PhCHO, or BzCl also gives (IV). (V) is converted by SOCl₂ in CCl₄ into 1:2:3:4-dibenzfluorenone, m.p. 186—187°, whilst (VI) is dehydrated (AcOH—conc. H₂SO₄) to -phenyl-1:2:3:4-dibenzfluorene (VII), m.p. 210—211°.

The Na compound (A., 1933, 1042) from 3-phenyl-1-diphenyleneindene is 9-sodio-9-phenyl-1:2:3:4-dibenzfluorene (VIII), since it is hydrolysed (H₂O) to (VII). (VII) is oxidised (CrO₃, AcOH) to a compound (IX), C₂₇H₁₈O₃, m.p. 188—189°, a small amount of a substance, m.p. 207—208°, and a resinous acid. (IX) and HI-AcOH give an I-containing substance, m.p. 185—187° (darkens at 125°), whilst dissolution in boiling 5% EtOH-NaOH and acidification (dil. HCl) affords a compound, C₂₇H₁₆O₂, m.p. 184—186°. (VIII) and BzCl give 9-benzoyl-9-phenyl-1:2:3:4-dibenzfluorene, m.p. 228—229°, also prepared by successive treatment of (VII) with 40% Na-Hg and BzCl.

H. B.

***p*-Methoxy- and 3:4-dimethoxy-phenylurethanes.** O. BRUNNER and R. WOHL (Monatsh., 1934, 63, 374—384).—From *p*-OMe·C₆H₄·NCO (prepared in 80% yield from *p*-OMe·C₆H₄·CO·N₃ by the Curtius method) are obtained: *methyl*-, m.p. 90°, *ethyl*-, m.p. 65°, *n*-, m.p. 69°, and *iso-propyl*-, m.p. 63°, *n*-, m.p. 45°, and *iso-butyl*-, m.p. 71°, *n-amyl*-, m.p. 53°, *n-hexyl*-, m.p. 60°, *n-heptyl*-, m.p. 78°, *n-octyl*-, m.p. 77·5°, *n-decyl*-, m.p. 78°, *n-dodecyl*-, m.p. 80°, *n-tetradecyl*-, m.p. 83°, *n-hexadecyl*-, m.p. 88·5°, *n-octadecyl*-, m.p. 92°, *n-docosyl*-, m.p. 98°, *n-tetracosyl*-, m.p. 102°, *allyl*-, m.p. 41°, *phenyl*-, m.p. 151°, *benzyl*-, m.p. 99·5°, and *cholesteryl*-, m.p. 152° (not sharp), *p-methoxyphenylurethane*. Similarly from 3:4-dimethoxyphenylcarbimide, b.p. 142—143°/16 mm. (from the hydrazide, m.p. 145°, of veratric acid), the corresponding -3:4-dimethoxyphenylurethanes are obtained, their m.p. being, respectively, 81°, 78·5°, 62°, 88°, 58°, 68°, 67°, 67°, 67·5°, 67°, 73°, 83°, 79·5°, 85°, 87°, 92·5°, 96·5°, 68°, —, 108°, and 160°. *s-Di*-(3:4-dimethoxyphenyl)carbimide has m.p. 215°.

J. W. B.

Synthesis of pharmacologically important amines. VIII. Substances similar to papaverine. K. KINDLER and W. PESCHKE [in part with O. BENECKE] (Arch. Pharm., 1934, 272, 60 70; cf. A., 1933, 1288).—Protocatechualdehyde, NaOEt, and EtBr in EtOH at 130° give 3:4-C₆H₃(CHO)(OEt)₂ (I), b.p. 158°/16 mm. [also obtained from pyrocatechol Et₂ ether ("ethylguaiacol") by Gattermann's method]. (I) with EtOAc and Na gives Et 3:4-diethoxycinnamate, m.p. 62°, which by hydrogenation (Pd-black) at 18° and hydrolysis affords β -3:4-diethoxyphenylpropionic acid, m.p. 107°; the NH₄ salt of this acid in NH₃ at 200° gives the *amide* (II), m.p.

111°, also obtained from (I) and MeOAc by way of Me 3:4-diethoxy-cinnamate, b.p. 205—207°/15 mm., m.p. 73°, and -phenylpropionate, m.p. 43°, the latter giving (II) by shaking with 25% aq. NH₃. (I) leads to acetyl-3:4-diethoxymandelonitrile, b.p. 205—207°/15 mm., which is reduced (Pd-black; 2 atm.) in AcOH-H₂SO₄ to β -3:4-diethoxyphenylethylamine (III), b.p. 162°/13 mm. (*hydrochloride*, m.p. 195° after sintering at 130°; *picrate*, m.p. 142—143°), also obtained from (II) in 61% yield. Hydrogenation (Pd-black; 60°; 2 atm.) of 3:4-dimethoxyphenylacetonitrile in EtOH gives a 92% yield of *di*- β -3:4-dimethoxyphenylethylamine (IV), m.p. 55—56° (*hydrochloride*, m.p. 201°). BzCN, veratrole, and AlCl₃ in hot ligroin give 3:4:3':4'-tetramethoxytriphenylacetonitrile, m.p. 124°, which is hydrogenated (Pd-black; 80°; 2 atm.) in AcOH-H₂SO₄ to $\beta\beta\beta$ -3:4:3':4'-tetramethoxytriphenylethylamine, (V), m.p. 113—113·5°. Pyrogallol Me₃ ether gives similarly 2:3:4:2':3':4'-hexamethoxytriphenyl-acetonitrile, m.p. 149°, and -ethylamine (VI), m.p. 139—140°. Nine primary, *sec.*, and *tert.* β -alkoxyphenylethylamines, including (III), (IV), (V), and (VI), resemble papaverine in pharmacological action and are highly toxic to paramoecia.

R. S. C.

Oxidation of isosafrole. M. IMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 26—29B).—Oxidation of isosafrole with alkaline KMnO₄ at 80—90° gave 79·5% of piperonylic acid (I), m.p. 226—227·5°. Addition of various "catalysts" diminished the yield. Oxidation with HNO₃ [15% at 75—100°; 25%+Hg(OAc)₂ at 50—100°] gave (I) in poor yield, piperonal, and H₂C₂O₄.

H. A. P.

Phthalates of quinol mono-ethers.—See B., 1934, 187.

Manufacture of derivatives [phosphates of mono-ethers] of dihydroxybenzenes.—See B., 1934, 232.

Rate of oxidation of quinol with atmospheric oxygen.—See this vol., 370.

Inositolphosphoric acid compounds II. Compounds of iron inositol phosphate with salts of hydroxy-acids. S. OTOLSKI (Rocz. Chem., 1934, 14, 78—86).—Na lactate, malonate, and citrate form sol. compounds with Fe^{III} inositol phosphate.

R. T.

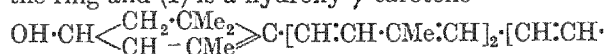
Molecular rearrangements of optically active radicals. E. S. WALLIS and P. I. BOWMAN (J. Amer. Chem. Soc., 1934, 56, 491).—When the OH group in *l*-CPhMeEt·CH₂·OH is replaced by Cl, rearrangement occurs with production of a *d-tert.* chloride.

E. S. H.

Triphenylmethane series. I. LIFSCHITZ (Rec. trav. chim., 1934, 53, 191—196).—Polymethoxytriphenylcarbinols, *e.g.*, the 2:4:6:2':4':6'-(OMe)₆ (*perchlorate*); *cyanide*, m.p. 152—153° and 2:4:6:2':4':6':4''-(OMe)₇-derivatives, are conveniently prepared by oxidation of the corresponding triphenylmethane [2:4:6:2':4':6':4''-(OMe)₇-compound, m.p. 142°] with PbO₂ in AcOH. Exposure to ultra-violet light with quinol in C₆H₆ gives derivatives of the type 2CAr₃C₆H₄O₂·2—2·5H₂O; of these the 4:4':4''-(OMe)₃-, m.p. 143°, and

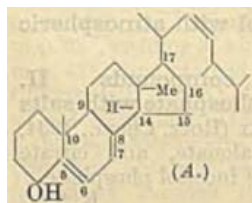
2:4:6:2':4':6'-(OMe)₆-, m.p. 141°, -compounds are described. H. A. P.

Rubixanthin, a new xanthophyll C₄₀H₅₆O. R. KUHN and C. GRUNDMANN (Ber., 1934, 67, [B], 339—344).—*Rubixanthin* (I), C₄₀H₅₆O, is present in hips and haws accompanied by considerable amounts of lycopene and carotenes. The ripe fruits of *Rosa rubinosa* are a particularly suitable source. Isolation is effected by chromatographic adsorption using Al₂O₃ which adsorbs (I) more readily than any of the carotenoids. (I) has m.p. 160° (Berl). Its absorption bands in various media are exactly coincident with those of γ-carotene. In distribution phenomena it very closely resembles kryptoxanthin (II). Catalytic hydrogenation causes union with 12 H₂. Since O is present as OH, (I) is monocyclic. Degradation with O₃ affords 1 mol. of COMe₂. Since (I) does not promote growth of rats fed on a diet free from vitamin-A, OH is probably attached to the ring and (I) is a hydroxy-γ-carotene



CH:CMe]₃·CH₂·CH₂·CH:CMe₂. Although the formula contains asymmetric C, (I) does not appear to be optically active ([α]_D ± 10° in C₆H₆), thus resembling (II). The xanthophyll from *Calendula officinalis* appears identical with (I). H. W.

Ring-system of sterols and bile acids. V. Constitution of ergosterol and its irradiation products. O. ROSENHEIM and H. KING (Chem. and Ind., 1934, 196—200; cf. A., 1933, 497).—The structure assigned to ergosterol (I) by Windaus and Langer (this vol., 186) does not contain the ·CH:C< group (which is necessary to account for the production and properties of ergostadienetriol), does not meet the requirements of X-ray analysis or the measurements of unimol. films, and offers no explanation for the intense ultra-violet absorption of (I). Structure (A), which is now assigned to (I), meets the above requirements and explains (a) the reduction of 22:23-dihydro-ergosterol to γ- and α-ergosterol by Na+EtOH and Pt+H₂, respectively, (b) the reduction (H₂, Pt) of β-ergostadienetriol to ergostenetriol, and (c) reduction (Zn, KOH) of 22:23-dihydro-ergosterol peroxide to isoergostenetriol (double linking between C₇ and C₈). Reductions (as above) involving Pt+H₂ probably involve the formation of an "inert" double linking between C₈ and C₉, and thus explain the difficulty of reduction (catalytic) of (I) to ergosterol; a similar isomerisation occurs in the change β- → α-pinene (A., 1926, 1148). The close association of the OH with the conjugated system accounts for the absorption of (I); the max. at 280 mμ is also found for oxycholesterilene (C:C·C:C·CO), whilst cholesterilene (C:C·C:C·C), like dihydrobenzene, shows a max. at 250 mμ. The ready loss of H₂O from (I) (by treatment with POCl₃ or C₆H₅Me·SO₂Cl), the ease of pinacol formation, and catalytic reduction of neoergosterol to a hydrocarbon [and similar reduction (unpublished) of cholestene-3:4-diol to cholestan-3-ol and cholestane]



favours the C₄·OH formulation. The adduct ergosterol-maleic acid can thus undergo γ-lactonisation [which might account for the anomalous titration results (Windaus and Langer, *loc. cit.*)].

The changes (caused by irradiation) (I) → lumisterol (II) → protachysterol (III) → tachysterol (IV) → calciferol (V) may involve the movement of the conjugated system, viz., C₅:C₆:C₇:C₈ (I) → C₆:C₇:C₈:C₉ (II) → C₆:C₇:C₈:C₁₄ (III) → C₇:H₈:C₁₄:C₁₅ (IV) → C₈:C₁₄:C₁₅:C₁₆ (intermediate) → C₁₄:C₁₅:C₁₆:C₁₇ (V). At the same time, inversion of the OH occurs [in (II)–(V)] and (II)–(V) probably contain C₅-H and C₁₀-Me *cis* to one another (*i.e.*, transition from the steric configuration of the sterols to that of the bile acids). H. B.

Dehydrogenation of œstrin. J. W. COOK and A. GIRARD (Nature, 1934, 133, 377—378).—Reduction of the CO< of ketohydroxyœstrin (I) to CH₂< and dehydrogenation of the "deoxo" compound yielded a non-acidic substance by a secondary change involving the OH. Methylation of the OH before dehydrogenation gave a OMe-compound, m.p. 76—77°, which when heated with Se and distilled over Na in a vac. yielded (from EtOH) colourless needles or plates, the analysis of which corresponded with a methoxycyclopentenophenanthrene (II), m.p. 134.5—136° [orange-red picrate, m.p. 135—136.5°; golden-orange C₆H₃(NO₂)₃ complex, m.p. 160—161°]. If the OH and the five-membered ring in the current formula for (I) are correctly oriented, (II) must be 7-methoxy-1:2-cyclopentenophenanthrene. L. S. T.

Marine products. II. Sterols of molluscs. W. BERGMANN (J. Biol. Chem., 1934, 104, 317—328).—A new sterol, *ostreasterol* (I), m.p. 142—143°, [α]_D²⁰ —43.57° in CHCl₃, has been isolated from the unsaponifiable fraction (10%) of the fat from the whole osyter (*Ostrea virginica*) as well as from its individual organs, and from the common round clam (*Venus mercenaria*) and the mussel *Modiola*. It is present with cholesterol (III) in the gastropods *Fulgur carica* and *F. canaliculata*, and is believed to be widely distributed among other mollusca, in which it replaces (III).

(I), C₂₇H₄₆O or C₂₇H₄₄O, gives an *acetate*, m.p. 134.5°, [α]_D²⁰ —45.94° in CHCl₃ (*Br₃-derivative*, C₂₉H₄₅O₂Br₃ or C₂₉H₄₇O₂Br₃, m.p. 122°), *propionate*, m.p. 113—114°, and *benzoate*, m.p. 145—147° to a turbid liquid which then turns blue, green, and again colourless, clearing at 152°; cf. benzoate of (III). Titration with BzO₂H shows two double linkings. "*Ostreasterol II*," m.p. 122° (*acetate*, C₂₇H₄₅OAc, m.p. 104—105°, [α]_D²⁰ —15.9° in CHCl₃), which is found in the acetylation mother-liquors from (I), does not give insol. Br-derivatives. Both (I) and "II" give positive Liebermann-Burchard and Salkowski reactions. W. S.

Microciona prolifera.—See this vol., 316.

4-Aminocyclohexylacetic acid. E. FERBER and P. LEONHARDT (Ber., 1934, 67, [B], 245—249). Treatment of CH₂Ph·CN with HNO₃ (d 1.5) affords *p*-nitrophenylacetonitrile, m.p. 116°, in 60—72% yield, converted by 77% EtOH and HCl into *Et p*-nitrophenylacetate (I), m.p. 65—66°, in 91% yield. (I) is also obtained by nitration of CH₂Ph·CO₂H and esteri-

fication of the crude product. Reduction of (I) by SnCl_2 and HCl in EtOH leads to the compound, $2\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}, \text{H}_2\text{SnCl}_6$, whence *Et p-aminophenylacetate*, m.p. 49.5° (*hydrochloride*, m.p. 215°). Hydrogenation of (I) at $60^\circ/2.5$ atm. (Skita) leads to a mixture (II) of aminotetrahydro-ester and acid, hydrolysed by 5N-HCl at 100° to the acid (*Cu salt*). Treatment of (II) with BzCl in CHCl_3 and 5% NaOH gives an oil (III) from which *Et 4-benzamidocyclohexylacetate* (IV), m.p. 142° , slowly separates. (IV) is hydrolysed by aq. Ba(OH)_2 to *trans-4-benzamidocyclohexylacetic acid*, m.p. $190\text{--}191^\circ$ (*Ba salt*, m.p. $278\text{--}279^\circ$). Further cooling of (III) causes deposition of crystals, m.p. (indef.) 35° , transformed at 200° into (IV). Treatment of (II) with *d-tartaric acid* in EtOH leads to *cis-d-4-aminocyclohexylacetic acid H tartrate*, m.p. $153\text{--}155^\circ$, $[\alpha]_D^{+40}$ in H_2O , whence *cis-d-4-aminocyclohexylacetic acid*, m.p. 289.5° (decomp.), $[\alpha]_D^{+11}$ in H_2O . *trans-4-Aminocyclohexylacetic acid*, m.p. $308\text{--}310^\circ$, is obtained by hydrolysis of (IV) by boiling Ba(OH)_2 —50% MeOH . H. W.

Phenylcarbimide derivatives and their immunological properties. III. The amino-acid derivatives and serological inhibition tests. S. J. HOPKINS and A. WORMALL (*Biochem. J.*, 1934, 28, 228—236).— PhNCO reacts with α - (I) and ϵ -amino-*n*-hexoic acid (II) to yield α - and ϵ -phenylcarbamido-*n*-hexoic acids, m.p. $140\text{--}141^\circ$ and $126\text{--}127^\circ$, respectively. $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NCO}$ yields with glycine, alanine, leucine, (I), (II), lysine (III), cystine (IV), aspartic acid, and tyrosine the corresponding phenylcarbamido-acids [bis-derivatives of (III) and (IV)], which decompose at $200\text{--}210^\circ$, $181\text{--}183^\circ$, $162\text{--}164^\circ$, $181\text{--}182^\circ$, $170\text{--}172^\circ$, $176\text{--}177^\circ$, $174\text{--}175^\circ$, $175\text{--}176^\circ$, and $197\text{--}199^\circ$, respectively. The reaction between phenylcarbamido-proteins (cf. A., 1933, 846) and the corresponding antisera in precipitin and complement fixation reactions is inhibited by the phenylcarbamido-acids, but not by the parent NH_2 -acids. The most highly active are those derived from (II) and (III). It is therefore probable that a large no. of the $\epsilon\text{-NH}_2$ -groups of the lysine components of the intact protein are free. W. O. K.

Alkaline halogenation. I. Chlorination of sodium benzoate. J. C. SMITH (*J.C.S.*, 1934, 213—218).—Chlorination of NaOBz by aq. NaOCl gives 47% of *o*-, 33% of *m*-, and 20% of *p*-Cl-derivative. It is suggested that the order is due to activation by the negative charge on the $\cdot\text{CO}_2\cdot$ of the benzoate anion of all positions, the effect falling with distance. Excess of BzOH was used, the products were esterified, and the esters fractionally distilled. The regenerated acid mixtures were analysed thermally. F. R. S.

Perkin reaction. I. First phase of the reaction. S. ISHIKAWA and R. KOJIMA. II. Condensation of β -methylcrotonic anhydride with aldehydes. S. ISHIKAWA and H. KATOH (*Sci. Rep. Tokyo Bunrika Daigaku*, 1934, 1, 289—296, 297—305).—I. Determinations of the active H by the Zerevitinov method show that Ac_2O , $(\text{PrCO})_2\text{O}$, $(\text{Bu}^i\text{CO})_2\text{O}$ (I), $(\text{CH}_2\text{Ph}\cdot\text{CO})_2\text{O}$ (II), and $(\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$, all of which contain a $\cdot\text{CO}\cdot$ group adjacent to a Me or $\cdot\text{CH}_2\cdot$ group, react in $\text{C}_5\text{H}_5\text{N}$ solution giving vals. increasing from 0.14 (40°) for (I) to 1.21 (40°) for (II).

Similar but lower vals. are obtained in anisole and still lower vals. in xylene. Maleic and β -methylcrotonic anhydrides (III), in which the $\cdot\text{CH}_2\cdot$ group is absent, give no reaction. Thus the primary reaction in the Perkin synthesis is the enolisation of the anhydride. $\text{CH}_2\text{Ph}\cdot\text{CN}$ acts in the tautomeric form and fluorene also reacts slightly, but CH_2Ph_2 has no action.

II. (III) and PhCHO in presence of NEt_3 at 150° give α -isopropenylcinnamic acid, m.p. 132° (yield 38%), reduced with Pd-BaSO_4 and H_2 to β -phenyl- α -isopropylpropionic acid, b.p. $155\text{--}160^\circ/5$ mm. (*chloride*, b.p. $136\text{--}141^\circ/21$ mm.; *anilide*, m.p. 128.3°). Less satisfactory yields are obtained when other bases or KOAc are used as condensing agents. The following are prepared in a similar manner, the appropriate aldehyde being given in parentheses: δ -phenyl- α -isopropenyl- $\Delta^{\alpha\gamma}$ -pentadienoic acid, m.p. 167° (cinnamic); α -isopropenyl-*o*-nitro-, m.p. 192° (*o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$), α -isopropenyl-*p*-methoxy-, m.p. 175.6° (*p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$), and α -isopropenyl-3 : 4-methylenedioxy-cinnamic acid, m.p. 154.8° (piperonal); α -isopropenylfurfurylideneacetic acid, m.p. 127° (furfural). Vanillin gives a resin under these conditions.

S. C.

Degradation of α -bromo-acids to aldehydes and ketones. J. VON BRAUN [with E. ANTON, F. FISCHER, W. KELLER, and G. MANZ] (*Ber.*, 1934, 67, [B], 218—225).—Reaction follows the course $\text{CR}_2\text{Br}\cdot\text{CO}_2\text{H} \rightarrow \text{CR}_2\text{Br}\cdot\text{COCl} \rightarrow \text{CR}_2\text{Br}\cdot\text{CO}\cdot\text{N}_3 \rightarrow [\text{CR}_2\text{Br}\cdot\text{CO}\cdot\text{N} <] \rightarrow \text{CR}_2\text{Br}\cdot\text{N}\cdot\text{C}\cdot\text{O} \rightarrow \text{CR}_2\text{Br}\cdot\text{NH}_2 \rightarrow \text{CR}_2\cdot\text{O}$. The aldehyde or ketone is obtained in about 60% yield. Hexahydrobenzoyl chloride and Br at 125° yield 1-bromohexahydrobenzoyl chloride, readily hydrolysed to 1-bromohexahydrobenzoic acid, b.p. $120\text{--}122^\circ/0.7$ mm., m.p. 61° , whence by SOCl_2 the pure 1-bromohexahydrobenzoyl chloride (I), b.p. $105\text{--}107^\circ/15$ mm. (I) and NaN_3 (activated by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) in C_6H_6 , PhMe , or $\text{C}_5\text{H}_5\text{N}$, react at about 80° and the product is treated successively with cold KOH-EtOH and HCl , thereby giving cyclohexanone. Bromination of α -butyl-*n*-hexoic acid smoothly affords α -bromo- α -butyl-*n*-hexoic acid, b.p. $168\text{--}171^\circ/15$ mm., whence the corresponding chloride, b.p. $126\text{--}127^\circ/15$ mm., and ultimately COBu_2 (semicarbazone, m.p. 89°) in 71—77% yield. Dicyclopentylacetic acid (II), P, and Br yield α -bromodicyclopentylacetic acid, b.p. $175^\circ/12$ mm., m.p. 32° , whence dicyclopentyl ketone (III), b.p. $110\text{--}112^\circ/12$ mm. (semicarbazone, m.p. $158\text{--}162^\circ$). Dicyclopentyl ketoxime, m.p. 92° , is reduced by Na and EtOH to dicyclopentylmethylamine (IV), b.p. $120\text{--}122^\circ/14$ mm. [*hydrochloride* (V), m.p. $193\text{--}194^\circ$; *picrate*, m.p. 127°]. (IV) is obtained in 70% yield by treating (II) in conc. H_2SO_4 with N_3H or by the action of activated NaN_3 in C_6H_6 on dicyclopentylacetyl chloride, b.p. $143\text{--}144^\circ/13$ mm., followed by HCl . Di(dicyclopentylmethyl)carbamide has m.p. 288° after softening at 280° . (V) is transformed by NaNO_2 into a mixture of $\text{C}_{11}\text{H}_{19}\cdot\text{OH}$ and $\text{C}_{11}\text{H}_{18}$, from which (III) is not obtained by oxidation. (III) is not smoothly prepared by the dry distillation of Ca cyclopentanecarboxylate or from α -bromodicyclopentylacetamide, Br, and KOH . *n*-Hexyl bromide is converted successively into *Et n-hexylmalonate*, b.p. $150\text{--}155^\circ/20$ mm., *n-hexylmalonic acid*, m.p. $103\text{--}105^\circ$, α -bromo-*n*-hexylmalonic acid, m.p. $119\text{--}121^\circ$ (decomp.),

α -bromo-octioic acid, b.p. 118—121°/0.5 mm., α -bromo-octyl chloride, b.p. 112—114°/15 mm., and heptaldehyde mixed with α -heptylideneheptaldehyde. Et cyclopentylmalonate is hydrogenated and hydrolysed to cyclopentylmalonic acid, m.p. 162°, whence successively α -bromocyclopentylacetic acid, b.p. 121—123°/0.5 mm., m.p. 50°, α -bromocyclopentylacetyl chloride, b.p. 130—132°/16 mm., and cyclopentylformaldehyde (semicarbazone, m.p. 124°). α -Bromo-8-phenylvaleryl chloride, b.p. 172°/16 mm., gives γ -phenylbutaldehyde, b.p. 120—122°/16 mm. (semicarbazone, m.p. 105°), in 58.5% yield. H. W.

1-Methylhydrindene-4-carboxylic acid. H. HOYER (J. pr. Chem., 1934, [ii], 139, 242—244).—4-Bromohydrindone (in 90% yield by cyclisation of o -C₆H₄Br·CH₂·CH₂·COCl with AlCl₃ in CS₂) with MgMeBr gives 4-bromo-1-hydroxy-1-methylhydrindene, b.p. 135—136°/25 mm., m.p. 33—34°, reduced by red P+HI (*d* 1.7) at 150—160° to 4-bromo-1-methylhydrindene (not pure), b.p. 245°, the Grignard compound of which with CO₂ affords 1-methylhydrindene-4-carboxylic acid, m.p. 138—139°. J. W. B.

Derivatives of 8-bromo- and 8-chloro-1-naphthoic acids and their orientation by dehalogenation and decarboxylation. H. G. RULE, W. PURSELL, and (in part) R. R. H. BROWN (J.C.S., 1934, 168—171).—Nitration of 8-bromo-1-naphthoic acid (I) (improved prep.; Et ester, m.p. 52°) gives the 5-NO₂, m.p. 245° (Me ester, m.p. 97°; Et ester, m.p. 103°), and the 4 : 5-(NO₂)₂, (II), m.p. 250—252° (Me ester, m.p. 155°; Et ester, m.p. 127—128°), -derivative. The Br is removed by boiling with Cu in PhMe. Thus (II) gives 4 : 5-dinitro-1-naphthoic acid, m.p. 265° (Et ester, m.p. 143—144°), decarboxylated in boiling quinoline with Cu. Bromination of (I) in AcOH at 150° gives 5 : 8-dibromo-1-naphthoic acid.

F. R. S.

Constitution of dinitroacenaphthenequinone and of dinitronaphthalic acid. Preparation of a new dinitronaphthalene. H. G. RULE and R. R. H. BROWN (J.C.S., 1934, 171—174).—Oxidation of 3-nitroacenaphthenequinone to the corresponding dinitronaphthalic anhydride, followed by mercuration and treatment of the product with Br, gives 8-bromo-4-nitro-1-naphthoic acid, m.p. 201—203°; similar treatment of dinitroacenaphthenequinone (I) leads to 8-bromo-4 : 5-dinitro-1-naphthoic acid (preceding abstract), thus establishing (I) as the 3 : 4-(NO₂)₂-compound. 3-Nitronaphthalic acid similarly treated yields a mixture, giving a fraction m.p. 240—242°, apparently 8-bromo-3-nitro-1-naphthoic acid (II), since when heated with Cu in PhMe it gave 3-nitro-1-naphthoic acid, m.p. 268—269°. (II) gives a Me ester, m.p. 173°, and Et ester, m.p. 155—156°. Dinitronaphthalic acid yields 8-bromo-3 : 6-dinitro-1-naphthoic acid, m.p. 273—275° (Me ester, m.p. 137—138°; Et ester, m.p. 205—207°), the mercuri-compound being converted by HCl into 3 : 6-dinitro-1-naphthoic acid, m.p. 273.5—274° (Me ester, m.p. 196—197°; Et ester, m.p. 145—146°), decarboxylated to 2 : 7-dinitronaphthalene, m.p. 234°. F. R. S.

Preparation of naphthastyryl from 8-bromo-1-naphthoic acid. H. G. RULE and R. R. H. BROWN (J.C.S., 1934, 137).—8-Bromo-1-naphthoic acid with

aq. NH₃, NH₄NO₃, KClO₃, and a little Cu at 130—150° under pressure gives naphthastyryl, m.p. 181° (yield 82%; less under atm. pressure, or in the absence of the inorg. salts). A. A. L.

Reactivity of atoms and groups in organic compounds. XIII. Influence of structure on the pyrolysis of esters of triphenylacetic acid. J. F. NORRIS and A. CRESSWELL (J. Amer. Chem. Soc., 1934, 56, 423—426).—The temp. quoted in parentheses after the following esters of CPh₃·CO₂H are those at which signs of decomp. are shown when the esters are heated for 1 hr.: Me (I), m.p. 184—185° (196°), Et, m.p. 116—117° (188°), Pr^a, m.p. 98—99° (169°), Pr^β, m.p. 83.5—84.5° (154°), Bu^a, m.p. 99—99.6° (183°) sec.-Bu, m.p. 101—102° (163°), Bu^β, m.p. 88—89° (149°), n-amyl, m.p. 76—76.5°, isoamyl, m.p. 77.5—78°, n-hexyl, m.p. 84—84.5°, benzyl (II), m.p. 99—99.5° (179°), and β -phenylethyl, m.p. 92.5—93° (157°). For the first six esters, the effect of the alkyl group on the thermal stability is similar to that of the same alkyl group in CPh₃·Oalk (A., 1930, 470). The Bu^β, ·CH₂Ph, and ·CH₂·CH₂Ph groups exert opposite effect in the two series. The above esters [except (I) and (II)] when heated to boiling decompose thus: CPh₃·CO₂·CH₂·CH₂R \rightarrow CHPh₃+CO₂+CH₂·CHR; (I) gives 61.9% of CH₂O and 8% of CO, whilst (II) affords 42.4% of CO. H. B.

Ring-chain tautomerism of β -p-bromobenzoyl-crotonic esters. R. E. LUTZ and A. W. WINNE (J. Amer. Chem. Soc., 1934, 56, 445—447).—*cis*- β -p-Bromobenzoylcrotonyl chloride (γ -chloro- γ -p-bromophenyl- β -methyl- γ -crotonolactone) (A., 1933, 502) and MeOH give γ -methoxy- γ -p-bromophenyl- β -methyl- γ -crotonolactone (cyclic Me β -p-bromobenzoylcrotonate) (I), m.p. 64°, also formed (cf. loc. cit.) from *cis*- β -p-bromobenzoylcrotonic acid (II) and MeOH·HCl. The cyclic Et ester (III), b.p. 165—168°/5 mm., is prepared similarly. (I) and (III) are hydrolysed (EtOH·NaOH) to (II), which is reduced (Na₂S₂O₄) to β -p-bromobenzoylbutyric acid [Me (IV), b.p. 193—194°/20 mm., and Et (V), m.p. 34.5°, esters]. The open-chain Me (VI), m.p. 69° (corr.), and Et, m.p. 42°, esters of (II) are prepared by the Ag salt method and are reduced (Zn, AcOH) to (IV) and (V), respectively. Exposure of Me *trans*- β -p-bromobenzoylcrotonate (VII) in EtOH to sunlight gives (VI); (VI) in CHCl₃ containing a little I similarly affords (VII). (VI) is converted by MeOH·conc. H₂SO₄ into (I). It is suggested that the free acid (II) (in the solid state) has the lactone structure, since it dissolves extremely slowly in aq. NaHCO₃. Preliminary work on the reduction (Zn, AcOH) of (I) and (III) is reported. H. B.

Amido- and imido-chlorides of non-aromatic acids. VIII. [cyclopentyl and cyclopentenyl derivatives].—See this vol., 393.

cycloButane-1 : 2-dicarboxylic acids. H. BODE (Ber., 1934, 67, [B], 332—335; cf. Kuhn et al., A., 1928, 885).—In agreement with Perkin (J.C.S., 1894, 65, 583), decarboxylation of cyclobutane-1 : 1 : 2 : 2-tetracarboxylic acid at 200° and treatment of the product with AcCl affords *cis*-cyclobutane-1 : 2-dicarboxylic anhydride, m.p. 77—78°, transformed by warm H₂O into the *cis*-acid (I), m.p. 138—139°. Treatment

of (I) with conc. HCl at 190° gives the *trans*-acid (II), m.p. 130—131°. The dissociation consts. of (I) and (II) have been measured.

H. W.

2-Nitrohomoveratric acid. K. H. SLOTTA and F. LAUERSON (J. pr. Chem., 1934, [ii], 139, 220—228).—The improved prep. of 2-nitrohomoveratric acid (I) [29% overall yield from vanillin (II)] by the stages, (II) \rightarrow Ac derivative \rightarrow 2-NO₂-derivative, \rightarrow 2-nitrovanillin \rightarrow 2-nitro-3:4-dimethoxybenzaldehyde, reduced by Al(OEt)₃ in C₆H₆ in N₂ or in abs. EtOH to the alcohol (III), which with HCl at room temp. gives the chloride, converted through the nitrile, iminoether, and Me ester into (I), is described. With 50% aq. HBr at 30—40°, (III) gives a 99% yield of the bromide. Similarly Al(OEt)₃ effects quant. reduction of *o*-NO C₆H₄·CHO to the alcohol.

J. W. B.

Preparation of homopiperonylic acid. K. H. SLOTTA and G. HABERLAND (J. pr. Chem., 1934, [ii], 139, 211—219).—*Me* 3:4-methylenedioxy mandelate, m.p. 99° (I) [prep. as for Et ester (Bayer et al., J.C.S., 1909, 95, 552) improved], with SOCl₂ in dry C₆H₆ gives *Me* α -chloro-3:4-methylenedioxyphenylacetate, b.p. 173°/10 mm., converted by boiling 2% NaOH-MeOH into the corresponding α -OMe-acid, m.p. 80°, and reduced (Zn-H₂O in boiling COMe₂) to homopiperonylic acid (30—36% yield) and 3:4-methylenedioxy mandelonitrile (53—60%). 3:4-Methylenedioxy mandelonitrile [intermediate in prep. of (I)] with Ac₂O-AcOH-C₆H₅N gives its O-Ac derivative, converted by MeOH-HCl into the iminoether hydrochloride, m.p. 131° (decomp.), hydrolysed (H₂O) to the O-Ac derivative, m.p. 102°, of (I). Similarly the O-Ac derivative of 3:4:5-trimethoxymandelonitrile (Kindler et al., A., 1932, 1126) gives the iminoether hydrochloride, m.p. 120°, and the O-Ac derivative, m.p. 82°, of *Me* 3:4:5-trimethoxymandelate.

J. W. B.

2:5-Dimethoxy-3:4:6-trimethylbenzoic acid. L. I. SMITH and R. O. DENYES (J. Amer. Chem. Soc., 1934, 56, 475—476).—Diaminodurylic acid, m.p. 221—222° (corr.; decomp.) (lit. 210°), prepared by reduction (Fe powder, aq. AcOH) of the (NO₂)₂-acid, is oxidised (FeCl₃, dil. HCl) to trimethyl-*p*-benzoquinonecarboxylic acid. Reduction (H₂SO₃) and subsequent methylation (Me₂SO₄, MeOH-KOH) gives the *Me* ester, m.p. 39—41°, of 2:5-dimethoxy-3:4:6-trimethylbenzoic acid (I), m.p. 100—101° (Ag salt), oxidised by HNO₃ (d 1.4) to nitrotrimethyl-*p*-benzoquinone. (I) could not be prepared by oxidation of 2:5:3:4:6-(OMe)₂C₆Me₃·CHO.

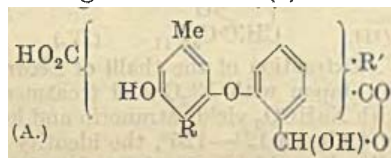
H. B.

Phenylmalonic and nitrophenylmalonic acids and esters. S. BASTERFIELD and L. A. HAMILTON (Trans. Roy. Soc. Canada, 1933, [iii], 27, III, 125—131).—CHPh(CO₂Me)₂ (I) (cf. A., 1894, i, 376) in Et₂O when shaken with 2—4% aq. Na₂CO₃ during 1 hr. affords the acid (II). Nitration of (I) at 0—10° with H₂SO₄-HNO₃ during 3 hr. affords *Me p*-nitrophenylmalonate (III), m.p. 95° (oxidised by KMnO₄ to *p*-NO₂·C₆H₄·CO₂H), and an oil which probably contains the *o*- and *m*-isomerides (cf. A., 1927, 558). Hydrolysis of (III) affords *p*-nitrophenylacetic acid. (II) with fuming HNO₃ at 0° gives *o*- and *m*-NO₂·C₆H₄·CO₂H, but with H₂SO₄-HNO₃ at 0° gives

o-nitrophenylmalonic acid, m.p. 133° (decomp.) (oxidised to *o*-NO₂·C₆H₄·CO₂H). *Me p*-carbethoxyaminophenylacetate, Na, and Me₂C₂O₄ in dry C₆H₆ at 60° during 6 hr. afford an oil which when heated loses CO to give *Me p*-carbethoxyaminophenylmalonate (?), b.p. about 110°/5 mm. *Me* 2:4-dinitrophenylmalonate (cf. A., 1916, i, 15) is reduced by (NH₄)₂S in boiling EtOH during 2 hr. to *Me* 2-(or 4-)nitro-4-(or 2-)amino-, m.p. 131°, and *Me* 4-(or 2-)nitro-2-(or 4-)amino-phenylmalonate, m.p. 190°.

J. L. D.

Saxatilis acid. G. KOLLER and A. KLEIN (Monatsh., 1934, 64, 80—86).—Pptd. by hot H₂O from COMe₂ solution saxatilis acid (I) gives a monohydrate, becoming anhyd. at 120°/12 mm., analysis of which agrees best with C₁₈H₁₄O₁₀·H₂O. Reduction of the alcoholysis product C₂₂H₂₀O₁₀ of (I) with a weakly active Pd-C catalyst gives a dihydro-compound, m.p. 168° (decomp. in vac.), which no longer reacts with NH₂Ph (·CHO \rightarrow ·CH₂·OH), nor gives atranol with Zn-NaOH. Hence the lactone ring is attached to ring 2. Fusion of (I) with KOH at 300°



gives orcinol and α -resorcylic acid. Reduction of (I) with a 1% Pd-C catalyst in AcOH affords dihydro-saxatilis acid, C₁₈H₁₆O (A; R=CH₂·OH, R'=CH₂·OH or >CH·OH) (*m*-bromoanilide), but with a 10% Pd-C catalyst, dideoxydihydrosaxatilis acid, C₁₈H₁₆O₈ (A; R=Me, R'=Me or >CH₂) (*m*-bromoanilide), and with a very active Pd-C catalyst a substance C₁₈H₁₆O₇, which no longer reacts with NH₂Ph (CH·OH of lactone ring \rightarrow CH₂). (I) is assigned the partial formula (A; R=·CHO, R'=·CH₂·OH or >CH·OH).

J. W. B.

Capraric acid. G. KOLLER and K. PÖPL (Monatsh., 1934, 64, 1—2).—Alcoholysis of capraric acid (I) (introduction of OEt with fission of H₂O) affords cetraric acid (II), identified as *Me* dimethylcetrarate (A., 1929, 1459). In (I) the oxide ring is intact, whereas in (II) it has undergone fission with introduction of OEt.

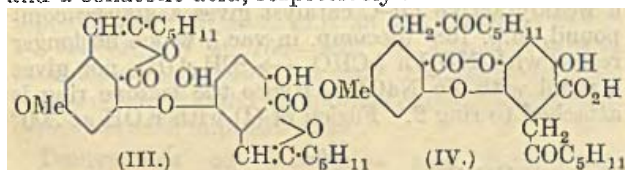
J. W. B.

Ramalic acid. G. KOLLER, E. KRAKAUER, and K. PÖPL (Monatsh., 1934, 64, 3—5).—Ramalic acid, extracted from *Ramalina farinacea*, is identical with protocetraric acid, since alcoholysis affords cetraric acid, identified as *Me* dimethylcetrarate and decomposed to atranol.

J. W. B.

Lichen substances. XXXIV. Constitution of alectoronic and α -collatolic acid. XXXV. Identity of α -collatolic acid and lecanorolic acid. Y. ASAHINA and F. FUJIKAWA (Ber., 1934, 67, [B], 163—168, 169—170; cf. A., 1933, 713).—XXXIV. Treatment of *Me* collatolate Me₂ ether, m.p. 114°, with conc. KOH-EtOH causes loss of two hexoyl groups; CO₂H is also involved, but its complete elimination requires subsequent treatment with HCO₂H and leads to *alectol Me₃ ether* (I), C₁₇H₂₀O₄, m.p. 96°, not identical with deoxyhyposalazolin Me₃ ether. (I) is converted by PCl₅ in PhNO₂ at 160° into *dichloroalectol*

Me_3 ether, $C_{17}H_{18}O_4Cl_2$, m.p. 125° , and by PCl_5 in $CHCl_3$ at 100° into trichloroacetol Me_3 ether, m.p. 185 – 188° . Tribromoacetol Me_3 ether, m.p. 179° , is obtained from (I) and Br in AcOH at room temp. Treatment of (I) with HI (*d* 1.7) and PhOH at 150° leads to orcinol. (I) is transformed by molten KOH into orcinol and α -resoreyic acid and oxidised by $Na_2Cr_2O_7$ in AcOH to 6-methoxy-2-methyl-*p*-benzoquinone, m.p. 151° [obtained by converting orcinol Me ether (II) into the NH_2 -derivative which is oxidised by $Na_2Cr_2O_7$ or by oxidation of orcinol Me_2 ether]. Treatment of the K derivative of (II) with bromo-orcinol Me_2 ether, m.p. 57° , leads to 3:4':6'-trimethoxy-5:2-dimethyldiphenyl ether, identical with (I). Arising from these results, the amended constitutions (III) and (IV) are assigned to collatolone and α -collatolic acid, respectively:



XXXV. Extraction of the thalli of *Lecanora atra*, Ach., from Japan with Et_2O and treatment of the extract with $NaHCO_3$ yields atranorin and lecanorolic acid, m.p. (anhyd.) 124 – 125° , the identity of which with α -collatolic acid is proved by determination of mixed m.p. and by conversion by HCO_2H in glycerol into collatolone. H. W.

Structure of reactants and extent of acetal formation. II. R. E. DUNBAR and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 442–444).—Equilibrium consts. for the reactions between 1 mol. of hexahydrobenzaldehyde (I), $PhCHO$ (II), CMc_3CHO (III), and cyclopentylaldehyde (IV) with 5 and/or 11 mols. of (usually) $EtOH$, Pr^iOH , octan- β -ol, cyclohexanol, and cyclohexylcarbinol in presence of a little HCl are determined and compared with the consts. for other aldehydes (A., 1933, 280). A progressive decrease in the extent of acetal formation is found with $MeCHO$, Pr^iCHO , and (III). (IV) resembles (III) in its affinity for acetal formation. The relationship between (I) and (II) is similar to that between tetrahydrofurfuraldehyde and furfuraldehyde (*loc. cit.*); acetal formation occurs to a much greater extent with the saturated aldehyde in each case. There appears to be a fundamental difference between the cyclopentyl and cyclohexyl groups irrespective of whether the group is in the aldehyde or alcohol. The following are described: hexahydrobenzaldehyde Me_2 , b.p. $63^\circ/25$ mm., $183^\circ/753$ mm., Et_2 , b.p. 94 – $95^\circ/12$ mm., 115 – $117^\circ/20$ mm., Bu^a_2 , b.p. 134 – $136^\circ/8$ mm., 149 – $150^\circ/22$ mm., diisooamyl-, b.p. 168 – $169^\circ/8$ mm., di- β -octyl-, b.p. 215 – $217^\circ/8$ mm., di- γ -2-tetrahydrofurylpropyl-, b.p. 236 – $238^\circ/10$ mm., di-cyclohexyl-, b.p. 202 – $203^\circ/20$ mm., and dicyclohexylmethyl-, b.p. 234 – $235^\circ/20$ mm., -acetals; trimethylacetaldehyde Et_2 , b.p. 146 – $148^\circ/742$ mm., and dicyclohexylmethyl-, b.p. 194 – $195^\circ/22$ mm., -acetals. H. B.

Condensation of aldehydes with hydrazones. IX. A. GIACALONE (Gazzetta, 1933, 63, 870–872).—Condensation of $NPhMe \cdot NH$, with $PhCHO$ yields

pp'-bis-(α -methyl- β -benzylidenhydrazino)triphenylmethane, m.p. 163° , different from the compound, m.p. 136° , to which this structure is assigned by Ciusa (A., 1932, 1132). E. W. W.

Basic properties of hydrazones. VIII. R. CIUSA and G. OTTOLINO (Gazzetta, 1933, 63, 884–886; cf. A., 1932, 51).—When the compound $CHPh:N \cdot NMe \cdot C_6H_4 \cdot CPh:NMeCl \cdot N:CHPh$ (I) is treated with dil. H_2SO_4 the Cl is replaced by HSO_4 , giving the compound $C_{35}H_{31}N_4 \cdot HSO_4 \cdot 2H_2O$ (II), m.p. 205° , which is also in part hydrolysed to the compound $NH_2 \cdot NMe \cdot C_6H_4 \cdot CPh:NMe(HSO_4) \cdot NH_2$ (III), which condenses with $PhCHO$ to form (II), and with cinnamaldehyde to form the compound $C_{39}H_{35}N_4 \cdot HSO_4 \cdot 2H_2O$, m.p. 197° . E. W. W.

Nitration of 3:5-dichlorobenzaldehyde and 3:5-dichlorobenzoic acid. F. ASINGER (Monatsh., 1934, 63, 385–393).—3:5- $C_6H_3Cl_2 \cdot CHO$ is converted by HNO_3 (*d* 1.48) at 0° into its 2- NO_2 -derivative (I), m.p. 91.5° (oxime, m.p. 97° ; phenylhydrazone, m.p. 175°), oxidised ($KMnO_4$) to 3:5-dichloro-2-nitrobenzoic acid, m.p. 194° (corr.) (*Me*, m.p. 73° , and *Et*, m.p. 69° , esters; *Ca* + $4.5H_2O$, *Ba* + $2.5H_2O$, and *Ag* salts; chloride, m.p. 94.5° ; amide, m.p. 180°), also obtained by nitration of 3:5- $C_6H_3Cl_2 \cdot CO_2H$ with HNO_3 (*d* 1.48) at 70° . With PCl_5 in C_6H_6 (I) affords 3:5-dichloro-2-nitrobenzylidene chloride, m.p. 45° (also by nitration of 3:5- $C_6H_3Cl_2 \cdot CHCl_2$), and with Ac_2O - $NaOAc$ at 180° , 3:5-dichloro-2-nitrocinnamic acid, m.p. 227° , is obtained. Reduction of (I) ($FeSO_4 \cdot NH_3 \cdot H_2O$ - $EtOH$) gives 3:5-dichloro-2-aminobenzaldehyde, m.p. 123° (oxime, m.p. 175° ; phenylhydrazone, m.p. 118°). With 1% NaOH in $COMe_2$ at -5° to 25° , (I) gives 5:7:5':7'-tetrachloroindigotin. J. W. B.

2-Hydroxy-6-methylbenzaldehydeanil. T. LOVE (J.C.S., 1934, 244).—The prep. of 2-hydroxy-4- and -6-methylbenzaldehydes from *m*-cresol by the Reimer-Tiemann reaction, and their conversion into anils, are described; the anil of the latter has m.p. 51.5° . H. A. P.

Condensation products of aromatic hydroxyaldehydes. T. PAVOLINI (Riv. Ital. Ess. Prof., 1933, 15, 171–173; Chem. Zentr., 1933, ii, 2260).—Condensation products of barbituric acid (I) with vanillin (II), dehydrovanillin, and coniferylaldehyde (III) pass from yellow into red in alkaline medium. (I) and lignin (IV) or piperonal (V) afford a yellow, amorphous product unchanged by alkali, owing to blockage of the OH group. The (I) reaction can be carried out with pulverised wood, and can be used for the detection of lignified material. (I) in AcOH has been condensed with $PhCHO$ (light yellow), salicylaldehyde (straw), (V) (yellow), (II) and (III) (orange-red), and dehydrovanillin (crimson) [all 2(I):1 aldehyde]. With (IV) (1:1) an orange-red powder is obtained. A. A. E.

Lignin. XVII. Tetraconiferaldehyde. P. KLASON (Ber., 1934, 67, [B], 302–303).—Treatment of pine wood with $NaHSO_3$ at 96 – 98° followed by HCl leads to a sulphonic acid sol. in H_2O which with α - $C_{10}H_7 \cdot NH_2$ gives the salt $4(C_{10}H_{10}O_3) \cdot H_2SO_3 \cdot C_{10}H_7 \cdot N \cdot H_2O$. Contrary to Freudenberg, the individuality of the tetraligninsulphonic

acid is as pronounced as that of the other lignin-sulphonic acids. The composition of this acid considered in conjunction with the acid

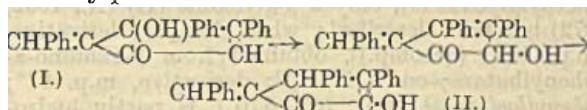
$3(\text{C}_{10}\text{H}_{10}\text{O}_3)\cdot\text{H}_2\text{SO}_3$ leads to the conclusion that the mol. wt. of α -lignin corresponds with $(\text{C}_{10}\text{H}_{10}\text{O}_3)_{12}$ and that of the total lignin of wood is > 3640 . Treatment of wood with 0.2% H_2SO_4 at 96–98° removes hemicellulose, giving a product which with $\beta\text{-C}_{10}\text{H}_7\text{-NH}_2$ affords the *anil* ($\text{C}_{10}\text{H}_{10}\text{O}_3$)₃· $\text{C}_{10}\text{H}_9\text{N-H}_2\text{O}$. Since the action of H_2SO_3 on lignin is similar to that of acids on polysaccharides, tetraconiferaldehyde is regarded as $\text{OH}\cdot\text{R}\cdot\text{C}_2\text{H}_2\cdot\text{CH}(\text{OH})\cdot[\text{O}\cdot\text{R}\cdot\text{C}_2\text{H}_2\cdot\text{CH}(\text{OH})]_2\cdot\text{O}\cdot\text{R}\cdot\text{C}_2\text{H}_2\cdot\text{CHO}$ (R=anisole residue). H. W.

Preparation of cyclic unsaturated ketones and hydrocarbons. H. BERGS [with C. WITTFELD and, in part, E. WILDT] (Ber., 1934, 67, [B], 238–244; cf. Cook *et al.*, A., 1933, 1042).—1-Phenylacetyl- Δ^1 -cyclohexene (I), b.p. 171–176°/12 mm., m.p. 47°, is obtained from $\text{CH}_2\text{Ph}\cdot\text{COCl}$, tetrahydrobenzene, and SnCl_4 in CS_2 at -10° to -5° , or with a substance, m.p. 204°, from $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ and tetrahydrobenzoxynitrile (II) in Et_2O . (I) yields a *semicarbazone*, m.p. 175–176°, and an *oxime*, m.p. 124°, transformed by 25% H_2SO_4 at 80–90° followed by addition of Br and loss of HBr into stilbene. (II) and MgEtBr afford 3:4:5:6-tetrahydrophenyl Et ketone (oxime, m.p. 48°, of 3:4:5:6-tetrahydrophenyl Me ketone are described. 1- β -Phenylethylcyclohexan-1-ol, b.p. 168–169°/16 mm., m.p. 56°, from cyclohexanone and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}$, is converted by ZnCl_2 at 160–165° into β -phenylethylcyclohexene (III), b.p. 136–137°/12 mm. (III) is transformed by AlCl_3 at 40° into 1:2:3:4:9:10:11:12-octahydrophenanthrene, b.p. 149–152°/12 mm. The prep. of $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ from $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{OH}$ and PCl_5 or PBr_3 , respectively, is described. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{MgCl}$ and the requisite ketone afford 1- β -phenylethyl-2-, b.p. 181–183°/20 mm., -3-, b.p. 171–172°/18 mm., and -4-methyl-, b.p. 179°/22 mm., -cyclohexan-1-ol, and 1- β -phenylethyl-1:2:3:4-tetrahydro- α -naphthol, b.p. 212–214°/20 mm. H. W.

Selective catalytic reduction of ketones. II. N. D. ZELINSKI, K. PACKENDORFF, and L. LEDER-PACKENDORFF (Ber., 1934, 67, [B], 300–302; cf. A., 1933, 715).—Hydrogenation of α -CO or α -OH-compounds in presence of Pt activated with Pd gives the corresponding CH_2 or Me substances. The following examples are cited: indan-1-one or -1:3-dione to indane; 1:5-diketophenylheptamethylenedicarboxylic ester to the 1:5-(OH)₂-compound; PhCNO and $\text{CH}_2\text{Ph}\cdot\text{OH}$ to PhMe , furfuraldehyde to silvane; $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ to $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$; $\text{OH}\cdot\text{CHPh}\cdot\text{CN}$ to $\text{CH}_2\text{Ph}\cdot\text{CN}$, and thence in poor yield to $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$. H. W.

Ammonolysis of fluorenone and fluorenone-anil. L. A. PINCK and G. E. HILBERT (J. Amer. Chem. Soc., 1934, 56, 490).—Prolonged interaction of fluorenone and Na-dried liquid NH_3 at room temp. gives fluorenoneimine (I); COPh_2 , 9:9-dichlorofluorene, and $\alpha\beta$ -dichloro- $\alpha\beta$ -di(diphenylene)ethane do not react under similar conditions. (I) and NH_2Ph at 120° afford fluorenoneanil, which with NH_4Cl in liquid NH_3 at 60° for 4 days gives some (I). H. B.

Anionotropic and prototropic changes in cyclic systems. II. Hydroxy-3:4-diphenyl-5-benzylidenecyclopentenones. III. Isomeric chloro-3:4-diphenylcyclopentenones. IV. Hydroxy-3:4-diphenyl-5-isopropylidenecyclopentenones. H. BURTON and C. W. SHOPPEE (J.C.S., 1934, 197–201, 201–205, 205–207).—II. The conversion of 4-hydroxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone (I) into the 2-hydroxy-compound (II) occurs by successive anionotropic and prototropic changes. Owing to dissymmetry, there are three pairs of theoretically possible alcohols:



The isolation of five of the six possible Me ethers is described. (Ia), m.p. 232° (cf. Gray, J.C.S., 1909, 95, 2138), Ag_2O , and MeI afford 4-methoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone, m.p. 158° (4-OEt., m.p. 159°), whilst (Ib), m.p. 213.5°, yields the 4-OMe-compound, m.p. 122°. (IIa), m.p. 216°, is methylated to 2-methoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone, m.p. 112° (2-OEt., m.p. 122–123°), whilst (IIb), m.p. 223°, gives the 2-OMe-compound, m.p. 124°. (Ia) and SOCl_2 afford 2-chloro- (III), m.p. 175°, and 2:4-dichloro-3:4-diphenyl-5-benzylidene- Δ^3 -cyclopentenone (IV), m.p. 175°. (III) with MeOH and AgOAc yields the 2-OMe-derivative, m.p. 143°, and with AcOH-AgOAc forms the 2-OAc-compound. (IV) with MeOH- AgOAc is converted into 2-chloro-4-methoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone, m.p. 155°, and with AcOH-AgOAc into the 4-OAc-derivative, m.p. 160°, and 3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentene-1:2-dione, m.p. 198–199° [osazone, m.p. 179–180° (decomp.)]. 3:4-Diphenyl- Δ^3 -cyclopentenone and PhCHO-NaOEt give the 2:5-dibenzylidene derivative, m.p. 202°. 4-Hydroxy-3:4-diphenyl-5-benzylidene-2-methyl- Δ^2 -cyclopentenone with Ac_2O and H_2SO_4 yields 3:4-diphenyl-5-benzylidene-2-methylene- Δ^3 -cyclopentenone (which gives CH_2O on ozonolysis) and a substance, $\text{C}_{50}\text{H}_{38}\text{O}_2$, m.p. 225°.

III. Anhydroacetonebenzil (V) and AcCl give 4-chloro-3:4-diphenyl- Δ^2 -cyclopentenone (VI) and a dimeride, $\text{C}_{34}\text{H}_{24}\text{O}_2$; (VI) and MeOH-AgOAc afford 4-methoxy-3:4-diphenyl- Δ^2 -cyclopentenone, m.p. 123.5°, which is also obtained from (V) by methylation, and with Br yields a compound, $\text{C}_{17}\text{H}_{10}\text{OBr}_4$, m.p. 145°. (V) and EtOH-HCl afford 2-chloro-3:4-diphenyl- Δ^2 -cyclopentenone, (VII), m.p. 128–129°, which is reduced (Zn-AcOH) to a substance, $\text{C}_{34}\text{H}_{28}\text{OCl}$, m.p. 210° (decomp.). The conclusions of Allen and Spanagel (A., 1933, 67) are shown to be incorrect with regard to (VII). 3:4-Diphenyl- Δ^3 -cyclopentenone with SOCl_2 gives 2-chloro-3:4-diphenyl- Δ^3 -cyclopentenone, m.p. 48°, and with Cl_2 forms a monochlorodimeride (VIII), $\text{C}_{24}\text{H}_{23}\text{O}_2\text{Cl}$, m.p. 216°. (VIII) is oxidised with NaOBr to diphenylmaleic anhydride.

IV. Mesityl oxide and benzil (cf. Japp and Knox, J.C.S., 1905, 87, 673) give 4-hydroxy-3:4-diphenyl-5-isopropylidene- Δ^2 -cyclopentenone (IX) and a substance, m.p. 251–252° (decomp.). (IX) forms 2-acetoxy-3:4-diphenyl-5-isopropylidene- Δ^3 -cyclopentenone.

tenone (X), reduced (HI) to a ketone, m.p. 171° (*benzylidene* derivative, m.p. 234°). (X) with HCl forms 2-*chloro-3 : 4-diphenyl-5-isopropylidene-Δ²-cyclopentenone* (?), m.p. 188° [which with KOH-EtOH gives the 2-*OH*-derivative (XI), m.p. 252°], and the 2-*OH*-Δ³-compound (XII), m.p. 207°. The transformation of (IX) into (XI) occurs by successive anionotropic and prototropic stages, the intermediate compound being (XII).

F. R. S.

Dioximes. CIII. F. S. DE PAOLINI and G. ARMITANO (Gazzetta, 1933, 63, 917—923).—Of benzylmethylglyoxal (I), only a β-glyoxime (II) (A., 1932, 272) has been described; when this [*Bz*₂ derivative, m.p. 167° (decomp.)], obtained from β-oximino-α-phenylbutan-γ-one (III), (*Bz* derivative, m.p. 67°; *phenylhydrazone*, m.p. 169—170°), is partly hydrolysed by dil. HCl at 40—50°, γ-oximino-α-phenylbutan-β-one (IV), m.p. 94° (*Bz* derivative, m.p. 90°; *phenylhydrazone*, m.p. 144—145°), is formed, but an α-dioxime cannot be obtained from either (III) or (IV), both of which with N₂O₄ in Et₂O yield (I). When, however, the product of further action of N₂O₄, 4-*benzyl-3-methyl-1 : 2 : 5-oxadiazole 2-oxide* (V), m.p. 67°, is reduced by Zn and AcOH, α-*benzylmethylglyoxime*, (VI), m.p. 94—95° (*Bz*₂ derivative, m.p. 134°; *Ni* salt insol. in dil. AcOH), is obtained, which is converted into (II) when heated. Reduction of (V) by SnCl₂ gives the *oxadiazole*, b.p. 154°/17 mm.; treatment of (V) with NaOEt yields 4-*imino-5-hydroxy-3-benzylisooxazoline*, m.p. 141° (*Bz* derivative, m.p. 136—137°).

E. W. W.

Tautomerism of α-diketones. II. Phenyl benzhydryl diketone. E. P. KOHLER and N. WEINER (J. Amer. Chem. Soc., 1934, 56, 434—438).—α-Benzoyl-β-diphenylethylene oxide (I) is converted by short treatment with MeOH-NaOMe in EtOH and subsequent acidification (dil. H₂SO₄) into *Ph benzhydryl diketone* (II), m.p. 49—50° [*quinoxaline*, m.p. 198—199°, from *o*-C₆H₄(NH₂)₂; *oxime*, m.p. 135—136], which is completely ketonic, is oxidised (H₂O₂ in aq. MeOH-NaOH) to *BzOH* and CHPh₂·CO₂H, and readily undergoes the “benzilic acid” rearrangement to α-*hydroxy-αβ-triphenylpropionic acid* (III), m.p. 243—245° (decomp.) (*Me* ester, m.p. 186°). (III) is best obtained from (I) and conc. MeOH-KOH. Methylation (Me₂SO₄, aq. MeOH-NaOH) of (II) gives *Ph α-methoxy-β-phenylstyryl ketone*, m.p. 103—104°, whilst benzoylation (*BzCl* and C₅H₅N or aq. NaOH-dioxan) affords *Ph α-benzoyloxy-β-phenylstyryl ketone*, m.p. 161°. (II) is reduced (H₂, PtO₂, EtOAc or Zn, acid) to diphenylacetylphenylcarbinol (A., 1931, 354) (*oxime*, m.p. 159°). (I) and HCl in cold AcOH give 1-*chloro-1 : 3-diphenylindan-2-one*, m.p. 174° (decomp.), oxidised (Na₂CrO₄, AcOH) to *o*-C₆H₄Bz₂ and converted by EtOH into the 1-*OEt* derivative, m.p. 133°. MgMeI (1 equiv.) and (II) give α-benzoyl-α-benzhydryl-ethyl alcohol, m.p. 178° (lit. 188°), which with MgPhBr affords αβ-*dihydroxy-ααγ-tetraphenyl-β-methylpropane*, m.p. 173°, also prepared from MgPhBr and *Me α-hydroxy-ββ-diphenyl-α-methylpropionate*, m.p. 87—88° (from MgMeI and CHPh₂·CO·CO·Me). (II) and an excess of MgMeI give α-*diphenylacetyl-α-phenylethyl alcohol*, m.p. 72—73°, which is converted by HI into 1 : 3-*diphenyl-1-methylindan-2-one*, m.p. about 185°

(decomp.), and with MgPhBr affords βγ-*dihydroxy-ααβγ-tetraphenylbutane*, m.p. 184°. (II) and an excess of MgPhBr give α-benzoyl-αββ-triphenylethyl alcohol.

H. B.

4 : 6- and 2 : 4-Diacetylresorcinol. W. BAKE (J.C.S., 1934, 71—73).—*m*-C₆H₄(OAc)₂ and FeCl₃ by an improved process give 4 : 6-diacetylresorcinol (I) (m.p. 182° (yield 32.4%) (*Bz*₂ derivative, m.p. 118° (A., 1933, 155), oxidised by H₂O₂ in NaOH in the absence of air to 2 : 4 : 5-trihydroxyacetophenone which is isolated as the Me₃ ether, better obtained by similar treatment of the Me ether of (I). Resaceto-phenone with Ac₂O and NaOAc gives 7-acetoxy-3-acetyl-2-methylchromone, converted by AlCl₃ in PhNO₂ into 7-hydroxy-8-acetyl-2-methylchromone, m.p. 185—186.5°. “Diflavone” (A., 1931, 1305) is shown to be 3 : 3'-dibenzoyldiflavone, and the structures of other products obtained from (I) are discussed.

A. A. L.

Tetramethyl-*o*-benzoquinone. L. I. SMITH and L. R. HAY (J. Amer. Chem. Soc., 1934, 56, 477—478).—Dinitroprehnitene, m.p. 176° (from prehnitene method, A., 1926, 729) is reduced (SnCl₂, conc. HCl, EtOH) to diaminoprehnitene (I), m.p. 144°. Treatment of the hydrochloride of (I) with Cl₂ in AcOH-conc. HCl, removal of the pptd. NH₄Cl and excess of Cl₂ (in a vac.), and subsequent treatment with SnCl₂ and conc. HCl gives *dihydroxyprehnitene*, m.p. 111° (*diacetate*, m.p. 175°; *dibenzoate*, m.p. 157° *Me₂ ether*, m.p. 21°), which is oxidised (dry Ag₂O in Et₂O) to tetramethyl-*o*-benzoquinone (*prehnitenequinone*) (II), m.p. 110—111° (darkens at 80°). (II) decomposes when kept for a few hr. even at low temp. in a vac. 1 : 2 : 3 : 4-*Tetramethyl*, m.p. 217°, and *octamethyl*, m.p. 279°, -phenazines are prepared from (II) and *o*-C₆H₄(NH₂)₂ and (I), respectively.

H. B.

Quinamines. K. FRIES, R. BÖCKER, and F. WALLBAUM (Annalen, 1934, 509, 73—102).—The following are prepared from 1 : 5-dibromo-4-keto-1 : 4-dihydro-*m*-xylene (A., 1928, 888) and the requisite NH₂Ar (2 mols.): 5-*bromo-1-o*- (I), m.p. 120° (decomp.), -*m*- (II), m.p. 110° (decomp.), and -*p*- (III), m.p. 109° (decomp.), -*toluidino*-, -1-*p*-*bromoanilino*- (IV), m.p. 131° (decomp.), -1-3'-*bromo-p-toluidino*- (V), m.p. 118° (decomp.), -1-3'-*chloro-p-toluidino*- (VI), m.p. 143° (decomp.), -1-3' : 5'-*dibromo-p-toluidino*- (VII), m.p. 118° (decomp.), -1-*m*-4-*xylydino*- (VIII), m.p. 107° (decomp.), and -1-*o*-*carboxyanilino*- (IX), m.p. 135° (decomp.), -4-*keto-1 : 4-dihydro-m-xylene*. 3 : 5-Dibromo-1-anilino- (X), m.p. 136° (decomp.) (cf. *loc. cit.*) -1-*o*-, m.p. 126° (decomp.) (lit. 112°), and -*p*- (XI) -*toluidino*-, -1-*m*-*toluidino*- (XII), m.p. 121° (decomp.) (previous blackening), -1-*p*-*bromoanilino*- (XIII), m.p. 138° (decomp.), -1-*m*-4-*xylydino*- (XIV), m.p. 111° (decomp.), -1-3'-*chloro-p-toluidino*- (XV), m.p. 146° (decomp.), and -1-*o*-*carboxyanilino*- (XVI), m.p. 163° (decomp.), -4-*keto-1 : 4-dihydro-toluene* are similarly obtained from 1 : 3 : 5-tribromo-4-keto-1 : 4-dihydro-toluene (XVII) (*loc. cit.*). The above quinamines containing no *p*-substituent in the arylamino-group are rearranged by conc. HCl in AcOH or EtOH to (mainly) diphenyl ethers. Thus (X) gives (cf. *loc. cit.*) 2 : 6-dibromo-4'-amino-4-methyldiphenyl ether (XVIII) and a little 5'-*chloro-3-bromo-2'-amino-2*-

hydroxy-3-methyldiphenyl (XIX), m.p. 168° (Ac_2 derivative, m.p. 195°); the amount of (XIX) rises with increased concn. of HCl. (XVIII) is debrominated (Zn dust) to 4'-amino-4-methyldiphenyl ether, m.p. 126° (Ac derivative, m.p. 131°), also prepared by reduction (Sn, conc. HCl, EtOH) of the 4'- NO_2 -derivative, m.p. 68° (obtained from $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OK}$, $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NO}_2$, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{OH}$ in $C_{10}H_8$ at 230°). Similarly, (II) and cold EtOH-conc. HCl give 5-bromo-4'-amino-2:4:2'-trimethyldiphenyl ether, m.p. 108° (Ac derivative, m.p. 155°), whilst (XII) affords 70% of 3:5-dibromo-4'-amino-4:2'-dimethyldiphenyl ether, m.p. 146° (Ac derivative, m.p. 191°), and 6% of 3:5'-dibromo-2'-amino-2-hydroxy-5:4'-dimethyldiphenyl, m.p. 211° ($N\text{-Ac}$ derivative, m.p. 175°). (I) yields 6-bromo-4'-amino-2:4:3'-trimethyldiphenyl ether, m.p. 131° (Ac derivative, m.p. 198°), whilst (IX) furnishes 6-bromo-4'-amino-5'-carboxy-2:4-dimethyldiphenyl ether (63%), m.p. 221° (decomp.) (Ac derivative, m.p. 148°), and 2-chloro-3:5-dimethyldiphenylamine-2'-carboxylic acid (XX) (27%), m.p. 327° (Me ester, m.p. 163°). Reaction of (IX) with HCl is considered to give $o\text{-NH}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ and 1-chloro-5-bromo-4-keto-1:4-dihydro-*m*-xylene, which then afford the 1-chloro-5-*o*-carboxyanilino-4-keto-derivative; further addition of HCl to CO and subsequent elimination of HOCl affords (XX). Distillation of (XX) with Zn dust gives (probably) an impure dimethylcarbazole, m.p. about 95°; 6-chloro-2:4-dimethyldiphenylamine-2'-carboxylic acid, m.p. 233° (from 5-chloro-*m*-4-xylylene and $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$), similarly affords 2:4-dimethyldiphenylamine, whilst 3:5-, m.p. 205°, and 2:6-, m.p. 204°, -dimethyldiphenylamine-2'-carboxylic acid furnish 3:5-, m.p. 57°, and 2:6-, m.p. 55°, -dimethyldiphenylamine, respectively. (XVI) is converted (EtOH-conc. HCl) into 2:6-dibromo-4'-amino-5'-carboxy-4-methyldiphenyl ether, m.p. 232° (Ac derivative, m.p. 183°), and a little 6-chloro-5-bromo-3-methyldiphenylamine-2'-carboxylic acid, m.p. 360°.

Diphenyl derivatives are obtained as the main products from several of the quinamines, especially the *p*-substituted-arylamino-derivatives. Thus, (III) gives 2'-amino-2-hydroxy-3:5:5'-trimethyldiphenyl, m.p. 135° (Ac_2 derivative, m.p. 116°), and a compound, $C_{15}H_{14}ONBr_3$, m.p. 181° (decomp.); distillation of the former with Zn dust affords 1:3:6-trimethylcarbazole, m.p. 126° (NO -derivative, m.p. 139°). (XI) gives 3-bromo-2'-amino-2-hydroxy-5:5'-dimethyldiphenyl, m.p. 176° ($N\text{-Ac}$ derivative, m.p. 184°) (converted by Zn dust into 3:5-dimethylcarbazole), and some 6-chloro-5:6'-dibromo-3:4'-dimethyldiphenylamine, m.p. 188°, whilst (IV) yields 70% of 5'-bromo-2'-amino-2-hydroxy-3:5-dimethyldiphenyl, m.p. 148° (Ac_2 derivative, m.p. 94°), and (XIII) furnishes 3:5'-dibromo-2'-amino-2-hydroxy-5-methyldiphenyl, m.p. 205° ($N\text{-Ac}$ derivative, m.p. 110°) [convertible (Zn dust) into 3-methylcarbazole], and some 2:6:5'-tribromo-2'-amino-4-methyldiphenyl ether, m.p. 105° (Ac derivative, m.p. 204°).

Most of the *op*-substituted-arylamino-compounds give (usually) *O*-free diphenylamines. Thus, (V) affords 2-chloro-2'-bromo-3:5:4'-trimethyldiphenylamine (80%), m.p. 153° [convertible (Zn dust) into 2:4:6-trimethylcarbazole, m.p. 198°]; (VI) yields 2:2'-dichloro-3:5:4'-trimethyldiphenylamine

(80%), m.p. 141°; (XV) furnishes 2:2'-dichloro-3-bromo-5:4'-dimethyldiphenylamine, m.p. 169°. (VIII), however, gives 2'-amino-2-hydroxy-3:5:3':5'-tetramethyldiphenyl, m.p. 98° (Ac_2 derivative, m.p. 117°), and (XIV) similarly affords 3-bromo-2'-amino-2-hydroxy-5:3':5'-trimethyldiphenyl, m.p. 128° ($N\text{-Ac}$ derivative, m.p. 195°), and some 2-chloro-3-bromo-5:2':4'-trimethyldiphenylamine, m.p. 135°. Unlike any of the other quinamines, (VII) yields a derivative of *m*-hydroxydiphenylamine, viz., 4:2':6'-tribromo-3-hydroxy-2:6:4'-trimethyldiphenylamine, m.p. 110° (Ac derivative, m.p. 141°), which is indifferent to $FeCl_3$. $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$ and (XVII) in cold EtOH do not give a quinamine but afford the rearrangement product 3:5-dibromo-*p*-tolyl 4-amino- α -naphthyl ether, m.p. 170° (Ac_2 derivative). H. B.

Reaction between duroquinone and sodiummalonic esters. II. Synthesis and reactions of 2:5-dimethoxy-3:4:6-trimethylbenzaldehyde. L. I. SMITH (J. Amer. Chem. Soc., 1934, 56, 472—474).—3:6-Dinitro- ψ -cumene (obtained by deamination of its 5- NH_2 -derivative) is reduced ($SnCl_2$; cf. A., 1926, 729) to 3:6-diamino- ψ -cumene stannichloride, which is oxidised ($FeCl_3$ in dil. HCl) to trimethyl-*p*-benzoquinone (ψ -cumoquinone), m.p. 29—30° (lit. 11° and 32°). Trimethylquinol, m.p. 168—170° (decomp.) [*dibenzoate*, m.p. 179.5—180.5°; diacetate, m.p. 108.5—110° (lit. 112°)], is methylated (Me_2SO_4 , $MeOH\text{-}KOH$) to the Me_2 ether, b.p. 144°/30 mm., m.p. 35.5—36°, which is converted by the method of Adams *et al.* (A., 1924, i, 51, 860) into 2:5-dimethoxy-3:4:6-trimethylbenzaldehyde (A., 1926, 836) [oxime, m.p. 134—135° (lit. 129—131°)]. Condensation ($MeOH\text{-}NaOMe$) of this with $CH_2(CO_2Me)_2$ followed by hydrolysis give the -benzylidenemalonic acid, identical with that previously obtained (*loc. cit.*) from duroquinone and $CHNa(CO_2R)_2$. H. B.

Santonin series. XIX. Behaviour of santonic acid on oxidative degradation. E. WEDEKIND and I. JACKH (J. pr. Chem., 1934, [ii], 139, 129—140).—Oxidation of santonic acid (I) with alkaline H_2O_2 gives aposantonic acid, $C_{14}H_{20}O_3$, m.p. 164—165° [oxime, m.p. 185—186°; H_2 -derivative, m.p. 205—206° (oxime, m.p. 188—189°); Clemmensen reduction gives an oil], a ketomonocarboxylic acid, further oxidised by $CrO_3\text{-}AcOH$ to a diketolactone, $C_{14}H_{18}O_4$, m.p. 159—160° (oxime, decomp. 228°), hydrolysed by alkali to the free acid, $C_{14}H_{20}O_5$, decomp. 200—202°. (I) is slowly oxidised by aq. $KOBr$ at room temp. to hydroxysantonic acid, $C_{15}H_{20}O_6$, m.p. 198° (+0.5 H_2O , decomp. 215°) [Me_2 ether-ester, m.p. 87—90° (decomp.)]; Ac_2 derivative, decomp. 192° (Me ester, m.p. 142°)], which appears to be free from CO and lactone groups. No identifiable products were obtained from (I) and O_3 . Distillation of santonic acid (A., 1892, 1352) with Ac_2O gives a cyclic ketone, $C_{12}H_{14}O_4$, m.p. 203—204° [oxime, m.p. 223° (decomp.)]. Santolic acid, $C_{15}H_{20}O_5$, decomp. 178—180° [lit. $C_{15}H_{22}O_5$, m.p. 166—167° (*loc. cit.*)], is conveniently prepared by action of 25% H_2SO_4 on the oxime of (I) and unlike (I) gives a H_2 -derivative, decomp. 160° ($H_2\text{-PtO}_2$). Its hydroxamic acid anhydride has m.p. 235° (decomp.) (lit. 226—227°). H. A. P.

Toad poisons. VI. Ch'an su, the dried venom of the Chinese toad, and the secretion of the tropical toad, *Bufo marinus*. H. JENSEN and E. A. EVANS (J. Biol. Chem., 1934, 104, 307—316; cf. A., 1930, 1205).—Fresh analyses have necessitated a revision of all empirical formulae and these now conform with derivatives. Cinobufagin (I), $C_{25}H_{32}O_6$, m.p. 222—223° (Ac derivative, m.p. 195—196°), is a lactone, contains two double linkings, $\cdot CH\cdot OH$, and $\cdot OAc$. (I) gives a *tetrahydro*-derivative, m.p. 230° (Ac derivative, m.p. 238°); on oxidation with CrO_3 it affords a ketone, *cinobufagone*, $C_{25}H_{30}O_6$, m.p. 240—241°. *N*-NaOH-EtOH opens the lactone ring and hydrolyses the $\cdot OAc$, cinobufaginic acid, $C_{23}H_{30}O_6$ (amorphous), being produced. Bufagin (II), $C_{24}H_{32}O_5$, m.p. 212—213° (Ac derivative, m.p. 203—204°), resembles (I) but does not contain OAc . The formation of CH_2O by the treatment of (II) with 70% H_2SO_4 and of HCO_2H with *N*-NaOH-EtOH suggest the presence of $\cdot CH_2\cdot C(\cdot CH_2)\cdot CH_2\cdot$; the latter hydrolysis also opens the lactone ring, *bufaginic acid*, $C_{23}H_{34}O_6$ (amorphous), being produced. (II) forms a *tetrahydro*-derivative, m.p. 210—211° (Ac derivative, m.p. 213—214°), and, with 5% H_2SO_4 in 50% EtOH, gives *dianhydrobufagin* (III), $C_{22}H_{28}O_3$, m.p. 245—246°. *Marinobufotoxin* (IV), $C_{38}H_{58}O_{10}N_4$, m.p. 204—205°, and *N*-HCl-EtOH give (III), suberic acid, and arginine. *Gamabufagin chloride* (V), $C_{24}H_{33}O_4Cl$, previously termed *bufotalin chloride*, is now held to be derived from *gamabufogenin*, $C_{24}H_{34}O_5$ (cf. Wieland and Vocke, A., 1930, 1466), since on treatment with Ac_2O -NaOAc (V) loses HCl and is acetylated to *acetylanhydrogamabufagin*, $C_{26}H_{34}O_5$, m.p. 225—226° (*hexahydro*-derivative, m.p. 180°), and with 25% KOH in MeOH gives *anhydrogamabufaginic acid*, $C_{23}H_{32}O_4$, m.p. 215°, HCO_2H and Cl^- being eliminated. W. S.

Resins and resin substances. IX. β -Amyrin and manila elemi resin. VI. A. ROLLETT and R. PETTER (Monatsh., 1934, 63, 311—316).—From the $COMe_2$ mother-liquor of the molozonides of β -amyrin benzoate (I) (A., 1931, 1299), a *cryst. substance*, $C_{37}H_{52}O_4$ (II), m.p. 333°, is isolated; (II) is a peroxide (I from KI) of an oxy- β -amyrin benzoate and on hydrolysis (5% KOH-EtOH) and acetylation of the product gives an Ac derivative, m.p. (indef.) 265—275°, probably identical with oxy- β -amyrin acetate (A., 1923, i, 588). With Br vapour in the dark β -amyrin and (I) give indefinite products containing, respectively, approx. 12 and 14 atoms of Br. J. W. B.

Constitution of hederagenin and oleanolic acid. V. Z. KITASATO (Acta Phytochim., 1933, 7, 169—186; cf. A., 1933, 612).—With CrO_3 in AcOH, diacetylhederagenin gives ketodiacylhederagenin lactone, m.p. 197°, hederagenonediacid (I) gives *ketohederagenonediacid monolactone*, $C_{29}H_{42}O_6$, m.p. 140° [*dioxime*, m.p. 221° (decomp.)], and the Me ester of (I) gives *γ -ketohederagenonediacid Me ester* (II), $C_{31}H_{46}O_6$, m.p. 178° [*dioxime*, m.p. 225° (decomp.)]. Hydrolysis of the monobromolactone of (I) with KOH in EtOH and methylation likewise gives (II), which is also obtained on oxidation of ketohederagenin with Beckmann's mixture. Hedratricid (III) Me ester by oxidation or the monobromolactone of (III) by hydro-

lysis and methylation affords the γ -*keto*-derivative, $C_{31}H_{46}O_7$, m.p. 163° [*oxime*, m.p. 227° (decomp.)]. Oxidation of hederagone Me ester gives the γ -*keto*-derivative, m.p. 237°, whilst oleanolic acid monobromolactone (IV) gives *oleanonic acid monobromolactone* (V), $C_{30}H_{45}O_3Br$, m.p. 251° (decomp.) [*oxime*, m.p. 267° (decomp.)]. (V) with Zn-AcOH yields oleanonic acid, $C_{30}H_{46}O_3$, m.p. about 190° [*oxime*, m.p. 280° (decomp.)]; Me ester *oxime*, m.p. 246° (decomp.). Acetyloleanolic acid with CrO_3 -AcOH gives as intermediate product (cf. A., 1932, 1035) *ketoacetyloleanolic acid*, $C_{32}H_{48}O_5$, m.p. 287° (decomp.). With CrO_3 -AcOH, Me keto-oleanolate (VI) yields *Me keto-oleanonate* (VII), m.p. 175° [*oxime*, m.p. 270°]; hydrolysis (KOH in MeOH) and methylation of (IV) affords (VI), which, when dissolved in EtOH and poured into dil. H_2SO_4 gives an *isomeride*, m.p. 198—200° (Ac derivative, m.p. 193—195°). (VII), when poured into dil. HCl, also gives an *isomeride*, m.p. 210° [*oxime*, m.p. 255° (decomp.)]. Oleanolic acid lactonediacid gives a Me ester, m.p. 213°.

J. H. B.

Convallarin. J. LINDNER and A. TORGLER (Monatsh., 1934, 63, 335—346).—Repeated extraction of convallarin (I) (Merck) with H_2O extracts approx. 60%, and with EtOAc approx. 45%, of sol. material. (I) is thus separated into H_2O -sol. (II) (C 58.4, H 8.17%), EtOAc-sol. (III) (C 60.82, 61.15, H 7.98, 7.92%), and H_2O - and EtOAc-sol. (IV) portions. The small difference in C and H content of (II) and (III) and other facts render it improbable that the fractions correspond with a neutral, acid, and preformed saponin (Hirschberg), (I) being a complex mixture the composition of which may differ according to its (commercial) source. Hydrolysis of the saponin fraction of (I) with 5% H_2SO_4 gives small yields of *cryst. material* containing at least two different substances (cf. A., 1915, i, 571), and only by examination of these *cryst. products* can the glucosides of the lily of the valley be investigated. J. W. B.

Caoutchouc. XVI. A. R. Kemp's method of determining iodine values in the case of caoutchouc. R. PUMNERER and H. STARK (Ber., 1934, 67, [B], 292—294; cf. A., 1933, 1054).—Caoutchouc (I) in pure CS_2 under N_2 is mixed with an excess of 0.2*N*- ICl -AcOH (which may attain 70%) at 0°. After 2—4 hr. the mixture is treated with 10% KI and anhyd. EtOH (to avoid emulsions) and titrated with $Na_2S_2O_3$. $CMe_2\cdot CHMe$ behaves similarly to (I), but γ -ethyl- Δ^8 -pentene, like the terpenes, cannot be determined thus. H. W.

Isoprene and caoutchouc. XLI. Hydrogenation of caoutchouc and balata. H. STAUDINGER and E. O. LEUPOLD (Ber., 1934, 67, [B], 304—311; cf. A., 1932, 1089).—The sp. viscosity (I) of squalene and perhydosqualene in C_6H_6 is the same; this is true also for hemicolloidal balata and hydrobalata obtained therefrom. This confirms the conclusion that (I) depends only on the length and no. of the mols. and is independent of their chemical nature. Cautious hydrogenation of undegraded balata and euolloidal caoutchouc leads to partly reduced compounds $(C_5H_9)_x$ and completely hydrogenated polypranes $(C_5H_{10})_x$ which, in equally conc. solution, have

the same (I) as the non-hydrogenated compounds. Since the size of the particles remains unchanged, all the C atoms which form the colloidal particles are united by normal co-valencies and the particles are mols. in the sense of the classic theory. The mols. of polyprenes and polypranes must necessarily have the same thread formation. The physical properties of the hydrocaoutchoucs, including elasticity, are identical with those of the polymeric-analogous caoutchoucs. Elasticity is not shown by degraded products and hence is conditioned by mol. size; only very complex compounds are elastic. Hydrobalata of mol. wt. 40,000 is as stable as any other paraffin. Eucolloidal hydrocaoutchouc is unaffected by exposure to air and light during many days when solid or in solution.

H. W.

Reactions of eucalyptol. L. EKKERT (Pharm. Zentr., 1934, 75, 145).—Colour reactions obtained when eucalyptol and furfuraldehyde, anisaldehyde, salicylaldehyde, vanillin, cinnamaldehyde, piperonal, *p*-NMe₂·C₆H₄·CHO, or α -C₁₀H₇·OH in EtOH are treated with conc. H₂SO₄ are described. S. C.

Preparation of pure *d*-neomenthol from *l*-menthol. W. J. GRUBB and J. READ (J.S.C.I., 1934, 53, 52—53T).—When *l*-menthone, prepared by oxidising *l*-menthol (I), is reduced with Ponndorf's reagent (A., 1926, 520) it readily yields a mixture of *d*-neomenthol (II) and (I), containing about 70% of (II). *p*-Nitrobenzoyl chloride reacts 16.3 times as rapidly with (I) as with (II), so that partial esterification leaves a residual menthol containing about 95—98% of (II). One recrystallisation of the *p*-nitrobenzoate of this material yields pure *d*-neomenthyl *p*-nitrobenzoate, from which pure (II) is easily obtained. *l*-Menthone yields about 35% of its wt. of pure (II) in this way.

Constituents of Indian turpentine from *Pinus longifolia*, Roxb. III (contd.). A. E. BRADFIELD, E. M. FRANCIS, and J. L. SIMONSEN (J.C.S., 1934, 188—197).—Ozonisation of longifolene (I) in CCl₄ at 0° affords CH₂O and an ozonide, which when decomposed and treated with H₂O₂ affords α -longifolic acid, m.p. 140—142° (labile form, m.p. 121—122°), [α]_D²⁰ —31° in EtOH (Me ester, an oil), stereoisomeric with longifolic (II) and isolongifolic acids, which are *cis-trans*-isomerides (cf. J.C.S., 1923, 123, 2642). (I) therefore has a vinyl side-chain. (I) with MnO₂ in boiling dil. H₂SO₄ in 18 hr. affords an acid, decomp. 264—265° (Me ester, m.p. 145—147°), and trimellitic acid, whereas with dil. HNO₃ first at room temp. and then at 100° for 5 days it affords a mixture of solids (III) and an oil from which *as*-dimethylsuccinic acid and CMe₂(CO₂H)₂ are isolated. CHCl₃ extracts from (III) a dibasic acid, C₁₁H₁₈O₄, m.p. 183—185°; the residue is separated by COMe₂ into a very weak tribasic acid, C₁₄H₁₈O₆, decomp. 283—285° (from HCO₂H) and decomp. 272—273° (from MeOH) (Me ester, m.p. 73—74°), stable to KMnO₄, HBr in AcOH at 180°, and Se at 300°, which indicates that the CO₂H groups are attached to quaternary C atoms and are derived by oxidation of the CH:CH₂ and two Me groups (one of which comes from the ·CMe₂· group) not attached to the same C atom, a tribasic acid (IV), C₁₅H₂₀O₆, decomp. 222—224° (Me ester, an oil)

[probably formed by addition of H₂O (or HNO₃) to CH:CH₂ followed by oxidation to give CH₂·CO₂H], stable to similar reagents, and occasionally an *isomeride* of (IV), m.p. 199—200° (sintering at 190°), which with AcCl gives an *anhydride*, m.p. 103°. Longifolamide (V) (prep. described) (cf. *ibid.*, 2656) easily affords *longifonitrile*, b.p. 145—150°/2 mm., which is the main product of the interaction of the acid chloride of (II) and NH₃, and is hydrolysed to (V) with hot 90% H₂SO₄. The urethane from (V) (improved prep.) with Na amyloxide at 160° during 8 hr. affords *l*-amino-1-methyl-longifane (VI), b.p. 150°/18 mm. [hydrochloride, decomp. 280—282° (sintering at 258°); nitrile, decomp. 132°; α - and β -Ac derivatives, m.p. 191—192° and 163—165°, respectively; 3:5-dinitrobenzoate, m.p. 199—200°; α -, m.p. 258—259°, and β - (VII) -methiodides (+1H₂O, decomp. 184°)]. (VII) with Ag₂O in H₂O at 60° during 12 hr. affords an oil which when heated gives 1-dimethylamino-1-methyl-longifane [hydrochloride (VIII), m.p. above 280°]. The NH₄ base corresponding with the α -isomeride affords (VIII) and some NMe₃. (VI) with NaNO₂ in H₂O—H₃PO₄ at 100° during 2 hr. affords a hydrocarbon-alcohol mixture, converted by KHSO₄ at 200° into a hydrocarbon (IX), C₁₃H₂₀, b.p. 124°/20 mm. (54.8% of unsaturation) (hydrochloride, an oil), and an unchanged alcohol which cannot be dehydrated even by 2-C₁₀H₇·SO₃H and does not react with *o*-C₆H₄(CO)₂O at 100—120°; this indicates it is a *tert.* alcohol and confirms that the CO₂H in (II) is linked to a quaternary C. (IX) with KMnO₄ in H₂O—NaOH at 0° during 10 hr. affords a dibasic acid, C₁₃H₂₀O₄, m.p. 235—236° (converted by AcCl into an oily anhydride), and a lactone, m.p. 190°, probably obtained by lactonisation of the hydrolytic product of (X) (below). Ozonisation of (IX) in EtOAc below 0°, followed by decomp. of the ozonide with H₂-Pd (cf. A., 1932, 1113), affords CH₂O (which indicates ·CH₂·), an acid, m.p. 166° (converted by NaOH into an acid, m.p. 132°), and an oil, separated into three fractions: 1-methyldehydrolongifane, b.p. 125—127°/25 mm. (liquid hydrochloride) (which probably contains a cyclopropane ring), probably longif-1-one (X), identified as its semicarbazone, m.p. 208—209°, and liquid OH·CH₂· derivative (semicarbazone, m.p. 199°) (which indicates ·CH₂·CO), and an unidentified ketone (2:4-dinitrophenylhydrazone, m.p. 250—251°). Interaction of (VI) in COMe₂ at 30—35° with KMnO₄ affords the α -NHAc-compound (XI) and an acid, C₁₆H₂₅O₃N, m.p. 122—124° (semicarbazide, decomp. 179—180°), converted by loss of CO₂ into a substance, m.p. 144°, isomeric with (XI) and converted into (XI) by heating with EtOH—H₂SO₄. A mechanism is suggested for these reactions. A formula is proposed for (I).

J. L. D.

Carvone series. I. Some ketones and amines.

J. READ and R. G. JOHNSTON (J.C.S., 1934, 226—233).—Reduction [Pd(OH)₂—CaCO₃—H₂; cf. A., 1916, ii, 534] of *d*-carvone in MeOH during 2 hr. affords a product, [α]_D²⁰ —30.62° in CHCl₃; when prepared by Rupe's method (cf. A., 1919, i, 29) this has [α]_D²⁰ —24.9° to —25.1° in CHCl₃ (cf. A., 1926, 1147) and is an equilibrium mixture of *l*- (I) and *l*-iso-carvomenthone (II). *d*-Carvomenthol (obtained from *d*-carvomenthylamine and HNO₂) with Beckmann's reagent (A., 1889,

721) affords *l*-carvomenthone, b.p. 96—96.5°/16 mm., $[\alpha]_D^{25}$ —6.0° in CHCl_3 , [oxime, (III), m.p. 99—100°; semicarbazone, m.p. 192°]. (II) with conc. HCl at room temp., 90% H_2SO_4 , or Na in cold EtOH , formed some (I), although 40% NaOH or heat had practically no effect. (I) affords some (II) with cold NaOEt-EtOH . (III) with Na in boiling EtOH affords *d*-carvomenthylamine hydrochloride, m.p. > 250°, converted into the free base, b.p. 89.8—90°/16.5 mm., $[\alpha]_D^{25}$ +12.47° in CHCl_3 , [formyl, m.p. 95°; *Ac*, m.p. 160—161°; propionyl, m.p. 128—129°; *n*-butyryl, m.p. 123—124°; *n*-hexoyl, m.p. 104°; *n*-octoyl, m.p. 97—98°; phenylacetyl, m.p. 177°; *Bz* (IV), m.p. 161°, and *d*-camphor-10-sulphonyl derivatives, m.p. 95°; carbimide, m.p. 206—207°; formate, m.p. 152°; *H* *d*-tartrate, m.p. 143—144°; *d*-, m.p. 138—140°, and *l*-camphor-10-sulphonate, m.p. 144—145°, together with (V) (below) and possibly another carvomenthylamine (*Bz* derivative, m.p. 151—152°). Interaction of (I) and (II) with HCO_2NH_4 at 130° during 48 hr. affords dicarvomenthylamine, b.p. 178—179°/11 mm., $[\alpha]_D^{25}$ —3.5° in CHCl_3 (which is probably a mixture of isomerides), and a mixture of formates from which *l*-neocarvomenthylamine (V), b.p. 87.8—88.0°/16 mm., $[\alpha]_D^{25}$ —20.13° in CHCl_3 (hydrochloride, $[\alpha]_D^{25}$ —31.9° in H_2O ; formyl, m.p. 50°; *Ac*, m.p. 114°; propionyl, m.p. 101°; *n*-butyryl, m.p. 98°; *Bz*, m.p. 126°; phenylacetyl, m.p. 81°, and salicylidene derivatives, m.p. 36—37°; formate, m.p. 131.5—132°; *H* *d*-tartrate, m.p. 162°), is isolated. Reduction of *d*-carvoxime with Na in EtOH (cf. A., 1893, i, 595) affords a mixture; fractional crystallisation of the formate affords *d*-dihydrocarvylamine formate, m.p. 145°, converted into the free base, b.p. 111°/35 mm., $[\alpha]_D^{25}$ +16.4° in CHCl_3 [*Bz* derivative, m.p. 182°, hydrogenated to (IV); salicylidene derivative, m.p. 58°]. Interaction of the appropriate acid chloride with a hydroxyaldehyde in dry $\text{C}_5\text{H}_5\text{N}$ affords the following: *d*-camphor-10-sulphonyl-*m*-hydroxybenzaldehyde, m.p. 67°; *vanillin*, m.p. 128°; β -naphthalenesulphonyl-salicylaldehyde, m.p. 74—75°; *vanillin*, m.p. 98°; *salicylidene-d*-carvomenthylamine, m.p. 104°. A stereochemical analogy between the menthone and carvomenthone series is discussed.

J. L. D.

Carvone series. II. Some unsaturated alcohols. R. G. JOHNSTON and J. READ (J.C.S., 1934, 233—237).—Reduction of *d*-carvone with Pr^{OH} and $\text{Al}(\text{OPr}^{\text{OH}})_3$ at 110° during 8 hr. (cf. A., 1926, 520) affords a carveol; fractional crystallisation of the 3 : 5-dinitrobenzoate gives *d*-trans-, m.p. 111.5°, and *d*-cis-carveyl-3 : 5-dinitrobenzoate, m.p. 92.5°, which are hydrolysed by boiling 5% KOH-MeOH to *d*-trans-carveol (I), b.p. 102.2—102.4°/10 mm., $[\alpha]_D^{25}$ +213.1° in CHCl_3 [*p*-nitrobenzoate (II), m.p. 77°; *Ac* derivative, b.p. 106—106.5°/9 mm.] (dehydrated by *d*-camphor-10-sulphonyl chloride to a mixture of a terpene and *p*-cymene), and *d*-cis-carveol (III), m.p. 24—25°, $[\alpha]_D^{25}$ +23.9° in CHCl_3 [*p*-nitrobenzoate, m.p. 26.5—28°; *Ac* derivative, b.p. 108—108.5°/10 mm.], respectively. A mixture of (I) and (III) having α_D +70.74° in $\text{C}_5\text{H}_5\text{N}$ with *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-COCl}$ at 15—30° affords more (II), which supports its *trans*-structure. Similarly, *l*-carvone affords *l*-trans- and *l*-cis-carveol. Equal wts. of *d*- and *l*-trans-carveyl 3 : 5-dinitrobenzoates in hot EtOH-EtOAc afford *dl*-trans-carveyl 3 : 5-dinitro-

benzoate, m.p. 119° (*dl*-cis-compound, m.p. 91.5°), hydrolysed to *dl*-trans-carveol, b.p. 108°/16 mm. [*p*-nitrobenzoate, m.p. 101°] (*dl*-cis-compound, b.p. 108°/16 mm.; *p*-nitrobenzoate, m.p. 94°). (I) is unattacked by Na in boiling EtOH , but $\text{H}_2\text{-Pd}$ (cf. J.C.S., 1923, 123, 2916) affords a product isolated as carvotanacetyl 3 : 5-dinitrobenzoate (?), m.p. 109—110°. Complete hydrogenation of (I) and (III) affords four carvomenthols. Reduction of *d*-carvone with Na in EtOH affords *d*-dihydrocarveol (cf. A., 1902, i, 630) [*p*-nitro-, m.p. 37°, and 3 : 5-dinitrobenzoate, m.p. 121.5—122°], readily hydrogenated to *d*-carvomenthol, whereas with Zn and EtOH-KOH it gives *l*-dihydrocarvone (IV), further reduced by $\text{Al}(\text{OPr}^{\text{OH}})_3$ and Pr^{OH} to a mixture of dihydrocarveols separated by means of 3 : 5-(NO_2) $_2\text{C}_6\text{H}_3\text{-COCl}$ into a dihydrocarveol, b.p. 99—100°/13 mm. [*p*-nitro-, m.p. 83—84°, and 3 : 5-dinitrobenzoate, m.p. 106—107°], and *l*-neodihydrocarveol, b.p. 101—102°/18 mm. (3 : 5-dinitro-, m.p. 138—138.5°, and *p*-nitrobenzoate, m.p. 107°; *d*-camphor-10-sulphonate, m.p. 91—93°, decomposed at 125° into α -phellandrene and *d*-camphor-10-sulphonic acid), hydrogenated to *l*-neocarvomenthol. (IV) with hot dil. H_2SO_4 (cf. A., 1895, i, 621) affords *dl*-carvenone, reduced by $\text{Al}(\text{OPr}^{\text{OH}})_3$ to *dl*-carvenol (3 : 5-dinitro-, m.p. 75—76°, and *p*-nitrobenzoate, m.p. 65°). J. L. D.

Catalytic hydrogenation of diosphenol. J. WALKER and J. READ (J.C.S., 1934, 238—242; cf. A., 1924, i, 862).—Reduction of diosphenol (I) (cf. A., 1922, i, 667) with Pd-H_2 affords dihydrodiosphenol (II), b.p. 108—115°/12 mm. [semicarbazone, m.p. 210—211° (decomp.); *p*-toluenesulphonate, m.p. 106—107°; *d*-camphor-10-sulphonate (III), an oil]. (III) at 150° in vac. affords *dl*-piperitone and *dl*- Δ^4 -menthenone-3, b.p. 90—97°/10 mm. [oxime identical with the product of Richtmann and Kremers (cf. A., 1897, i, 84)], which indicates that (II) is 2-hydroxymenthone. The *p*-toluenesulphonate of (I), m.p. 76°, or of (II), is unattacked by $\text{H}_2\text{-Pd}$ or $\text{H}_2\text{-Adams'}$ catalyst. *dl*-Piperitone oxide with $\text{H}_2\text{-Pd}$ affords *l*-hydroxymenthone (?), m.p. 88.5—90.5°. Similarly, *dl*-carvenone oxide affords 4-hydroxycarvomenthone (?), m.p. 72.5—74°. J. L. D.

***d*- $\Delta^{3,8(9)}$ -*p*-Menthadiene from *d*-pulegone.** W. J. GRUBB and J. READ (J.C.S., 1934, 242—243; cf. A., 1931, 230).—Reduction of *d*-pulegone with $\text{Al}(\text{OPr}^{\text{OH}})_3$ in dry Pr^{OH} (cf. A., 1926, 520) affords no pulegol, but *d*- $\Delta^{3,8(9)}$ -*p*-menthadiene (cf. J.C.S., 1906, 89, 848; 1911, 99, 537), b.p. 69°/14 mm., $[\alpha]_D^{25}$ +140.6° in CHCl_3 (which gives no solid derivatives, but adds on 2 Br), oxidised ($\text{KMnO}_4\text{-COMe}$, at 0°) to β -methyladipic acid. J. L. D.

Optical resolution of externally compensated alcohols. J. WALKER and J. READ (J.S.C.I., 1934, 53, 53—54r).—Chloromethylene-*d*-camphor, prepared from hydroxymethylene-*d*-camphor, reacts with Na l - and *dl*-menthoxide to yield *cryst. l*-, m.p. 74—75°, $[\alpha]_D^{25}$ +109.3° in EtOH , and *dl*-, m.p. 75—76°, $[\alpha]_D^{25}$ +150.0° in EtOH , *menthoxymethylene-d*-camphor; the *dl*-compound is a partial racemate. The corresponding *dl*-3-methylmenthyl and *dl*-m-methylcyclohexyl ethers do not crystallise. The pos-

sible application of such derivatives to the optical resolution of suitable *dl*-alcohols is pointed out.

Constituents of campherol. Y. ASAHINA and M. ISHIDATE (Proc. Imp. Acad. Tokyo, 1933, 9, 596—598; cf. this vol., 79).—The 5- is more reactive than the 2-CO group in 5-ketocamphor (I), since (I) adds HCN exclusively to the former and its monosemicarbazone, m.p. 238—240°, gives (Wolff-Kishner) *d*-borneol. Similarly (I) with cold Na-Hg in presence of CO₂ gives 5-hydroxycamphor, m.p. 210°, $[\alpha]_D^{25} +47.4^\circ$ (*Ac* derivative), the semicarbazone of which (Wolff-Kishner) gives probably impure *epiborneol* and may thus be a mixture of isomerides. Me *trans*- π -apocamphor-7-carboxylate semicarbazone, when reduced (Na-EtOH) and then hydrolysed by HCl, gives *trans*- π -hydroxycamphor, m.p. 233°, $[\alpha]_D^{25} +62.2^\circ$. The corresponding *cis*-ester gives similarly *cis*- π -hydroxycamphor, m.p. 233°, $[\alpha]_D^{25} +40.68^\circ$.

R. S. C.

Determination of configuration in the terpene and camphor series. VI. J. VON BRAUN and P. KURTZ (Ber., 1934, 67, [B], 225—230; cf. A., 1932, 43).—(+)-Camphor is transformed by two treatments with NaNH₂ and MeI into dimethylcamphor and thence by NaNH₂ into dimethylcampholamide (I). Treatment of (I) with Br and KOH leads to the

carbimide $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CHPr}^a-\text{CMe} \end{array} > \text{CMe} \cdot \text{N} : \text{C} : \text{O}$, b.p. 109—112°/14 mm., $[\alpha]_D^{25} +16.5^\circ$ in EtOH [*di*(dimethylcamphelyl)-carbamide, m.p. 154°], hydrolysed by HCl to dimethyl-

camphelylamine (II), $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{CHPr}^a-\text{CMe} \end{array} > \text{CMe} \cdot \text{NH}_2$, b.p.

90°/14 mm., $[\alpha]_D^{25} +22.31^\circ$, $[\alpha]_D^{25} +33.06^\circ$ in EtOH [*picrate*, m.p. 202°; *hydrochloride*; *sulphate*; *phosphate* (III)]. (I) is hydrolysed by conc. HCl at 150° to dimethylcampholic acid (III), b.p. 137—140°/0.5 mm., $[\alpha]_D^{25} +47.8^\circ$ in EtOH (re-converted into the amide by action of NH₃ on the *chloride*, b.p. 100°/0.5 mm.). Treatment of (III) in H₂SO₄ with NH₃-CHCl₃ gives partly racemised (II). Dry distillation of (III) gives a smaller amount of somewhat racemised (II) and a larger quantity of 1 : 2 : 2-trimethyl-3-isopropyl- Δ^5 -cyclopentene (IV), b.p. 168—170°, $[\alpha]_D^{25} -15.49^\circ$, probably containing a small amount of a semicyclic impurity. Ozonisation in AcOH of (IV) followed by treatment with Zn dust leads to 8-keto- $\gamma\gamma$ -dimethyl- β -isopropylhexaldehyde (V), b.p. 117—120°/12 mm., $[\alpha]_D^{25} +43.39^\circ$ (*p*-nitrophenylhydrazone, m.p. 179—180°; *semicarbazone*, m.p. 218°), with a small proportion of (?) 2 : 2-dimethyl-3-isopropylcyclohexanone (*semicarbazone*, m.p. 200°). (V) is the first example of an open-chain, optically active degradation product of camphor in which C₁ of camphor has been inactivated, whereas C₄ retains its original configuration.

H. W.

Electrolytic reduction of camphoric acid imide.—See this vol., 373.

Fenchene series. V. *sec.*- and *tert.*-Fenchyl chlorides. G. KOMPPA and S. BECKMANN (Annalen, 1934, 509, 51—60).—The rate of elimination of HCl (by 0.5N-KOH-EtOH at 20—24°) from the following is: *dl*- α -fenchene hydrochloride (I) > *dl*-cyclofenchene hydrochloride > *dl*- β -fenchene hydrochloride > “isofenchyl chloride” (II) > “fenchyl chloride”

(III). (I) thus regenerates α -fenchene; careful hydrolysis gives methyl- α -fenchocamphorol. (III), prepared from *dl*-fenchyl alcohol and PCl₅, is a mixture of *sec.*- and *tert.*-chlorides; the composition varies according to the method of prep. Thus, rapid treatment with PCl₅ gives 20—30% of β -fenchene [and (probably) some γ -fenchene], which then adds HCl to give the *tert.*-chloride. When (III) is kept in contact with the acid reaction mixture for a relatively long time, *isofenchyl chloride* results; elimination of HCl from this gives (mainly) β -fenchene (cf. Qvist, A., 1919, i, 165). Treatment of (III) with aq. Ca(OH)₂ at 50—60° gives unchanged *sec.*-chloride (*i.e.*, true *sec.*-fenchyl chloride or its rearrangement product *isofenchyl chloride*) and β -fenchene hydrate (A., 1933, 830); similar results are obtained using AgOAc (and subsequent hydrolysis). (II) is also a mixture containing a considerable amount of *tert.*-chloride. *dl*-isofenchyl *H* phthalate has m.p. 153—154°. H. B.

Super-aromatic properties of furan. III. Nitration. H. GILMAN and R. V. YOUNG (J. Amer. Chem. Soc., 1934, 56, 464—466).—Ph 2-furyl ketone and HNO₃ (*d* 1.5) in Ac₂O at < -8° give Ph 5-nitro-2-furyl ketone, m.p. 111°, also prepared from 5-nitro-2-furoyl chloride (improved prep.), C₆H₅, and AlCl₃, which is oxidised (KMnO₄) to 5-nitro-2-furoic acid and a little BzOH. 2-Furyl 2-thienyl ketone (*semicarbazone*, m.p. 150°) similarly affords 5-nitro-2-furyl 2-thienyl ketone, m.p. 161°, which when heated with 10% NaOH (to effect destruction of the nucleus containing the NO₂-group) and then oxidised (KMnO₄) gives 2-thienoic acid. These and previous results (A., 1933, 1300) show that 2-furyl, 2-thienyl, and Ph are decreasingly aromatic. Fur-2' : 4' : 6'-tribromoanilide, m.p. 164°, and -N-methylanilide, m.p. 125°, and 5-nitro-2-fur-2' : 4' : 6'-tribromoanilide, m.p. 191—192°, are described; attempted nitration gives resinous products.

H. B.

Decarboxylation temperatures of furoic acids. H. GILMAN, A. M. JANNEY, and C. W. BRADLEY (Iowa State Coll. J. Sci., 1933, 7, 429—431).—M.p. and decarboxylation temp. (determined by Norris' graphical method) are: 2-furoic acids: unsubstituted 132°, 158°; 5-Me 107°, 122—125°; 5-Bu^o 105°, 125—127°; 5-Cl 175°, 180—182°; 5-Br 185°, 177—179°; 3 : 5-Cl₂ 156—157°, 168—170°; 3 : 5-Br₂ 168—168.5°, 174°; 5-I 193°, —; 5-NO₂ 186°, 201—203°. 3-Furoic acids: unsubstituted 122°, 152°; 2-Me 101°, 101—103°; 2 : 4-Me₂ 114°, 129°; 5-NO₂-2-Me 154.5°, 172°; 5-NO₂-2 : 4-Me₂ 182°, 185—186°. *o*-Anisic acid 98°, 213—215°; *p*-anisic acid 106—107°, 243—245°.

CH. ABS.

Synthesis of 6- β -*d*-glucosidokojic acid. R. M. HANN (J. Amer. Chem. Soc., 1934, 56, 485—486).—Acetobromoglucose, kojic acid, and EtOH-KOH in CHCl₃ give 5- β -tetra-acetyl-*d*-glucosidoxy-2-hydroxymethyl-1 : 4-pyrone, m.p. 201° (corr.), $[\alpha]_D^{25} -88.3^\circ$ in CHCl₃, de-acetylated (MeOH-NaOMe in cold CHCl₃) to 5- β -*d*-glucosidoxy-2-hydroxymethyl-1 : 4-pyrone (5- β -*d*-glucosidokojic acid), m.p. 197—198° (corr.), $[\alpha]_D^{25} -107.3^\circ$ in H₂O.

H. B.

Natural coumarins. X. Synthesis of osthol. E. SPATH and H. HOLZEN (Ber., 1934, 67, [B], 264—265; cf. A., 1933, 614).—2-Hydroxy-4-methoxybenz-

aldehyde is transformed by successive treatment with Na in C_6H_6 at 80° and γ -methyl- Δ^2 -butenyl bromide into 2-hydroxy-4-methoxy-3- γ -methyl- Δ^2 -butenylbenzaldehyde, b.p. $118-122^\circ/0.6$ mm., converted by NaOAc and Ac_2O at $155-160^\circ$ into 7-methoxy-8- γ -methyl- Δ^2 -butenylcoumarin, m.p. $82-83^\circ$, identical with osthol (I). Immediately after distillation (I) has m.p. $62-63^\circ$, but passes slowly when preserved, rapidly when heated at $50-60^\circ$ and seeded or crystallised from ligroin or Et_2O , into the modification, m.p. $83-84^\circ$.

H. W.

Synthesis of dihydro-osthol from a degradation product of rotenone. E. SPATH, S. TAKEI, and S. MIYAJIMA (Ber., 1934, 67, [B], 262-263).—2-Hydroxy-4-methoxy-3- γ -methylbutylbenzoic acid (tetrahydrotubaic acid Me ether) is decarboxylated at $220-230^\circ/vac.$ to 3-methoxy-2- γ -methylbutylphenol (tetrahydrotubanol Me ether), b.p. $120^\circ/7$ mm., converted by malic acid (I) and conc. H_2SO_4 into 7-methoxy-8- γ -methylbutylcoumarin (dihydro-osthol), m.p. $85-85.5^\circ$, identical with the substance obtained by hydrogenation of osthol (Pd-C in AcOH). 1:3-Dihydroxy-2- γ -methylbutylbenzene and (I) give 8- γ -methylbutylumbelliferone in poor yield. H. W.

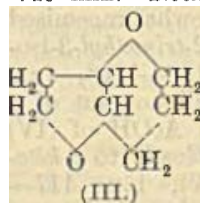
Constitution of tannins. I. Reduction products of chalcones and the synthesis of a typical phlobatannin. A. RUSSELL (J.C.S., 1934, 218-221).—Gallacetophenone 3:4-Me₂ ether (I) with piperonal affords 2-hydroxy-3:4-dimethoxy-3':4'-methylenedioxy-chalkone, m.p. 175° . Similarly (I) and p -OH- C_6H_4 -CHO give 2:4'-dihydroxy-3:4-dimethoxychalkone, m.p. 106° . Gallacetophenone Me₂ ether and anisaldehyde afford 2:3:4:4'-tetramethoxychalkone (II), m.p. 94° . 2-Hydroxy-3:4:4'-trimethoxychalkone in boiling EtOH-AcOH containing Zn during 1 hr. affords 4-hydroxy-7:8:4'-trimethoxyflavan, decomp. $> 85-95^\circ$. Similarly prepared, 4-hydroxy-7:8:3':4'-tetramethoxy-, 4-hydroxy-7:8-dimethoxy-3':4'-methylenedioxy-, and 4:4'-dihydroxy-7:8-dimethoxy-flavan have m.p. $90-110^\circ$, $110-125^\circ$, and $120-125^\circ$, respectively. These flavans closely resemble the methylated natural phlobatannins. Reduction of chalkone (as above), 4'-hydroxychalkone, and (II) gives compounds, m.p. 192° , $204-205^\circ$, and 168° , respectively. Resacetophenone dibenzoate and protocatechualdehyde dibenzoate in dry EtOAc containing HCl at 0° during many hr. afford, after treatment with boiling KOH, 2:4:3':4'-tetrahydroxychalkone, m.p. 212° [identical with butein (cf. J.C.S., 1904, 85, 1459; A., 1912, i, 30)], reduced (Zn-AcOH) to 4:7:3':4'-tetrahydroxyflavan (or the 4:4-bis-compound), indistinguishable from natural phlobatannins. J. L. D.

Synthetic experiments with methyltrihydroxybenzenes. I. Synthesis of 2:6-dimethylpolyhydroxyflavones. S. FUJISE and S. MITUI (Bull. Chem. Soc. Japan, 1934, 9, 24-26).—2:4-Dimethylphloroglucinol with piperonylacrylyl chloride and $AlCl_3$ gives 5:7-dihydroxy-3':4'-methylenedioxy-6:8-dimethylflavone, m.p. 207° (chalkone, m.p. 222° —carbethoxyferulyl chloride yields the -3-methoxy-4'-hydroxy-flavone, m.p. $254.5-255.5^\circ$). Absorption spectra are given. F. R. S.

Pigments of the benzopyrylium type. II. Absorption spectra of flavylum chlorides. K.

HAYASHI (Acta Phytchim., 1933, 7, 143-168; cf. A., 1933, 832).—Absorption curves were obtained for the following flavylum chlorides prepared by cold hydrolysis of the 5-Bz derivatives with 10% aq. NaOH: 5:7-dihydroxy-, 5:7-dihydroxy-2'-methoxy- (+2H₂O), 5:7:3'- and 5:7:4'-trihydroxy-, 5:7-dihydroxy-2':4'-dimethoxy-, m.p. $> 290^\circ$ (+H₂O), 5:7:4'-trihydroxy-3'-methoxy-, m.p. $> 290^\circ$ (+1.5H₂O), 5:7-dihydroxy-3':4'-methylenedioxy-, not decomp. $< 290^\circ$ (+1.75H₂O), 5:7-dihydroxy-2':5'-dimethoxy-, m.p. $< 290^\circ$ (+1.75H₂O), 5:7-dihydroxy-2':6'-dimethoxy-4'-methyl-, brown prisms (+H₂O), orange needles (+1.75H₂O), m.p. $< 270^\circ$, 5:7-dihydroxy-2':3':4'-trimethoxy- (+0.5H₂O), decomp. $< 260^\circ$, 5:7-dihydroxy-3':4':5'-trimethoxy- (+2H₂O), m.p. $> 270^\circ$, 5:7-dihydroxy-2':4':6'-trimethoxy- (+2.5H₂O), not decomp. at 270° , 5:7-dihydroxy-2':4':5'-trimethoxy- (+1.5H₂O), decomp. 260° , 5:7-dihydroxy-2':3':4':6'-tetramethoxy- (+3H₂O), decomp. $> 270^\circ$, 3:5:7:4'-tetrahydroxy- (+H₂O), 3:5:7-trihydroxy-4'-methoxy- (5-Bz derivative from ω -acetoxy-4-methoxyacetophenone, m.p. $60-61^\circ$). The observations on the influence of OH-substitution in the Bz compounds are here confirmed. A band at frequency 3000-3300 is characteristic of 4'-substitution (OH or OMe), but may be neutralised by 3'-substitution. Other bands are sp. for 2':5'-dimethoxy- (or methylenedioxy-) and pelargonidin derivatives. J. H. B.

Hydrogenation and hydrogenolysis of furan derivatives. H. E. BURDICK and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 438-442).— β -2-Furyl aldehyde (I) is reduced [H_2 (100-200 atm.), Nikelselguhr catalyst (a), 160°] to 2-ethyltetrahydrofuran (3%), b.p. $105-107^\circ/740$ mm., γ -2-tetrahydrofurylpropyl alcohol (II) (38%), b.p. $105-106^\circ/10$ mm., 221-224 $^\circ/741$ mm., and 1:5-dioxactahydroindene (III) (33%), b.p. $49-50^\circ/10$ mm., $156-157^\circ/740$ mm.



Reduction [H_2 , Raney Ni (b), EtOH at 23°] of (I) affords β -2-furylpropionaldehyde (IV) (46%), b.p. $69-70^\circ/14$ mm., $179-180^\circ/740$ mm., and some γ -2-furylpropyl alcohol, b.p. $93^\circ/10$ mm. (II) and (III) are also produced from (IV) (method a). Small amounts of (III) are also formed from (I) using Cu-Cr oxide in EtOH; at 200° (no solvent) (II) (22%), n -heptyl alcohol (4%), heptane- $\alpha\delta$ -diol (V) (29%), b.p. $127-130^\circ/6$ mm., and heptane- $\alpha\eta$ -diol (VI) (20%), b.p. $148-149^\circ/11$ mm., are produced. (V) and (VI) are further reduced (method b at 250°) to hexan- γ -ol, b.p. $130-132^\circ/740$ mm., and n -pentane (21%), respectively; (II) similarly affords H_2O , n -pentane (1%), and 2-ethyl- (60%) and 2- n -propyl-tetrahydrofuran (1%), b.p. $132-133^\circ/739$ mm. (also prepared by reduction of Mg γ -2-tetrahydrofurylpropyl chloride). Furfurylidene acetate is reduced (method a) to 2-methyltetrahydrofuran (10%), b.p. $78-79^\circ/740$ mm., tetrahydrofurfuryl acetate (41%), b.p. $88-90^\circ/18$ mm., $192-194^\circ/740$ mm., and tetrahydrofurfurylidene acetate (24%), b.p. $134-136^\circ/16$ mm. (lit. $133^\circ/29$ mm.). Similarly, furfuryl alcohol gives 85% of tetrahydrofurfuryl alcohol, b.p. $80-82^\circ/20$ mm.; fur-

furoin affords a mixture of $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-2-tetrahydrofurylethanes (Kaufmann and Adams, A., 1924, i, 197); furfurylideneacetone yields 89% of γ -hydroxy- α -2-tetrahydrofurylbutane, b.p. 95°/6 mm.; furfurylideneacetophenone furnishes γ -phenyl- α -2-tetrahydrofurylpropane (VII) (31%), b.p. 160°/28 mm., and its γ -OH-derivative (25%), b.p. 177—181°/12 mm.; (VII) gives γ -cyclohexyl- α -2-tetrahydrofurylpropane, b.p. 121—122°/6 mm., 150—151°/28 mm.; Et β -2-furylacrylate, b.p. 132—133°/18 mm., yields Et β -2-tetrahydrofurylpropionate, b.p. 115—116°/18 mm.; (III) affords some (II).

(III) and 48% HBr give (probably) 3-bromo-2- γ -bromopropyltetrahydrofuran, b.p. 142°/5 mm., which with Zn-Cu and aq. EtOH regenerates (III). (III) and HI afford a compound, $C_7H_{12}OI_2$, m.p. 45°. γ -2-Furylallyl alcohol has b.p. 85—87°/4 mm. (cf. Bray and Adams, A., 1927, 973). H. B.

Piperidine metavanadate.—See this vol., 375.

Electrolytic oxidation of piperidine.—See this vol., 373.

Introduction of pyridine into the inner sphere of quadrivalent platinum. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Ann. Inst. Platine, 1933, No. 11, 63—71).—The product of reaction of $enPtCl_4$ (I) and C_5H_5N at room temp. is $[enCl_4Pt](C_5H_5N)_2$ and not, as Schleicher *et al.* (A., 1923, i, 1120) supposed, $[en(C_5H_5N)_2Cl_2Pt]Cl_2$; at 100° the product is $[enCl_3(C_5H_5N)Pt]Cl$. Schleicher *et al.* based their supposition on the observation that the salt obtained by treating (I) successively with C_5H_5N and en had the composition en_2PtCl_4 ; in reality, a 1 : 1 mixture of en_2PtCl_4 and $enPtCl_4$ is obtained. R. T.

Derivatives of 2-aminopyridine. K. FEIST [with W. AWE, J. SCHULTZ, and F. KLATT] (Arch. Pharm., 1934, 272, 100—113).—2-Aminopyridine (I), m.p. 57° (modified prep.; dibromide, m.p. 195—197°), with o -OH- C_6H_4 ·CHO (0.5 mol.) in cold EtOH (not with other proportions or in presence of dehydrating agents) gives the salicylidene derivative, m.p. 65° (dibromide, m.p. 170°; blue $FeCl_3$ colour), which is hydrogenated (Pd-black) in Et_2O to the N - o -hydroxybenzyl derivative, m.p. 105° (picrate, m.p. 185°; $HgCl_2$ -derivative, +6H₂O, m.p. 134°; does not give a colour with $FeCl_3$ and thus probably exists in the betaine form). (I) with CCl_3 ·CHO (II) (1.5 parts) in cold $CHCl_3$ yields 2-pyridyl-($\beta\beta$ -trichloro- α -hydroxyethyl)amine (III), m.p. 106°, but with 0.75 part of (II) in $CHCl_3$ without cooling gives $\alpha\alpha\alpha$ -trichloro- $\beta\beta$ -di-(2-pyridylamino)-ethane, CCl_3 ·CH(NH- C_5H_4N)₂, m.p. 172° (lit. 160°) [picrate, m.p. 185° (decomp.)], also obtained from (III) at 110°. When heated with the appropriate thiocarbimide (I) gives substituted 2-pyridylthiocarbamides, C_5H_4N ·NH·CS·NHR, in which R is *allyl*, m.p. 98°, b.p. 201—205°/18 mm. (picrate, m.p. 144°), *Me*, m.p. 146°, and *Bu* ^{β} , m.p. 97°, whence by NaOH-EtOH-Pb(OAc)₂-H₂O were obtained the corresponding carbamides, m.p. 102°, 148°, and 102°, respectively. *N*-Phenyl-*N'*-2-pyridylcarbamide, m.p. 187° (lit. 180°), was similarly prepared. (I) and CS₂ in cold Et_2O yield slowly an iso-form, m.p. 147°, of *s*-di-2-pyridylaminothiocarbamide; this and its isomeride, m.p. 163°, give the same carbamide, m.p. 175°, and thus are probably

CS(NH· C_5H_4N)₂ and C_5H_4N ·NH·C(SH)·N· C_5H_4N , or *vice versa*. ω -Chloro-3 : 4-dihydroxyacetophenone, m.p. 173°, and (I) (2 mols.) in hot EtOH give 3 : 4-dihydroxy- ω -2-pyridylaminoacetophenone, an unstable oil with no sympathomimetic action [hydrochloride, +4H₂O, decomp. 300° after darkening at 250°, and anhyd.; picrate, m.p. 231° (decomp.); $HgCl_2$ -derivative, +17H₂O, m.p. 209° after sintering at 190°, and anhyd.; sulphate, sinters at 160°; Ac₂ derivative, cryst. (hydrochloride, +2H₂O, m.p. 199° after previous sintering, and anhyd.)], which is hydrogenated (Pd-C) to 2-(β -hydroxy- β -2' : 4'-dihydroxyphenylethylamino)pyridine (hydrochloride, m.p. 300—301°). 2 : 3 : 4-Trihydroxy- ω -2-pyridylaminoacetophenone, an unstable oil [hydrochloride, +H₂O, m.p. 265° after sintering, and anhyd.; picrate, m.p. 190° (decomp.); $HgCl_2$ -derivative, +8H₂O, m.p. 231°, and anhyd.], was similarly prepared. R. S. C.

Acyl derivatives of polymeric indoles and [precaution in] determination of active hydrogen. O. SCHMITZ-DUMONT and K. HAMANN (J. pr. Chem., 1934, [ii], 139, 167—179).—Treatment of polymeric indoles (I) with acid anhydrides or chlorides gives α - (II) or β -acyl derivatives (III); (III) are generally formed at higher temp., but not by rearrangement of (II). (II) contain 1 active H < (I) and are true *N*-acyl derivatives, being readily hydrolysed to (I) by hot aq. EtOH-KOH. (III) are produced without loss of active H and with certain exceptions (e.g., the β -Ac and Bz derivatives of tri-indole) do not regenerate (I) with alkali; they do not seem to be *C*-derivatives, however, as they do not give CO reactions, even with MgMeI. Many of these derivatives are, however, affected by MgMeI, and Zerevitinov determinations need to be conducted with care, and should be checked by regeneration of the compound. The following are described: α -Ac, m.p. 158.5°, α -CO₂Et, m.p. 130—131°, α -Bz, m.p. 178—179°, β -Bz, m.p. 197—198°, and (? α)p- C_6H_4 MeSO₂, m.p. 186—187°, derivatives of di-indole; α -Bz, m.p. 212°, α -CO₂Et, m.p. 155—156°, and α -p- C_6H_4 MeSO₂, m.p. 188—189°, derivatives of diskatole; and β -carbethoxytri-indole, m.p. 163—164°. H. A. P.

Derivatives of 8-aminoquinoline as anti-malarials. III. Influence of branching of the chain in position 8. O. J. MAGIDSON, N. M. DELEKTORSKAYA, and I. M. LIPOVITSCH (Arch. Pharm., 1934, 272, 74—84; cf. this vol., 82).—Branching of the chain in position 8 in five cases greatly depresses the toxic index of this type of substance. 8-Amino-6-methoxyquinoline (I), NaNH₂, and isoamyl bromide in Et_2O give the 8-isoamyl-amino- and 8-diisoamylamino-derivatives, b.p. 163—165°/4 mm. and 172—183°/4 mm., respectively (hydrochlorides, m.p. 205° and 136—138.5°, respectively). (I) with NEt₂·CH₂·CH₂Cl, HCl at 125—130° gives the 8- β -diethylaminoethylamino-derivative, b.p. 197—203°/4 mm., D_{tol}/D_{cur} = 6. Et α -bromoiso-valerate, NHEt₂, and NaI (not without NaI or with Cu, with or without solvents) at 60° give slowly Et dimethylacrylate and Et α -diethylaminoisovalerate, b.p. 80—85°/10—11 mm., reduced (Na-EtOH) to β -diethylaminoisoamyl alcohol, b.p. 87—93°/14 mm., which with SOCl₂ in $CHCl_3$ gives the chloride, b.p.

85—88°/14 mm., the hydrochloride of which with (I) at 125—130° gives 8-N- β -diethylaminoisoamylamino-6-methoxyquinoline, b.p. 198—205°/1 mm., $D_{\text{tol.}}/D_{\text{cur.}}=4$. isoAmylene and cold aq. $\text{Ca}(\text{OCl})_2$ give α -chloro- γ -methylbutan- β -ol (35% yield), b.p. 140—145°, which with boiling aq. NH_4Et_2 gives α -diethylamino- γ -methylbutan- β -ol (39% yield), b.p. 181—184°. α -Nitro- γ -methylbutan- β -ol (obtained in 70% yield from MeNO_2 and Pr^iCHO), b.p. 78—82°/2—3 mm., with Al-Hg and EtOH (not Zn-AcOH) (8% yield), Zn and HCl (41% yield), or Fe and HCl (53% yield) gives α -amino- γ -methylbutan- β -ol, b.p. 79°/6—7 mm., m.p. 34—35° (oxalate, m.p. 223°; carbonate, cryst.), which yields the α -diethylamino-alcohol, b.p. 181—184°/760 mm., 84—88°/24 mm., and thence by SOCl_2 in C_6H_6 β -chloro- α -diethylamino- γ -methylbutane, b.p. 70—72°/12 mm. The hydrochloride of the last-mentioned base and (I) at 125—130° give 8-(α -diethylaminomethyl- β -methylpropylamino-6-methoxyquinoline, b.p. 187—191°/3 mm., non-curative. α' -Bromoneopentanol, b.p. 184—187° (obtained from the Ac derivative by KOH -EtOH, not by NH_4Et_2), and NH_4Et_2 at 140—150° form the α' - NEt_2 -compound, b.p. 88—89°/8 mm. (41% yield), giving with SOCl_2 in hot C_6H_6 α -chloro- α' -dimethylaminoneopentane, b.p. 69—71°/11 mm., the hydrochloride, m.p. 105°, of which with (I) at 125—130° gives 8- γ -diethylaminoneopentylamino-6-methoxyquinoline, b.p. 196—200°/1—1.5 mm., $D_{\text{tol.}}/D_{\text{cur.}}=2$ (hydrochloride, an oil; meconate, m.p. 134—136°). *N*-Diethyl-leucine Et ester gives (Na-EtOH) a 75% yield of β -diethylamino-8-methylpentan- α -ol, which led to the chloride, b.p. 69—75°/15 mm. (hydrochloride, cryst.), and 8- β -diethylamino-8-methyl-*n*-amylamino-6-methoxyquinoline, b.p. 200°/1.5 mm., $D_{\text{tol.}}/D_{\text{cur.}}=4$ [meconate, m.p. 153—154° (decomp.)]. R. S. C.

Hydroxyquinolines. I. Iodo-derivatives of 8-hydroxyquinoline. F. PIRRONI and A. CHERUBINO (Atti R. Accad. Lincei, 1933, [vi], 18, 311—313).—Treatment of boiling EtOH solution of 8-hydroxyquinoline (I) with I in EtOH yields the hydriodide of (I), m.p. 174—175° (decomp.), and 5-iodo-8-hydroxyquinoline, m.p. 114—116° or 124—126° (+aq.), which forms a hydrochloride, m.p. 206—208° (decomp.), picrate, m.p. 162—163°, sulphate, m.p. 208—209°, 1-MeI derivative, m.p. 136—137°, pale yellow Cu and greenish-yellow Ni salts (cf. Matsumura, A., 1927, 467). T. H. P.

isoQuinoline derivatives. III. isoQuinoline-3-carboxylic acids. H. J. HARWOOD and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 468—469).—Me α -benzamido- β -3:4-dimethoxyphenylpropionate (Hartmann and Kagi, A., 1923, i, 604) and P_2O_5 in boiling xylene give the Me ester (I), m.p. 120.5—121.5°, of 6:7-dimethoxy-1-phenyl-3:4-dihydroisoquinoline-3-carboxylic acid (II) [the Et ester, an oil, is similarly prepared from Et α -benzamido- β -3:4-dimethoxyphenylpropionate, m.p. 100—101°, which is obtained by reduction (H_2 , PtO_2) of Et veratrylidene-*n*-appurate, m.p. 118—119°]. (II) heated in C_6H_6 gives 6:7-dimethoxy-1-phenyl-3:4-dihydroisoquinoline, m.p. 10.5—121.5°, also obtained from benz- β -3:4-dimethoxyphenylethylamide, m.p. 90—91°, and POCl_3 in IhMe . Successive treatment of (II) with SOCl_2

and MeOH affords the Me ester (III), m.p. 172—173°, of 6:7-dimethoxy-1-phenylisoquinoline-3-carboxylic acid, m.p. 216—216.5° (the β -diethylaminoethyl ester, m.p. 158.5—159°, is similarly prepared). (III) is also formed when (I) is oxidised by Pictet and Kay's method (A., 1909, i, 513). Successive treatment of (II) with PCl_5 (in C_6H_6) and MeOH gives (I).

H. B.

Synthesis of cincophens [2-phenylquinoline-4-carboxylic acids] from phenacylideneoxindoles. R. N. DUPUIS and H. G. LINDWALL (J. Amer. Chem. Soc., 1934, 56, 471—472).—3-Phenacylideneoxindole (A., 1933, 164) is converted by warm aq. EtOH-HCl into 2-phenylquinoline-4-carboxylic acid (4'-Cl-, m.p. 243—245°, 4'-Br-, and 4'-Me derivatives, all similarly prepared). H. B.

Quinoline derivatives. XLIII. α -Alkylated *p*-2-quinolylanilinoacetic acids. H. JOHN (J. pr. Chem., 1934, [ii], 139, 183—188).—*p*-2-Quinolylanilinoacetic acid, m.p. 218° (Me, m.p. 152°, and Et, m.p. 144°, esters), is prepared by gradual addition of aq. CH_2O to NaCN and 4'-amino-2-phenylquinoline (I) in abs. EtOH. It is decarboxylated at > its m.p. to 2-*p*-methylaminophenylquinoline, m.p. 82° (hydrochloride, m.p. 186°). The following are prepared from (I) and the appropriate α -Br-acid at 140°: α -*p*-2-quinolylanilino-propionic, m.p. 215—217° (Et ester, m.p. 86°; 2-*p*-ethylaminophenylquinoline, m.p. 110°), -*n*-, m.p. 187°, and -iso-butyric, m.p. 192—195°, -*n*-, m.p. 163—165° (Et ester, m.p. 108°), and -iso-valeric, m.p. 180—182°, and -stearic acid, m.p. 127—128° (Et ester, m.p. 65°).

H. A. P.

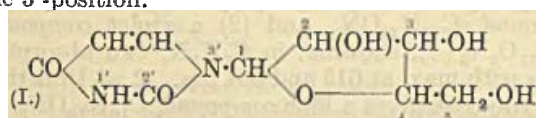
Quinoline derivatives. XLIV. Synthesis of α -aryl-*p*-2-quinolylanilinoacetic acids. H. JOHN and (in part) E. PIETSCH. XLV. Derivatives of 2-phenyl-4-quinolylaminoacetic acid. H. JOHN and G. BEHMEL (J. pr. Chem., 1934, [ii], 139, 237—241, 284—288).—XLIV. By the action of the appropriate aldehyde and NaCN on 2-*p*-aminophenylquinoline (this vol., 304) in EtOH and hydrolysis (without isolation) of the nitrile are obtained: *p*-2-quinolylanilino-phenyl-, m.p. 178—180° (Et ester, m.p. 173°), -*p*-tolyl-, m.p. 158—162° (Et ester, m.p. 95°), and -*p*-isopropylphenyl-, m.p. 102—105°, -acetic acid, α -(*p*-2-quinolylanilino)- β -phenylpropionic acid, m.p. 120°, and - γ -phenyl-*n*-butyric acid, m.p. 170—190°, all of the type $\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{N}=\text{C}(\text{C}_6\text{H}_4)\text{NH}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$.

XLV. By usual methods the following derivatives of 2-phenyl-4-quinolylaminoacetic acid (A., 1933, 165) are obtained: *Pr*^a, m.p. 91°; *Bu*^a, m.p. 74.5°; *Bu* ^{β} , m.p. 105°; isoamyl, m.p. 76°, and *Ph*, m.p. 108°, esters: benzylamide, m.p. 187°; *p*-phenetidide, m.p. 127°; α -pyridylamide, m.p. 233°, and piperidide, m.p. 189—190°. J. W. B.

ψ -Bases. IV. Mechanism of formation of bimolecular ethers from ψ -bases. Aromatic nature of heterocyclic compounds. J. G. ASTON and P. A. LASSELLE (J. Amer. Chem. Soc., 1934, 56, 426—433).—The rates of formation of bimol. ethers from 1-methyl- (I) and 1:2-dimethyl-quinolinium hydroxides (from the corresponding iodides and aq. NaOH) are determined at 25° by a conductometric

method (A., 1931, 742); they are proportional to the product of the squares of the concns. of quinolinium and OH ions. Reaction occurs much faster with (I). The formal heat of activation for the reaction with (I) is calc. from measurements at 33.8° to be 10,420 g.-cal. 1:2-Dimethylpyrazolinium and 1:2-dimethylpyridinium hydroxides are strong electrolytes; the conductivity of solutions does not change appreciably at 25°, indicating the absence of ether formation. Decreased conjugation of the ring system favours ether formation. 1:2-Dimethylpyrazolinium iodide appears to be new. H. B.

N-Methyluridine and its bearing on the structure of uridine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1934, 104, 385—393).—The 1'-position of the uracil residue in uridine (I) is shown to be vacant, so that the ribose residue is attached at the 3'-position.

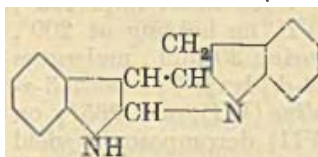


CPh₃Cl and (I) in C₅H₅N give 5-triphenylmethyluridine, m.p. 200°, [α]_D²⁵ +9.5° in COMe₂, +18.8° in MeOH (cf. Brederick, A., 1933, 149), the 2:3-Ac₂ derivative, a glass, [α]_D²⁷ +50.9° in MeOH, of which gives with CH₂N₂ in Et₂O 2:3-diacetyl-5-triphenylmethyl-N-methyluridine (II), glassy flakes, [α]_D²⁵ +55.3° in MeOH. Hydrolysis of (II) with Ba(OMe)₂ in MeOH gave N-methyl-5-triphenylmethyluridine, m.p. 173—174°, [α]_D²⁷ +17.1° in COMe₂. (II) and 0.5% HCl in MeOH give N-methyluridine, m.p. 108—110°, [α]_D²⁵ +16.5° in H₂O, hydrolysed by 10% H₂SO₄ to l-methyluracil, m.p. 174—175°, identical with a specimen prepared from 6-hydroxy-2-ethylthiol-1-methylpyrimidine (Johnson and Heyl, A., 1907, i, 728). W. S.

Polymembered cyclic compounds. VIII. cycloDitridecamethylenedi-imine and preparation of hexamethyleneimine. A. MÜLLER [with E. RÖLZ and M. WIENER] (Ber., 1934, 67, [B], 295—300; cf. A., 1932, 1262).—Erucic acid (improved prep.) is treated with conc. HNO₃ and the mixture of acids is esterified, thereby giving Me brassylate, which is reduced by Na and EtOH to tridecane-α-diol, m.p. 74°, whence α-dibromotridecane (I). Treatment of (I) and p-C₆H₄Me·SO₂·NH₂ with KOH in boiling KOH-EtOH leads to di-p-toluenesulphonyl-cycloditridecamethylenedi-imine (II), m.p. 163°, α-di-p-toluenesulphonamido-n-tridecane (III), m.p. 92° (corr.), and (?) p-toluenesulphonimidocyclotridecamethylene. (II) is hydrolysed by conc. HCl at 155° to cycloditridecamethylenedi-imine, NH<[CH₂]₁₃>NH, b.p. 183—185° (bath)/0.01 mm., m.p. about 52° [hydrochloride; aurichloride; picrate; Bz₂, m.p. 95° (corr.), and (SO₂Ph)₂, dimorphous, m.p. 122.2° (corr.) after softening at about 111° and m.p. about 111° derivatives]. (III) is hydrolysed to α-diamino-n-tridecane (IV), b.p. 172—173°/9 mm., m.p. 51° (corr. vac.) [di-p-toluenesulphonate, m.p. 198° (corr.); aurichloride, decomp. about 150° after softening; platinchloride, decomp. about 225°; picrate, m.p. 145—146°

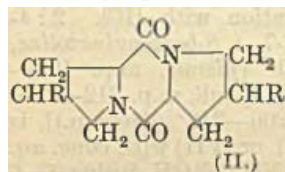
(corr.); Bz₂ derivative, m.p. 124—125° (corr.); hydrochloride, decomp. 321—324°; n-tridecane-α,α-diphenylthiocarbamide, m.p. 118—119° (corr.)]. (IV) is also obtained from α-phthalimido-n-tridecane, m.p. 102—103° (corr.). H. W.

Pyrrole-indole group. Series II. XVIII. Polymerisation of indole, and constitution of di-indole. B. ODDO (Gazzetta, 1933, 63, 898—907).—



A summary of work on polymerides of indoles, with new interpretations the introduction of Ac and NO groupings. Oddo's formula for di-indole (annexed; cf. A., 1913, i, 755) is preferred to that of Schmitz-Dumont (A., 1933, 959). E. W. W.

Grignard reaction on l-proline, l-hydroxyproline ester, and diketopiperazines. J. KAPPHAMMER and A. MATTHES (Z. physiol. Chem., 1934, 223, 43—52).—L-Proline Et ester (I), m.p. 78°, on keeping over H₂SO₄ in vac. or after 24 hr. at 177°, gives l-proline anhydride (II; R



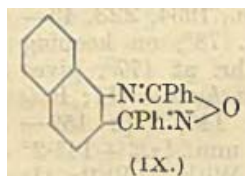
H), m.p. 146, b.p. 152—153°/0.16 mm., [α]_D¹⁵ —147.2° in H₂O. With MgPhBr, (I) affords pyrrolidyl-diphenylcarbinol, m.p. 83° (hydrochloride, m.p. < 240°; Bz derivative, m.p. 183°), with MgEtBr, pyrrolidyl-diethylcarbinol isolated as the hydrochloride, m.p. 158°. With MgPhBr, l-proline anhydride affords Ph (N-pyrrolidyl-diphenylmethyl)pyrrolidyl ketone (picrate, m.p. 174—175°). l-Hydroxyproline Et ester, b.p. 112—114°/1 mm. [hydrochloride (III), m.p. 147—148°], changes spontaneously into l-hydroxyproline anhydride (II; R=OH), m.p. 245—246° (decomp.), [α]_D¹⁸ —153.4° in H₂O. With MgPhBr, (III) affords hydroxy-pyrrolidyl-diphenylcarbinol, m.p. 187—188°; sarcosine anhydride (IV) yields methylaminoacetophenone (picrate, m.p. 145—146°, hydrochloride) and the sarcosyl derivative (picrate). With MgEtBr, (IV) gives 1:4-dimethyl-2:2:5:5-tetraethylpiperazine (picrate; hydrochloride). J. H. B.

Complex salts with 2:2'-dipyridyl.—See this vol., 379.

Action of benzoyl chloride on α-naphthylamine.

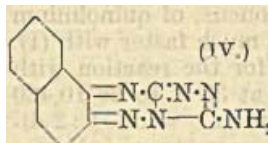
K. DZIEWONSKI and L. STERNBACH (Rocz. Chem., 1933, 13, 704—719).—α-C₁₀H₇·NH₂ (I) and BzCl yield on heating during 3—5 min. at 175—180° with anhyd. ZnCl₂ 1-benzamido-4-benzoylnaphthalene (II), m.p. 178° (2-Bz derivative, m.p. 224—226°), which on hydrolysis gives 4-benzoyl-α-naphthylamine, m.p. 105—106° (picrate, m.p. 142°); this, on diazotising and coupling with β-C₁₀H₇·OH, yields 4-benzoyl-1-naphthylazo-β-naphthol, m.p. 229°, and on coupling with PhN₂Cl yields 2-benzeneazo-4-benzoyl-α-naphthylamine, m.p. 209—210°, from which 4-benzoylnaphthylene-1:2-diamine (III), m.p. 198°, is prepared. (III) condenses with phenanthraquinone to yield phenanthrobenzoylnaphthazarin, m.p. 252—255°. The double salt, m.p. 310°, of ZnCl₂ and 2:4-diphenyl-7:8-benzo-3-α-naphthylquinazoline 3-chloride (IV) is obtained by heating the original reaction mixture from which (II)

was prepared during 2 hr. at 240°, by heating together (II), α -C₁₀H₇·NHBz, and ZnCl₂ at 180°, or by heating a mixture of iso-1-benzamido-2-benzoylnaphthalene (V) (prepared as below), m.p. 161—162°, and ZnCl₂ at 180°. The double salt yields with boiling aq.-alcoholic KOH 4-hydroxy-2:4-diphenyl-7:8-benzo-3- α -naphthyl-3:4-dihydroquinazoline (VI), m.p. 184° [hydrochloride, m.p. 209°; 4-Et ether, m.p. 224° (hydrochloride, m.p. 292°); 4-Me ether, m.p. 193°; picrate, m.p. 260—261°]. (VI), on heating at 200°, or on boiling with PhNO₂ during 30 min., undergoes conversion into 2-hydroxy-2:4-diphenyl-7:8-benzo-3- α -naphthyl-3:4-dihydroquinazoline (VII), m.p. 265°; on acid hydrolysis (VI) and (VII) decompose to yield (V) and (I). (V), on heating with aq.-alcoholic KOH during 10 hr. at 170°, yields 2-benzoyl- α -naphthylamine, b.p. 263—265°/14 mm. [picrate, m.p. 200—201°; N-Ac, m.p. 194—195°; N-Bz derivative, m.p. 202° [oxime, m.p. 211° (decomp.)]; oxime (VIII), m.p. 178°]. AcOH solutions of (VIII) yield the substance (IX), m.p. 186—189° (HgCl₂ salt, m.p. 209°), on saturation with HCl. 2:4-Diphenyl-7:8-benzoquinazoline, m.p. 160° [picrate, m.p. 168—170°; HgCl₂ salt, m.p. 212—215° (decomp.)]; ZnCl₂ salt, m.p. 206—212° (decomp.), is prepared by boiling (IV), (VI), or (VII) with conc. aq. NH₃, or by heating (V) with NH₃-EtOH during 4—6 hr. at 180°.



Guanazole. R. STOLLE and W. DIETRICH (J. pr. Chem., 1934, [ii], 139, 193—210).—Guanazole, $\text{N} \begin{smallmatrix} \text{C}(\text{NH}_2)_2 \cdot \text{NH} \\ \text{C}(\text{NH}_2)_2 \cdot \text{N} \end{smallmatrix}$, and tautomeric forms (I) [Ac₂, not melting at 300°, Bz₂, sinters 295°, m.p. 300° (decomp.), and monobenzylidene, m.p. 234°, derivatives; dinitrate, decomp. 145°] with 1 mol. of C₅H₁₁·O·NO (II) in EtOH gives its 3-NO-derivative, decomp. 172°, but 2 mols. of (II) in HCl-EtOH afford the 3:5-(NO)₂-derivative, decomp. 187°, reduced (SnCl₂-HCl) to the hydrochloride, m.p. 217° (decomp.), of 3-amino-5-hydrazino-1:2:4-triazole (III); this with PhCHO gives 5-benzylidenehydrazino-3- α -hydroxybenzylamino-1:2:4-triazole, m.p. 232° (previous sintering), with loss of H₂O (best at 139°/vac.), to give the 3:5-dibenzylidene derivative, m.p. 232°, of (III). With NaNO₂ at 0° (III), as its hydrochloride, gives 5-azido-3-nitrosoamino-1:2:4-triazole, detonates at 134°, isomerised by 2N-HCl to the 5-azido-3-diazonium chloride, which couples with β -C₁₀H₇·OH to give 5-azido-3-(β -hydroxynaphthyl-1-azo)-, m.p. 195° (decomp.), and with NPhMe₂ to give 5-azido-3-p-dimethylaminobenzeneazo-, decomp. 185°, -1:2:4-triazole. Diazotisation of (I) affords a mixture containing the 3-NH₂-5-diazonium chloride (30%), the 3:5-bisdiazonium chloride (60%), and, by decomp., 3:5-dichloro-1:2:4-triazole, m.p. 148°, and the hydrochloride, m.p. 112°, decomp. 130°, of 5-chloro-3-amino-1:2:4-triazole, since by coupling with PhOH 3:5-di-p-hydroxybenzeneazo-, m.p. 270° (decomp.) [OO-Ac₂-derivative, m.p. 235° (4-N-Ac-derivative, m.p. 167°)], and 3-amino-5-p-hydroxybenzeneazo- + H₂O and anhyd., m.p. 260° (decomp.) (hydrochloride + H₂O, decomp. 240°), -1:2:4-triazole are isolated. With bleaching-powder solution

at 0° (I) affords 3:5-dichloroimino-3:5-dihydro-1:2:4-triazole, detonates at 135°, which when boiled with EtOH- β -C₁₀H₇·NH₂ gives a dye, m.p. 285° (decomp.), the structure of which (IV) is assigned. With PbO in boiling EtOH thiosemicarbazide gives aminoguanazole (monobenzylidene derivative, m.p. 184°), identical with the product of Pellizzari *et al.* (A., 1908, i, 65).

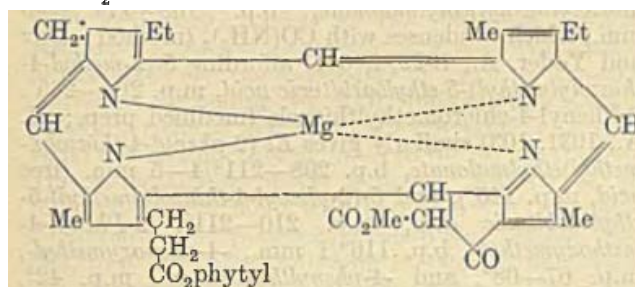


J. W. B. **Condensation products of isatin with pyrrole (pyrrole-blue).** P. PRATESI (Atti R. Accad. Lincei, 1933, [vi], 17, 954—960).—In boiling AcOH solution isatin gives no blue condensation product with 1-methyl-, 1-ethyl-, 1-phenyl-, 1-acetyl-, 2:5-dimethyl-, or 2:4:5-trimethyl-3-ethyl-pyrrole. 2:3-Dimethylpyrrole gives a blue, cryst. compound C₁₄H₁₂ON₂. 3-Methyl-4-ethylpyrrole yields (1) a blue compound, C₁₅H₁₄ON₂, and (2) a violet compound C₂₃H₁₇O₂N₃ (?), showing, in C₆H₅N, two absorption bands with max. at 613 and 564 m μ . 2:4-Dimethyl-3-ethylpyrrole gives a blue compound, C₁₆H₁₆ON₂.

T. H. P. **Chlorophyll. XL. Oxoporphyrins: structure of chlorophyll a.** H. FISCHER, J. RIEDMAIER and J. HASENKAMP. **XLI. Conversion of phaeoporphyrin a₅ into phaeoporphyrin a₆ and neophaeoporphyrin a₆.** H. FISCHER and J. HECKMAIE (Annalen, 1934, 508, 224—249, 250—262).—XL Pyrophaeophorbide a (improved prep. given) is degraded by cold HI-AcOH to (mainly) oxophylloerythrin, C₃₃H₃₂O₄N₄ [Me ester, m.p. 275° (dioxime haemin)], and some phylloerythrin (which is the sole product at 65°). Dihydrophaeophorbide a similarly gives phaeoporphyrin a₅; a little isophaeoporphyrin a₅ (A., 1933, 959) [now termed oxophaeoporphyrin a₅ (I) is formed when the reaction mixture is kept for several days. The oxime, m.p. 257°, of oxochlorophyllin Me₃ ester (*loc. cit.*) is readily converted (fusion; heating in C₆H₅N) into the oxime of the Me ester of (I). Allomerised (I in AcOH) phaeophorbide is degraded by HI-AcOH at 65° to neophaeoporphyrin a₆, phaeoporphyrin a₇, and rhodoporphyrin (II); i.e. the cold, oxorhodoporphyrin (III), C₃₂H₃₂O₅N₄ [Me ester, m.p. 274° (oxime, decomp. 268°)], is also formed (III) is also obtained when oxoneophaeoporphyrin a₆ is kept in 14% HCl for 24 hr.; oxophaeoporphyrin a₆ is probably an intermediate (oxidative fission) product. (III) is reduced (Wolff-Kishner) to (II) an reduced (KOH in a little EtOH) to hydroxyrhodoporphyrin. The products formed by similar degradation of the following compounds are quoted in parentheses: chlorin e (chloroporphyrin e₅ and oxochloroporphyrin e₅); chlorin e Me₃ ester (chloroporphyrin e₆ and oxochloroporphyrin e₆); 10-ethoxymethylphaeophorbide (oxophaeoporphyrin a₆); phaeopurpurins 7 and 18 [an oxoporphyrin spectroscopically identical with (III); the former gives a second oxoporphyrin]. The formation of the above oxo-derivatives is considered to involve the following reactions: CH₂:C <—> CH₂I·CH <—> CH₂I·Cl <—> OH·CH₂:C <—> OH·CH:C <—> CHO·C <—> C> is C₁ of the porphin structure.

The presence of CO in (native) methylphaeophorbide

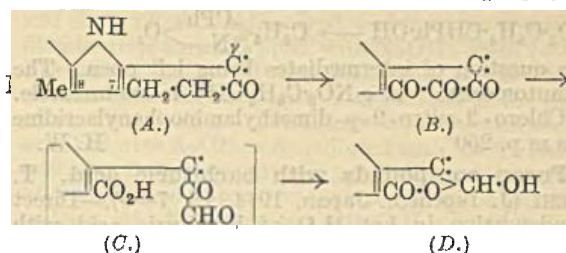
a is shown by the prep. of an *oxime* (IV), which is degraded by HI-AcOH at 65° to a small amount of phæoporphyrin *a*-oxime and hydrolysed (14% HCl) to phæophorbide. Oximation of methylchlorophyllide *a*+*b* in C_5H_5N , dilution with Et_2O , washing with H_2O and 6% HCl, and subsequent extraction with 14% HCl gives (IV). Structures are suggested for many of the above compounds. Chlorophyll *a* is assigned the following constitution; the position of the CH_2 is uncertain.



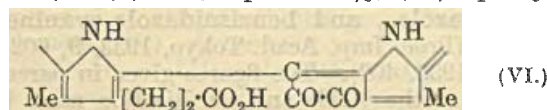
XLI. Phæoporphyrin *a*₅ (Me_2) ester (I) is oxidised (I, NaOAc, EtOH) to *acetylneophæoporphyrin a*₆ Me_2 ester (II), $C_{38}H_{40}O_4N_4$, m.p. 305° [*Cu* salt, m.p. 305° (decomp.)]; *p*-nitrobenzoate, m.p. 257°; *benzoate*, m.p. 292° (corr.)], which is also prepared from and hydrolysed (cold conc. H_2SO_4 in N_2) to *neophæoporphyrin a*₆ [and a little phæoporphyrin *a*₇ (III)]. Hydrolysis ($MeOH-KOH$ in $EtOH-C_5H_5N$) of (II) gives (mainly) *allophæoporphyrin a*₇ (IV). Oxidation (I, Na_2CO_3 , EtOH) of (I) affords phæoporphyrin *a*₆ Me_2 ester, which is hydrolysed (15% HCl) to *isophæoporphyrin a*₇ (V) and a little (IV). Methylphæophorbide *a*, I, and NaOAc in EtOH give allomerised *acetylphæophorbide a* Me_2 ester, decomp. about 300°, which is degraded (HI-AcOH at 65°) to (II). Prolonged treatment of chlorophyllin *e*₇ lactone Me_2 ester with cold oleum (30% SO_3) and subsequent esterification (CH_2N_2) affords the Me_3 ester of (IV); the Me_1 ester, I, and NaOAc in EtOH give (after esterification) the Me_3 ester of (III). The Me_3 ester of (V) and oleum afford (III). H. B.

Chlorophyll. XLII. Mesorhodin and its conversion into chlorophyll-porphyrins; oxidation of phyloerythrin. H. FISCHER and J. EBERSBERGER (Annalen, 1934, 509, 19—37).—Mesorporphyrin Me_2 ester (from hæmin) is converted by approx. 10% oleum into *mesorhodin* (I), $C_{34}H_{36}O_3N_4$ [*oxime*; *Me* ester, m.p. 269° (corr.) (*oxime*)], which is oxidised ($KMnO_4$, 10% NaOH, C_5H_5N) to chlorophyllin *e*₅ (II) (18%) [*Me*₁ ester; *Me*₂ ester (III), m.p. 288° (corr.) (*Fe* and *Cu* salts), prepared using $MeOH-HCl$; *Me*₂ ester, m.p. 286° (*Fe* and *Cu* salts), using CH_2N_2], rhodoporphyrin- γ -carboxylic acid (IV) (0.5%), and a crude “diketone” (about 1.5%). (II) and its derivatives are spectroscopically identical with “natural” chlorophyllin *e*₅ and its derivatives; mixed m.p. show depressions indicating that (I) and (II) are (probably) mixtures of isomerides. (III) is degraded by 30% $MeOH-KOH$ in C_5H_5N at 180° to pyrroporphyrin IX, indicating that (I) contains the group (A) and that oxidation to (II) (as D) proceeds through the triketone (B), which undergoes hydrolytic fission to (C) (this is then oxidised to the gly-

oxylic acid which subsequently loses CO_2). (II) is oxidised (O_2 in dil. HCl) to (IV) and rhodoporphyrin



(V), and reduced (HI-AcOH) to chlorophyllin *e*₄. (IV) and boiling HCO_2H give (V). (II) (as Me_1 ester) is reduced ($TiCl_3$, conc. HCl; absence of air) to *hydroxymethylrhodoporphyrinlactone*, $C_{34}H_{36}O_4N_4$, m.p. 250—256°, also prepared (with m.p. 256°) from chlorophyllin *e*₅ Me_1 ester (prepared from chlorin *e*). Phæoporphyrin *a*₇ is similarly reduced to chlorophyllin *e*₇-lactone. Oxidation (SeO_2 , EtOH) of phyloerythrin gives hydroxyphyloerythrin and *phyloerythrin diketone* (VI) [*Me* ester, $C_{34}H_{34}O_4N_4$, m.p. 273° (corr.) (*oxime*, m.p. > 300°)]; (VI) is partly



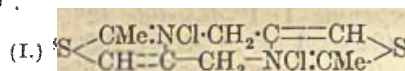
converted by prolonged treatment with 20% HCl in absence and presence of air into (II) and (IV), respectively. H. B.

Metal complex salts of hæmatoporphyrin. F. BANDOW (Z. physiol. Chem., 1934, 223, 71—73).—The formation of metal complex compounds of hæmatoporphyrin in the lower fatty acids was examined spectroscopically. Various centres in the porphyrin mol. are affected by the presence of the metal. J. H. B.

New derivative of chlorophyll with hypnotic action; diethylamine salt of phæophorbide. M. CUFFARO (Giorn. Chim. Ind. Appl., 1934, 16, 7—9).—The protracted action of HCl on chlorophyll yields phæophorbide, the $(NH_4)_2$ salt of which swells above 100°, chars at 240°, and shows hypnotic properties. T. H. P.

Occurrence of chlorophyll derivatives in an oil-shale from the upper Trias.—See this vol., 387.

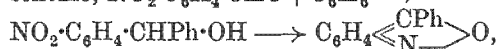
Polymerisation of 2-methyl-4-chloromethylthiazole. XII. F. E. HOOPER and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 470—471).—Thioacetamide and $CO(CH_2Cl)_2$ give (cf. A., 1931, 103) 2-methyl-4-chloromethylthiazole, b.p. 65—67°/3 mm., which polymerises slowly at room temp. and more rapidly at 110—115° to the compound (I), not melted at >300°.



H. B.

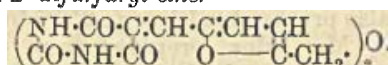
Formation of C-phenylanthranils and acridones from o-nitrobenzaldehydes and aromatic hydrocarbons. K. LEHMSTEDT (Ber., 1934, 67, [B], 336—339).—Mainly a reply to Tanasescu (A., 1933, 956). At present, the formation of C-arylanthranils from

o-nitrobenzaldehydes is best explained by Kliegl's scheme, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO} + \text{C}_6\text{H}_6 \rightarrow$



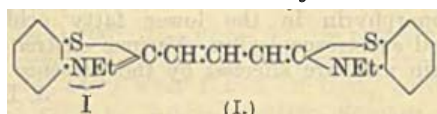
the question of intermediates being left open. The "tautomerism" of *o*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ is inadmissible. 6-Chloro-3-nitro-9-*p*-dimethylaminophenylacridine has m.p. 250°.

Furan compounds with barbituric acid. T. ISEKI (J. Biochem. Japan, 1934, 19, 7—9).—Direct condensation in hot H_2O of barbituric acid with 5-hydroxymethylfurfuraldehyde or 5:5'-di(furylmethyl) ether 2:2'-dialdehyde (cf. A., 1933, 719) affords 5-hydroxymethyl-2-furfurylidenebarbituric acid (I), m.p. 274° (uncorr.), and 5:5'-di(barbiturylidene-methyl)-2:2'-difurfuryl ether



Orally ingested (I) in dogs and rabbits is partly (15—20%) excreted as hydroxymethylfuroic acid (cf. A., 1927, 1107; 1929, 450).

Cyanine dyes. VI. Benzthiazolo-, thiazolo-, benzoxazolo-, and benzimidazolo-cyanines. T. OGATA (Proc. Imp. Acad. Tokyo, 1933, 9, 602—605; cf. A., 1933, 402).—The figures given in parentheses below are the yields and sensitisation max. in μ , respectively. 2-Methylbenzthiazole ethiodide and $\text{NPh} \cdot \text{CH} \cdot \text{NPh}$ in piperidine (method A) at 65° (20%) or $\text{Ac}_2\text{O} \cdot \text{NaOAc}$ (method B, usually with KOAc) at 165° (100%) give 1:1'-diethyltrimethinebenzthiazolocyanine iodide (I), m.p. 269° (decomp.) (590). Similar starting materials give by the method named: 1:5:1':5'-tetramethyltrimethinethiazolo-



cyanine iodide (B, 125°, 45%), m.p. 268° (decomp.) (590); 1:1'-dimethyltrimethinebenzoxazolocyanine iodide (B, 51%), m.p. 282° (decomp.) (520); 1:1'-diethylpentamethinebenzthiazolocyanine iodide (B, 61%), m.p. 253° (decomp.) (700); 1:1'-di- (A, 5%), m.p. 215° (decomp.) (690), and 1:5:1':5'-tetra-methylpentamethinebenzthiazolocyanine iodide (A, 24%), m.p. 226° (690); 1:1'-diethylheptamethinebenzthiazolocyanine iodide (A, 15%), m.p. 240° (800); 1:1'-dimethylheptamethinebenzthiazolocyanine iodide (A, 10%), m.p. 152° (decomp.) (780); 1:5:1':5'-tetramethylheptamethinebenzthiazolocyanine iodide (A, 27%), m.p. 174° (decomp.) (780); 1:3:1':3':1'':3''-hexamethyl-9-benziminazolytrimethinebenziminazolocyanine 1:1'-di-iodide (B, 170°, 5%), m.p. 230° (570). By variations of the Et_3 orthoformate method were prepared 1:1':1''-triethyl-9-benzthiazolytrimethinebenzthiazolocyanine 1:1'-di-iodide (2%), m.p. 256° (decomp.) (640), 1:1':1''-tri- (40%), m.p. 250° (decomp.) (640), and 1:5:1':5':1'':5''-hexamethyl-7-thiazolytrimethinebenzthiazolocyanine 1:1'-di-iodide (42%), m.p. 283° (decomp.) (640). 2:3-Dimethylbenziminazole methiodide, $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$, and NaOEt in hot EtOH give 1:3:1':3'-tetramethyltrimethinebenziminazolocyanine iodide (13%), m.p. 303° (530). Methods A and B give zero yields when

applied in the cases not specified above. *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ and Ac_2O at 140° give an 82% yield of 2-methylbenziminazole, the methiodide of which is obtained in 42% yield by MeI and MeOH at 110°.

R. S. C.

Cyanine dyes.—See B., 1934, 268, 314.

Synthesis of thiazolybarbituric acids. XIII. F. E. HOOPER and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 484—485).—2-Methyl-4-chloromethylthiazole and $\text{CNaEt}(\text{CO}_2\text{Et})_2$ give *Et* (2-methyl-4-thiazolylmethyl)ethylmalonate, b.p. 168—174°/4—5 mm., which condenses with $\text{CO}(\text{NH}_2)_2$ (method: Dox and Yoder, A., 1922, i, 681) affording 5-(2-methyl-4-thiazolylmethyl)-5-ethylbarbituric acid, m.p. 264—265°. 2-Phenyl-4-chloromethylthiazole (modified prep.; cf. A., 1931, 103) similarly gives *Et* (2-phenyl-4-thiazolylmethyl)ethylmalonate, b.p. 208—211°/4—5 mm. (free acid, m.p. 145°), and 5-(2-phenyl-4-thiazolylmethyl)-5-ethylbarbituric acid, m.p. 210—211°. 2-Phenyl-4-methoxymethyl-, b.p. 116°/1 mm., -4-phenoxy-methyl-, m.p. 67—68°, and -4-phenylthiomethyl-, m.p. 42°, -thiazoles have been prepared.

H. B.

Anabasis aphylla alkaloids. A. P. OREKHOV and S. S. NORKINA (Khim. Farm. Prom., 1933, 109—113).—1-Nitrosoanabesine is reduced with Zn and AcOH to 1-aminoanabesine. Anabesine is prepared by heating anabesine sulphate in closed tubes at 200° for 120 hr. and distilling in vac.

CH. ABS.

Alkaloids of Anabasis aphylla. VII. Amination of anabesine and N-methylanabesine with sodamide. G. MENSCHIKOV, A. GRIGOROVITCH, and A. OREKHOV (Ber., 1934, 67, [B], 289—292; cf. A., 1932, 952).—Treatment of anabesine with NaNH_2 in xylene at 150° affords much resin, *r*-anabesine, and *r*-aminoanabesine [2-(2'-amino-3'-pyridyl)piperidine], m.p. 111°. Similar treatment of *N*-methylanabesine yields a substance, b.p. 100—102°/6 mm. (picrate, m.p. 231—232°), 1-methyl-2-(2'-amino-3'-pyridyl)piperidine (I), m.p. 95—95.5° [picrate, m.p. 234—235° (decomp.)], and the non-cryst. (?) 1-methyl-2-(6'-amino-3'-pyridyl)piperidine (very hygroscopic hydrochloride; picrate, m.p. 220—221°). Diazotisation of (I) in HCl (*d* 1.19) leads to 1-methyl-2-(2'-chloro-3'-pyridyl)piperidine, b.p. 145—146°/8 mm., oxidised by aq. KMnO_4 to 2-chloropyridine-3-carboxylic acid, m.p. 192°.

H. W.

Alkaloids of white hellebore. I. Isolation of constituent alkaloids. K. SAITO, H. SUGINOME, and M. TAKAOKA (Bull. Chem. Soc. Japan, 1934, 9, 15—23).—Separation by EtOH of the alkaloids from the roots of *Veratrum album* gives jervine, m.p. 240—241°, $[\alpha]_D^{25} -177.5^\circ$ in EtOH [acetate (+0.5 H_2O), m.p. 234—238°, $[\alpha]_D^{25} -126.8^\circ$ in EtOH], as the only cryst. product. Hydrolysis with HCl of the amorphous base obtained affords tiglic acid or with H_2O under pressure or with $\text{EtOH} \cdot \text{KOH}$ yields another amorphous base and angelic acid. Separation of the alkaloids by HPO_3 similarly gives only jervine.

F. R. S.

Alkaloids of Vinca pubescens. A. OREKHOV, H. GUREVITSCH, and S. NORKINA [with N. PREIN] (Arch. Pharm., 1934, 272, 70—74).—*V. pubescens* (I) contains 0.34% of alkaloids, whence with difficulty were separated *vinine* (II), $\text{C}_{19}\text{H}_{26}\text{O}_4\text{N}_2$, m.p. 211.5—213°, $[\alpha]_D^{25} -70.12^\circ$ in dry EtOH [hydrochloride, m.p. 212° (decomp.)]; *sulphate*, m.p. 229—230° (decomp.);

platinichloride, m.p. 226—227° (decomp.), *pubescine*, $C_{20}H_{26}O_4N_2$, m.p. 227—228°, $[\alpha]_D -134.2^\circ$ in dry EtOH, and a small amount of an *alkaloid*, m.p. 194—195°. (I) and (II) depress the blood-pressure. V. *minor* also contains alkaloids. R. S. C.

Constitution of isochondodendrine. VI. F. FALTIS and H. DIETERICH (Ber., 1934, 67, [B], 231—238; cf. A., 1932, 1047).—Ozonisation of α -isochondodendrimethine, m.p. 205° (*loc. cit.*), in dil. H_2SO_4 followed by treatment with spongy Pt and hydrogenation (Pd— $BaSO_4$) leads to the non-cryst. 3:4-dimethoxy-2-p-aldehydophenoxy-6- β -dimethylaminoethylbenzaldehyde (I), the *methiodide* of which is smoothly converted by boiling 5% KOH into the oily *o*-vinylaldehyde reduced (Pd—C) to the ethylaldehyde which could not be smoothly oxidised to the carboxylic acid. The *methochloride* of (I) with aq. $KMnO_4$ at 20° followed by treatment with boiling 5% KOH affords 3:4-dimethoxy-2-p-carboxyphenyl-6-vinylbenzoic acid (II), m.p. 192° after softening at 189°, in 64% yield, thus showing that the isochondodendrine (III) mol. is composed of two similar components. (II) is decarboxylated by Cu powder in boiling quinoline and the dimethoxyvinylidiphenyl ether thus produced is directly oxidised by $KMnO_4$ in $COMe_2$ at 0° to 3:4-dimethoxy-5-phenoxybenzoic acid (IV), m.p. 161° after softening at 158° [*Me* ester (V), m.p. 69° after softening at 66°]. The constitution of (IV) is established by the synthesis of (V) by the condensation of *Me* 5-bromoprotocatechuate and KOPh in presence of Cu powder and anhyd. $Cu(OAc)_2$ at 160—180° followed by hydrolysis. The constitution assigned previously (*loc. cit.*) to (III) is regarded as established, at any rate in so far as the *O*-Me derivative is concerned. H. W.

Cactus alkaloids. XI. Synthesis of pelletine. E. SPATH and F. BECKE (Ber., 1934, 67, [B], 266—268; cf. this vol., 87).—2-Hydroxy-3:4-dimethoxyacetophenone is converted by NaOMe and CH_2PhCl in boiling MeOH into 2-benzyloxy-3:4-dimethoxyacetophenone, b.p. 175—180°(bath)/0.2 mm., m.p. 47—48.5° (vac.), transformed by aminoacetal at 165° into the Schiff's base (I), $CH_2Ph \cdot O \cdot C_6H_4(OMe)_2 \cdot CMe:N \cdot CH_2 \cdot CH(OEt)_2$, b.p. 180—200°(bath)/0.02 mm. Treatment of (I) with 73% H_2SO_4 followed by warm H_2O leads to 8-hydroxy-6:7-dimethoxy-1-methylisoquinoline, m.p. 180—182° (vac.), the *methiodide*, m.p. 188—189.5°, of which is reduced by pptd. Zn and 12% HCl to 8-hydroxy-6:7-dimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, m.p. 110—112° (vac.), identical with natural pelletine. H. W.

Composition of strychnine phosphomolybdate. C. ANTONIANI (Giorn. Chim. Ind. Appl., 1934, 16, 9).—The observation that strychnine and NH_4 phosphomolybdates show different vals. for the ratio $MoO_3 : P_2O_5$ (A., 1928, 1265) is confirmed and Tetamanzzi's contrary statement refuted. T. H. P.

Separation of the opium alkaloids. S. BUSSE and V. BUSSE (Khim. Farm. Prom., 1933, 127—129). The combined filtrate after separation of resins from 1 kg. of opium is treated with NaOAc (200 g.) and NaCl (200 g.); the pptd. papaverine is collected, dissolved in aq. AcOH, and the neutralised solution treated with NaOAc (100 g.) and NaCl (100 g.). The

pptd. papaverine is collected and the filtrates are combined. The resin (40—50 g.) is dissolved in AcOH and NaCl, filtered, redissolved, and from the combined filtrates papaverine is pptd. with NaOH; yield 7—9 g. Thebaine is pptd. with aq. NH_3 from the combined filtrates from the first pptn. and purified in the usual way; yield 3—4 g. The filtrate from the thebaine is acidified with AcOH, conc., diluted with EtOH (50%), and after 2 days morphine is pptd. The main portion of the filtrate after removal of thebaine contains codeine, which is extracted with C_6H_6 ; yield 6—8 g.

CH. ABS.

Oxidation of thebaine with manganic acetate. F. VIEBOCK (Ber., 1934, 67, [B], 197—202).—Since crotonic, itaconic, and oleic acids are scarcely attacked by $Mn(OAc)_3$, it appears that the double linking must be activated to permit reaction. Treatment of thebaine (I) with $N \cdot Mn(OAc)_3$ at about 60—70° causes addition of OH and OAc at the double linking 8, 14 with production of the substance (II), $C_{21}H_{25}O_6N$, m.p. 198° (Cu block) after softening at 196°. Under the action of 20% HCl, (II) loses OMe and Ac, yielding the compound (III), $C_{18}H_{21}O_5N$, m.p. 171° (block) (*chromate*; *oxime*, m.p. 212—215°), and a small amount of oxycodone (IV). Protracted treatment of (I) or (II) with HCl or of (III) with KOH—EtOH yields (IV) almost exclusively. It is suggested that the oxidation of (I) by H_2O_2 to (IV) may proceed through (III). Unexpectedly (III) does not yield reducing substances when acted on by $Pb(OAc)_4$. The behaviour of $Pb(OAc)_4$ towards (I) is similar to that of $Mn(OAc)_3$, but the yield is lower and operations are more difficult. Codeine and (IV) appear only to lose the N chain under the action of $Mn(OAc)_3$. H. W.

Specific rotations of alkaloid and alkaloid salt solutions. R. LILLIG (Pharm. Ztg., 1934, 79, 198—200).—A review. S. C.

Action of hydrobromic acid on phenylarsinic and *p*-aminophenylarsinic acids. J. PRAT (Compt. rend., 1934, 198, 583—585).—The action of HBr on $AsPhO(OH)_2$ takes the following course:

- (1) $AsPhO_2H_2 + HBr \rightarrow [AsPh(OH)_3]Br$;
- (2) $[AsPh(OH)_3]Br + 3HBr \rightarrow (AsPhBr_3)Br + 3H_2O$;
- (3) $(AsPhBr_3)Br \rightarrow AsPhBr_2 + Br_2$;
- (4) $(AsPhBr_3)Br \rightarrow PhBr + AsBr_3$.

All these compounds, except $AsPhBr_4$, have been isolated. HBr has an analogous action on $p-NH_2 \cdot C_6H_4 \cdot AsO_3H_2$ with the additional formation of $2:4-C_6H_3Br_2 \cdot NH_2 \cdot HCl$. P. G. M.

Reactions of organo-arsenic, -antimony, -tin, and -lead compounds with mercuric chloride in neutral and alkaline medium. A. N. NESMEJANOV and K. A. KOZESCHKOV (Ber., 1934, 67, [B], 317—324).—In boiling EtOH, $HgCl_2$ and $SnAr_4$ react: $SnAr_4 + HgCl_2$ (I) = $SnAr_3Cl$ (II) + $HgArCl$ (III); (II) + (I) = $SnAr_2Cl_2$ (IV) + (III); (IV) + (I) = $SnArCl$ (V) + (III); (V) + (I) = $SnCl_4$ + (III). In the cases of (IV) and (V) reaction is instantaneous and quant.; with $SnAr_4$ it is markedly slower. With Pb compounds the stage $PbAr_2Cl_2$ cannot be passed even with excess of $HgCl_2$ and very protracted heating. With $SbAr_2Hal_2$ and $SbAr_2Hal$ (VI) reaction occurs as with Sn compounds, being accompanied in the case of (VI) by the oxidation $(V) + 2(I) = SbAr_2Cl_2Hal + 2HgCl$. Reaction does not

take place with derivatives of Sb or with compounds of As^{III} or As^V. With HgO in boiling H₂O-EtOH-NaOH the following changes are typical: $\text{SnAr}_2\text{O} + \text{HgO} + 2\text{NaOH} = \text{HgAr}_2 + \text{Na}_2\text{SnO}_3 + \text{H}_2\text{O}$; $4\text{SbArO} + 2\text{HgO} = 2\text{HgAr}_2 + 2\text{Sb}_2\text{O}_3$; $2\text{AsPhO} + \text{HgO} = \text{HgPh}_2 + \text{As}_2\text{O}_3$; $2\text{PbAr}_2\text{OH} + \text{HgO} = \text{HgAr}_2 + 2\text{PbAr}_2\text{O} + \text{H}_2\text{O}$. Reaction generally proceeds as rapidly as that in neutral solution and its rate depends on the solubility of the initial material. The protracted action with PbPh_2Cl_2 is accompanied by production of PbO_2 and $\text{HgPh}\cdot\text{OH}$. With SbArO and SbAr_2OH the normal process is accompanied by oxidations. Compounds of Sb^V are stable towards HgO. AsPhO reacts normally to the extent of 25–30%, the remainder is oxidised to AsPhO_2H_2 ; oxidation occurs exclusively with $(\text{AsPh}_2)_2\text{O}$. The de-alkylating power of $\text{HgAr}\cdot\text{OH}$ in contrast with HgArCl is shown by the reactions $\text{HgPh}\cdot\text{OH}$ (VII) + $\text{SbPhO} + \text{NaOH} = \text{HgPh}_2 + \text{NaSbO}_2 + \text{H}_2\text{O}$; (VII) + $\text{AsPhO} + 2\text{NaOH} = \text{HgPh}_2 + \text{Na}_2\text{HASO}_3 + \text{H}_2\text{O}$; $\text{SnPh}_n\text{Hal}_{4-n} + n\text{HgPhHal} + 6\text{NaOH} = n\text{HgPh}_2 + \text{Na}_2\text{SnO}_3 + 4\text{NaHal} + 3\text{H}_2\text{O}$. The possibility of thus preparing compounds $\text{HgAr}\cdot\text{Ar}'$ is discussed. The interactions of (I) with arylboric acids, arylsulphinic acids, and arylhodo-compounds are analogous and individual instances of the above general reaction. H. W.

Organic compounds of selenium. IV. Confirmation of structure of 4:4'-dihydroxy-3:3'-dicarbomethoxydiphenyl selenide dichloride. R. E. NELSON and R. G. BAKER (J. Amer. Chem. Soc., 1934, 56, 467).—The dichloride (I) (A., 1933, 407) is reduced (Zn) to the selenide (II) (*loc. cit.*), which is then hydrolysed to 4:4'-dihydroxy-3:3'-dicarbomethoxydiphenyl selenide (III) (Morgan and Burstall, A., 1929, 202). Esterification (MeOH) of (III) gives (II), reconverted into (I) through the dibromide and dihydroxide. (III) and Br in CHCl_3 give 3:5-dibromosalicylic acid. H. B.

Selenonaphthen. G. KOMPPA and G. A. NYMAN (J. pr. Chem., 1934, [ii], 139, 229–236).—3-Hydroxy-selenonaphthen (Lesser *et al.*, A., 1912, i, 642) (*picrate*, m.p. 120°; *semicarbazone*, m.p. 245°) is reduced (58% yield) by 4% Na-Hg in boiling 50% EtOH to selenonaphthen (I), b.p. 238.5–240°/775 mm., m.p. 50–51° (*picrate*, m.p. 156–157°; *styphnate*, m.p. 146–147°). With Br in CHCl_3 (I) gives its 3-Br-derivative, b.p. 286–289°/768 mm. (*picrate*, m.p. 128–129°), and, with excess of Br-H₂O, its 2:3-Br₂-derivative, m.p. 129–130°. Passage of Cl₂ into a CCl_4 solution of (I) gives a (? 2:3:4-)Cl₃-derivative, b.p. 143°/8 mm. (*picrate*, m.p. 135–136°). With Ac_2O -fuming HNO_3 at 0° (I) gives its 3-NO₂-derivative, m.p. 97°, and with AcCl-AlCl_3 in CS_2 at 0° is obtained 3-selenonaphthenyl Me ketone, m.p. 91–93° [*semicarbazone*, m.p. 254–256° (uncorr.)], converted by NaOBr in C_6H_6 into selenonaphthen-3-carboxylic acid, m.p. 270–280° (decomp.). When condensed with benzoic acid in $\text{AcOH-H}_2\text{SO}_4$ (I) affords diphenyl-3-selenonaphthenylacetic acid, m.p. 254–255°. All m.p. are corr. J. W. B.

Action of vanadium oxytrichloride on various organic compounds. R. E. NELSON and A. H. McFADDEN (Proc. Indiana Acad. Sci., 1933, 42, 119–122). VOCl_3 and NH_2Ph give $\text{VO}(\text{NHP})_3$ and a

compound, containing C, H, and N, m.p. 236°. PhCHO and VOCl_3 afford $(\text{C}_6\text{H}_4\cdot\text{CHO})_2\text{VCl}_3$.

CH. ABS.

Physico-chemical studies on proteins. VIII. Rotatory dispersion of three gliadin preparations peptised by different solutions. H. O. WILES and R. A. GORTNER (Cereal Chem., 1934, 11, 36–48).—Gliadin prepared by three different methods (*cf.* A., 1933, 730) was peptised by 10% and 70% EtOH, distilled H₂O, *N*-K⁺I⁻, and *N*-K⁺Br⁻, and $[\alpha]$ of the resulting sols determined at five different vals. of λ . The differences in the rotatory dispersions of the three protein preps. are > the experimental errors (*E*). *N*-KCl, *N*-NaCl, *N*-LiCl, and *N*-K₂SO₄ did not peptise enough gliadin to yield a readable α . The peptising agent appears to have no effect on the rotatory dispersion; if a Hofmeister series exists, its effect is > that of *E*. E. A. F.

Analyses of azoproteins: casein, gelatin, and zein coupled with arsanilic acid. W. C. BOYD and S. B. HOOKER (J. Biol. Chem., 1934, 104, 329–337).—Determinations of As.N support but do not confirm Pauly's theory (A., 1904, i, 1068; 1915, i, 725) that proteins couple with diazo-compounds in virtue only of their tyrosine and histidine residues, each of which attaches two R-N=N- groups. Unlike azo-dyes, azoproteins yield all their N to the Kjeldahl treatment. W. S.

Determination of the membrane potentials of protein solutions and the valency of protein ions. G. S. ADAIR and M. E. ADAIR (Biochem. J., 1934, 28, 199–221).—When solutions of haemoglobin of sheep or ox, serum-albumin (I), acid haematin, kathemoglobin, and edestin (II) are equilibrated at 0° with dialysates of well-defined [H⁺] with p_H vals. ranging from 2.0 to 7.8, and salt concns. from 0.005 to 0.16M, the observed membrane potential *E* is approx. proportional to the concn. *C* of protein (III) expressed in g. per 100 ml. solvent, when *E* is < 2.0 mv. From a full theoretical discussion, it appears that the mean valency n_p of the protein ions may be calc. by the formula $n_p = 0.00425MJ(E/C)_0$ [*M*—mol. wt. of protein, *J*—sum of concns. of ions in dialysate \times squares of valencies, $(E/C)_0$ is the limiting val. of the ratio for *C*=0]. In the case of (II) and Congo-red, this formula is consistent with other observations, whilst in the case of (I) the results can be reconciled with the investigations of the distribution of ions on the assumption that the protein exists as a zwitterion and that some of the positive charges are neutralised by phosphate ions. W. O. K.

Action of papain on ovalbumin.—See this vol., 450.

Methods of organic chemical analysis by [catalytic] hydrogenation and oxidation. H. TER MEULEN (Rec. trav. chim., 1934, 53, 118–125).—Use in analysis by catalytic methods (*e.g.*, for As or Hg) of the van den Berg (this vol., 162) in place of the Fletcher furnace simplifies procedure in many cases. Even heating of the whole or part of a tube is secured by use of Al blocks bored centrally to carry the tube and heated by a Bunsen burner. In the determination of O by hydrogenation the use of Ni spirals in place of asbestos is recommended with

difficultly reduced compounds (e.g., cholesterol). The slow reduction of NiO is obviated by use of (less of) the highly active Ni-ThO₂ (10 : 1). The Ni spirals retain S but not halogens, which must be absorbed in Ag₂SO₄ if present. Ni-ThO₂ is the best catalyst for determination of N, except in oils, where pure Ni is best. For S Pt spirals are used as catalyst, and if N is also present ZnSO₄ + NaOAc as absorbent for the H₂S to avoid errors due to (CN)₂; if the sample carbonises badly it is mixed with Pt-black. In the determination of C and H by combustion with O₂ and MnO₂ a Pt spiral is recommended to volatilise the substance completely before it reaches the MnO₂. In the determination of S by Heslinger's method SO₂ fog is passed through aq. NH₃; although the fog persists it is then an (NH₄)₂SO₄ fog, and the alkali used can be determined by titration. H. A. P.

Schobel's heating mortar for Pregl carbon-hydrogen determinations. H. LIEB (Mikrochem., 1934, 14, 263—264).—An all-glass cymene boiler is described. J. S. A.

Attempt to apply a new principle to organic micro-analysis. K. SCHWARZ (Mikrochem., 1934, 14, 271—279).—The attempt is made to apply measurement of the vol. change on combustion in O₂, and the vol. and pressure at which the H₂O vapour formed reaches saturation, to C, H, O, and N determinations using min. quantities of material. J. S. A.

Semi-micro-Kjeldahl methods. J. A. SCARROW and C. F. H. ALLEN (Canad. J. Res., 1934, 10, 73—76).—For certain substances which give low results by the ordinary method a preliminary reduction with P and HI is recommended. A. G.

Determination of nitrogen in organic substances. N. POROV (Khim. Farm. Prom., 1933, 218—220).—Anderson and Jensen's method (A., 1931, 638) is slightly modified. CH. ABS.

Detection of nitrogen, phosphorus, sulphur, and halogens in organic compounds by means of sodium peroxide. O. HOGL (Mitt. Lebensmitt. Hyg., 1933, 24, 164—170; Chem. Zentr., 1933, ii, 1225—1226).—5—10 mg. of the substance (I) are placed in a depression in Na₂O₂ contained in a Ni spoon, which is then inverted over a red-hot Ni crucible so that (I) is covered by Na₂O₂. After heating to bright redness and cooling, the melt is treated with 6—8 c.c. of H₂O, and the Na₂O₂ destroyed by heating. P, S, N, and the halogens are then confirmed as usual. Volatile substances, e.g., CHCl₃ and CS₂, can be tested with certainty in this way. L. S. T.

Determination of halogens in organic substances. K. REVVA (Khim. Farm. Prom., 1933, 147—148).—The sample is treated with H₂SO₄ and air is passed through the boiling liquid for 1 hr., the halogen being collected in dil. aq. NaOH and determined by Fresenius' method. CH. ABS.

Determination of iodine in organic compounds. J. L. GOLDBERG (Mikrochem., 1934, 14, 161—166).—Combustion is effected by Pregl's method, and I' absorbed in Na₂CO₃, without NaHSO₃. I' is oxidised by Br-H₂O to IO₃', which is determined iodometrically. The acidity requires control; excess of Br is removed by PhOH. J. S. A.

Micro-determination of phosphorus in organic material. A. VILA (Compt. rend., 1934, 198, 657—659).—0.2—2 mg. P is determined in 0.5 hr. by measuring the vol. of the NH₄ phosphomolybdate ppt. formed. In the absence of Si and As, the error is 2—5%. J. L. D.

Micro-method of determining methoxyl and ethoxyl groups. H. R. NANJI (Analyst, 1934, 59, 96—98; cf. A., 1932, 928).—A modification of Pregl's micro-Zeisel apparatus is used. The substance is boiled with HI and PhOH in CO₂, and the alkyl iodide absorbed in Br-H₂O. The HIO₃ formed is determined as usual. E. C. S.

Fractional separation of unsaturated hydrocarbons. F. N. VORONOV (Sintet. Kautschuk, 1932, 1, 7—13; Chem. Zentr., 1933, ii, 2483).—Components of a complex hydrocarbon mixture are adsorbed on active C in the reverse order to their volatility. The process is followed with an interferometer. Desorption follows in the reverse order, and may be applied in separating the mixture. H. J. E.

Determination of chloroform. M. SCHTSCHIGOL (Khim. Farm. Prom., 1933, 150—151).—10 drops of CHCl₃ in 5 c.c. of PhMe are treated for 2 hr. with 0.5N-EtOH-KOH; after dilution and acidification with HNO₃ the Cl' is determined by Volhard's method. CH. ABS.

Titration of betaine.—See this vol., 338.

Determination of nitrotoluene. K. LESNICHENKO (Chem. Obzor, 1932, 7, 246—248, 265—268; Chem. Zentr., 1933, ii, 2710).—The HNO₃ used to convert C₇H₇·NO₂ into C₇H₆(NO₂)₂, using as nitrating mixture 35% H₂SO₄, 15% HNO₃, and 50% H₂O, is measured with a nitrometer. C₇H₆(NO₂)₂ and C₇H₅(NO₂)₂ are without influence. H. J. E.

Detection and determination of small quantities of cholesterol and other sterols. A. WASITZKY (Mikrochem., 1934, 14, 289—310).—A review.

2 : 4-Dinitrophenylhydrazine as a quantitative reagent for carbonyl compounds. I. Benzaldehyde. R. E. HOUGHTON (Amer. J. Pharm., 1934, 106, 62—64).—2 : 4-Dinitrophenylhydrazine in dil. H₂SO₄ is added to a solution of PhCHO in aq. EtOH. A. E. O.

Microchemical and microscopical identification of santonin. M. WAGENAAR (Pharm. Weekblad, 1934, 71, 260—264).—Santonin (I) forms characteristic, oblong crystals when pptd. from solution in H₂SO₄, glycerol (II), or especially C₅H₅N. Dichroic crystals are obtained with I-KI solution. The most characteristic microchemical reactions are the violet coloration with H₂SO₄ and a trace of Fe^{III} salt and the rose coloration when a solution of (I) in (II) is treated with freshly-ignited CaO. S. C.

Use of silicotungstic acid for the detection and determination of novocaine. G. VALETTE (Bull. Sci. pharmacol., 1933, 40, 28—33; Chem. Zentr., 1933, ii, 2300).—Pptn. of 12W₃SiO₃·2H₂O·2C₁₃H₂₀O₂N₂·3H₂O (anhyd. from hot solution) in characteristic crystals is optimal at room temp. in 0.5N-HCl. The novocaine content of a solution is given (±1%) by : 0.1916(p+0.000033V),

where p is the residue on ignition of the ppt. and V is the vol. of solution and wash- H_2O . A. A. E.

Determination of nicotine. A critical investigation. P. KOENIG and W. DORR (Z. Unters. Lebensm., 1934, 67, 113—144).—The physiological, colorimetric, and nephelometric methods are not accurate. Of the volumetric methods only Kissling's (A., 1916, ii, 587) is reasonably accurate. Pptn. with silicotungstic acid gives accurate results if certain specified precautions are taken, the most important of which is the maintenance of a particular [HCl]. Pfyl and Schmitt's method (B., 1927, 955), depending on pptn. of nicotine (I) with picric acid, is recommended when many routine determinations are to be made. Minor improvements are suggested. The more important of these are: by gradual addition of (II) in feebly acid solution a more easily filterable ppt. is formed; by cooling in ice a further 0.5 mg. of (I) per 200 c.c. of solution can be separated; addition of PhMe is necessary only when large quantities of (I) are present. The eosin titration can be dispensed with. E. C. S.

Determination of nicotine. M. G. RUITKOV (Khim. Farm. Prom., 1933, 140—142).—The sample dissolved in 50 c.c. is distilled with steam and 2 g. of fresh MgO into dil. HCl. An aliquot of the distillate is treated with 1.5 c.c. of HCl and 3 c.c. of 12%

$H_2Si(W_2O_7)_6 \cdot 22H_2O$. The ppt. is formed in 3 min. 85° and is ready for filtration after 2 hr. CH. ABS.

Dimethylaminobenzaldehyde test for atropine. A. A. O'KELLY and C. F. POE (J. Lab. Clin. Med., 1918, 1235—1241).—Compounds which mask or interfere with the test are listed. CH. ABS.

Determination of quinine.—See this vol., 346.

Otto test for strychnine. C. F. POE and J. BAILEY (J. Lab. Clin. Med., 1933, 19, 40—46).—Compounds which mask or interfere with the test listed. CH. ABS.

Determination of alkaloids. Y. FIALKOV and S. BABICH (Khim. Farm. Prom., 1933, 148—149).—2 c.c. are dispersed with 70 c.c. of $CHCl_3$ and 5 g. anhyd. Na_2SO_4 ; aq. NH_3 is then added, the mixture shaken, the $CHCl_3$ filtered and evaporated, and the residue dissolved in 0.02N-acid, the excess of which is titrated with 0.02N-NaOH. CH. ABS.

Homoneurine derivatives of the cinchona alkaloids as reagents for iodide ions.—See this vol., 380.

Determination of nitrogen in sericin. C. BARONI (Boll. Uff. R. Staz. sperim. Seta, 1933, 28—29; Chem. Zentr., 1933, ii, 2478).—The N determination of sericin in the high-temp. H_2O extract of silk gives the same results as an indirect determination. H. J. E.

Biochemistry.

Determination of hæmoglobin. H. SCHULTEN (Münch. med. Woch., 1933, 80, 1017—1019; Chem. Zentr., 1933, ii, 1226). L. S. T.

Food and hæmoglobin regeneration. III. Eggs compared with whole wheat, prepared bran, oatmeal, ox-liver, and -muscle. M. S. ROSE, E. McC. VAHLTEICH, and G. MACLEOD (J. Biol. Chem., 1934, 104, 217—229).—For hæmoglobin regeneration (I) of 10—11 g. in 6 weeks from 4 to 6 g. per 100 c.c. of rat blood, < 0.25 mg. Fe, and 0.05 mg. Cu per day are required; on these levels only whole wheat, oatmeal, and prepared bran are effective. In egg-yolk (II) the first limiting factor is Cu. In liver and, in a smaller degree, in (II) another factor is the form of combination of Fe; for equiv. (I), twice as much Fe in the form of liver as of whole wheat is necessary. H. G. R.

Red blood-cell count and hæmoglobin in the adolescent male. S. M. GOLDHAMER and A. I. FRITZELL (J. Lab. Clin. Med., 1933, 19, 172—177).—The blood of boys (12—17 years) contains 3.28—5.8 (average 4.718) $\times 10^6$ erythrocytes per cu. mm. The hæmoglobin (I) content is 9.80—13.58 (average 11.55) g. per 100 c.c. The average (I) coeff. is 12.35 g. per 100 c.c. and colour index 0.87. CH. ABS.

Factors causing variation in the hæmoglobin level with age in the first year of life. H. M. M. MACKAY (Arch. Dis. Child., 1933, 8, 251—264).—Hæmoglobin (I) varies inversely with birth-wt. (II)

during the first week of life, i.e., it varies inversely with maturity at birth, the post-natal fall in (I) commencing normally *in utero*. This fall, which may amount to 50%, is more rapid in infants of low (II). The breakdown products are in part stored, and increase the content of the liver. After 2—3 months, cell regeneration occurs to a degree and for a period determined by the reserve stores and Fe content of the diet, and complete only on a sufficient supply of Fe.

NUTR. ABS. (b)

Relation of hæmoglobin to bilirubin and hæmatin in normal and diseased men. DUESBERG (Arch. exp. Path. Pharm., 1934, 174, 305—327).—Hæmoglobin (I) and hæmatin (II) were injected into the veins, transudates, and exudates of normal and diseased men and the contents of (I), (II), and bilirubin (III) in the serum and fluids were determined after 1—24 hr. The results indicate that the formations of (II) and (III) are two distinct routes of (I) decomp. and that (I), whether in the blood-stream or not, may quantitatively yield (III). In disease, (I) yields (II), but the formation of (III) from (II) does not occur. The mechanism of the decomp. of (I) is discussed. F. O. H.

Chemical composition of Herzog's "hæmatoprostheticin." F. HAUROWITZ (Z. physiol. Chem., 1934, 223, 74—75; cf. A., 1933, 1180).—The composition of "hæmatoprostheticin" corresponds with that of a half anhydride of oxyhæmin (cf. Hämik, 1927, 1100). J. H. B.

Hæmin prepared with the help of formic acid. J. BRUCKNER (Biochem. Z., 1934, 268, 181—186; cf. Partos, A., 1920, i, 773).—Heat-coagulated horse-blood or horse-oxyhæmoglobin on rapid extraction with cold MeOH or EtOH containing 3—4% HCO_2H yields a solution which deposits cryst. hæmin formate (I), $\text{C}_{35}\text{H}_{20}\text{O}_6\text{N}_4\text{Fe}\cdot 2\text{EtOH}$ (yield 1.3 g. per 1000 c.c. blood). (I), which is purified by dissolution in $\text{C}_5\text{H}_5\text{N}\cdot\text{CHCl}_3$ and addition of HCO_2H in EtOH, is not esterified.

W. McC.

Hæmoerythrin from *Sipunculus*. J. ROCHE (Bull. Soc. Chim. biol., 1933, 15, 1415—1435).—Cryst. hæmoerythrin (I) is obtained from the celomic fluid of *Sipunculus* by repeated dissolution in aq. NaCl and dialysis. The absorption spectrum (II) of methæmoerythrin is unchanged on treatment with CO; the large band at 3500 Å. observed by Florkin for (I) (A., 1933, 81) was not seen. (I) has a solubility min. (III) at p_{H} 5.7 and a min. of cataphoresis at p_{H} 5.8. From the titration curve (I) behaves as a univalent base of p_{K} 2.9 and a multivalent acid of p_{K} 6.6, 8.0, and 10.5 approx. Keeping (I) for 2—20 min. at p_{H} 1.8 and 16° reduces the solubility and shifts (III) to lower p_{H} . The val. of p_{H} 4.8 of Florkin (*loc. cit.*) for the (III) obtained in AcOH-NaOAc buffers is explained by denaturation. A protein-free compound containing Fe, hæmoferin (IV), is separated from (I) by pptn. with CoMe_2 and dissolution in HCl and CoMe_2 and purified by means of EtOH and $\text{C}_5\text{H}_5\text{N}$. (IV) gives pyrrole reactions; its ultra-violet (II) is similar to that of (I) and is unchanged in acid solution.

H. D.

Combination of carbon monoxide with hæmocyanin. R. W. ROOT (J. Biol. Chem., 1934, 104, 239—244).—The affinity of CO for *Limulus* hæmocyanin is about 1/20 that of O_2 , and the compound formed is less stable. As in oxyhæmocyanin, 1 mol. CO corresponds with 2 atoms Cu.

H. G. R.

Fibrinogen formation in the animal body. E. HORI (Sei-i-kwai Med. J., 1932, 51, No. 8, 97—111).—Venous blood contains more fibrinogen (I) than arterial blood. In the rabbit (I) is formed chiefly from the leucocytes by the liver.

CH. ABS.

Origin of the plasma-proteins. H. A. REIMANN, G. MEDES, and L. C. FISHER (J. Clin. Invest., 1933, 12, 968).—Leucocytes (I) disintegrated by freezing with liquid air contained proteins with the salting-out characteristics of fibrinogen (II), globulin (III), and albumin (IV). Destruction of (I) *in vivo* in rabbits by C_6H_6 injections led to marked increase of plasma- (III) and -(II), generally at the expense of the -(IV). The marked leucopenia produced by X-rays caused little change in the plasma-proteins apart from some increase in (II). (III) and (II) may in part be derived from the decomp. of (I) in the circulation or hæmatopoietic system.

NUTR. ABS. (b)

Micro-determination of blood-plasma-proteins. G. MEDES (Amer. J. Clin. Path., 1933, 3, 439—442).—The method consists in fractional pptn. with anhyd. Na_2SO_4 , pptn. of protein in the various filtrates with $\text{CCl}_3\cdot\text{CO}_2\text{H}$, dissolution of the ppts. in NaOH, and determination of N in aliquot parts of the solutions.

CH. ABS.

Condition of hydration of serum-protein. M. SIGNON (Z. ges. exp. Med., 1933, 89, 211—214; Chem. Zentr., 1933, ii, 2157).—A new expression is based on the viscosity and albumin : globulin content of serum; a nomogram is given.

A. A. E.

Specific gravity of synthetic solutions of serum-albumin and -globulin. R. L. NUGENT and L. W. TOWLE (J. Biol. Chem., 1934, 104, 395—398).—The d of a protein solution plotted against the protein concn. gives a straight line which is identical for both ox serum-albumin and -globulin.

H. D.

Effect of deamination on the combination curves of serum-albumin and -globulin. E. B. R. PRIDEAUX and D. E. WOODS (Proc. Roy. Soc., 1933, B, 114, 110—123).—Ox-serum-albumin and -globulin were deaminated using HNO_2 . The products contained no free $\text{NH}_2\text{-N}$, and some slight introduction of NO-groups had occurred. Their isoelectric points were at p_{H} 4.0 ± 0.1 and 4.3 ± 0.2 , respectively. They were capable of combination with acid, and combined with more alkali than the original proteins, suggesting combination at peptide linkings. On allowing for hydrolysis, the max. difference between the alkali or acid taken up by 1 g. of natural and deaminated protein was approx. equiv. to the $\epsilon\text{-NH}_2$ of lysine, which is lost on deamination. The effect of CH_2O on the titrations of natural and deaminated serum-albumin favoured the “zwitterion” theory of combination; the titration of the deaminated protein was complete at p_{H} 8.5, consistent with absence of $\epsilon\text{-NH}_2$ of lysine.

Effect of ultra-violet radiation and heat on protein solutions of low concentrations. M. SPIEGEL-ADOLF (Biochem. J., 1934, 28, 372—379).—Electrolyte-free serum-albumin and -pseudoglobulin (0.2—0.002%) are almost completely pptd. by heat or by ultra-violet irradiation, but in the latter case the filtrate contains a substance (I), probably proteose in nature, which coagulates colloidal Au. When a conc. solution of (I) is added to normal spinal fluid the mixture gives a Au sol reaction similar to that obtained in general paralysis. The filtrates obtained from protein solutions (0.2—0.5%) containing acid or alkali, after irradiation, neutralisation, and heat-coagulation, do not show a positive reaction with colloidal Au.

W. O. K.

Basic amino-acids of serum-proteins. II. Effect of heating to 58°. R. J. BLOCK. III. Chemical relationship between serum-proteins of various origins. R. J. BLOCK, D. C. DARROW, and M. K. CARY (J. Biol. Chem., 1934, 104, 343—346, 347—350).—II. The amount and the basic NH_2 -acid composition of the protein fraction pptd. from cattle-serum by half saturation with $(\text{NH}_4)_2\text{SO}_4$ are the same in serum unheated, and heated at 58° for 3 hr. Albumins obtained from cattle-serum by means of aq. $(\text{NH}_4)_2\text{SO}_4$ yield more lysine than the globulins.

III. Determination of albumin, globulin, and basic NH_2 -acid (I) content of various samples of mammalian serum indicates that although the total amount of protein and the albumin content may vary widely, the (I) content of the protein is const. both in abs. and relative amount. Serum-protein,

like the keratins, might therefore be classified according to the mol. ratio of NH_2 -acids it yields on hydrolysis. Probably the proteins obtained from blood-serum are not of const. (I) composition, but are artefacts produced by reagents employed in their prep. A. L.

Zeiss interferometer and Hirsch's interferometric method. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1933, 15, 1392—1414).—The use of the Zeiss interferometer, with special reference to Hirsch's method of determining the changes in the molar concn. of sera produced by gland extracts, is described. The most trustworthy results are obtained by direct comparison of pathological and normal sera. The methods of correction of Durupt and Schlesinger (A., 1933, 1331) are criticised. H. D.

Changes in blood-glutathione at high altitudes. G. DELRUE and A. VISCHER (Compt. rend. Soc. Biol., 1933, 113, 942—944).—The glutathione content (I) of the blood increases at high altitude (3400 m.) (in three cases from 17 to 50 mg. per 100 c.c.). The relative increase in (I) is $>$ that in red blood-cells. NUTR. ABS. (m)

Depressor substance of blood. C. H. FISKE (Proc. Nat. Acad. Sci., 1934, 20, 25—27).—Blood is deproteinised at 0° with $\text{CCl}_3\text{CO}_2\text{H}$ and the filtrate neutralised with saturated aq. NaOH. The Hg salt of the active principle is then pptd. by $\text{Hg}(\text{OAc})_2$ and decomposed with H_2S ; the Ag salt is next pptd. by $5N\text{-AgNO}_3$ and decomposed with H_2S (repeated twice), and finally the acid Ca salt is pptd. by CaCl_2 and EtOH . By this method 6.45 mg. (as P) of the acid Ca salt of adenosine triphosphate were isolated from 100 c.c. of blood. The acid Ag salt has the composition $\text{C}_{10}\text{H}_{13}\text{O}_{13}\text{N}_5\text{P}_3\text{Ag}_3$. All operations must be carried out at a low temp. to minimise deamination of the adenine to hypoxanthine. The depressor principle of blood (adenylic acid) is present exclusively as adenosine triphosphate. P. G. M.

Acetylcholine in ox-blood. K. GOLLWITZER-MEIER (Arch. exp. Path. Pharm., 1934, 174, 456—467).—No acetylcholine-like substance (I) occurs in fresh blood (II) or in normal or deproteinised plasma, but is found in deproteinised extracts of fresh (II) (0.01—0.07 mg. per litre) and in lysed (II) (0.005—0.013 mg. per litre) when the (II) is previously treated with eserine or kept for 1—2 hr. Hence (I) originates in the red corpuscles, where it is either preformed and bound, or arises by a reaction of the (II) constituents. F. O. H.

Determination of non-protein-nitrogen with special reference to the Koch-McMeekin method. C. A. DALY (J. Lab. Clin. Med., 1933, 18, 1279—1285).—A slight modification for blood of the Koch-McMeekin method is described. The chief differences from Folin's original method (I) are the use of H_2O_2 previously added to the H_2SO_4 for digestion of the protein-free filtrate and the addition of gum ghatti and Na citrate to the slightly modified Nessler solution. The results agree with those obtained by (I). NUTR. ABS. (m)

Titrimetric micro-determination of non-protein-nitrogen of blood without distillation.

F. RAPPAPORT (Klin. Woch., 1933, 12, 1184—1185).—Blood (0.1—0.2 c.c.) is deproteinised, the filtrate is ashed with phosphomolybdic acid or a $\text{Ti}(\text{SO}_4)_2\text{-H}_2\text{SO}_4$ reagent, the free acid is neutralised, and after addition of buffered aq. NaOBr, KI, and HCl, titration with $0.01N\text{-Na}_2\text{S}_2\text{O}_3$ follows. Excellent agreement with distillation methods is found. NUTR. ABS. (m)

Deproteinisation with cadmium hydroxide and blood-sugar. C. DUMAZERT (Compt. rend. Soc. Biol., 1933, 113, 1061—1062).— $\text{Cd}(\text{OH})_2$ is recommended as a protein precipitant in determining the true (i.e., fermentable) sugar in blood. The ratio of free sugar in the cells to that in the whole blood is with normal subjects about 8, with diabetics, a little $>$ 6. NUTR. ABS. (m)

Distribution of sugar between plasma and corpuscles in animal and human blood. A. ANDREEN-SVEDBERG (Skand. Arch. Physiol., 1933, 66, 113—190).—Vals. for the corpuscle: plasma (I) distribution of true sugar are given for the blood of seventeen different vertebrates. With the exception of the goose-fish, human blood (II) shows the highest ratio. In (II), in hyperglycaemia (III), or when large quantities of glucose have been added to the blood *in vitro*, the (I) ratio rises, but in fish, dogs, and rabbits, under similar conditions, it falls. An increase is observed in rabbit's and dog's blood in (III). These results support the theory that sugar is adsorbed at the surface of animal blood corpuscles, but in man is probably partly adsorbed, partly dissolved in the H_2O of the corpuscles, and to some extent chemically bound to the lipins of the cell wall. NUTR. ABS. (m)

Determination of animal lipins and their components. H. PATZSCH (Pharm. Zentr., 1934, 75, 98—102, 116—120).—A summary of suitable known methods for determination (in blood and serum) of cholesterol, cholesteryl esters, lecithin, choline, lipin-P, and fat. P. G. M.

Precipitation of albumins and lipins from serum by neutral salts as function of p_H . G. SANDOR, A. E. BONNEFOI, and P. GORET (Bull. Soc. Chim. biol., 1933, 15, 1472—1482).—Machebœuf's method of pptn. (A., 1931, 1447) is approx. quant. between p_H 3.34 and 2.30 for the horse and sheep. Albumin (I) left at p_H 3 for 1 hr. is not denatured. The pptn. of (I) from conc. $(\text{NH}_4)_2\text{SO}_4$ solutions shows a max. at p_H 6.55 and a min. at 4.8. The ppt. formed at p_H 6.55 redissolves on further acidification. The presence of a protein of isoelectric point 6.55 in serum is suggested. H. D.

Lipin- and inorganic phosphorus in the blood after irradiation with artificial sunlight. H. STIEMENS and G. C. HERINGA (Nederland. Tijdschr. Geneesk., 1933, 77, 1635).—Irradiation of the skin of young men, with few exceptions, did not affect the lipin-P of the blood, but inorg. P increased slightly. NUTR. ABS. (b)

Absorption of ether by serum. F. SEELICH (Biochem. Z., 1934, 268, 34—45; cf. A., 1932, 1053).—Aq. solutions of Na oleate (I) and Na glycocholate (II) resemble serum in taking up Et_2O on shaking. The amount taken up is const. for given quantity

(III) of substance and concn. (IV) of solution, and is dependent for (II) on (III) and (IV), but for (I) on (III) only. The Et_2O no. (V) (amount of Et_2O taken up by 1 c.c. of solution or serum) of solutions of (I) and (II) of unknown (IV) may be used for deducing (IV). The decrease in (V) produced by heating for 10 min. at $>50^\circ$ can be partly counteracted by CO_2 treatment. There appears to be a relation between (V) and hæmolytic complement action. W. McC.

Variations in blood-cholesterol due to sunlight. S. MALCZYNSKI (Compt. rend. Soc. Biol., 1933, 113, 1300—1302).—Exposure of the shaved backs of two dogs for 20—30 min. to summer sunlight daily for 9 days caused an immediate rise in blood-cholesterol from 167 to >200 mg. per 100 c.c. after the first exposure; for 3 weeks after the ninth exposure the level was high (180 mg.), but fluctuating, and thereafter fell to pre-exposure level. NUTR. ABS. (b)

Determination of the iodine value of unsaturated fatty acids in blood. W. BRANDT, K. HINSBERG, and G. HOLLAND (Z. ges. exp. Med., 1933, 90, 216—224).—Extraction with EtOH -light petroleum (9:1) is best. All types of saponification lower the I val.; the use of NaOEt is most advantageous. Rupp's modification of Winkler's method yields figures nearest the theoretical vals.; other methods give low vals. for blood and tissues. NUTR. ABS. (m)

Hydrogen-ion concentration in blood of healthy and sick horses. A. MEYER (Arch. wiss. pr. Tierheilk., 1933, 66, 512—520).—The p_{H} of normal horse blood was 7.38—7.54 (average 7.46). Vals. are given for cases with various diseases. The variations were not sp. for the type of disease. NUTR. ABS. (b)

Potassium of serum. H. WAELSCH and S. KITTEL (Kolloid-Z., 1934, 66, 200—205).—Experiments in Furth's high-tension apparatus (A., 1925, ii, 1057) show that K in serum migrates to the anode even at p_{H} 4, at which the albumin migrates to the cathode. Combination of K with serum-albumin is excluded under these conditions. E. S. H. NUTR. ABS. (m)

Bound calcium of blood-serum. F. ROSENTHAL (Klin. Woch., 1933, 12, 1140—1141).—The hypothesis underlying Berensy and Hermann's method of determining protein-bound Ca is untenable. When aq. CaCl_2 is added to serum, part (5—50%) of the added Ca is pptd. with the protein. NUTR. ABS. (m)

Blood-phosphate during work. H. GUNTHER (Z. ges. exp. Med., 1933, 90, 479—488).—A small rise in serum- PO_4''' occurs, due to concn. The chief cause of the increased val. for whole blood- PO_4''' during work is a relative increase in the proportion of red cells. NUTR. ABS. (b)

Total and ultrafilterable calcium and the acid-soluble phosphate content of the blood-serum of children. M. S. NEEDLES and C. M. MARBERG (J. Lab. Clin. Med., 1933, 18, 1227—1234).—Serum-Ca, total and diffusible, is slightly lower in the spring than in autumn in children on standard diet, but there is little or no seasonal variation in children

receiving, in addition, orange and lemon juice daily. Serum-inorg. P shows no seasonal variation in either case, but is lower in older children. No correlation can be found between total Ca, ultrafilterable, Ca or inorg. P of the blood-serum and the incidence of dental caries. NUTR. ABS. (m)

Thiocyanogen metabolism I. Thiocyanogen content of blood. B. STUBER and K. LANG (Deut. Arch. klin. Med., 1933, 175, 564—567).—The normal SCN content of blood, determined as $\text{Cu C}_5\text{H}_5\text{N}$ thiocyanate, is 0.1—0.2 mg. per c.c. It is greatly reduced in thyroid disease, but not in renal insufficiency. NUTR. ABS. (m)

Level, distribution, and physico-chemical state of bromine in blood in normal subjects and conditions other than mental disease. C. O. GUILLAUMIN and B. MEREJKOWSKY (Compt. rend. Soc. Biol., 1933, 113, 1428—1430).—The average ratio of Br in blood-corpuscles to that in the plasma is 0.36. The Br content of the blood is 2—20 mg. per litre (average 10). Apparently 63—88% of the Br in blood resists ultra-filtration and is therefore present either as an adsorption complex or in org. combination. NUTR. ABS. (m)

Blood-chlorine in the normal dog. V. ROBIN, A. BRION, and R. MONPERT (Compt. rend. Soc. Biol., 1933, 113, 1174—1176).—The Cl content of the serum (I) of normal dogs fed on a normal diet is 0.320—0.350 g. per 100 c.c. and 0.200—0.220 g. for whole blood (II). The ratio of Cl in (II) to that in (I) is 0.65—0.70. NUTR. ABS. (m)

Penetration of erythrocytes by anions. M. MAIZELS (Biochem. J., 1934, 28, 337—350).—Erythrocytes (I) were exposed to a solution containing Cl' and a second anion (II), the amount of (II) entering (I) being usually found indirectly on the assumption (experimentally verified) that in 5 min. the sum of all the anions entering (I) = amount of Cl' entering (I) suspended in aq. KCl at the same p_{H} . The order of permeation of inorg. ions into (I) is $\text{CNS}' > \text{I}' > \text{NO}_3', \text{Cl}' > \text{SO}_4'' > \text{PO}_4'''$ (a lyotropic series), the permeation rate (III) of (II) relative to Cl' increasing with $[\text{H}']$. Anions of lower fatty acids permeate more readily than Cl' at low p_{H} , but the presence of additional polar group(s) (IV) decreases (III), especially if α to CO_2H . In the aromatic series, (IV) enhances (III). $\text{C}_2\text{O}_4''$ permeates more rapidly than Cl' or any other anion at low p_{H} . Substances permeating rapidly are usually poorly dissociated, have a relatively high $\text{Et}_2\text{O}-\text{H}_2\text{O}$ partition coeff., and are capillary-active. The problem of the nature of the membrane of (I) is discussed in the light of these results. A. E. O.

Passage of chlorine from erythrocytes to plasma under influence of sodium citrate. S. RASZEJA and A. SLAVINSKI (Bull. Soc. Chim. biol., 1933, 15, 1569—1571).—Addition of Na citrate to horse blood fails to alter the plasma or erythrocyte $[\text{Cl}']$. H. D.

Influence of trisodium citrate on migration of chlorine between corpuscles and plasma of human blood. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1933, 15, 1572—1574).—The criticisms of Raszeja and

Slavinski (see preceding abstract) against the author's work (A., 1930, 944) are rebutted. H. D.

Retardation of blood-coagulation by trisodium citrate. M. LARGET, J. P. LAMARE, R. C. WEYL, and R. LECOQ (Bull. Sci. pharmacol., 1933, 40, 408—416; Chem. Zentr., 1933, ii, 2284).—Of the substances which retard blood-coagulation *in vitro*, only Na₂ citrate is suitable for use *in vivo* (8—16 g. in 4% solution orally). A. A. E.

Temporary inhibition of coagulation in the blood of insects. W. E. SHULL and P. L. RICE (J. Econ. Entom., 1933, 26, 1083—1089).—Exposure to AcOH vapour inhibits the coagulation of the blood of cockroaches, the intensity of the action varying with temp. and period of exposure. A. G. P.

Antigens. J. G. FITZGERALD (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 1—9).—A lecture. F. O. H.

Nature of antibodies. J. MARRACK (Nature, 1934, 133, 292—293).—Tetrazotised benzidine coupled with R salt and with the proteins of an agglutinating serum gives a deep red compound (I), but the agglutinin is not wholly destroyed. If the agglutinins (II) of the serum are proteins (I) should be adsorbed specifically by homologous bacteria, but actually the protein dyes thus formed are adsorbed non-specifically. When dil. solutions are used, however, a marked quant. difference can be observed between the degree of adsorption by homologous and heterologous bacteria. This sp. adsorption of the dye from the homologous coloured agglutinin agrees with the view that (II) are proteins. Other alternatives are mentioned. L. S. T.

Application of f.-p. measurements to the dilution of antitoxic globulin. E. M. TAYLOR and P. J. MOLONEY (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 193—196).—The f.p. of 0.4—1.0% aq. NaCl is lowered proportionately by the addition (10—20%) of pseudoglobulin (I) from the serum (II) of immunised animals and also by the further addition (0.3%) of "tricrosol" (III). With (I) the effect is due to the vol. of H₂O it occupies, and is slightly more marked with KCNS than with NaCl. Addition of approx. 0.7% of NaCl to 18—20% aq. (I) containing 0.38% of (III) yields a solution isotonic with the average human (II) (f.p. —0.55°). F. O. H.

Carrier-function of serum-proteins and its significance in serological reactions. E. KYLIN (Arch. exp. Path. Pharm., 1934, 174, 483—489).—Cataphoresis of serum with a positive serological reaction (I) (e.g., Wassermann, Kahn) yields pure albumin (II), a mixture of (II) and globulin (III), a protein-free fluid, and (III). The (III)-containing fractions, but not the protein-free serum nor (II), give a positive (I), and hence (III) appears to be the carrier on which the factors responsible for (I) are adsorbed. F. O. H.

Organ-specificity of a hæmoglobin-precipitating antiserum. K. YORIMITSU (Tohoku J. Exp. Med., 1933, 22, 1—6). CH. ABS.

Immunological study of native, denatured, and reversed serum-albumin. B. F. MILLER (J. Exp. Med., 1933, 58, 625—633).—Native and reversed

horse serum-albumin are indistinguishable by t precipitin reaction. CH. ABS.

Phenylcarbimide derivatives and their immunological properties. III.—See this vol., 405.

Organ-specificity. T. ISHIKAWA and H. YAMAMOTO (Tohoku J. Exp. Med., 1933, 21, 524—531).—The lens (I), vitreous humour (II) and cornea of fish (I) and (II) of fowl, and the naked nuclei of fowl red cells contain a common antigenic factor. The nuclei of the hepatic cells, freed from protoplasm by peptic digestion, are organ-sp. CH. ABS.

Post-mortem glycogenolysis in human infant and foetus. W. HERTZ (Z. Kinderheilk., 1933, 55, 410—420).—The rate of glycogenolysis, determined under strictly sterile conditions in buffered media, is very rapid in the livers of 15-week-old foetuses (I) but less rapid in the livers of older (I) and of new-born infants which have not breathed; the small liver glycogen content of young (I) is thus explained. NUTR. ABS. (m)

Phosphoric esters in normal and malignant tissue. E. L. OUTHOUSE (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 123—133).—The tissue (I) is extracted with 4% aq. CCl₃CO₂H and the extract is fractionated by means of the Ba, Hg^{II}, and boric salts. Normal avian muscle (II) yields hexose mono- (but not di-)phosphate and adenylic acid, the carbohydrate residue from light (II) containing 75% and from dark (II) 66% of aldose. Data are given for the partition of P in human and bovine tumour. Fibrous (I) has a low content of acid-sol. P. Malignant (I) contains an org. phosphate, the Pb and Ba salts of which are sol. in EtOH and Et₂O, which appears to be absent from muscle. F. O. H.

Glycerophosphoric acid. II. Glycerophosphoric acid of the naturally-occurring phosphatides. J. J. RAE (Biochem. J., 1934, 28, 151—156).—Brain-lecithin and -kephalin and Ca phosphatidate contain mainly the α -form, egg-lecithin the β -form, whereas liver-lecithin contains about equal amounts of the two forms. H. G. R.

Constitution of ovomucin. T. ISEKI (J. Biochem. Japan, 1934, 19, 1—5).—Ovomucin (cf. A., 1927, 372) was digested with trypsin, the digest pptd. with HgCl₂, and the resulting filtrate freed from Hg and pptd. with basic Pb acetate. The material regenerated from this ppt. on pptn. from conc. aq. solution by EtOH afforded a substance (22.5% yield with 5.35% N, free from NH₂-acids, giving a marked biuret reaction, and containing 49.43% of glucosamine.

Paraffin in the egg of Bombyx mori. D. ONGARO (Annali Chim. Appl., 1933, 23, 567—572).—The unsaponifiable portion of the Et₂O extract of silkworms' eggs contains a saturated hydrocarbon, C₂₈H₅₈, m.p. 62°, similar to that obtained from the chrysalis, and a sterol. T. H. P.

Sterols of molluscs.—See this vol., 404.

Pigments of animal fats. L. ZECHMEISTER and P. TUZSON (Ber., 1934, 67, [B], 154—155).—The isolation of a mixture of α - and β -carotene from the kidney-fat of an aged cow is described. H. W.

Reducing substance found in chromophilic adenomas and in the normal anterior pituitary. T. J. PUTNAM and H. B. WILCOX (Amer. J. Path., 1933, 9, 649—650).—The substance reduces methylene-blue, but does not reduce Benedict's solution or give other common tests for sugar. CH. ABS.

Thyroglobulin. III. Thyroglobulin content of the thyroid gland. B. O. BARNES and M. JONES (Amer. J. Physiol., 1933, 105, 556—558).—Of the I in thyroids from pigs and dogs >95% is present as thyroglobulin. The % remains the same irrespective of the total I content. NUTR. ABS. (m)

Iron content of thyroid gland.—See this vol., 382.

Composition of pig's thymus. E. KATAOKA (J. Biochem. Japan, 1934, 19, 21—24).—The fresh glands (64.1% H₂O) contain 9.3% of fat, a constituent of which is α -palmitodistearin. Hydrolysis of the fat-free dry substance yields alanine (1.19%), valine (0.81%), leucine (3.24%), isoleucine (1.28%), proline (0.84%), glutamic+aspartic acid (2.8%), lysine (1.58%), arginine (2.0%), and histidine (0.21%).

F. O. H.

Composition of the pancreas. E. KATAOKA (J. Biochem. Japan, 1934, 19, 25—32).—The following data are given for ox- and pig-glands, respectively: H₂O, 69.0—74.2, 68.5—69.5%; fat, 9.5—14.2 (partly β -stearodipalmitin), 10.6—11.3% (partly β -laurodistearin). Hydrolysis of the fat-free dried tissue yields mainly lysine (2.89—3.56, 3.01—3.94%), arginine (2.45—2.60, 2.33—2.54%), leucine (5.44, 5.34%), and glutamic acid (1.93, 1.23%).

F. O. H.

Histamine in canine gastric tissues. G. GAVIN, E. W. MCHENRY, and M. J. WILSON (J. Physiol., 1933, 79, 234—238).—The mucous membrane of the dog's stomach contains relatively large amounts of histamine (I), the gastric muscle much less. The fundic mucosa (II) contains about 80% of the (I) contained in the stomach. Extracts of dog's (II) and pyloric tissue (III) have secretagogue powers, which are lost after incubation of the solutions with histaminase. (II) contains more secretagogue material than the (III). NUTR. ABS. (b)

Distribution and origin of sulphur in wool. I. Methionine. J. BARRITT (Biochem. J., 1934, 28, 1—5).—The methionine content of the degreased wools from a no. of breeds of sheep, determined by Bernstein's method (A., 1932, 1149), was 0.44—0.67% of the dry wt. and represented 2.4—4.8% of the total S.

H. D.

Phenomena occurring in solutions of collagen at the limits of action of acids and neutral salts. L. GUYON (Compt. rend., 1934, 198, 975—977).—Solutions of the collagen from the tendons of the tails of rats form a homogeneous gel when dialysed against 0.01% AcOH. NaCl inhibits gel formation. With 0.1% NaCl and 0.001% AcOH, spherules (A) and birefringent fibres are formed. With 0.1% NaCl in 0.0001% AcOH or 0.03% NaCl in H₂O, only (A) are obtained. R. S. C.

Basic amino-acids of keratins. R. J. BLOCK (J. Biol. Chem., 1934, 104, 339—341).—The mol. ratios of histidine, lysine, and arginine present in human

finger-nails and cattle horn are 1 : 5 : 15 and 1 : 5 : 13, respectively, indicating that these tissues have a composition resembling that of keratinoid tissue. These vals. do not agree with those of Abderhalden and Heyns (A., 1932, 637).

A. L.

Nucleotide component of mammalian cardiac muscle. I. Composition and chemical properties of the nucleotide. F. BEATTIE, T. H. MILROY, and R. W. M. STRAIN. II. Biological and co-enzyme properties of the cardiac dinucleotide. R. W. M. STRAIN (Biochem. J., 1934, 28, 84—90; 90—93).—The chemical composition and behaviour on hydrolysis at 100° with *N*-HCl show that the nucleotide of cardiac (I) differs from that of voluntary (II) muscle in being more closely allied to a dinucleotide composed of 1 mol. each of adenosine-di- and -tri-phosphoric acids. Approx. 60% of its total P is labile. The only distinctive difference in the pharmacological action of the two nucleotides is obtained with intestinal musculature, when (I) lowers the tone without a subsequent rise, whilst (II) has the double action. (I) has a more powerful co-enzyme action in reactivating inactive extracts of both voluntary and cardiac muscle. P. W. C.

Crystalline myoglobin. II. Sedimentation constant and mol. wt. III. Light absorption by oxy-, carbon monoxide-, meta-, and reduced myoglobin. IV. Myoglobin in equilibrium with oxygen and carbon monoxide. V. Fixation of oxygen by myoglobin. H. THEORELL (Biochem. Z., 1934, 268, 46—54, 55—63, 64—72, 73—82; cf. A., 1932, 1054).—II. Myoglobin (I) from expressed muscle juice of horse, ox, or cat has sedimentation const. (II) 2×10^{-13} . The mol. wt. of (I) from horse muscle is 34,800 but aq. extracts of horse heart contain in addition a (I) having (II) $= 4 \times 10^{-13}$ and probable mol. wt. 68,000. Within the p_H range 6.0—13 (I) is stable. It is probably the low mol. wt. of (I) which enables it to diffuse so readily in the kidney.

III. The light absorption curves of these forms of myoglobin are plotted and the max. and min. recorded. The curve for metamyoglobin yields vals. which vary with $[H^+]$ (p_H 6.2, 7, and 8 chosen).

IV. Vals for the tensions (III) at 20° and 37° and p_H 7.4—6.0 (as well as in absence of salts and in presence of phosphate buffer) of O₂ and CO in (I) solutions are given. The order of magnitude of (III) differs greatly from that of the corresponding vals. for haemoglobin (IV), although as regards effect of temp. and $[H^+]$ (effect insignificant) the pigments behave similarly.

V. The strictly hyperbolic O₂ dissociation curve (V) of (I) solutions shows that, at p_H 7.4, the affinity of (I) for O₂ is six times p_H that of (IV). (V) is little affected by $[H^+]$ and affected by temp. changes < the corresponding (IV) curve. (I) acts physiologically as an O₂ reservoir. At 37° (I) solutions are half-saturated with CO when its pressure is 0.2 mm.

W. McC.

Extractives of muscle. XXXVIII. Dromæus sp. N. TOLKATSCHEVSKAYA (Z. physiol. Chem., 1934, 223, 57—60; cf. A., 1929, 1479).—The flesh of an exotic bird, *Dromæus sp.*, contains anserine,

methylguanidine, creatinine, xanthine, carnitine (?), and choline (?). Carnosine is absent. J. H. B.

Ratio of calcium to phosphorus content of fish. A. DE CLERCQ (Natuurwetensch. Tijds., 1934, 15, 229—236).—The P:Ca ratio is remarkably high in fish (0.29—1.58). In herrings the ratio increased from 0.28 to 0.78 from Nov. to Jan. S. C.

Colour reactions of the aqueous solution of the cocoon layer. H. KANEKO (Bull. Sericult. Japan, 1932, 4, No. 3, 10—12).—A flavone-like compound, glycine, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, $(\text{NH}_4)_2\text{CO}_3$, and a small quantity of aspartic acid are probably present. CH. ABS.

Aqueous solution of domestic cocoons. XI. Nitrogen distribution of sericin-A and -B. XII. Solubility of sericin. H. KANEKO (J. Agric. Chem. Soc. Japan, 1933, 9, 45—49, 301—311).—XI. Sericin-A is rich in arginine. High arginine content of the aq. solution indicates good reelability. Sericin-A and -B contain, respectively, tyrosine 2.62, 5.53; glycine 6.18, 4.89 (fibroin 33.5)%.

XII. Sericin is more sol. in aq. solutions of Na salts of org. acids than in those of salts of inorg. acids. Sericin-A is least sol. in HCl at p_H 4.5 and -B at p_H 4.7; for H_2SO_4 , 4.4, 4.6. CH. ABS.

Toad poisons. VI. Ch'an su, the dried venom of the Chinese toad, and the secretion of the tropical toad, *Bufo marinus*.—See this vol., 412.

Electrical phenomena of the cornea. I. Potential differences against electrolytes. II. Potential of the cornea. K. HAYASHI (J. Biochem. Japan, 1934, 19, 145—163, 165—172).—I. No significant p.d. exists between the posterior and anterior chambers of the eye (ox). That between the vitreous humour and an aq. electrolyte (I) in contact with the outside of the cornea depends on the character of (I), CuCl_2 , AlCl_3 , H^+ , SO_4^{--} , and $\text{Fe}(\text{CN})_6^{--}$ yielding small or negative vals. and KSCN , KNO_3 , KBr , and NaOH yielding high positive vals.

II. The p.d. between two different concns. of (I) in contact with the two sides of the cornea (fresh or formolised) was determined for various (I).

F. O. H.

Calcium content of the aqueous and vitreous humours and serum. P. W. SALIT (J. Biol. Chem., 1934, 104, 275—280).—The Ca content of the aq. and vitreous humours (I) and serum (II) of young calves is 5.82, 8.34, and 11.54 mg. per 100 g., whilst for aged cattle the vals. are 4.60, 6.75, and 9.69, respectively. The Ca content of (I) is directly dependent on the Ca of (II). H. G. R.

Porphyrin content of human amniotic fluid. R. FIKENTSCHER (Arch. Gynäkol., 1933, 154, 129—146).—The coproporphyrin content of human amniotic fluid rises from zero in the first few weeks to a max. about the middle of pregnancy, falling to zero again in the last month. Uroporphyrin is absent.

NUTR. ABS. (m)

Chemical origin of the biliary elements. G. RANZOLI (Boll. Chim. Farm., 1934, 73, 41—46).—A review. R. C.

Isolation of bilirubin. C. E. MAY, R. MARTINDALE, and W. F. BOYD (J. Biol. Chem., 1934, 104, 500—507). Bilirubin (I) is pptd. from dil. aq. solu-

tion with BaCl_2 and Na_2HPO_4 or Na_3PO_4 . With diazo-chlorides (I) gives stable coloured products, whereas biliverdin does not react. H. G. R.

Effect of diet on hydrogen-ion concentration of bile. H. BRONNER (Klin. Woch., 1933, 12, 1562—1563).—Cholecystectomised patients were fed alternately on vegetarian (I) and meat (II) diet and the p_H was determined electrometrically in the bile collected by drainage of the bile duct. In cases with no liver damage the p_H was approx. 7.5 on (I) and 6.5 on (II). In cases with liver disease, bile was acid even with (I). NUTR. ABS. (b)

Complete absorption of chlorine from the gall-bladder of the dog. E. CHABROL, R. CHARONNAT, M. MAXIMIN, and J. COTTET (Compt. rend. Soc. Biol., 1933, 113, 1347—1348).—In fasting dogs in which the cystic duct had been ligated, the bile from the gall-bladder was much more conc. than the hepatic bile and contained practically no Cl. The urea content was unchanged. NUTR. ABS. (b)

Gastric secretion. T. TEORELL (Skand. Arch. Physiol., 1933, 66, 225—317).—In decerebrated cats which had previously been starved for 24 hr., secretion of gastric juice (I) was induced by slow and continuous intravenous infusion of histamine. The flow of (I) continued even when the blood-pressure was very low, and was unaffected by complete denervation of the stomach (II). Long-continued gastric secretion tended to cause acute gastric ulceration. An "alkaline tide" in the blood as the result of secretion of HCl into the (II) is doubtful. The regulation of the acidity of the (I) depends neither on dilution of the gastric contents nor on neutralisation by alkaline juices from the duodenum. The diminution of gastric acidity is due to diffusion of H^+ into the (II) mucosa, and so into the blood, and to the passage of anions from the blood into the (II) contents. NUTR. ABS. (b)

p_H of the arterial blood during gastric secretion. C. E. BRUNTON (J. Physiol., 1933, 79, 4—5P).—Gastric secretion excited by meat extracts caused no change in the p_H of human blood. NUTR. ABS. (b)

Mode of action of secretagogues (liver extract) in promoting gastric secretion. M. S. KIM and A. C. IVY (Amer. J. Physiol., 1933, 105, 220—240).—Liver and meat extracts, either with or without vasopressor (I) substances, had approx. the same secretagogue (II) action after direct application to dogs, but when given by mouth (Pavlov pouch dogs) or into the intestine, the (I) extracts were more effective than the (I)-free. Both types of extract excited gastric secretion on intravenous injection, but the (I)-free was less effective. (II) action in the stomach did not, but in the intestine did, depend on absorption of the extract. NUTR. ABS. (b)

Proteins as stimulants for the secretion of pepsin. E. R. B. SMITH and G. R. COWGILL (Amer. J. Physiol., 1933, 105, 697—705).—When two basal rations of a commercial dog food and nine artificial diets, in which the protein varied, were fed to Pavlov-pouch dogs, vol. and rate of secretion of gastric juice varied widely, but free and total acidity and total Cl were const. NUTR. ABS. (b)

Secretory activity of the gastric mucosa in the region of the lesser curvature. A. ALLEY (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 71—78).—Following ingestion of meat, milk, or bread by dogs, the vol., pepsin content, and acidity of the secretion from the mucosa of the lesser curvature region of the stomach are $>$ those of the greater curvature region. F. O. H.

Changes in acid secretion by the stomach at high altitudes. G. DELRUE and J. P. BOUCKAERT (Compt. rend. Soc. Biol., 1933, 113, 940—942).—At high altitudes (3400 m.) the acidity of gastric secretion in dogs with gastric fistulae was reduced—from p_H 1.02 to 3.6, in one case—during the first 4 days. Acclimatisation and exercise increased the acidity.

NUTR. ABS. (b)

Acidity of the stomach contents of premature infants. S. SEYFFARTH (Jahrb. Kinderheilk., 1933, 140, 164—179).—Gastric acidity (I) in 50 premature infants after the ingestion of breast milk was low for the first two months of life, increased to the fourth month, and then fell to the limits found in full-time infants of the same age. (I) was max. about 2 hr. after a feed. In 16 infants the p_H after 1 hr. was $>$ 3.7, and of the infants over 4 weeks the p_H was $<$ 3.7 in all cases in 2 hr. When the p_H was $<$ 4.0, only a slight growth of *B. coli* could be got from the gastric contents. No const. correlation was found between (I) and parenteral infection, dyspepsia, or type of faecal flora.

NUTR. ABS. (b)

Gastric digestion of fresh and ripe cheese. F. RAMOND, G. GUITTONNEAU, E. NICHOLAS, and M. BÉJAMBES (Compt. rend. Soc. Biol., 1933, 113, 1023—1025).—Gastric analyses were conducted on man, using Camembert (I), Gruyère (II), and white cheese (III). Practically all the HCl secreted was bound by (I) and (II). The results were confirmed *in vitro*. (I) and (II) therefore contain larger proportions of degraded proteins than (III).

NUTR. ABS. (b)

Acid-combining power of gastric juice and its significance for the regulation of gastric acidity. H. SCHWARZ and M. TAUBENHAUS (Z. ges. exp. Med., 1933, 89, 506—528).—Marked acid-combining power (I) was shown by anacid juices, particularly unfiltered specimens, but not by acid juices. Max. (I) was obtained when the final p_H was 2.4—1.6; thereafter no more acid was bound. The Cl⁻ behaved as if the juice were a solution of inorg. salts. There was no significant correlation between (I) and N content. Mucus had a definite (I), but did not account for nearly all.

NUTR. ABS. (b)

Buffering action and protective power of gastric mucus. B. GROÁK (Z. ges. exp. Med., 1933, 89, 86—96).—Electrometric titration of the gastric juice, with and without contained mucus, from patients with gastritis showed that the mucus had no buffering action, except above p_H 2.5.

NUTR. ABS. (b)

Thiocyanic acid in gastric juice. H. R. KANITZ (Arch. Verdauungs-Krankh., 1933, 54, 42—52).—In Pavlov pouch dogs, HCNS secretion, unlike that of HCl, is not sustained at a uniform level, but falls gradually. The concn. of CNS⁻ varied from 0.2 to 2.3 mg. per 100 c.c. of juice.

NUTR. ABS. (b)

Enzymic activity of dogs' intestinal juice and its relation to intestinal digestion. F. A. CAJORI (Amer. J. Physiol., 1933, 104, 659—668).—The enzymic activity (I) of the intestinal juices from Thirty loops in the jejunum and ileum showed wide variations, even in samples from the same loop, which could not be correlated with physiological conditions, but were related to the quantity of juice secreted. (I) of juice from jejunal loops was $>$ that from the low ileal loops. Histamine subcutaneously increased the vol. of secretion and decreased enzyme concn. No correlation was found between (I) and food intake, any difference being related to the quantity of juice secreted. Peptone, starch, sucrose, and lactose, inserted into jejunal loops, were readily absorbed, whilst ovalbumin, inulin, raffinose, and glucoscuride were recovered unchanged. The absorption rate of peptone, sucrose, and lactose was $>$ would have been predicted on the basis of the (I) of the juice, whilst that of starch was commensurate with the amylase content.

NUTR. ABS. (b)

Relation between nutrition and lactation. V. ZAGAMI (Atti R. Accad. Lincei, 1933, [vi], 17, 973—979).—Further experiments on rats (A., 1933, 743) on various diets emphasise the close connexion between nutrition and lactation. Under some conditions lactation may be affected while all other functions, including reproduction, remain normal.

T. H. P.

Absence of a second phase in milk secretion. S. FILIPOVIC (Milch. Zentr., 1934, 63, 1—4, 17—20, 29—33).—The work of Isaachsen is refuted.

E. B. H.

Nutritional deficiencies of cow's milk and various milk preparations. E. GLANZMANN (Z. Vitaminforsch., 1934, 3, 2—27).—Young rats fed for a year solely on full-cream milk or milk powder showed subnormal growth, atrophy of the sexual glands, sterility, and lactational deficiency; rickets did not occur. When glass cages were used, there occurred an alimentary anaemia which was cured by administration of Fe+Cu, but not by either alone. A supplement of 0.05% Mn to the diet removed the lactation deficiency, whilst addition of black bread restored growth, fertility, and lactation. A diet of sweetened (but not of unsweetened) condensed milk caused pellagra, which was cured by feeding coagulated ovalbumin. Separated milk powder was still more inadequate, glucose or sucrose being necessary to correct the deficiency of fat. Buttermilk powder produced a protein intoxication which ultimately proved fatal.

F. O. H.

Effect of milk products on p_H of intestinal contents of domestic fowl. D. W. ASHCRAFT (Poultry Sci., 1933, 12, 292—298).—Rations containing milk products [20% and 40% buttermilk (I), 28% dried whey (II), 40% dried skim milk (III), and 20% lactose (IV)] as compared with a ration containing 20% meat scrap increased the p_H of the duodenal contents from 5.96 to 6.23—6.5, and that of the ileal contents from 7.13 to 7.16—7.68. The p_H of the caecal contents, however, fell from 7.06 to 5.1—6.7, and that of the contents of the large intestine from 7.26 to 7.04—6.28; 20% (IV) was the most effective agent, followed in order by (III), (II), and (I). The effect produced

was not proportional to the (IV) content of the ration.

NUTR. ABS. (b)

Rôle of the mineral salts of milk in nutrition.

O. B. WANSCHENK and E. J. DOLAN (Med. J. Rec., 1933, 138, 172—173).—Protein-Ca, extracted from sour whey, obtained in the manufacture of cream cheese, should be added to sweet whey from renneting in order to restore its mineral balance. The product is of high nutritive val. either in the liquid or the dried state.

NUTR. ABS. (m)

Iodine content of milk. I. Effect of desiccation and storage. Z. M. HANFORD, G. C. SUPPLEE, and R. E. REMINGTON. **II. Variation in the mixed milk of herds.** R. E. REMINGTON and G. C. SUPPLEE (J. Dairy Sci., 1934, 17, 15—18, 19—28).—I. The I content of milk dried either by the roller process or by slow evaporation after addition of NaOH was 60—80% of the initial val. Drying (by either process) of milk to which free I had been added resulted in the retention of approx. 83% of the total initial I. Changes in acidity within the range suitable for roller-drying did not influence the amount of I retained. No loss of I from dried milk occurred during storage for 7 months.

II. The average I content of 117 samples of milk from various sources was 572 ± 16 pts. per 10^{12} . Variations due to locality and season are recorded.

A. G. P.

Crystalline globulin from the albumin fraction of cow's milk. A. H. PALMER (J. Biol. Chem., 1934, 104, 359—372).—After removal of the caseinogen, the whey is conc. by freezing and the globulin fraction removed by pptn. with Na_2SO_4 (18 g. per 100 c.c.). The filtrate at 30° again treated with an equal amount of Na_2SO_4 gives a ppt. which, when dissolved in H_2O and dialysed at p_{H} 5.2, yields a cryst. protein (I). Since this is insol. in salt-free H_2O between p_{H} 4.5 and 5.5, it is considered to be a globulin. Solubilities of (I) in salt solutions are recorded. The distribution gives vals. similar to those for lactalbumin.

A. L.

Pus in milk. F. WIEDMANN (Z. Unters. Lebensm., 1934, 67, 174—178).—In certain cases, e.g., advanced mastitis, the Tromsdorff (T) sediment consists largely of casein (I) and its vol. is therefore no indication of the pus content of the milk. (I) is removed by digestion for 5 min. with pepsin and HCl, the sediment centrifuged again in the T tube, and its vol. measured. Normal milks having T vals. (T.V.) between 0.1 and 0.6 have Wiedmann vals. (W.V.) between 0.05 and 0.3. Milk from a cow suffering from advanced mastitis had a T.V. of 300—400, a W.V. of 5—7. Pasteurisation increases the T.V. from a mean of 0.3 to a mean of 1.0, the W.V. remaining unaltered.

E. C. S.

Albuminuria in the normal male rat. M. E. BELL (J. Physiol., 1933, 79, 191—193).—A protein, coagulable by heat, was found in the urine of normal adult male rats, in a concn. of 0.5—0.8 g. per litre. The protein was not identified, and was not present in the urine of female rats on the same régime.

NUTR. ABS. (b)

Determination of urobilin in urine by Terwen's method. (MLLE.) CHRISTOPHE (J. Pharm. Chim., 1934, [viii], 19, 105—111).—Details are given for

determining urobilin (> 1 mg. per litre) in urine within $\pm 5\%$, with special directions for urine containing albuminoids and indole. The presence of novocaine invalidates the method.

R. S. C.

Detection and determination of the bile acids in urine. G. RANZOLI (Boll. Chim. Farm., 1934, 73, 81—83).—A review of the surface tension methods. A 5-c.c. microburette, with a tap calibrated to deliver 5 c.c. of distilled H_2O in 100 drops at 15° , is recommended as a substitute for the Duclaux drop-counter.

R. N. C.

Rennin content of infants' urine. G. SERENYI and L. VESZELSZKY (Orvosi Hctilap, 1933, 77, 757—759).—Urine (I) of infants contains no rennin (II) when they are fed with human milk. If about half of the necessary milk is replaced by other food, (II) appears in the (I). This also occurs, independently of the food ingested, in toxicosis.

NUTR. ABS. (m)

Iodometric determination of cystine in urine. R. W. VIRTUE and H. B. LEWIS (J. Biol. Chem., 1934, 104, 415—421).—The method of Okuda (A., 1929, 730) requires, as optimal conditions for reaction, low temp., 2% HCl, and only a min. excess of I. In applying the method to determinations in urine the latter is decolorised with norit. Satisfactory recovery vals. for added cystine were obtained.

H. D.

Excretion of ammonia and neutrality regulation. A. P. BRIGGS (J. Biol. Chem., 1934, 104, 231—238).—Administration of KCl causes the urine to become more alkaline, because of excretion (I) of more fixed base (II) than mineral acid (III), with diminished (I) of NH_3 . Na_2SO_4 causes (I) of more (III) than (II) with an increased (I) of NH_3 . It is suggested that the mechanism of (I) of NH_3 is not controlled by acid-base changes in the tissues.

H. G. R.

Fixation of, and chemical and optical methods of staining, urinary sediments. Permanent preparations. P. SCHUGT (Pharm. Ztg., 1934, 79, 228—231).—The choice of a fixative and the techniques involved in chemical and optical methods of staining urinary sediments are discussed.

P. G. M.

Sugar tolerance in experimental acidosis and the effect of insulin and vitamin-B. S. TATSU-ZAWA (Sei-i-kwai Med. J., 1932, 51, No. 8, 1—16).

CH. ABS.

Production of acidosis and alkalosis by salts and diet. H. DENNIG, H. J. GOTTSCHALK, and L. TEUTSCHER (Arch. exp. Path. Pharm., 1934, 174, 468—475).—Diets yielding an acidic or basic ash produce in man a slight acidosis (I) or alkalosis (II), respectively. Soya-bean meal produces a fairly marked (II), but in all cases relatively small amounts of acid- or base-forming salts influence the result. NH_4Cl and Na citrate have an influence on (I) and (II) $>$ those of CaCl_2 and NaHCO_3 , respectively.

H

Sulphur content of hair and nails in abnormal states. Therapeutic value of hydrolysed wool. I. Hair. H. BROWN and J. V. KLAUDER (Arch. Dermatol. Syph., 1933, 27, 584—604).—Hair normally contains 4.6—5.1 (average 4.86)% S. In alopecia areata it contains 4.38%, and after hydrolysed wool

therapy 5.5%. Loss of hair is not necessarily associated with low S. The metabolism of S (cystine) is not exclusively concerned in hair loss. Dietary deficiency as a cause of hair loss is more apparent in laboratory animals than in man. CH. ABS.

Calcium and inorganic phosphorus in the blood in arthritis with ankylosis. J. MORELLE (Rev. belge Sci. méd., 1933, 5, 417—425).—In arthritis deformans, rhizomelic spondylitis, and vertebral rheumatism, serum-Ca (I) usually exceeds 11 mg. per 100 c.c. Plasma-phosphate is within normal limits and does not vary inversely with (I).

NUTR. ABS. (m)

Plasma-proteins, -calcium, and -cholesterol in beriberi. G. V. VILLELA (Compt. rend. Soc. Biol., 1933, 113, 1277—1279).—In five cases of wet beriberi the serum-albumin rose with the disappearance of oedema, whilst the serum-globulin was unchanged. Ca and cholesterol were normal in seven cases.

NUTR. ABS. (b)

Soil and mineral supplements in the treatment of bush sickness. T. RIGG and H. O. ASKEW (Empire J. Exp. Agric., 1934, 2, 1—8).—Sheep in bush-sick areas were maintained in perfect health by drenching with a suspension of a soil containing 6% of Fe_2O_3 sol. in $\text{H}_2\text{C}_2\text{O}_4$. Except in one instance drenching with $\text{Fe}^{\text{III}}\text{NH}_4$ citrate prevented sickness, but the wts. of sheep varied considerably under experiment. Suspensions of limonite were ineffective. A. G. P.

Experimental production of cancer by dust obtained from tarred roads. J. A. CAMPBELL (Lancet, 1934, 226, 233—234).—Road dust containing approx. 2% of tar causes cancer of the skin in mice with metastases sometimes in the lungs.

L. S. T.

Prevention of mineral oil and tar dermatitis and cancer. C. C. TWORT and J. M. TWORT (Lancet, 1934, 226, 286—287).—Textile grades of mineral oil are, on the whole, the most carcinogenic. Internal-combustion lubricating oils are of relatively low carcinogenic power (I), and "spirits," whilst capable of causing dermatitis, had no (I). In crude oils, (I) varies markedly with the geographical source, and, in general, is less the more fully hydrogenated is the oil. Treatment with H_2SO_4 or SO_2 , or, in general, any process which tends to hydrogenate or saturate the oils decreases (I). Refractivity is closely related to (I), and in most cases its determination can replace animal tests. Where exposure to carcinogenic oils is unavoidable, protection of exposed surfaces by lanolin and olive oil is effective. L. S. T.

Serum-calcium, -potassium, and -inorganic phosphate in cancer. Effect of X-ray irradiation. H. JACKSON, jun., and F. H. L. TAYLOR (Amer. J. Cancer, 1933, 19, 379—388).—Blood-Ca was normal in 52% and low in 48% of cases. Low vals. appear to result from disturbed nutrition associated with advanced carcinoma. Vals. for K and inorg. PO_4 were normal. After X-ray therapy K, Ca, P, Ca : P, and K : P were unaltered. CH. ABS.

Possibility of glycolysable haptene in tumour. W. R. FRANKS (Trans. Roy. Soc. Canada, 1933, [iii],

27, V, 135—140).—Attempts to demonstrate the presence of a glycolysable haptene in mouse tumour or Rous sarcoma failed. F. O. H.

Cataract as a result of dietary deficiency in larval *Amblystoma tigrinum*. E. M. PATCH (Science, 1934, 79, 57—58).—In larvæ of the tiger salamander fed on highly-purified milk powder-casein diets the lenses of the eyes turn milky-white, and pass through stages like those of senile cataract of the cortical type. The disease is due to inadequacy of the basic milk diet, and is not prevented by an increase in vitamin-A or $-B_2$. L. S. T.

Blood- and skin-cholesterol in dermatoses with atypical keratosis. T. CHORAZAK (J. Physiol. Path. gen., 1933, 31, 408—413).—In psoriasis, eczema, lupus, etc. administration of Ca, As, or fat or ultra-violet irradiation causes increase in skin- (I) and blood- (II) -cholesterol. No direct relationship between (I) and (II) can be traced, but there is a well-defined relation between (II) and Ca content.

NUTR. ABS. (m)

Abnormalities of calcium deposition in diabetes mellitus. H. F. ROOT, P. WHITE, and A. MARBLE (Arch. Int. Med., 1934, 53, 46—53).—Diabetes may be accompanied by osteomalacia and by abnormal Ca deposits in the body. Adequate Ca intake is essential. W. O. K.

Availability of fructose in normal and diabetic animals. M. ABE (J. Biochem. Japan, 1934, 19, 69—110).—With normal dogs the min. amount of fructose (I) necessary to cause fructosuria (II) is < that of glucose (III) necessary to cause glycosuria; the degree of hyperglycæmia (IV) is also lower with (I) than with (III). Hence the renal threshold (V) for (I) is low compared with that for (III). With diabetic dogs, (V) is increased, and the degree of (II) and (IV) indicates that the diabetic organism utilises (I) more readily than (III). F. O. H.

Choline and liver-fat in diabetic dogs. C. H. BEST, G. C. FERGUSON, and J. M. HERSEY (J. Physiol., 1933, 79, 94—102).—In depancreatized dogs on a lean beef diet plus vitamins, the symptoms associated with accumulation of liver-fat (I) and degeneration of liver cells, were prevented by giving choline. The decrease in (I) which also occurred was sometimes accompanied by increased sugar excretion. NUTR. ABS. (b)

Liver and the respiratory metabolism of pancreatic diabetes. G. C. RING and C. W. HAMPEL (Amer. J. Physiol., 1933, 105, 306—310).—The raised metabolism (I) of the depancreatized cat persists after the formation of an Eck fistula or the removal of 50—70% of the liver tissue. It seems unlikely, therefore, that processes occurring in the liver are responsible for the high (I), and the results support the previous conclusion that protein catabolism is not alone responsible. NUTR. ABS. (b)

Protein metabolism in pancreatic diabetes. G. C. RING and C. W. HAMPEL (Amer. J. Physiol., 1933, 105, 300—305).—Following pancreatectomy, with insulin administration, in most cases the post-absorptive urinary N excretion (I) of cats was increased, although the metabolism (II) was normal; withdrawal of insulin produced the usual rise of (II),

but no significant increase of (I). The raised (II) of the diabetic cat is not completely explained by the sp. dynamic action of protein. NUTR. ABS. (b)

Hyperglycæmia, glycosuria, and the respiratory quotients following insulinisation of non-diabetics. W. D. PAUL, B. B. CLARK, and C. MARTIN (Amer. J. Physiol., 1933, 105, Proc. 79).—Non-diabetic individuals on mixed diet tolerate insulin (I) up to 75 units daily, without hypoglycæmia. On discontinuing (I), glucose-tolerance curves of a mild diabetic type are obtained, together with lowered R.Q. Return to the normal state is progressive over several days. NUTR. ABS. (m)

"Fatty diarrhoea," with special reference to nitrogen metabolism. A. G. ANDERSON and A. LYALL (Quart. J. Med., 1933, 2, 339—351).—Although both types of fatty diarrhoea showed a grossly negative total N balance, only in the type with a pancreatic lesion was there high N excretion by the bowel. NUTR. ABS. (b)

Chemical composition of exudates. J. S. HEPBURN and H. B. FEGLEY (Amer. J. Pharm., 1934, 106, 16—17).—A pleural exudate and a peritoneal exudate (I) contained, respectively, total solids 5.96, 5.64; moisture 94.04, 94.36; ash 0.40, 0.48; fat 0.72, 0.83; total N 0.03, 0.20. Neither contained blood; (I) contained amylase but not esterase. W. O. K.

Reduced glutathione content of organs in artificially-produced fever [in dogs]. L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1933, 113, 124; Chem. Zentr., 1933, ii, 1200).—Intravenous injection of $\text{ONa} \cdot \text{C}_6\text{H}_5(\text{NO}_2)_2$ in dogs produces a rise in temp. to 44°. The SH-glutathione content of the liver is markedly increased, whilst those of the spleen and lungs are decreased. L. S. T.

Blood-sugar in scarlet fever, measles, and varicella. L. MANZONI (Riv. clin. pediatr., 1932, No. 12).—Blood-sugar rises during the febrile stage of scarlet fever and measles. No change was found in varicella. CH. ABS.

Diazo-urine. III. Composition of urine in scarlet fever. IV. Composition of urine in measles. S. NAKAYAMA (J. Biochem. Japan, 1934, 19, 33—38, 39—43; cf. A., 1927, 170).—III. 9.7 litres of diazo-urine (I) from scarlet-fever patients yielded 7.18 g. of antoxyproteic acid (II) (A., 1906, i, 122), 1.07 g. of oxyproteic acid (III), 0.02 g. of histidine (IV), 0.08 g. of arginine (V), 0.25 g. of lysine (VI), and $(\text{NH}_2)_1$ -acids equiv. to 0.56 g. of N.

IV. 6.8 litres of (I) from measles patients yielded 6.5 g. (as Ba salt) of (II), 4.5 g. (as Ba salt) of (III), 3.08 g. (as picrolonate) of (IV), 0.32 g. (as picrate) of (V), and 0.55 g. (as picrate) of (VI). F. O. H.

Goitre and drinking water in Switzerland. T. VON FELLEBERG (Mitt. Lebensmitt. Hyg., 1933, 24, 123—142; Chem. Zentr., 1933, ii, 1201).—No relation between the frequency of goitre (I) and the I content or the inorg. constituents could be established for the 57 principal tap H_2O (II), which were poor in I (0.2 to 1.8×10^{-8} g. per litre). In general, but not invariably, (I) increases with an increase in wt. of dried residue from (II), and especially with hardness. It

decreases with the age of the geological formation from which the H_2O is drawn. Since the places supplied with lake H_2O , in spite of the softness of the H_2O , are not free from (I), it appears that factors other than hardness which partly decrease with age of the rocks are responsible for (I). An Fe-containing (II) lost most of its I in the removal of Fe by de-aeration. L. S. T.

Lactic acid metabolism in disturbed thyroid function. I. Variations in blood-lactic acid after injection of lactate. II. Lactic acid and gas metabolism during muscular work. III. Lactic acid metabolism in the liver after injection of lactate. K. KATO (Tohoku J. Exp. Med., 1933, 21, 238—256, 257—279, 280—297).—I. Oxidation and resynthesis of intravenously injected Na lactate are disturbed in hyperthyroid and thyroidectomised rabbits, and in exophthalmic goitre.

II. Increase in blood-lactic acid and O_2 consumption caused by muscular contraction in hyperthyroid is $>$ in normal animals. Resynthesis of lactic acid (I) is delayed. The effect of exercise in thyroidectomised rabbits is normal.

III. (I) is resynthesised to glycogen during its passage through the liver. Normal (I) vals. are: arterial $>$ portal $>$ hepatic venous; hyperthyroid vals. are: venous $>$ portal $>$ arterial, glycogen being mobilised more rapidly than it is synthesised. CH. ABS.

Blood-catalase in heart disease. I. J. C. HEALY and H. BAKER (J. Lab. Clin. Med., 1933, 19, 133—141).—Blood-catalase is increased in rheumatic heart disease and scarlatinal endocarditis, and normal in cases of scarlet fever and diphtheria which show no heart damage. CH. ABS.

Quantity of the glomerular filtrate. II. Cardiac insufficiency and hypertension. F. NAKAZAWA, J. IZUMI, and I. SEKI (Tohoku J. Exp. Med., 1933, 22, 159—166).—In cardiac decompensation and in hypertension with kidney disease the quantity of glomerular filtrate and creatinine excretion decrease. CH. ABS.

Possibility of a pressor principle in the blood in hypertension. A. H. ELLIOT and F. R. NUZUM (J. Lab. Clin. Med., 1933, 18, 1255—1260).—Intravenous injection of large amounts of fresh citrated blood from normal persons into rabbits usually produces a transitory rise in blood-pressure followed by a prolonged fall. Injection of blood from patients with hypertension produces a higher initial rise. Injection of EtOH , Et_2O , and H_2O -sol. fractions of blood cause a transitory fall. CH. ABS.

Blood-sugar in experimental hypertension. E. NETER (Klin. Woch., 1933, 12, 1317—1318).—Since section of the aortic nerves and the nerves of the carotid sinus of rabbits and dogs has usually no effect on the blood-sugar, the view that the rise of blood-pressure in these circumstances is due to adrenalinæmia is not supported. NUTR. ABS. (m)

Colloid-osmotic pressure of the blood in normal and pathological conditions. VIII. Hunger. J. HATAFUKU and F. NAKAZAWA (Tohoku J. Exp. Med., 1933, 21, 226—237).—Blood-protein (I) in fasting dogs is increased, but the colloid-osmotic pres-

sure (II) per unit protein first decreases and then increases. In hyperthyroid dogs (I) increases and (II) decreases, hunger producing an increase in both factors.

CH. ABS.

Hunger hypoglycæmia in infants. III. Blood-sugar following administration of acid or alkali during fasting. H. SCHONFELD (Jahrb. Kinderheilk., 1933, 140, 215—218).—Administration of 0.1N-HCl or -NaHCO₃ during a hunger period of 4 or 16 hr. decreases the fall in the fasting blood-sugar level. The cause may be reduced glycolysis in the tissues.

NUTR. ABS. (m)

Disturbances of metabolism in acute under-nutrition in infants. III. Creatine excretion and basal metabolism. IV. Creatine excretion and specific dynamic action. L. GAROT (Rev. franç. Pédiat., 1933, 9, 273—312, 313—333).—III. Determinations of the basal metabolic rate (I) in healthy infants and those in the first stage of hypothyrepsia yield vals. (47.8—57.6; average 51.0 g.-cal. per kg. actual wt. per 24 hr.) very similar to those obtained by Benedict and Talbot. In those infants in the second stage of hypothyrepsia the vals. of group A with a normal excretion of total creatinine compounds are high, whilst in group B with reduced excretion of creatinine the (I) is reduced. In group B there is a qual. as well as a quant. disturbance (II) of metabolism, whereas in group A the increase in (I) per kg. body-wt. is due to loss of "inactive" tissue and not to any change in the metabolic processes. The use of wt. loss as a criterion of hypothyrepsia is valueless, since it is no indication of the nature of (II).

IV. In healthy infants receiving buttermilk containing 5% of maltose the sp. dynamic action (III) is 20% of the basal metabolism, lasting for 3 hr. after the ingestion of the feed. In hypothyrepsia of the second stage (III) is increased (25.2—30.7%) in group A. In group B (III) is markedly reduced (6.7%).

NUTR. ABS. (m)

Colloid-osmotic pressure of the blood in normal and pathological conditions. VIII. Experimental ileus. J. IZUMI (Tohoku J. Exp. Med., 1933, 22, 149—158).—In rabbits the serum-protein increases, but the colloid-osmotic pressure per unit protein decreases.

CH. ABS.

Effect of obstruction of the bile-duct on the bilirubin content of serum and on the number of erythrocytes. A. VISCHER (Biochem. Z., 1934, 268, 116—120).—In rabbits the very low (< 0.1 mg. per 100 c.c.) bilirubin content of the blood-serum increases greatly (> 10-fold in 24 hr.) when the duct is obstructed.

W. McC.

Liver insufficiency and amino-acid metabolism. K. HOESCH and C. STEVERT (Klin. Woch., 1933, 12, 1357—1358).—The intravenous injection of 1.0 g. of glycine followed by the determination of free and combined NH₂-N and blood-urea is a suitable test of liver function. In liver injury the primary rise of free NH₂-N is prolonged, and the subsequent rise of combined NH₂-N and blood-urea delayed.

NUTR. ABS. (b)

Galactose in physiological and pathological conditions. V. Significance of galactose and glucose in the blood after ingestion of galactose

for the diagnosis of liver function. H. KOSTERLITZ (Z. ges. exp. Med., 1933, 90, 465—478).—After ingestion of 40 g. of galactose (I) by healthy subjects the blood-(I) rose to about 40 mg. per 100 c.c. (max. 63) in 1 hr., falling to nil at 2 hr.; blood-glucose (II) rose by 40 mg. per 100 c.c. In icterus simplex the (I) rose to 150 mg., whilst the rise in (II) was normal or less. In diabetes mellitus the rise of (I) was normal, that of (II) excessive. In hepatic diseases the (I) curve was abnormal only when there was cellular damage. In Graves' disease the curve may be normal or of the hepatic or diabetic types. Ordinarily examination of the urine for (I) after ingestion of (I) suffices as a test, but a blood curve gives more information.

NUTR. ABS. (b)

Diagnostic value of serum-protein changes in kala-azar. M. R. G. MUDALUJAR, S. K. SUNDARAM, and A. S. RAMACHANDRAN (Indian J. Med. Res., 1933, 21, 361—378).—Serum-globulin increases, -albumin decreases, and -eu-: -total globulin increases. Determinations of serum-protein and -albumin: -globulin are valuable, but not diagnostic.

CH. ABS.

Lipolytic activity of rat lepromas during treatment with various antileprotics. G. EMERSON, H. H. ANDERSON, and C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1933, 31, 18—20).—The low lipase content of rat lepromas and of other tissues of infected rats is probably due to the invasion of normal tissue by *Mycobacterium lepræ muris*. The lipolytic activity of lepromas was unchanged by treatment with various antileprotics.

CH. ABS.

Derivatives of 8-aminoquinoline as anti-malarials. III.—See this vol., 417.

Mechanism of Henry's reaction [for paludism]. V. CHORNE and R. GILLIER (Ann. Inst. Pasteur, 1934, 52, 193—216).—This reaction depends on the state of non-equilibrium between dissolved substances (slightly sol. in distilled H₂O) and the mol. concn. of the serum. Dialysis increases the ability to undergo flocculation, whilst addition of salts diminishes it. In paludism globulins and the Et₂O-sol. substances of the serum are increased, and negative sera become "positive" on addition of globulin, lecithin, cholesterol, or uric acid. No sp. antibody is involved and melanin serves merely as a suitable indicator.

P. G. M.

Osteitis deformans. H. D. KAY, S. L. SIMPSON, and G. RIDDOCH (Arch. Int. Med., 1934, 53, 208—248).—During osteitis deformans the contents of fat and org. matter of the bones increase, whilst the ash content decreases. The % Ca and Mg are < normal. Whilst the serum-Ca and -P are approx. normal, the serum-phosphatase is markedly increased. A retention of Ca, Mg, and P in the body, but a loss of S, occur.

F. O. H.

Blood in normal pregnancy. II. Hæmoglobin, hæmatocrit, and erythrocyte determinations. W. J. DIECKMANN and C. R. WEGNER (Arch. Int. Med., 1934, 53, 188—207).—During pregnancy in women, the hæmoglobin (I) per kg. body-wt. slightly increases, but the (I) per 100 c.c. of blood decreases by a max. of 15% (26th to 35th week); at 2 and 8 weeks *post partum*, it is 17 and 14%, respectively, < normal. Similar changes occur in the

haematocrit val. (II) and the erythrocyte count. Although (I) and (II) experience a relative decrease, there is an abs. increase in both owing to the large increase in plasma vol. Thus the total amount of (I) shows an average increase of 13% and of (II) 20%.

F. O. H.

Choline in the human uterus in pregnancy and non-pregnancy; relations between the choline content of the human uterus and uterine contraction. L. CATTANEO (Atti R. Accad. Lincei, 1933, [vi], 17, 968—973).—The results of previous workers and those now given indicate that choline cannot be regarded as a normal constituent of either the pregnant or the non-pregnant uterus, and that the hypothesis that choline is the hormone of uterine peristalsis is without foundation.

T. H. P.

Sexual hormone in women with gynaecological diseases, particularly menstrual disturbance. R. BOMPIANI (Rass. Clin. Terap. Sci. aff., 1933, 31, 149—158; Chem. Zentr., 1933, ii, 2155).—Zondek and Aschheim's reaction 3 is almost exclusively confined to pregnancy. Reaction 1 is frequently given by women with carcinoma of the genital organs, after surgical and X-ray castration, after the natural menopause, and in anomalous menstrual function.

A. A. E.

Carbohydrate metabolism in pruritus and chronic urticarias. J. G. PRIETO and M. G. REY (Arch. med. chirurg. espec., 1932, 35, No. 52).—Hypoglycaemia was found in 10 of 16 cases.

CH. ABS.

Investigation of scalding. S. NICOLAU and P. POINCELOUX (Ann. Inst. Pasteur, 1934, 52, 217—240).—In the blood of rabbits which have been scalded an increase in the no. of mononuclear and primordial cells can be observed, together with a slight increase in Turck cells and the appearance of some Rieder cells. A toxin appears in the blood which, on intraperitoneal injection in mice, causes death; it is also present in the liver. The blood exhibits a definite flocculation phenomenon.

P. G. M.

Silicic acid content of the lungs of quartz workers in Styria. H. LIEB and E. SCHADENDORFF (Arch. Gewerbepath. Gewerbehyg., 1933, 4, 576—579; Chem. Zentr., 1933, ii, 2701).—SiO₂ constituted 0.3—1.46% of the dry residue or 4.6—22.8% of the ignited residue from the lung, the normal vals. being 0.08—0.21% and 1.28—4.0%, respectively.

H. J. E.

Effect of splenectomy on blood-calcium and -potassium. L. BOUISSET and G. DUCLOS (Compt. rend. Soc. Biol., 1933, 113, 1358—1360).—The alkali reserve (I) and the total and plasma-Ca of the blood of dogs fall slightly after splenectomy, the vals. returning to normal after about 45 days. No regular variations occur in the K content of whole blood or plasma. The changes occurring in (I) and Ca may be associated with the hypertrophy of Aselli's pancreas and the hæmal glands associated with the digestive tract.

NUTR. ABS. (m)

Cerebrospinal fluid-sugar and -chlorides in neurosyphilis. G. BREWER (Amer. J. Syphilis, 1933, 17, 382—386).—The normal ratio cerebrospinal fluid : blood-sugar is 0.647, and of Cl' 1.48. The Cl' ratio is significantly decreased in neurosyphilis only in severe meningeal irritation or damage; in general

paresis the average ratio is 1.36. The sugar ratio (in paresis 0.519) tends to decrease with increasing meningeal damage.

CH. ABS.

Relation of amino-acid-nitrogen to the Wassermann reaction. G. BREWER (Amer. J. Syphilis, 1933, 17, 221—227).—In neurosyphilis the blood : cerebrospinal fluid-NH₂-acid-N was 0.261 (0.171—0.335); normal vals. were 0.260 (0.163—0.431). NH₂-acid-N is apparently not related to the Wassermann reaction.

CH. ABS.

Vitiation of the Wassermann reaction and other reactions by tannic acid from cork stoppers of sample tubes. F. PLAUT (Münch. med. Woch., 78, 1125—1126; Chem. Zentr., 1933, ii, 2693).—Interference with the Wassermann reaction and protein and colloid reactions of blood and cerebrospinal fluid may occur. The use of rubber stoppers is recommended.

H. J. E.

Cork and complement binding. W. RIMPAU and G. SCHNEIDER (Zentr. Bakt. Par., 1932, I, 124, 568—571; Chem. Zentr., 1933, ii, 2694).—Plaut's results (see above) were not confirmed.

H. J. E.

Cork and complement binding. F. PLAUT (Zentr. Bakt., Par., 1932, I, 126, 135—137; Chem. Zentr., 1933, ii, 2694).—A reply to Rimpau. Tannic acid solutions and aq. extract from cork are shown to hinder hæmolysis in the complement-binding reaction.

H. J. E.

Mapharsen (m-amino-p-hydroxyphenylarsine oxide) as an antisymphilitic agent. A. L. TATUM and G. A. COOPER (J. Pharm. Exp. Ther., 1934, 50, 198—215).—The max. tolerated and min. lethal doses, and therapeutic index of mapharsen (I), for rats, rabbits, cats, and dogs, were const., whereas those of mixtures such as the arsphenamines (II) varied considerably. Slow oxidation of (I) reduced the toxicity, whilst those of (II) were increased. In experimental syphilis in rabbits, (I) had a curative action in 1/30 the amount of neoarsphenamine required. The single sterilising dose of (I) was 6 mg. per kg.

R. N. C.

Glucose-tolerance curves in pulmonary tuberculosis. D. W. KRAMER (J. Lab. Clin. Med., 1933, 18, 1212—1220).—Tolerance for glucose is increased. High or diabetic types of curve were found in 17%, low curves in 24%, and normal curves in 59% of the 100 patients examined.

CH. ABS.

Serum-proteins in pulmonary tuberculosis. I. SATO (Tohoku J. Exp. Med., 1933, 22, 116—125).—The globulin : albumin ratio increases.

CH. ABS.

Vitamin therapy in pulmonary tuberculosis. III. Effect of viosterol on absorption, retention, and excretion of calcium. P. D. CRIMM, J. W. STRAYER, H. L. WATSON, and G. HEIMANN (Amer. Rev. Tuberc., 1933, 28, 202—216).—During early administration, in man, urinary Ca (I) and faecal Ca (II) decrease; on continued administration serum-Ca and (I) increase, whilst (II) decreases.

CH. ABS.

Auto-antibodies in tuberculosis. O. FISCHER (Z. Tuberk., 1933, 68, 5—6).—Certain tuberculous sera gave a positive complement fixation reaction with EtOH lung extracts. The reaction may be due to the presence of lung-lipin antibodies in the sera or to serum lability.

CH. ABS.

R and S types of tubercle bacilli in pulmonary tuberculosis. G. B. REED, C. E. RICE, and J. H. ORR (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 225—227).—The ratio of the complement fixation with *S* and *R* tubercle bacilli antigens ("S/R index") (cf. following abstract) is high in active tuberculosis in man, but low in chronic or improving cases. F. O. H.

Complement-fixing antibodies in rabbits immunised with *S* and *R* tubercle bacilli. G. B. REED, C. E. RICE, and B. G. GARDINER (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 219—224).—The serum of rabbits treated with heat-killed *S* bacilli gives approx. twice as much complement fixation (I) with *S* antigens (II) as with *R* (II). Parallel experiments with *R* organisms, however, yield the same degree of (I) with both *S* and *R* (II). Hence the *S* type contains two (II), one *S*-sp. which reacts only with *S* antibodies (III), and another which reacts equally with *S* and *R* (III), whilst the *R* form contains the species- but not the *S*-sp. (II). F. O. H.

Blood-sugar in typhoid. E. V. KASSATKIN (Wien. Arch. inn. Med., 1933, 24, 85—100).—Hypoglycæmia is common in typhoid, occurring usually after the fifteenth day, and resulting from exhaustion of glycogen reserves by starvation. A high-carbohydrate diet is therefore important.

NUTR. ABS. (m)

Chemical processes in embryonic induction. M. W. WOERDEMAN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 842—849).—Introduction of suitable agents (rat and human cancer tissue, human muscle, gelatin gels containing glycogen) into the blastocœle of axolotl gastrulæ results in the formation of a secondary neural plate, in a thickening of the ectoderm, etc. Induction by localised rise of temp. occurred in only a few instances. Whilst effective inductors are generally associated with a high glycogen content or with marked glycolysis, the phenomenon probably depends on a localised change of the metabolism of the ectodermal cells (cf. A., 1933, 630, 855, 1074). F. O. H.

Metabolism in the sea-urchin embryo. P. E. LINDAHL (Naturwiss., 1934, 22, 105).—An inhibitory action of Li on respiration may be observed 3 hr. after fertilisation of eggs of the sea-urchin. This effect, which also occurs in yeast, is counteracted by K.

R. K. C.

Urochrome and the part played by lyochromes in cellular respiration. T. WAGNER-JAUREGG and H. WOLLSCHITT (Naturwiss., 1934, 22, 107; cf. Stern and Greville, A., 1933, 1324).—Urine contains very small amounts of a lumiflavin. Urochrome is not a flavin. Lactoflavin does not convert hæmoglobin into methæmoglobin: the effect observed by Stern and Greville is due to impurities or to flavin and an activator.

R. K. C.

Tissue respiration and the indophenol-oxidase reaction of serous membranes. K. KIYOHARA and S. KAGIYAMA (J. Biochem. Japan, 1934, 19, 59—68).—The O₂ consumption of various tissues (omentum, mediastinum, pericardium, mesentery, pleura, and peritoneum) of the dog and rabbit is approx. proportional to the no. of oxidase granules present.

F. O. H.

Variations in oxidation and reduction activities of tissues with sex. V. Influence of the organs of reproduction. S. KAGIYAMA (J. Biochem. Japan, 1934, 19, 45—58).—With embryonic, young, or adult rabbits, the oxidation and reduction activities of the tissues of the male are respectively > and < those of the female. Castration and transplanting experiments indicate that these differences are correlated with the sexual organs (cf. A., 1933, 527).

F. O. H.

Diurnal cycle in the liver of the white rat. II. Food, a factor in its determination. G. M. HIGGINS, J. BERKSON, and E. FLOCK (Amer. J. Physiol., 1933, 105, 177—186).—There is a diurnal cycle in the glycogen, protein, and H₂O contents, and the total wt. of the liver of the white rat. The position of the two peaks in the curve is determined by the time of food intake.

NUTR. ABS. (m)

Effects of chlorophyll in the diet of the albino rat. F. R. EDWARDS and K. T. HOLLEY (Georgia Agric. Exp. Sta. Bull., 1932, No. 173, 1—11).—Addition of chlorophyll (I) to Sherman's diet *B* for rats produced no significant difference in body-wt. increases, although a slight lowering of the food requirement per unit gain in wt. was apparent. The major part of the ingested (I) was eliminated in the faeces as phæophytin.

A. G. P.

Digestibility of Steffen sugar-beet slices by fowls. E. MANGOLD and H. BRUGGEMANN (Arch. Geflügelk., 1933, 7, 161—170).—When 20, 25, or 40% of the total ration is replaced by the slices (I), their digestibility is < that of the normal ration. N-free extractives, which total 77% of the dry matter and include 35% sugar, give only 54% digestibility. Good results with (I) must be due to a "dietetic" effect.

NUTR. ABS. (m)

Food value of seeds of *Vicia faba*, L. V. ZAGAMI (Atti R. Accad. Lincei, 1933, [vi], 18, 327—329).—For growing rats these seeds are an incomplete food, being deficient in salts and in vitamin-A and -D; vitamin-B and -E are present in suitable proportions.

T. H. P.

Biological value of proteins of peas. I. P. TSCHUKITSCHEV and M. N. TSCHUKITSCHEV (Biochem. Z., 1934, 268, 83—92).—The proteins (I) of peas are as satisfactory for maintaining life and growth in rats as is caseinogen. The contradictory results of Osborne *et al.* (A., 1912, ii, 1190) and McCollum may be due to differences in methods of prep. and physical properties of (I).

W. McC.

Soya-bean milk and chicken protein. J. S. HEPBURN, K. S. SOHN, and L. P. DEVLIN (J. Franklin Inst., 1934, 217, 213—221).—Soya-bean milk (I) contains protein 3.5%, carbohydrate 0.61, fat 2.35, Ca 0.034, and P₂O₅ 0.091 [cow's milk (II) 3—4, 4.6—5.0, 3—6, 0.120, 0.23]. (I) curdles at a lower *c_H* than (II) and cannot replace (II) in a basal diet so efficiently, although no avitaminosis occurs. Chicken protein is a less efficient protein than caseinogen in the diet of young rats.

P. G. M.

Relationship of the metabolic nitrogen of the faeces to body-weight and to food intake for rats. B. H. SCHNEIDER (Biochem. J., 1934, 28, 360—

364).—The metabolic N (I) in the faeces of rats depends partly on the food intake and partly on the body-wt., but for intakes of food above a certain min. val. the ratio of (I) to the intake of dry food assumes a practically const. level. W. O. K.

Validity of the Terroine-Sorg-Matter law on endogenous protein metabolism in cold-blooded animals. R. BONNET (Arch. internat. Physiol., 1933, 37, 104—120).—The ratio (I) N output : respiratory exchange per kg. body-wt. per hr. is const. between 0° and 30° for turtles and frogs. The metabolism of the tortoise per kg. body-wt. at any temp. is > that of the frog. (I) approaches more closely, in the tortoise, than in the frog, to that of the homeotherms (II). Reptiles are intermediate, physiologically and biochemically, between poikilotherms and (II). NUTR. ABS. (m)

Chemical separation of urine and faeces in birds and its use in determining the digestibility of proteins. H. STOTZ (Arch. Tierernähr. Tierzucht, 1933, 9, 426—437).—A method for the separate analysis of faecal and urinary N in birds is based on the oxidation of uric acid from the urine by HNO_3 , and is utilised in determining the digestibility of cereal proteins by hens. The digestibility of crude protein in wheat (I), barley (II), oats, and rye (III), and that of the crude fibre of (II) and (III), was higher for summer than for winter varieties. In (I) the fibre of winter varieties had much the higher digestibility. A. G. P.

Digestibility of nutrients in commonly used feeding-stuffs by hens, with special reference to protein as examined by a new method. H. PETERS (Arch. Tierernähr. Tierzucht, 1933, 9, 438—469).—Digestibility trials with a no. of cereals and fish meal are recorded. Vals. obtained for crude protein digestibility by Stotz's method (preceding abstract) differ in some cases from those usually accepted. A. G. P.

Fate of *d*-l-methionine, glycine, *d*-glutamic acid, and *l*-pyrrolidonecarboxylic acid in the dog. J. A. STEKOL and C. L. A. SCHMIDT (Univ. California Pub. Physiol., 1933, 8, 31—42).—In dogs receiving a const. diet, methionine caused an increased excretion of urea (I), SO_4 , and creatinine (II). Both *d*- and *l*-forms were metabolised. Glycine caused an increased excretion of (I), (II), and sometimes SO_4 . *d*-Glutamic acid caused an increased excretion of (I) and SO_4 . Pyrrolidonecarboxylic acid had no effect on the urinary excretion beyond a decrease in the output of SO_4 . It probably combined with SO_4 and was excreted in the bile. NUTR. ABS. (b)

Formation of sulphate from cysteine and methionine by tissues *in vitro*. N. W. PIRIE (Biochem. J., 1934, 28, 305—312).—Slices of rat liver (I) and kidney (II) (cf. A., 1933, 856) when shaken in 95% O_2 with a solution of cysteine (III) in NaHCO_3 -Ringer solution oxidise (III) to SO_4 (IV) at a rate comparable with that calc. from feeding tests with the intact animal (cf. A., 1932, 646). Cystine is oxidised only after reduction to (III), and glutathione (V) only after hydrolysis. (II) has a much greater power of oxidising (V) than (I), and its peptide-splitting enzymes make (III) available more rapidly than it can

be oxidised. Methionine (VI) is oxidised to (IV) at approx. the same rate by both (I) and (II), but much more slowly than (III), and there is little quant. relation between *in vitro* and *in vivo* rates of oxidation of (VI). Ethylcysteine is very slowly oxidised at relatively high concn. and ergothioneine and thiocarbamide not at all, nor do these last act as catalysts in the oxidation of other S compounds. Blood, testis, spleen, heart, and lung are inactive. A mechanism for the oxidation of (III) and (VI) is proposed. A modification in the technique of colorimetric micro-sulphate determination is described (cf. A., 1931, 1177).

A. E. O.

Increase of liver-proteins by mixed diet containing a natural mixture of amino-acids. C. GAUTIER (Bull. Soc. Chim. biol., 1933, 15, 1563—1565).—On a diet containing a natural mixture of NH_4 -acids and glucose the frog's liver increases in wt. by 2—4 times and the liver-proteins by 90—125%.

H. D.

Tryptophan metabolism. IV. Influence of optical activity on the utilisation of tryptophan for growth and for kynurenic acid production. C. P. BERG (J. Biol. Chem., 1934, 104, 373—384).—*d*- and *l*-Tryptophan (I) and acetyl-*l*-tryptophan are equally effective in promoting the growth of the rat, whilst acetyl-*d*-tryptophan is not utilised in this way. Of these substances only *l*-(I) leads to kynurenic acid excretion, acetylation reducing its convertibility very considerably. A. L.

Effect of oral administration of creatinine on blood and urine. J. D. S. CAMERON (Quart. J. Exp. Physiol., 1933, 23, 351—366).—On an "ordinary diet" with an average of 95 g. of protein per day the blood-creatinine (I) level was const. (1.35—1.55 mg. per 100 c.c.) with an average urinary output of 1.48 g. On a protein-free diet, the (I) was 1.15—1.55 mg. per 100 c.c. and the urinary creatinine (II) 1—1.3 g. per day. The ingestion of pure creatinine (III) was followed by a sharp rise in the (I) and (II) curves with a slow fall to normal level. The whole of the administered (III) was found in the urine within 24 hr. Raised (I) concn. alone does not cause "uræmic" symptoms. NUTR. ABS. (b)

Nitrogen balance. H. PENAU and J. GAUDUCHON (Bull. Soc. Chim. biol., 1933, 15, 1483—1497).—Intake of N in man is determined on a dried, powdered, aliquot portion of the total daily ingesta. The Dumas technique gave results > a no. of others.

H. D.

Purine metabolism. I. Exogenous. II. Endogenous. K. TOMITA (Sei-i-kwai Med. J., 1932, 51, No. 5, 95—136; No. 6, 37—118).—I. Feeding purine (I) to guinea-pigs does not increase uric acid excretion, although total N is proportionally increased. The average uricolytic index of the normal guinea-pig is 98.8 and the (I) coeff. 309. The end-product of (I) metabolism is allantoin (II).

II. The end-product, chiefly (II), is low in summer and high in winter. Partial removal of the liver or blockage of the reticulo-endothelial system diminishes (I) metabolism. CH. ABS.

Purine metabolism. J. PAROULEK (Acta med. Scand., 1933, 80, 127—135).—The peripheral tissues

in man did not absorb uric acid injected into the portal and/or peripheral veins.

NUTR. ABS. (b)

Real value of endogenous purine metabolism. E. F. TERROINE and G. MOUROT (Compt. rend., 1934, 198, 772—774).—Purine metabolism accounts for only 16—23% of the purine compounds and 2% of the total N excreted by rats subjected to protein starvation.

R. S. C.

Lipin metabolism. I. Hypercholesterolaemia in omnivora and herbivora caused by parenteral dosage with colloidal cholesterol and lecithin. I. REMESOV and N. TAVASTYERNA. **II. Blood-sugar curves in carnivora and herbivora during experimental lipaemia.** **III. Changes in lipin metabolism caused by adrenaline, insulin, and some alkaloids.** I. REMESOV and D. MATROSSOVITSCH. **IV. Relation between cholesterol and carbohydrate metabolism in herbivora and omnivora.** I. REMESOV and O. SEPALOVA. **V. Blood-lipase in carnivora and herbivora during experimentally-produced lipaemia.** I. REMESOV and N. TAVASTYERNA. **VI. Influence of cholesterol on pepsin secretion.** I. REMESOV and D. MATROSSOVITSCH (Z. ges. exp. Med., 76, 419—462; 77, 67—86, 87—98, 100—119; 1933, 87, 613—622, 623—624; Chem. Zentr., 1933, ii, 2695—2696).—I. Colloidal cholesterol (I) causes hypercholesterolaemia (II) in rabbits, (I) being absorbed in the lungs. Parenterally administered lecithin causes lecithinaemia in herbivora and carnivora; simultaneous (II) occurs in herbivora.

III. Intravenous adrenaline injection causes hyperglycaemia (III) and a fall in blood-(I). A change from carbohydrate to lipin is indicated. Injection of nicotine, adonidin, and strophanthin causes similar results. Hypoglycaemia after insulin injection occurs with diminution of the blood-sugar, showing a change from lipin to carbohydrate.

IV. Intravenous injection of (I) sol with glucose and fructose solution causes strong (III) and a simultaneous fall in (I) in herbivora and omnivora. In the latter, glucose also causes (II).

V. In vitro and in vivo (I) sol hinders the action of blood-lipase (IV) in carnivora and herbivora, owing to adsorption. Reactivation of the adsorbate is caused by Mn or Ni sols. Bi sol is feebly active, Au, Pt, Fe, and Ag sols and KCNS are inactive, whilst Se and Cu have the opposite action. Lecithin inactivates (IV) *in vivo* in carnivora. Adrenaline and nicotine also inactivate (IV). Insulin strengthens the lipase action and produces hypocholesterolaemia and hypoglycaemia.

VI. (I) dissolved in oil inactivates, and in the colloidal state activates, the action of pepsin in dogs.

H. J. E.

Degradation of cholesterol by the animal organism. III. Excreted degradation products. K. BOSSERT, I. H. PAGE, and W. MENSCHICK (Biochem. Z., 1934, 268, 93—103; cf. A., 1933, 857).—The faeces of rabbits and cats to which cholesterol (I) has been fed contain increased amounts of unsaponifiable matter (II) which has low m.p. and is not pptd. by digitonin. (II), which is dextrorotatory, and gives modified colour reactions of sterols, closely resembles

material extracted from hay. Although a good part of the degraded (I) is not found in (II), the increased excretion of (II) may account for part of the degradation.

W. McC.

Fat metabolism. J. B. BROWN (Ohio J. Sci., 1933, 33, 359—371).—A review. Fatty acids of high mol. wt. undergo the same reactions as fats.

CH. ABS.

Fat metabolism. II. P. E. VERKADE and J. VAN DER LEE (Biochem. J., 1934, 28, 31—40; cf. A., 1933, 417).—Administration of triundecoin, trinonoin, tridecain, or trilaurin together with adequate carbohydrate to healthy individuals gave quantities of undecanedioic, azelaic, sebacic, and dodecanedioic acids decreasing in this order. Tristridecain gave no diacid in the urine. Thus there is no contrast in the behaviour of triglycerides of acids containing odd and even nos. of C atoms. H. D.

Fat metabolism. III. P. E. VERKADE and J. VAN DER LEE (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 876—887; cf. A., 1933, 417, 742).—Ingestion of the glycerides of the fatty acids, trioctoin to trilaurin, is followed by excretion of dicarboxylic acids ("diaciduria"), especially with triundecoin and tridecain (I); tristridecain is not diacidogenic. No significant ω -oxidation occurs with either "diafat" (mainly tridecoic acid or its triglyceride) or "intarvin" (A., 1930, 1206). Ingestion of the oil (II) from the seeds of *Ulmus campestris* [which contains approx. 50% of (I)], but not of coconut oil [containing mainly low fatty acids (B., 1928, 23)], produces diaciduria [mainly sebacic acid with (II)].

F. O. H.

Effects of high-fat diets on respiratory metabolism and ketosis. E. E. HAWLEY, C. W. JOHNSON, and J. R. MURLIN (Amer. J. Physiol., 1933, 105, Proc. 46—47).—In man and the pig R.Q. vals. too low to be accounted for by the formation of sugar from protein (max. depression of R.Q. 0.025) or glycerol (max. depression 0.003) or by the ketosis (I) produced (max. depression 0.005) occur. Using butter-fat (II), the combined effect of these factors would not account for a R.Q. < 0.69. Possible explanations of low R.Q. vals. are given and attention is directed to the sp. dynamic action of (II), to the absence of any relationship between R.Q. and (I), and to the influence of cold in producing a low R.Q.

NUTR. ABS. (m)

Relationship between carbohydrate and fat metabolism. H. FESTEN (Diss., Utrecht, 1933, 160 pp.).—Micro-chemical methods are given for the determination of fats (I) (fatty acids), cholesterol (II), and phosphatides (III) in 0.2—0.4 c.c. of blood. To determine the (II) content, the light petroleum extract is evaporated to dryness and saponified so as to prevent a brown discoloration in the Liebermann-Burchard test. (III) are pptd. from the EtOH-Et₂O extract with COMe₂ and MgCl₂, and H₃PO₄ is determined in the ppt. by Tisdall's method. In normal dogs fasted for 14 hr. (I) varies between 381 and 1089, (II) between 128 and 180, and (III) between 313 and 350 mg. per 100 c.c. blood. Vals. are similar in the same animal on different days. After injection of insulin (IV) no significant change occurs in the fat

or lipin content. After a meal of 100 c.c. olive oil, there is a rise in (I), which reaches its highest val. after 5—6 hr. After 9 hr. it falls to the initial val. or below. (II) increases and then decreases, the lowest val. corresponding with the highest for (I). A regular increase follows. After removing the pancreas, tolerance for fat is considerably diminished; it increases after (IV). **NUTR. ABS. (m)**

Biochemistry and physiology of glycuronic acid. IV. (a) Occurrence of conjugated glycuronic acids in the animal body. (b) Conjugation of *d*- and *l*-borneol. J. PRYDE and R. T. WILLIAMS. V. Site and mechanism of the formation of conjugated glycuronic acid. A. HEMINGWAY, J. PRYDE, and R. T. WILLIAMS (Biochem. J., 1934, 28, 131—135, 136—142).—IV. The normal occurrence of glycuronic acid (I) in the urine and blood of various animals is examined and a preferential conjugation of (I) *in vivo* with *d*- rather than *l*-borneol is demonstrated.

V. A technique for perfusing liver, spleen, and hind limbs in combination with the kidney is described. The main, if not the only, site of conjugation of (I) is in the liver. The process of conjugation is abolished by CN⁻. The hypothesis that the production of a glucoside is an intermediate stage in glycuronide formation is not supported.

P. W. C.

Carbohydrate metabolism. J. R. MURLIN (Ohio J. Sci., 1933, 33, 335—358).—A review. Fats were converted into carbohydrates in the germinating bean and in persons having a high fat tolerance.

CH. ABS.

Carbohydrate metabolism of the warm-blooded organism in muscular activity. E. JOKL (Pflüger's Archiv, 1933, 232, 687—702; Chem. Zentr., 1933, ii, 1290).—After running for several hr. the muscle- and liver-lactic acid (I) of rats has fallen, whilst the blood-(I) has risen; muscle- and liver-glycogen have fallen, whilst blood-sugar (II) remains const. Exhausting exercise causes a further fall in muscle- and liver-(I) and, with almost complete disappearance of the glycogen store in the muscle and liver, of (II) also. In exercise, muscle- and liver-hexose monophosphoric acid decreases, whilst phosphagen increases.

A. A. E.

Factors determining the glucose-tolerance curve. S. SOSKIN and D. ALLWEISS (Amer. J. Physiol., 1933, 105, Proc. 89).—Sugar-tolerance tests on (a) hepatectomised dogs receiving a const. intravenous injection of glucose (I) sufficient to keep the blood-sugar level (II) const., and (b) depancreatized dogs receiving a const. intravenous injection of insulin (III) or (III) and (I) sufficient to maintain a const. (II), yield results indicating that (a) the liver plays the major role in determining the normal (I) tolerance curve (IV), (b) no (III) secretion, beyond that necessary to maintain a const. (II), need be predicated to account for (IV). **NUTR. ABS. (m)**

Abnormal sugar tolerance curves. L. POLLAK (Wien. med. Woch., 1933, 83, 1245—1247, 1290—1292).—The alimentary rise in blood-sugar depends on the permeability of the liver to sugar (I), the rate of assimilation by peripheral organs, and the rate

of liberation of (I) by the liver. These processes cannot be separated by glucose-tolerance tests, but may be by using galactose (II). In that case blood-glucose is derived from the liver; the (II) curve measures the rate of removal of (I).

NUTR. ABS. (m)

Oxidation of glucose after fasting. W. H. CHAMBERS and M. DANN (Amer. J. Physiol., 1933, 105, Proc. 18).—The efficacy of various foods in restoring the normal carbohydrate metabolism of the dog after a 3 weeks' fast has been studied. Improvement in the ability to oxidise carbohydrate was determined by the rise in R.Q. during the second, third, and fourth hr. following a test meal of glucose given 18—24 hr. after the food studied. The height of the R.Q. increases with the size of the carbohydrate mol. fed, *i.e.*, from monosaccharide to starch. 50 g. of wheat flour are more effective than 6 units of insulin per kg. The effects obtained are not in proportion to the vitamin-B content of the foods. **NUTR. ABS. (m)**

Absorption of glucose by chronic loops of colon. G. E. BURGET, P. H. MOORE, and R. W. LLOYD (Amer. J. Physiol., 1933, 105, 187—190).—Sugar was absorbed more rapidly from 20% than from 5 or 10% solutions, and the rate of absorption tended to increase with time.

NUTR. ABS. (b)

Absorption of glucose by closed loops of colon. G. E. BURGET, P. MOORE, and R. W. LLOYD (Amer. J. Physiol., 1933, 105, Proc. 15).—Isotonic solutions of glucose (5%) were absorbed at a rate which increased directly with time, by a closed loop of colon; 0.7 g. of glucose was absorbed from 10 c.c. of a 20% solution per hr. The absorption is slower than for loops of small intestine.

NUTR. ABS. (b)

Serum- and muscle-phosphate changes following glucose injection. H. POLLACK (Amer. J. Physiol., 1933, 105, Proc. 79—80).—The changes in serum-PO₄ during continuous injection of glucose are described for normal, adrenalectomised, dehepatized, and demuscle animals and for perfused preps. with and without insulin.

NUTR. ABS. (m)

Regulation of blood-sugar after administration of carbohydrate. J. MELKA (Z. ges. exp. Med., 1933, 90, 22—27).—Gargling (I) with 10—20% aq. glucose (II) causes a rise of blood-sugar in only a few subjects, but in all, after 30 min., there is a fall which does not occur when the oral mucosa are anaesthetised with 5% cocaine. Ingestion of (II) after (I) causes less marked hyperglycemia than usual both in diabetic and non-diabetic patients. The presence of (II) in the mouth produces a reflex increase in the secretion of insulin by way of the nerves of taste and the vagus.

NUTR. ABS. (m)

Conversion of glycerol into glucose by the animal organism. F. H. LASHMET and L. H. NEWBURGH (J. Clin. Invest., 1933, 12, 968).—< 30% of glycerol, and hence only 2—3% (not 10%) of fat, is converted into glucose.

NUTR. ABS. (m)

Relation between blood-lactic acid and sugars or sugar-forming substances. T. KOIKE (J. Biochem. Japan, 1934, 19, 111—143).—Intraperitoneal injection of glucose (I), fructose (II), mannose (III), maltose (IV), and galactose (V), but not of

lactose, arabinose, or xylose, produces in rabbits an increase in the blood-lactic acid (VI). The hyperglycæmia due to (IV) or (V) is more prolonged than that due to (I), (II), or (III). A blood-sugar (VII) level of approx. 0.20% is attained before (VI) appreciably increases; the max. of the two curves, however, occur practically simultaneously. With sorbose and glycerol, (VI) increases even when (VII) is < 0.20%, and attains higher levels than with the hexoses. With adrenaline, (VII) reaches its max. before (VI), the ratio (VI)/(VII) being < those with the sugars. Injection of Na lactate increases (VII) but does not significantly influence (VI). The mechanism of these changes is discussed. F. O. H.

Carbohydrate metabolism of the liver. I. Glycogen and other carbohydrates in decapitate cats. C. TSAI (Chinese J. Physiol., 1933, 7, 215—227).—Ether anaesthesia and decapitation cause a reduction in glycogen (I) and other polysaccharides in the liver (II) and a rise in (II)- and blood-sugar. With initial low (I) content, sugar in the circulation is > can be accounted for by loss from (II), and the regeneration of (I) is more rapid. H. G. R.

Assimilation of sugar in Eck-fistula dogs. Glycosuria after administration of sugar *per os* or intravenously. S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (Compt. rend. Soc. Biol., 1933, 113, 1393—1395).—Ingestion of 100 g. of glucose causes more marked hyperglycæmia (I) in Eck-fistula than in normal dogs. Lactose (70 g.) and fructose (20 g.) cause only very slight (I) and are removed in the urine. NUTR. ABS. (m)

Assimilation of sugar in Eck-fistula dogs. Blood-sugar after administration of sugar *per os*. S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (Compt. rend. Soc. Biol., 1933, 113, 1396—1398).—Glucose, either *per os* or intravenously, is not excreted in the urine of normal (I) or Eck-fistula (II) dogs. Lactose and fructose are excreted particularly in (II), in which also the glycogen content of the liver is < in (I). The liver of the dog retains more lactose and fructose than all the other tissues combined. NUTR. ABS. (m)

Effect of injection of glucose on blood-sugar of normal and vagotomised pigeons. E. MORACCI (Riv. Patol. sper., 1933, 10, 443—458).—Vagotomy (I) increases and prolongs the hyperglycæmia (II) which follows intramuscular injection (III) of glucose. When the interval between (I) and (III) is increased from 1—2 to 3—5 days, (II) is more marked, and serious general disturbance, ending in death, results. The prolonged inanition (due to the inability of the vagotomised pigeon to take food) is not responsible for these results, which are probably due to an impairment in the glycogenic function of the liver. NUTR. ABS. (m)

Carbohydrate metabolism and specific dynamic action in partly hypophysectomised dogs. A. G. EATON and R. G. DAGGS (Amer. J. Physiol., 1933, 105, Proc. 29).—Partly hypophysectomised dogs show a decreased glucose tolerance. Post-insulin hypoglycæmia is more prolonged in these than in normal dogs. NUTR. ABS. (m)

Ovarian cycle and carbohydrate metabolism. J. BLOCH and A. BERGEL (Wien. Arch. inn. Med., 1933, 24, 29—51).—Blood-sugar in many women rises immediately preceding and during the first days of menstruation. This may be correlated with thyroid activity. NUTR. ABS. (m)

Renal excretion of sucrose when injected intravenously in man. N. M. KEITH, M. H. POWER, and R. D. PETERSON (Amer. J. Physiol., 1933, 105, Proc. 60—61).—After intravenous injection of 5 g. of sucrose in the adult, recovery of sugar in the urine was quant., 40% of the dose appearing in 1 hr. and 19% in the second hr. NUTR. ABS. (b)

Metabolism of galactose. II. Behaviour of the rat towards galactose. V. J. HARDING, G. A. GRANT, and D. GLAISTER (Biochem. J., 1934, 28, 257—263; cf. A., 1933, 307).—Galactose (I) fed to rats [1.2 g. of (I) per kg. body-wt.] disappears from the intestine almost completely within 1, and from the tissues within 3, hr. Excretion of (I) into the urine is proportionately much > in man. Muscle- and liver-glycogen formed after ingestion of (I) give only glucose on hydrolysis. No evidence of the conversion of (I) into any other reducing carbohydrate was obtained. A. E. O.

Inositol metabolism in mammalian heart. L. B. WINTER (Biochem. J., 1934, 28, 6—10).—Inositol (I) is determined by disintegrating the tissue with 10% KOH, clearing with Pb(OAc)₂, pptn. of (I) with EtOH—Ba(OH)₂, and weighing the recryst. (I) after decomp. of the Ba ppt. The method has an average error of 13%; 73% of added (I) is recovered. The (I) obtained from the heart increases with the length of treatment with KOH, and in hearts kept in N₂ for 90 min. at 37° was > in those immediately treated. Mincing and incubating the tissue in HPO₄'' buffer increase the yield of (I). H. D.

Wool growth in sheep as affected by the carbohydrate content of the diet. A. H. H. FRASER and J. E. NICHOLS (Empire J. Exp. Agric., 1934, 2, 9—19).—Addition of maize starch to a maintenance ration resulted in an increase in body-wt. and gross fleece-wt. The latter was reflected in the wt. of clean wool, and was due to increased fibre thickness, a slight increase in fibre length, and possibly to a larger proportion of follicles actively elaborating fibres. A. G. P.

Wood digestion by insect larvæ. K. MANSOUR and J. J. MANSOUR-BEK (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 795—799).—Wood-eating larvæ are not dependent on micro-organisms for the digestion of wood. Larvæ of *Xystrocer a globosa* obtain their carbohydrates from the sugar and starch in the wood, whilst *Macrotoma palmata* obtain them from the decomp. of cellulose by intestinal enzymes. The latter species can live on woods poor in sugar and starch. J. W. S.

Chemistry of active heart-muscle. B. WEICKER (Arch. exp. Path. Pharm., 1934, 174, 383—404).—The active surviving cold- (frog) or warm-blooded heart (I) (rabbit, cat) under aerobic conditions shows a slight rise in phosphagen (II) and a fall in lactic acid (III), whilst the adenylypyro- (IV) and hexose-phos-

phoric acids (V) remain approx. const.; under anaerobic conditions (II) and (IV) are decreased and (III) is increased. Poisoning of (I) aerobically with $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ slightly lowers the O_2 consumption (VI), (III) and (IV) decreasing, and the total acid-sol. PO_4 increasing. Lack of O_2 increases the production of (V). The fall in free adenylic acid (VII) is parallel with that in work efficiency (VIII) and with the compensatory rise in (III). Perfusion with media containing (VII) increases (VI) and (VIII) in the hypodynamic, but not in the fully active, heart.

F. O. H.

Changes in composition of muscle, blood, and liver of the dog after muscular work. T. CAHN and J. HOUGET (Compt. rend. Soc. Biol., 1933, 113, 1132—1133).—Prolonged exercise does not alter the H_2O or P content of muscle (I). Glycogen is greatly reduced in both (I) and liver. Lactic acid (II) is also reduced in (I), and since there is only a small increase in blood and liver, most of the (II) formed appears to be oxidised.

NUTR. ABS. (m)

Relation between the electrical stimulation of muscle and the creatinephosphoric acid decomposition. Y. RENQVIST and C. E. RAIHA (Skand. Arch. Physiol., 1933, 66, 78—91; Chem. Zentr., 1933, ii, 2419).—The effect of electrical stimulation of muscle is attributed to the decomp. of creatinephosphoric acid.

H. J. E.

Muscle-calcium during calcium-free perfusion. G. TAUBMANN (Arch. exp. Path. Pharm., 1934, 174, 476—482).—Perfusion (I) of the frog's gastrocnemius (II) with Ca-free Ringer's solution (III) does not produce a permanent loss of total or ultrafilterable Ca from the muscle. Ca is removed by (III) and the excitability of (II) decreases, but cessation of (I) is followed by a replacement of the Ca from the bone, and the response to stimulation returns to normal.

F. O. H.

Methods of determining the degree of calcium deficiency of sheep. A. H. H. FRASER, W. GODDEN, and D. W. AUCHINACHIE (Biochem. J., 1934, 28, 157—161).—The arrest of growth on a Ca-deficient ration is due to a decreased consumption and insufficient utilisation of food. Serum-Ca is lower, but returns to normal with supplements of cod-liver oil (I) and chalk, their effects being additive. The effect of (I) in retaining a normal serum-Ca is > its effect in increasing Ca retention or rate of growth.

H. G. R.

Serum-calcium and -magnesium level in the ovarian cycle of the laying hen. E. CHARLES and L. HOGGEN (Quart. J. Exp. Physiol., 1933, 23, 343—349).—In sexually immature White Leghorn pullets the serum-Ca averages 11.4 mg. and the Mg 2.4 mg. per 100 c.c. In the interval between oviposition and the next ovulation Ca varies from 14.7 to 19.6 mg. (average about 17) and Mg from 1.9 to 2.9 mg. In hens having an egg in the oviduct (I) with no shell formed, the Ca varies from 12.9 to 19.4 mg. In hens where the egg is in the shell gland and the shell in different stages of deposition the Ca varies from 10.4 to 28.5 mg. During shell secretion (II) Mg vals. appear to be > when no egg is present in (I) or when shell formation is complete. Possibly the presence of the egg in (I) stimulates

the mobilisation of Ca in the tissues during (II), producing a transitory rise in blood-Ca.

NUTR. ABS. (m)

Simultaneous administration [to rats] of lime and phosphoric acid with a colloidal lime-phosphoric acid-protein preparation. M. GÜRSCHING (Münch. med. Woch., 1933, 80, 1143—1144; Chem. Zentr., 1933, ii, 1204).—The Ca and P metabolism of rats treated with a colloidal Ca phosphate-milk protein prep. has been investigated. Ca and P retention and bone formation are better than when Ca and P are added as ordinary $\text{Ca}_3(\text{PO}_4)_2$.

L. S. T.

Feeding lucerne and timothy hays to dairy cows. Milk-production values and calcium and phosphorus utilisation of the hays after balancing the protein in the ration. C. W. HOLDAWAY, W. B. ELLET, J. F. EAHEART, and H. G. CUNNINGHAM, jun. (Virginia [Blacksburg] Agric. Exp. Sta. Tech. Bull., 1932, No. 45, 27 pp.).—A lucerne-grain ration (I) proved superior to a timothy-grain ration (II) in point of yields of milk and butter-fat and the net food energy required per kg. of milk and fat. Differences in the protein digestion coeffs. of the two rations and in the actual protein consumption were small, but the Ca contents diverged considerably (Ca:P=2.1:1 and 1.06:1, respectively). The Ca balance of the cows was positive in nearly all cases, but the body-gain in Ca of cows receiving (I) was > that of those receiving (II). These differences became more marked as the lactation period advanced. During the fourth to ninth months of lactation the P retention with (I) was much > during the first to fourth months.

A. G. P.

Phosphorus requirement of dairy cattle when lucerne furnishes the principal source of protein. C. F. HUFFMAN, C. W. DUNCAN, C. S. ROBINSON, and L. W. LAMB (Michigan Agric. Exp. Sta. Tech. Bull., 1933, No. 134, 1—75).—Heifers receiving a low-P ration of lucerne-maize silage-maize supplemented with bone meal required 10—12 g. of P daily for growth and maintenance. The demand for milk production averaged 0.5—0.7 g. of P per lb. of milk. The P requirement for growth is not directly proportional to body-wt., but depends also on the rate of growth. The most pronounced symptom of P deficiency was anorexia usually preceded by a lowered org. P content of the blood.

A. G. P.

Effect of decalcium phosphate, without vitamin-D, in the nutrition of chicks. G. M. HIGGINS and C. SHEARD (Anat. Rec., 1933, 56, 395—408).— $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$, in absence of vitamin-D, does not maintain growing chicks or protect against results of disturbed Ca metabolism.

CH. ABS.

Copper in Chinese food materials. W. H. ADOLPH and T. P. CHOU (Chinese J. Physiol., 1933, 7, 185—188).—The Cu content of forty Chinese food materials corresponds closely with that of similar American products.

H. G. R.

Influence of alkalinity on the respiratory level of *Telphusa* and the crayfish. A. RAFFY (Compt. rend., 1934, 198, 680—681).—*T. fluviatilis* progressively lowers its O_2 consumption as the salinity of its environment varies from that of fresh H_2O (I) to that of sea- H_2O (II). Its respiratory level is regained in (I)

after immersion in (II). The crayfish is not so adaptable. J. L. D.

Effect of pyocyanine on the respiration of normal tissues and tumours. E. A. H. FRIEDHEIM (Biochem. J., 1934, 28, 173—179).—The increase due to pyocyanine (I) in respiration (II) of tissues with aerobic glycolysis is dependent on the presence of glucose. With CO_3 Ringer, (II) of rat kidney is not affected by (I), but there is a considerable increase with PO_4 Ringer, the PO_4 fundamentally altering the oxidation mechanism of the cell. (I) is less toxic than methylene-blue. H. G. R.

Effect of guanidine derivatives on tissue respiration. C. BANU and N. GAVRILESCU (Biochem. J., 1934, 28, 270—272).—Guanidine (I) and methylguanidine (II), in 0.05% concn., depress the O_2 uptake of isolated tissues (brain, liver, muscle) and of rat's brain *in vivo*. The general toxic effect of (I) leading to tetanic symptoms is ascribed in part to depression of tissue metabolism, particularly of the brain. No direct antagonistic action between parathyrin and (I) or (II) was observed. A. E. O.

Natural reversible oxidation-reduction systems as accessory catalysts in respiration: juglon and Lawson. E. A. H. FRIEDHEIM (Biochem. J., 1934, 28, 180—188).—Lawson (I) (the colouring matter in the leaves of the henna plant) in the oxidised form, and juglon (II) (the colouring matter in the husks of walnuts) in the reduced form, act as true intracellular reversible oxidation-reduction systems. The potentials in the semi-reduced condition at p_{H} 7.0 are: (I) -0.139, (II) +0.033. Whereas both (I) and (II) increase the respiration of erythrocytes, only (II) oxidises hæmoglobin to methæmoglobin. H. G. R.

Tissue metabolism. III. Effect of oxidised 1:2:5:6-dibenzanthracene. E. BOYLAND and M. E. BOYLAND (Biochem. J., 1934, 28, 244—256).—A H_2O -sol. oxidation product of 1:2:5:6-dibenzanthracene (A., 1932, 1156) has similar inhibitory effects on oxidation and glycolysis in both normal and malignant rat tissues. A. E. O.

Effect of carbohydrate content on cardiac muscle. I. Agents directly affecting sugar metabolism. II. Cardiacs. F. LASCH and K. TRIGER (Z. ges. exp. Med., 1932, 85, 390—399; 1933, 88, 588—592; Chem. Zentr., 1933, ii, 1211, 1212).—I. The effect of insulin (I), glucose, and phloridzin on the total carbohydrate content (II) of cardiac muscle in comparison with that of the liver has been investigated for rats and guinea-pigs in short- and long-period experiments. (II) is affected to only a limited extent. (I) reduces (II) in short-period experiments with guinea-pigs, and in long- but not in short-period experiments with rats. Glucose does not increase in rats, but in one short-period experiment with guinea-pigs an increase was observed.

II. In rats neither caffeine nor hexeton alters the (II) of cardiac muscle or the liver, but in guinea-pigs strophanthin raises (II) in both cases. L. S. T.

Peptone hyperglycæmia in animals deprived of suprarenals or suprarenal medulla. T. KAIWA (Tohoku J. Exp. Med., 1933, 21, 1—12).—Bilateral adrenalectomy in rabbits and removal of the supra-

renal medulla in dogs, 3—6 weeks previous to intravenous injection of peptone (I) (0.1—0.3 g. per kg. in 0.9% aq. NaCl), results in a decrease and an increase, respectively, in the usual vals. for (I) hyperglycæmia (II). When adrenaline hydrochloride (III) is given subcutaneously to adrenalectomised rabbits immediately after administration of (I) the (II) produced is < with (III) alone, but similar to that with (I) alone, whilst the length of the (II) period and the time of greatest intensity coincide with those obtained with (III) alone. NUTR. ABS. (m)

Effect of spices on the movements of the intestinal villi and the absorption of glucose. E. DE KOKAS and G. DE LUDANY (Orvosi Hetilap, 1933, 77, 638—639).—Spices (cloves, garlic, onions, pepper, paprika) in low concn. stimulate the movements of the intestinal villi. Absorption of glucose in the small intestine was accelerated by spices; the most effective were those which had the greatest stimulating effect on the movements of the villi. NUTR. ABS. (b)

Diffusion of alcohol in the organism. Bound water. M. NICLOUX (Compt. rend., 1934, 198, 983—985).—The ratio 0.85—0.90 for the EtOH content of the tissues of gudgeon in equilibrium with dil. EtOH is explained by the assumption that some of the H_2O in the tissues is bound by the proteins, and then does not dissolve EtOH. The quantity thus bound is much < that usually known as "bound," is very sensitive to electrolytes, and is reduced to 0 by death or destruction of the tissues. R. S. C.

Configuration and anæsthetic activity of aromatic alcohols. P. K. KNOEFEL and G. A. ALLES (Proc. Soc. Exp. Biol. Med., 1930, 30, 1076—1077).—Increase in length of the straight C chain and/or transformation into *sec.*- or *tert.*-alcohol increased the anæsthetic activity. CH. ABS.

[Physiological effect] of acetophenone and certain derivatives. G. FLORENCE (Bull. Sci. pharmacol., 1933, 40, 325—336; Chem. Zentr., 1933, ii, 2123—2124).—The solubility in H_2O , distribution between olive oil and H_2O , and physiological effects have been determined. The following are new: 3:4-dichloroacetophenone, m.p. 74° ; m-, m.p. 146° , and p-, m.p. 148° , -ureidoacetophenone; acetophenone-m-, m.p. 187° , and p-, m.p. 201° , -ureide. p-Methylacetophenone is more active than acetophenone, but further substitution by Me diminishes the activity. Substitution by Et or halogen destroys the narcotic power. Certain halogen derivatives are toxic. None of the N-derivatives is active. A. A. E.

Adrenaline secretion and blood-sugar in dogs after chloralose. H. SATO and F. OHMI (Tohoku J. Exp. Med., 1933, 21, 433—443).—Chloralose causes hypoglycæmia and decreased adrenaline secretion, but does not increase blood-pressure. CH. ABS.

[Physiological] action of isomerides of amyl nitrite. B. E. READ, K. Y. YU, and T. M. P'ENG (Chinese J. Physiol., 1933, 7, 253—268).—By intravenous injection the order of potency is *iso*-. (I), *n*-. (II), *sec*-. (III), and *tert*-. (IV); by inhalation the order is (III), (IV), (II), (I). (III) and (IV) are least toxic in producing vaso-constriction and (IV) is the best for therapeutic purposes. H. G. R.

Combination of avertin with magnesium chloride. W. KEIL (Arch. exp. Path. Pharm., 1934, 174, 490—492).—Subcutaneous injection of sublethal doses of $MgCl_2$ into rats lowers both the min. lethal dose and the min. narcotic dose (by as much as approx. 45%) of subsequently administered avertin. F. O. H.

Assay of analgesics. F. HILDEBRANDT (Arch. exp. Path. Pharm., 1934, 174, 405—415).—The method depends on the reaction of guinea-pigs to the application of heat to the skin. Opium derivatives have an analgesic power much > that of acetylsalicylic acid, quinine, atophan, etc. F. O. H.

Effect of methylprotocatechualbarbituric [5-4'-hydroxy-3'-methoxybenzylidenebarbituric] acid in rabbits. E. KATASKA (J. Biochem. Japan, 1934, 19, 11—13).—Vanillin with barbituric acid in hot H_2O yields 5-4'-hydroxy-3'-methoxybenzylidenebarbituric acid (I). Following ingestion (2—3 g. daily) of (I) by rabbits, vanillic acid appears in the urine to the same extent as after ingestion of the equiv. amount of vanillin. F. O. H.

Central blood-sugar regulation. I. Effect of pyramidone on blood-sugar. II. Veronal or luminal. III. Small quantities of pyramidone. IV. Magnesium salts. F. HOGLER (Z. ges. exp. Med., 1932, 84, 14—23, 29—49, 50—61, 62—73; cf. A., 1933, 411).—I. Pyramidone (I) hyperglycaemia is prevented or diminished by veronal (II) and luminal (III), arrested by ergosterol, and increased by atropine, Ca salts, and parathormone. (I) hypothermy is unaffected.

II. Blood-sugar is practically unaffected by (II) and (III), but adrenaline hyperglycaemia is increased. Ergotamine (in doses otherwise inactive) with (II) causes hypo- and atropine (IV) hyper-glycaemia. Hypoglycaemia following small (not large) doses of insulin (V) is increased and extended by both hypnotics.

III. Small doses of (I) cause hypoglycaemia and hyperthermy.

IV. Mg hyperglycaemia is restrained by ergotamine, but scarcely affected by (II), (III), (IV), or (V). Ca interrupts Mg narcosis and hyperglycaemia; parathormone retards it. A. A. E.

Relation between constitution and chemical or pharmacological properties. I. Reactions between nitrogenous compounds and phenols. R. LABES (Arch. exp. Path. Pharm., 1934, 174, 255—285).—The pptn. reactions of various phenols ($PhOH$, $p-C_6H_4Cl.OH$, 2:4:6- $C_6H_2Cl_3.OH$, resorcinol) with cyclic N compounds (quinoline, antipyrine, pyramidone, and C_6H_5N) are correlated with their solubility products and with the limiting mol. solubility of the complex produced. F. O. H.

Chemical constitution and physiological action. Comparative effects of benzyl- β -phenylethyl- and di-(β -phenylethyl)-amines and some of their derivatives. A. M. HJORT (J. Pharm. Exp. Ther., 1934, 50, 131—150).—Benzyl- β -phenylethylamine (I), di-(β -phenylethyl)amine (II), and many of their derivatives containing one or more OH, OMe, or CH_2O_2 groups in either ring, were examined and compared with one another and with adrenaline (III) and other

β -phenylethylamine (IV) derivatives. The toxicities of (I) and (II) were lowered by the introduction of substituent groups, whilst the tone-depressant effects on isolated intestinal muscle were increased, the extent of the increase or decrease varying with the no., nature, and positions of the substituent groups. None of the (I) or (II) derivatives exhibited any tone-depressant effect comparable with that of (III), although comparable with other (IV) derivatives. Most of the (I) and (II) derivatives lowered the blood-pressure, a few producing a slight initial rise. The effects on the melanophores, pulse, and respiration varied.

R. N. C.

Synthesis of substances similar to papaverine.—See this vol., 403.

Toxicity of nitriles of α -amino-acids. C. SAN-NIÉ (Bull. Soc. Chim. biol., 1933, 15, 1436—1461).—In the fatty acid series lengthening the chain or the introduction of Ph at the extremity decreases the toxicity. Straight-chain compounds are less toxic than their isomerides. A MeO group in the C_6H_5 nucleus or a double linking in the aliphatic group increases the toxicity. The amounts of HCN liberated from the alkaline solutions of the NH_2 -nitriles on exposure to air are not large enough to be toxic.

H. D.

Action of tetramethylammonium and tetraethylammonium iodides on the vessels of the posterior limbs of the frog. G. COLANTUONI (Arch. Farm. sperim., 1934, 57, 36—43).—Introduction of NMe_4I (I) into the vessels of the posterior limbs of the frog produced a slight vaso-dilatation (II), followed by an intense vaso-constriction (III). Increasing the concn. of (I) produced an increased (III) without (II). With solutions of NEt_4I equimol. to those of (I), (II) lasted longer, whilst (III) was less intense than for (I). R. N. C.

Chemotherapy of derivatives of harmine and harmaline. II. C. E. COULTHARD (Biochem J., 1934, 28, 264—267; cf. A., 1933, 859).—The amoebicidal val. of *O*-*n*-nonylharmol (the most lethal of 14 *O*-alkylharmols tested) is much < that of emetine (I) under optimal conditions for (I), but is comparable with that of (I) at p_H 6.2 or 6.3, the probable *in vivo* p_H in amoebic dysentery. A. E. O.

Enhanced action of morphine in experimental nephrosis after oral ingestion of magnesium sulphate. A. D. HIRSCHFELDER (Proc. Soc. Exp. Biol. Med., 1933, 30, 1057—1058). CH. ABS.

Effect of morphine on the adrenaline output, blood-sugar, and blood-pressure in dogs. H. SATO and F. OHMI (Tohoku J. Exp. Med., 1933, 21, 411—432).—Subcutaneous injection of morphine into dogs (10—40 mg. per kg.) causes a 5—25-fold increase in adrenaline secretion and somewhat retarded hyperglycaemia. Blood-pressure is not regularly affected. CH. ABS.

Physiological action of nucleic acids and their derivatives. O. FLOSSNER (Arch. exp. Path. Pharm., 1934, 174, 245—254).—The following compounds, prepared from both yeast- and thymus-nucleic acids, were investigated: adenylic, guanylic, and inosic acid (I), adenosine (II), guanosine, inosine, xanthine,

adenine, hypoxanthine, guanine, pancreatic nucleic acid, "vicin" (2:5-diamino-4:6-dihydroxypyrimidine glucoside), and 4:5-diamino-2:6-dihydroxypyrimidine. All [especially (II)] lower the blood-pressure and [especially (I)] retard the heart, whilst some increase and others decrease the strength of the heart-beat. With the intestine and uterus, tonus-increasing and -decreasing actions, respectively, generally occur.

F. O. H.

Comparative effects of various diuretics in dogs, with special reference to the excretion of urine, chloride, and urea. M. N. FULTON, H. A. VAN AUKEN, R. J. PARSONS, and L. F. DAVENPORT (J. Pharm. Exp. Ther., 1934, 50, 223—239).—The greatest increase in both vol. of urine excreted and urinary Cl' was produced by salyrgan (I) both with and without NH_4Cl , the others, in diminishing order of potency, being novasurol (II), NH_4Cl (III), digitan (IV), urea (V), theophylline- $\text{C}_2\text{H}_4(\text{NH}_2)_2$ (VI), theocin (VII), caffeine, and theobromine- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$. Increase in urinary Cl' was given by (I), (II), (III), (V), (VI), and (VII). Blood-Cl' remained const. except in cases of excessive Cl' excretion. The effects of the diuretics on urea excretion were not consistent. Blood-urea generally fell during the periods of action of the drugs, but except in cases of small urine vols. the blood-urea clearance was unaffected. Pituitrin inhibited the increased excretion of urine after (II), but not the Cl' excretion.

R. N. C.

Influence of panax ginseng on serum-calcium and -potassium. II. Effects of convulsants. K. IN (J. Chosen Med. Assoc., 1933, 23, 725—732).—Injection into normal rabbits of camphor, picrotoxin, caffeine, or strychnine increases serum-Ca. If the rabbit has been fed with ginseng the effect is greater.

CH. ABS.

Toxic constituent of *Ryania acuminata*. S. NAKARAI and T. SANS (Arch. Pharm., 1934, 272, 1—4).—Injection of ryanin (I), m.p. < 100°, extracted from the root of *R. acuminata*, into frogs (0.00001 g./10 g.), mice (0.000005 g./10 g.), rabbits (0.00025 g./kg.), cats, and dogs (min. lethal dose in parentheses) has no influence on the heart and blood, but acts first as a stimulant and then as a paralytic poison to the respiratory system, death being due to suffocation. Death is delayed when (I) is injected into a narcotised ($\text{CCl}_3\cdot\text{CHO}$) animal.

J. W. B.

Tests of the potency of digitalis preparations on man. E. EDENS (Klin. Woch., 1933, 12, 1012—1015; Chem. Zentr., 1933, ii, 2701).—The quantity of the digitalis prep. necessary to give the same effect as a definite quantity of strophanthin must be measured.

H. J. E.

Chemico-therapeutic interference phenomena. A. HASSKÓ (Z. ges. exp. Med., 1933, 87, 567—577; Chem. Zentr., 1933, ii, 1209—1210).—Of the nine CHPh_3 dyes investigated, only brilliant-green (I) gives a therapeutic interference phenomenon (III) in rats after a period of 1 hr. The trypanflavine (II) test shows that fuchsin, parafuchsin, and (I) after 1 hr. hinder the union between (II) and the trypanosome cell. (III) depends on a process of saturation of the parasite protoplasm probably through a change in the physico-chemical cell-structure.

L. S. T.

Toxicity of fish-liver oils and fish oils, and the antitoxic effect of yeast. I. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1—2).—The retardation of the growth of rats fed on a basal diet to which 10—15% of liver or fish oils are added as the sole source of fat, together with a quantity of oryzanin solution, can be alleviated by addition of yeast. Substitution of butter or olive oil gives better growth. Skate-liver oil, which is more potent in vitamin-A (I) than cod-liver oil, is less toxic. The toxicity of an oil is not reduced by removal of (I), and is associated with the fatty acids.

P. G. M.

Spectroscopic investigation of the action of poisons in the blood. C. L. CARBONESCHI (Semana méd., 1933, II, 1187—1196).—Absorption spectra of blood treated with CO , N_2O , C_2H_2 , H_2S , PhNO_2 , and F compounds are recorded. Spectroscopic characteristics of methæmoglobin, hæmatin, hæmochromogen, and hæmatoporphyrin are discussed.

CH. ABS.

Arsine poisoning: blood changes in experimental animals. F. FRETWURST, S. HORWITZ, and R. ROSENBAUM (Z. klin. Med., 1933, 123, 703—730; Chem. Zentr., 1933, ii, 1212).—In cats poisoned by AsH_3 , a strictly regular dependence of morphological structural changes of the red and white constituents of blood on the poisoning action was not observed. The characteristic symptoms of the acute AsH_3 poisoning are mainly hæmolysis with the appearance of methæmoglobin and incidental hæmatin in the blood, the separation of oxyhæmoglobin, and different degrees of leucocytosis. The principal attendant phenomena are the appearance of erythrocytes (III) in the urine and an increase in the residual-N content of the blood. The AsH_3 is mainly taken up by (III), the As content of the plasma increasing with the degree of hæmolysis.

L. S. T.

Adsorption, distribution, and excretion of injectable bismuth preparations. M. R. THOMPSON, C. I. ICHNIOWSKI, and B. S. ROBERTS (Amer. J. Syphilis, 1933, 17, 205—220).

CH. ABS.

Deposition of lead in the kidney. F. RAUH (Arch. exp. Path. Pharm., 1934, 174, 352—356).—Oral administration of Pb salts to guinea-pigs is followed by Pb deposition (I) in the intercalary region and ascending tube of Henle's loop (II), but seldom in the cortical region. Subcutaneous administration produces (I) in the vessels and capillary endothelium, the descending tube of (II) being practically free from Pb.

F. O. H.

Detection and determination of radium in living persons. IV. Retention of soluble radium salts administered intravenously. H. SCHLUNDT and J. T. NERANCY (Amer. J. Roentgenol., 1933, 30, 515—522).—In psychiatric patients receiving RaCl_2 intravenously, 4.3% was retained 6 months after treatment and 1.9% 6 months later. Precautions in making the necessary γ -ray measurements are described.

CH. ABS.

Distribution and excretion of thorium after injection of Thorotrast. T. LEIPERT (Wien. klin. Woch., 1933, 46, 994—996; Chem. Zentr., 1933, ii, 2023).—Th is found principally in the spleen and

liver; smaller amounts are present in the lungs and the red marrow. A. A. E.

Toxicity of sodium chromate and dichromate. A. RABBENO (Boll. Soc. Eustach., 1933, 31, 57—58; Chem. Zentr., 1933, ii, 2023).—On intravenous injection into rabbits $\text{Na}_2\text{Cr}_2\text{O}_7$ is twice as toxic as Na_2CrO_4 . A. A. E.

Formation of methæmoglobin by sodium chromate and dichromate *in vivo*. A. RABBENO (Boll. Soc. Eustach., 1933, 31, 59—62; Chem. Zentr., 1933, ii, 2023—2024).—< 70% conversion was observed; > 70% is fatal. A. A. E.

Formation of methæmoglobin by sodium and potassium dichromate. M. MATTUCCI (Boll. Soc. Eustach., 1933, 31, 121—128; Chem. Zentr., 1933, ii, 2141).—The change takes place in very dil. solution; the effects of time and $[\text{CrO.}']$ are recorded. A. A. E.

Iodine distribution after injection of Abrodil. II. J. OLIVET (Klin. Woch., 10, 2396—2397; Chem. Zentr., 1933, ii, 2700).—Intravenous injection of 20—40 g. of Abrodil results in a uniform I distribution in the organs in 0.25—1.5 hr. H. J. E.

Mechanism of absorption of sodium fluoride by roaches. G. L. HOCKENYOS (J. Econ. Entom., 1933, 26, 1162—1169).—Although a lethal dose of NaF may be absorbed by roaches through the body integument, the rate of absorption is too low to be an effective factor in control measures. When the antennæ and tarsi are coated with NaF dust, sufficient may be taken in through the mouth to cause death. A. G. P.

Blood-calcium after the administration of sodium oxalate to normal and thyro-parathyroidectomised cats. W. SALANT, W. M. PARKINS, and L. E. SHEPPARD (J. Lab. Clin. Med., 1933, 19, 142—152).—Fall in serum-Ca of normal cats after injection of $\text{Na}_2\text{C}_2\text{O}_4$ is due to injury of the parathyroid gland. Decrease in serum-Ca caused by intravenous injection of 30—40 mg. per kg. after thyro-parathyroidectomy is 0.25 as great as that produced by injection of the same amounts into normal cats. The reduction produced by injection of large amounts is < 0.5 as great. CH. ABS.

Effects of feeding sodium bicarbonate or lactic acid on the sex ratio in rats. F. E. D'AMOUR (Science, 1934, 79, 61—62).—Rats bred on stock diet to which was added NaHCO_3 or lactic acid showed no variation in the sex ratio due to feeding with acid or base. L. S. T.

Variations in mineral composition of blood due to irradiation by sunlight. S. MALCZYNSKI (Compt. rend. Soc. Biol., 1933, 113, 1297—1300).—Irradiation with summer sunlight does not appreciably affect the P or Na content of the blood of dogs, but causes immediate increase (I) in the Ca content. (I) persists for several weeks, but the accompanying increase in the K content soon disappears. NUTR. ABS. (m)

Spectral erythemic reaction of the untanned human skin to ultra-violet radiation. W. W. COBLENTZ and R. STAIR (Bur. Stand. J. Res., 1934,

12, 13—14).—Data for the erythemic response of skin are revised and extended. A. G.

Effect of X-rays on substances of biological importance. J. P. BECKER and S. FREYTAG (Pflüger's Archiv, 1932, 231, 26—32; Chem. Zentr., 1933, ii, 2278).—The fluorescence power of ovalbumin, a mixture of various NH_2 -acids, and histidine (I) was increased. The effect on the absorption spectrum of (I) is similar to that caused by ultra-violet irradiation, a physiologically active substance being produced. A. A. E.

Vital oxidation of succinic acid in air and in pure oxygen with change in p_{H} . J. LEHMANN (Skand. Arch. Physiol., 1933, 65, 291—303; Chem. Zentr., 1933, ii, 1195).—The oxidation of succinic acid with succinodehydrogenase from horse muscle in air and in O_2 has been studied at different p_{H} vals. At p_{H} 7.4 approx. O_2 consumption is independent of the partial pressure; at p_{H} > 7.4 it is smaller, and at < 7.4 greater, in O_2 than in air. L. S. T.

Xanthine-oxidase. XI. Xanthine-oxidase and lactoflavin. D. E. GREEN and M. DIXON (Biochem. J., 1934, 28, 237—243).—Rate of O_2 uptake (I), and the ratio of (I) and rate of reduction of methylene-blue (II) by milk xanthine-oxidase (III) are both unaffected by lactoflavin (IV). (II) is reduced by (III) anaerobically 64 times as fast as (IV), which cannot be a catalytic flavin (cf. this vol., 109). O_2 probably reacts directly with the activated substrate.

Alcohol dehydrogenase from yeast. II. D. MULLER (Biochem. Z., 1934, 268, 152—157; cf. A., 1933, 982).—At p_{H} 6.3 the activity (I) of the dehydrogenase (II) is reduced by 50% on heating to 58°. (I) is optimal between 7.5 and 10, decreases slowly between 7.5 and 3.5, and reaches a min. between 10 and 11. KCN has little effect on (I), which is reduced only 50% even by 0.1N solution. The reduction of methylene-blue in presence of extract containing (II) is accelerated by many org. compounds (mono- and poly-hydric alcohols, aldehydes, ketones, pentoses, hexoses, neutral salts of acids), but no succino-, triose-, or xanthine-(II) is present. W. McC.

Quinones as enzyme models. XII. Metal salts as activators. B. KISCH and K. SCHUWERTH (Biochem. Z., 1934, 268, 158—163; cf. A., 1933, 979).—Low concns. (0.001—0.0000005M) of AlCl_3 , TiCl_3 , FeCl_3 , CoSO_4 , NiSO_4 , HgCl_2 , CuSO_4 , AgNO_3 , AuCl_3 , PtCl_4 , and especially CdCl_2 activate the oxidative deamination of glycine in presence of hydroxyquinol, resorcinol, adrenaline, pyrocatechol, and gallic acid. The degree of activation varies with the salt used, its concn., $[\text{H}^+]$, the catalyst, and the buffer used. W. McC.

Formation of urea from uramido-acids, hydroantoin, and proteins by the action of enzymes (reductases) in neutral solution. M. WADA (Proc. Imp. Acad. Tokyo, 1934, 10, 17—20; cf. A., 1933, 1063).—Urea (I) is formed in small yield when citrulline, prollysine, carbamyl-leucine (II), carbamylphenyl-alanine (III), ovalbumin, gelatin, and various hydroantoin are incubated, in neutral solution at 65°, with fresh milk (IV), blood-serum, or liver or pancreas extracts. The last-named all contain small amounts

of (I), not increased by heating at 100°. 80% yields of (I) from (II) and (III) are obtained in presence of CH_2O at 35°, using a filtrate (conc. by evaporation) from (IV) treated with citric acid. The (I)-producing activity runs parallel with reducing power. A. E. O.

Nature of lysozyme action. K. MEYER, R. THOMPSON, J. W. PALMER, and D. KHORAZO (Science, 1934, 79, 61).—Lysozyme (I) appears to be an enzyme or enzyme mixture which splits off reducing sugar from certain mucoids and from the polysaccharides derived from them. The occurrence of (I) in tears, nasal, bronchial, and gastro-intestinal mucus, egg-white, and semen can thus be understood, the bacteriolytic action being incidental. L. S. T.

Enzymic amylolysis. III. Crystalline hexaose from starch. E. WALDSCHMIDT-LEITZ and M. REICHEL (Z. physiol. Chem., 1934, 223, 76—80; cf. A., 1932, 304).—From the products of pancreatic hydrolysis of erythroamylose, there was isolated in 7—11% yield a cryst. *hexaose*, m.p. 258—263° (decomp.), $[\alpha]_D +183^\circ$. It is hydrolysed by α -amylase to α -maltose, and by β -amylase to β -maltose, but not by maltase. J. H. B.

Inactivation of animal amylase by plant paralyzers and the presence of inactivating substances in solutions of animal amylase. T. CHRZASZCZ and J. JANTOCKI (Biochem. J., 1934, 28, 296—304).—Plant sistoamylase (A., 1933, 749, 980, 1080, 1343) inhibits the action of animal amylase (I) of saliva and pancreas, dried preps. being more active than undried. Animal sistoamylases (II) occur together with (I) in nature, inactivating $\frac{2}{3}$ and $\frac{1}{3}$ of salivary and pancreatic (I), respectively. Sistoamylase-amylase systems can be reactivated by addition of eleuto-substances, notably peptone, which are regarded as causing elution of (I) from the adsorbing (II). C. G. A.

Biological significance of enzymic activation. E. WALDSCHMIDT-LEITZ (Bohm. Bierbrauer, 1933, 60, 299—302, 317—319; Chem. Zentr., 1933, ii, 2683).—Enzyme activity depends on the presence of activators (or inhibitors). Amylokinase, occurring in malt, is an activator for α - and β -amylase. H. J. E.

Activity of technical invertase preparations. R. WEIDENHAGEN (Chem.-Ztg., 1934, 58, 185—187).—The enzyme val. of a prep. is defined as the time in min. taken by 1 g. of the prep. to effect 50% inversion of 2.375 g. of sucrose at 4.62 and 30° in a total vol. of 50 c.c. P. G. M.

Glyoxalase. I. Manometric method for the study of glyoxalase. M. E. PLATT and E. F. SCHROEDER (J. Biol. Chem., 1934, 104, 281—297).—The manometric method (A., 1932, 1287) is suitable for determination of glyoxalase (I) activity. With low concn. of glutathione (II) and AcCHO (III), the rate (IV) of enzyme reaction is directly proportional to the amount of (I) present. With high concn. of (II), (IV) is independent of (I) and proportional to (III). In pure solution (II) and (III) react and reach equilibrium; it is suggested that this complex forms the enzymic substrate. $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ inhibits COME_2 -yeast (I) by destroying (II), (I) not being affected.

Glyoxalase activity of tissues. M. JOWETT and J. H. QUASTEL (Biochem. J., 1934, 28, 162—172).—The glyoxalase activity of tissue slices is proportional to the surface area and is inhibited by O_2 . AcCHO and glucose probably compete as substrates.

H. G. R.

Conversion of glyceraldehydephosphoric acid into methylglyoxal and lactic acid. M. KOBEL and H. COLLATZ (Biochem. Z., 1934, 268, 202—204).—Under the conditions most favourable for the production from hexose diphosphate of AcCHO yeast produces only traces of it from glyceraldehydephosphoric acid (I), lactic acid being almost quantitatively formed. During fermentation of sugars, AcCHO is thus a primary product, and is not derived from (I).

W. McC.

Influence of arsenate and arsenite on the enzymic breakdown of phosphoric acid esters. L. B. PETT and A. M. WYNNE (Biochem. J., 1934, 28, 365—371).—Of the phosphatase systems of *Cl. acetobutylicum*, *P. jensenii* (I), *B. subtilis*, *B. lactis aërogenes*, yeast, takadiastase, pig kidney, and ox erythrocytes, the only one in which the action on Na glycerophosphate was accelerated by AsO_4''' (II) and AsO_3''' (III) is that of (I). With hexose diphosphate as substrate, (II) and (III) sometimes, but not always, increase the rate of liberation of inorg. P, but in this case the effect on the glycolytic enzyme is a complicating factor. F' , which up to 0.01M does not inhibit the phosphatase action of (I), reduces the accelerating effect of (II). W. O. K.

Urinary phosphatases. A. DMOCHOWSKI (Compt. rend. Soc. Biol., 1933, 113, 956—957).—The activity of hexosediphosphatase (optimum p_{H} 4.8—5.8) found in normal urine has been studied, using substrates of (1) Na glycerophosphate, (2) the Na salt of yeast-nucleic acid, (3) thymus-nucleic acid, and (4) $\text{Na}_4\text{P}_2\text{O}_7$, the P being determined by the method of Lohmann and Jendrassik. Large variations occur in normal and pathological urines of the same sp. gr., as well as in the same sample over several hr. Dialysis and dilution of the urine greatly increase the activity of the enzyme, whilst pptn. of the urinary PO_4''' with Mg decreases it. Nucleophosphatase shows little activity either in normal or pathological urines, whilst pyrophosphatase, which has an optimum p_{H} of 5.5, is completely inactivated at p_{H} 9. NUTR. ABS. (b)

Serum-lipases. N. FIESSINGER, M. ALBEAUX-FERNET, and A. GAJDOS (Ann. Med., 1933, 34, 101—135).—Decrease of total serum-lipases occurs in cases of rapid emaciation. Increase of quinine-resistant lipase frequently occurs in hepatic disorders, and increased atoxyl-resistant lipase in pancreatic disorders. These changes are not, however, characteristic of the respective disorders, and are influenced by the thyroid and probably by other internal secretory glands. NUTR. ABS. (b)

Relative concentration of esterase and lipase in adipose tissue. J. S. HEPBURN and H. M. MOORE (Amer. J. Pharm., 1934, 106, 14—15).—In adipose tissue both esterase (I) and lipase (II) are present, (I) being predominant in goose, lamb, and man and (II) in chicken and turkey. W. O. K.

Determination of pancreatic lipase. E. WALDSCHMIDT-LEITZ and R. JUNOWICZ (Biochem. Z., 1934, 268, 178—180).—Steudel's criticisms (A., 1933, 981) of the method of Willstätter *et al.* (A., 1923, i, 403) are unfounded, since his curves show wt. of gland instead of wt. of lipase. W. McC.

Lipase and esterase action of pancreatic juice. H. P. WOLFEKAMP and K. GRIFFIOEN (Z. physiol. Chem., 1934, 223, 36—42).—In pancreas there appear to be at least two esterases, (I) and (II), hydrolysing tributyrin and EtOAc, respectively. Heating at 67° destroys (II) more rapidly than (I). The rates of inactivation at p_H 9.92 are about equal; at p_H 3.3 (II), but not (I), is inactivated in 1 hr. J. H. B.

Intracellular enzymes of tissues and glands. IV. **Pancreatic lyo- and desmo-lipases.** E. BAMANN and P. LAEVERENZ (Z. physiol. Chem., 1934, 223, 1—20; cf. this vol., 108).—In extraction of COMe₂-dried preps. of pancreas with aq. glycerol (I), the yield of lyo-enzyme varies with the H₂O present, being max. with 50% (I). With 100% (I) the yield is only 2—3%. From fresh minced tissue 100% (I) extracts only 1.5% of the total lipase; the effect of H₂O is much less. The yield is increased when autolysed tissue or the dried prep. from it is used. Extracts with high (I) content show the greatest activatability (II). The (II) of dried is > that of minced tissue. Autolysed preps. give solutions of low (II). Differences in the colloidal carrier are the cause of the variations in (II). J. H. B.

Adsorption of enzymes on protein. II. **Inhibition and activation of pancreatic enzymes.** H. DYCKERHOFF, H. MIEHLER, and V. TADSEN (Biochem. Z., 1934, 268, 17—33; cf. A., 1933, 535).—Pig pancreas contains substances (I), some sol. in solvents usually employed for extracting the enzymes (II), which inhibit the action of lipase, amylase, and trypsin (III). (I) are only partly or not at all removed during the process used for determination of (II). Another inhibitor (IV) for (III) accompanies it. (IV) is inactivated by enterokinase (V). (III) hydrolyses proteins even in the absence of (V). W. McC.

Proteolytic enzyme in cucumber (*Cucumis sativus*). R. N. CHOPRA and A. C. ROY (Indian J. Med. Res., 1933, 21, 17—23).—Cucumber juice contains an ereptic enzyme (I), capable of hydrolysing Witte's peptone and caseinogen, forming tryptophan, but without action on fibrin. (I), which also liquefies gelatin and clots milk, acts best at p_H 5.4—6.2. The endocarp has a higher concn. of (I) than the mesocarp and the juice of mature fruit shows a higher activity than that of immature or ripe fruit. Activation by HCN is not sp. NUTR. ABS. (m)

Ultracentrifugal study of the action of papain on ovalbumin. T. SVEDBERG and I. B. ERIKSSON (J. Amer. Chem. Soc., 1934, 56, 409—412; cf. A., 1933, 427).—The action of papain (I) activated by HCN on ovalbumin (II) gives three types of degradation products: (a) non-centrifugable material (probably containing lower polypeptides and NH₂-acids), (b) a centrifugable substance [sedimentation const. (III) about 0.6×10^{-13}] with a mol. wt. of the same order as that of the protamines, and (c) a substance [(III)

about 2.7×10^{-13}] having the same mol. wt. as (II) but a highly unsymmetrical mol. (which probably arises by the weakening of some of the linkings in the original mol.). (II) is unaffected by inactivated (I).

H. B.

Action of oxidising and reducing agents on papain. II. **Effect of light, organo-arsenicals, and ascorbic acid.** T. BERSIN (Z. physiol. Chem., 1933, 222, 177—186; cf. A., 1933, 1203).—Ultra-violet light activates oxidised papain (I) by reduction of ·S·S· to ·SH. *p*-Aminophenylarsine oxide similarly activates by reduction, but *p*-acetamido- and *p*-aminophenylarsinic acid oxidise ·SH, and hence inactivate the enzyme. Ascorbic acid, which is unable to reduce ·S·S· to ·SH, does not activate (I). J. H. B.

Chemical nature of rennin. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1934, 104, 259—266).—Rennin (I) is completely digested by pepsin (II) and trypsin, but not by erepsin, and may be easily separated from (II) by this method. Absorption on cryst. edestin indicates that, in the case of (I), no exchange of carrier is taking place. H. G. R.

Activation of pro-rennin. R. EGE and E. LUNDSTEEN (Biochem. Z., 1934, 268, 164—173; cf. A., 1933, 1081).—Aq. extracts (I) of calf's stomach contain only small amounts (5—10% of total enzyme) of active rennin. Activation (II) is induced by acid reaction beginning at $p_H < 5$; hence at the optimal p_H (5—6) no (II) takes place. The rate of (II) increases rapidly (from 30 min. at 3.4 to 1.5 min. at 3) as the p_H decreases. Spontaneous (II) occurs even at p_H about 7 when (I) are kept, probably as a result of bacterial proteolysis. Pancreatin produces similar (II). W. McC.

Trypsin. I. **Chemical nature.** II. **Effect of trypsin on caseinogen.** I. S. KLEINER and H. TAUBER (J. Biol. Chem., 1934, 104, 267—270, 271—274).—I. By complete autolysis of pancreatic tissue for 18 months, a protein-free trypsin (I) prep. has been obtained.

II. (I) will coagulate milk at low concn. only, otherwise the casein stage is passed without formation of Ca caseinate, and no clot can be obtained with rennin (II). The velocity of coagulation is proportional to [H⁺] for (I), (II), and pepsin. H. G. R.

Dilatometric studies in the proteoclastic degradation of proteins. I. **Tryptic hydrolysis.** M. SREENIVASAYA, B. N. SASTRI, and H. B. SREERANGACHER (Biochem. J., 1934, 28, 351—355).—During the tryptic digestion of solutions of caseinogen (I) and of gelatin (II), the ratio of the change in vol. measured by the two-bulbed dilatometer (A., 1932, 880) to the NH₂ groups set free varies during the early stages, but is const. after 30 or 40 min., when the dilatometric depression per millimol. of NH₂-N set free is for (I) 10.8 cu. mm. and for (II) 8.7 cu. mm. W. O. K.

Specificity of dipeptidase and aminopolypeptidase. W. GRASSMANN and H. BAYERLE (Biochem. Z., 1934, 268, 214—219).—Dipeptides (I) obtained from asparagine (II) and aspartic acid (III) by introducing natural NH₂-acid radicals into their NH₂ groups are hydrolysed by dipeptidase (IV), but are

not attacked by aminopolypeptidase (V) from yeast or intestine. Diglycylasparagine is attacked by (V), but not by (IV). Erepsin, obtained from intestine by the method of Waldschmidt-Leitz and Schaffner (A., 1926, 323), behaves as a mixture of (IV) and (V). (I) from (III) are more resistant to hydrolysis than are (I) from (II). Asparagyl-*l*-tyrosine, asparagylglycine, and *d*-leucyl-*l*-asparagine are not hydrolysed by (IV). W. McC.

Effect of preservatives on enzyme action. T. SABALITSCHKA (Z. Unters. Lebensm., 1934, 67, 203—204).—A criticism of Kluge (this vol., 108). Pancreatic trypsin is not inhibited by esters of p -OH·C₆H₄·CO₂H. Infusions of coffee and 1% NaCl both inhibit peptic digestion *in vitro*, but have no deleterious effect on digestion *in vivo*. E. C. S.

Effect of preservatives on avitaminotic animals. H. CREMER (Z. Unters. Lebensm., 1934, 67, 205; cf. this vol., 108).—The esters of p -OH·C₆H₄·CO₂H have no deleterious effect on either normal or scorbutic animals. E. C. S.

[Effect of preservatives on enzyme action etc.] H. KLUGE (Z. Unters. Lebensm., 1934, 67, 205—206).—A reply (cf. preceding abstracts). E. C. S.

Phase changes in enzyme systems: azotase activity in relation to p_H . D. BURK and H. LINEWEAVER (J. Physical Chem., 1934, 38, 35—46).—Azotase activity in *Azotobacter* varies abruptly with p_H , and a characteristic zero limit at p_H 5.97 is approached reversibly and practically perpendicularly. By applying the phase rule, it may be regarded as a two-component heterogeneous system with three phases in equilibrium at the crit. p_H : H₂O, active non-aq. (basic) (I), and inactive non-aq. (acidic) (II). (I) exists above the crit. p_H and (II) below. Slight phase non-homogeneity may occur between p_H 5.97 and 6.37. The conditions are similar to those which obtain in the dissociation of a hydrated salt. Phase-rule applications to micro-heterogeneous systems, surfaces, and problems of general enzyme reaction velocity and stability are considered. M. S. B.

Arginase. I. Relation between activity of enzyme and concentration of hydrogen ions. A. HUNTER and J. A. MORRELL. **II. Influence of hydrogen-ion concentration on the stability of the enzyme.** A. HUNTER and J. A. DAUPHINEE (Quart. J. Exp. Physiol., 1933, 23, 89—117, 119—126).—I. The activity of arginase determined by a two-stage method described is unsymmetrically arranged about an optimum p_H (I) of 9.8 with a second less marked optimum (II) between 7 and 8. (II) persists in arginase complexes extracted from fresh liver and left for 3 or 4 weeks, whilst (I) becomes less evident. These results may be explained by assuming the existence of two arginases or, better, by supposing that ionisation of the protein complex associated with the enzyme occurs. The activity curve of arginase thus becomes the alkali titration curve of the enzyme-protein ion.

II. As regards its stability at various [H⁺] in the absence of its substrate arginase is not destroyed at p_H 6.6—7.8, but on either side of this zone it undergoes

progressive destruction. Below 4 and above 12, it is completely inactivated at 37° in 10 min.

NUTR. ABS. (m)

Uricase. VII. Soluble uricase. R. TRUSZKOWSKI (Biochem. J., 1934, 28, 62—67).—Ro's conclusion (A., 1932, 428) that uricase (I) is indissociable from traces of alkali-sol. protein (II) and his method of prep. of sol. (I) have been confirmed. The activity varies in proportion to the (II) in the solution. The non-extractability of (I) is due to the presence of lipins, and after their removal (I) may be extracted with dil. aq. Na₂CO₃. H. G. R.

Isolation of heteroxanthine [7-methylxanthine] from yeast. P. W. WIARDI and B. C. P. JANSEN (Rec. trav. chim., 1934, 53, 205—208).—The yeast is extracted with HCl at p_H 4.5 and the extract stirred with fuller's earth, which is then separated and extracted with iced aq. Ba(OH)₂. This extract is acidified to p_H 4.8, pptd. with Na silicotungstate, and the ppt. decomposed with Ba(OH)₂. Acidification of the resulting solution to p_H 2 and pptn. with AgNO₃ gives 7-methylxanthine. H. A. P.

Acid production in autolysis of yeast. H. HAEHN and H. LEOPOLD (Z. Unters. Lebensm., 1934, 67, 50—58).—Between 30° and 55° the total acid production in alkaline media is > that in acid media, but the NH₂-acid production is less, owing to deamination. In normal yeast autolysates at these temp. the acids produced inhibit the growth of putrefactive bacteria. E. C. S.

Inhibition of fermentation in maceration extract by oxygen in presence of a positive oxidoreduction system. F. LIPMANN (Biochem. Z., 1934, 268, 205—213; cf. A., 1933, 1202).—Fermentation (I) in Lebedev's maceration extract (II) is inhibited by amounts of I which are more than equiv. to the SH content. (I) of (II), which is not sensitive to the action of O₂, is inhibited by O₂ in presence of dichlorophenol-indophenol. Vals. for the oxidoreduction potential are given, and the effect on them of addition of traces of thionine and naphtholsulphonate-indophenol (III) is measured. When (III) and O₂ are present (I) ceases, but not because of resynthesis. W. McC.

Bios from lecithin. E. JANSSENS (Arch. internat. Physiol., 1933, 37, 70—86).—The presence of "bios" in choline-free lecithin from egg yolk was demonstrated by fermentation experiments, using the method of Wildiers. An attempt was made to separate the "bios" from the lecithin complex, but the substance appeared to be present as a salt or soap of the lipophosphoric acid, which could not be separated from other similar compounds occurring in egg yolk.

NUTR. ABS. (b)

Influence of dyes on the functions of cells and organs. V. Poisoning of zymase and its specific groups. F. AXMACHER and G. OPETZ (Arch. exp. Path. Pharm., 1934, 174, 427—439).—Benzidine diazo-compounds which inhibit glucose fermentation (I) by isolated zymase (II) (cf. A., 1933, 531) also inhibit the decarboxylation of AcCO₂H to MeCHO. Of various arylsulphonic acids, only SO₃H·C₆H₄·NH·NH₂ and sulphosalicylic acid inhibit (I); other ·CO-reagents (NHPh·NH₂, NH₂OH, and

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ in 0.008*M* solution) act similarly on (II) but to only a slight extent on the living cell. Experiments on (I) by (II) preps. after reacting with $(\text{PhN}_2)_2\text{SO}_4$, Ac_2O , Bz_2O , BzCl , $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\text{Cl}$, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, or CH_3N_3 , yielded no conclusive results.

F. O. H.

Biological action of ultra-short electromagnetic waves. I. Alcoholic fermentation of sucrose solutions by brewer's yeast in a Lakhovsky oscillatory circuit. F. PIRRONE (L'Ind. Chimica, 1934, 9, 16—21).—Exposure to an oscillatory circuit of wave-length 188.5 cm. for 1—2 days raises the vol. of CO_2 produced to 101—105% of that obtained with the control, and after 6—7 days to 127%.

H. F. G.

Biological action of ultra-short electromagnetic waves. II. Alcoholic fermentation of sucrose solutions by beer yeast exposed to electromagnetic waves of $\lambda=1.7$ metre. F. PIRRONE (L'Ind. Chimica, 1934, 9, 167—173).—Aq. suspensions of the yeast were exposed, and for the subsequent fermentations of 10% sucrose solutions, 10% of yeast was used. Although weaker and somewhat variable, the action of Lakhovsky oscillating circuits is analogous to that of wireless transmitters capable of emitting waves of $\lambda=1.7$ m. For exposures of 10—40 min. if continuous, or up to 90 min. if broken, these waves enhance the rate of fermentation and cell-multiplication, but the effects diminish with more prolonged exposures.

T. H. P.

Micro-calorimeter for measurement of the heat output of mould cultures. H. TAMIYA and A. YAMAMOTO (Acta Phytochim., 1933, 7, 245—263).—The mould is grown in an air-tight culture bomb which serves as calorimeter. The respiratory exchange is determined by measuring the vol. change of the gas mixture (originally 85% O_2 , 15% N_2) in the bomb and the CO_2 evolved.

J. H. B.

Germination [of fungus spores]. R. G. TOMKINS (Trans. Brit. Mycol. Soc., 1932, 17, 147—149).—The latent period of germination is slightly prolonged in presence of narcotics and certain acids, and markedly prolonged in presence of MeCHO , HCN , H_2S , NH_3 , and heavy-metal salts.

CH. ABS.

Phoma species. M. GRIMES, M. O'CONNOR, and H. A. CUMMINS (Trans. Brit. Mycol. Soc., 1932, 17, 97—111).—*P. hibernica* (described) grows well on nutrient lactose agar at p_{H} 7.0 or 3.5. Litmus milk becomes slightly alkaline (6 days) and gelatin is slightly liquefied (3 weeks). No diastatic action on starch in various cultures was observed, and no gas is produced from glucose, lactose, mannitol, dextrin, or glycerol.

CH. ABS.

Nitrogen assimilation by *Aspergillus niger*. H. HARDTL (Biochem. Z., 1934, 268, 104—115).—The rate and extent of N assimilation by *A. niger* vary with the kind (org. and inorg.) and amount of N source, and also with the amount of C source (sugar). After the first few days increase in the abs. amount of N assimilated is accompanied by decrease (I) in the % N content. (I) runs parallel with increase in amount of N and C source supplied. The N of the medium is never completely consumed. Sugar serves to intensify

respiration as well as growth, and is extensively utilised. Production of citric acid continues throughout the period of growth when the N supply is small, but occurs only during early stages when it is large.

W. McC.

Acids produced from sugar by a *Penicillium* parasitic on *Aspergillus niger*. J. L. YUILL (Biochem. J., 1934, 28, 222—227).—When grown on a sucrose medium containing chalk, *Penicillium* "R.B." (I), a mould parasitic on *A. niger*, produces Ca citrate and a small quantity of Ca oxalate as well as the Ca salt of an insol. acid, $\text{C}_{18}\text{H}_{30}\text{O}_7$, probably glauconic acid I (Wijkman, A., 1931, 523). This acid is also formed in an acid medium, but no citrate or oxalate is then produced. When grown on a glucose or fructose medium, (I) produces the insol. acid. Citric acid is also formed when chalk is present.

W. O. K.

Biochemistry of micro-organisms. XXXVI. Metabolic products of *Penicillium Charlesii*. G. SMITH. P. W. CLUTTERBUCK, W. N. HAWORTH, H. RAISTRICK, G. SMITH, and M. STACEY (Biochem. J., 1934, 28, 94—110).—A new mould species, *P. Charlesii*, G. Smith, isolated from Italian maize, when grown at 24° on a Czapek-Dox or Raulin-Thom medium containing glucose as the sole carbohydrate gave the following products: a *polygalactose*, $[\alpha]_{5790} -84^\circ$ in H_2O ; a *polymannose*, $[\alpha]_{5790} +63^\circ$ in H_2O ; *carolic acid*, $\text{C}_9\text{H}_{10}\text{O}_4$, m.p. 132°, $[\alpha]_{5461} +84^\circ$ in H_2O , monobasic; *carolinic acid*, $\text{C}_9\text{H}_{10}\text{O}_6$, m.p. 123°, $[\alpha]_{5461} +60^\circ$ in H_2O , dibasic; *carlic acid*, $\text{C}_{10}\text{H}_{10}\text{O}_9$, m.p. 176°, $[\alpha]_{5461} -160^\circ$ in H_2O , dibasic; *carlosic acid*, $\text{C}_{10}\text{H}_{12}\text{O}_8$, m.p. 181°, $[\alpha]_{5461} -160^\circ$ in H_2O , dibasic; *ramigenic acid*, $\text{C}_{16}\text{H}_{20}\text{O}_6$, m.p. 171°, $[\alpha]_{5461} +28^\circ$ in EtOH, lactonic acid; *verticillic acid*, $\text{C}_{26}\text{H}_{32}\text{O}_{12}$, m.p. 171°, $[\alpha]_{5461} -53^\circ$ in EtOH, lactonic acid. The acids were isolated from the metabolism solution by taking advantage of their differing solubilities and precipitability by various metallic salts. The variety of products obtained from the metabolism solutions of moulds isolated from spoiled Italian and American maize suggests a possible connexion with human pellagra.

P. W. C.

Cytochrome and the supposed direct spectroscopic observation of oxidase. D. KEILIN (Nature, 1934, 133, 290—291; cf. this vol., 109).—Further spectroscopic observations on bacteria are recorded. All the absorption bands of hæmatin (I) compounds seen by direct spectroscopic observation of the cells of different organisms belong either to free (I) or to the different components of cytochrome. None can be ascribed to the oxidase or the O_2 -transporting enzyme.

L. S. T.

Spectroscopic detection of the oxygen-carrying enzyme in *Azotobacter*. E. NEGELEIN and W. GERISCHER (Biochem. Z., 1934, 268, 1—7; cf. preceding abstract).

W. McC.

Significance of cytochrome in the physiology of cell respiration. K. SHIBATA and H. TAMIYA (Acta Phytochim., 1933, 7, 191—231).—In the oxygenation (I) of cytochrome (II), the O_2 mol. probably forms a complex with several (II) mols., and CO combines only with a certain fraction of the (II) mols., thus hindering (I). The formula relating CO inhibition to

the ratio of concns. of O_2 and CO derived on this basis agrees with the results of Meyerhof and Schulz (A., 1932, 1067) for the respiration of *Azotobacter chroococcum*. The spectroscopic properties and genetic relationships of the (II) components are considered. Warburg's respiratory enzyme is probably component α of (II). The function of (II) as O_2 carrier is not regarded as depending on valency change of the Fe atom.

J. H. B.

Cytochrome spectrum of various micro-organisms. H. TAMURA and S. YAMAGUCHI (Acta Phytochim., 1933, 7, 233—244).—The type of cytochrome spectrum given by various bacteria and yeasts is systematically described.

J. H. B.

[Bacterial] nitrogen assimilation. A. ISAKOVA (Bull. Acad. Sci. U.R.S.S., 1933, 1493—1504).—Both *Azotobacter Winelandii* and *A. chroococcum* assimilate NH_3 in presence of glucose, mannitol, NaOAc, or NaOBz, the mechanism of the action being the same in the two cases, although the action is more rapid with the former organism. The bacteria were grown in neutral or faintly alkaline media, which exclude autolysis, and the assimilation of the NH_3 must be regarded as a function of the vital activity of the organisms. The experiments with NaOBz show that the NH_3 may be assimilated as deaminated NH_2 groups and as N_2 . Deamination occurs also with NH_2 -acids, but to a smaller extent than was observed by Kostytshev and Brilliant (A., 1923, i, 659). Experiment shows that development of NH_3 is possible under approx. natural conditions, the rapidity of the process and the amount of NH_3 formed depending largely on the nature of the substance supplying the energy. This observation has a bearing on the rapid accumulation by higher plants of N_2 assimilated by azotobacteria.

Rhizobium species in relation to nodule formation on the roots of Florida legumes. W. R. CARROLL (Soil Sci., 1934, 37, 117—135).—Modifications of cultural methods are described and cross-inoculation data for a no. of species are recorded and discussed.

A. G. P.

Physiology of the acetic acid bacteria. I. Gluconic acid fermentation. K. TANAKA (Acta Phytochim., 1933, 7, 265—297).—The O_2 uptake by *Bacterium aceti* shows a much greater increase than the CO_2 output on addition of glucose (I), owing to the formation of gluconic acid (II). The increased CO_2 production is due to alcoholic fermentation, since it is repressed by $CH_2I \cdot CO_2Na$. The absence of the fermentation $EtOH$, normally oxidised to $AcOH$, causes a slight decrease in O_2 consumed. The aerobic oxidation of (I) is independent of (I) concn., but sensitive to p_H (optimum 5—6). The production of (II) is greater when the bacteria have been grown in absence of (I) than when cultivated on media containing (I). Mannose, galactose, and maltose, but not fructose, sucrose, and lactose, can serve as substrates. (I) is oxidised more rapidly than $EtOH$ when both are present. Methylene-blue, O_2 , and benzoquinone (III) act as H acceptors, the activity increasing in that order. The (I) fermentation in presence of O_2 is inhibited by KCN, CO, and PhMe, but in presence of (III), not by KCN, indicating that cytochrome (IV) probably takes part

in the fermentation as O_2 carrier, but since fermentation of (I) is less sensitive to inhibitors than that of $AcOH$, part of the O_2 may react without intervention of (IV).

J. H. B.

Metabolism of propionic acid bacteria. I. Degradation of phosphoric esters by *Propionibacterium Jensenii* (van Niel). L. B. PETT and A. M. WYNNE (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 119—122).— $AcCHO$ is formed by the action of the dried organism on 1% aq. Mg hexose phosphate at p_H 6.1 or Na β -glycerophosphate at p_H 7.0; with the latter glyceraldehyde (or dihydroxyacetone) is probably also formed.

F. O. H.

Chemistry of *Lactobacillus acidophilus*. II. Composition of neutral fat. J. A. CROWDER and R. J. ANDERSON (J. Biol. Chem., 1934, 104, 399—406; cf. A., 1932, 1066).—The neutral fats in the $EtOH \cdot Et_2O$ extract of *L. acidophilus* contain glycerides of lauric, myristic, palmitic, stearic, and oleic acids. The unsaponifiable matter contains cholesterol. A phosphatide is pptd. from the extract with $COMe_2$.

H. D.

Enzymic formation of hydrogen sulphide by certain heterotrophic bacteria. II. H. L. A. TARR (Biochem. J., 1934, 28, 192—198).—Extraction of $COMe_2$ -dried *P. vulgaris* cells with PO_4''' buffer yields 2—3% of the enzyme (I) which produces H_2S from org. S compounds. In the intact cells (I) requires the presence of an NH_2 group before it can become active. The activity is nil at p_H 5.5, max. at p_H 7.8—9.0, and 20% at p_H 12. The optimum temp. is 40° and aerobic conditions are most favourable.

H. G. R.

Factors preventing the synthesis of a bacterial pigment. A. GROORTEN and N. BEZSSONOV (Compt. rend., 1934, 198, 987—989).—The development of colour in *Bacillus laticus* at p_H 7 and 20° is prevented by nineteen substances containing an OH (a *tert.* group being most effective), enolisable CO, or C·O·C group. The final p_H , which normally rises to 8.4 in a week, is then 6.2—8.0. Substances with k 4—10 are generally more effective than those with low k , and a lowering of the temp. increases the effect.

R. S. C.

Influence of salt on diffusion from bacterial cells. C. E. A. WINSLOW and H. H. WALKER (Proc. Soc. Exp. Biol. Med., 1933, 30, 1033—1035).—NaCl at low concn. (0.05—0.08M) increases viability of *Es. coli* and the diffusion of NH_3 outwards through the cell wall; higher concns. ($> 2M$) have an opposite and toxic effect.

CH. ABS.

Influence of cations on aerobic sporogenesis in a liquid medium. F. W. FABIAN and C. S. BRYAN (J. Bact., 1933, 26, 543—547).—Chlorides of Na, Li, NH_4 , and K, and also Na lactate stimulated spore production in *B. cereus*, *B. subtilis*, *B. mesentericus*, and *B. megatherium*. Chlorides of a no. of bi- and ter-valent metals were without effect. Slightly acid media appeared to favour spore formation, although in the range p_H 5.0—7.5 the influence of reaction was very small.

A. G. P.

Tropical soil microbiology. I. Evolution of carbon dioxide from the soil and the bacterial growth curve. A. S. CORBET (Soil Sci., 1934, 37,

109—115).—Evolution of CO_2 from soil under laboratory conditions and at const. temp. is represented by the equation $y = Ft^m$ (y = total yield of CO_2 after time t , m is a const. expressing the retardation of CO_2 production due to laboratory conditions, and F is a const. representing CO_2 produced during the initial unit of time in the experiment). Vals. for F and m are determined for a no. of soils. Curves showing daily yield of CO_2 with advancing time correspond with the phase of decrease of bacterial growth. During this phase only a portion of the total organisms present are concerned in the production of CO_2 . A. G. P.

Poisonous principles of so-called Bongkrek poisoning of Java. A. G. VAN VEEN and W. K. MERTENS (Rec. trav. chim., 1934, 53, 257—266).—The yellow cryst. substance, m.p. 171—172° (decomp.) (cf. A., 1933, 1206), formed alone by cultivation of the appropriate bacteria in glycerol-peptone media is accompanied in most other media (e.g., glycerol-agar or stearic acid-agar) by a colourless amorphous substance, which is N-free, has acidic properties (H_2O -sol. Na salt), and when injected intraperitoneally is toxic to rats in doses of < 0.1 mg. The isolation of the latter is described. It is separated from accompanying fatty acids only with difficulty, and when pure is very sensitive to heat and oxidation. H. A. P.

Poisons and disease and some experiments with the toxin of the *Bacillus tetani*. J. J. ABEL (Science, 1934, 79, 63—70, 121—129).—An address. L. S. T.

Lysis of tubercle bacilli *in vitro*. H. J. CORPER (Amer. Rev. Tuberc., 1933, 28, 138—143).—Loss of acid-fastness in tissues sterilised with H_2SO_4 is due to acid retained by the tissues, and not to the action of autolytic enzymes. CH. ABS.

Detoxifying effect of ox bile on diphtheria toxin. M. D. SMITH and P. J. MOLONEY (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 183—186).—Diphtheria toxin is detoxified by ox bile (I) when fresh, but not when heated at 100° for 20 min. Extraction of (I) by Et_2O at p_{H} 2.0 yields a heat-stable detoxifying agent (II). The residue on neutralisation and addition of AcOH to p_{H} 3.6 gives a ppt. which contains a heat-labile detoxifying agent (III). Whilst neither (II) nor (III) alone is significantly effective, (II)+(III) detoxify equally as well as (I). F. O. H.

Enzymic capabilities and anaerobic growth of paratyphoid-*B* bacillus. K. AARON (Biochem. Z., 1934, 268, 121—151).—Many org. compounds (I) (alcohols, acids, carbohydrates, NH_2 -acids, peptides, and other N compounds) are dehydrogenated by the bacillus (II), including some (e.g., HCO_2H , EtCO_2H) which cannot serve as C source (III) for its growth. Conversely, some (I) (e.g., *l*-tartaric acid, rhamnose) are not dehydrogenated, but can serve as sole (III) during aerobic growth. In presence of Na lactate and (II), NaNO_3 , Na fumarate, Na *l*- and *i*-malate, Na aspartate, and asparagine (but not Na *l*- and *d*-tartrate, Na mesotartrate, and Na citrate) act as H acceptors. For the anaerobic growth of (II) in presence of Na lactate and NO_3^- , leucine, serine, aspartic acid, asparagine, glutamic acid, lysine, arginine, phenylalanine, tryptophan, histidine, proline, and glycyl-

glycine, but not NH_4Cl , glycine, alanine, urea, and uric acid, act as N sources. When glucose is the C source, glycine also serves as N source. When serine is the N source, the presence of NaNO_3 is unnecessary. Strains of (II) which grow feebly anaerobically with NH_4Cl as N source can, however, be propagated. In presence of Na aspartate and NaNO_3 , acetates, succinates, fumarates, *i*- and *l*-malates, *l*-tartrates, citrates, and glycerol (but not EtOH) serve as C sources for the anaerobic growth of (II). AcCO_2H maintains anaerobic growth even in the absence of a H acceptor when the N source is serine, Na glutamate, histidine, proline, or NH_4Cl . W. McC.

Biochemical and serological properties of *B. typhi flavum*. J. SEYDEL (Ann. Inst. Pasteur, 1934, 52, 179—192).—*B. typhi flavum* (I) exhibits several points of difference from Eberth's bacillus (liquefaction of gelatin, production of H_2S , etc.). Serologically at least three groups can be distinguished, and the *flavum* strains are agglutinated more often by anti-typhoid and paratyphoid sera (80%) than by antisera to (I) (55%). P. G. M.

Soluble specific substance of *Pneumococcus*.
I. **Acetylpolysaccharide of *Pneumococcus* type I.** O. T. AVERY and W. F. GOEBEL (J. Exp. Med., 1933, 58, 731—755).—In the isolation of the acetylpolysaccharide (I), excess of alkali is avoided. (I) contains 4.85% N, of which 45% is liberated in the NH_2 form with HNO_2 in the cold. Hydrolysis affords a polysaccharide identical with that hitherto termed the sol. sp. substance. Immunological reactions are described. CH. ABS.

Antigenic structure of *Vibrio cholerae*. III. **Specific carbohydrates.** R. W. LINTON and D. L. SHRIVASTAVA. IV. **Carbohydrates in rice-water faeces.** R. W. LINTON, D. L. SHRIVASTAVA, and B. N. MITRA (Indian J. Med. Res., 1933, 21, 379—384, 385—388).—III. On hydrolysis, 5 strains (from patients) yielded galactose (I) and 5 (from H_2O) yielded arabinose (II).

IV. Polysaccharides afforded on hydrolysis probably (I) and (II). CH. ABS.

Ramon flocculation reaction and fixed amounts of antigen or antiserum. W. TIMMERMAN (Ann. Inst. Pasteur, 1934, 52, 146—154).—The different results obtained by taking either a fixed amount of diphtheria toxin or a fixed amount of antiserum are due entirely to the varying vols. of saline added to give a const. total vol. P. G. M.

Effect of resection of the stomach on the bacteriology and chemistry of the small intestine and its clinical significance. E. HERTEL and F. SARTORIUS (Arch. klin. Chirurg., 1933, 176, 197—235).—Experiments on dogs with intestinal fistulae (duodenum or lower ileum) showed that after gastric resection (Billroth I and II) the organisms of the upper and middle portions of the small intestine tended to increase in no. and to resemble those of the large intestine: differences between the two operations were principally apparent at the duodenal fistula. There was also an increase in the indole of the intestinal contents, and of urinary indican, particularly after a meat diet; indole was diminished after whey and mu-

especially sour milk. Resection produces abnormal fermentation and foulness in the upper parts of the gut.

NUTR. ABS. (b)

Method of counting bacteria in milk. W. M. BOGDANOFF (Lait, 1934, 14, 37—48).—The milk of suitable dilution is mixed in a known proportion with a standard suspension of stained *Schizosaccharomyces pombe* (I), and is then stained in the usual manner. On several "fields" the bacteria and the (I) are separately counted, and from the known count of the latter and the proportion of mixing of the two liquids the bacterial count may be calc.

E. B. H.

Bacteriostatic action of gentian-violet and its dependence on the oxidation-reduction potential. M. A. INGRAHAM (J. Bact., 1933, 26, 573—598).—Bacteriostasis caused by gentian-violet is closely related to its controlling effect on the oxidation-reduction potential of the medium. It affects the cultures only in the lag phase.

A. G. P.

Influence of colloidal lecithin on microbial cytolysis by bacteriophage. B. S. LEVIN and I. LOMINSKI (Compt. rend., 1934, 198, 989—991).—The cytolytic action of antistaphylococcal bacteriophage (I) is partly or completely inhibited by colloidal lecithin. This may account for the greater effect of (I) *in vitro* than *in vivo*.

R. C. S.

Internal secretion of the parotid gland. L. TAKÁCS (Orvosi Hetilap, 1933, 77, 659—661).—Fresh, minced parotid gland is extracted with EtOH and Et₂O and the residue taken up in 0.4% HCl. After neutralising and concn., a yellow substance is obtained, insol. in EtOH, Et₂O, C₆H₆, PhMe, readily sol. in H₂O or dil. acids and alkalis. Injected into rabbits starved for 24 hr., material from 0.5—5.0 g. of fresh gland causes hypoglycæmia within 1—3 hr. Blood-sugar is lowered by 30—70% and remains low for > 24 hr. despite continued abundant feeding. Hypoglycæmic symptoms are not observed although vals. of 30 mg. per 100 c.c. are recorded.

NUTR. ABS. (m)

Effect of injection of spleen extract on sugar-tolerance test in the normal and splenectomised dog. F. RATHERY and I. COSMULESCO (Compt. rend. Soc. Biol., 1933, 113, 1115—1118).—Intravenous injection (I) of spleen extracts considerably diminishes the hyperglycæmia which normally follows (I) of glucose and causes the "bound" blood-sugar to fall slightly. With splenectomised dogs there are similar but less intense effects.

NUTR. ABS. (m)

Influence of spleen extract on blood-sugar and experimental hyperglycæmia in dogs depancreatized before or after splenectomy. F. RATHERY and I. COSMULESCO (Compt. rend. Soc. Biol., 1933, 113, 1430—1433).—Spleen extract, intravenously injected into the depancreatized dog, has the same slightly hypoglycæmic effect (free sugar) as in normal and splenectomised dogs. When the dog is both depancreatized and splenectomised, the effect is greatly intensified.

NUTR. ABS. (m)

Liver-glycogen and splenectomy. F. RATHERY, P. M. DE TRAVERSE, and (MLE.) PATIN (Compt. rend.

Soc. Biol., 1933, 113, 1433—1435).—Splenectomy sometimes affects liver-glycogen in the dog.

NUTR. ABS. (m)

Glycolytic hormone of the spleen. N. FIESINGER and R. CATTAN (J. Physiol. Path. gen., 1933, 31, 380—399).—In the dog and rabbit, splenectomy and injection of extracts of spleen (I) indicate that (I) produce a hormone (not insulin) which causes hypoglycæmia.

NUTR. ABS. (m)

Glycolytic hormone of the spleen. II. Application to human pathology. N. FIESINGER, S. GOTHÉ, and H. R. OLIVIER (J. Physiol. Path. gén., 1933, 31, 759—765).—Intravenous injection of 2 c.c. of deproteinised splenic extract produces an inconst. fall in blood-sugar in normal and diseased subjects. Splenic feeding in diabetic patients gives no const. results.

NUTR. ABS. (m)

Influence of the parathyroid on the metabolism of creatine and phosphoric acid. C. G. IMRIE and C. N. JENKINSON (J. Physiol., 1933, 79, 218—225).—The creatine phosphate of the muscles (I) of thyroparathyroidectomised cats is < normal, and its rate (II) of resynthesis after stimulation of the (I) is reduced. After the administration of parathormone (II) is normal.

NUTR. ABS. (m)

Influence of desiccated thyroid gland, thyroxine, and inorganic iodine on the storage of glycogen in the liver of the albino rat. H. C. COGGESHALL and J. A. GREENE (Amer. J. Physiol., 1933, 105, 103—109).—Liver-glycogen (I) is reduced following administration of desiccated thyroid gland (II) and thyroxine (III), but remains practically unaltered after KI. The reduction after (II) or (III) is not proportional to the dose, although the effect is in general greater with greater doses. When given in doses of equiv. I content, (III) lowers (I) more than does (II), except in myxœdema, when both are equally effective.

NUTR. ABS. (m)

Absorption of thyroxine from the gastrointestinal tract, with special reference to the effect of alkali. W. O. THOMPSON, P. K. THOMPSON, S. G. TAYLOR, and L. F. N. DICKIE (J. Clin. Invest., 1933, 12, 990).—Pure thyroxine given orally or intraduodenally has little effect on the B.M.R.; as Na salt given orally it has about $\frac{1}{2}$ the effect when given intravenously. When given in solution with excess NaOH (*i.e.*, as Na₂ salt) oral administration has almost as great an effect as intravenous.

NUTR. ABS. (m)

Calorigenic action of thyroglobulin and its constituents. J. LERMAN and W. T. SALTER (J. Clin. Invest., 1933, 12, 973—974).—In patients with myxœdema treated with thyroglobulin (I) obtained from hyperplastic or colloid glands the calorigenic response is proportional to the total I content. Since di-iodotyrosine (II) peptone obtained by peptic digestion of (I) is inactive in cases where thyroxine peptone obtained in this way is active in proportion to its I content, it follows that no calorigenic activity is lost in the isolation of (I) from whole thyroid gland and that (II) loses its activity in the first stage of proteolytic digestion of (I).

NUTR. ABS. (m)

Peculiarity of thyroid extracts in exophthalmic goitre with respect to the increase in oxygen

consumption. I. Increased oxygen consumption in rabbits following the injection of thyroid extracts from cases of exophthalmic goitre, [commercial] thyroid preparations, and extracts of normal glands. II. Variations in the oxygen consumption of rabbits after injection of splenic extracts, spleen preparations, and solutions of potassium iodide. K. SAITO (Tohoku J. Exp. Med., 1933, 22, 85—104, 105—115). CH. ABS.

Alteration of muscle metabolism in relation to the increase of muscular work by the adrenal cortex hormone. K. LANG (Naturwiss., 1934, 22, 91).—After treatment with cortin, isolated frog's muscle develops tensions approx. 30% > normal, and its phosphagen content increases. W. O. K.

Effect of insulin and adrenaline on the amino-acid content of the blood of adrenalectomised rabbits. B. L. DAVIS, jun., and W. VAN WINKLE, jun. (J. Biol. Chem., 1934, 104, 207—215).—A lowering (I) of the blood- NH_2 -acid of adrenalectomised rabbits is caused by adrenaline (II), but not by insulin (III). It is concluded that the (I) observed in normal animals following injection of (III) is caused by an increased secretion of (II). H. G. R.

Adrenaline liberation during insulin hypoglycaemia. T. J. YEN, T. AOMURA, and T. INABA (Tohoku J. Exp. Med., 1933, 21, 542—555).—Intravenous injection of insulin into dogs (0.25—10 units per kg.) increases the secretion of adrenaline. Blood-pressure falls somewhat, body temp. rises, and respiratory rate increases. CH. ABS.

Effect of insulin in accelerating the discharge of adrenaline. H. SATO, F. OHMI, and S. KANO-WOKA (Tohoku J. Exp. Med., 1933, 22, 53—64). CH. ABS.

Effect of adrenaline and insulin on the lactic acid metabolism in the liver. K. KATO and K. KIMURA (Tohoku J. Exp. Med., 1933, 21, 298—313).—Adrenaline increases the formation of lactic acid (I) in muscle and in organs drained by the portal vein, arterial and portal blood-(I) being correspondingly increased. Mobilisation of liver-glycogen and the attendant liberation of (I) exhibit an even greater acceleration. Splanchnicotomy decreases this effect. Insulin (II) increases hepatic venous blood-(I), but does not greatly affect arterial or portal blood-(I). (II) hypoglycaemia depends largely on the transformation of glucose into (I), and mobilisation of glycogen causes a further increase in venous blood-(I). Splanchnicotomy has no effect. CH. ABS.

[Precipitation of insulin.] V. D. YANKOVSKI and S. S. BRYUKHONENKO (Bull. Nauch. Issledov. Khim.-Farm. Inst., 1931, 223—228).—Insulin is completely pptd. from aq.-EtOH, but not from EtOH, solution by Benzoehtrosa 2BL. The red double compound with NH_3 can be used for its colorimetric determination. CH. ABS.

Sugar in blood and subcutaneous lymph following insulin administration. J. W. HEIM and B. N. BERG (Amer. J. Physiol., 1933, 105, 674—677).

In dogs the lymph-sugar (I) is usually > or = the sugar in arterial plasma; it is never significantly lower. Injection of insulin causes a fall in plasma- and (I), the vals. remaining very close together. The diffusion of

sugar from blood to lymph is similar in the normal and diabetic dog. NUTR. ABS. (m)

Insulin and sugar tolerance in thin people. H. BLOTNER (Arch. Int. Med., 1934, 53, 153—158).—Administration of insulin (small doses during several weeks) to certain thin normal persons results in a temporary decrease of sugar tolerance, evidenced by glycosuria with or without an abnormally high blood-sugar curve after a glucose test-meal. W. O. K.

Significance of the action of insulin on the respiratory quotient of the diabetic heart. E. W. H. CRUICKSHANK (J. Physiol., 1933, 79, 2—4p).—Addition of insulin to the perfusing blood of the isolated heart is followed by a rise in the R.Q. to 1, an increase in the rate of disappearance of blood-sugar, and a slight increase in O_2 consumption, whilst the glycogen content of the heart remains high. These results support the view that a failure in the oxidation of carbohydrate is the primary defect in pancreatic diabetes. NUTR. ABS. (m)

Effect of insulin on the serum-inorganic phosphate in normal and adrenalectomised dogs. R. ELLSWORTH and A. WEINSTEIN (Bull. Johns Hopkins Hosp., 1933, 53, 21—30).—The fall in serum-inorg. PO_4''' in a given interval after insulin injection is approx. the same in completely adrenalectomised dogs maintained on cortical extract, as in normal dogs. After the fall in PO_4''' there is a rise to a level > the control val. NUTR. ABS. (m)

Effect of previous hypophysectomy on the diabetes resulting from pancreatectomy. J. F. REGAN and B. O. BARNES (Amer. J. Physiol., 1933, 105, Proc. 83).—In two hypophysectomised dogs subsequent pancreatectomy did not produce the usual hyperglycaemia. In another which survived for 5 weeks there was no glycosuria, blood-sugar was about normal, and a small dose of insulin produced convulsions. NUTR. ABS. (m)

Influence of insulin-free pancreatic extract on the gaseous exchange of the white rat. C. J. CARR, J. E. SCHMIDT, and W. HARNE (J. Pharm. Exp. Ther., 1934, 50, 151—156).—Insulin-free pancreatic extracts, injected subcutaneously into the fasting rat, increased R.Q. without significantly affecting O_2 consumption (I). Mixtures of the extract and adrenaline produced a slight increase in R.Q., but the extract did not antagonise the increased (I) produced by adrenaline. Intravenous injection of the extract in rabbits showed marked hypoglycaemic effects. R. N. C.

Effect of the pituitary hypolipæmic substance on man. W. RAAB (Z. ges. exp. Med., 1933, 89, 588—615; Chem. Zentr., 1933, ii, 2263—2264).—The effects of various pituitary preps. on the blood-fat after administration of arachis oil have been studied. The factor responsible, lipotrin, is not identical with any previously described pituitary hormone. A. A. E.

Relation of the posterior pituitary hormone to carbohydrate metabolism in man. S. THAD-DEA (Z. klin. Med., 1933, 125, 175—194; Chem. Zentr., 1933, ii, 2415).—After subcutaneous injection of orasthin the blood-sugar is unchanged, but it increases after subcutaneous tonephin injection, and then falls. This is a result of increased insulin secretion, and con-

sequently does not occur in diabetes mellitus. In exophthalmic goitre and severe liver parenchyma disease no rise in the blood-sugar occurs. Tonerphin will prevent insulin hypoglycaemia in healthy subjects, but not in cases of exophthalmic goitre and liver diseases.

H. J. E.

Effect of Loeb's anterior pituitary extract on the basal metabolism of dogs. J. G. BUENO and B. O. BARNES (Amer. J. Physiol., 1933, 105, Proc. 15).—In normal dogs daily injections of the extract cause a rise in basal metabolism which reaches a peak of about 30% above normal on the fourth or fifth day. Other changes observed include increased respiration and heart rate, thirst, and polyuria. All the symptoms disappear about 5 days after the last injection. None of these changes occurs in the thyroidectomised dog.

NUTR. ABS. (m)

Preparation, identification, and assay of prolactin—a hormone of the anterior pituitary. O. RIDDLE, R. W. BATES, and S. W. DYKSHORN (Amer. J. Physiol., 1933, 105, 191–216).—A hormone ("prolactin") is prepared from the anterior lobe of the pituitary by methods described. It is obtained free from the gonadotropic and thyrotropic substances and probably also from growth-promoting activity. It excites lactation in a mature non-lactating mammary gland and also leads to sp. enlargement and activity of the crop gland of pigeons, a fact made use of in the assay. It has not been detected in tissues other than the pituitary.

NUTR. ABS. (m)

Pituitary substance giving increased gonadotropic effects when combined with prolan. H. M. EVANS, M. E. SIMPSON, and P. R. AUSTIN (J. Exp. Med., 1933, 58, 545–559).—The synergic factor itself possesses slight gonadotropic activity. The substance is unaffected by digestion with trypsin, or with trypsin followed by short digestion with crepsin, but is inactivated by pepsin.

CH. ABS.

Gonad-stimulating hormones. II. Influence of length of period of administration of certain extracts. C. F. FLUHMAN (Proc. Soc. Exp. Biol. Med., 1933, 30, 1014–1016).

CH. ABS.

Influence of the gonads on protein metabolism. IV. Effect of ovariectomy and of injections of gonadal and anterior pituitary extracts on urinary creatinine in female rabbits. I. SCHRIER and H. ZWARENSTEIN (Biochem. J., 1934, 28, 356–359).—In ovariectomised (I) adult rabbits (II) the excretion of creatinine (III), const. for 5 months, had slightly increased 9 months after the operation. Administration of extracts of ovaries or testicles causes a larger fall in the high (III) of (I) than in the (III) of normal (II), whilst extracts of the anterior lobe of the pituitary increase the output of (III) in normal (II), but have little effect on (I) (II).

W. O. K.

(A) Biological characteristics of ovary-stimulating extracts made from blood of pregnant women. (B) Induction of ovarian growth with an extract made from blood of pregnant women. C. F. FLUHMAN (Proc. Soc. Exp. Biol. Med., 1932, 29, 1193–1195; 1933, 30, 149–150).

CH. ABS.

Recognition and comparison of prolan and prolan-like substances. H. M. EVANS, M. E.

SIMPSON, and P. R. AUSTIN (J. Exp. Med., 1933, 58, 561–574).—The gonadotropic hormone of the blood of the pregnant mare is conc. by adsorption on active $Al(OH)_3$ followed by elution. Biological effects of its injection are described.

CH. ABS.

Preparation of prolan, theelin, and theelol from the same urine. P. A. KATZMANN and E. A. DOISY (Proc. Soc. Exp. Biol. Med., 1933, 30, 1196–1197).—Prolan is adsorbed on $BzOH$. The filtrate, acidified with HCl , is kept for a few days and the supernatant liquid is extracted (continuously) with $BuOH$. The residue on evaporation of the $BuOH$ is extracted with C_6H_6 , which is removed by distillation. The residue from 100 gals. of urine is dissolved in 1500 c.c. of 80% $EtOH$ containing 150 c.c. of conc. HCl ; after boiling for 4 hr. the $EtOH$ is distilled off and solid $NaOH$ is added in excess (phenolphthalein). The solution is extracted with $BuOH-C_6H_6$ (50%), and the process continued as from stage 3 of Doisy and Thayer's method (A., 1931, 879). Theelol (yield 2–5 mg. per gallon of urine) is purified as the Na salt.

CH. ABS.

League of Nations ; Committee of Hygiene. International standard for oestrogenic hormone. C. LORMAND (Bull. Soc. Chim. biol., 1933, 15, 1566–1568).—The unit of oestrogenic activity is defined as that contained in 10^{-7} g. of ketohydroxyoestrin.

H. D.

Oestrogenic activity of condensed-ring compounds in relation to other biological activities. J. W. COOK, E. C. DODDS, C. L. HEWETT, and W. LAWSON (Proc. Roy. Soc., 1934, B, 114, 272–286).—Condensation of the appropriate Mg alkyl halide with 1 : 2 : 5 : 6-dibenzanthraquinone affords 9 : 10-dihydroxy-9 : 10-diethyl-9 : 10-dihydro-1 : 2 : 5 : 6-dibenzanthracene (I), m.p. 248–250°, and its homologues, -9 : 10-di-n-propyl- (II), m.p. 245–247° [stereoisomeride (?), m.p. 192–195° (III)], -9 : 10-di-n-amyl- (IV), m.p. 178–179°, and -9 : 10-di-n-hexyl- (V), m.p. 164–165°. Phenanthraquinone and 1 : 2-benzanthraquinone with $MgBu^iBr$ similarly yield 9 : 10-dihydroxy-9 : 10-di-n-butyl-9 : 10-dihydrophenanthrene, m.p. 134–134.5°, and -9 : 10-dihydro-1 : 2-benzanthracene, m.p. 126°. *Et* 2 : 4-diketo-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene-1-carboxylic acid, m.p. 133–134°, is obtained from *Et* Δ^1 -dihydro-1-naphthoate and CH_3AcCO_2Et . Oestrogenic activity (VI) is shown by (I), (II), [40,000 rat units per g., max. of this series], (III) [20,000 rat units per g.], their Bu^i analogue (A., 1931, 612), and, to a smaller extent, by 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, neoergosterol, calciferol, ergosterol, 5 : 6-cyclopenteno-1 : 2-benzanthracene, 1 : 2-benzpyrene, and 1 : 9-dimethylphenanthrene. A large no. of inactive polycyclic compounds include (IV), (V), the Me_2 analogue (*loc. cit.*), fluorene, chrysene, retene, 1 : 2-benz-, and 1 : 2 : 5 : 6-dibenzanthracene, and 1 : 2-cyclopentenophenanthrene. The (VI) of varied mol. types is discussed, in relation to their carcinogenic or antirachitic activities.

A. C.

Sex change in plumage of Brown Leghorn capons following injection of certain oestrus-producing compounds. J. W. COOK, E. C. DODDS, and A. W. GREENWOOD (Proc. Roy. Soc., 1934, B 114, 286–290).—Injection of 1-keto-1 : 2 : 3 : 4-tetra-

hydrophenanthrene or 9:10-dihydroxy-9:10-di-*n*-butyl-9:10-dihydro-1:2:5:6-dibenzanthracene causes the appearance of female characteristics in the plumage of Brown Leghorn capons. No acceleration in comb growth is observed. A. C.

Progestin in placental extract. A. A. ADLER, P. DE FREMERY, and M. TAUSK (Nature, 1934, 133, 293).—The presence of progestin has been demonstrated in human and animal (cow) placenta. L. S. T.

Assay of vitamin-A. J. B. ORR and M. B. RICHARDS (Nature, 1934, 133, 255).—In a series of assays by the curative method of the vitamin-A content (I) of fish oils and dried milk, it was found that in most cases the wt. curve did not give a trustworthy indication of the state of depletion of the vitamin-A (II) reserve of an animal, and that an increase in wt. after administration of a supplement could not always be ascribed to its (I). Further, when (II) is the only known factor absent from the diet there is no cessation of growth (increase in size). (II) cannot be considered more essential for growth *per se* than any other of the many factors responsible for an increase in wt. The characteristic loss in wt., termed "cessation of growth," is apparently due to pathological conditions (III) arising from the (II) deficiency, and the diversity of (III) which may arise during the preliminary depletion period makes it impossible to secure uniformity at the beginning of a test period. This makes the curative method of (II) assay of doubtful val. L. S. T.

Spectrophotometric method for the assay of carotene and vitamin-A in butter. A. E. GILLAM (Biochem. J., 1934, 28, 79—83).—The average ratio of carotene (I) to xanthophyll (II) in butter, from determinations on 70 samples, is 14:1 by wt. and the (I) content can be calc. with sufficient accuracy by assuming that 94% of the light absorption of the unsaponifiable fraction at 455—460 m μ is due to (I). In this way, the removal of (II) before determination of (I) is avoided and the author's method (A., 1933, 848) is shortened, permitting its use for routine purposes. P. W. C.

Chemical evaluation of the vitamins. A. L. BACHARACH and E. L. SMITH (Analyst, 1934, 59, 70—81).—A review. E. C. S.

Determination of vitamin-A. N. EVERS (Analyst, 1934, 59, 82—85).—48 samples of cod-liver oil gave a mean "true blue val." calc. from the intensity of absorption at 328 m μ 2.17 times the actual mean blue val. of the oils. The determination of the blue val. of ordinary commercial oils is adequate to express the approx. vitamin-A content. E. C. S.

Relationship between the Carr-Price value and the 328 m μ absorption coefficient of preparations containing vitamin-A. S. K. CREWS and S. J. COX (Analyst, 1934, 59, 85—90).—The blue val. of liver-oil (I) when determined on the unsaponifiable fraction is usually > when determined on the oil itself, but in neither case is the vitamin-A content (II) so determined as great as (II) calc. from the absorption at 328 m μ (the *E* val.). The inhibiting substances present in (I) cause a depression of the blue val. > any in-

crease due to chromogenic substances other than vitamin-A. The apparatus and technique employed in the determination of the *E* val. are described. Vitamin-A has a max. absorption between 325 and 330 m μ , carotene at 450 m μ approx., and vitamin-D between 265 and 270 m μ . The colour given with SbCl₃ by (I) is pure blue or violet-blue, by concentrates of (I), greenish-blue. E. C. S.

Chemical tests for vitamins. L. J. HARRIS (Analyst, 1934, 59, 93—95).—For accurate determination of the vitamin-A content of a foodstuff by the SbCl₃ method it is essential to saponify first and make the test on the unsaponifiable fraction. The blue val. is then determined by the tintometer. Semi-chemical tests for vitamin-B₁, and a modification of Tillmans' method (cf. A., 1933, 433) for -C, are described. E. C. S.

Carotene. VII. Physical properties of carotenes from different plant sources. J. H. C. SMITH and H. W. MILNER (J. Biol. Chem., 1934, 104, 437—447; cf. A., 1933, 1151).—The m.p. of different samples of carrot-root carotene (I) are plotted against their $[\alpha]$, giving a typical two-component m.-p. curve. Mixed m.p. of α - (II) and β -carotene (III) lie on the curve. The inactive carotenes from sunflower, chard, and cauliflower leaves have approx. identical m.p. and solubilities; the solubilities of mixtures of leaf carotene and (I) lie between those of the pure components. The ultra-violet absorption (IV) max. of (II) are 4472 and 4755 Å., and of (III) are 4529 and 4796 Å. The (IV) curves of mixtures of (II) and (III) shift quantitatively towards the violet as their $[\alpha]$ increases. H. D.

Physical and chemical properties of biosterin (vitamin-A) and its physiological significance. V, VI, and VII. Z. NAKAMIJA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 3—5).—V. Fractional distillation in vac. of methylperhydrobiosterin from cod-liver oil yielded a hydrocarbon (b.p. 50—90°) and a no. of fractions containing OMe (b.p. 90—193°), indicating the presence of OH in the original biosterin.

VI. Nonacosane and a liquid hydrocarbon were obtained from perhydrobiosterin.

VII. 90% of biosterin condensed with maleic anhydride in 20 hr. at 140°, whilst 15—20% condensed with citraconic anhydride at room temp. in 1 month (35% of the vitamin-A fraction of "Ischinagi" oil condensed in 8 days). The non-condensing fraction gave a *hydrochloride*, m.p. 131—132° (Cl 32.4%), and a *bromide*, darkens above 170° (Br 62.5%). Biosterin-maleic acid may be acetylated and hydrogenated; ozonisation yields geronic and succinic acids. P. G. M.

Carotene-vitamin-A in man. W. VON DRIGALSKI (Z. Vitaminforsch., 1934, 3, 37—74).—The liver (I), whether normal or diseased, is the main storehouse of vitamin-A-carotene (II). Following saturation of (I) with (II), (II) passes into the blood, the highest level attained being 0.00027%; such a condition is due to excess ingestion of (II) and is not pathological. The blood-(II) varies considerably. Small amounts of (II) are found in transudates, more in exudates, but none in sweat, bile, semen, cerebrospinal fluid, faeces, or urine. Destruction (by oxidation) of (II) probably

occurs in (I). The protection of epithelial tissue by (II) is emphasised.

F. O. H.

Vitamin-A and carotene. XI. Distribution of vitamin-A in the organs of the normal and hypervitaminotic rat. A. W. DAVIES and T. MOORE (Biochem. J., 1934, 28, 288—295).—The vitamin-A (I) content of the organs of rats receiving differing amounts of (I) and of carotene (II) was determined. Kidneys (III) and lungs (IV) contained small amounts even when the liver (V) content was low. Administration of large but non-toxic doses of (I) to adult rats caused extremely high concn. in (V), that in (IV) being increased to about the normal (V) level, whilst the (III) level remained low. Distribution of (I) in young rats given toxic doses of (I), causing emaciation, hæmorrhagic rhinitis, lung and bone lesions, was similar to that in rats given non-toxic doses, except that the concn. in (IV) was even higher. It was impossible to produce hypervitaminosis-A by feeding (II), rats receiving 8 mg. per day growing normally; storage of (I) in (V) was moderately high and in (III) and (IV) very low.

C. G. A.

Growth investigations with carotenoids. H. VON EULER, P. KARRER, and A. ZUBRYS (Helv. Chim. Acta, 1934, 17, 24—29).—PBr₃ added to a dry C₆H₆ solution of zeaxanthine (I) and xanthophyll (II) causes partial replacement of OH by Br and partial elimination of HBr from the product. Extraction with 90% MeOH of the ligroin extract of the residue from the washed C₆H₆ solution removes unchanged (I) and (II), giving products (P_I and P_{II}) containing 2—5% Br, the absorption spectra of which differ but slightly from those of (I) and (II). Daily doses of P_I (40 × 10⁻⁶ g.) or P_{II} (10 × 10⁻⁶ g.) caused wt.-increase of 1.4 g. and 0.8 g. per day, respectively, in rats. Growth promotion by α- and β-carotene is greatly dependent on the composition of the basic diet, the min. daily doses being 5 and 2.5 × 10⁻⁶ g., respectively. Ca(OH)₂ adsorption of purest vitamin-A preps. gives a main β-fraction (growth increase 0.7 g. per day for a dose 0.3 × 10⁻⁶ g.) and a small α-fraction, *heparanthine* (absorption spectrum with SbCl₃ gives max. at 580 mμ), which is much less active (dose 3 × 10⁻⁶ g. per day).

J. W. B.

Vitamin-A content of pasteurised milk and native [Puerto Rican] cheese. D. H. COOK and J. H. AXTMAYER (Puerto Rica J. Pub. Health, 1933, 9, 90—92).—Vals. for pasteurised milk and whole milk cheese are, respectively, 2 units per c.c. and 20 units per g.

CH. ABS.

Fat metabolism in vitamin-A deficiency: blood-serum-esterase. H. N. GREEN (Biochem. J., 1934, 28, 16—24).—Esterase activity (I) was determined by titration of the acid liberated from esters by incubation with the serum. (I) decreases in vitamin-A (II) deficiency and infection in rats and dogs, increases with excess of (II) in the diet, and is unaffected by vitamin-B deficiency.

H. D.

Fat metabolism in vitamin-A deficiency: utilisation of fat and desaturation of fat in the liver. H. N. GREEN (Biochem. J., 1934, 28, 25—30).—Large quantities of fat can be absorbed by vitamin-A (I) deficient rats. The lowering of the % of fat in

the liver and the raising of its I val. by (I)-deficiency are similar to the effects of inanition and infection.

H. D.

Vitamin content of fish fat. II. Antirachitic value of the fat of the Japanese sardine and cat-fish. S. N. MATZKO (Z. Unters. Lebensm., 1934, 67, 172—174; cf. A., 1932, 887).—The vitamin-D content of the fat of the Japanese sardine is < 10 units per g., that of the visceral fat of the cat-fish 50—65 units per g.

E. C. S.

Vitamin-D activity of butter. II. Complex nature of the antirachitic action of butter. III. Nature of the labile factor in butter antirachitic for the rat. Antirachitic potency of lard, olive oil, egg oil, and the fatty acids of butters and lard. S. K. KON and R. G. BOOTH (Biochem. J., 1934, 28, 111—120, 121—130).—II. At least two factors antirachitic to the rat are present in butter, one which is not recoverable in the non-saponifiable residue, and the other (vitamin-D) which is resistant to saponification. By exposure to summer conditions or by feeding to cows irradiated yeast or cod-liver oil, the concn. of the stable, but not of the labile, factor is greatly increased. Direct irradiation of the butter also leads to the formation of the stable factor only. > 75% of the potency of autumn and winter butters is either destroyed or diverted to another fraction on prep. of the non-saponifiable residue. Attempts to separate the two factors by Zucker's method were unsuccessful.

III. A sample of home-rendered lard had almost the same antirachitic activity (I) for rats as winter and autumn butter, and an American sample was as active as summer butter. The (I) of lard is impaired by saponification. Fatty acids prepared from various butters possessed a slight but definite (I) which was not due to incomplete removal of non-saponifiable residue (II). Butter incorporated in the diet had a lower (I) than when fed separately. Autumn butter loses a large part of its (I) on saponification, but its (I) is almost completely recovered when the administration of (II) is accompanied by feeding the fatty acid fraction (III). Loss of (I) on saponification may be explained in terms of loss of a new labile factor but is more simply accounted for in terms of loss of the antirachitic effect on the rat of (III). The bearing of these results on the interpretation of the vals. usually obtained in feeding experiments is discussed.

P. W. C.

Occurrence of antirachitic vitamin in green plants. O. RYGH (Nature, 1934, 133, 255).—Meadow hay from Oslo gave an extract possessing the same antirachitic effect as a high-quality cod-liver oil. Vitamin-D in this extract has the same characteristics as have been described (A., 1933, 1089) for that in butter.

L. S. T.

Influence of fat-soluble vitamin on the amounts of cholesterol substances in the bile in rabbits. S. KUSAKA (Japan. J. Gastroenterol., 1933, 5, 31—35).—Excess of cholesterol is excreted by the liver.

CH. ABS.

Products of ultra-violet irradiation of ergosterol. A. V. TRUFANOV (Khim. Farm. Prom., 1933,

196—203).—The products were tested for vitamin efficiency on rats. CH. ABS.

Enrichment of vitamin-D in yeast by ultra-violet irradiation. S. N. MATZKO (Arch. Tierernähr. Tierzucht, 1933, 9, 623—636).—The vitamin-D content of baker's yeast may be raised to 5000—10,000 units per g. by irradiation. When prepared in presence of atm. O_2 and CO_2 , the material has no toxic action if administered in customary amounts. The vitamin potency remained unchanged during storage for 2 months, but weakened somewhat after 4 months. A. G. P.

Calcium compound in serum following overdosage with parathyroid hormone or ergosterol. N. B. TAYLOR, C. B. WELD, and J. F. SYKES (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 247—252).—When normal blood or Ca-free saline is transfused into hypercalcaemic dogs, the high serum-Ca (I) is maintained. This is probably due to the rapid transference of Ca from the tissue-fluids to the blood. Similarly, when part of the blood of parathyroidectomised dogs is replaced by that from parathyroid-treated dogs, (I) immediately increases, the same effect being obtained by the infusion of an equiv. amount of Ca as Ca gluconate. Hence the parathyroid gland does not appear to control the formation of a non-diffusible Ca compound (cf. A., 1925, i, 857). The anomaly of a high kidney threshold for Ca is explained by reabsorption in the tubules. F. O. H.

Effect of activated ergosterol administration on the cerebrospinal fluid-calcium. C. R. K. JOHNSTON and E. J. KING (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 87—89).—Oral administration of large doses of activated ergosterol to dogs is followed by a rapid rise in the serum-Ca, which reaches a max. after 48—60 hr., when the cerebrospinal fluid-Ca commences to increase. Both levels gradually decrease during the third to fifth day, and secondary rises occur from the fifth to eighth day, after which the levels very slowly return to normal. The theory that vitamin-D acts through the parathyroid hormone is supported. F. O. H.

Hypervitaminosis in the chicken. Mobilisation of calcium by irradiated ergosterol. G. E. HALL and E. J. KING (Trans. Roy. Soc. Canada, 1933, [iii], 27, V, 149—158).—Oral administration of large amounts of irradiated ergosterol produces a loss in body-wt. and an increase in serum-Ca, whilst calcification occurs in the stomach wall and kidney. Addition of 10% of $Ca_3(PO_4)_2$ to the diet considerably enhances the above Ca changes, whilst the imperfect bone calcification due to hypervitaminosis-D is reduced. The mechanism of the changes in bone-Ca is discussed. F. O. H.

Fat-soluble vitamins : their relation to growth and resistance to disease. R. SUTHERLAND (Diss., Aberdeen, 1933).—School-children given daily doses of radiostoleum (vitamin-A and -D) for 6 months showed a slight superiority, regarded as statistically significant, in height, and possibly also in wt. and nutritive condition, over controls, but no decreased susceptibility to infection or increased resistance to established disease. NUTR. ABS. (b)

Mortality among tropical fish. J. I. SPIRA (Science, 1934, 79, 140—141).—High infant and adult mortality among tropical fish is prevented by the addition of viosterol to a diet of desiccated shrimp, beetle, and ground fresh liver. Deeper pigmentation, increased activity, and recovered rigidity of deformed vertebrae also result. L. S. T.

Recent developments of sterol chemistry in relation to biological problems. J. PRYDE (Nature, 1934, 133, 237—239).—A review. L. S. T.

Lipins and vitamins-B. I. Role of vitamins-B in utilisation of lipins by the organism. R. LECOQ. II. Influence of constitution of lipins on progress of avitaminosis in pigeon. General need of vitamins-B in utilisation of lipins. R. LECOQ and J. SAVARE. III. Are alcohol-water-soluble vitamins-B equally lipin-soluble? J. SAVARE (Bull. Soc. Chim. biol., 1933, 15, 1498—1507, 1508—1516, 1517—1519).—I. Pigeons fed on a vitamin-B-deficient diet (I) containing muscle powder lived longer than those fed on a similar diet containing muscle peptones. High doses of lipins failed to prevent the onset of polyneuritis, which was, however, cured rapidly by the administration of yeast.

II. Pigeons on (I) containing muscle peptones live longer when fed with difficultly digestible lipins than when fed with easily digestible ones.

III. Olive oil left in contact with a yeast extract for 10 days was not antineuritically active. H. D.

Physiology of vitamins. XXIII. Effect of lack of the vitamin-B complex on the secretion of gastric juice in dogs with gastric pouches. G. R. COWGILL and A. GILMAN (Arch. Int. Med., 1934, 53, 58—70).—The gastric activity, as evidenced by response to histamine injection, of three dogs with Pavlov pouches was decreased when the diet was deficient in vitamin-B, but a dog with a Heidenhain pouch (vagus innervation interrupted) was not thus affected by lack of vitamin-B. The factor involved is probably B_1 and not B_2 . W. O. K.

Growth-vitamin-B in egg-yolk. C. SZYMANSKA (Bull. Soc. Amis Sci. Poznan, 1932, B, Sci. math. nat. No. 5, 15—37; Chem. Zentr., 1933, ii, 2287).— H_2O extracts 40% of the vitamin-B from defatted, dry egg yolk, but the residue is inactive; on reunion of extract and residue the original activity is attained. The vitamin is considered to be compound in nature. A. A. E.

Physiology of vitamins. XXII. Effect of experimentally-induced hyperthyroidism on the vitamin-B requirement of pigeons. G. R. COWGILL and M. L. PALMIERI (Amer. J. Physiol., 1933, 105, 146—150).—After hyperthyroidism had been induced in pigeons by the administration of desiccated thyroid, the min. dose of a vitamin B_1 concentrate needed to maintain wt. and prevent anorexia was much increased. The relative increase varied widely in individual birds. The vitamin- B_1 requirement is probably related to the caloric intake. NUTR. ABS. (b)

Vitamin- B_1 and the conception of a beri-beri quotient (Q_b). G. AMANTEA (Atti R. Accad. Lincei, 1933, [vi], 18, 317—323).—The beri-beri quotient is

defined as the ratio of the total consumption to the initial wt. of the animal, and is given by $Q_b = (\text{rice retained body-wt. lost}) / \text{initial wt.}$ Although Q_b may vary between 0.7 and about 1 for different pigeons, yet, under similar experimental conditions, it is sufficiently const. for one and the same animal to serve as an index in quant. experiments on vitamin- B_1 .

T. H. P.

Extractability of vitamin- B_2 from yeast by acetone-water and methyl alcohol-water mixtures. P. L. DAY [with W. J. DARBY] (J. Amer. Chem. Soc., 1934, 56, 452—454).—Vitamin- B_2 (I) is not extracted from dry baker's yeast by 80 and 99.5% COMe_2 or abs. MeOH; 60% COMe_2 and 60% MeOH extract about 50% and 80% MeOH removes about 20% of (I). All % are by wt. Yeast extracts which do not promote growth do not prevent the onset of cataract, keratitis, and conjunctivitis. H. B.

Vitamin- B_2 . B. C. GUHA and P. N. CHAKRAVORTY (Indian J. Med. Res., 1933, 21, 211—219).—Extracts of ox- and buffalo-kidney and of fowl-liver were good sources of vitamin- B_2 (I), and "Hilsha" fish was a poor source. Extracts of liver were most potent if made at p_H 5. (I) in the ox-kidney extract was largely destroyed by heating at 100° for 15 min. at p_H 10.5. NUTR. ABS. (b)

Vitamin- B_2 . P. GYORGY, R. KUHN, and T. WAGNER-JAUREGG (Klin. Woch., 1933, 12, 1241—1245).—Lactoflavin (I) and ovoidflavin may be identical with one constituent of vitamin- B_2 (II), and vitamin- B_4 (Reader) a second constituent. Warburg and Christian's oxidation enzyme from yeast, in which "yeast flavin" is united with a polysaccharide, was rich in (II) even after the enzyme was destroyed by boiling. The flavin group, after irradiation, was sol. in CHCl_3 and showed a composition and absorption spectrum similar to that of pure (I) but no (II) activity. The (II) activity of (I) and of boiled food extracts was also destroyed by irradiation with visible light, filtered from ultra-violet rays. The relation of (II)-deficiency to pellagra, anaemia, and sprue is discussed. Treatment of a condition resembling sprue in older infants with (II) (as cooked meat extract or yeast extract) and Fe was successful. NUTR. ABS. (b)

Behaviour on oxidation-reduction and a colour reaction of lactoflavin (vitamin- B_2). R. KUHN and T. WAGNER-JAUREGG (Ber., 1934, 67, [B], 361—363).—Reduction of lactoflavin (I) by Zn, Sn, or Na-Hg, in 10% HCl does not immediately yield the leuco-compound, an intense red, comparatively stable intermediate product being formed. Analogy with pyocyanine indicates this to be due to a radical-like H_2 -compound. The biological importance of the behaviour of (I) on oxidation-reduction is discussed; in addition, its vitamin properties are determined by peculiar constitutive features, notably the sugar-like side-chain $[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}_2\text{OH}$. H. W.

a. Distribution of vitamin- B_2 in the animal body. b. Preparation of vitamin- B_2 concentrates. P. GYORGY, R. KUHN, and T. WAGNER-JAUREGG (Z. physiol. Chem., 1934, 223, 21—27, 27—35).—a. Various tissues showed vitamin- B_2 activity decreasing in the order: ox-heart, calf's heart, fowl's

leg, veal, beef, fowl's breast. Ox-spleen has a high, carcinomatous tissue a low, activity. Boiled juices have 50—80% of the activity of the tissue, but the wt. curve of the test animal rapidly flattens owing to the absence of a $\text{H}_2\text{O-insol. accessory factor R}$.

b. Vitamin- B_2 , is conc. by pptn. methods or by adsorption on fuller's earth in N -acid solution and elution of the adsorbate with dil. $\text{C}_5\text{H}_5\text{N}$ (cf. A., 1933, 1090). J. H. B.

Relative vitamin- B_2 content of lactose feed (dried whey) and dried skim-milk. V. HEIMAN and L. C. NORRIS (Poultry Sci., 1933, 12, 332).—Growth tests on White Leghorn chicks showed that lactose (I) feed contained 50% more vitamin- B_2 (II) than dried skim-milk (III). Cheese that had been made from the same milk sample also contained but little (II). When fed in limiting amounts (2.5%), better hatching took place with the (I) feed than with (III), but with 5% of either no difference was detected. (I) feed could be used as a source of (II) in practical chicken rearing. NUTR. ABS. (b)

Relation of vitamin- B_2 complex to hatchability and nutritive value of eggs. R. M. BETHKE, P. R. RECORD, and D. C. KENNARD (Poultry Sci., 1933, 12, 332—333).—The vitamin- B_2 (I) complex had a beneficial effect on hatchability (II). The (I) potency of eggs from differently fed hens varied, but could be correlated with the (II) of the eggs. NUTR. ABS. (b)

Vitamin- B and vitamin- C content of egg-plants and pumpkins. P. JURIST and A. CHANTIN (Problems of Nutrition [U.S.S.R.], 1933, 2, No. 4, 12—14).—The two vegetables were nearly equal in vitamin- C content, about 15 g. daily of the fresh substance protecting guinea-pigs from scurvy. As a source of vitamin- B_1 , 30 g. of fresh egg-plant (I) protected pigeons from polyneuritis, but wt. was lost. 7—8 g. of (I) (dry wt.) equalled in vitamin val. 0.5 g. of dried brewer's yeast. The vitamin- B_1 content of pumpkins was similar to that of (I). NUTR. ABS. (b)

Behaviour of vitamin- C (ascorbic acid) and other reductones towards cathepsin and other enzymes. H. VON EULER, P. KARRER, and F. ZEHENDER (Helv. Chim. Acta, 1934, 17, 157—162).—The activating power of vitamin- C (I) for proteases of the cathepsin type (II) (A., 1933, 873) is effective in H_2 , is increased by Fe^{++} , Fe^{+++} , and Ca^{++} , but inhibited by Cu^{++} , but the smaller activating power of reductone and reductic acid is slightly decreased by Fe and Ca. Hexose diphosphate also activates (II), but dehydro-ascorbic acid neither activates nor inhibits. (I) inhibits wheat-amylase and catalase, but has no action on guanase. Possible mechanisms for the action of (I) are discussed. J. W. B.

Separation of cysteine from ascorbic acid by mercuric acetate. A. EMMERIE (Biochem. J., 1934, 28, 268—269).—Cysteine, a source of error in the determination of ascorbic acid by 2 : 6-dichlorophenol-indophenol indicator, is quantitatively pptd. by $\text{Hg}(\text{OAc})_2$. Ergothioneine is also pptd. A. E. O.

Vitamin- C in the ovary and the corpus luteum. A. GIROUD, C. P. LEBLOND, and M. GIROUX (Compt. rend., 1934, 198, 850—851).—The presence of

vitamin-*C* (I) in the interstitial tissue of the male genital organs (rodents) and in the corpus luteum is demonstrated by its reduction of AgNO_3 . By this test (I) is proved to be absent from the follicles and the oocytes of the normal animal. (I) is completely absent in avitaminosis. J. W. B.

Vitamin-*C* in the chick embryo. S. N. RAY (Biochem. J., 1934, 28, 189—191).—There is no vitamin-*C* (I) in the fresh egg, but after 4 days' incubation considerable amounts of reducing substance are formed. Injection of (I) into the egg does not affect the growth rate of the embryo.

H. G. R.

Distribution of a reducing substance (vitamin-*C*) in the tissues of fluorine-fed cows. P. H. PHILLIPS and F. T. STARE (J. Biol. Chem., 1934, 104, 351—358).—Vitamin-*C* (I) as determined by the method of Bessey and King (A., 1934, 227) is widely distributed in the various organs and tissues of the dairy cow. The content is low in striated and heart muscle, but high in the suprarenal cortex (II) and the anterior lobe of the pituitary (III). After ingestion of 0.088% F with the grain mixture an increase in (I) content was observed in the kidney, liver, (II), and (III). In chronic F toxicosis, total cellular respiration in (II) is lowered as indicated by O_2 uptake determinations, and the anaerobic phase, as indicated by the effect of CN' , is increased considerably. A. L.

Alleged vitamin-*C* of Rygh. B. SPUR (Z. Vitaminforsch., 1934, 3, 27—37).—Methylnornarcotine does not replace vitamin-*C* (lemon-juice) in the diet of guinea-pigs (A., 1932, 1294). F. O. H.

Antiscorbutic value of black-currents preserved in sugar. G. P. SCHELESNY and E. S. KANEVSKA (Problems of Nutrition [U.S.S.R.], 1933, 2, No. 4, 21—23).—Black-currant jam was devoid of vitamin-*C*, but black-currents preserved raw in sugar for 9 months apparently contained it.

NUTR. ABS. (b)

Fresh and pickled cucumbers as antiscorbutic vitamin carriers. N. JARUSOVA (Problems of Nutrition [U.S.S.R.], 1933, 2, No. 4, 25—28).—About 12 g. of fresh cucumber daily provided the min. prophylactic dose of vitamin-*C* for a guinea-pig. Pickled cucumbers were devoid of the vitamin.

NUTR. ABS. (b)

Antiscorbutic factor. W. M. CAHILL (Bull. Soc. Chim. biol., 1933, 15, 1462—1471).—Unfermented grape juice, kept for 6 months with $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ and Et glycol bromoacetate as preservative, when treated by the method of Szent-Gyorgyi (A., 1929, 98) gives an acid similar to ascorbic acid but lacking antiscorbutic activity (I). 5-Ketogluconic acid has no (I).

H. D.

Determination of the antiscorbutic potency of vegetable products, chiefly berries, grown in Norrland. G. F. GOTHLIN (Acta med. Scand., 1933, Suppl. 53, 1—120).—The berries (tested on guinea-pigs on the Sherman diet) gave the following vals. calc. as min. daily protective ration for a human adult of 60 kg.: fresh black-currents 30—40 g., fresh cloudberries 60—85 g., cloudberry beverage (stored 7 months) 85—120 c.c., cultivated raspberries 100—140

g. Blueberries, arctic raspberries, and red whortleberries were less potent. NUTR. ABS. (b)

Titration of vitamin-*C* in citrus juices. A. H. BENNETT (Analyst, 1934, 59, 91—93; cf. A., 1933, 1090).—The method of prep. of the indicator solution used in Tillmans' method (cf. A., 1933, 433) is described. The vitamin-*C* (I) content of lemon juices (II) can vary by 100%. (II) pasteurised and preserved in a vac. lost only 20% of its (I) in 35 days, whilst pasteurised (II) exposed to air (in a tube stoppered with cotton wool) lost 100% in 12 days. Preserved with SO_2 , 30% was lost after 56 days, 40% after 110 days in a vac., 100% after 26 days when exposed to air. E. C. S.

Experimental scurvy. XVI. Purine metabolism of guinea-pigs fed on a vitamin-*C*-free diet. K. TOMITA (Sei-i-kwai Med. J., 1932, No. 7, 1—12).—Urinary total N, purine bases, uric acid (I), and allantoin decrease during the course of scurvy, but [except (I)] increase at the terminal state. Urea is parallel with total N, but NH_3 increases with the progress of the disease. CH. ABS.

Vitamin-*E*. I. Chemical and physiological properties. H. S. OLCOTT and H. A. MATTILL (J. Biol. Chem., 1934, 104, 423—435).— $5\frac{1}{2}$ times the min. dose of vitamin-*E* (I) required to produce fertility (II) in rats is insufficient to preserve (II) for more than a second gestation. The paralysis of the suckling young of (I)-deficient mothers is uninfluenced by administration of (I). A (I)-active concentrate, b.p. 200—233°, from the unsaponifiable lipins of lettuce was obtained, similar in properties to that of Evans and Burr (Mem. Univ. Calif., 1927, 8) from wheat-germ oil (III). The Evans-Burr prep. of (I) from (III) is modified by vac.-distillation of the MeOH extract of the unsaponifiable residue from which the sterols have been removed. The product so obtained is further conc. by freezing out impurities from COMe_2 and still further by adsorption on Al_2O_3 . Br and KMnO_4 destroy, whilst acetylation, benzoylation, AgNO_3 , and H_2 do not influence, the activity of (I). In a rancid food mixture (I) is stable for 4 weeks. From comparison of the effects of hebin (IV) and (I) on immature female rats, it is concluded that (I) and (IV) play entirely different roles in the physiology of reproduction. H. D.

Chlorophyll content as an index of the productive capacity of selfed lines of maize and their hybrids. H. W. SPRAGUE and N. CURTIS (J. Amer. Soc. Agron., 1933, 25, 709—724).—The chlorophyll (I) and carotene contents of leaves of maize were highest in the uppermost and least in the lowest leaves. The gradient was regular and vals. for middle leaves were fairly representative of the whole plant. Xanthophyll vals. were very erratic. Correlation between mean (I) contents, genetic factors, and productivity are examined. A. G. P.

Oxidation potential and protein change in the leaf. K. MOTHES (Flora, Karsten Festschr., 1933, 58—98).—High O_2 tension stabilises the protein, protects it from decomp., and furthers its synthesis. Low O_2 tension renders the protein subject to the attack of leaf proteinases. CH. ABS.

Formation of protein in plants. O. LOEW (Angew. Bot., 1933, 15, 518—539).—The synthesis of protein from asparagine with the intermediate formation of the di-aldehyde of aspartic acid is discussed.

A. G. P.

Formation of alkaloids in the plant. T. WEEVERS (Chem. Weekblad, 1934, 31, 19—24).—Pictet's theory that alkaloids are built up from the degradation products of proteins, particularly proline, tyrosine, and tryptophan (cf. A., 1905, i, 541; 1907, i, 954), is extended and discussed from a physiological-phytochemical point of view. Experiments on *Ricinus* plants and seeds are described.

S. C.

Transformation of nicotine in the ripening of tobacco seeds. G. ILJIN (Biochem. Z., 1934, 268, 253—259).—Nicotine is formed in the early ripening processes of the seeds, the amount then rapidly diminishing during the regeneration of reserve protein.

P. W. C.

Method of formation of grains of wheat-flour in the grasses, and the production therein of hydroxyflavones and anthocyanins. J. CHAZE (Compt. rend., 1934, 198, 840—842).—Mainly botanical. Hydroxyflavone derivatives are first formed in the vacuoles and may become converted into anthocyanins during maturation.

J. W. B.

Effect of yeast extract on the growth of plants. A. I. VIRTANEN and S. VON HAUSEN (Nature, 1934, 133, 383; cf. A., 1933, 1093, 1342).—The factor which stimulates blooming of the pea is sol. in Et₂O, and is equally effective in sterile H₂O cultures and in the usual pot cultures with quartz sand.

L. S. T.

Effect of female sex hormones on plant growth. M. M. JANOT (Compt. rend., 1934, 198, 1175—1178).—The growth of hyacinths and lilies is increased by watering with saturated aq. solutions of equilin, equilenin, folliculin (I), and dihydrofolliculin. Similar results are obtained by using a solution containing 4 mg. per litre, but trihydroxycestrin is toxic under these conditions. (I) is the least effective of the compounds used.

P. G. M.

Influence of boron and of other complementary elements on the growth of flax. M. J. SCHKOLNIK (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1163—1188).—Normal growth was obtained in nutrient solutions containing, in addition to the usual salts, 0.5 mg. B, 1.5 mg. Mn, 0.5 mg. Al, 0.125 mg. Cu, and 0.25 mg. I per litre of distilled H₂O (I); previous attempts at cultivating flax in solutions of salts in (I) failed owing to the absence of the above elements. Of these, B is the most important, development of the root system failing in its absence; concns. of > 0.5 mg. B per 100 c.c. are toxic. Al, Mn, Cu, and I are of only secondary importance.

R. T.

Influence of the temperature of germination on the chemical composition of cereal seedlings. E. GAUMANN (Z. Bot., 1932, 25, 385—361; Bied. Zentr., 1933, A, 4, 199—200).—Increasing germination temp. (I) is associated with rising fresh wt. and declining dry matter content in seedlings. The total carbohydrate in seedlings is unaffected by (I) between 3° and 15° but varies irregularly with temp. above this. Differences in glucose, sucrose, and amylose con-

tents with varying (I) are traced. The crude fat and total N increase with rising (I). The mobilisation and transport of N and the proportions of NH₂-, amide-, protein-, and humin-N show little variation, but polypeptide- and residual N are definitely related to the (I). Increasing (I) results in lower proportions of K and P but not of Ca in the plants. Low (I) followed by slow seedling growth induces the formation of much cell-wall material containing relatively higher proportions of cellulose, lignin, and cutin and less xylan than when (I) is high and subsequent growth rapid. The latter conditions favour the dissolution of the cell wall by enzymes of *Fusarium*.

A. G. P.

Degradation of amino-acids in flowers. W. GRASSMANN and H. BAYERLE (Biochem. Z., 1934, 268, 220—228).—Some pulped flowers or extracts (I) (e.g., from *Rosaceae*) partly decompose NH₂-acids although no decarboxylation occurs and primary amines are not produced. NH₃ is the only recognisable reaction product. No decomp. occurs anaerobically. For each mol. of NH₃ produced almost 0.5 mol. of O₂ is consumed. The extent of deamination is < one tenth of that produced by kidney. Thermostable catalysts are involved. There is no appreciable difference in the rate of decomp. of optical antipodes. Peptides (glycyl-alanine, -leucine, and -asparagine, diglycyl-asparagine) are deaminated 2—3 times as rapidly by (I) as are corresponding mixtures of the appropriate NH₂-acids.

W. McC.

Acidity of epidermal cells and stomata in *Rumex acetosa* in light and in darkness. J. PEKAREK (Planta [Z. wiss. Biol.], 1933, 21, 419—446).—Both stomatal and surrounding epidermal cell saps have *p_H* approx. 6.0 in daylight. In darkness there is a change of *p_H* of stomatal cells towards the acid region and in epidermal cells towards the alkaline side.

A. G. P.

Relationships between geo-electric effects and geotropism. H. U. AMLONG (Planta [Z. wiss. Biol.], 1933, 21, 211—250).—Geotropic effects are examined in relation to the p.d. induced by differences in electrolyte concn. of the cell sap and that of external liquids with which the tissues are in contact. "Electrotropic" effects produced by roots and shoots of seedlings when placed in an electrostatic field are recorded.

A. G. P.

Action of salts in water cultures [of plants]. K. SCHMALFUSS (Flora, Karsten Festschr., 1933, 197—210).—The effects of various mineral deficiencies on the growth of *Callisia repens* in H₂O have been studied. Fe chlorosis is favoured by the presence of easily sol. phosphates, alkaline reaction, and excess of Ca⁺⁺.

CH. ABS.

Role of mineral and organic matter in plant life. II. Mineral and organic metabolism in leaves and shelled seed of *Aesculus hippocastanum* during growth. N. T. DELEANO and C. BORDEIANU (Beitr. Biol. Pflanzen, 1932, 20, 179—197; Bied. Zentr., 1933, A, 4, 205).—By means of the "biometric" method, three phases of leaf development are differentiated. In the initial "development" stage the dry wt. per leaf increases steadily, remaining unaltered during the second period of "protoplasmic constancy," and declining in the final

stage of "negative translocation." The length of each stage is sp. for each species of plant and for each plant organ. The depletion of mineral and org. constituents from old leaves may be as high as 50% of the max. content, and is unrelated to the elimination of H_2O , which begins at an earlier stage when the cell walls are still semipermeable.

A. G. P.

Cellulose and xylan. Constitution and relation between the material, form, and function [of the plant membrane]. M. LÜDTKE (Biochem. Z., 1934, 268, 372—393).—The relationship between the cellulose (I) and xylan (II) constituents of plant membranes and the change of the membrane due to various factors within and without the plant are investigated. The isolated parenchymatous cells (III) of bamboo canes and beechwood contain more (II) than the fibrous cells, the relationship appearing to be a general one. The acid val. of (III) and the loss on fractionation with NaOH are $>$ for fibrous cells. The residue after removal of material sol. in 0.2% NaOH does not appear to be a chemical individual. The view that (I) and (II) are combined as an ester is negated.

P. W. C.

Starch formation in the leaves of sugar cane. W. M. COELINGH and V. J. KONINGSBERGER (Arch. Suikerind. Ned.-Indie, 1932, 1325—1340; Bied. Zentr., 1933, A, 4, 221—222).—Starch (I) formed during normal CO_2 assimilation occurs only in the bundle sheaths (II). In darkness leaves placed in solutions of maltose, sucrose, glucose, or fructose produce (I) mainly in the palisade cells of the parenchyma. Such (I) is partly translocated to (II) on exposure of leaves to sunlight in a CO_2 -free atm. Leaves placed in sugar solutions in daylight but in the absence of CO_2 accumulated (I) in (II).

A. G. P.

Regularities in the carbohydrate composition of barley grain. L. R. BISHOP and D. MARX (J. Inst. Brew., 1934, 40, 62—74).—A regular relation is found between amounts of pentosan (Kröber) (I), "insol. carbohydrate" (II), and extract (III), respectively, and total carbohydrate (IV) of Plumage-Archer barley, all quantities being calc. as g. per 1000 corns. Similar regularities hold for other barley varieties, although abs. amounts may differ. With increase in (IV), (I), (II), and (III) also increase regularly, the last the most rapidly. For 2-rowed barleys (III) is higher, (I) and (II) are regularly lower, than with 6-rowed, for any given val. of (IV). There is a definite arrangement of carbohydrate, typical of each barley variety, during development and at maturity. The regularities observed are analogous to those previously described for barley proteins. The curve relating reserve protein (hordein) with total protein is of the same form as that for (III) and (IV), and similarly with the curves for non-reserves in each case plotted against total protein or carbohydrate. During malting, decomp. of protein leads ultimately to formation of asparagine, whilst decomp. of carbohydrates leads to production of sucrose.

I. A. P.

Physiology of the cold-resistance of winter cereals. E. CONSTANTINESCU (Planta [Z. wiss. Biol.], 1933, 21, 304—323).—In plants maintained at const. temp. the total dry matter, sugar content, and osmotic pressure of the cell sap in the first three leaves

remain const. Transition from a high to a low temp. induces an increase in osmotic pressure, a small increase in sugar, and a slight increase in dry matter. Differences in the case of varieties of varying hardness are small.

A. G. P.

Seasonal variations in the sulphur content of pastures. ANON. (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932—1933, 25).—There is a seasonal variation in the S content (I) which rises as a rule to a max. during the dry season and falls to a min. in the wet. (I), which was always very low, showed a parallelism with the Ca content. NUTR. ABS. (m)

Beginning of hydrolysis of agar-agar. A. KORENTZVIT (Khim. Farm. Prom., 1933, 153).—The process is followed colorimetrically on addition of EtOH—I.

CH. ABS.

Comparison of plant and animal chitin. L. ZECHMEISTER and G. TÓTH (Z. physiol. Chem., 1934, 223, 53—56).—From *Boletus edulis* chitin, octa-acetylchitobiose, and undeca-acetylchitotriose were obtained, identical with the products from crab chitin.

J. H. B.

Scillin of *Scilla maritima* and the fructoside of *S. nutans*. H. COLIN and A. CHAUDUN (Bull. Soc. Chim. biol., 1933, 15, 1520—1526).—A fructoside, $[\alpha]_{5461} - 32^\circ$, is prepared from *S. maritima* by clearing the EtOH extract with H_2WO_4 and pptn. with Ba(OH)₂ and EtOH; another, $[\alpha]_{5461} - 51.4^\circ$, prepared from *S. nutans* by clearing with Pb(OAc)₂ and pptn., appears to yield a mixture containing 97% of fructose and 3% of glucose on hydrolysis.

H. D.

Ovary liquid of the corn cockle (*Agrostemma githago*, L.) and its relation to the seminal tegument. M. MOLLIARD and R. ECHEVIN (Compt. rend., 1934, 198, 780—783).—When kept in EtOH the fluid (100 c.c.) (I) expressed from the capsules of *A. githago* deposits a H_2O -sol. gum, $[\alpha]_D + 149^\circ$ (0.472 g. after desiccation), hydrolysed by 2% H_2SO_4 at 120° to a reducing sugar giving an osazone resembling galactosazone; the sol. matter (4 g.; ash 0.166 g.) consists of glucose (2.043 g.), fructose (1.668 g.), and sucrose (II) (0.438 g.). As the capsules develop, the total sugars, and especially (II), diminish (7.104—2.458 g. per 100 c.c.), (II) being absent when (I), originally colourless, has become brown.

J. W. B.

Constituents of hornbeam bark. O. BRUNNER and G. WIEDEMANN (Monatsh., 1934, 63, 368—373).—In agreement with Zellner *et al.* (A., 1926, 983) the ligroin extract of the unsaponifiable fraction of an EtOH extract of the bark of *Carpinus betulus*, L., affords ceryl alcohol, a phytosterol, m.p. 136° (Ac derivative, m.p. 122°), shown by Windaus' bromination method to be a sitosterol containing no stigmasterol, and betulin.

J. W. B.

Chemical composition of "St. John's root" [*Berberis laurina*, Billb. (Thunb.)]. O. DE A. COSTA and R. D. DA SILVA (Rev. Soc. Brasil. Quím., 1933, 4, 199—201).—The root contains hydrastine (I) as well as berberine (II); the analysis by the Dragendorff-Schlagdenhauffen method is detailed. Besides its use in the dye industry, the root might be used as a commercial source of (II), and possibly as a sub-

stitute for *Hydrastis canadensis*, on account of its content of (I). E. L.

Fatty oil of seeds of *Cydonia vulgaris*. A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 24—27).—The fatty acids (94.2%) comprise saturated acids (8.6%), oleic (42.5%), linoleic (39.2%), and linolenic acid (3.9%). A trace of OH-acid may be present but there is no evidence of the existence of the acid $C_{17}H_{32}(OH) \cdot CO_2H$ of Herrmann (A., 1899, i, 822). H. A. P.

Fatty oil of seeds of *Cassia occidentalis*. L. A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 28—30).—The oil contains unsaponifiable matter 7.4%, saturated acids 19.7%, oleic 30.7%, linoleic 31.4%, and linolenic acids 6.3%. H. A. P.

Fatty oil of millet (*Panicum miliaceum*). A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 41—44).—The oil contains 3.3% of unsaponifiable matter and 88.7% of fatty acids comprising saturated acids 10.7%, oleic 23.9%, linoleic 46.9%, and linolenic acid 7.2%. A small amount of OH-acid is probably present, but no evidence of the existence of "Hirseolsaure" is found. H. A. P.

Coffee oil. A. HEIDUSCHKA and R. KUHN (J. pr. Chem., 1934, [ii], 139, 269—276).—The ligroin-extracted fat (I) of unroasted coffee beans contains 96.95% of total fatty acids (Hehner), analysis of which (full details) gives the following composition of (I): linoleic 37.60%, oleic 20.20% (total liquid fatty acids, 59.59%), palmitic 23.60%, carnaubic 14.25%, stearic 1.05%, and *n*-decoic 0.35% (total solid fatty acids 40.47%). J. W. B.

Dark-coloured duramen of ebony. K. GRIFFOEN (Proc. K. Akad. Wetensch. Amsterdam, 1933, 36, 897—988).—A large part of the colouring matter of ebony woods consists of ulmic acids. C. W. G.

Tomato pigments. Pigment in American red and purple tomatoes (*Lycopersicum esculentum*). M. B. MATLACK and C. E. SANDO (J. Biol. Chem., 1934, 104, 407—414).—The pigment from American-grown tomatoes is identical with the lycopene obtained from an Italian variety. H. D.

Plant pigments. LV. Presence of α - and β -carotene in various natural products. P. KARRER and W. SCHLIENTZ. LVI. Autumn colours of leaves. P. KARRER and O. WALKER (Helv. Chim. Acta, 1934, 17, 7—8, 43—54).—LV. Differential chromatic absorption of the carotene from spinach, paprika, nettle, and corpus luteum confirms the conclusion of Kuhn *et al.* (A., 1931, 1421) that it is almost pure β -carotene, only traces of the α -form being detected spectroscopically.

LVI. The methods of differential chromatic absorption, extraction with 90% MeOH and ligroin, and pptn. the carotenoids with I (and regeneration with $Na_2S_2O_3$) are applied to the examination of the pigments present in green and yellow leaves of *Aesculus hippocastanum*, *Acer pseudoplatanus*, *Ginkgo biloba*, and *Ulmus campestris*. The unhydrolysed pigment extract is pptd. with I and pptd. carotenoids are regenerated with $Na_2S_2O_3$: free phytoanthin (I) is removed from the extract with MeOH and the ligroin-sol. pigments are hydrolysed with NaOMe or

NaOH-MeOH. The resulting pigments remain almost exclusively in the ligroin layer, thus disproving the hypothesis that the production of autumn tints is due to increased esterification of the xanthophyll (II). Whilst both carotene (III) [as *isocarotene* (IV) after regeneration from the I-compound] and (II) can be isolated from the green autumnal leaves, the yellow leaves give only spectroscopic traces of (IV), and a little (II) mixed with some violaxanthin. The "autumn (II)" can be extracted from ligroin solution by large vols. of 90% MeOH, and *vice versa*. Thus during autumn necrosis the (III) and (I) decrease, the former more rapidly, due to oxidative destruction, "autumn (II)" containing the oxidation products, but intermediate compounds could not be isolated.

J. W. B.

Enzymic clarification of fruit juices and sweet wines. I. Changes in fruit juices during spontaneous clarification and on treatment with filtration enzymes. II. Determination of pectolase action of filtration enzymes. A. MEHLITZ and M. SCHEUER (Biochem. Z., 1934, 268, 345—354, 355—363).—I. Enzymic clarification of fruit juices consists of the complete hydrolysis of pectins.

II. Pectolysis in pectin solutions can be followed with a fair degree of accuracy in terms of changes of viscosity and the liberation of CHO groups by I titration. Determination of residual pectin by pectase coagulation gives inaccurate, but by the Ca pectate method accurate, results. The action of pectolase may also be followed polarimetrically. P. W. C.

Chemistry of the brown algæ. I. M. HEILBRON, R. F. PHIPERS, and H. R. WRIGHT (Nature, 1934, 133, 419).—*Fucosterol*, $C_{29}H_{48}O$ or $C_{30}H_{50}O$, m.p. 124° (acetate, m.p. 119°; propionate, m.p. 104°), isolated from *Fucus vesiculosus* and from *Pelvetia canaliculata*, contains two double linkings. L. S. T.

Choline in marine algæ. A. ZELLER (Biochem. Z., 1934, 268, 187—188).—The micro-chemical detection of choline in some marine algæ is reported.

W. McC.

Determination of chlorophyll. N. T. DELEANO and J. DICK (Biochem. Z., 1934, 268, 317—321).—The method depends on the separation of chlorophyll from the EtOH extract by means of $CHCl_3$, with determination of the nuclear Mg as $MgNH_4AsO_4 \cdot 6H_2O$, from which the chlorophyll content is calc. P. W. C.

Micro-analytical tobacco determinations. V. Determination of ammonia. J. BODNAR, V. L. NAGY, and L. BARTA (Biochem. Z., 1934, 268, 174—177; cf. A., 1931, 132).— NH_3 is determined in a HCl extract of 0.25 g. of finely powdered tobacco after pptn. of nicotine with silicotungstic acid, by subjecting the filtrate to steam-distillation in presence of MgO , using excess of 0.01N-HCl for trapping the NH_3 and back-titrating with 0.01N-NaOH. W. McC.

Mineral composition of plantains of varying degrees of keeping quality. ANON. (Sci. Rep. Govt. Agric. Chem., Coimbatore, 1932—1933, 21—22).—In the better keeping varieties of plantain the mineral ash (especially K) content is > that in poorer keeping qualities. Plantains manured with ashes give fruit which keeps better and tastes sweeter.

NUTR. ABS. (m)

Analyses of the ash of bean seed and of leaves of different varieties of vines : potassium compounds in the respective ashes. A. TEGOROULOS (Z. Pflanz. Düng., 1934, A, 33, 95—98).—Ash of vine leaves contains K in H_2O -sol., HCl -sol., and HCl -insol. (probably silicate) forms. The last named is absent from bean ash. A double salt similar to that produced by heating K_2CO_3 with Ca phosphate may exist in plants. A. G. P.

Nitrate content of grasses and legumes. G. DE VITO (Italia Agricola, 1932, 69, 1028—1029; Bied. Zentr., 1933, A, 4, 203).—Analyses of various species of grasses and legumes in different stages of growth show that the relatively high NO_3 contents of young plants decline rapidly with advancing growth. A. G. P.

Determination of phosphorus fractions of plants. M. JAVILLIER and Y. COLIN (Bull. Soc. Chim. biol., 1933, 15, 1552—1562).—The proportions of the total P in the lipin, nucleotide, and phytin fractions of wheat germ were 9, 28, and 42% and in lentil powder 12, 11, and 51%, respectively. H. D.

Use of cresol-blue in systematic mycology. R. KÜHNER (Compt. rend., 1934, 198, 843—846).—The colour reactions of cresol-blue with various species of agaric and boletus are described. J. W. B.

Aldehydes as cytological fixatives. C. ZIRKLE (Protoplasma, 1933, 20, 169—179).—The use is described of a no. of the simpler aliphatic aldehydes in conjunction with $AcOH$, HCO_2H , Cu propionate, lactate, dichromate, Müller's fixative, etc. for the fixation of root tips of *Zea mays*. A. G. P.

Effect of mosaic disease on certain metabolic products in the tobacco plant. H. CORDINGLEY, J. GRAINGER, W. H. PEARSALL, and A. WRIGHT (Ann. Appl. Biol., 1934, 21, 78—89).—Diseased leaves contained more N and less carbohydrate than healthy ones, differences being more marked during photosynthesis. The decrease in carbohydrate during storage of leaves in the dark falls mainly on insol. carbohydrates in healthy leaves and on disaccharides in diseased leaves. In the latter protein breakdown is retarded and insol. substances are less readily hydrolysed. A. G. P.

Possible chemical nature of tobacco mosaic virus. E. BARTON-WRIGHT and A. M. MCBAIN (Nature, 1934, 133, 260).—A reply to criticism (this vol., 337). L. S. T.

Physiology of potato leaf roll. I. Respiration of healthy and leaf-roll-infected potatoes. T. WHITEHEAD (Ann. Appl. Biol., 1934, 21, 48—77).—Except for a short period at the end of the dormant period until the first unfolding of leaves infected plants had the higher respiratory rate. The latter is related to the amount of available respirable substrate present, and thus only indirectly to the effect of the virus. A. G. P.

Plant tumours and polyploidy produced by bacteria and other agents. D. KOSTOFF and J. KENDALL (Arch. Mikrobiol., 1933, 4, 487—508).—Tumours produced by *B. tumefaciens* are similar in

structure to those formed by injection of various chemicals into the internodal cavities of *Ricinus*. The action of chemicals in producing tumours is paralleled by their ability to cause pptn. in tissue extracts.

A. G. P.

Effect of various elements on bacterial tumours of *Pelargonium*. A. GOSSET, J. MAGROU, and A. TCHAKIRIAN (Compt. rend., 1934, 198, 1097—1100).—Inoculation with *B. tumefaciens* gives rise to a uniform production of tumours in *P. zonale*. Introduction of compounds of Ge, Ce, Mo, Sn, Zr, and Al into the tumour tissue produces rapid and permanent necrosis without, in suitable doses, any harmful effect on the plant. P. G. M.

Chlorophyll-containing parasites. J. RICHTER (Pharm. Zentr., 1934, 75, 157—163, 176—179).—The development and morphological relationships of the parasite, particularly the mistletoe and those of the genera *Cuscuta* and *Orobancha*, to their particular hosts are discussed. E. H. S.

Photometer. A. H. SANFORD, C. SHEARD, and A. E. OSTERBERG (Amer. J. Clin. Path., 1933, 3, 405—420).—A new type of apparatus and its use in determining blood-haemoglobin, -glucose, and -creatinine are described. CH. ABS.

Photo-electric colorimeter.—See this vol., 383.

Horizontal micro-burette.—See this vol., 384.

Rapid dialysis. I. A. NELSON and I. H. NELSON (Amer. J. Clin. Path., 1933, 3, 447—453).—Two types of apparatus, applicable to blood, are described. CH. ABS.

Incineration of small laboratory animals for bismuth determinations. C. DESGREZ, M. GLAUME, and R. WOLFF (Bull. Soc. Chim. biol., 1933, 15, 1527—1534).—The method of incineration of Desgrez and Meunier (A., 1920, ii, 554) is applied to whole guinea-pigs. H. D.

Detection of elements in tissues. VII. Determination of gold in tissues by spectrum analysis, with histochemical comparisons. W. GERLACH, K. RUTHARDT, and L. PRUSENER (Beitr. pathol. Anat., 1933, 91, 617—642).—For the detection and determination of traces of heavy metals and for diagnostic purposes, the spectrographic method is unsurpassed. In the determination of Au in animal organs the method is more trustworthy than histochemical methods. NUTR. ABS. (m)

Micro-determination of bromine in blood and organs. A. SALVATORI (Atti R. Accad. Lincei, 1933, [vi], 18, 324—326).—Pincussen and Roman's method (A., 1929, 713) is untrustworthy. T. H. P.

Margosches' quick iodine value method. H. MOHLER and H. BENZ (Mitt. Lebensm. Hyg., 1933, 24, 277—280).—25 c.c. of 0.2N-I in EtOH are mixed with 0.2—0.4 g. of fat dissolved in 10 c.c. of EtOH; 200 c.c. of H_2O are added, with shaking, and the closed flask is kept for 5 min. Without addition of KI the liquid is titrated, with starch as indicator. This method gives the same results as are obtained by the Hanus method. NUTR. ABS. (m)

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1934.

General, Physical, and Inorganic Chemistry.

Fine structure of the Balmer lines. W. V. HOUSTON and Y. M. HSIEH (Physical Rev., 1934, [ii], 45, 263—272).—A new method of treating interferometer patterns of doublets, involving measurements of the intensities of min. between the members of the doublet and between successive orders of interference, is applied to the Balmer series. The separations of the centres of gravity for the lines $H_{\beta, \gamma, \delta, \epsilon}$ are much < the calc. vals., and explanations of the discrepancy are discussed. N. M. B.

Mathematical representation of the energy levels of the secondary spectrum of hydrogen. I. SANDEMAN (Proc. Roy. Soc. Edin., 1932—1933, 53, 347—353).—Assuming certain vals. for the coeffs. of the higher powers of $J(J+1)$, where J is the quantum no., it is proposed to write the energy term form for the rotational spectra of diat. mols. as $F(J)=[B_e J(J+1)]/[1+u^2 J(J+1)]$, where $u=2B_e/\omega_e$, B_e is a const., and ω_e is the equilibrium val. of the vibration frequency. The expression fits the simpler states of H_2 , and is equiv. to Kratzer's potential energy expression. An extension is suggested for states to which the simple form is not applicable. N. M. B.

Polarisation effect in helium D terms. Dipole and quadrupole effects. E. A. HYLLERAAS (Z. Physik, 1934, 88, 108—113).—Theoretical. A. B. D. C.

Spectrum of the carbon arc in the red region. H. BIRKENBEIL (Z. Physik, 1934, 88, 1—13).—The region 6000—9000 Å. has been photographed and analysed. A. B. D. C.

Rydberg's potential energy function and transition probabilities. N. R. TAWDE (Current Sci., 1934, 2, 293—294).—Band intensity measurements on the N_2 spectrum agree far better with the Condon parabola of max. probabilities based on Rydberg's function than with Morse's function, confirming Johnson and Dunstan's conclusions (A., 1933, 884). D. R. D.

Intensities in the spectrum of O II. K. G. EMELEUS (Proc. Nat. Acad. Sci., 1934, 20, 115—117).—In order to explain the absence of the multiplets $\lambda\lambda$ 4956, 4406, and 2419 and the presence of 4950 in the negative glow of a cold-cathode discharge with low c.d., spectra from other sources were examined. The possibility of simultaneous dissociation, ionisation, and excitation of the O_2 mol. by electron impact is considered. N. M. B.

Anomalous dispersion for the doublet H, K of ionised calcium. L. PUCCIANI (Atti R. Accad.

Lincei, 1934, [vi], 19, 13—15).—Anomalous dispersion measurements show that the intensity of the $1S-2P_1$ line of Ca^+ is double that of the $1S-2P_2$ line. O. J. W.

Arc spectrum of chromium under reduced pressure. H. WERRES (Z. wiss. Phot., 1934, 32, 278—282).—The spectra in air and under reduced pressure are mapped from 2900 to 4400 Å. The "vac." lines, although close to those of the solar spectrum, do not entirely correspond with them. J. L.

Multiplets in the spectrum of Cu III. B. V. R. RAO (Z. Physik, 1934, 88, 135—138). A. B. D. C.

Paschen-Back effect. I. L-S coupling; the $3P^3D$ multiplets of Zn and Cd. J. B. GREEN and D. E. GRAY (Physical Rev., 1934, [ii], 45, 273—276).—Observed frequencies and intensities are in good agreement with those calc. by Darwin's method. N. M. B.

Absorption of light by adsorbed bromine. J. F. H. CUSTERS and J. H. DE BOER (Physica, 1934, 1, 265—270; cf. A., 1933, 656).—Br adsorbed on CaF_2 at low pressures gives absorption max. at 2670, 2520 Å., attributed to dissociation into two normal and into one normal and one excited atom, respectively. The energy difference between the max. corresponds with that between the $2P_{3/2}$ and the $2P_{1/2}$ states of Br. The displacement of these two bands towards the ultra-violet represents an energy of 1.9 e.v. H. J. E.

Nuclear moment of indium. F. PASCHEN and I. S. CAMPBELL (Naturwiss., 1934, 22, 136—137).—Fine structure of lines in the In II spectrum leads to the conclusion that the nuclear moment of In is $9/2$, in agreement with Jackson (A., 1933, 200). There is no evidence of any new isotope of In. A. J. M.

Nuclear moment of tellurium and selenium isotopes. S. RAFAŁOWSKI (Acta. phys. polon., 1933, 2, 119—123; Chem. Zentr., 1933, ii, 3096—3097).—Hyperfine structure in the line spectra of Te and Se has been measured. The isotopes have zero nuclear moment. H. J. E.

Absorption spectra due to excitation of inner electrons. VI. The Cs spectrum between 1020 and 600 Å. due to excitation of the $(5p)^6$ shell ($Cs I^b$). H. BEUTLER and K. GUGGENHEIMER (Z. Physik, 1934, 88, 25—42). A. B. D. C.

Regularities in the spectrum Ce III. V. D. DABHOLKAR (Current Sci., 1934, 2, 286).—A note (cf. this vol., 2). D. R. D.

Arc spectrum of osmium. W. ALBERTSON (Physical Rev., 1934, [ii], 45, 304—308).—Complete classifications as transitions between 137 terms of Os I are tabulated for > 1050 lines, and J vals. are assigned. The normal state of Os is $5d^5 6s^2 (^5D_4)$; the ionisation potential is approx. 8.7 volts.

N. M. B.

Illumination of rarified gases by high-frequency currents. F. ESCLANGON (Ann. Physique, 1934, [xi], 1, 267—406).—The gases are contained in discharge tubes at the centre of a solenoid carrying a high-frequency current of wave-length range 50—150 m. Two stages of illumination are found, one for weak excitation, and a brilliant one appearing only for intense excitation and low pressure. Variations of the field components show that the first is due primarily to the electrostatic field, and the second to induced currents. The induced field alone is incapable of exciting the discharge, but can sustain the second stage when initiated. Data are given for O_2 , and for Ne, A, He, H_2 , and N_2 . Spectroscopic observations, and the excitation, by high-frequency currents, of at. jets, and Doppler broadening are discussed.

N. M. B.

Theory of positive column with moving striations. M. J. DRUYVESTEYN (Physica, 1934, 1, 273—280).—Theoretical.

H. J. E.

K series of aluminium and magnesium. H. KARLSSON and M. SIEGBAHN (Z. Physik, 1934, 88, 76—82).

A. B. D. C.

Weak lines in $K\beta$ spectra of molybdenum, rhodium, and silver. H. HULUBER and (MLLE.) Y. CAUCHOIS (Compt. rend., 1934, 198, 1222—1223).—Seven lines, β_0 , β_{1-9} , of each of these elements have been measured, of which two, β_8 and β_9 , are new (cf. A., 1933, 548, 881).

C. A. S.

Probability of double ionisation in the X-ray range. F. WISSEK (Physikal. Z., 1934, 35, 301—302).—Examination of the $K\alpha_1$ and $K\alpha_2$ lines of Cu shows that the probability of double ionisation for a potential of 30 kv. is 2×10^{-5} .

A. J. M.

Ionisation in nitrogen at high pressures. S. CHYLINSKI (Physical Rev., 1934, [ii], 45, 309—313; cf. Broxon, A., 1932, 3; Compton, *ibid.*, 556).—The ionisation-pressure relation for γ - and residual rays was investigated up to 120 atm., and a series of saturation characteristics up to 109 atm. for the intensity range 7—1200 ions per c.c. per sec. per atm. was determined.

N. M. B.

Ionisation functions of the inert gases. H. FUNK (Physikal. Z., 1934, 35, 302—303).—The at.-ray method (A., 1930, 268) has been applied to the inert gases. Max. ionisation occurred at potentials of 120, 130, and 85 volts for He, Ne, and A, respectively.

A. J. M.

Self energy of the electron. G. WATAGHIN (Z. Physik, 1934, 88, 92—97).—Theoretical.

A. B. D. C.

Electron affinities. P. P. SUTTON and J. E. MAYER (J. Chem. Physics, 1934, 2, 145—146).—The electron affinity of an electronegative gas X_2 can be found from the equilibrium const. of the reaction $> X + e^-$, when the gas comes in contact with

a hot metallic surface, obtained from the surface temp., gas pressure, and ratio of the currents carried by the ions and electrons. Results for I_2 are in good agreement with those calc. from the lattice energies of the alkali iodides.

N. M. B.

New transition produced by electron impact in helium. R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1934, 2, 491).—A line has been observed in the electron spectrum in He corresponding with an energy loss of 59.2 volts. It is not due to three successive transitions $1'S_0-2'P_0$ corresponding with energy loss of 63.3 volts.

H. S. P.

Emission of electrons under the influence of chemical action. II. General conclusions and a further study of the case of carbonyl chloride. A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1934, A, 144, 46—75; cf. A., 1931, 994).—The energy distribution of the electrons emitted in the reaction between K_2Na and twenty-two gases has been studied. The results can be interpreted by the equation $E_m - E_c - \phi$, where E_m is the max. energy of the emitted electrons, E_c is the energy of the corresponding chemical reaction responsible for E_m , and ϕ is the work function of the metal. This relation is general, and is similar to the fundamental law of photoelectricity.

L. L. B.

Electron and positron. W. H. FURRY and J. R. OPPENHEIMER (Physical Rev., 1934, [ii], 45, 245—262).—Mathematical. Dirac's interpretation of the negative kinetic energy states in his theory of the electron is developed to give a consistent theory of electrons and positrons.

N. M. B.

Production of positive electrons. J. CHADWICK; P. M. S. BLACKETT, and G. P. S. OCCHIALINI (Proc. Roy. Soc., 1934, A, 144, 235—248).—The emission of positive electrons (positrons) has been observed from a Pb target exposed to the γ -rays of Th-C'', from a source of the active deposit, and from a Pb target exposed to the radiations (γ -rays and neutrons) emitted by Be, B, and F when bombarded by Po α -particles. The observations of the energies of the positrons ejected by the γ -rays of Th-C'' support the view that an electron and a positron of equal mass are produced simultaneously by the interaction of a γ -ray and an atom. They are probably produced in the electric field outside, rather than inside, the nucleus.

L. L. B.

Physical properties of the positron. Annihilation of matter and radiation of dematerialisation. J. THIBAUD (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 36—52).—A full account of work already noted (cf. A., 1933, 993; this vol., 4, 126, 341).

J. W. S.

Emission of alkali atoms from various ammonia catalysts. A. K. BREWER (J. Chem. Physics, 1934, 2, 116—118).—The rate of emission of alkali as positive ions and neutral atoms is measured (cf. A., 1931, 1106; this vol., 233). When the temp. of the catalyst is first raised to the emission point, the no. of emitted atoms far exceeds that of ions, but falls to a negligible val. after several min. heating. Atom emission is much more persistent from catalysts containing Al_2O_3 , and the temp. for equiv. ion

currents is higher. Both atom and ion emission increase when sintering occurs, since the alkali can diffuse more readily to the surface. Factors determining the ratio of atoms to ions are discussed.

N. M. B.

Slow ions and neutral rays. A. ROSTAGNI (*Z. Physik*, 1934, **88**, 55—75).—Formation of neutral rays by A^+ and H_2^+ was studied for grazing incidence at a metal target with velocities between 100 and 600 volts, and the effective cross-section of A^+ , Ne^+ , and He^+ was determined for transference of charge when passing through the same gas at velocities between 600 and 6 volts. The efficiency of H_2 , A , Ne , and He for releasing electrons from metal surfaces at velocities from 600 to 6 volts was obtained for the ionic and neutral rays.

A. B. D. C.

Distribution of initial velocities of positive ions from tungsten. G. J. MUELLER (*Physical Rev.*, 1934, [ii], **45**, 314—319).—Data and curves for eighteen temp. (1300—3000° abs.) are given; distribution is Maxwellian.

N. M. B.

Optical investigation of mercury atom beams. S. YEN (*Helv. phys. Acta*, 1933, **6**, 250—252; *Chem. Zentr.*, 1933, ii, 3392).—The resonance radiation from a beam of Hg atoms illuminated with λ 2536 Å., and the effect of a magnetic field perpendicular to the beam, have been studied.

H. J. E.

Curves for collisions between neutrons and protons. G. MONOD-HERZEN (*J. Phys. Radium*, 1934, [vii], **5**, 95—96; cf. Auger, this vol., 235).—The distribution of slow and swift protons as a function of their direction with that of the incident neutron is determined from an examination of 6000 photographs. The curve for swift protons is symmetrical with a max. at 54°, and for slow protons it is asymmetrical with a max. at 70°.

N. M. B.

At. wts. of iodine, carbon, and sodium. Ratio of iodine pentoxide to sodium carbonate. G. P. BAXTER and A. H. HALE (*J. Amer. Chem. Soc.*, 1934, **56**, 615—617).—By assuming two of the at. wts. involved the third is calc. for several possible vals. of each element. It is concluded that the at. wt. of I is \approx 126.92 and that of C is probably > 12.00 .

E. S. H.

Discussion on heavy hydrogen. (*Proc. Roy. Soc.*, 1134, A, **144**, 1—28).—(LORD) RUTHERFORD discussed the history of the discovery of heavy hydrogen and its probable constitution: two protons and an electron, or a neutron and a proton. Also the question as to whether the fields of force near the H^1 and H^2 nuclei are the same. The use of H^2 nuclei as swift projectiles for the study of the transmutation of the elements was mentioned.

N. V. SIDGWICK discussed the at. vol. of H^2 , and the equilibrium const. for the reactions in which it takes part.

F. W. ASTON pointed out what a very small discrepancy of at. wts. and masses enabled the discovery to be made.

P. HARTECK demonstrated the differences in v.p. and f.p. between H_2O and D_2O , and discussed the prep. of D_2O by the electrolysis of alkaline solutions with Ni electrodes.

F. SODDY criticised the extension of the term "isotope" to H^2 , and other supposed examples revealed only by band spectra. "Isotope" is a term applied to the individuals of a group of two or more chemically identical elements existing together in const. natural proportion and separable only by a few physical methods which depend directly on the masses of the mols. Aston's work on the non-radioactive elements and his discovery of the whole-no. rule give the best proof of this conception, particularly the constancy of the natural ratio. H^2 does not appear to be in sufficient proportion to give concordance between the chemically and physically determined at. wts. The marked difference of chemical character discovered for H^2 destroys the basis of the prediction. In the determination of the combining ratio of H_2 to O_2 , differences in purification would lead to differences in at. wt. determinations which have not been observed. The case under discussion appears more analogous to the separation of a pair of homologues, e.g., Zr and Hf, than isotopes.

M. PÓLANYI discussed the catalysed (Pt-black) interchange between the H^2 and the H^1 in H_2O . The results throw light on the nature of overvoltage and point to its cause being the transition of the H ion to its at. form adsorbed on the Pt. The generally assumed view that H^2 will react more slowly than H^1 is not always correct.

E. K. RIDEAL described work carried out by L. and A. Farkas on the equilibrium $H^1 + H^2 \rightleftharpoons 2H^1H^2$ by a thermal conductivity method. The equilibrium const. does not change much above room temp. and up to 600°, and lies between 3 and 4. The two possible mechanisms for the reaction (1) $H_2 + H^2 \rightleftharpoons 2H^1H^2$, and (2) $H^1 + H_2^2 \rightleftharpoons H^1H^2 + H^2$, $H^2 + H^1 \rightleftharpoons H^1H^2 + H^1$, are discussed. The kinetics of the $H_2^2 + H_2O$ reaction have been investigated, also the diffusion of the isotopes through Pd. H^1 passes through more rapidly than H^2 . The gas evolved on dissolving Zn in dil. H_2SO_4 (30% H^1 - H^2 water) has $H^1 : H^2 = 3.5$.

R. H. FOWLER discussed the separation of H^1 and H^2 by electrolysis.

R. P. BELL described measurements carried out with J. H. Wolfenden. The nature of the cathode metal, the temp., and the c.d. exert no appreciable influence on the efficiency of separation of H^1 and H^2 by electrolysis, as expressed by the factor α in the equation $l \log H^2 - \alpha d \log H^1$.

J. D. BERNAL. The cell measurements (X-ray) of a crystal of ice from 91% H_2O show a definite small difference from those of ordinary ice determined under the same experimental conditions. The apparent mol. vol. of H_2O is slightly $>$ that of D_2O , whilst the apparent mol. vol. of heavy ice is slightly $<$ that of ordinary ice. The reason for this difference is discussed.

W. JEVONS discussed recent spectroscopic investigations on H^2 .

L. L. B.

Isotopic ratio in oxygen. W. R. SMYTHE (*Physical Rev.*, 1934, [ii], **45**, 299—303).—An improved mass-spectrometer is described (cf. A., 1932, 668). The ratio $O^{16} : O^{18}$ in O_2 prepared by the

decomp. of PbO_2 is 503 ± 10 . The divergence from available vals. is attributed to the method of prep.
N. M. B.

Measurements of pressure dependence of ionisation currents. P. KRAUS (Z. Physik, 1934, 88, 99—102).—These measurements should be corr. for change in capacity of the ionisation chamber with pressure.
A. B. D. C.

Physical relationship between the "Rontgen" (r) and the so-called radium dosage "mgeh/cm." R. JAEGER (Physikal. Z., 1934, 35, 273—275).—The relationship between the "Rontgen" (r) and the radium dosage unit mgeh/cm. (mg. Ra element-hr. at a distance of 1 cm. from the prep.) has been derived using the Eve const. (no. of ion-pairs produced per c.c. in free air by the γ -radiation from 1 Curie of Ra-C at a distance of 1 cm. from the prep.). If this is 4.28×10^9 at n.t.p., 1 mgeh/cm. = 7.35 r ; this depends to a certain extent on the filtration adopted.
A. J. M.

Mobility of radioactive atoms on the surface of solids. H. JĘDRZEJOWSKI (Acta phys. polon., 1933, 2, 137—142; Chem. Zentr., 1933, ii, 3091—3092).—A deposit of Po on one part of a Pt foil was found (photographically) to be almost uniformly distributed over the Pt surface after heating to 910° . An evaporation process is excluded, and surface diffusion must have occurred. No such diffusion occurs on Au up to 1000° .
H. J. E.

Distribution of Ra-A, -B, and -C in radioactive equilibrium with radon in a spherical vessel. W. MUND and A. LUYCKX (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 24—29).—Theoretical.
J. W. S.

Diffusion of Th-C''. (MLLE.) C. CHAMIE (J. Phys. Radium, 1934, [vii], 5, 54—56; cf. this vol., 5).—Curves for the diffusion of Th-C'', obtained by the recoil method from Th-C and received on an uncharged plate, show that the amount diffusing in air is very small, and decreases rapidly with the distance between the receiver and the source. Diffusion conditions differ widely from those of emanations.
N. M. B.

Activation by diffusion. P. LANGEVIN (J. Phys. Radium, 1934, [vii], 5, 57—60).—Mathematical. The results of Chamie (see preceding abstract) lead to a hyperbolic law of variation of activation as a function of the distance between the receiver and the source.
N. M. B.

Penetrating radiation from potassium. F. D. GREEVES (Proc. Roy. Irish Acad., 1933, A, 41, 129—136).—Using an arrangement of counter, screens, and small source, and having regard to the background effect varying with meteorological conditions, the β and fast γ radiations from K were examined. The absorption coeff. of the γ radiation in Pb was 0.60 cm.⁻¹
N. M. B.

Absolute energy measurement in the β spectrum of active thorium deposit. R. ARNOULT (J. Phys. Radium, 1934, [vii], 5, 67—70).—A focalisation method gives for the most intense ray the val. $hR=1381.5$ gauss cm. corresponding with an energy 146.88 electron kv.
N. M. B.

Scattering of hard gamma-rays by lead, and the annihilation of positive electrons. E. J. WILLIAMS (Nature, 1934, 133, 415).—An experiment which supports the hypothesis that the nuclear scattering of hard γ -rays by heavy elements is due to the annihilation of positive electrons produced by the γ -rays is described.
L. S. T.

Absorption of penetrating γ -rays. W. GENTNER (J. Phys. Radium, 1934, [vii], 5, 49—53; cf. this vol., 5).—The absorption in Pb of γ -rays of wavelengths 4.7, 5.9, 6.6, 7.9, and 9.3 Å. was measured. Comparison of the experimental and theoretical absorption curves gives the nuclear absorption as a function of the wave-length.
N. M. B.

Scattering of hard γ -rays. L. MEITNER (Naturwiss., 1934, 22, 174).—Scattering of γ -rays with no change of wave-length should occur at electrons with negative energy in the presence of an at. nucleus.
A. J. M.

Neutron. A. BRAMLEY (Science, 1934, 79, 160).—A discussion.
L. S. T.

Photographic detection of spontaneous neutron emission. S. PIENKOWSKI and J. STARKIEWICZ (Acta phys. polon., 1933, 2, 105—110; Chem. Zentr., 1933, ii, 3090—3091).—No emission from Sb, Bi, and La was detectable photographically.
H. J. E.

Angular distribution of protons ejected by neutrons. N. A. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 179—181).—The angular distribution of protons ejected by a parallel beam of neutrons (from Rn+Be) from a paraffin plate inside a Wilson chamber is in better agreement with the results of Curie (Physical Rev., 1933, [ii], 44, 463) than with those of Auger and Monod-Herzen (A., 1933, 551). The greater angle scattering observed by Dunning and Pegram (Physical Rev., 1933, [ii], 43, 497) may be due to C of the paraffin.
J. W. S.

Photographic method, and artificial disintegration of atoms. (MLLE.) M. BLAU (J. Phys. Radium, 1934, [vii], 5, 61—66).—A photographic plate is sensitive to H -rays, and shows trajectories, from the lengths of which the speed of the rays can be found. Velocity distributions of H -rays from at. disintegrations, and excited by neutrons, are thus investigated. Results are given for H -rays from disintegration of Al, and for transmutation neutrons of Be.
N. M. B.

Artificial production of a new kind of radioelement. F. JOLIOT and I. CURIE (Nature, 1934, 133, 201—202; cf. this vol., 234, 343).—The transmutation of B, Mg, and Al α -particles gives rise to new radio-elements emitting positrons. *E.g.*, for B, there occurs the nuclear reaction ${}^5\text{B}^{10} + {}^2\text{He}^4 = {}^{13}\text{N}^{13} + {}^0\text{e}^{+1}$, where ${}^{13}\text{N}^{13}$ is the radioactive nucleus disintegrating with emission of positrons, giving a stable nucleus ${}^{13}\text{C}^{13}$. With Al and Mg the radioactive nuclei would be ${}^{30}\text{P}^{30}$ and ${}^{27}\text{Si}^{27}$, respectively, produced in the ratio of 10^{-7} or 10^{-6} of the no. of α -particles. A Po prep. of 100 millicuries gives approx. 10^5 atoms of the new radioactive elements. The NH_3 obtained by heating irradiated BN with NaOH carries the activity with it, as does the H_2 liberated

by action of HCl on irradiated Al. Pptn. of the activity in this case with Zr phosphate indicates that the radio-element is an isotope of P.

L. S. T.

Artificial radioactivity discovered by Curie and Joliot. L. MEITNER (Naturwiss., 1934, 22, 172—174).—The artificial radioactivity (*i.e.*, nuclear disintegration continuing after removal of bombarding particles) discovered by Curie and Joliot (see above) has now been directly observed in the Wilson cloud chamber. Photographs of the process are given. Positive electrons were found to be emitted from Al 9 min. after shutting off the Po α -rays, and from B 12 min. after. No negative electrons were produced, so that the reaction discussed by Curie and Joliot, $\text{Si}^{30}_{14} = \text{Si}^{29}_{14} + e^+ + e^-$, does not occur.

A. J. M.

Nuclear spin and maintenance of rotation impulse for nuclear processes. H. RAETHER (Naturwiss., 1934, 22, 151).—By considering the nuclear processes: $\text{H}^2 + \text{Li}^6 = 2\text{He}^4$, $\text{H}^1 + \text{Li}^7 = 2\text{He}^4$; $\text{H}^2 + \text{Li}^7 = 2\text{He}^4 + n^1$, $\text{B}^{11} + \text{He}^4 = \text{N}^{14} + n^1$, $\text{Be}^9 + \text{He}^4 = \text{C}^{12} + n^1$, it is shown that the application of the law of maintenance of rotation impulse to nuclear processes agrees with the calculation of nuclear spin from spectroscopic data. The last three processes indicate that the neutron has a nuclear spin involving

A. J. M.

Transmutation effects observed with heavy hydrogen. M. L. OLIPHANT, P. HARTECK, and (LORD) RUTHERFORD (Nature, 1934, 133, 413).—When NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, and H_3PO_4 in which H^1 has been largely displaced by H^2 are bombarded by an intense beam of protons no marked differences from H^1 compounds are observed. When ions of H^2 are used, however, there is a large emission of fast protons detectable even at energies of 20,000 volts. The proton group has a range of 14.3 cm., corresponding with an energy of emission of 3×10^6 volts. There is also a short-range group of singly-charged particles of approx. 1.6 cm. range and numerically equal to the 14-cm. group. A large no. of neutrons, max. energy approx. 3×10^6 volts, also result, but the reaction by which they are produced is probably less frequent than that which produces the protons. An interpretation of the results is put forward and the possible reactions $\text{H}_2 + \text{H}_2 \rightarrow \text{H}_3 + \text{H}_1$ or $\text{H}_2 + \text{H}_2 \rightarrow$ are discussed.

L. S. T.

Ranges of disintegration particles from lithium and boron by bombardment with rapid protons. F. KIRCHNER and H. NEUBER (Physikal. Z., 1934, 35, 292—293; cf. A., 1933, 1098).—The ranges of the disintegration particles from Li and B were determined by a cloud-chamber method. For Li, particles of ranges 7, 9, and 12 mm. were found in the short-range group, whilst the range of the long-range group was 18.4 cm. The total no. of short-range particles was about twice that of the long-range. For B, the previous observations have been confirmed. There was a group with a max. at 22 mm., and another at 45 mm.

A. J. M.

Atomic disintegration of metallic sodium. A. KONIG (Naturwiss., 1934, 22, 150—151).—A thin layer of Na on Au, protected from atm. oxidation by

a layer of Ag, was bombarded with Po α -rays. The emitted protons fall into four groups. A. J. M.

Disintegration of deuterons by high-speed protons and the instability of the deuteron. G. N. LEWIS, M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (Physical Rev., 1934, [ii], 45, 242—244).—A comparison of the effect of proton bombardment on pairs of targets containing H and H^2 in the form of $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH}^2)_2$ gave an excess of long-range protons from the targets containing H^2 , and attributed to disintegration of the deuteron by the bombarding protons. The range of protons requires a neutron mass of approx. 1.

N. M. B.

The deuteron and disintegration. H. J. WALKER (Phil. Mag., 1934, [vii], 17, 793—800).—A neutron-proton combination (the deuteron) may be a stable nuclear sub-unit for elements up to S. Two deuterons should unite to form an α -particle. Nuclear structures are suggested and correlated with results on disintegration.

H. J. E.

Interpretation of the relation between cosmic and atomic quantities. K. SITTE and W. GLASER (Z. Physik, 1934, 88, 103—107).—Theoretical.

A. B. D. C.

New hard component of the cosmic ultra-radiation. A. CORLIN (Nature, 1934, 133, 419; cf. this vol., 128).

L. S. T.

Cosmic rays under 600 metres of water. W. KOLHORSTER (Nature, 1934, 133, 419).—Measurements in the Stassfurt salt-mine show that the hardest cosmic rays penetrate also to 600 m. of H_2O . The apparent mass absorption coeff. is $< 5 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1}$ with an upper limit $1.8 \times 10^{-5} \text{ cm}^2 \text{ g}^{-1}$ (cf. A., 1933, 1100).

L. S. T.

Stellar atmospheres with and without oxygen. P. SWINGS (Bull. Acad. roy. Belg., 1934, [v], 20, 137—139).—Possible classification of stars according to their O_2 spectra is discussed.

J. W. S.

Absence of molecular hydrogen bands in the spectra of sun-spots. P. SWINGS (Bull. Acad. roy. Belg., 1934, [v], 20, 132—136).—It is shown theoretically that the concn. of mol. H_2 in sun-spots may be too low for the absorption bands to appear in the astronomical spectral region.

J. W. S.

Free paths and transport phenomena in gases and the quantum theory of collisions. II. Determination of the laws of force between atoms and molecules. H. S. W. MASSEY and C. B. O. MOHR (Proc. Roy. Soc., 1934, A, 144, 188—205; cf. A., 1933, 1101).—The form and magnitude of the interaction energy between two He atoms are considered in terms of observations of the viscosity of He at different temp. The interaction between a He atom and ion is discussed with reference to the mobility of He ions in He. Free paths are calc. for various laws of force between gas atoms.

L. L. B.

Relativistic theory of atoms with many electrons. J. SOLOMON (Compt. rend., 1934, 198, 1023—1025; cf. A., 1933, 660).

C. A. S.

Materialisation of polarised æther. V. POSEPAL (Compt. rend., 1934, 198, 914—916; cf. this vol., 236).

C. A. S.

Interaction of two helium nuclei. W. M. ELSASSER (J. Phys. Radium, 1934, [vii], 5, 71—74; cf. this vol., 6).—Mathematical. N. M. B.

The atom as a system quantised in time and space. G. BECK (Helv. phys. Acta, 1933, 6, 309—314; Chem. Zentr., 1933, ii, 2634).—Theoretical. H. J. E.

Velocity of light. M. E. J. G. DE BRAY (Nature, 1934, 133, 464). L. S. T.

Wave equation of photon. Y. MIMURA and T. MAEKAWA (J. Sci. Hiroshima Univ., 1934, A, 4, 41—45).—Mathematical.

Vector model for almost-closed shells. M. H. JOHNSON, jun. (Proc. Nat. Acad. Sci., 1934, 20, 117—120).—Mathematical. The formulation of the properties of a group of equiv. electrons in terms of the corresponding holes, or electrons missing from a partly filled shell, is examined. N. M. B.

Atmospheric water vapour band 6324 Å. in the solar spectrum. V. N. KONDRATEEV and D. I. EROPKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 170—175).—235 new lines have been measured over an interval of 170 Å. around 6300 Å. in the spectra of the sun near the horizon. By comparison with the same spectral region for the sun higher in the sky some of these lines have been identified as due to terrestrial H₂O vapour, and three others as new lines of the O, band α . From measurements of the 6324 Å. H₂O band of the 3, 1, 1 vibration state, vals. of the fine structure const., and moments of inertia of the H₂O mol. are calc. The valency angle and O—H distance are 104.18° and 1.016×10^{-8} cm., respectively. J. W. S.

Band spectrum of aluminium deuteride. W. HOLST and E. HULTHÉN (Nature, 1934, 133, 496).—Preliminary results for the spectra of AlH¹ and AlH² are given. The application of the data to the question of isotopes is discussed. L. S. T.

Spectrum of MgF. F. A. JENKINS and R. GRINFELD (Physical Rev., 1934, [ii], 45, 229—233).—Consts. for the $^2\Sigma, ^2\Sigma$ and $^2\Pi, ^2\Sigma$ systems are evaluated from measurements of the band heads and of the partly resolved rotational structure. The isotope effect of Mg is observed in the +1 sequence of $^2\Sigma, ^2\Sigma$ bands. N. M. B.

Absorption [spectrum] of liquid oxygen. R. GUILLIEN (Compt. rend., 1934, 198, 1223—1225; cf. A., 1931, 404; this vol., 123).—The spectrum between $\lambda\lambda$ 3500 and 8400 Å. has been examined using thicknesses of liquid O, up to 109 cm. A new band with max. at λ 7307 was found. C. A. S.

Line spectrum of chromic oxide and absorption spectra of chromium glasses. G. JOOS and K. SCHNETZLER (Z. physikal. Chem., 1934, B, 24, 339—392).—Cr₂O₃ at -190° exhibits five ill-defined absorption lines characteristic of the lattice. B₂O₃ glass with 1% Cr₂O₃ shows the same lines, but if alkali is added, the lines disappear, and the spectrum, despite the low temp., then resembles that of an aq. solution of a Cr salt, indicating the absence of periodicity in the structure of the glass. R. C.

Absorption [spectrum] of chromyl chloride. M. KANTZER (Compt. rend., 1934, 198, 1226—1227; cf. A., 1933, 791).—103 lines between $\lambda\lambda$ 5894 and 5050.5 Å. have been measured, and classified as affected by varying temp. (0—270°) and pressure.

Absorption band spectra of polyatomic molecules in solution. I. Absorption due to the double linkings O:C:OH, O:C:H, :C:C, :N:N, and :C:N. S. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 256—263).—The two absorption bands attributed to the groups :C:O etc. in polyat. mols. are shifted towards the red relative to the absorption of the CO mol., whilst the difference between the threshold frequencies of the bands is approx. equal to the difference between the $^3\Pi$ and $^1\Pi$ levels of the CO mol. R. S.

Infra-red absorption spectra of phosphine. L. W. FUNG and E. F. BARKER (Physical Rev., 1934, [ii], 45, 238—241).—Data are given for the 10 μ absorption region showing three bands with centres at 1121, 992, and 990 cm.⁻¹ The 4.3 μ band centre is at 2327 cm.⁻¹ Weak bands were observed at 2.9 μ (3428 cm.⁻¹) and 2.2 μ (4541 cm.⁻¹). Doubling found in corresponding NH₃ bands is not shown; hence the P atom cannot pass readily through the plane of the three H atoms. The perpendicular type bands have intense central max., indicating that PH₃ behaves like a spherical top. N. M. B.

Vibrational energy level system of the linear molecule HCN. A. ADEL and E. F. BARKER (Physical Rev., 1934, [ii], 45, 277—279).—The complete vibrational energy level scheme of the normal HCN mol., determined with the help of the newly-discovered rotation-vibration bands in the infra-red (cf. this vol., 129), is in good agreement with theory. The fundamental frequencies of the isotopic mol. H²CN are predicted from those found for HCN. N. B.

Infra-red absorption spectrum of some cyclic and chain organic compounds. R. FREYMAN and A. NAHERNIAC (J. Phys. Radium, 1934, [vii], 5, 75—84).—A recording spectrometer for the region 0.8—1.2 μ is described, by means of which data are obtained for the absorption bands of C₆H₆, PhI, PhBr, PhCl, PhNO₂, PhMe, CHCl₃, CH₂Cl₂, MeOH, cyclohexane, C₆H₁₄, and CHCl·CCl. A new classification system of the C₆H₆ bands is proposed, and the mol. structure is discussed. N. M. B.

Smekal-Raman effect and molecular structure. K. W. F. KOHLRAUSCH (Naturwiss., 1934, 22, 181—189, 196—204).—A review.

Raman spectrum of nitric acid. H. ANDERHOLD and H. E. WEISS (Z. Physik, 1934, 88, 83—91).—The variation of the Raman spectrum of HNO₃ with concn. is not entirely due to dissociation, but to the formation of OH·NO₂ in the conc. acid; the frequency characteristic of $\dot{\text{N}}\text{O}_3$ is absent from the pure acid spectrum. A. B. D. C.

Raman frequencies of the ammonium group. I. R. RAO and C. S. RAO (Z. Physik, 1934, 88, 127—134).—NH₄Cl, NH₄NO₃, and (NH₄)₂SO₄ were investigated in the cryst. form and in solution; the

Raman displacements for the NH_4 group are 3117, 3169 (?), 3220 cm^{-1} for crystals, and 3157, 3221, 3275 (?) cm^{-1} for solutions. A. B. D. C.

Changes in the Raman spectrum of sulphuric acid on dilution. L. A. WOODWARD and R. G. HORNER (Proc. Roy. Soc., 1934, A, 144, 129—143).—Microphotometer curves of the Raman spectra of H_2SO_4 are given for the concn. range 100—10%. The frequencies 910, 978, and 1121 cm^{-1} (characteristic of the H_2SO_4 mol. and present in the pure acid) rapidly vanish on dilution, whilst the frequency 1036 (characteristic of the HSO_4' ion) appears and increases in intensity. At 50% acid the frequency 982 (characteristic of the SO_4'' ion) appears and becomes stronger. The behaviour of the continuous background supports the view that it consists mainly of a true continuous Raman effect due to vibrations of mol. complexes. L. L. B.

Raman spectrum of arsenic trifluoride and the molecular constants of AsF_3 , AsCl_3 , and PCl_3 . D. M. YOST and J. E. SHERBORNE (J. Chem. Physics, 1934, 2, 125—127).—The Raman spectrum of AsF_3 consists of four lines with frequencies $\omega_1(1)$, 707; $\omega_2(1)$, 341; $\omega_3(2)$, 644; and $\omega_4(2)$, 274 cm^{-1} . The selection rules require a pyramidal mol. Electron diffraction data for AsF_3 , AsCl_3 , and PCl_3 are used to establish linking angles. Entropies are calc., and free energies of formation of liquid and gaseous AsCl_3 are —65,190 and —62,718 g.-cal., respectively, at 25° (± 500 —1400 g.-cal.). N. M. B.

Raman spectrum of lead tetramethyl. A. B. F. DUNCAN and J. W. MURRAY (J. Chem. Physics, 1934, 2, 146).—The lines 135, 458, 472, 766, 930, 1155, 1169, 2921, and 3000 were found and provisionally assigned. N. M. B.

Raman spectra of ring compounds. II. Poly-substituted benzene compounds. J. W. MURRAY and D. H. ANDREWS (J. Chem. Physics, 1934, 2, 119—124; cf. this vol., 10).—Data are given for PhF , 1:2:4- $\text{C}_6\text{H}_3\text{Cl}_3$, 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$, C_6HCl_5 , C_6Cl_6 , and C_6Me_6 . Relations to the vibrations of the C_6H_6 ring are discussed. N. M. B.

Raman effect. II. Raman effect of phenylacetates, phenylpropionates, cinnamates, phthalates, salicylates, and phenylmethylcarbinol. K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1934, 9, 88—108; cf. this vol., 130).—Data refer to the Me, Et, and Pr^s esters and $\text{CHPhMe}\cdot\text{OH}$. The frequency 3060 cm^{-1} of the C-H linking in the C_6H_5 ring is influenced little by groups or atoms other than those adjacent to the C in the ring, and is raised by neighbouring double linkings. The intensities of the lines attributed to the C=O linking are enhanced by the proximity of the C-C linking, and the frequency 1720 cm^{-1} is diminished to 1672 cm^{-1} by $\cdot\text{OH}$, e.g., in the salicylates. The C_6H_6 ring frequencies 615 and 1000 cm^{-1} are absent from the di-derivatives, but other frequencies appear. The frequency of the $\cdot\text{C}\cdot\text{O}\cdot\text{CH}_2\cdot$ grouping is 845 cm^{-1} . J. G. A. G.

Raman effect. XXX. Raman spectra of aliphatic ketones and aldehydes. K. W. F. KOHLRAUSCH and F. KOPPEL (Z. physikal. Chem., 1934,

B, 24, 370—388; cf. this vol., 346).—The frequencies 510 and 1390 are assigned to the group H-CO and the frequency 590 cm^{-1} to the Me-CO group in addition to the CO frequency and the internal vibrations of the Me group. In compounds $\text{R}\cdot\text{CO}\cdot\text{X}$, where R is alkyl and X represents H, Cl, Me, OH, OMe, or OEt, the CO frequency ~ 1700 cm^{-1} is independent of the length of the R chain when this is straight, and the effect of branching in the α position is small compared with that of varying X. Examination of the frequencies of R, where this group is not branched in the α position, has shown that when R=*iso*amyl, two forms of mol. probably exist, owing to free rotation about the axis of the $\text{CH}\cdot\text{CH}_2$ linking.

R. C.

Application of the Raman effect. II. Conjugate ethylenic and benzenic double linking in the hydroaromatic ring. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 274—287).—Progressive substitution of ethylenic compounds is accompanied by an increase in the mean Raman frequency associated with the double linking (I). These frequencies can be separately identified in compounds containing two non-conjugated (I), but when (I) are conjugated, the frequencies are diminished. Measurements of the Raman spectra of dihydronaphthalene and indene show that conjugation of a (I) in the hydroaromatic nucleus with a benzenic (I) produces a still greater diminution in the frequency.

R. S.

Molecular scattering of light in liquids: fluctuations in orientation of homopolar and heteropolar molecules. A. ROUSSET (Compt. rend., 1934, 198, 1227—1229).—An explanation of the more extensive continuous background on each side of the exciting line in the light scattered by a homopolar liquid (e.g., CS_2 , C_6H_6) than in that scattered by a heteropolar liquid (e.g., PhNO_2 , AcOH) is based on the stronger orientation of, and consequent smaller amplitude of vibrations induced in, heteropolar as compared with homopolar mols. The inference as regards gases is shown to be in conformity with recent results for compressed O_2 (cf. A., 1929, 985; 1933, 998; this vol., 10). C. A. S.

Phenomena of metachromasis. L. LISON (Bull. Acad. roy. Belg., 1933, [v], 19, 1332—1341).—Metachromatic colouring matters all contain at least one not entirely substituted NH_2 group. Such compounds only are capable of forming an imine base or of existing in two tautomeric forms, (a) of "normal" colour and (b) of colour near that of the imine base and probably directly related to it chemically.

J. W. S.

Variation of properties of zinc oxide as a result of mechanical treatment. A. KUTZELNIGG (Monatsh., 1934, 64, 61—73).—The changes of colour and luminescence of ZnO brought about by pressure vary with the method of prep.; the most sensitive to pressure is the sublimed form and the least sensitive that prepared in the wet way. When the compressed product is powdered and ignited, it regains its original colour, but luminescence is regained incompletely. Light has no influence on the colour change.

E. S. H.

Fluorescence of zinc oxide at the temperature of liquid air. A. KUTZELNIGG (Monatsh., 1934, 64, 74—75).—The fluorescence of ZnO, prepared in different ways, is increased strongly at low temp.

E. S. H.

Indications and reproducibility of fluorescence phenomena in solids and application to determinations of concentration. J. EISENBRAND and G. SIEWERT (Arch. Pharm., 1934, 272, 428—440).—The distribution of spectral intensity may be used to classify the fluorescence of solids, since it is almost independent of the size of the powder particles. The intensity of the fluorescence depends on the size and surface of the particles; consequently determinations of concn. in mixtures are uncertain.

H. S. P.

Luminescence of pharmaceutical zinc oxide. J. EISENBRAND and G. SIEWERT (Arch. Pharm., 1934, 272, 440—451).—Luminescence produced by Hg radiation decreases with the size of particle, as measured by sedimentation and the adsorption of Congo-red.

H. S. P.

Emission of Lenard phosphors in the red and infra-red. E. LOES (Ann. Physik, 1934, [v], 19, 489—500).—The emission of various phosphors in the red and infra-red was photographed up to 950 m μ . The long-wave bands were similar in structure to those found already in the visible and ultra-violet. Many emission bands were found in the infra-red. The temp. displacement of these bands is like that of the visible bands.

A. J. M.

Photo-electric effect of crystalline semiconductors. I. Argentite, achantite, and cuprite. G. ATHANASIU (J. Phys. Radium, 1934, [vii], 5, 85—94).—Photo-electric sensitivity for radiations in the range 0.4—1.4 μ was measured; max. were shown at 1.15, 1.2, and 0.64 μ for argentite (I), achantite (II), and cuprite, respectively. The influence of an auxiliary potential on the val. and sense of the photo-electric effect was investigated for (I). Evidence is given of residual phenomena supporting the theory of electrolytic decomp. of the crystal under the influence of the current. For (I) and (II), the radiation giving the max. photo-electric effect coincides with that inducing max. photo-conductivity at low temp.

N. M. B.

Ionising power of compounds of light elements. A. DORABIALSKA (Rocz. Chem., 1934, 14, 105—114).—The ionising power of a no. of compounds has been measured, using piezoelectric quartz in a large ionising chamber, with a paraffin screen. Compounds of Se, Y, La, As, Sb, Bi, F, Nb, and Ta give rise to feeble currents, whilst Sb and compounds of Li, Ca, Al, Si, and Ti are inactive.

R. T.

Mobility of metallic ions in alkali halide crystals. S. A. ARZYBYSHEV and A. S. TOPORETZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 176—178).—When a potential is applied between two metal plates in contact with opposite faces of a NaCl crystal at a high temp., a coloured layer forms on the side in contact with the positively-charged plate, the thickness of the layer formed at const. temp. being proportional to the time of application of the potential. The effect is attributed to distortion of the crystal lattice

by diffusing Cu ions, and it is deduced that at 700° the mobility of Cu⁺⁺ ions is about 130 mu. per sec.

J. W. S.

Variation with time of current in semi-conducting material with low voltage. G. DECHÈNE (Compt. rend., 1934, 198, 1021—1023; cf. A., 1930, 129; 1933, 884).—With yellow HgO, PbCl₂, ZnO, or effloresced Na₂CO₃ as semi-conducting material and Hg electrodes, the counter-e.m.f. increases slowly with increase in the d.c.; with low voltage resistance increases with time at the anode, and decreases at the cathode, but on reversal shows an increase followed by a decrease.

C. A. S.

Electrical conductivity of Cu-Pd alloys with disordered and ordered atomic distributions at low temperatures (with an appendix on Cu₃Pt). H. J. SEEMANN (Z. Physik, 1934, 88, 14—24).—Measurements of the resistance of Cu-Pd alloys containing 38—53 at.-% Pd at room, liquid N₂, and liquid H₂ temp. show that although the resistance of the ordered atom alloy is < that of the disordered at room temp., the resistance of the ordered decreases less rapidly with fall in temp.

A. B. D. C.

Resistance of manganese arsenide. L. F. BATES (Phil. Mag., 1934, [vii], 17, 783—793; cf. A., 1933, 1109).—The resistance of Mn₃As₂ changes abruptly at a temp. between 30° and 50°, depending on the previous heat-treatment. The relation between this change and changes in the energy of spontaneous magnetisation is discussed.

H. J. E.

Electromagnetic waves of 1.1 cm. wave-length and the absorption spectrum of ammonia. C. E. CLEETON and N. H. WILLIAMS (Physical Rev., 1934, [ii], 45, 234—237).—Using magnetron-type oscillators as the source of continuous short-wave radiation, the absorption spectrum of NH₃ was mapped for the wave-length region 1—4 cm. The absorption max. was at 1.25 cm. The calc. effective collision diameter of the mol. is 8.8 × 10⁻⁸ cm.

N. M. B.

Resonance frequency of oscillatory circuits with leaky condenser, and its bearing on the measurement of the dielectric constant of ionised gas. S. S. BANERJEE (Phil. Mag., 1934, [vii], 17, 834—843).—The apparent increase in the dielectric const. is due to the conductivity of the ionised gas.

H. J. E.

Determination of dipole moments in solution. S. SUGDEN (Nature, 1934, 133, 415—416).—When mol. polarisation P_2 is plotted against vol. polarisability $(\epsilon-1)/(\epsilon+2)$ for solutions of PhCN, PhNO₂, and PhCl in non-polar solvents, the points for each substance all lie near a straight line through the entire range of solutions to the pure liquid. The measured polarisation appears to be < the true val. of P_2 , which should be obtained by extrapolating the curve to $(\epsilon-1)/(\epsilon+2)=0$. Vals. for μ obtained from the curve are given. The dipole moments calc. from $\propto P_2$ in a solvent may be erroneous when the dipole moment is large.

L. S. T.

Two types of dielectric polarisation. S. O. MORGAN (Trans. Electrochem. Soc., 1934, 65, 185—192).—Dielectric polarisation of the Debye type (I),

due to orientation of dipoles, usually occurs at high frequencies, but it may be found at low frequencies with highly viscous materials. Polarisation of the Maxwell-Wagner type (II), due to heterogeneity, is generally to be sought at low frequencies, but it may occur at high frequencies if either component of the dielectric has a high conductance. The two types may be distinguished, however, by their being affected by temp. in opposite senses. Data at various temp. show that anomalous dispersion in glycerol is attributable to (I), but that in "halowax" and paper to (II).

H. J. T. E.

Dipole moment of associated molecules and validity of mass law for association. I. SAKURADA (Z. physikal. Chem., 1934, B, 24, 437—444).—Assuming that when an associating liquid is dissolved in a non-polar solvent the associated mols. are either all double mols. or all triple mols. and that the mass law is valid for the association, equations are derived permitting the calculation from the orientation polarisation of the solute of the dipole moment of the polymerised mols. and the dissociation const. The equations have been verified from existing data. PhCl , EtOAc , MeOAc , and CHCl_3 are stated to form dipole-free double mols., whilst PhNO_2 forms dipole-free triple mols.

R. C.

Dielectric constant studies. IV. Moments of some inorganic compounds. (Miss) M. G. MALONE and A. L. FERGUSON (J. Chem. Physics, 1934, 2, 99—104; cf. this vol., 363).—The dipole moments of SbCl_3 , SbBr_3 , SbI_3 , AsBr_3 , AsI_3 , AsF_3 , PI_3 , and LiClO_4 have been determined in various solvents. The vals. agree fairly well with those derived from a consideration of the electronegativity of the elements.

N. M. B.

Electric moment of dioxan. C. H. SCHWINGEL and E. W. GREENE (J. Amer. Chem. Soc., 1934, 56, 653—654).—Data recorded for dielectric const. and polarisation of 1:4-dioxan vapour at temp. between 337° and 487° abs. indicate zero electric moment.

E. S. H.

Dielectric measurements with dipole liquids. J. L. SNOEK (Physikal. Z., 1934, 35, 196—203).—The dipole contribution to the vol. polarisation has been determined for different concns. of the following substances in various solvents (CCl_4 , C_6H_{14} , or C_6H_6): MeNO_2 , PhNO_2 , $\text{C}_5\text{H}_{11}\text{NO}_2$, EtNO_2 , EtOAc , PhF , MeCN , $\text{CH}_2\text{Cl}\cdot\text{CN}$, $\text{CHCl}_2\cdot\text{CN}$, $\text{CCl}_3\cdot\text{CN}$, pyrazine, 2:5- and 2:6-di- and tetra-methylpyrazine, 2-methyl- and 2:3-dimethyl-quinoxaline, $\text{C}_6\text{H}_4\text{Br}_2$, and $\text{C}_2\text{H}_4\text{Cl}_2$.

A. J. M.

Dipole moments of acetic anhydride and of some fatty acids. A. PIEKARA and B. PIEKARA (Compt. rend., 1934, 198, 1018—1020).—The mol. polarisation, P_∞ , of Ac_2O , deduced from several concns. in CS_2 solution, is 196.5 at 5° and 187.5 at 25° ; dipole moment, μ , 2.82×10^{-18} , or from temp. variation of P_∞ , 2.46×10^{-18} . P of AcOH and EtCO_2H in C_6H_{14} at 10° and 30° show increases with both concn. and temp., but P_∞ is independent of temp. (cf. A., 1930, 523, 824; 1933, 888, 1240).

C. A. S.

Derivatives of normal pentane and normal heptane. III. Dipole moments of the bromoethoxy- and the dibromo-derivatives. M. L.

SHERRILL, M. E. SMITH, and D. D. THOMPSON (J. Amer. Chem. Soc., 1934, 56, 611—614; cf. A., 1930, 888).—Data are recorded for b.p., d , n , dielectric const., and electric moment of six bromoethoxy- and five Br_2 -derivatives.

E. S. H.

Polarity of chemical compounds. V. K. HIGASI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 16—17; cf. A., 1933, 1230).—The dipole moment of $(\text{-CH}_2\text{Cl})_2$ dissolved in C_6H_6 (I) and in amylene (II) has been measured at different temp. The abnormally high, almost const. moment in (I) is attributed to the influence of the (I) ring itself. Data from the (II) solution show normal behaviour and are considered to be trustworthy in view of its small moment, 0.37 , in (I). The moment of $\text{CH}_2\text{Cl}\cdot\text{CH}_2\text{Br}$ is 1.52 and 1.17×10^{-18} e.s.u. in (I) and C_6H_{14} solution, respectively, at 25° .

R. S.

Dielectric constants of polar solutions. J. WYMAN, jun. (J. Amer. Chem. Soc., 1934, 56, 536—544).—Data are recorded for solutions of NH_3 -acids and polypeptides in H_2O , aq. EtOH , aq. $\text{CO}(\text{NH}_2)_2$, and other solvents. In all cases the dielectric const. is a nearly additive property of the solutions. A theoretical interpretation is advanced.

E. S. H.

Volumes of substances in the free state and in solution. I. I. SASLAVSKI (J. Gen. Chem. Russ., 1933, 3, 897—903).—The apparent mol. vol. (I) of non-electrolytes diminishes on dissolution; that of electrolytes may increase or diminish, according to the nature of the individual salt. These effects are due chiefly to change in vol. of the solvent. Certain periodic variations in the magnitude of the effect obtained are found for salts of the same anion with cations of increasing at. no. Where the cation is const. (Na^+), and the anion is varied, the % diminution in (I) increases in the series $\text{I}^+ = \text{ClO}_3^+ < \text{BrO}_3^+ < \text{NO}_3^+ < \text{OAc}^+ < \text{Br}^+ = \text{N}_3^+ < \text{Cl}^+ < \text{NO}_2^+ < \text{HCO}_2^+ < \text{MeO}_4^+ < \text{WO}_4^+ < \text{SO}_4^+ < \text{SeO}_4^+ < \text{CO}_3^+ < \text{PO}_4^+ < \text{AsO}_4^+ < \text{OH}^+ < \text{S}^+$.

R. T.

Physical properties and chemical constitution. I. Esters of normal dibasic acids and of substituted malonic acids. A. I. VOGEL (J.C.S., 1934, 333—341).—Data are given for n_D , d , r , σ , at 20° , mol. refraction coeffs., parachors, and dispersion, and for the density and surface tension over a temp. range for the Me and Et esters of malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids, and for the Me esters of substituted malonic and of cyclic 1:1-dicarboxylic acids. The vals. for an increment of CH_2 for the mol. refraction coeffs. for the mol. refractivities of the C, D, F, and G' lines agree with available data, but the mean difference for the parachor is 40.3 , giving at. parachors C— 11.5 , H— 14.4 , calc. from existing data on the normal hydrocarbons.

N. M. B.

Molecular refractions and dispersions in the ultra-violet of salts and of ions in water solution. G. S. FORBES and H. B. ELKINS (J. Amer. Chem. Soc., 1934, 56, 516—521).—Data have been determined for KCl , KBr , KI , KNO_3 , NaNO_3 , Na_2SO_4 , Na_2SeO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , LiClO_4 , NaClO_4 , NaClO_3 , NaBrO_3 , NaIO_3 , LiIO_3 , LaCl_3 , AgClO_4 , TiClO_4 , TlNO_3 , $\text{Hg}_2(\text{ClO}_4)_2$, $\text{Hg}(\text{ClO}_4)_2$, $\text{Pb}(\text{ClO}_4)_2$, $\text{Pb}(\text{NO}_3)_2$, and CdSO_4 .

E. S. H.

Analysis of the dispersion curves of substituted propionic acids. P. A. LEVENE and A. ROTHEN (J. Amer. Chem. Soc., 1934, 56, 746).—Data are recorded for four pairs of optically active, configuratively related derivatives. The partial rotations of the significant chromophoric group and of the rest of the mol. remain the same in sign. E. S. H.

Polarimetric researches on narcotine. PARISELLE (Compt. rend., 1934, 198, 928–930).—For Hg λ 5461 in aq. HCl solution $M[\alpha]$ of narcotine increases with excess of HCl to $+240^\circ$; in CHCl_3 with HCl to $+650^\circ$, but alone in CHCl_3 it is -1006° . In aq. NaOH $M[\alpha]$ is $+273^\circ$, diminishing on addition of HCl until with formation of the normal hydrochloride of the Na salt it is -587° . Further addition of HCl causes mutarotation, $M[\alpha]$ after 48 hr. becoming $+230^\circ$. The changes of sign are attributed to rotation of the meconic group around its linking with the isoquinoline nucleus. C. A. S.

Absolute configuration of optically active compounds. W. KUHN and K. BEIN (Z. physikal. Chem., 1934, B, 54, 335–369; cf. A., 1933, 211).—By means of models the optically active behaviour of compounds of the type of pentaerythritoldipyrvic acid and $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$ (I) in absorption bands in the near ultra-violet and visible has been calc. The fundamental assumption is that the coupling forces which are effective between various parts of the mol. in optical oscillations can be deduced, at least as far as sign is concerned, from the polarisability of the various parts of the mol. and the vibrational scattering moments in the adjoining parts. This affords a semi-quant. explanation of the observed behaviour of (I). Relations are deduced permitting the calculation of the anisotropy factor of an absorption band having a scattering moment of any form. With asymmetric compounds the optical activity of which is due to unsymmetrical arrangement of like symmetrical parts, the absorption bands are resolved into parts the anisotropy factors of which for a given band differ in magnitude and at times in sign. This has been detected with the two absorption regions of (I) in the visible, and from comparison of the optical properties of (I) with those of a model, it has been possible to deduce the abs. configuration of the isomeride which is laevorotatory in Na-D light. These conclusions have been confirmed by measurements of the absorption, rotation, and circular dichroism at 2600–9000 Å. R. C.

Solvent action. VIII. Rotatory powers of the *l*-menthyl esters of *o*-nitro-, 2:4-dinitro-, and *p*-nitro-benzoic acids in relation to the solvent, concentration, temperature, and wavelength of light. A. McLEAN (J.C.S., 1934, 351–360; cf. A., 1933, 1110).—Solutions of the first two groups of esters in benzenoid solvents show rotatory powers varying inversely as the dipole moment of the solvent, the relation being quant. for solvents of weak or medium polarity, and becoming qual. with strongly polar solvents, indicating solvent influence through dipole association between solvent and solute. No regularity is observed for the effect of solvents on the rotation of the *p*-nitro-ester. For non-polar solvents, an explanation of the effects of concn. and temp. on

rotatory power is advanced in terms of dipole association. For the series of related solvents, the consts. in three-const. Drude equations are calc. from dispersion data; for approx. const. solute concn., the dispersion const. λ^2 increases with the polarity of the solvent. An explanation in terms of dipole association is given. N. M. B.

Stereochemical structure. VI. The isomeric (–)-menthyl α -naphthylglycolates. R. ROGER and E. R. L. GOW (J.C.S., 1934, 130–137).—The dispersions of (–)- α -naphthylglycolic acid and (–)-menthyl (–)- α -naphthylglycolate (I) are normal and slightly complex, whilst that of the (+)- α -naphthylglycolate (II) is normal and definitely complex. The dispersion of (–)-menthyl *dl*-naphthylglycolate (purified by treatment of the Et_2O solution with C) is normal and almost simple, and identical with that found for equimol. mixtures of (I) and (II), for (I) and (II) superimposed in separate tubes, and may be calc. by superposition of the vals. from (I) and (II). This and other examples of superposability are discussed, and it is concluded that it is not related to the formation of *dl*-compounds. A. A. L.

Kasolite. J. MELON (Bull. Acad. roy. Belg., 1934, [v], 20, 178–182).—The orientation of the optical axes of kasolite ($3\text{PbO} \cdot 3\text{UO}_2 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$) has been measured. The crystal is strongly birefringent. J. W. S.

Magnetic rotation of hydrogen selenide. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1934, 198, 1030–1031).—Verdet's const. is 61×10^{-6} (λ 5780), and the mol. rotation 40×10^{-5} ; the resultant at. rotation of Se is 36×10^{-5} . C. A. S.

Kerr effect with benzene derivatives. G. OTTERBEIN (Physikal. Z., 1934, 35, 249–265).—The determination of the Kerr effect in dil. solutions is discussed, and a mixture formula is derived. A simple apparatus, employing the Brace compensation method, for determining the Kerr const. in dil. solutions is described. Observations with C_{10}H_8 and 1- and 2- $\text{C}_{10}\text{H}_7\text{Cl}$ show that a simple addition of polarisation tensors does not always lead to correct results. A. J. M.

Spectroscopy and valency. II. Periodic groups of non-hydride diatomic molecules. C. H. D. CLARK (Proc. Leeds Phil. Soc., 1934, 2, 502–512; cf. A., 1932, 901).—A system of classification of diat. mols. is suggested which emphasises the relations between mols. of similar kinds. The spectroscopic features of the mols. which should occupy gaps in the table can be forecast. H. S. P.

Primary and secondary valencies of nitrogen as deduced from the crystal structure of hexamethylenetetramine. R. REINICKE (Z. Krist., 1934, 87, 417–422).—The author's theory of tetrahedral domains (cf. A., 1931, 1001; 1932, 563; 1933, 450) is shown to give a satisfactory explanation of the mol. and crystal structure of $(\text{CH}_2)_6\text{N}_4$. C. A. S.

Theory of the structure of ethylene. Structure of ethane. W. G. PENNEY (Proc. Roy. Soc., 1934, A, 144, 166–187).—Two methods, that of electron pairs and that of mol. orbits, used to determine the structure of the C_2H_4 mol. give consistent results. The

most stable arrangement has all six nuclei coplanar, with a large HCH angle (about 130°). Similar calculations on the C_2H_6 mol. show that it is only the H-H repulsions which prevent free rotation of the Me group about the C-C axis. L. L. B.

Hydrazoic acid. E. C. FRANKLIN (J. Amer. Chem. Soc., 1934, 56, 568—571).—Numerous reactions of HN_3 are consistent with the constitution H·N·N·N·.

E. S. H.

Molecular structure of carbon suboxide. H. BOERSCH (Naturwiss., 1934, 22, 172).— C_3O_2 is probably $O=C\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}C$; $a=1.2$, $b=1.3$, $c=1.2$, $d=1.51$, $e=1.13$, $f=1.3$ Å.

A. J. M.

Comparative chemistry. III. Binary compounds of hydrogen. IV. Binary compounds of halogens. V. Didactic importance. I. N. LONGINESCU (Bul. Chim. Soc. Romana Științe, 1932, 35, 21—24, 45—51, 103—106).—Theoretical. Four kinds of combination are suggested. R. T.

Apparent molecular association of some aliphatic acids. G. BROUGHTON (Trans. Faraday Soc., 1934, 30, 367—372).—The apparent mol. association of a no. of aliphatic acids has been determined cryoscopically in cyclohexane (I). HCO_2H and $AcOH$ have an association factor > 2 because their solutions in (I) deviate from ideal. More ideal solutions might have been expected with a lengthening chain, but $C_{15}H_{31}CO_2H$ and $C_{13}H_{27}CO_2H$ deviate from Raoult's law to an extent $> C_5H_{11}CO_2H$, $C_7H_{15}CO_2H$, and $C_{11}H_{23}CO_2H$, the last having a min. deviation. Lateral adhesion between chains may take place when these are long. M. S. B.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1933, [v], 19, 1364—1376; cf. A., 1933, 1232; this vol., 133).—Theoretical. J. W. S.

Chemical formulæ of compounds containing hydrogen and oxygen isotopes. R. A. GORTNER (Science, 1934, 79, 203—204). L. S. T.

Naming hydrogen isotopes. W. A. BOUGHTON (Science, 1934, 79, 159—160). L. S. T.

Natural classification of chemical elements and compounds. F. M. SCHEMJAKIN (Uspekhi Khim., 1933, 2, 630—642).—A review. CH. ABS.

Law of multiple proportions. A. ROSE (Science, 1934, 79, 206; cf. this vol., 234). L. S. T.

Magnetic susceptibility of liquid ozone and of mixtures thereof with liquid oxygen. P. LAINE (Compt. rend., 1934, 198, 918—919; cf. A., 1933, 449).—By similar methods the magnetic susceptibility of O_3 at temp. near that of liquid air is determined to be about 1.5×10^{-7} and its thermal variation to be $< 1/3$ of that required by the Curie law. By maintaining a vac. above an agitated mixture of liquid O_2 and O_3 , liquid O_3 containing $< 0.01\%$ O_2 can be obtained. C. A. S.

Magnetism of B_2H_6 . L. FARKAS and H. SACHSSE (Trans. Faraday Soc., 1934, 30, 331—333).—The conversion of para- into ortho- H_2 in presence of B_2H_6 at different temp. has been studied. The reaction velocity coeffs. and collision efficiencies

indicate that the observed conversion is not caused by the paramagnetism of B_2H_6 . At 195° abs. there is no conversion, hence the ground level of B_2H_6 must be diamagnetic. It is suggested that the para- H_2 conversion effected by B_2H_6 in the homogeneous reaction must be due to exchange of the para- H_2 with part of the H of B_2H_6 . M. S. B.

Magnetic study of hydrated thoria. F. BOURLON and (Mlle.) D. BEAU (Compt. rend., 1934, 198, 916—918).—The magnetic susceptibility varies linearly with the content of H_2O , indicating a mixture and not a true hydroxide (cf. A., 1923, ii, 25; 1929, 20). C. A. S.

Diamagnetism of nitroso-compounds. E. B. WILSON, jun. (J. Amer. Chem. Soc., 1934, 56, 747).— $NOCl$, $PhNO$, and $p-NMe_2 \cdot C_6H_4 \cdot NO$ are diamagnetic. It is inferred that these compounds are in singlet states. E. S. H.

Paramagnetism of rare-earth ions. C. J. RODDEN (J. Amer. Chem. Soc., 1934, 56, 648—649).—Magnetic susceptibilities at room temp. are recorded for $Pr_2(SO_4)_3 \cdot 8H_2O$, $Nd_2(SO_4)_3 \cdot 8H_2O$, Nd_2O_3 , $NdFe(CN)_6 \cdot 4H_2O$, $Sm_2(SO_4)_3 \cdot 8H_2O$, Sm_2O_3 , and $Yb_2(SO_4)_3 \cdot 8H_2O$. The results are discussed in the light of Van Vleck's theory of paramagnetism. E. S. H.

Energetics of ferromagnetic materials. R. GANS (Magnetismus, Leipziger Vorträge, 1933, 91—110; Chem. Zentr., 1933, ii, 2651).—A review of the energy relations in ferromagnetic phenomena. H. J. E.

Ferromagnetism in the oxide obtained by dehydration of gamma ferric oxide hydrate. L. A. WELO and O. BAUDISCH (Phil. Mag., 1934, [vii], 17, 753—768; cf. A., 1932, 709).—Dehydration of paramagnetic $\gamma-Fe_2O_3 \cdot H_2O$ was studied by measurements of the magnetic properties of the ferromagnetic $\gamma-Fe_2O_3$ formed. Dehydration is slow at 180° , and rapid at 240° , whilst at 285° $\gamma-Fe_2O_3$ forms paramagnetic $\alpha-Fe_2O_3$. From X-ray measurements the crystals of $\gamma-Fe_2O_3$ are very small initially. They grow, and simultaneously change their magnetic characteristics, above 180° . Colloidal $\gamma-Fe_2O_3$ shows a similar dependence of permeability and susceptibility on particle size. H. J. E.

Shape of molecules. N. V. SIDGWICK (Proc. Roy. Inst., 1934, 28, 35—45).—A lecture.

Parachor of sulphur hexafluoride and the single electron linking. A. H. SPONG (Chem. and Ind., 1934, 312).—The parachor of SF_6 cannot be considered as sufficient evidence for the structure (I) suggested by Pearson and Robinson (this vol., 132); (I) is improbable owing to the singlet linkings involved, and, on certain assumptions, the ordinary symmetrical non-polar structure would lead to the parachor 147.0 [actual val. 143.3; val. calc. for (I) 148.6]. D. R. D.

Dissociation of diatomic molecules with $p-p$ binding. H. LESSHELM and R. SAMUEL (Z. Physik, 1934, 88, 276).—Corrections to an earlier paper (cf. A., 1933, 996).

Relation between internuclear distances and linking force constants. R. M. BADGER (J. Chem.

Physics, 1934, 2, 128—131).—For diat. mol. the relation between linking force const. k_0 and inter-nuclear distance r_e is $k_0(r_e - d_{ij})^3 = 1.86 \times 10^5$, where d_{ij} is a const. depending only on the rows in the periodic table in which the two elements comprising the mol. are located. The expression holds for the normal and, with a few possible exceptions, all excited states. Uses, and an extension to polyat. mol., are discussed. N. M. B.

Energies of the atomic linkings in methane, ethane, methyl and ethyl alcohols. F. D. ROSSINI (J. Chem. Physics, 1934, 2, 145).—Data on heats of combustion show that the energy of breaking a C-H linking in the R-CH₃ mol., and forming R-CH₂-OH is appreciably affected by the nature of R, and that the energies of the at. linkings in these and homologous compounds are not additive. N. M. B.

Connexion between chemical constitution and K-X-ray absorption spectra. XIV. K-X-Ray absorption spectra of stereoisomerides. II. O. STELLING (Z. physikal. Chem., 1934, B, 24, 407—428; cf. this vol., 133).—The Cl absorption spectrum of org. Cl-compounds, which consists of two edges similar to those of inorg. Cl-compounds with non-ionic Cl, has been studied. With saturated CH₄ derivatives the short-wave edge shifts towards shorter waves with increase in the no. of Cl atoms attached to the central C atom. In Cl₁-substituted C₂H₄ derivatives the short-wave edge of the Cl is influenced principally by the group in the *cis* position to the Cl, CO₂H shifting the edge to considerably shorter wave-lengths, whilst Me causes a slight shift in the opposite direction; the *trans* group is of little moment. Of isomeric $\alpha\beta$ -Cl₂-substituted C₂H₄ derivatives the isomeride with Cl in the *cis* position has the hardest short-wave edge. With C₆H₆ derivatives the hard edge becomes increasingly soft in the order $o < m < p$. The position of the long-wave edge is the same for all saturated compounds, but different from that of the corresponding edge of Cl linked to -C:C. Nuclear-substituted C₆H₆ derivatives give the same edge as C₂H₄ derivatives. R. C.

Liquid crystals. (SIR) W. BRAGG (Proc. Roy. Inst., 1934, 28, 57—92).—A lecture.

Liquid crystals obtained by rapid evaporation of an aqueous solution. P. GAUBERT (Compt. rend., 1934, 198, 951—953; cf. this vol., 18).—Both liquid and solid crystals of tartrazine are hydrated. The birefringence of its smectic state is $<$ that of calcite, and $>$ that of its nematic state. Certain dyes, e.g., Na alizarinsulphonate, increase the stability of the nematic constitution. A solution of brilliant-crocoine gives rise to a viscous birefringent liquid. C. A. S.

Comparative X-ray and optical investigations with the anisotropic and isotropic melts of *p*-azoxyanisole. W. KAST (Ann. Physik, 1934, [v], 19, 571—581).—X-Ray photographs of diffraction of monochromatic rays at the liquid cryst. and normal liquid phases of *p*-azoxyanisole (I) show that in both cases only one ring is obtained, and that the variation of intensity in the rings is the same. The difference between the two phases must lie in the different

structures of the mol. aggregates, being isotropic in the case of the normal melt, and anisotropic in that of the liquid cryst. The solid cryst. phase of (I) shows a very high val. of the double refraction, like the liquid-cryst. phase. A. J. M.

Crystallisation of melts. J. MEYER and W. PFAFF (Z. anorg. Chem., 1934, 217, 257—271).—By careful filtration through fine sintered glass filters crystallisation nuclei can be removed from fused salol, thymol, C₆H₅, *o*- and *m*-cresol, C₆H₅Me, and guaiacol so that the supercooled melt no longer shows a readiness to crystallise, even on freezing and introducing some of the solid into the supercooled liquid and remelting. The nuclei apparently consist of foreign particles removable by filtration. For this reason no conclusions can be reached by means of crystallisation experiments regarding the polymorphic relations of the crystallising substances, as has hitherto been done erroneously for *allocinnamic acid*. M. S. B.

Modification of form of crystals grown in solutions containing foreign materials. L. ROYER (Compt. rend., 1934, 198, 949—951). C. A. S.

Manner of separation of small quantities of foreign substances in crystallising salts. O. HAIN, H. KADING, and R. MUMBRAUER (Z. Krist., 1934, 87, 387—416; cf. A., 1931, 1225, 1230; 1932, 359).—Photographs, taken at intervals, of the same crystal as it grows in a solution containing, in addition to the main substance, a suitable radioactive isotope, e.g., Th-B, Ra-X, or Po, show the distribution of the latter. C. A. S.

Differences in lattice constant between single crystals and polycrystalline materials. P. WIEST (Metallwirtsch., 1933, 12, 255; Chem. Zentr., 1933, ii, 2499).—Phillips and Brick's results (A., 1933, 1234) have been confirmed for Ag-Cu alloys. Lattice consts. are not functions of the grain size, but of the mechanical and thermal treatment. H. J. E.

Primary crystallisation of metals. Influence of temperature gradients on the orientation of zinc single crystals. V. D. KUZNETZOV and D. D. SARATOVKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 248—255).—Crystal orientation from Zn melts in glass tubes (0.3—0.5 cm. diameter) has been correlated with conditions of cooling; both single and poly-crystals form, depending on conditions. Single crystals are oriented with the hexagonal axis perpendicular to the greatest temp. gradient, influenced by the no. of crystallisation centres. H. J. E.

Change of shape of alternately twisted cadmium crystals. W. FAHRENHORST and H. EKSTEIN (Z. Metallk., 1933, 25, 306—308).—When a round, single-crystal Cd wire is subjected to 100,000 alternate twists of $\pm 5^\circ$ the cross-section becomes distorted (S-shaped), two sharp ridges appearing at opposite ends of a diameter. A crystallographic analysis of the stresses causing this change of shape is given. A. R. P.

Influence of the shaping process on the crystal orientation in [metal] wires. G. VON VARGHA

and G. WASSERMANN (Z. Metallk., 1933, 25, 310—313).
A. R. P.

Lattice constants of cubic space-centred β -tungsten. M. C. NEUBURGER (Z. anorg. Chem., 1934, 217, 154—156).—The longer-known cubic space-centred modification of W is formed from the more recently discovered modification (A., 1931, 805) above 600—650°, and therefore the latter is more suitably described as α -W and the cubic space-centred form as β -W. The following vals. for the lattice consts. of β -W have been determined: a 3.1589 \pm 0.0004 Å. at 20°, in good agreement with previous determinations, the shortest at. distance 2.7357 Å., at. radius 1.368 Å., no. of atoms in unit cell 2, and d_{calc} 19.24 at 20° (cf. A., 1933, 665).
M. S. B.

Nomenclature [of the two modifications of tungsten]. F. EBERT and H. HARTMANN (Z. anorg. Chem., 1934, 217, 156).—Since the new modification of W has already been described in the literature as β -W, confusion would be avoided by retaining the name α -W for the cubic space-centred form, contrary to Neuburger's suggestion (cf. preceding abstract).
M. S. B.

Structure of cold-worked threads of silver chloride, and their recrystallisation. V. CAGLIOTI (Atti R. Accad. Lincei, 1933, [vi], 18, 570—574).—X-Ray investigation shows that in cold-worked AgCl threads the crystallites are oriented partly along the (111) axis, but mainly along the (100) axis. The latter arrangement is still more marked in the recryst. structure after heat-treatment at 250°. O. J. W.

Fibrous structure in ionic lattices. G. R. LEVI and M. TABET (Atti R. Accad. Lincei, 1933, [vi], 18, 574—579).—Threads of AgCl and AgBr formed under pressures of 3.4—3.5 atm. show a marked fibrous structure. AgCl is oriented along the (111) and AgBr along the (100) axis. TlCl, TlBr, and AgI threads show no fibrous structure.
O. J. W.

Crystal hydrates. I. Structure of magnesium chloride and bromide hexahydrates. K. R. ANDRESS and J. GUNDERMANN (Z. Krist., 1934, 87, 345—369).—These are monoclinic, with 2 mols. in the unit cell, and respectively a 9.90, b 7.15, c 6.10, β 94°, and a 10.25, b 7.40, c 6.30, β 93° 30'; space-group C_{2v} — $C/2m$. The 6H₂O are arranged octahedrally around a Mg atom, each such group is surrounded by eight halogen atoms, six in the same plane with the Mg, of which four are distant therefrom 4.7₅, and two 4.8₅ Å., whilst two are vertically above and below the Mg and distant 4.1₅ Å.; these last two are the two in direct connexion with that Mg atom.
C. A. S.

Crystal structure of anhydrous zinc sulphate. K. SCHIFF (Z. Krist., 1934, 87, 379—386).—ZnSO₄ is rhombic, a 8.58, b 6.73, c 4.76 Å., with 4 mols. in the unit cell.
C. A. S.

Calcium sulphate hemihydrate and soluble anhydrite. P. GALLITELLI [with W. BUSSEM] (Periodico Mineralogia, 1933, 4, 1—42; Chem. Zentr., 1933, ii, 3391).—The hemihydrate is monoclinic (a 11.94, b 6.83, c 12.70 Å., 12 mols. CaSO₄·0.5H₂O in unit cell; space-group C_{2v}). Anhydrite made by dehydration of the hemihydrate has the same structure,

characterised by chains of CaSO₄ mols. along the c axis, between which the H₂O mols. are accommodated.
H. J. E.

Structure of the trithionate group (S₃O₆)⁻². W. H. ZACHARIASEN (J. Chem. Physics, 1934, 2, 109—111; cf. A., 1932, 903).—The group structure is found from the crystal lattice of the K compound; two of the S atoms form four linkings each, three with O atoms and one with S, and are directed to the corners of a tetrahedron. The third S atom forms only two linkings, both with S atoms; the angle is 103°. The S—O distance is 1.50, and S—S 2.15 Å. N. M. B.

Crystal structure of barium nickelocyanide. H. BRASSEUR, A. DE RASSENFOSSE, and J. PIERARD (Compt. rend., 1934, 198, 1048—1050).—BaNi(CN)₄ crystallises with 4H₂O, not 3 (cf. A., 1871, 389), is monoclinic, d_{20} 2.383. X-Ray examination gives a 11.89, b 14.08, c 6.54 Å., β 103° 42', with 4 mols. in the unit cell, identical with the structure of BaPt(CN)₄·4H₂O. [Ni(CN)₄]²⁻ is therefore planar with the Ni in the centre of a square formed by 4(CN) (cf. A., 1933, 1107).
C. A. S.

Structure and formula of 12-phosphotungstic acid. J. F. KEGGIN (Proc. Roy. Soc., 1934, A, 144, 75—100).—The structure of the mol. of 12-phosphotungstic acid, H₃[PW₁₂O₄₀] _{n} · n H₂O, has been found by X-ray analysis, using the powder method. The anion consists of a central PO₄ tetrahedral group surrounded by 12 WO₆ octahedral groups, linked by shared O atoms. The positions of the atoms are given. The symmetry is O_h . In the partly dehydrated acid ($n=5$) the anions pack together with cubic symmetry (O_h), the edge of the unit cube being 12.14 \pm 0.005 Å. There are 2 mols. of acid per unit cell. Most of the chemical evidence supports this formula. L. L. B.

Crystal structure of thallic dimethyl halides. H. M. POWELL and (Miss) D. M. CROWFOOT (Z. Krist., 1934, 87, 370—378).—TlMe₂Cl, d_4^{25} 3.445, TlMe₂Br, d_4^{25} 3.790, and TlMe₂I, d_4^{25} 3.909, are tetragonal. The unit cells are body-centred tetragonal, a 4.29, 4.47, 4.78; c 14.01, 13.78, 13.43 Å., respectively, and contain 2 mols.
C. A. S.

Polymorphic phenomena and crystal structure. T. F. W. BARTH (Amer. J. Sci., 1934, [v], 27, 273—286).—Polymorphic manifestations are classified. Potash feldspar is trimorphous. A structural relation between orthoclase and microcline is suggested.
C. W. G.

Crystal structure of 1 : 3 : 5-triphenylbenzene. K. S. KRISHNAN and S. BANERJEE (Nature, 1934, 133, 497).—The magnetic susceptibilities along the a , b , and c axes support the view (this vol., 134) that the C₆ rings are inclined to the (001) plane at an angle of 24°. The optical consts. also support this orientation.
L. S. T.

Films of cellulose nitrate and their polymorphism. J. J. TRILLAT (J. Chim. phys., 1934, 31, 125—137).—Films of cellulose nitrate (I) containing 13% N and prepared with COMe₂ (II) and EtOAc (III) exhibit X-ray diagrams characteristic of two different cryst. forms, one of which disappears rapidly and the other more slowly as drying proceeds. (I) with < 13% N is amorphous. Butyl and amyl

acetate alone and mixed with COMe_2 afford (I) of the ordinary structure, showing that (I) probably forms cryst. additive products with (II) and (III). Dissolution and re-formation of the film reproduce the same series of phenomena. Experiments with stretched films show that the swelling and contraction are due to addition and removal of solvent mols. perpendicularly from the direction of the C chains.

J. G. A. G.

Electron diffraction by cellulosic films. J. J. TRILLAT (Compt. rend., 1934, 198, 1025—1027).—When 20—25-kv. electrons pass through films of cellulose nitrate (13% N), acetate, propionate, and butyrate, the diagrams show that the film when freshly prepared is usually amorphous, but that microcrystals appear in a few hr., and that in a few days the whole film is cryst. The cellulosic chains lie parallel and flat in the film with equiv. atoms at the nodes of a monoclinic network with a 7.10, b 4.68, c 2.5 or 5.0 Å.

C. A. S.

Diffraction of rapid electrons by talc. G. AMINOFF and B. BROOME (Arkiv Kemi, Min., Geol., 1934, 11 B, No. 25, 5 pp.).—Talc is hexagonal or pseudohexagonal, with a 5.25 Å.

D. R. D.

General proof of certain fundamental equations in the theory of metallic conduction. H. JONES and C. ZENER (Proc. Roy. Soc., 1934, A, 144, 101—117).

Magneto-caloric effect in superconducting tin. K. MENDELSSOHN and J. R. MOORE (Nature, 1934, 133, 413).—Measurements of the adiabatic magnetisation and demagnetisation of superconducting Sn at 2.5—4.0° abs. show a cooling effect on magnetisation and heating on demagnetisation.

L. S. T.

Piezoelectric properties of Rochelle salt. P. D. SHULBAS-SOROKINA (J. Tech. Phys., U.S.S.R., 1931, 1, 756—760).—The val. of the modulus is 10 times that given by Valasek (Physical Rev., 1924, 24, 560).

CH. ABS.

Discontinuities of resistance associated with the Barkhausen effect. C. W. HEAPS (Physical Rev., 1934, [ii], 45, 320—323).—A Ni wire under bending stress shows a jump of magnetoresistance associated with the magnetisation jump.

N. M. B.

Light absorption by metals. A. SMAKULA (Z. Physik, 1934, 88, 114—126; cf. A., 1933, 1226).—Chemically related metals show similar absorption curves.

A. B. D. C.

Elastic behaviour and elastic constants of zinc single crystals. A. W. HANSON (Physical Rev., 1934, [ii], 45, 324—331).—For each crystal orientation there is a limited region of proportionality between an initially increasing stress and the corresponding strain, and this is a min. for crystals of 45° orientation. Elastic hysteresis occurs for bending, but not for torsion. Elastic const., differing appreciably, are given for two grades of 99.99+ % pure Zn. The behaviour of the single-crystal form is definite, but variable for the polycryst. and technical forms.

N. M. B.

Is liquid benzene allotropic? E. COHEN and J. S. BUY (Proc. K. Akad. Wetensch. Amsterdam,

1934, 37, 55—61).—From a consideration of published work it is inferred that no allotropic change occurs between 0° and 70° (cf. this vol., 353).

E. S. H.

Magneto-thermo-electrical effects in nickel and iron: theoretical interpretations. A. PERRIER and (Mlle.) T. KOUSMINE (Compt. rend., 1934, 198, 920—921; cf. this vol., 353).—The thermo-electric anisotropies (ΔE_{\parallel} — ΔE_{\perp}) of Ni and Fe are, respectively, 43.7 and 14.8×10^{-8} volt per degree; Both ΔE_{\parallel} and ΔE_{\perp} are intrinsic properties of the metal independent of contact potential.

C. A. S.

Thermal power generated by twisting zinc and cadmium wires. G. TAMMANN and G. BANDEL (Ann. Physik, 1934, [v], 19, 582—584).—The differences between Zn and Cd and other metals as regards the thermal power produced by twisting are discussed.

Superconductivity. I. C. J. GORTER and H. CASIMIR (Physica, 1934, 1, 306—320).—Theoretical.

H. J. E.

Intensity determinations for the explanation of the depolymerising action of ultrasonic waves. A. SZALAY (Physikal. Z., 1934, 35, 293—296).—Highly polymerised substances, such as starch, in aq. solution, are hydrolysed when exposed to ultrasonic waves. By comparing the energy imparted to the system by direct heating and that imparted by the waves, it was found that the effect of placing the solution in the ultrasonic beam was the same as heating it to 100°.

A. J. M.

Softening of vitreous substances. E. RENCKER (Compt. rend., 1934, 198, 934—936; cf. B., 1934, 351).—Differential cooling curves for B_2O_3 , HPO_3 , etc. show that at the transformation or softening point there is merely a change in the sp. heat; this coincides with the change in the coeff. of dilatation (cf. B., 1921, 347; A., 1928, 354; 1930, 862).

C. A. S.

Para-ortho conversion of deuterium. A. FARKAS, L. FARKAS, and P. HARTECK (Science, 1934, 79, 204).—The thermo-conductivity method shows the para-ortho conversion of H_2 at 78°, 53°, and 20.4° abs., changes in readings relative to normal H_2 being in the ratio 3 : 11 : 30, respectively. This agrees with the Bose-Einstein statistics if the nuclear spin of the deuteron is one which gives excess concn. of 3.3, 11.1, and 31.2%, respectively, of ortho- H_2 at these temp. relative to normal H_2 . The velocity coeff. of reconversion of ortho- H_2 by O_2 (0.57 litre per mol. per min.) at room temp. is $\frac{1}{15}$ that of para- H_2 .

L. S. T.

Ortho- and para-states of hydrogen of mass 2. Temperature variation of heats of rotation of H_2 . H. MOTZ and F. PATAT (Monatsh., 1934, 64, 17—20).—Theoretical. The equilibrium proportions of ortho- and para- H_2 are calc. for the range 10—110° abs.

E. S. H.

International Bureau of Physico-chemical Standards. Physical constants of twenty organic compounds. J. TIMMERMANS and (Mlle.) Y. DELCOURT (J. Chim. phys., 1934, 31, 85—124).—The following data for b.p./760 mm., m.p., and d_{15}^{15} have been determined: MeI 42.50°, —66.45°, 2.29300,

Pr^aI 102.45°, -101.3°, 1.75840, Pr^βI 89.45°, -90.1°, 1.71371, CCl₂Me₂ 70.5°, -34.4°, 1.09843, Bu^aI 130.40°, -103.0°, 1.62366, Bu^βI 121.0°, -93.5°, 1.61176, Bu^βBr 91.20°, -111.9°, 1.26808, *sec.*-BuI 120.0°, -104.0°, 1.60584, Bu^βCl 50.7°, -27.1°, 0.84739, Bu^βBr 73.25°, -16.2°, 1.22861, PrOH 97.15°, vitreous in liquid air, 0.80749, Pr^βOH 82.40°, -89.5°, 0.78916, Bu^βOH 82.50°, 25.55°, *d*²⁰ 0.78670, Pr^βCO₂H 154.70°, -46.1°, 0.95296, Et malonate 199.30°, -51.5°, 1.06040, EtCN 97.20°, -91.9°, 0.78673, Pr^βCN 117.9°, -111.9°, 0.79544, Pr^βCN 103.85°, -71.5°, 0.77511, Bu^βCN 141.30°, -96.0°, 0.80350, Bu^βCN 130.5°, -100.85°, 0.79490. The data include the relation between b.p. and pressure, coeffs. of dilatation, r_{λ}^{λ} , viscosity coeffs., and surface tensions. Earlier data are tabulated. J. G. A. G.

Exact measurement of the specific heat of solid substances at higher temperatures. XIII. Specific heats of vanadium, niobium, tantalum, and molybdenum from 0° to 1500°. F. M. JAEGER and W. A. VEENSTRA. XIV. Specific heats and thermal retardation phenomena of beryllium. F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 61—66, 67—76).—XIII. The following true sp. heats have been determined: V 0.11846 + 0.313734 × 10⁻⁴t - 0.675396 × 10⁻⁸t² + 0.14184 × 10⁻¹¹t³; Nb 0.06430 + 0.772766 × 10⁻⁵t + 0.234774 × 10⁻⁸t²; Ta 0.033218 + 0.4198 × 10⁻⁵t + 0.3295 × 10⁻⁹t²; Mo 0.061046 + 0.0616043 × 10⁻⁴t + 0.0345454 × 10⁻⁸t².

XIV. The apparent sp. heat of cast Be varies with the thermal treatment. When Be is reduced to fine powder const. vals. are obtained at a given temp. represented by $c_p = 0.414032 + 0.719894 \times 10^{-3}t - 0.2221422 \times 10^{-6}t^2 - 0.1436704 \times 10^{-8}t^3 + 0.156547 \times 10^{-11}t^4$. E. S. H.

Does the fusion of crystalline substances depend on the previous and subsequent history? M. LE BLANC and E. MOBIUS (Ber. Verh. Sachs. Akad. Wiss., math.-phys. Kl., 1933, 85, 75—96; Chem. Zentr., 1933, ii, 3106).—Samples of pure C₆H₆ and C₂H₄Br₂ exhibit a rise of sp. heat just below the m.p., due to residual impurities. The sp. heat of liquid C₆H₆ has a min. val. (for the range 5.15—30°) at 18°. A change in mol. state is excluded by the const. val. of $C_p - C_v$, and the min. val. is attributed to residual orientation in the liquid. C₂H₄Br₂ has a similar min. H. J. E.

Heat conduction in a solid in contact with a well-stirred liquid. A. N. LOWAN (Phil. Mag., 1934, [vii], 17, 849—854).—Theoretical. H. J. E.

Thermodynamic properties of helium gas. J. R. ROEBUCK and H. OSTERBERG (Physical Rev., 1934, [ii], 45, 332—340).—Joule-Thomson coeffs. (cf. A., 1932, 218) and *p**v* data are used to calculate variation of sp. heat with pressure, sp. vol., coeff. of vol. expansion, elastic coeff., coeff. of free expansion η , and intrinsic energy variation with vol, λ . Simple relationships exist between η and λ . η is independent of pressure *p* and λ is proportional to *p*² except at low temp. Both η and λ are zero at about -70°, and are positive below and negative above this temp. The pressure and temp. behaviour of η and λ is explained kinetically. N. M. B.

V.p. of fluorine. W. H. CLAUSSEN (J. Amer. Chem. Soc., 1934, 56, 614—615).—The v.p. (6.3—75.2 cm.) is given by $\log_{10} P(\text{cm.}) = -462.66/T + 8.7202 - 0.016567T$. F₂ has b.p. 85.21 ± 0.1° abs., calc. heat of vaporisation 1560 g.-cal. per mol.

E. S. H.

Vapour pressure of benzanthrone and of quinizarin. W. WENZEL and H. PIRAK (Coll. Czech. Chem. Comm., 1934, 6, 54—59).—Data, by the gas saturation method, are recorded for the ranges: benzanthrone 180° (0.17 mm.) to 280° (6.10 mm.) and quinizarin 200° (1.15 mm.) to 260° (11.0 mm.).

J. G. A. G.

Saturation pressure of radium emanation at low temperatures. L. WERTENSTEIN (Acta phys. polon., 1933, 2, 131—136; Chem. Zentr., 1933, ii, 3107).—At the b.p. of liquid O₂ the v.p. was 0.05 bar. H. J. E.

Low-pressure data of state of nitric oxide and of nitrous oxide between their b.p. and room temperature. H. L. JOHNSTON and H. R. WEIMER (J. Amer. Chem. Soc., 1934, 56, 625—630).—Apparatus and technique are described. Data of state have been determined for NO between 122° and 308° abs., and for N₂O between 197° and 298° abs., and the second virial coeffs. have been calc. for each gas. The data for both gases are represented by $PV_m = RT + BP$, where $B = 20 + 5881.5/T - 5.7639 \times 10^6/T^2 + 8.4301 \times 10^{10}/T^4 - 9.2783 \times 10^{14}/T^6$ c.c. per mol. for NO and $B = 32 - 5611.5/T + 3.9424 \times 10^6/T^2 - 3.9145 \times 10^{11}/T^4 + 3.0747 \times 10^{15}/T^6$ for N₂O. E. S. H.

Nernst's form of the equation for free energy. H. SCHMOLKE (Z. Physik, 1934, 88, 139—142).—Nernst's expression for free energy is shown to lead to exact results. A. B. D. C.

Dependence of the coefficient α of van der Waals' equation on temperature. IV. K. JABŁCZYŃSKI (Rocz. Chem., 1934, 14, 93—97).—Van der Waals' equation is formulated $f_2(w)T/w^2[(w-b)=RT]$, where *w* is the vol. of 1 mol. of gas. R. T.

Physical researches in the neighbourhood of absolute zero. F. HENNING (Chem.-Ztg., 1934, 58, 308—309).—A review.

Dilatation of fused silica. L. DUNOYER (Compt. rend., 1934, 198, 909—911, 1132—1134).—The method used depends on determining the form of the meridian line of a tube of the material when a definite temp. difference is maintained between two opposite generatrices of the tube. Applied to glass and fused SiO₂ it gave as the coeff. for temp. approx. between 0° and 40° 6.9 × 10⁻⁶ and -6.6 × 10⁻⁸, respectively. C. A. S.

Viscosity of *n*-heptadecane, tetra-*n*-butylmethane [ζ -di-*n*-butylnonane], and cycloheptadecane. P. KARRER and C. FERRI (Helv. Chim. Acta, 1934, 17, 358—362).—The prep. of the above compounds is described. The viscosity (η) of the first two in the fused condition at 30° has been determined, and also the sp. η of solutions of all three in C₆H₆ at two different concns. The results indicate that the space configuration of the mol. has a great influence on the η . η measurements can be used only for the deter-

mination of mol. wts. in homologous series of completely analogous structure. M. S. B.

Application of Batschinski's formula to the viscosity of fused salts at high temperatures. M. P. VOLAROVITSCH (Bull. Acad. Sci. U.R.S.S., 1933, 1431—1437).—For KNO_3 between 348° and 542°, Batschinski's formula $v=0.50315+0.000958\phi$ (A., 1913, ii, 928) gives results $\pm 0.98\%$ from the observed vals.; with Dantuma's interpolation formula (A., 1928, 1208), the mean deviation is $\pm 0.94\%$. For NaCl at 816—997°, $v=0.6066+0.000672\phi$. As Batschinski's formula holds only for non-associated liquids, fused KNO_3 and NaCl must be non-associated. For associated liquids the η - t relation is in accordance with Lasarev's form of Le Chatelier's formula, $\log \log \eta/\eta_0 - a - bt$. T. H. P.

Effect of magnetic field on the inner friction of oxygen. H. SACK [with H. ENGELHARDT] (Magnetismus. Leipziger Vortrage, 1933, 25—35; Chem. Zentr., 1933, ii, 3105).—The diminution in the inner friction by a field is $< 0.4\%$ for O. and air and $< 0.01\%$ for H_2 , N., and CO_2 . The effect is independent of pressure from 30 to 760 mm., and reaches a saturation val. with a field of 6000—8000 Oersteds. H. J. E.

Transport phenomena in degenerate gases. A. GANGULI and P. MITRA (Current Sci., 1934, 2, 295). D. R. D.

System aluminium-barium. E. ALBERTI (Z. Metallk., 1934, 26, 6—9).—The system contains a compound with $> 50\%$ Ba which forms a simple eutectiferous series with pure Al, the eutectic containing 2% Ba and melting at 651°. The liquidus rises sharply from this point, and reaches 1013° at 36.5% Ba; alloys with $> 5\%$ Ba could not be prepared. A. R. P.

System copper-silicon. K. SAUTNER (Forschungsarb. Metallkunde Röntgenmetallogr., No. 9, 30 pp.; Chem. Zentr., 1933, ii, 2226—2227).—Over the range 0—13% Si, thermal and X-ray data reveal six intermediary phases: α (Si 5.2%), cubic face-centred, a 3.60 Å.; β (Si 5.99%), hexagonal, a 2.40, c 3.91 Å., with 16 atoms per unit cell; ζ (Si 7.6%, stable at $> 760^\circ$), a 2.58, c 3.91 Å., identical with Westgren's β -phase; γ (Cu_3Si , Si 8.12%), m.p. 815°, a 6.21 Å.; 20 atoms per unit cell; d 7.95; δ , lattice consts. not determined; η (Cu_3Si , Si 12.8%), stable at high temp., cubic body-centred; a 9.69 Å., with 19 mols. per unit cell; ϵ ($\text{Cu}_{20}\text{Si}_3$, Si 12.26%), tetragonal body-centred, a 9.21 Å., $a:c$ 0.87, with 76 atoms in the unit cell. A. A. E.

Manganese-silicon equilibrium diagram. R. VOGEL and H. BEDARFF (Arch. Eisenhüttenw., 1933—1934, 7, 423—425).—A re-investigation of this system up to 35% Si by thermal analysis and micrographic observations shows it to be much more complex than found by Doerincel (A., 1906, ii, 676). The existence of MnSi (m.p. 1275°) and a eutectic (E_2) at 30% Si and 1235° have been confirmed, but the second constituent of E_2 is Mn_3Si_3 (m.p. 1280°) and not Mn_2Si , which does not exist. Mn_3Si_3 reacts with Mn-rich liquid at 1075°, forming the compound Mn_2Si , which can retain up to 1% Mn in solid solution.

Mn_2Si forms a eutectic with β -Mn saturated with Si at 12% Si and 1040°. The $\beta \rightleftharpoons \gamma$ transformation temp. of Mn is raised by addition of Si from 1100° to 1155° with 3% Si, and the $\alpha \rightleftharpoons \beta$ transformation from 770° to 900° with 10% Si; with increasing Si the $\alpha + \beta$ range becomes broader. With rise in temp. the α -($\alpha + \text{Mn}_3\text{Si}$) boundary is displaced towards the Si end. In the $\beta + \text{Mn}_3\text{Si}$ field with alloys containing 9—13% Si a heat effect occurs at 980°, the exact cause of which has not been elucidated, although it appears to be due to the formation of Mn_3Si .

A. R. P.

X-Ray investigation of alloys of silicon with chromium, manganese, cobalt, and nickel. B. BOREN (Arkiv Kemi, Min., Geol., 1934, 11 A, No. 10, 28 pp.).—The following compounds are formed in the system Cr-Si: Cr_3Si , cubic crystals with a 4.555 Å. and 8 atoms in the unit cell; a phase of uncertain composition and structure, stable only at $< \text{about } 1000^\circ$; CrSi, cubic, a 4.620 Å., space-group T^1 , 8 atoms in the unit cell, structure analogous to that of FeSi; CrSi_2 , hexagonal, a 4.422, c 6.351 Å., space-group D^1 . System Mn-Si: Mn_3Si , hexagonal, a 6.898, c 4.802 Å., 16 atoms in the unit cell; MnSi, with the FeSi structure, a 4.548 Å.; MnSi_2 , tetragonal, a 5.513, c 17.422 Å., probably 48 atoms in the unit cell. System Co-Si: Co_2Si , rhombic, a 3.730, b 4.908, c 7.095 Å., space-group C^2 , or V^6 , 12 atoms in the unit cell; CoSi, with the FeSi structure, a 4.438 Å. The investigation of the system Ni-Si is not yet completed, but NiSi has been shown to have the FeSi structure with a 4.437 Å. At. co-ordinates are given. Si dissolves Co and Ni, and Cr dissolves a little Si, with contraction of the lattice. Cr and Mn are insol. in Si. D. R. D.

Equilibrium diagram of the system nickel-zinc. II. K. TAMARU and A. OSAWA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 13—14; cf. A., 1932, 801).—The lattice structures of the α , β , γ , δ , and ϵ solid solutions have been determined by X-ray analysis. α is face-centred cubic; the parameter increases rapidly up to 20% Zn and reaches 3.592 Å. at 38.9% Zn. β is body-centred tetragonal, a 2.724, c 3.168 Å., c/a 1.163. γ , probably $\text{Ni}_3\text{Zn}_{10}$, is body-centred cubic, a 8.927 Å., 52 atoms in unit cell. δ -solid solution is face-centred tetragonal; a 3.867, c 3.203 Å., c/a 0.8278. ϵ is tetragonal, a 8.922, c 9.254 Å., c/a 1.0372; 50 atoms in unit cell. The ϵ phase, $\text{Ni}_3\text{Zn}_{22}$, contains 10.9% Ni. A peritectic reaction occurs at 517° between γ and the melt, forming ϵ . The reaction range lies between 13.5 and 0.5% Ni. Alloys containing 10—11% Ni increase in vol. by 3% with the formation of the ϵ phase. R. S.

Germanium. XV. Germanium-copper phase diagram. R. SCHWARZ and G. ELSTNER (Z. anorg. Chem., 1934, 217, 289—297).—The m.p. of Ge is 940°, which is $<$ that given by previous investigators. Several series of mixed crystals are formed. The eutectic is at 650° and 65 at.-% Cu. A compound Cu_3Ge , silver-white with a bluish tinge, is formed and probably undergoes an α - β transformation at 615°. Alloys up to 17 at.-% Ge are golden-yellow, and the yellowish tinge persists up to 24 at.-%; above that they are greyish-white. All the alloys are resistant

to HCl, attacked by conc. HNO_3 up to 25 at.-% Ge, but above that by aqua regia only; they are slowly decomposed by boiling H_2SO_4 . They are harder and more brittle than Cu, and Ge-rich alloys can be powdered in a mortar. M. S. B.

Praseodymium-magnesium alloys. G. CANNERI (Metallurg. ital., 1933, 25, 250—252; Chem. Zentr., 1933, ii, 2227).—Thermal and micrographical analysis indicates the existence of PrMg , m.p. 767° , and PrMg_3 , m.p. 798° ; Pr_2Mg is stable only between 528° and 752° . A. A. E.

Recrystallisation of iron alloys with a closed γ -field at the A3 and A4 points. A. HEINZEL (Arch. Eisenhüttenw., 1933—1934, 7, 479—482).—The recrystallisation during polymorphic transformation of alloys of Fe with Al, Si, V, and W in the γ -field has been studied. During cooling from the liquid state the no. of nuclei at the A4 transformation is independent of the amount of alloying element (E) present; grain refinement in the γ -field takes place only in the range up to $4/5$ of the saturation limit of E , and the crystallites formed at A4 become more regularly oriented with increase of E , until finally the fully oriented δ is converted first into regularly oriented γ , and then into regularly oriented α . The disappearance of the grain refinement is associated with the fall in the A4 temp. produced by addition of E , and therefore the recrystallisation of Fe at the A4 point is comparable with the recrystallisation of cold-worked metals. An explanation is given for the absence of recrystallisation at the A3 point and for the formation of α -veining instead. A. R. P.

Heat effects in the austenite-martensite transformation. H. ESSER and W. BUNGARDT (Arch. Eisenhüttenw., 1933—1934, 7, 533—536).—The heat contents of Ag, 20 : 80 Mn-Fe alloy, and steels with 0.5, 0.8, and 1.4% C between 300° and 900° have been determined with the aid of a new type of H_2O calorimeter, and from the results the heat effect at the austenite (A)-martensite transformation at 721° has been calc. as 13.6 g.-cal. per g. for steel with 0.5% C (I), 11.9 for steel with 0.82% C (II), and 11.4 for steel with 1.4% C (III). Magnetic measurements show that the A content of quenched (I) is always 2%, that of (II) falls from 8% after quenching at 750° to 6% after quenching at 1000° , and that of (III) rises from 6 to 25% in the same temp. range. A. R. P.

System Fe- Fe_3C -ZrC- Fe_3Zr_2 . R. VOGEL and K. LOHBERG (Arch. Eisenhüttenw., 1933—1934, 7, 473—478).—The system is divided into two similar sections by the line Fe-ZrC, which constituents form a pseudobinary system with a eutectic at Fe 88.82, Zr 9.88, and C 1.3%, 1460° , and a eutectoid at Fe 99.14, Zr 0.76, and C 0.1%, 780° ; the solid solubility of C as ZrC in the γ -phase rises from 0.1 at 780° to 0.8% at 1460° . In the pseudoternary system Fe- Fe_3C -ZrC (A) there is a eutectic plane at 1145° in which the binary Fe-C liquid is in equilibrium with a solid solution of C, Fe_3C , and ZrC in γ -Fe; similarly in the pseudoternary system Fe-ZrC- Fe_3Zr_2 (B) there is a eutectic plane at 1330° in which the binary Fe-Zr liquid is in equilibrium with a solid solution of Zr, ZrC, and Fe_3Zr_2 in γ -Fe. In A a plane of 4-phase

equilibrium occurs at 780° corresponding with the decomp. of γ with 0.1% C and 0.8% Zr into almost pure α -Fe and Zr in the presence of Fe_3Zr_2 , the quantity of which remains practically const.; in B a 4-phase equilibrium occurs at 721° corresponding with the eutectoid temp. of pearlite. In Zr steel the separation of Fe_3Zr_2 is accompanied by a reduction in hardness (H), but with increase in the ZrC content H increases; the structure of quenched Zr steels is martensitic, and the steels are much less brittle than plain martensitic steels. A. R. P.

Theory of alloys in the γ -phase. H. JONES (Proc. Roy. Soc., 1934, A, 144, 225—234).—Large diamagnetic susceptibilities and Hall coeffs. are to be expected for alloys in the γ -phase. These properties are related to the crystal structure of the alloys, and to the fact that the composition within the γ -phase follows the Hume-Rothery electronic rule. A reason is shown to exist for the ratio 21/13 of the no. of approx. free electrons to that of atoms. L. L. B.

Effect of X-ray analysis on the development of physical metallurgy. U. DEHLINGER (Arch. Eisenhüttenw., 1933—1934, 7, 523—526).—The use of X-rays in investigating the equilibrium diagrams and structure of alloys, the nature of transformations and pptns. in the solid state, and the effects of mechanical and heat-treatment on metals and alloys is briefly reviewed. A. R. P.

Mixtures of dipole liquids with dielectric constants independent of temperature. A. E. VAN ARKEL and J. L. SNOEK (Physica, 1934, 1, 271—272).—A solid substance is chosen which, when suspended in the liquid, changes the dielectric const. of the solvent (due to increasing solubility) sufficiently to compensate for the normal temp. coeff. of dielectric const. A mixture of $o\text{-C}_6\text{H}_4\text{Cl}_2$ and glyceryl triacetate with suspended $m\text{-C}_6\text{H}_4(\text{OBz})_2$ shows this behaviour. Al_2O_3 or TiO_2 stabilises the suspension. H. J. E.

New table of refractive index of pure glycerol at 20° . L. F. HOYT (Ind. Eng. Chem., 1934, 26, 329—332).—The measured vals. are given by: 0.44% glycerol, $n_D = 1.33303 + 0.001124x + 0.05605x^2 - 0.07555x^3$; $45\text{--}79\%$, $n_D = 1.32359 + 0.00149x$; $80\text{--}100\%$, $n_D = 0.90799 + 0.0154x - 0.03155x^2 + 0.0576x^3$. The temp. coeff. for 99.84% glycerol is 0.000225 per 1° for the range $10\text{--}20^\circ$. G. H. C.

Gas analysis and confining liquids. A. NAHOCZKY (Banyasz. kohás. Lapok, 1933, 66, 332—335; Chem. Zentr., 1933, ii, 3163).—The absorption coeff. of CO_2 at 15° in four org. liquids and in seven saturated aq. solutions and their mixtures has been measured. H. J. E.

Velocity of gas exsorption from liquids. A. GUYER and B. TOBLER (Helv. Chim. Acta, 1934, 17, 257—271).—A formula has been deduced for the mean concn. of a gas at any given time in its undisturbed solution when the osmotic pressure of the gas in the solution is $>$ the partial pressure above it. The formula has been found to be valid for CO_2 and H_2S . The results show that the rate of diffusion through the liquid is the determining factor in the velocity of exsorption, and not the rate of escape from the surface. M. S. B.

Chemical and physico-chemical properties of polonium. II. Diffusion coefficient of polonium in solution. Apparatus. M. SERVIGNE (J. Chim. phys., 1934, 31, 147—161).—The rate of diffusion of Po from aq. HCl into a superimposed column of aq. HCl is deduced from the rate of discharge, R , of a superposed electroscope. With a homogeneous liquid, R is directly proportional to concn. of Po. Full details of the technique are given. The air-solution interface is a film of H_2O with underlying Po ions. J. G. A. G.

Solubility of sulphite in presence of sodium hydroxide and β -naphthol. I. M. KOGAN, A. N. PLANOVSKI, and A. N. EVDOKIMOV (Anilinokras. Prom., 1934, 4, 34—37).—The solubility of Na_2SO_3 in H_2O falls from 90° to 106° , and is greatly depressed by the presence of NaOH and $NaO \cdot C_{10}H_7$. R. T.

Physico-chemical analysis of systems containing diamines. V. Mutual solubility of ethylenediamine and certain C_6 hydrocarbons. A. S. BROWN. VI. Viscosity and fusion diagrams of the systems ethylenediamine-butyl alcohols. D. E. DIONISIEV (J. Gen. Chem. Russ., 1933, 3, 973—975, 976—989).—V. Solubility data are recorded for n - and cyclo-hexane at 25° .

VI. The viscosity isotherms suggest formation of 1:2 compounds in the case of Bu^oOH and Bu^sOH at 0° and 25° , but not at 50° ; the fusion diagrams indicate similar compounds with all four alcohols, m.p. -34° (primary) -33° (sec.), -21° (tert.), and -31.5° (iso). R. T.

Relation between solubility and inverse fusion point. J. N. BRONSTED (Rec. trav. chim., 1934, 53, 421—424).—Theoretical. A reply to Voogd (A., 1933, 897). H. S. P.

Relation between solubility and inverse fusion point. N. H. J. M. VOOGD (Rec. trav. chim., 1934, 53, 425—429).—Theoretical. A reply to Bronsted (see above). H. S. P.

Double sulphates $M^I_2SO_4 \cdot M^{II}SO_4 \cdot nH_2O$. A summary. R. M. CAVEN (J. Roy. Tech. Coll., 1934, 3, 218—222).—The solubility isotherms of the systems $M^I_2SO_4 \cdot M^{II}SO_4 \cdot nH_2O$, where M^I is Na, K, or NH_4 , and M^{II} is Mn, Co, Ni, Cu, and Zn, are compared to show the influence of the different metallic ions on the range of stability and the degree of hydration of the salts. H. S. P.

Behaviour of the magnesium ion towards ammonia in aqueous solution. I. H. FREDHOLM (Z. anorg. Chem., 1934, 217, 203—213).—Distribution experiments between $CHCl_3$ and aq. NH_4Cl of const. concn. and varying NH_3 and $MgCl_2$ concn. indicate the existence of the Mg ammine ion $[Mg(H_2O)_nNH_3]^+$. Since the co-ordination no. of Mg is usually 6, n is probably 5. M. S. B.

Adsorption of gases on solid surfaces at low temperatures. C. ZICKERMANN (Z. Physik, 1934, 88, 43—54).—Absorption isotherms for N_2 and A adsorbed on mica and glass between 77.7° and 40.2° abs. and 10^{-5} to 5×10^{-4} mm. indicate that proportionality of adsorbed quantity and pressure does not hold between 1.5 and 3×10^{-4} mm.; this is

attributed to the most efficient active centres becoming saturated. A. B. D. C.

Adsorption of carbon dioxide and hydrogen on bare and oxygen-covered silver surfaces. L. C. DRAKE and A. F. BENTON (J. Amer. Chem. Soc., 1934, 56, 506—511).—On bare Ag, CO_2 shows instantaneous physical adsorption with a heat change $= 5$ kg.-cal. Physical adsorption of H_2 is very small even at -183° , but activated adsorption occurs at $> 200^\circ$, and is removable by evacuating at 300° . When the Ag surface is covered with adsorbed O_2 , slow activated adsorption of CO_2 occurs at 0 — 200° with an energy of activation of 4—5 kg.-cal. Ag surfaces covered by Ag_2O react with CO_2 to form Ag_2CO_3 at $> 56^\circ$, with a heat of formation of 17.3 kg.-cal. and an energy of activation of 13 kg.-cal. The rate of formation of Ag_2CO_3 is proportional to the pressure of CO_2 , and independent of the amount of Ag_2O . Activated adsorption of CO_2 occurs below the equilibrium pressure of Ag_2CO_3 . E. S. H.

Adsorption at high pressures. I. A. S. COOLIDGE. II. A. S. COOLIDGE and H. J. FERNWALT (J. Amer. Chem. Soc., 1934, 56, 534—561, 561—568).—I. Theoretical.

II. The adsorption of CO_2 , N_2O , and SiF_4 by C has been investigated over a wide range of temp. and pressure, with particular attention to the region near the crit. point. The behaviour of CO_2 is in agreement with the predictions of Pólaný's theory. E. S. H.

Adsorption of hydrogen by zinc oxide, zinc chromite, and zinc oxide-molybdenum oxide. H. S. TAYLOR and C. O. STROTHER (J. Amer. Chem. Soc., 1934, 56, 586—590).—With ZnO, van der Waals adsorption (I) is observed between liquid air temp. and -78° , slow adsorption from 0° to 100° , requiring an activation energy of 5 kg.-cal., and further slow adsorption from 100° to $> 300^\circ$, having an activation energy of 12 kg.-cal. Addition of Cr_2O_3 increases the amount of (I), and only one form of activated adsorption is observed, beginning at -78° . Adsorption is a max. at 218° . Addition of MoO_3 renders ZnO less active. (I) occurs at liquid air temp.; no adsorption occurs between -78° and 200° . H_2 is adsorbed slowly above 200° , with an activation energy of 17 kg.-cal. Max. adsorption occurs at 400° . E. S. H.

Gas-solid equilibria. V. Pressure-concentration equilibria between silica gel and (1) oxygen, (2) nitrogen, (3) mixtures of oxygen and nitrogen, determined isothermally at 0° . B. LAMBERT and D. H. P. PEEL (Proc. Roy. Soc., 1934, A, 144, 205—225).—The adsorption of N_2 and O_2 by SiO_2 gel at 0° is directly proportional to the pressure except for a very slight divergence at pressures < 100 mm. The pressure-concn. isothermals are completely reversible up to 1 atm. At corresponding pressures the adsorptive power of SiO_2 gel for N_2 is $>$ for O_2 . With mixtures of N_2 and O_2 at 0° , the adsorptive power of SiO_2 gel for O_2 is greater (up to 15%) in presence of N_2 than with O_2 alone, but the adsorptive power for N_2 is less in presence of O_2 than with N_2 alone. The total amount of gas

adsorbed from the mixture is always slightly < the sum of the separate amounts of the pure gases absorbed singly at the same pressures. L. L. B.

Adsorption. VII. Form of the isothermals of vapour on charcoal and its relation to hysteresis. L. J. BURRAGE (Trans. Faraday Soc., 1934, 30, 317—325).—Adsorption isotherms have been determined for CCl_4 and MeOH on charcoal A and for MeOH , EtOH , PrOH , and HCO_2H on charcoal N1. In all cases a reversible hysteresis loop has been observed and the pressure determined at which it closes. The factors influencing the form of the isotherms are discussed and Lindau's const. (A., 1932, 1084) is criticised. M. S. B.

Relation between activity and binding power of active charcoal. F. KRČIČ [with H. WEJROCH] (Kolloid-Z., 1934, 67, 37—40).—With C from the same source and subjected to the same activation treatment, the activity towards methylene-blue, PhOH , and I runs parallel with the adsorption of C_6H_6 and the heat of wetting. Such a relation does not exist between the activity or the heat of wetting and the binding power. E. S. H.

Active charcoal. II. Constitution of the surface and the activated adsorption of water. C. OCKRENT (J.C.S., 1934, 291—301).—Analysis of three activated ash-free charcoals has shown that, at 500° , C and H_2O only are present. The latter forms an adsorption layer consisting of two parts, a low-temp. and a high-temp. adsorption layer (I). (I) is the chief component, and is desorbable above 500° only. The total H_2O forms an approx. unimol. layer. The results indicate that the "oxide" theory of activation is untenable. Differences in adsorptive properties are associated with the presence or absence of (I), and a mechanism for its formation is suggested. (I) is an example of activated adsorption, and its desorption curve is discontinuous with temp. These discontinuities are evidence for the existence of a no. of activated energies of adsorption anticipated on theoretical grounds. M. S. B.

Heat of adsorption of carbon monoxide on copper. R. A. BEEBE and E. L. WILDER (J. Amer. Chem. Soc., 1934, 56, 642—645).—Differential heats of adsorption, determined at 0° , show a marked decrease in the initial stages as successive small portions of the gas are adsorbed. E. S. H.

Adsorption and diffusion phenomena of gases at points of contact of solid substances. E. HABANN (Ann. Physik, 1934, [v], 19, 501—512; cf. A., 1931, 671; 1932, 985).—If the gas possesses electron affinity, the adsorbed gas forms a space charge, and this is shown in the p.d. For strong currents, the space charge is destroyed, and the potential falls rapidly. From observations on the decrease of potential, the amount of adsorbed gas can be calc. Part of the neutralised gas is retained by the contact spaces by adsorption forces, but some diffuses into the solid substances. A. J. M.

Mathematical and experimental studies on repeated extraction of adsorption systems, which are in equilibrium. I. J. VOICU (Kolloid-Z.,

1934, 66, 322—328).—After q extractions the concn. x^p of a substance in adsorption equilibrium in the solution, and the total amount 0^p of the same substance are given by $x^p = A_x(1-r)^{pq} + K$ and $0^p = A_0(1-r)^{pq} + K_0$, where A_x , A_0 , r , p , K , and K_0 are consts. These relations, derived theoretically, are verified experimentally for several adsorption systems.

E. S. H.

Transference of surface changes to the interior of crystals. III. D. BALAREV [with B. SREBROV] (Kolloid-Z., 1934, 66, 317—322; cf. A., 1933, 122).—Kinetic and microscopical studies of the thermal decomp. of KClO_3 in presence of MnO_2 are explained with reference to the mosaic structure of the KClO_3 crystals. No thermal effect is produced on mixing powdered KClO_3 and MnO_2 . E. S. H.

Adsorption of organic substances at the surfaces of crystals. N. A. HELD and V. DJATSCHKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 193—198).—The adsorption of $\text{C}_3\text{H}_7\cdot\text{CO}_2\text{H}$ on BaSO_4 is of an ionic type, being increased by the presence of adsorbed Ba^{++} on the surface, and decreased by SO_4^{--} . The electrokinetic potential at the surface of BaSO_4 crystals has been measured for different concns. of BaCl_2 and Na_2SO_4 and shown to be related to the $\text{C}_3\text{H}_7\cdot\text{CO}_2$ adsorption. Adsorbed cation appears to act as an activator of adsorption, whereas the anion has the reverse effect, this being confirmed by the relative effects of Ba^{++} and K^+ on the above system. Applications to flotation problems are discussed.

J. W. S.

Formation and properties of precipitates. I. Theory of co-precipitation. I. M. KOLTCHOFF [with R. MOLTZAU] (Chem. Weekblad, 1934, 31, 102—103; cf. A., 1932, 908).—Co-pptn. may involve adsorption, occlusion, or the formation of a chemical compound, whilst a further case is presented by the subsequent deposition of the second substance on the original ppt. The catalytic influence of HgS on the pptn. of ZnS is so pronounced that if both metals are present the Zn may be completely pptd. by H_2S from 0.1N- HCl ; the presence of N-HCl is necessary for complete separation to be effected. In more dil. acid solutions the cryst. HgS which is first pptd. begins to adsorb ZnS and becomes difficult to filter if the passage of the H_2S is continued, but on ageing (24 hr.) the adsorbent power of the HgS diminishes. HgS also adsorbs H_2S strongly. ZnS adsorbs HgS from, e.g., solutions in Na_2S , whilst if a suspension of HgS in H_2O is shaken with Na_2HgS_4 solution, free Na_2S appears in the solution, i.e., HgS adsorbs H_2S from such solutions, and the solubility of HgS in Na_2S solutions is a function of the surface of the solid phase. H. F. G.

Capillary penetration of fibrous materials. R. L. PEEK, jun., and D. A. McLEAN (Ind. Eng. Chem. [Anal.], 1934, 6, 85—90).—The rate of capillary rise of liquids into porous materials varies inversely with the height of rise; the slope of the straight-line plot of these quantities is proportional to γ/η , where γ is the penetration tension (the product of the surface tension and the cosine of the contact angle) and η the viscosity of the liquid. The proportionality const. depends on the average pore size and on the

range of pore sizes. Results are given for the rise of several org. liquids in strips of paper. E. S. H.

Interfacial activity of salts of the higher fatty acids and other emulsifiers. A. LOTTERMOSER and H. WINTER (Kolloid-Z., 1934, 66, 276—288).—A ring-torsion balance for the determination of surface and interfacial (I) tensions, having a sensitivity of 0.01 dyne per cm., is described. (I) against paraffin oil of Na or K acetate, butyrate, valerate, hexoate, octoate, deoate, laurate, myristate, palmitate, stearate, and oleate have been determined at 20° and 80° and concns. 0.01—10%. The max. lowering of (I) is almost attained in 0.2% solutions. Similar determinations with solutions of carrageen, gum arabic, tragacanth, gelatin, and saponin show that the max. lowering is attained in 0.5% solutions.

E. S. H.

Structure and growth of thin surface layers on metals by atmospheric oxidation. A. STEINHEIL (Ann. Physik, 1934, [v], 19, 465—483).—The properties, chemical composition, structure, and growth of thin surface layers formed on Al and Sn on exposure to air at room and higher temp. have been investigated. The layer forming on Al has a face-centred cubic lattice, a 5.35 Å.; it corresponds with ϵ -Al₂O₃, previously unknown. By melting the metal, oxide layers 4×10^{-5} cm. thick, consisting of γ -Al₂O₃, are produced. Sometimes surface lattice interference occurs. This is due to single crystals of hexagonal β -Al₂O₃ which possess an unusually long c -axis. When Sn foil is melted, the layer consists of SnO and SnO₂ in varying proportions. The rate of growth of the layer on Al has been studied.

A. J. M.

Optical observations on the passivity of iron and steel in nitric and chromic acids. L. TRONSTAD and C. W. BORGMANN (Trans. Faraday Soc., 1934, 30, 349—361).—The surface films on Fe and on ordinary and unstainable steels have been studied by Drude's optical method during immersion in conc. HNO₃, 0.01M-CrO₃, and M-K₂CrO₄+0.1M-KCl. The natural films are strengthened or replaced by denser films in accordance with the oxide theory of passivity. The approx. thickness of the film on steel in conc. HNO₃ is 100 Å., on purer Fe 25—35 Å., and on austenitic unstainable steel about 10 Å. In CrO₃ and K₂CrO₄-KCl mixtures the films are of the same order as previously obtained during anodic treatment, i.e., 30—40 Å.

M. S. B.

Optical observations on the protective films on aluminium in nitric, chromic, and sulphuric acids. L. TRONSTAD and T. HÖVERSTAD (Trans. Faraday Soc., 1934, 30, 362—366; cf. preceding abstract).—In CrO₃ and K₂CrO₄-KCl mixtures only small changes are observed in the optical properties of the natural oxide film. The films are not protective in conc. H₂SO₄, and there is alternate formation and breakdown of the protective film in conc. HNO₃. The mean thickness of the natural oxide film is about 100 Å.

M. S. B.

Physical chemistry of wetting phenomena and flotation processes. XII. Parallelism between wetting isotherms and flotation curves. M. LIPETZ, P. REHBINDER, and M. RIMSKAJA (Kolloid-

Z., 1934, 66, 273—276; cf. this vol., 141).—The parallelism is demonstrated for the system malachite-H₂O-air.

E. S. H.

Kinetics of penetration. VIII. Temporary accumulation. W. J. V. OSTERHOUT and S. E. KAMERLING (J. Gen. Physiol., 1934, 17, 507—516).—Aq. solutions of HCl and KOH are separated by a mixture of guaiacol and *p*-cresol, whereby a temporary accumulation of K⁺ occurs in the HCl phase together with an increase in vol. up to a steady state. Lowering the p_H of the acid phase increases accumulation.

H. D.

Electrolytic dissociation by the Raman effect. II. Nitrates. I. R. RAO (Proc. Roy. Soc., 1934, A, 144, 159—165; cf. A., 1930, 1370).—Raman frequencies of nitrates in the cryst. state and in solution are given. The frequencies in the cryst. state are different for different cations, but the same for all nitrates in solution. For the same cation, the frequency in the solid state is higher than for the solution, with the exception of NH₄NO₃ and possibly KNO₃. No trace of any additional line due to undissociated mols. is found in the spectra of conc. solutions of NaNO₃ and NH₄NO₃. The ratio of intensity of the NO₃-line of NaNO₃ to the concn. is const. The evidence points to the hypothesis of complete dissociation of nitrates even at high concns.

L. L. B.

Properties of electrolytic solutions. X. F.p. of solutions of an electrolyte in a non-polar solvent. C. A. KRAUS and R. A. VINGEE (J. Amer. Chem. Soc., 1934, 56, 511—516).—An apparatus for use between 0° and 25°, giving an accuracy of about 1% with concns. down to 10⁻³N. is described. F.-p. curves for solutions of CHPh₃ in C₆H₆ and dioxan indicate that the f.-p. const. of C₆H₆ is 5.065° and that of dioxan is 4.63°. The f.-p. curve of 0.001—0.011N-tetraisoamylammonium nitrate in dioxan deviates greatly from linearity, due probably to the association of the ion-pairs to more complex aggregates.

E. S. H.

Derivation of distribution functions in problems of Brownian motion. L. S. ORNSTEIN and W. R. VAN WIJK (Physica, 1934, 1, 235—254).—Theoretical.

H. J. E.

Mechanical properties of disperse systems. III. Effect of vibrations on the deformation of disperse, powdered substances. G. I. POKROVSKI and I. S. FEDEROV (Kolloid-Z., 1934, 66, 270—272; cf. A., 1932, 901).—A theoretically derived relation between velocity of deformation of coarsely disperse substances and the frequency and strength of vibrations is verified experimentally for sand saturated with H₂O.

E. S. H.

Chromatic, disperse two-phase systems, with special reference to their application as light filters. E. KNUDSEN (Kolloid-Z., 1934, 66, 257—266).—The theory of the production of colour in disperse systems in which the two phases have equal n and different dispersions is treated with reference to numerous examples. The variation of colour with temp. is discussed. The least temp.-variable systems are solid-solid. Such systems can be formed

by dispersing glass in solutions of lacquers, celluloid, etc., and evaporating the solvent, by emulsifying molten colophony in molten grape sugar and subsequently cooling, or in the manufacture of glass under certain conditions. E. S. H.

Dust and smoke. R. WHYTLAW-GRAY (Proc. Roy. Inst., 1934, 28, 149—163).—A lecture.

Conditions for the production of fog in the neutralisation of a volatile acid or alkali. C. N. JACKSON and J. C. PHILIP (J.C.S., 1934, 341—346).—The view previously expressed (A., 1930, 855) as to the mechanism of the formation of the fog produced when an air-HCl stream is passed through aq. NaOH containing a trace of NH_3 has been confirmed. The amount and composition of the fog have been determined and the influence of the v.p. of the aq. NaOH on its formation is considered. Similar observations and measurements have been made when an air- NH_3 stream is passed into HCl. Observations have also been made on the less stable fogs produced when an air- SO_2 stream is passed into aq. NaOH containing NH_3 . M. S. B.

Colloidal gases. II. Determination of particle size of colloidal air. A. KRAUSE and K. KAPITANCZYK (Kolloid-Z., 1934, 66, 288—292; cf. A., 1931, 1230).—Colloidal particles of air in aq. NaOH have a radius about 0.14 μ . E. S. H.

Viscosity of froth. J. O. SIBREE (Trans. Faraday Soc., 1934, 30, 325—331).—A froth behaves similarly to a coarse emulsion. The viscosity (η) varies with the velocity gradient and becomes const. above a certain val. of the latter. In the const. region (η) is expressed by the formula $\eta_e = \eta_0/[1 - \sqrt[3]{(1.2\phi)}]$, where η_e and η_0 are (η) for the froth and continuous phase, respectively, and ϕ is the val. of the disperse phase in unit vol. of the froth. A curve showing the size-distribution of the bubbles is given.

M. S. B.

Plasticity of powdered slate from Solnhofen and the thixotropic behaviour of its suspensions. H. FREUNDLICH and F. JULIUSBURGER (Trans. Faraday Soc., 1934, 30, 333—338).—Finely-powdered slate from Solnhofen containing about 95% CaCO_3 and 2% clay gives, when mixed with either sea- H_2O or pure H_2O , a highly plastic thixotropic paste. Thin layers dry on a porous surface without cracking, and this property is probably necessary for the formation of the Solnhofen petrification. Finely-powdered quartz gives a thixotropic paste within a very narrow range of concn. with sea- H_2O or an aq. solution if an electrolyte (e.g., MgCl_2). With pure H_2O , on the contrary, the Osborne-Reynolds phenomenon is observed. The conditions producing the two different phenomena are contrasted.

M. S. B.

Residual tension in layered dielectrics, especially in colloid systems. E. L. LEDERER [with F. DANNMEYER and J. SCHUBERT] (Kolloid-Z., 1934, 67, 63—65).—The apparatus and technique described allow the detection of small quantities of degradation products, particularly of photochemically sensitive substances. E. S. H.

Influence of traces of Na_2S in preparation of colloidal gold by the formaldehyde method (Zsigmondy's Au_F). Preparation at room temperature. R. WERNICKE and R. B. LOSSEN (Anal. Assoc. Quim. Argentina, 1933, 21, 149—155; cf. A., 1931, 303).—Using Na_2S , it is difficult to obtain Au sols of consistent properties at the b.p., but at room temp. optically empty ruby-red sols are obtained by using larger proportions of Na_2S . AuCl_3 (100 c.c. of 0.01%) is treated with 1.4 c.c. of 0.18N- K_2CO_3 , and after 20 min. 0.5—0.6 c.c. of 0.02M- Na_2S , and after 24 hr. 1 c.c. of 1.2% CH_2O . R. K. C.

Influence of heat on structure formation in ferric hydroxide sols. A. RABINERSON (Kolloid-Z., 1934, 66, 303—311).—When 4.5—10% $\text{Fe}(\text{OH})_3$ sols are heated under various conditions, partial solidification occurs, the system returning to the liquid state subsequently at room temp. either spontaneously or after shaking. The cause of these phenomena is attributed to the increasing degree of hydrolysis of the intermicellar FeCl_3 , which lowers the ζ potential. After cooling the hydrolysis is reversed. E. S. H.

Colloid chemistry of arsphenamine solutions: viscosity and conductivity measurements. C. ROBINSON and C. A. MORRELL (Trans. Faraday Soc., 1934, 30, 339—349).—Viscosity (η) and conductivity (λ) measurements have been made on aq. arsphenamine dihydrochloride (I) in an atm. of N_2 . The vals. depend on the history of the solution. After cooling for some time, both η and λ for a 0.5% solution at 25° are > in a solution recently heated, but both return in time to the equilibrium val., which is always reproducible after a sufficient length of time at const. temp. This slow reversible equilibrium has not hitherto been observed with other colloidal electrolytes. The increased vals. are probably to be explained by the aggregation of the cations into complex ions of high valency and mobility. In the hot solutions (I) may exist in true solution. In a 2% solution λ does not change in the same direction as η . Probably this concn. corresponds with concns. above the max. in λ curves for soaps or mobility curves for dyes. The existence of structural η could not be proved. Reproducible vals. were also observed for solutions of the Na_2 salt. Equilibrium is reached rapidly. M. S. B.

Colloid-chemical processes in the formation of colour lakes. F. PAVELKA and F. HEISNAR (Kolloid-Z., 1934, 66, 340—351).—Experiments on the taking up of dyes by the hydroxides of Zr, Bi, Th, Sn, and Al show that an adsorption process is involved; no stoichiometric relation exists, and the concn. variation is in accordance with the usual adsorption isotherm. E. S. H.

Colloid-chemical properties of sulphur dyes. L. J. BELENKI (Kolloid-Z., 1934, 67, 79—87).—The leuco-solutions are highly-dispersed, negative colloids. The p_H of the bath is lowered by the presence of wool fibre. At lower p_H the dyes tend to become lyophobic; their pptn. at the surface of the fibre explains why they are not fast to rubbing. E. S. H.

Transference of the disperse phase from one dispersion medium to another by demulsification. II. A. JANEK and A. SCHMIDT (Kolloid-Z., 1934, 66, 296—302; cf. A., 1930, 1368).—The systems studied consist of hydrosols of Au, to a const. amount of which varying amounts of an alcohol and a third org. liquid (PhNO_2 , PhMe , CHCl_3) are added. Demulsification occurs on cooling, and at certain mixture relations a zone is reached in which the Au is transferred from the aq. to the org.-liquid phase. In some cases the concn. of the colloidal Au is increased 300—400 times in this process. Certain resins, especially sandarac, facilitate the transference.

E. S. H.

Electrochemistry of colloids. W. PAULI and E. VALKÓ (Kolloid-Z., 1934, 66, 312—316).—A review of published work.

E. S. H.

Quantitative relations in the lyotropic series. I. Introduction. E. H. BUCHNER. II. Lyotropic numbers and their explanation. E. M. BRUINS (Rec. trav. chim., 1934, 53, 288—291, 292—307).—I. The method of Bruins, which enables the flocculation concns. for one colloid to be calc. from those for another, is considered.

II. The method of deducing lyotropic nos. is explained, and these nos. are placed on a physical basis by means of a general coagulation theory. The flocculation vals. of salts and a simple method of determining the hydration energy are considered.

H. S. P.

Regularities in the formation of Liesegang rings. M. P. LAKHANI and R. N. MATHUR (Kolloid-Z., 1934, 67, 59—62).—When the concns. of gel and K_2CrO_4 are const. the distance between successive rings is expressed by $\log X_n - nK$, where X_n is the distance for the n th ring. The val. of K increases with the concn. C of the AgNO_3 in accordance with $K\sqrt[3]{C} = A$, where A is a const.

E. S. H.

Potentiometric studies of colloidal solutions. I. Stearic acid hydrosols. M. P. U. IYER (J. Mysore Univ., 1932, 6, 188—196).—The sols were prepared by dissolving stearic acid in MeOH, adding to H_2O , and boiling off the MeOH. The p_H of the intermicellar liquid is found to depend on the size of the particles, but not on the concn. of the acid. Potentiometric titration with NaOH or $\text{Ba}(\text{OH})_2$ shows no evidence of a stoichiometric acid-alkali relation; the amount of alkali required varies with the time of contact. An adsorption theory of these phenomena is outlined.

E. S. H.

Dependence of the state of division of dissolved fatty acid salts (soaps) in water on concentration. G. JANDER and K. F. WITTENDORF (Angew. Chem., 1934, 47, 197—200).—The variation of the diffusion coeff. of Na decaate and laurate with concn. has been determined in presence of a large excess of NaOH and NaCl and compared with that of $\text{Bu}^n\text{CO}_2\text{Na}$. With increasing concn. soap particles of colloidal dimensions are gradually built up from the unimol. soaps obtained in solution at low temp. The bimol. stage of aggregation is of especial importance in building up the higher stages. The diffusion coeff. of 0.12N-Na decaate indicates an aggregation of 24 decaate acid residues with a mean mol. wt. of at least 4000.

M. S. B.

High electrolyte sensitivity of the pasting process of potato starch and the colloid system produced thereby. E. WIEGEL (Kolloid-Z., 1934, 67, 47—55).—Neutral salts of uni- and bi-valent cations at a concn. of 0.0001N lower the viscosity of the system by 40—60%, whilst the effect is detectable in 0.00001N solutions. At the same time the presence of electrolytes hinders the dispersion of starch granules to a sol. The influence of valency of the cation is in the direction indicated by the Schulze-Hardy rule, but is not very pronounced; H^+ has a stronger effect, and also promotes hydrolysis. The viscosity of starch sols is increased when the electrolyte normally present is removed.

E. S. H.

Diffusion in silicic acid gels. Z. V. VOLKOVA (Kolloid-Z., 1934, 66, 292—295).—The diffusion coeff. K of glucose in SiO_2 gels decreases linearly with increasing concn. of SiO_2 , and increases with the age of the gel, probably as a result of widening of the pores. The width of the pores is about 1—4 μ .

E. S. H.

Combination of proteins with acids and bases. (Miss) D. J. LLOYD (J. Soc. Leather Trades Chem., 1933, 17, 245—258).—The preferential adsorption of OH ions by protein from solutions at p_H 7.0 is evidence of chemical combination. According to the zwitterion theory, isoelectric protein (I) should have one acid and two or more basic p_K vals. The acid p_K and one basic p_K are of the same order as those of aliphatic acids and primary aliphatic amines. At the isoelectric point, (I) carries equal and opposite charges, but there is considerable salt formation and an equilibrium between ionised and non-ionised acid groups, basic groups, and dissociated and associated salt linkings. The general titration curves of (I) can be explained on this basis.

D. W.

Colloid-chemical hydrolysis of albumins. I. S. J. DEJATSKHOVSKI and V. A. LIVANSKAJA (Kolloid-Z., 1934, 67, 41—47).—When aq. solutions of proteins are shaken with C_6H_6 , PhMe , or Et_2O , the concn. of the aq. phase diminishes; the effect increases with the dilution. The hydrolysis product thus extracted is amorphous and increases in amount with the duration of hydrolysis.

E. S. H.

Effect of deamination on combination curves of serum-albumin and -globulin.—See this vol., 427.

Change in the isoelectric point of collagen under the action of trypsin. N. I. GAVRILOV and A. M. SIMSKAYA (Ovrad. Tekh. Kozh. Proiz., 1931, No. 2, 23—24).—Trypsin causes a change from p_H 4.64 to p_H 3.7; oropon causes a change to 3.4—4.2, depending on the duration of bating.

CH. ABS.

Silk fibroin. G. RASTELLI (Kolloid-Z., 1934, 67, 55—59).—The isoelectric point of fibroin is p_H 4.6; the p_H of fibroin in the silk cocoon is 7.2. Fibroin has a slight solubility in H_2O and reacts with AgNO_3 .

E. S. H.

Simultaneous determination of the equilibrium constants of the reactions $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$; $2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CO}_2 + \text{CH}_4$; $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$; $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$ by using activated nickel catalysts. J. C. GHOSH, K. M.

CHAKRAVARTY, and J. B. BAKSHI (Z. anorg. Chem., 1934, 217, 277—283).—The experimental arrangement was similar to that previously described (A., 1931, 1376), but the gas mixture was passed much more slowly over the $\text{Ni-ThO}_2\text{-CeO}_2$ catalyst to ensure that the temp. of the gases should be the same as that of the furnace. The required equilibrium consts. were determined at temp. between 400° and 490° .
M. S. B.

Table for the methanol synthesis equilibrium. G. FRACASSO (L'Ind. Chimica, 1934, 9, 293—299).—Published vals. of the equilibrium const. for the synthesis of MeOH from $\text{CO}+2\text{H}_2$ differ widely among themselves and from the calc. vals. The discrepancies are due partly to secondary reactions and partly to errors in the theoretical treatment. All the available data are discussed and the relations between K_p , temp., and pressure are deduced. A nomographic table summarises the relations under the conditions of the industrial synthesis.
T. H. P.

Cryoscopic determination of hydration of ions of strontium chloride. E. ROUYER (Compt. rend., 1934, 198, 1156—1158; cf. this vol., 361).—The hydration of the ions in 0.5 and 0.25*M*. SrCl_2 corresponds with $\text{SrCl}_2 \cdot 26.7\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 30.3\text{H}_2\text{O}$, respectively.
C. A. S.

Calculation of dissociation constants from the electrometric titration of acids. E. SODERBACK (Arkiv Kemi, Min., Geol., 1934, 11 A, No. 8, 48 pp.).—A rigid derivation of the equations of Auerbach and Smolczyk (A., 1925, ii, 118).
D. R. D.

Constitution of homogeneous acids and the influence of solvents on their acidity. Investigations with indicators. A. MULLER (Z. anorg. Chem., 1934, 217, 113—153).—The relative acidity of acids in different org. solvents has been determined by comparing the extent of dilution necessary for the complete splitting up of an indicator salt formed from the acid and indicator base. The indicators *p*-dimethylaminoazobenzene and the less basic dicinnamylidenecyclohexanone have been used and, for single experiments, dianisylideneacetone and -cyclohexanone, and (*p*- $\text{NMe}_2 \cdot \text{C}_6\text{H}_4$) $_2\text{CH} \cdot \text{OH}$. The results are compared with those obtained by the kinetic diazo-ester method, and, although the indicator method is less sensitive, it is much simpler. The halogenated acetic acids, except the abnormal $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$, contain a great deal of active acidium salt. Aliphatic and aromatic mono- and poly-carboxylic acids are in general associated pseudo-acids, and therefore inactive towards diazo-ester and indicators. Anhyd. $\text{H}_2\text{C}_2\text{O}_4$ is an exception. Introduction of halogen or of a triple linking causes strong activity. The simple sulphonic acids are homogeneous, and strongly active in solution. They readily form oxonium salts or solvates. Aminosulphonic acids are inactive. Among inorg. acids HClO_4 , which is the strongest, is always active, whilst HNO_3 is completely inactive in Et_2O . Complex acids and hetero-poly-acids are, for the most part, active in the solid state, and not appreciably affected by inactivating solvents. The behaviour of

acid salts depends on the nature of the constituent acids. As a solvent AcOH has an inactivating action which is in accordance with Hantzsch's conception of it (A., 1927, 1011) as bimolar acetyl alcohol. $\text{N}_2\text{CH} \cdot \text{CO}_2\text{Et}$ is a strongly inactivating solvent on account of its unsaturation. The inactivating power of a solvent is greater in proportion to the degree of unsaturation of its mol. and to the weakness of the acid dissolved in it. The action of certain O-containing compounds, especially Et_2O , cincol, and acetal, is the most marked. Acids rich in acidium salt form solvates of varying stability in solution. Strong acids form true oxonium salts or acidium solvates with Et_2O and EtOH , whilst other acids give inactive "neutro-solvates."
M. S. B.

Interhalogen compounds: dissociation of halide complexes, dissociation, hydrolysis, distribution ratios in acid solution. J. H. FAULL, jun. (J. Amer. Chem. Soc., 1934, 56, 522—526).—The data recorded are: $[\text{IBr}][\text{Br}']/[\text{IBr}_2'] = 0.0027$; $[\text{IBr}][\text{Cl}']/[\text{IBrCl}'] = 0.023$, $[\text{ICl}][\text{Cl}']/[\text{ICl}_2'] = 0.0060$; distribution ratios between CCl_4 and H_2O , IBr 3.9, ICl 0.34; $[\text{I}_2][\text{Br}_2]/[\text{IBr}]^2 = 1.2 \times 10^{-5}$, $[\text{I}_2][\text{Cl}_2]/[\text{ICl}]^2 = 1.6 \times 10^{-10}$. Preliminary vals. for hydrolysis consts. are given. The results diverge from the rule that properties are intermediate between those of the component halogens.
E. S. H.

Equilibrium in the reaction $\text{Cl}_2 + \text{Br}_2 = 2\text{BrCl}$. H. G. VESPER and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 620—625).—In measurements of the absorption coeff. of BrCl , with wave-lengths near 0.50 the following vals. have been obtained at 28° : $K = [\text{Br}_2][\text{Cl}_2]/[\text{BrCl}]^2 = 0.107 \pm 0.002$, $\alpha = 0.384 \pm 0.006$. Equilibrium is attained after some hr. in the dark, but after 2 min. when illuminated with light of wave-length 0.365 μ . The steady state in the light is identical with the thermal equilibrium.
E. S. H.

Formation of high-molecular inorganic compounds in hydrolysing systems. G. JANDER and K. F. JAHR (Chem.-Ztg., 1934, 58, 247—249).—Data for aq. solutions of salts of weak bases with strong acids and of strong bases with weak acids show that salts of weak acids (e.g., Na_2WO_4) yield on acidification a series of definite anhydro-acid salts the anions of which are stable over a definite range of p_H , whereas the salts of weak bases [e.g., $\text{Fe}(\text{ClO}_4)_3$] give no definite complex cations, the mol. wt. of the complex increasing steadily with the p_H .
D. R. D.

Amphoteric behaviour of metallic hydroxides. VI. Plumbites. R. SCHOLDER and R. PATSCH (Z. anorg. Chem., 1934, 217, 214—224).—In alkaline plumbite solutions the complex ions $\text{Pb}(\text{OH})_3^-$, $\text{Pb}(\text{OH})_4^{2-}$, and $\text{Pb}(\text{OH})_6^{4-}$, are present in proportions depending on temp. and concn., but pure cryst. hydroxoplumbites cannot be separated. Decomp. takes place and PbO is formed. Stabilisation is brought about, however, by replacement of OH by halogen X up to a proportion of $1\text{Pb} : 0.5X$. It is especially effective, and mixtures of the following compounds can be obtained: $[\text{Pb}(\text{OH})_4]_2\text{Na}$; $[\text{Pb}(\text{OH})_4]_2\text{Na}_2$; $[\text{PbX}(\text{OH})_3]_2\text{Na}_2$; $[\text{Pb}(\text{OH})_4]_2\text{Ba}$; $[\text{PbX}(\text{OH})_3]_2\text{Ba}$; $[\text{Pb}(\text{OH})_6]_2\text{BaNa}_2$. Pure cryst. $[\text{Pb}(\text{OH})_4]_2\text{Na}_2$ has been obtained in presence of hot

and very conc. aq. NaOH, but cannot be isolated from this without decomp. M. S. B.

Hydrolysis of acetoxime. J. E. W. RHODES (J.C.S., 323—325).—The const. for the equilibrium between NH_2OH , COMe_2 , and acetoxime in dil. aq. solution is approx. 16×10^{-6} in neutral solution, but increases slightly in very acid solution. H^+ is evidently not involved in the equilibrium const., but may have a small influence on the active masses of the reactants. M. S. B.

Application of the van 't Hoff-Le Chatelier-Braun principle to chemical equilibria. K. POSTHUMUS (Rec. trav. chim., 1934, 53, 308—311).—Le Chatelier's new formulation (cf. A., 1933, 783) is incorrect, even if the ideal gas laws are assumed. H. S. P.

Thermodynamic deduction of the law of infinitely dilute gases. D. MATURO (Rev. fac. quim. ind. agric., Univ. nac. litoral, 1932, 2, 38—49).—Starting with $(\partial U/\partial v)_T=0$ and $(\partial H/\partial v)_T=0$, and assuming that in any real gas it is impossible to reach zero pressure by any finite reversible isometric process, it is shown that $\lim_{P=0} MPV=kT$. The application to the thermodynamic temp. scale and to the determination of mol. wts. is discussed. CH. ABS.

Activity coefficients of solutions. P. VAN RYSELBERGHE (Bull. Acad. roy. Belg., 1934, [v], 20, 234—238).—Theoretical. J. W. S.

Solubility of strong electrolytes in concentrated solutions. G. ÅKERLOF and H. C. THOMAS (J. Amer. Chem. Soc., 1934, 56, 593—601).—Simple relations between the thermodynamic activities of strong electrolytes in pure or mixed aq. solutions are considered with reference to the solubility of Ag_2SO_4 in H_2SO_4 and several sulphate solutions. Equations are derived for calculating the composition of the solution in three-component systems containing two strong electrolytes. E. S. H.

Equilibrium constants in terms of activities (cryoscopic). III. **Dissociation of quinoline *o*-chlorophenoxide in benzene and *p*-dichlorobenzene.** H. M. GLASS, W. M. MADGIN, and (in part) F. HUNTER (J.C.S., 1934, 260—263).—The vals. of the true equilibrium const. $K_a = a_{AB}/a_A a_B$ for the dissociation of quinoline *o*-chlorophenoxide in C_6H_6 and *p*- $\text{C}_6\text{H}_4\text{Cl}_2$ are 219.8 and 36.74, respectively, at the f.p. of the solvents. Hence the molal heat of formation is —6800 g.-cal., which is the same as for pyridine *o*-chlorophenoxide (this vol., 28). This equality is ascribed to the existence of the same type of valency linking in each compound, i.e., a co-ordinate linking between the N atom of the base and the H atom of OH in *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$. M. S. B.

Equations of state of water vapour. J. KUUSI-NEN (Forsch. Ingenieurwes., 1933, A, 4, 200—201; Chem. Zentr., 1933, ii, 2654).—Equations for the heat content (*i*), entropy (*s*), and pressure (*p*) are recorded. H. J. E.

Deliquescence and efflorescence. A. DAMIENS (Compt. rend., 1934, 198, 1233—1235). C. A. S.

Thermal dissociation of cadmium carbonate. P. Y. NARAYANA and H. E. WATSON (J. Indian

Inst. Sci., 1934, 17, A, 1—6).—The dissociation pressure falls steadily with increase in the proportion of CdO present. D. R. D.

Binary system, $\text{MnO}\text{--}\text{SiO}_2$. J. WHITE, D. D. HOWAT, and R. RAY (J. Roy. Tech. Coll., 1934, 3, 231—240).—The equilibrium has been derived from thermal observations and the phase changes confirmed by use of a high-temp. microscope. H. S. P.

Binary system $\text{TlNO}_3\text{--}\text{Ti}_2\text{CO}_3$. A. S. BROWN (J. Gen. Chem. Russ., 1933, 3, 998—1000).—The fusion diagram suggests formation of the compounds $2\text{TlNO}_3\cdot\text{Ti}_2\text{CO}_3$, m.p. 218° , and $\text{TlNO}_3\cdot\text{Ti}_2\text{CO}_3$, m.p. 214° . R. T.

Active oxides. LXXIII. Changes of the magnetic properties of a mixture of magnesium oxide with chromium oxide and calcium oxide with iron oxide during transformation into spinel. H. KITTEL and G. F. HUTTIG (Z. anorg. Chem., 1934, 217, 193—202).—Magnetic susceptibility data have been obtained for the above systems at different temp. and compared with the data previously obtained for other oxide mixtures. X-Ray spectroscopic observations have also been made on the system $\text{CaO}\text{--}\text{Fe}_2\text{O}_3$. M. S. B.

Thermal analysis of picrates. II. T. TUCHOLSKI (Rocz. Chem., 1934, 14, 125—140).—Dehydration and fusion temp., and those leading to explosion of the picrates of Be, Mg, Zn, Cd, Hg, Ca, Sr, and Ba are recorded. The following hydrates are recorded: Mg, $4\text{H}_2\text{O}$; Zn, $10\text{H}_2\text{O}$; Cd, 1 and $4\text{H}_2\text{O}$; Hg, 1 and $3\text{H}_2\text{O}$; Ca, $8\text{H}_2\text{O}$. Evidence is not found for the hydrates Mg, $5\text{H}_2\text{O}$; Zn, 1 and $5\text{H}_2\text{O}$; Cd, $5\text{H}_2\text{O}$; Ca, $3\text{H}_2\text{O}$; Ba, 2.5, 3, 4, and $4.5\text{H}_2\text{O}$, recorded by other authors. R. T.

Phase equilibria in hydrocarbon systems. II. Methane-propane. B. H. SAGE, W. N. LACEY, and J. G. SCHAAFSMA (Ind. Eng. Chem., 1934, 26, 214—217).—The system has been studied between 20° and 90° , and 1 and 200 atm. The results are given in full, with pressure-composition isotherms, const. composition curves on pressure-temp. and density-pressure diagrams, and isobars on the gas-liquid composition diagram. H. F. G.

Fusion diagram of the system carbamide-di-phenylamine. W. J. NIJVELD (Rec. trav. chim., 1934, 53, 430—432).—The diagram shows an extensive region of miscibility in the fluid state. This region meets the m.p. line of $\text{CO}(\text{NH}_2)_2$. H. S. P.

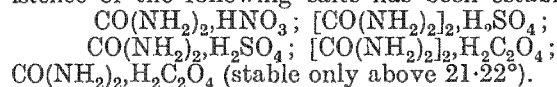
Binary systems. IV. J. H. KOERS and F. E. C. SCHEFFER (Rec. trav. chim., 1934, 53, 279—287).—Systems (*a*) with a stable quadruple point, (*b*) without a quadruple point, and (*c*) the transition case are considered theoretically. The systems $\text{CO}_2\text{--o-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, $\text{CO}_2\text{--}i\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$, and $\text{C}_6\text{H}_6\text{--p-C}_6\text{H}_4\text{ClBr}$ belong to type (*a*) and the systems $\text{CO}_2\text{--o-OH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ and $\text{C}_6\text{H}_6\text{--s-C}_6\text{H}_3\text{Cl}_3$ to type (*b*). H. S. P.

25° isotherms of the systems $\text{Na}_2\text{CO}_3\text{--NaHCO}_3\text{--H}_2\text{O}$ and $\text{Na}_2\text{CO}_3\text{--NaHCO}_3\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$. S. Z. MAKAROV and M. N. JAKIMOV (J. Gen. Chem. Russ., 1933, 3, 990—997).—The equilibrium relations are discussed. R. T.

Ternary system KI-PbI₂-H₂O at 0° and 25°. H. S. VAN KLOOSTER and P. A. BALON (J. Amer. Chem. Soc., 1934, 56, 591—592).—Only one double salt exists, KPbI₃·2H₂O. E. S. H.

Mixed crystals in the sulphate series. II. A. BENRATH and A. BLANKENSTEIN (Z. anorg. Chem., 1934, 217, 170—174).—Data are given for the system MnSO₄-ZnSO₄-H₂O. M. S. B.

Ternary systems of carbamide and acids. I. Carbamide, nitric acid, and water. **II.** Carbamide, sulphuric acid, and water. **III.** Carbamide, oxalic acid, and water. L. H. DALMAN (J. Amer. Chem. Soc., 1934, 56, 549—553).—The existence of the following salts has been established:



E. S. H.

Equilibria in binary and ternary systems of certain polynitro-compounds. K. HRYNAKOWSKI and Z. KAPUŚCIŃSKI (Rocz. Chem., 1934, 14, 115—124).—Contrary to Giua's findings (A., 1914, i, 817; 1915, i, 659) no compounds are formed in the systems *m*-C₆H₄(NO₂)₂ (I)-C₆H₃Me(NO₂)₂ (II), C₆H₂Me(NO₂)₃ (III), C₆H₂(OH)(NO₂)₃ (IV); (I)-(II); (II)-(IV); (III)-(IV); and (I)-(II)-(III). R. T.

Double decomposition in the absence of a solvent. XIX. A. P. OBUCHOV. **XX, XXI.** V. P. RADISCHTSCHIEV (J. Gen. Chem. Russ., 1933, 3, 787—791, 843—851, 852—864).—XIX. Fusion diagrams are given for the system NaI+KBr → NaBr+KI.

XX. The diagrams for NaCl-NaBr-NaI and KCl-KBr-KI suggest the formation of solid solutions which contain all three components.

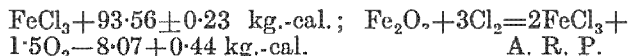
XXI. Diagrams are given for the system 2NaCl+K₂CO₃ → 2KCl+Na₂CO₃. R. T.

Double decomposition in the absence of a solvent. XXII, XXIII. O. S. DOMBROVSKAJA. **XXIV.** M. A. KLOTSCHKO (J. Gen. Chem. Russ., 1933, 3, 1007—1016, 1017—1025, 1026—1039).—XXII. The fusion diagrams for the systems KCl-K₂SO₄, KCl-LiCl, Li₂SO₄-LiCl, Li₂SO₄-KCl show no compound formation, whilst that for K₂SO₄-Li₂SO₄ indicates K₂SO₄·Li₂SO₄, m.p. 716°. The equilibrium relations for the system K₂SO₄+2LiCl ⇌ 2KCl+Li₂SO₄ are discussed.

XXIII. The diagrams for Cs₂SO₄+2KCl ⇌ K₂SO₄+2CsCl and 2RbCl+K₂SO₄ ⇌ Rb₂SO₄+2KCl do not suggest compound formation.

XXIV. The equilibrium relations in the system 2LiCl+Na₂SO₄ ⇌ 2NaCl+Li₂SO₄ are discussed. R. T.

Thermochemistry of iron. W. A. ROTR and F. WIENERT (Arch. Eisenhuttenw., 1933—1934, 7, 455—460).—The heat of reaction with aq. HCl at room temp. of finely-divided Fe and Fe₂O₃ [from Fe(CO)₅], Fe₃O₄ (from the reduction of Fe₂O₃ with H₂ and steam at 500°), and FeO (from anhyd. FeCl₂ and CaO) have been determined and the following thermochemical data derived: Fe+0.5O₂=FeO+64.65±0.12 kg.-cal.; 3Fe+2O₂=Fe₃O₄+266.76±0.22 kg.-cal.; 2Fe+1.5O₂=Fe₂O₃+195.19±0.20 kg.-cal.; FeO+Fe₂O₃=Fe₃O₄+6.94±0.33 kg.-cal.; Fe+1.5Cl₂=



A. R. P.

Thermometric study of formation of inorganic complexes. P. MONDAIN-MONVAL and R. PARIS (Compt. rend., 1934, 198, 1154—1156).—The curve obtained by plotting the temp. rise against the amount of aq. KI added to aq. HgCl₂ (cf. A., 1922, ii, 578) affords evidence of the formation of HgI₂ and K₂HgI₄ (cf. A., 1933, 37). Similarly when aq. KCN is added to aq. NiSO₄, ZnSO₄, or CoSO₄ breaks indicate the formation of (1) M^{II}(CN)₂ and (2) of K₂Ni(CN)₄, K₂Zn(CN)₄, and K₃Co(CN)₅, respectively (cf. A., 1910, ii, 458; 1924, ii, 704). C. A. S.

Heat of formation of silicon carbide and the existence of siloxicon. R. BRUNNER (Z. anorg. Chem., 1934, 217, 157—160).—The different vals. obtained for the heat of formation of SiC are discussed. It is not found possible to reconcile the val. of 39 kg.-cal. obtained dynamically (A., 1932, 341) with any of the calorimetric data. The existence of Si₂C₂O, as indicated by pressure data, is reaffirmed, contrary to the conclusions of Arndt and Hausmann (this vol., 42). M. S. B.

Heats of neutralisation of the amino-acids. G. DEVOTO (Atti R. Accad. Lincei, 1934, [vi], 19, 50—52).—The heats of neutralisation of thirteen NH₂-acids are recorded. The polar character of the various acids deduced from these data agrees with the results of other methods. O. J. W.

Conductance of aqueous solutions as a function of the concentration of potassium bromide and lanthanum chloride. G. JONES and C. F. BICKFORD (J. Amer. Chem. Soc., 1934, 56, 602—611).—Electrical conductance and *d* of 0.00025—3.75*M*-KBr and 0.00025—1.0*M*-LaCl₃ have been determined at 0° and 25°. The vals. of *d* are in accordance with an equation of the form given by Root (A., 1933, 347). The equation of Jones and Dole (A., 1930, 998) is applicable to the conductance data; Shedlovsky's equation (A., 1932, 699) fits the data for KBr up to 0.1*M*, but is not applicable to LaCl₃. E. S. H.

Guaiacol solutions. I. Electrical conductivity of sodium and potassium guaiacoxides. II. Distribution of sodium and potassium guaiacoxides between guaiacol and water. T. SHEDLOVSKY and H. H. UHLIG (J. Gen. Physiol., 1934, 17, 549—561, 563—576).—The vals. of *D* (=14.3), relative *η* (=7.23), and *ρ* (=1.1275) for a saturated solution of H₂O in guaiacol (I) and of *A* for solutions of Na and K guaiacoxide (II) in (I) are used to derive *Λ*_∞ and *K*, the dissociation const., of (II) in (I) by use of the Onsager equation (A., 1927, 517). Using an average val. of *Λ*_∞, the calc. vals. for *A* at various concns. agree with those obtained experimentally.

II. The distribution ratios for (II) between (I) and H₂O are determined by analysis and vals. for *K* derived in good agreement with those obtained conductimetrically. Bjerrum's equation for the variation of *r* with concn. (A., 1927, 1028) is modified by introducing the individual vals. of the radii of the ions, giving vals. for *r* of the same order as those obtained experimentally. H. D.

Electrochemical examination of the system $\text{AlBr}_3\text{--KBr}$ in the solid state. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Gen. Chem. Russ., 1933, 3, 869—871).—The compound $2\text{AlBr}_3\cdot\text{KBr}$ conducts electricity, and with Al electrodes Al is transported to the cathode. An increase in the KBr content of the electrolyte does not appreciably change the conductivity. R. T.

Electrochemical examination of solutions of aluminium chloride and potassium chloride in nitrobenzene. V. A. PLOTNIKOV and I. M. PODORVAN (J. Gen. Chem. Russ., 1933, 3, 782—786).—The sp. conductivity κ of PhNO_2 solutions of AlCl_3 is greatest when the concn. of AlCl_3 is 14%. κ rises on addition of KCl, to an extent proportional to its concn.; on electrolysis of such solutions K is deposited at the cathode, at a decomp. potential of 5 volts, as compared with 4.5 volts for solutions containing KCl alone. R. T.

Electrochemical properties of smooth films of electrolytically deposited platinum metals. I. I. SHUKOV (J. Gen. Chem. Russ., 1933, 3, 959—962).—Pt electrodes covered with a smooth layer of Pt (I) give better results in conductivity measurements than do those covered with Pt-black (II); the overpotentials obtained on electrolysis of aq. H_2SO_4 are of the same magnitude for (I) and (II). The active surface of (I) is > 10 times that present before platinising. R. T.

Superconductivity of films of tin. E. F. BURTON (Nature, 1934, 133, 459).—Thin films of Sn cease to show superconductivity (I) when they are plated over with a film of a non-superconducting metal such as Cu or Ni. When the film of Sn increases in thickness, a point is reached at which (I) is not lost by surface plating. L. S. T.

Persistent currents in superconductors. K. MENDELSSOHN and J. D. BABBITT (Nature, 1934, 133, 459—460). L. S. T.

Production of heat in superconductors by alternating currents. H. LONDON (Nature, 1934, 133, 497—498). L. S. T.

The antimony electrode. A. HOLMQUIST (Svensk Kem. Tidskr., 1934, 46, 2—10).—The potential attained in an acid solution of given p_{H} depends on whether the electrode is massive or powdered Sb, and varies with the nature of the acid, the greatest differences being observed between HCl and HClO_4 . The variations with different types of electrode are considered to be due to variable O_2 content of the solution. The oxidation-reduction potential for $\text{Sb}^{\text{III}}\text{--Sb}^{\text{V}}$ was measured in 3.8*N*-HCl, and data are given for the distribution of SbCl_3 between aq. HCl and Et_2O . R. P. B.

Effect of electrical leakage on the electromotive behaviour of the glass electrode. C. MORTON (J.C.S., 1934, 256—260).—Correct indications of the electromotive behaviour are obtained only by use of the quadrant electrometer or the electrometer triode valve. Other instruments distort the e.m.f. $\text{--}p_{\text{H}}$ graph to an extent depending on input impedances, but give satisfactory results in routine work provided

that the conditions obtaining during calibration are maintained const. by control of temp. and humidity.

M. S. B.
Cell lead|lead sulphate|cupric sulphate|copper. (MLLE.) M. QUINTIN and A. LEBETRE (Compt. rend., 1934, 198, 1140—1141).—Comparison of the normal potentials of the cells $\text{Pb}(\text{amalgam two phases})|\text{PbSO}_4(\text{s})|\text{CuSO}_4(\text{c})|\text{Cu}(\text{amalgam two phases})$ for $c=0.105\text{--}0.00105$, and $\text{Cu}(\text{amalgam two phases})|\text{CuSO}_4(\text{c})|\text{Hg}_2\text{SO}_4(\text{s})|\text{Hg}$ shows that the irregularities in the latter when c is $< 0.003M$ are determined by the solubility of Hg_2SO_4 . Similar irregularities occur in the former if c is $< 0.001M$ (cf. A., 1933, 781). C. A. S.

Thermodynamic study of dilute thallos chloride solutions by electromotive force measurements of the cell $\text{Ti--Hg}|\text{TiCl}(\text{m})|\text{AgCl}(\text{s}), \text{Ag}(\text{s})$. I. A. COWPERTHWAIT, V. K. LA MER, and J. BARKSDALE (J. Amer. Chem. Soc., 1934, 56, 544—549).—Data for the cell at 25° are: $E^\circ 0.55833$, $dE^\circ/dT 6.646 \times 10^{-4}$, $-\Delta F^\circ 12,877$ g.-cal., $-\Delta H^\circ 8307$ g.-cal. The curve obtained by plotting the logarithms of the activity coeffs. of TiCl against the square root of concn. is discussed in relation to the Debye-Hückel theory. E. S. H.

Thermodynamics of aqueous sodium sulphate solutions from electromotive force measurements. H. S. HARNED and J. C. HECKER (J. Amer. Chem. Soc., 1934, 56, 650—653).—Activity coeffs., relative partial mol. heat contents, and sp. heats of Na_2SO_4 have been calc. from e.m.f. determinations of the cells $\text{Pb}(\text{Hg})|\text{PbSO}_4(\text{s})|\text{Na}_2\text{SO}_4(\text{m})|\text{Na}_2\text{Hg}|\text{Na}_2\text{SO}_4(0.05)|\text{PbSO}_4(\text{s})|\text{Pb}(\text{Hg})$ at 5° intervals from 0° to 40° . E. S. H.

Electrometric measurements in solutions of quinine salts. H. L. PEDERSEN (Dansk Tidsskr. Farm. 1934, 8, 17—39).—On adding > 1 equiv. of acid to a solution of a pure quinine salt and then titrating with NaOH, the potential curve (measured with a quinhydrone electrode) has two points of inflexion, one (weak) corresponding with the di-acid salt, and one (strong) corresponding with the mono-acid salt. The p_{H} corresponding with the di-salt can be obtained from measurements with pure salt, and the amount of NaOH necessary to change the p_{H} from this val. to the mono-salt point of inflexion gives the amount of quinine present. If quinine is written $\text{B}_1\cdot\text{B}_2$, the acid dissociation consts. for the processes $\text{B}_1\text{H}^+\cdot\text{B}_2\text{H}^+ \rightarrow \text{B}_1\text{H}^+\cdot\text{B}_2+\text{H}^+$ and $\text{B}_1\text{H}^+\cdot\text{B}_2 \rightarrow \text{B}_1\cdot\text{B}_2+\text{H}^+$ are 4.3×10^{-5} and about 2×10^{-11} , respectively. R. P. B.

Electrolytic reduction potentials of organic compounds. XI. Reduction potentials of nitranilines. M. SHIKATA and E. TAGUCHI (Mem. Coll. Agric. Kyoto, 1934, No. 29, 1—17).—The electrolytic reduction potentials, P , of $10^{-3}\text{--}10^{-5}M$ -o- (I), -m- (II), and -p- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (III) determined polarographically with the dropping Hg cathode become more negative with increase of p_{H} from 1 to 10 and are independent of p_{H} in the range 10—13. Consistent with the weak basicity of the compounds, vals. of P for the ionic and the mol. forms are observed. The P of the ionic forms in 0.1*N*-HCl at 25° are (I)

—0.121, (II) —0.104, (III) —0.117 volt, which are more positive than P for PhNO_2 (IV), whilst for the mol. forms at p_H 7 the vals. are (I) —0.553, (II) —0.425, and (III) —0.507, which, excepting the val. for (II), are more negative than P for (IV). These results are related to the authors' negativity rule (cf. A., 1932, 231) and the theory of induced alternating polarity. J. G. A. G.

Electromotive behaviour of organic derivatives of arsenic and arsenious acids. H. ERLÉNMEYER and H. ARNI (Helv. Chim. Acta, 1934, 17, 308—311).—The potential of the oxidation-reduction system atoxyl acid $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$ and its reduction product $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_2\text{H}_2\text{O}$ has been determined at various concns. in 6*N*-HCl, 0.1*N*-HCl, and 0.0667*M*- KH_2PO_4 . M. S. B.

Oxidation-reduction properties of "evolved carbohydrates" in absence of oxygen. See this vol., 550.

Capacity of non-polarisable electrode with a.c. N. THON (Compt. rend., 1934, 198, 1219—1221).—By means of an arrangement similar to that of Jones and Josephs (cf. A., 1928, 595) it is shown that the capacity, C , of Hg electrodes in 0.5*M*- HgNO_3 varies as $1/\omega^2$ if the frequency, ν , is > 4200 per sec. ($\omega = \text{pulsatance}, = 2\pi\nu$); in 0.1*M*- HgNO_3 between $1/\omega^2$ and $1/\omega$, approaching $1/\sqrt{\omega}$ as the concn. of Hg diminishes; and in 2*M*- KNO_3 as $1/\sqrt{\omega}$. This disagrees with previous results (cf. A., 1873, 348; 1903, ii, 707). C appears to increase with depolarisation (cf. A., 1932, 24). C. A. S.

Arced gases. B. W. BRADFORD and G. I. FINCH (J.C.S., 1934, 360—365).—Apparatus is described for examining pre-arc'd jets of gases or mixtures, and for studying the interaction of two such jets, for preheating, and for determining the homogeneous and heterogeneous ignition temp. of various mixed arc'd and unarc'd gases. Arc'd jets of CO and O_2 both showed strong afterglows, and a bright characteristic glow appeared on mixing. No CO_2 was formed by direct combination of CO and O_2 . Pre-arc'ing of H_2 alone caused no appreciable formation of steam in mixed H_2 and O_2 jets, arc'ing of O_2 being also necessary. Moist arc'd H_2 gave the reactions of at. H. Arc'ing or otherwise of preheated jets had no effect on the ignition temp. of the mixed streams. It is concluded that H does not act as a promoter. N. M. B.

Influence of pressure on the spontaneous inflammation of hydrocarbons. H. F. COWARD (Nature, 1934, 133, 463—464).—Unpublished pressure-temp. curves by Dixon for the lag on ignition of C_3H_{12} vapour heated to a given temp. and issuing into the atm. at the same temp. show a break at 60 cm. pressure and are of the same general character as those obtained by Neumann and Estrovich (this vol., 259). L. S. T.

Movement of flame in firedamp explosions.—See B., 1934, 307.

Combustion of carbon monoxide. A. H. W. ATEN, jun. (Rec. trav. chim., 1934, 53, 269—278).—The theory is advanced that reactions in flames are due to ions. The extinction of flames by an electric

field, the influence of H_2O vapour and composition of the gas mixture on flame velocity, and the effect of pressure and composition of the mixture on ignition temp. are considered. H. S. P.

Kinetics of the thermal reaction of gaseous alkyl iodides with hydrogen iodide. R. A. OGG, jun. (J. Amer. Chem. Soc., 1934, 56, 526—536).—The reactions $\text{RI} + \text{HI} \rightarrow \text{RH} + \text{I}_2$, where R is Me, Et, or Pr^n , are homogeneous, free from appreciable side reactions, and proceed almost to completion at 250—320° and 3—360 mm. The order of reaction is complex, and appears to be controlled by two concurrent mechanisms—a bimol. reaction of RI with HI, and a unimol. dissociation of RI. The consts. for both reactions have been determined with the three materials. The unimol. coeff. for MeI and EtI falls at low pressures in accordance with the collision theories. E. S. H.

Spontaneous inflammability of fatty oils.—See B., 1934, 333.

Wave theory of periodic reactions. I. F. M. SCHEMJAKIN, V. K. NIKIFOROV, and P. F. MICHALEV. II. P. F. MICHALEV and F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1933, 3, 798—801, 1001—1004).—I. The expression $\lambda v = \text{const.}$, where λ is the distance between Liesegang rings forming from AgNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ in gelatin, and $\text{Pb}(\text{NO}_3)_2$ and KI in agar, and v is the velocity of propagation, is experimentally verified.

II. $\lambda v = \text{const.}$ is verified for MnCl_2 and $(\text{NH}_4)_2\text{S}$, and Na_2HPO_4 and CaCl_2 in gelatin (I), and for AgNO_3 and Na_2HAsO_4 in (I) and in agar (II). If a drop of aq. KI is placed on (I) or (II) containing HgCl_2 , a yellow ring appears, travels down the test-tube, and finally disappears at the bottom. This phenomenon is due to the successive reactions: $\text{HgCl}_2 + 2\text{KI} \rightarrow \text{HgI}_2 + 2\text{KCl}$; $\text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2\text{HgI}_4$. R. T.

Kinetics of the thermal *cis-trans* isomerisation. III. G. B. KISTIAKOWSKY and W. R. SMITH (J. Amer. Chem. Soc., 1934, 56, 638—642; cf. A., 1931, 1239).—Semi-quant. experiments with Me_2 citraconate at 280—360° and 500—30 mm. show that the reaction is similar to that previously described for Me_2 maleate. The activation energy increases with rise of temp., reaching about 25,000 g.-cal. at the highest temp. studied. The isomerisation of *iso*-stilbene (I) is a unimol. reaction, having an activation energy of 43,000 g.-cal., which does not fall with pressure down to 4 mm. ≤ 12 oscillators must participate in the isomerisation process. In the gaseous system stilbene \rightarrow (I) the equilibrium consts. near 600 Å. are about 0.07, from which 3000 σ -cal. is the calc. approx. heat of reaction. E. S. H.

Polymerisation processes. I. Kinetic investigations of aqueous solutions of formaldehyde. M. WADANO, C. TROGUS, and K. HESS (Ber., 1934, 67, [B], 174—190).—The kinetics of the establishment of the equilibrium $3(\text{CH}_2\text{O}, \text{H}_2\text{O}) \rightleftharpoons \text{C}_3\text{H}_5\text{O}_3, \text{H}_2\text{O} + 2\text{H}_2\text{O}$ (cf. Auerbach *et al.*, A., 1905, i, 859; 1908, i, 131) have been studied by the interferometer method controlled by cryoscopic determination of mol. wt. Reaction is balanced with reverse

change of a higher order. With $> 3\%$ CH_2O the change is unimol., the reverse action being negligible. The temp. coeff. of the velocity coeff. is 2.7 per 10° . OH^- is 10 times as powerful as H^+ as catalyst. Substances (e.g., MeOH) which diminish the ionic product of H_2O diminish the velocity coeff. markedly, whereas neutral salts have no observable effect. The energy of activation of the depolymerisation of CH_2O is practically identical with that of ester hydrolysis and mutarotation, but differs from that of glucoside fission. As in the case of depolymerisation, the velocity coeffs. pass through a min. at p_{H} 3—7 for mutarotation, p_{H} 3.8—4.6 for ester hydrolysis, and p_{H} 5.8—6.2 for amide hydrolysis. In all these cases within the region of moderate $[\text{H}^+]$ and $[\text{OH}^-]$ the reaction coeff. is directly proportional to the concn. of the ions; in contrast, fission of the glucosidic anion is accelerated only by H^+ . It is therefore established that the O linkings in polymeric CH_2O are of the same character as in esters, amides, and semi-acetals and that the mechanism of polymerisation and depolymerisation of CH_2O in H_2O is similar to that of the rupture and formation of such linkings. The acidic and basic dissociation consts. of $\text{CH}_2(\text{OH})_2$ are determined. In dil. solution the following equilibria are assumed, $\text{CH}_2(\text{OH})_2 \rightleftharpoons \text{CH}_2^+\text{OH} + 3\text{OH}^-$ (I); $\text{CH}_2(\text{OH})_2 \rightleftharpoons \text{CH}_2^+\text{O} + 3\text{H}^+ + 3\text{OH}^-$ (II); $\text{CH}_2(\text{OH})_2 \rightleftharpoons \text{OH}\cdot\text{CH}_2\text{O} + 3\text{H}^+$ (III). (I), (II), and (III) are favoured at $p_{\text{H}} < 2.6$, $2.6-4.5$, and > 4.5 , respectively. In conc. solution the following equilibria also exist: $(\text{OH}\cdot\text{CH}_2\text{O})_2\text{CH}_2$ (IV) $\rightleftharpoons \text{OH}\cdot\text{CH}_2\text{O}\cdot\text{CH}_2\text{O}\cdot\text{CH}_2^+ + \text{OH}^-$; (IV) $\rightleftharpoons \text{OH}\cdot\text{CH}_2\text{O}\cdot\text{CH}_2\text{O}\cdot\text{CH}_2^+\text{O} + \text{H}^+$; (IV) $\rightleftharpoons \text{CH}_2\text{O}\cdot\text{CH}_2\text{O}\cdot\text{CH}_2\text{O}\cdot\text{O} + \text{OH}^- + \text{H}^+$. It is estimated that the energy of formation of the C·O linking in polymerised CH_2O is $1/4$ to $1/5$ that of the normal C·O union. H. W.

Acid hydrolysis of ethyl malonate. (MLLE.) M. G. TER HORST (Rec. trav. chim., 1934, 53, 312—324).—When Et malonate is hydrolysed in a mixture of EtOH and H_2O , the ratio of the coeffs. of the two consecutive reactions is 1.59, whilst in H_2O the ratio is 1.57. The agreement between these two vals. shows that the ratio is independent of the medium, and is due to the structure of the acid. The ratio for the esterification of malonic acid is 2.34. H. S. P.

Rate of hydrolysis of bromoacetic acid in relation to its degree of ionisation. H. M. DAWSON and N. B. DYSON (Proc. Leeds Phil. Soc., 1934, 2, 495—498).—The reduced rate of hydrolysis of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ (I) in presence of strong acid is due to the gradual elimination of the reaction between (I) and $\text{CH}_2\text{Br}\cdot\text{CO}_2^-$ with increase of $[\text{H}^+]$. H. S. P.

Mutarotation of α -D-glucose in deuterium water. E. PASCU (J. Amer. Chem. Soc., 1934, 56, 745—746).—The velocity in H_2O at 20° is identical with that observed in H_2O at 10° . For the equilibrium solution in H_2O $[\alpha]_{\text{D}}^{20}$ is $+52.14^\circ$, as compared with 52.06° in H_2O . E. S. H.

Mutarotation of β -D-ribose and β -L-ribose. F. P. PHELPS, H. S. ISBELL, and W. PIGMAN (J. Amer. m. Soc., —748).—Measurements at 20° and 1° show that mutarotation takes place rapidly,

the direction of change being reversed after a few min., so that the initial and final rotations do not differ greatly. E. S. H.

Decomposition of malic acid by sulphuric acid. R. E. DERIGHT (J. Amer. Chem. Soc., 1934, 56, 618—620).—The rate of decomp. increases up to a certain point as H_2O is removed, and then decreases. The max. resembles that observed in the similar reactions of HCO_2H , $\text{H}_2\text{C}_2\text{O}_4$, and citric acid. The temp. coeff. at $35-45^\circ$ for 100% H_2SO_4 is 3.75. E. S. H.

Kinetics of the decomposition of trichloroacetates in various solvents. F. H. VERHOEK (J. Amer. Chem. Soc., 1934, 56, 571—577).—The velocities of decomp. of $\text{NH}_2\text{Ph}\cdot\text{CCl}_3\cdot\text{CO}_2\text{H}$ in H_2O , EtOH, and NH_2Ph , and of $\text{CCl}_3\cdot\text{CO}_2\text{Na}$ and $(\text{CCl}_3\cdot\text{CO}_2)_2\text{Ba}$ in H_2O and EtOH at 70° increase in the order given. The decomp. in H_2O and of the Na salt in EtOH are first-order reactions, but departures are observed in the remaining reactions, probably due to changes in the degree of dissociation. The reaction velocity depends on $[\text{CCl}_3\cdot\text{CO}_2^-]$. Temp. coeffs. in several solvents indicate that the stability of this ion is determined by the nature and extent of solvation. The formation of Cl^- in aq. and EtOH solutions of $\text{CCl}_3\cdot\text{CO}_2^-$ is due to oxidation of CHCl_3 produced by decomp. E. S. H.

Application of the ebullioscope to precise determination of coefficients of esterification. W. SWIENTOSŁAWSKI (Rocz. Chem., 1934, 14, 98—104).—Using an ebullioscopic method, which permits the elimination of a no. of sources of error inherent in the analytical methods, slightly higher vals. are obtained for velocity of formation of EtOAc . R. T.

Reaction of organic halides with piperidine. IV. Bromo-esters.—See this vol., 532.

Determination of enzyme dissociation constants.—See this vol., 558.

Influence of the surface of the oxidiser (I_2O_5) on the velocity of oxidation of carbon monoxide. ASTAPENJA, VARNIK, and ZEIKIN (J. Gen. Chem. Russ., 1933, 3, 839—842).—The optimum temp. of oxidation of CO by I_2O_5 varies with the degree of subdivision of the latter. R. T.

Measurement of reaction rates at high temperatures. J. H. CHESTERS and C. W. PARMELEE (J. Amer. Ceram. Soc., 1934, 17, 50—59).—The reactions $\text{quartz} \rightarrow \text{cristobalite}$ and $\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{spinel}$ were studied by measuring continuously the firing expansion ($1300-1500^\circ$) of test-pieces moulded at 10,000 lb. per sq. in. The products were identified by X-ray and microscopical examination, and the amounts present also calc. from the changes in d . Medina quartzite was completely converted into cristobalite after 2 hr. at 1500° ; addition of 2% of CaO increased the rate, and a further addition of 1.5% of $\text{Na}_2\text{O} + 1.5\%$ of Fe_2O_3 completed the change after 2 hr. at 1400° . A mixture of electrically fused MgO (grain size 0.15—0.06 mm.) and Al_2O_3 (3.59—0.15 mm.) contained 25% of MgO, Al_2O_3 after 2 hr. at 1500° ; addition of 2% of B_2O_3 increased the amount to 75%. A mixture containing only fine particles

(0.06 mm.) was completely converted after 10 min. at 1450°. Test-pieces moulded under high pressure increased in porosity during firing. J. A. S.

Rate of displacement of copper from solutions of its sulphate by cadmium and zinc. C. V. KING and M. M. BURGER (Trans. Electrochem. Soc., 1934, 65, 115—122).—Rates of dissolution of cylindrical specimens of pure Zn and Cd in dil. CuSO_4 solutions increase continuously with speed of rotation and show no sign of approaching a max. (cf. Centnerszwer, A., 1932, 1003). Observed differences in rates of dissolution of Zn and Cd in a given CuSO_4 solution and of Cd in CuSO_4 solutions of various concns. are attributed to differences in adhesion and physical character of the replaced Cu. H. J. T. E.

Theory of corrosion. II. Rusting of iron on the film theory of passivity.—See B., 1934, 324.

Corrosion of zinc in chloride solutions.—See B., 1934, 325.

Mechanism of detonation in lead azide crystals. T. C. SUTTON (Nature, 1934, 133, 463).—The unit cell of PbN_6 , space-group Q^{12} , contains 24 mols., arranged in eight groups each containing 3PbN_6 . The criterion for detonation is closely related to cryst. structure, and thermal decomp. appears to be due to the activation of 1 mol. of PbN_6 , whilst detonation requires the simultaneous activation of all three constituents of one of the complex groups $(\text{PbN}_6)_3$. L. S. T.

Detonation of explosives.—See B., 1934, 350.

Preservation of hydrogen peroxide.—See B., 1934, 318.

Induced oxidation of cyanide. B. K. HARNED and C. J. DEERE (J. Biol. Chem., 1934, 104, 727—736).—Oxidation of NaCN , yielding $\text{Na}_2\text{C}_2\text{O}_4$ and NH_3 , is induced by oxygenation of alkaline glucose solutions, utilising about 0.5 of the extra O, absorbed. H. G. R.

Catalysis of ethyl diazoacetate in very dilute solutions of organic acids. M. DUBOUX and P. MATAVULJ (Helv. Chim. Acta, 1934, 17, 245—257).—In very dil. org. acid solutions the velocity coeff. of hydrolysis of $\text{N}_2\text{CH}\cdot\text{CO}_2\text{Et}$ is not strictly proportional to $[\text{H}^+]$ as determined by conductometric methods. The accepted val. 38.5 for k_H in the equation $k=k_H[\text{H}^+]$ becomes 36.7 in 0.001*M*-acid and 35.5 in 0.0005*M*-acid. This diminution of k_H with concn. of acid is comparable with the behaviour observed in the inversion of sucrose in presence of org. acids. M. S. B.

Oxidation of sucrose to oxalic acid by the method of Naumann, Moeser, and Lindenbaum. W. DOMINIK and J. JANCZAK (Rocz. Chem., 1934, 14, 141—151).—70% yields of $\text{H}_2\text{C}_2\text{O}_4$ (I) are obtained from sucrose and HNO_3 (*d* 1.4) at 70°, using 0.006 g. NH_4VO_3 (II) per 100 c.c. as catalyst. The velocity of reaction can be increased by taking higher concns. of (II), which, however, also catalyses oxidation of (I). Satisfactory yields of (I) are also obtained at higher temp., using less conc. HNO_3 . The yields of (I) are not increased by conducting the reaction in an atm. of CO_2 . The intermediate products of oxidation are also convertible into (I), so that the

mother-liquors from crystallisation of (I) can be further utilised. Reduction of HNO_3 does not proceed further than to NO. The vol. of the reaction mixture can be reduced by adding only a fraction of the necessary quantity of HNO_3 , and introducing NO_2 during the reaction. R. T.

Oxidation of carbon monoxide with a silver catalyst. A. F. BENTON and R. T. BELL (J. Amer. Chem. Soc., 1934, 56, 501—505).—Experiments with reduced Ag at 80—140° show that the rate of reaction is proportional to the pressure of CO, independent of the CO_2 pressure, and independent of O_2 pressure when CO is in excess. The average energy of activation is 13.3 kg.-cal. The facts are consistent with measurements showing a very small adsorption of CO, no adsorption of CO_2 , and a slow, irreversible, activated adsorption of O_2 . The observed rates are $> 1/30$ of those calc., assuming that reaction occurs at every collision of CO with adsorbed O_2 , in which the joint energy exceeds the energy of activation. E. S. H.

Oxidation of phosphine in presence of tungsten and molybdenum. H. W. MELVILLE and H. L. ROXBURGH (J.C.S., 1934, 264—272; cf. A., 1933, 790).—The oxidation of PH_3 in presence of Mo and W filaments at pressures below the explosion limit appears to take place almost wholly on the surface. A faint glow indicates the presence of a trace of homogeneous reaction, but this is not measurable. Experiments with SiO_2 and Pyrex filaments were also unsuccessful, and the presence of P did not induce the reaction to leave the surface. The causes of the difference in the reaction of O, with P and with PH_3 are discussed. The catalytic decomp. of PH_3 and NH_3 is inhibited by the simultaneous bombardment of the filament with at. H. M. S. B.

Regeneration of vanadium catalysts.—See B., 1934, 273.

Effect of catalysts on the reaction between olefines and hydrogen sulphide.—See B., 1934, 265.

Mechanical activation at the surface of an electrode. K. M. GORBUNOVA and A. T. VAHRAMJAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 127—129).—A study of the deposition of metal on a Ag cathode in AgNO_3 solution, with a highly polished and with a scratched surface. In the latter case deposition tends to take place around the scratch, owing to an increased no. of active centres.

W. R. A.

Relation between oxygen overvoltage and catalysis. A. D. GARRISON and J. F. LILLY (Trans. Electrochem. Soc., 1934, 65, 171—184).—At a polished metal surface in 0.1*N*-NaOH a steady representative val. of the O overvoltage (η) at given c.d. (*I*) can be obtained by approach from either higher or lower c.d., and for given metal η —where k has the same val. for all metals examined. For different metals the overvoltage at zero c.d. η_0 increases in the order: Ni, Co, Fe, Ir, Pt, Au. When the same metal surfaces are cathodically polarised while air is bubbled around them, the single potential is also a linear function of *I*, and the slope

of this line (k_0) is taken as a measure of the catalytic effect of the given metal on the ionisation of O_2 . For the various metals k_0 increases in the reverse order to that for η_0 , and $\log k_0$ is a linear function of η_0 . The behaviour of Au at low cathodic c.d. is anomalous.

H. J. T. E.

Electrodeposition of metallic niobium, and its separation from tantalum. N. A. IZGARISCHEV and A. F. PREDE (J. Gen. Chem. Russ., 1933, 3, 831—838).—Mixtures of Ta_2O_5 and Nb_2O_5 are fused with $K_2S_2O_7$, and the melt is dissolved in 40% KOH, or in saturated aq. $H_2C_2O_4$ or citric acid. On electrolysis of these solutions, Nb is deposited quantitatively on the cathode, in the form of a bright, smooth, adherent coating. The industrial possibilities of Nb plating are discussed.

R. T.

Electrodeposition of cuprous oxide film.—See B., 1934, 330.

Chlorine in the lead storage battery.—See B., 1934, 330.

Electrodeposition of aluminium from non-aqueous solutions.—See B., 1934, 326.

Electrolysis of ether solutions of the Grignard compound.—See this vol., 517.

Electro-organic oxidations in concentrated aqueous organic salt solutions. Stability of the sulphonate solvents and the oxidation of benzaldehyde and benzyl alcohol. R. H. MCKEE and J. R. HEARD, jun. (Trans. Electrochem. Soc., 1934, 65, 135—139).—Conc. aq. solutions of Na salts of aromatic sulphonates are not appreciably oxidised at Pt or Ni anodes except when strongly acidified, and act as solvents for many substances insol. in H_2O , which can thus be subjected to anodic oxidation more effectively than if in suspension. $PhCHO$ is very sol. in these solvents, especially in the presence of $BzOH$, and in alkaline solutions is readily oxidised anodically to $BzOH$ without tar formation, especially in the presence of CuO as catalyst. In such solutions there is some direct production of $BzOH$ by the Cannizzaro reaction, and the $CH_2Ph\cdot OH$ simultaneously produced is probably the effective anodic depolariser. $CH_2Ph\cdot OH$ is very sol. in these solvents and is readily anodically oxidised to $PhCHO$ and $BzOH$, especially in the presence of hydroxides of Ni or Co as catalysts. With free NaOH in the solution $BzOH$ is the main product; with Na_2CO_3 , $PhCHO$. The efficiency of these oxidations under various conditions has been investigated.

H. J. T. E.

Electro-organic oxidations in concentrated aqueous organic salt solutions. Reactions with toluene, oleic acid, benzoin, and other substances. R. H. MCKEE and J. R. HEARD, jun. (Trans. Electrochem. Soc., 1934, 65, 161—170; cf. preceding abstract).—In alkaline solutions of Na salts of aromatic sulphonates benzoin is oxidised efficiently to $BzOH$ at a Ni anode. The efficiency of anodic oxidation of oleic acid is lower in slightly acid than in alkaline solutions, but the reverse is true with more unsaturated linseed fatty acids. Anodic oxidation of quinol and anodic halogenation of $PhMe$ in these solvents were also investigated.

H. J. T. E.

Chemical reactivity and light absorption. I. N. R. DHAR and A. K. BHATTACHARYYA (J. Indian Chem. Soc., 1934, 11, 33—43).—It is suggested that the presence of a second reactant sensitises mols. to radiation of longer wave-length. Examples are quoted.

R. S.

Correlation of the photosyntheses of phosgene and hydrogen chloride. G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 579—583).—Kinetic investigations show that the active form of Cl involved in the chain processes of the two reactions is the same and is probably Cl_2 . The calc. heat of dissociation of the reaction $Cl_3 \rightarrow Cl_2 + Cl$ is 5.0 ± 1.0 kg.-cal.

E. S. H.

Photolysis of nitrogen oxides: N_2O_5 , N_2O_4 , and NO_2 . H. H. HOLMES and F. DANIELS (J. Amer. Chem. Soc., 1934, 56, 630—637).—Absorption coeffs. have been determined from 436 to 265 m μ . N_2O_5 is decomposed by light of 280 and 265 m μ with a quantum efficiency 0.6. N_2O_4 is decomposed at 265 m μ with a quantum efficiency 0.4; λ 366 and 313 m μ are absorbed, but give no measurable decomp. NO_2 is decomposed by 313, 366, 405, and 436 m μ . He, A, N_2 , O_2 , H_2 , CO_2 , and N_2O decrease the photo-decomp., but are more effective in reducing the fluorescence of NO_2 . Photo-decomp. in CCl_4 solution is slight.

E. S. H.

Effect, on the latent image, of post-heating and of melting the gelatin. A. J. REARDON and H. P. GRIGGS (J. Opt. Soc. Amer., 1934, 24, 85—90).—Exposed plates, half of which were bathed in H_2O at 45° for 5 sec. and dried, were heated for const. time in an oven saturated with H_2O vapour, or for varying times at 70°. The results on development show that, for the bathed plates, a continuous decrease of the latent image is caused by increased heating, but with the unbathed plates an increase occurs up to about 30 min. heating at 70°, after which a rapid decrease sets in. The bathing treatment causes more immediate fluidity of the gelatin. The rate of decrease is the greater the greater is the initial exposure to light. The crystal-cracking hypothesis of the latent image is supported on the ground that heating causes increased cracking until the fluidity of the gelatin is sufficient to start filling the cracks, forming a less developable gelatin—Ag—AgBr surface.

J. L.

Formation of histamine by irradiation of histidine.—See this vol., 534.

Photochemical addition of chlorine to cinnamic acid. A. BERTHOUD and D. PORRET (Helv. Chim. Acta, 1934, 17, 237—245).—The above reaction follows the same laws as the photobromination of cinnamic acid (A., 1927, 528; 1930, 718). The velocity is practically independent of the concn. of acid, proportional to $[Cl_2]$ for total absorption of light and to $[Cl_2]^{1.5}$ for feeble absorption. It is also proportional to $I^{1/2}$. The quantum yield differs with experimental conditions. It was 2.4 in one case. The thermal coeff. (25—35°) is 1.5. The life of a reaction chain is < 0.02 sec.

M. S. B.

Photochemical reduction of methyl-red by phenylhydrazine using chlorophyll solution as photosensitiser. J. C. GHOSH and S. B. SEN-

GUPTA (J. Indian Chem. Soc., 1934, **11**, 65—77).—The reaction velocity, after an induction period, is of zero order with respect to Me-red (I) and $\text{NHPh}\cdot\text{NH}_2$ (II) in MeOH or C_6H_6 solution when $\lambda=5460 \text{ \AA.}$; γ is approx. 1. When $\lambda=4358 \text{ \AA.}$, the same holds in MeOH , but in C_6H_6 the velocity is unimol. with respect to (I) and (II), and $\gamma=0.05$. Using $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$ in MeOH , $\gamma=0.013$, and the rate is unimol. with respect to (I). In this case there is a measurable dark reaction. A mechanism based on the formation of an activated complex of chlorophyll and (I) is advanced. R. S.

Kinetics of photosynthesis and allied processes. E. C. C. BALY and L. B. MORGAN (Nature, 1934, **133**, 414).—Theoretical. L. S. T.

Influence of the intensity of irradiation on the ionic yield in reactions produced by alpha particles. W. MUND (Bull. Soc. chim. Belg., 1934, **43**, 100—110).—Theoretical. The general case is considered, followed by the case of a gas exposed to α -rays from a capsule of Rn within the gas, and that of a mixture of a gas with Rn. D. R. D.

Mechanism of reactions provoked by α -rays in gases. W. MUND (Ann. Soc. Sci. Bruxelles, 1934, **B**, 54, 30—35).—Theoretical. J. W. S.

Effect of lead content on the colouring of sodium and potassium chlorides when irradiated with radium radiations. O. HAHN and H. J. BORN (Naturwiss., 1934, **22**, 137—138).—Two processes occur when NaCl and KCl crystals containing Pb are irradiated with Ra radiations. Pb-free NaCl is coloured amber-yellow, but with increasing quantities of Pb an unstable yellow colour is first produced, which later changes to a stable blue colour. The stability of the primary yellow colour decreases with increasing Pb content. Pb-free KCl is coloured reddish-violet by Ra irradiation, but with increasing Pb content the colour becomes increasingly unstable, and a stable rose colour is produced. The effect of the addition of Pb to these crystals on the colour on irradiation is the same as that of pressure or temp. A. J. M.

Influence of the intensity of irradiation, pressure, mercury vapour, and nature of the walls on the radiochemical decomposition of ammonia. A. LUYCKX (Bull. Soc. chim. Belg., 1934, **43**, 117—159).—Experimental determinations of the ionic yield, M/I , using both central irradiation and admixture with Rn, are recorded. M/I decreases with increase of pressure, except for very low intensities, when the reverse is true. In Na_2O -glass vessels M/I increases with the size of the vessel. M/I is not affected by the presence of Hg vapour, but at low pressures it is decreased by the presence of a Hg mirror on the walls of the vessel. Etching of the walls with HF has no measurable effect on M/I . D. R. D.

Negative catalysis of the radiochemical decomposition of ammonia by platinised walls. A. LUYCKX (Bull. Soc. chim. Belg., 1934, **43**, 160—177).—The ionic yield is reduced by sputtering the walls of the glass vessel with Pt. The amount of adsorption by the Pt is negligible. The sphere of

activity of the Pt does not extend any appreciable distance into the gas, and it is probable that it must be actually struck by an α -particle in order to exhibit its activity. Pt has no effect on the radiochemical synthesis of NH_3 from its elements, but the negative catalytic effect of the Pt on the decomp. is destroyed by this process. D. R. D.

Fractionation of hydrogen by diffusion through palladium. V. LOMBARD and C. EICHNER (Compt. rend., 1934, **198**, 932—934; cf. A., 1932, 906).— H_2 which has diffused once through Pd diffuses again approx. 19% more quickly than that portion of the original stream of H_2 which did not diffuse. Accumulation of impurities was very improbable (cf. this vol., 156). C. A. S.

Exchange reactions of hydrogen atoms. N. F. HALL, E. BOWDEN, and T. O. JONES (J. Amer. Chem. Soc., 1934, **56**, 750).—When 2% H_2O in H_2O dissolves substances and is subsequently distilled off, (1) no interchange of H^1 with H^2 occurs with KCl , KH_2PO_4 , KOAc , KOBz , or H_2 during brief contact, (2) one third of H^1 is immediately exchanged in $(\text{CH}_2\cdot\text{OH})_2$, (3) exchange increases with time of contact with KOAc and H_2 . E. S. H.

Preparation of distilled water. R. KUMMER (Pharm. Ztg., 1934, **79**, 355—358).

Isotopic fractionation of water by distillation. N. F. HALL and T. O. JONES (J. Amer. Chem. Soc., 1934, **56**, 749—750).—Determinations of d and n show that considerable separation occurs in the distillation of H_2O - H_2O mixtures. E. S. H.

Preparation of beryllium.—See B., 1934, 325.

Boron hydrides. XVIII. Preparation of B_2H_6 from boron trichloride and hydrogen. A. STOCK, H. MARTINI, and W. SUTTERLIN. **XIX. Preparation of B_2H_6 from boron tribromide and hydrogen.** A. STOCK and W. SUTTERLIN (Ber., 1934, **67**, [B], 396—407, 407—411; cf. A., 1933, 34).—**XVIII.** The prep. of B_2H_6 from BCl_3 and H_2 by action of an electric discharge according to Schlesinger *et al.* (A., 1932, 350) has been examined in detail. Only $\text{B}_2\text{H}_5\text{Cl}$ appears to be formed in the region of the discharge; B_2H_6 in the gaseous product arises secondarily by decomp. of $\text{B}_2\text{H}_5\text{Cl}$ into B_2H_6 and BCl_3 . Complete removal of HCl formed during the reaction from B_2H_6 is effected with sufficient rapidity by K. B_2Cl_4 is found among the products of the reaction only, and then in very small amount, when a mixture of much BCl_3 and little H_2 is subjected to the electric discharge. Reaction between B_2H_6 and HCl leads through $\text{B}_2\text{H}_5\text{Cl}$ to an equilibrium between this and its decomp. products, B_2H_6 and BCl_3 . Small amounts of HCl and B_2H_6 disappear thereby practically completely. Reaction occurs with a B_2H_6 - HCl mixture obtained from the prep. of B_2H_6 much more rapidly than with one prepared from pure B_2H_6 and HCl ; the former contains therefore a catalytic accelerator of unknown type in small amount. Hg does not affect the rate of reaction. The equilibrium $6\text{B}_2\text{H}_5\text{Cl} \rightleftharpoons 5\text{B}_2\text{H}_6 + 2\text{BCl}_3$ has been examined quantitatively. BBr_3 is better adapted than BCl_3 to the prep. of B_2H_6 .

XIX. Details are given of the prep. of B_2H_6 from

BBr_3 and H_2 . Advantages claimed are that the saturation of H_2 with BBr_3 does not require a cooling bath, that reaction in the zone of discharge occurs more smoothly and with production of less B and solid B hydrides than when BCl_3 is used, and, mainly, that B_2H_6 and HBr can be separated completely from one another by fractional distillation. BBr_3 does not react as completely as BCl_3 in the zone of discharge. H. W.

Isolation of chlorodiborane: additions to the high-vacuum technique for chemical work with volatile substances. A. B. BURG (J. Amer. Chem. Soc., 1934, 56, 499—501).— $\text{B}_2\text{H}_6\text{Cl}$, prepared by reaction of B_2H_6 with BCl_3 followed by distilling through a U-tube at -150° , has m.p. -142° and v.p. 18 mm. at -78.5° . Apparatus and technique for fractional condensation are described. E. S. H.

Periodic efflorescence of alum. F. M. SCHEM-JAKIN (J. Gen. Chem. Russ., 1933, 3, 1005—1006).—A crystal of K Cr alum exhibited numerous points around which concentric zones (15—20) of efflorescence were evident. R. T.

Compounds of aluminium bromide with toluene, nitrobenzene, and metal bromides. V. A. PLOTNIKOV, Z. A. JANKELEVITSCH, and I. A. SCHEKA (J. Gen. Chem. Russ., 1933, 3, 802—807).—The compound $\text{CuBr}\cdot\text{AlBr}_3$ (I), m.p. 239° , is prepared by concentrating a C_6H_6 solution of CuBr and AlBr_3 ; the crystals separating from an analogous PhMe solution are $\text{CuBr}\cdot\text{AlBr}_3\cdot\text{PhMe}$ (II), decomposing at 140° to yield PhMe and $\text{C}_6\text{H}_5\text{MeCl}$, and dissociating into its constituents in H_2O , with partial oxidation of PhMe to PhCHO. The compound $\text{LiBr}\cdot 2\text{AlBr}_3\cdot 2\text{PhNO}_2$, m.p. 63° , obtained analogously from PhNO₂ solutions, decomposes at 265° , with copious evolution of gaseous products; on electrolysis its solutions in C_6H_6 or PhMe Li is deposited at the cathode. Compressed (II), but not (I), conducts electricity. R. T.

Formation of aluminium nitride from aluminium and amines. V. A. PLOTNIKOV and N. T. KALITA (J. Gen. Chem. Russ., 1933, 3, 872—873).—The reaction $2\text{AlCl}_3\cdot\text{NH}_3$ (I) + $2\text{Al} \rightarrow 2\text{AlCl}_3\cdot\text{AlN} + 3\text{H}_2$ takes place on adding Al to fused (I). R. T.

Preparation and properties of gallium and gallium trichloride. W. M. CRAIG and G. W. DRAKE (J. Amer. Chem. Soc., 1934, 56, 584—585).—The separation of traces of Ga from Pb dross is described. Ga has m.p. 29.755° , d_{25}^{25} 5.903, at. vol. 11.81. Pure Ga has little tendency to supercool. GaCl_3 has m.p. 76.65° , b.p. 199.6° . E. S. H.

Combustion of graphite. I. V. SIHVONEN (Suomen Kem., 1934, 7, B, 80—82).—A further discussion of previous work (cf. A., 1933, 1254).

Solubility of silicon in hydrofluoric acid. H. FUNK (Ber., 1934, 67, [B], 464; cf. Marchot and Funk, A., 1930, 1007).—The solubility of Si in HF is best judged by the evolution of H_2 . Bedel's method (this vol., 135) of measuring loss in wt. involves SiO_2 and other sol. impurities. H. W.

Preparation of rutile. H. RHEINBOLDT and W. WISFELD (Ber., 1934, 67, [B], 375—376).—Rutile is obtained when TiCl_4 vapour and O_2 are passed through a porcelain tube at about 700° ; oxychlorides do not appear to be formed at any stage of the reaction. H. W.

Preparation of hydrazine sulphate by Raschig's process. J. HENRION (Bull. Soc. chim. Belg., 1934, 43, 115—116).—The published methods for the prep. of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ from NH_3 , NaOCl , and H_2SO_4 are reviewed and the following improved method is recommended. Cl_2 is passed into 100 c.c. of 5% aq. NaOH , cooled in a freezing mixture, until 4 g. have been absorbed. The solution is exposed to the air for 12 hr. for all free Cl_2 to evaporate (essential for a good yield). The solution is then added to a mixture of 200 c.c. of saturated aq. NH_3 with 15—20 c.c. of aq. gelatin. The mixture is boiled down to half its vol. and then well cooled. 10 c.c. of conc. H_2SO_4 dissolved in 50 c.c. of H_2O are added, followed by sufficient EtOH to form a slight cloudiness. On keeping, crvst. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ is obtained in $> 70\%$ yield. D. R. D.

Action of sodium nitrite on sodium polysulphide. I. CHEMLNITSKAJA and V. VERCHOVSKAJA (Anilinokras. Prom., 1934, 4, 27—31).— NaNO_2 and Na_2S_x react as follows: $4\text{Na}_2\text{S}_{3.5} + 6\text{NaNO}_2 + 9\text{H}_2\text{O} \rightarrow 7\text{Na}_2\text{S}_2\text{O}_3(\text{I}) + 6\text{NH}_3$; if x is > 3.5 , the remaining S is pptd. as such, and, should NaOH be present, is also converted into (I), as follows: $4\text{NaOH} + 3\text{S}_2 \rightarrow 2\text{NaNO}_2 + \text{H}_2\text{O} \rightarrow 3\text{Na}_2\text{S}_2\text{O}_3 + 2\text{NH}_3$. R. T.

Dehydration and decomposition of the dithionates. J. SCHREIBER (Ann. Chim., 1934, [xi], 1, 88—127, 129—180).—The dehydration of the dithionates of the alkali, alkaline-earth, and certain heavy metals, prepared by crystallisation at room temp., has been studied at various const. temp. and at temp. rising linearly with time. Equilibrium is attained only slowly. $\text{Na}_2\text{S}_2\text{O}_6\cdot 6\text{H}_2\text{O}$ yields the dihydrate at 9.1° , $\text{Na}_2\text{S}_2\text{O}_6$ at about 70° , and Na_2SO_4 at 245° . $\text{Li}_2\text{S}_2\text{O}_6\cdot 4\text{H}_2\text{O}$ behaves similarly (27° , 87° , and 195°). $(\text{NH}_4)_2\text{S}_2\text{O}_6\cdot 2/3\text{H}_2\text{O}$ (lit. 0.5 and 1.5 H_2O) yields hemihydrate (25°) and anhyd. salt (55°); no other hydrate exists. Other new hydrates described include those of Ca, Sr, Ba ($1\text{H}_2\text{O}$), Mg, Mn, Ni, Zn, Cd (4 and $2\text{H}_2\text{O}$), Cu, Fe, and Co ($2\text{H}_2\text{O}$). The anhyd. Sr and Mg salts have been prepared. Monohydrated sulphates are obtained in many cases by thermal decomp. of heavy metal dithionates. $\text{PbS}_2\text{O}_6\cdot 4\text{H}_2\text{O}$ is exceptional in that it yields PbSO_4 at 45° . No tri- or penta-hydrates could be obtained, but all the bivalent metals studied yielded tetrahydrated dithionates. H. F. G.

Preparation of sulphur chlorides and of arsenic trichloride. T. D. IONESCU and A. G. SOARE (Bul. Chim. Soc. Romana Ştiinţe, 1932, 35, 25—31).—96% yields of SCl_2 are obtained by passing Cl_2 over dry pyrites at 130 — 140° , whilst gas-works spent oxide gives 96% yields of a product containing 35% S_2Cl_2 and 64% SCl_2 . Theoretical yields of AsCl_3 and SCl_2 are obtained analogously from realgar or orpiment. R. T.

Ammoniates of chromium compounds. F. EPHRAIM and C. ZAPATA (Helv. Chim. Acta, 1934, 17, 287—295).—CrCl₃ and CrBr₃ form *ammines* with similar decomp. curves. On charging both CrCl₃ and CrBr₃ with NH₃ the colour becomes first ash-grey, then violet, and finally bright green. In both cases at low temp. solid solutions of ammines with > 5NH₃ are formed. At 97° CrCl₃·5NH₃ is reached, and breaks up to form CrCl₂·3NH₃ at 98°. There is a gradual decomp. to CrCl₂·2NH₃ which is complete at 250°. At 333° there is a sharp fall to CrCl₂·NH₃. Practically all NH₃ has been removed at 410°. CrBr₃·5NH₃ decomposes to CrBr₂·3NH₃ at 135—143°. Up to 153° CrBr₂·2·5NH₃ appears to be gradually formed and to remain stable up to 300°. There is then further slow decomp., but 1·5NH₃ still remains at 400°. M. S. B.

Ammoniates of chromates and perchlorates. F. EPHRAIM and C. ZAPATA [with E. AMMANN] (Helv. Chim. Acta, 1934, 17, 296—308).—The following *ammines* have been prepared and the temp. of decomp. determined: Ag₂CrO₄·4NH₃ (known), decomp. 137° with reduction; CuCrO₄·5NH₃ 44—45°, 4NH₃ (known) 162—164°, possibly 2NH₃ and 0·5NH₃; ZnCrO₄·5NH₃ 55°, 4NH₃ forming solid solution with ZnCrO₄·3NH₃ from 59° to 77°, the latter then becomes stable to 150°; CdCrO₄·>6NH₃ 23°, 6NH₃ 40°, 5NH₃ 79°, 3NH₃ 122—124°, 2NH₃ 160°, reduction, but also formation of CdCrO₄·NH₃ at 200°; Ca(ClO₄)₂·6NH₃ 148—150°, 3NH₃, which gradually loses NH₃ until more extensive decomp. sets in at 307°; Sr(ClO₄)₂·>7NH₃ 53°, 6NH₃ 102°, 4NH₃ 110—123°, 3NH₃, which gradually loses NH₃ as temp. rises; Ba(ClO₄)₂·>6NH₃ 63°, 6NH₃ 74°, 3NH₃ 74—122°, 2NH₃ 129°; Cd(ClO₄)₂·6NH₃ (known) 154·5°, 4NH₃ 298—301° reduction then beginning; Zn(ClO₄)₂·6NH₃ 40°, 4NH₃ still stable at 300°; Ni(ClO₄)₂·6NH₃ (known) stable to 264° and then explodes. M. S. B.

Peroxides and per-acids of halogens. L. V. PISARSHEVSKI (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1121—1124).—Theoretical. R. T.

"Red hydrogen chloride." E. TIEDE [with H. REINICKE] (Ber., 1934, 67, [B], 492—494).—The red colour of HCl obtained from NaCl and H₂SO₄ and frozen in vac. is due to the substance, NO·HCl, formed from minute traces of NO in H₂SO₄. The reaction is much more sensitive than the NHPH₂ test. NO is completely removed from H₂SO₄ by partial treatment with NaCl. H. W.

Attacking powers of binary systems of organic liquids on metals. L. SLADOVIĆ (Monatsh., 1934, 64, 35—40).—Losses of wt. of metals in a large no. of org. liquids and their binary mixtures have been determined at 45° and 55°. No significant corrosion was observed with Fe or Al, but with Cu and the systems NH₂Ph—PhOH, NH₂Ph—PhNO₂, and C₅H₅N—PhOH the corrosive effect of the mixtures is considerably > that of either component. In the system NH₂Ph—C₆H₆, which does not form a mol. compound, the rate of corrosion is < that of the more corrosive component. E. S. H.

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Precipitation of cobalt from zinc sulphate solutions by means of zinc dust and metallic compounds. G. HANSEL (Wiss. Veröff. Siemens-Konz., 1934, 13, 55—60).—The use of various metals (Cu, Bi, Cd, Ag, Hg, Pb, and Sn) as pptg. agents for Co from ZnSO₄ solutions used in the electrolytic prep. of Zn was investigated. The best metal was Sn, which gave the same degree of pptn. as As or Sb. The method recommended is to add Zn dust and a solution of a Sn salt. A. J. M.

Precipitation of cobalt from zinc sulphate solutions used in the electrolytic preparation of zinc. A. GREVEL (Wiss. Veröff. Siemens-Konz., 1934, 13, 61—71).—The course of the reaction occurring when Co is pptd. from ZnSO₄ solutions by the addition of Zn dust and an Sb salt was investigated. The potential developed at a Zn surface in a dil. solution of ZnSO₄, alone, and after addition of various metallic salts, was measured. A cementation process takes place between the Zn and the Sb. Examination of Zn—Sb preparations by the X-ray method indicated that alloy formation also occurred. Other methods of causing the pptn. of Co were investigated; Zn—Cu couple in the presence of CuCN acts similarly to Zn—Sb. For the colorimetric detection of Co, 1 c.c. of the Co solution, 2 c.c. of eriochrome blue-black (0·02 g. per 100 c.c.), and 0·5 c.c. of NaNO₂ (3·5 g. per 100 c.c.) are mixed. The reagent is capable of detecting the Co in 1 c.c. of a solution containing 2 mg. per litre, in the presence of a Zn concn. 80,000 times as great. Cu, Cd, and Fe interfere. A. J. M.

Sulphoacetato-salts of complex hexammine-, pentammine-, and tetrammine-cobaltic salts.—See this vol., 517.

Simple and complex metallic salts of thio-sulphatopentacyanocobaltic acid. S. N. MAULIK (J. Indian Chem. Soc., 1934, 11, 1—4; cf. A., 1931, 1140).—The following *compounds* have been prepared: BeO·Be₂[(CN)₅CoS₂O₃]₂·2H₂O, orange-red; K₂Mn[(CN)₅CoS₂O₃]₄·4H₂O, pale yellow crvst. powder; Mn₂[(CN)₅CoS₂O₃]₆·6H₂O; [Cu(NH₃)₁₂]₂[(CN)₅CoS₂O₃], blue crystals; [Cu(NH₃)₁₂]₂[(CN)₅CoS₂O₃]₃·3H₂O, green; [Cu(NH₃)₁₂]₂[(CN)₅CoS₂O₃]; [Zn(NH₃)₁₂]₂[(CN)₅CoS₂O₃]; [Zn(NH₃)₁₂]₂[(CN)₅CoS₂O₃]₄·4H₂O; [Ni(NH₃)₁₂]₂[(CN)₅CoS₂O₃]₃·3H₂O, yellowish-green crystals; [Ni(NH₃)₁₂]₂[(CN)₅CoS₂O₃]₆·6H₂O, green; Ag₄[(CN)₅CoS₂O₃], light yellow powder; Ag₄[(CN)₅CoS₂O₃]₄·5NH₃·6·5H₂O, unstable crystals rapidly turning black. R. S.

Varying spectrographic sensitivity of an element alone or mixed with others. G. PICCARDI (Annali Chim. Appl., 1934, 24, 35—36).—The diminution in intensity or disappearance of the spectral lines of an element when other elements are present, observed by Gazzi (A., 1933, 581), is due to the fact that many of the lines used for analytical purposes belong to the ionised, and not to the neutral, atom. With a mixture of two elements, that with the lower ionisation potential generates a cloud of electrons which, by mass action, retard the ionisation of the other element. T. H. P.

Theory of mean values. H. NIKLAS and M. MILLER (Z. Pflanz. Düng., 1934, A, 33, 242—246).—A mathematical discussion. A. G. P.

Determination of concentration of surface-active substances. K. SCHULTZE (Kolloid-Z., 1934, 67, 26—35).—The ring method is adapted. Results are given for humic acid, medicinal soap, oleic acid, ovalbumin, and quinine sulphate. E. S. H.

Simple micro-ashing process. J. ERDÖS (Z. Unters. Lebensm., 1934, 67, 284—287).—A description of the method and apparatus, and the results of determination of Ca in ashed material, are given. E. C. S.

Colorimetric determination of p_H at higher temperatures. W. NEUMANN (Z. anal. Chem., 1934, 96, 175—183; cf. A., 1933, 1022).—Solutions of NaCl and KCl showed a p_H decrease on heating to the b.p., the extent of the change decreasing with increasing concn. of salt. J. S. A.

Silver electrodes "of the second kind" as comparison electrodes. W. HILTNER (Z. anal. Chem., 1934, 96, 193).—A reply to Hahn (cf. this vol., 160). J. S. A.

Nitrazine-yellow, a new indicator. H. WENKER (Ind. Eng. Chem., 1934, 26, 350).—Nitrazine-yellow (2':4'-dinitrobenzeneazo-2- α -naphthol-3:6-disulphonic acid) changes from yellow at p_H 6.0 to blue at p_H 7.0, and the colour change between p_H 6.4 and 6.8 is very sharp. It is very suitable for test papers. A. G.

Ter Meulen method of analysis.—See this vol., 540.

Indirect determination of halogen acids. T. I. PIRTEA (Z. anal. Chem., 1934, 96, 263—266).—The $Cl^- + Br^-$ (or I^-) are pptd. as $AgCl + AgBr$ (AgI). The weighed ppt. is dissolved in hot, saturated aq. KBr (KI) and repptd. as $AgBr$ (AgI) by adding HNO_3 and diluting. Where $Cl^- + Br^-$ and I^- are present, the ppt. is converted first into $AgBr + AgI$, then into AgI . J. S. A.

Negative catalysis and microchemistry. A. QUARTAROLI (Annali Chim. Appl., 1934, 24, 70—74).— 10×10^{-6} g. of $KClO_3$ may be determined, even in presence of KCl and $KClO_4$, by its negative catalytic action on the reaction between NO_3^- and HCO_2H . The alteration of pptd. $Cu(OH)_2$ occurs in two phases, characterised by darkening and contraction, both of which are retarded by traces of Mg, Ni, and Co, and accelerated by traces of H_2O_2 . A method for determining these substances in this way is outlined. T. H. P.

Colorimetric determination of fluorine. E. PEYROT (Annali Chim. Appl., 1934, 24, 74—78).—A combination of Treadwell and Koch's (A., 1904, ii, 841) and of Penfield's method (A., 1879, 829; see Steiger, A., 1908, ii, 426). The powdered substance, ashed if necessary, is mixed with SiO_2 and treated at about 160° in the Penfield apparatus with conc. H_2SO_4 ; the air circulated need not be purified. The evolved gas is collected in about 0.5N-NaOH, which converts it into NaF , this being determined colorimetrically as described by Steiger; CO_2 , SO_2 , SO_3 , and HCl do not interfere. T. H. P.

Detection and determination of small amounts of fluorine. Application of the zirconium purpurin test. I. M. KOLTHOFF and M. E. STANSBY (Ind. Eng. Chem. [Anal.], 1934, 6, 118—121).—The qual. test of De Boer and Basarat (A., 1926, 590) is modified, making it sensitive to 0.003 mg. F^- . Many anions interfere with the test, but by distilling as SiF_4 and collecting in the Zr-purpurin reagent 0.005 mg. F^- can be detected in presence of any other ion. F^- can be determined with an accuracy of 2% by titrating with $ZrOCl_2$, using purpurin as indicator. A colorimetric titration procedure for determining 0.01—0.05 mg. F^- with an accuracy of 0.002 mg. F^- is described. E. S. H.

Determination of fluorides in natural waters. J. M. SANCHIS (Ind. Eng. Chem. [Anal.], 1934, 6, 134—135).—Modifications of the $Zr(NO_3)_4$ -alizarin method (A., 1933, 477) are described. Cl^- , SO_4^{2-} , HCO_3^- , Na^+ , Ca^{2+} , and Mg^{2+} up to 500 p.p.m., Mn^{2+} up to 200 p.p.m., SiO_3^{2-} up to 50 p.p.m., PO_4^{3-} , B , Cu^{2+} , and Fe up to 5 p.p.m., and S^{2-} up to 2 p.p.m. do not interfere. E. S. H.

Determination of SO_4^{2-} in presence of rhodizonic acid as indicator. R. B. ROSCHAL (Anilinokras. Prom., 1934, 4, 37—38).— SO_4^{2-} is determined in solutions of technical sulphonic acids as follows: 2—3 g. of $NaOAc$, 5 c.c. of glycerol, 5 g. of NH_4Cl , 10 c.c. of 0.5N- $BaCl_2$, and 8 drops of 0.3% Na rhodizionate (I) are added to 10 c.c. of solution, and excess of $BaCl_2$ is titrated with 0.25N- H_2SO_4 . The solutions of (I) deteriorate rapidly, and should be freshly prepared every 24 hr. R. T.

Colorimetric determination of ammonia in small amounts of material. F. ALTEN, H. WEILANDT, and E. HILLE (Z. Pflanz. Düng., 1934, A, 33, 129—133).—Golub's method (B., 1927, 397) is unsatisfactory. The colour produced in ammoniacal solutions by Nessler's reagent (I) varies considerably with p_H . The sample of plant material (20—50 mg.) is digested with H_2SO_4 and K_2SO_4 , H_2O_2 being added during the digestion process. The product is diluted with H_2O and a portion neutralised with 0.5N-NaOH (thymolphthalein). A borate buffer solution is added, followed by (I). Colour comparisons are made after 1 hr. A. G. P.

Analytical method of separating dimethylamine and ammonia. E. KATTSCHER and M. VOROSCHLOVA (Anilinokras. Prom., 1934, 4, 39—41).—100 c.c. of H_2O , 15 c.c. of 8% aq. NH_3 , and 2.5—3 c.c. of CS_2 are added to 10 c.c. of the solution under analysis, and the well-shaken solution is titrated after 15 min. with 0.2N- $CuSO_4$ (I), the titration being completed when a drop of solution placed beside a drop of (I) on filter-paper does not give a dark brown demarcation line. This titration gives the $NHMe_2$ content: $2NHMe_2 + 2CS_2 + 2NH_3 \rightarrow 2NMe_2 \cdot CS \cdot SNH_4 \rightarrow [S \cdot CS \cdot NMe_2]_2 \cdot Cu$. Total alkalinity is determined in a second 10 c.c. of solution, and the NH_3 content is calc. by difference. R. T.

Determination of phosphoric acid by the phosphomolybdate method and its use for plant ashes. J. TISCHER (Z. Pflanz. Düng., 1934, A, 33, 192—242).—The Mo-blue colour developed in determinations of

PO_4''' reaches a max. early after the addition of the reducing agent (I), and subsequently falls to a stable intensity after approx. 30 min. The max. colour is reproduced by further additions of (I). Fe salts prevent its formation. With appropriate proportions of reagents a direct proportionality between the colour produced and the PO_4''' content of test solutions (up to 50×10^{-6} g. P) is demonstrated. The influence of $[\text{H}^+]$ and of varying proportions of different salts on the intensity of coloration is examined. Technique for the determination of PO_4''' in plant ashes is given.

A. G. P.

Determination of phosphoric acid with ammonium molybdate, and the application of the process in certain cases. A. BAURLE, W. RIEDEL, and K. TAUFEL (Z. Unters. Lebensm., 1934, 67, 274—279).—Excess of H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ is to be avoided. Titration of the ppt. with NaOH to phenolphthalein gives consistent results, and the method can be applied to foodstuffs treated by the wet combustion method. In the prep. of melted butter (I) the phosphatides are pptd., consequently (I) does not suffer from browning.

E. C. S.

Tabular method of reading arsenic strips. B. D. THOMAS (Ind. Eng. Chem., 1934, 26, 356).—The lengths of the stains on As test papers vary from one set of tests to another, but the ratio between the lengths for different wts. of As remains const. A set of tables can therefore be prepared, and the correct table for any series of tests is chosen by the sum of the lengths of the stains obtained for a series of wts. of As. This is more accurate than plotting the lengths against the wts. of As.

A. G.

Potentiometric determination of arsenates. W. E. HANSON, S. B. SWEETSER, and H. B. FELDMAN (J. Amer. Chem. Soc., 1934, 56, 577—579).—The procedure is satisfactory when a large excess (10 times the theoretical amount) of NaOAc is used in 50 vol.-% aq. EtOH as solvent.

E. S. H.

Determination of small quantities of carbon monoxide in medicinal oxygen and carbon dioxide.—See B., 1934, 299.

Determination of sodium by the uranyl method. S. Z. MAKAROV and V. V. BUKINA (J. Gen. Chem. Russ., 1933, 3, 881—891).—15 c.c. of a reagent (I), prepared by mixing 50 c.c. of a solution containing 10 g. of $\text{UO}_2(\text{OAc})_2$ and 6 c.c. of 30% AcOH with 50 c.c. of 60% $\text{Zn}(\text{OAc})_2$ containing 6% of AcOH, are added to the dry residue of the solution under analysis (containing ≥ 10 mg. Na), the ppt. of $\text{NaZn}(\text{UO}_2)_2(\text{OAc})_6 \cdot 6\text{H}_2\text{O}$ (II) is washed successively with several portions of (I), with 95% EtOH saturated with (II), and with Et_2O , dried, and weighed. The method gives good results for solutions containing only Na, as well as in presence of Ca, Ba, Sr, Mg, and of ≥ 20 mg. K per mg. Na.

R. T.

Manganese uranyl acetate as a reagent for the detection of sodium. T. C. CHANG and C. L. TSUNG (Sci. Quart. Nat. Univ. Peking, 1934, 4, 185—189).—Mn uranyl acetate (prep. described) detects 0.02 mg. of Na in 0.5 c.c., $\text{NaMn}(\text{UO}_2)_3(\text{OAc})_9 \cdot 6\text{H}_2\text{O}$ being pptd. K, Li (unless in large excess), Mg, alkaline earths, and NH_4 salts do not interfere.

R. S. C.

Analytical reactions of rubidium and caesium. W. J. O'LEARY and J. PAPISH (Ind. Eng. Chem. [Anal.], 1934, 6, 107—111).—Rb and Cs can be separated quantitatively from K by adding luteo-phosphomolybdic acid, which does not ppt. K. Cs is quantitatively pptd. in 6N-HCl in presence of Rb by adding silicotungstic acid; when PO_4''' is present it is more satisfactory first to concentrate as platinum-chlorides, a modified method for which is worked out.

E. S. H.

Gravimetric determination of magnesium as $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$. J. DICK and A. RUDNER (Z. anal. Chem., 1934, 96, 245—248).—Mg is pptd. cold from conc. solution by adding NH_4Cl and excess of Na_2HAsO_4 . The ppt. is dissolved in HCl, then neutralised with 2.5% aq. NH_3 (phenolphthalein), and 1/3 vol. of conc. aq. NH_3 is added (total 60—70 c.c.). The ppt. is filtered after 1 hr., washed with EtOH and Et_2O , and dried in an air stream. For semi-micro-determinations, the vol. should be ≥ 5 c.c.

J. S. A.

Rapid semi-micro-gravimetric determination of magnesium as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ or as $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$. L. W. WINKLER (Z. anal. Chem., 1934, 96, 241—245).— $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ is pptd. from hot solution (20 c.c.) by addition of 0.5 g. of NH_4Cl , 1 c.c. 20% aq. NH_3 , and 2 c.c. 10% Na_2HPO_4 . After 5 min. the solution is cooled, shaken vigorously, and filtered after 15 min. The ppt. is washed with EtOH and dried in an air stream. Ca if present is first pptd. by $(\text{NH}_4)_2\text{C}_2\text{O}_4$; the time of keeping is then doubled. $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ is pptd. cold and filtered after 30 min. shaking, addition of NH_4Cl being omitted after pptn. of Ca.

J. S. A.

Precipitation of zinc sulphide and aluminium hydroxide, and gravimetric separation of zinc from aluminium. C. MAYR (Z. anal. Chem., 1934, 96, 273—274).—Frers' claim of priority is rejected (cf. this vol., 161, and A., 1933, 478).

J. S. A.

Separation of metals of the second analytical group. G. L. CHABORSKI and E. PETRESCU (Bul. Chim. Soc. Romana—Științe, 1932, 35, 33—36).—Modifications of Longinescu and Theodorescu's procedure are proposed.

R. T.

Iodometric and potassium permanganate determinations of lead in lead acetate.—See B., 1934, 318.

Oxidation of thallous to thallic salts, and reduction of the latter by sodium arsenite for analytical purposes. F. ČUTA (Chem. Listy, 1934, 28, 58—59).— Tl^{I} is oxidised to Tl^{III} by Br, excess of Br is removed by boiling with HCl, the solution is made alkaline, and titrated with standard Na_3AsO_3 . The mean error is $\pm 0.2\%$. In the absence of Cl^- , Tl^{III} undergoes partial reduction to Tl^{I} when its solutions are heated, even if reducing agents are not present.

R. T.

Copper [borax and microcosmic] beads H. RAKETT (Z. anal. Chem., 1934, 96, 192—193).— 0.1×10^{-6} g. of Cu may be detected by means of small borax or $\text{NaNH}_4\text{HPO}_4$ beads, with addition of a particle of Sn to effect reduction.

J. S. A.

Detection and determination of copper in fresh waters.—See B., 1934, 350.

Determination of mercury in air and urine. A. M. FRASER (J. Ind. Hygiene, 1934, 16, 67—76).—Hg in air is determined by electrolytic deposition or micrometrically, after condensation by passage through a tube immersed in liquid air (cf. Stock and Heller, A., 1926, 703). In urine, Hg is determined as HgS after wet ashing with $\text{KMnO}_4 + \text{H}_2\text{SO}_4$.

H. G. R.

Potentiometric determination of mercurous salts. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 96, 188—192).—Titration of Hg by KIO_3 (cf. this vol., 270) may be performed potentiometrically, preferably in 30% EtOH. Use of 0.01N solutions is impossible, the Hg-coated Pt electrode becoming passivated.

J. S. A.

Determination of manganese in iron and steel or in ores.—See B., 1934, 279.

Colour reactions of rhenium. B. TOUGARINOFF (Bull. Soc. chim. Belg., 1934, 43, 111—114).—On adding a few drops of 5% aq. $\text{K}_4\text{Fe}(\text{CN})_6$ and 2—3 c.c. of a solution (I) of 25 g. of cryst. SnCl_2 in 100 c.c. of conc. HCl to a solution (II) containing ReO_4^- (not strongly alkaline) a brown coloration is produced. Re may be separated from metals which interfere (W, V, Mo, Nb, Cr) by distillation with conc. H_2SO_4 . On adding a few drops of a saturated solution of dimethylglyoxime in EtOH and 2—5 c.c. of (I) to 1 c.c. of (II), a yellow to red colour is produced and the solution develops a green fluorescence when heated. 0.01 mg. of Re may be detected by either of these reactions.

D. R. D.

Influence of nitric acid on the determination of iron by potassium permanganate. D. TOTORESCU (Z. anal. Chem., 1934, 96, 183—188).— NO_3^- can be totally removed only by evaporation to dryness with H_2SO_4 . If NO_3^- is present, reduction with $\text{Zn} + \text{H}_2\text{SO}_4$ gives NH_2OH , invalidating KMnO_4 titration.

J. S. A.

2-Aminopyridine in microchemical identification of some cations. A. SA (Anal. Farm. Biochim., 1933, 4, 77—80).—2-Aminopyridine gives characteristic cryst. compounds with salts of Co, Cu, Zn, and Cd and KCNS or NH_4CNS .

R. K. C.

Indirect potentiometric determination of nickel. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 96, 270—273).—The Ni solution is treated with 0.1N-KSCN and $\text{C}_5\text{H}_5\text{N}$, pptg.

$[\text{Ni}(\text{SCN})_2(\text{C}_5\text{H}_5\text{N})_4]$, which is filtered off. The filtrate is acidified with HNO_3 and excess KSCN titrated back potentiometrically with AgNO_3 .

J. S. A.

Separation of the components of the ammonium sulphide group. J. KUNZ (Helv. Chim. Acta, 1934, 17, 369—372).—An error in a previous communication (A., 1932, 827) is corr. The dark ppt. obtained by adding Cl_2 - or $\text{Br}-\text{H}_2\text{O}$ in AcOH to a Co salt solut on does not give a complete separation of Co from Ni but is an indication of the presence of Co^{+++} . The separation of Cr, Zn, Al, Mn, and Fe is effected by dissolving the pptd. sulphides in HCl, evaporating to dryness, oxidising Fe^{II} to Fe^{III} with HNO_3 , treating with boiling Na_2CO_3 , filtering, and

fusing the dried residue with KNO_3 and NaOH. If only one cation is present, the colour of the melt or of the solution in H_2O gives an indication of its nature. From a colourless solution Al is pptd. by an excess of $(\text{NH}_4)_2\text{CO}_3$ and Zn from the filtrate by Na_2S . After removing Al and Zn from a clear yellow solution, Cr is pptd. by acidifying with AcOH and adding $\text{Pb}(\text{OAc})_2$. A red powder in the melt or solution indicates Fe_2O_3 . If the solution of the melt is coloured bluish-green by Na_2MnO_4 , H_2O_2 is added and gives, on warming, pptd. $\text{Mn}(\text{OH})_4$, which may also contain Fe_2O_3 . The latter is left behind when the $\text{Mn}(\text{OH})_4$ is brought into solution by $\text{K}_2\text{S}_2\text{O}_5$. From the filtrate, freed from Mn and Fe, Al is separated as before; the filtrate is acidified with conc. HCl and Cr^{VI} reduced to Cr^{III} by $\text{K}_2\text{S}_2\text{O}_5$. From the green solution $\text{Cr}(\text{OH})_3$ is pptd. by aq. NH_3 . In the filtrate Zn is pptd. by Na_2S .

M. S. B.

Application of the potential-forming system metal/metal anion to potentiometric titrations. E. MULLER and K. MEHLHORN (Z. anal. Chem., 1934, 96, 173—175; cf. this vol., 49).—Titration of, e.g., CrO_4^{II} using a Cr reference electrode (I) can also be effected using (I) of Pt or Au. (I) actually functions as an O electrode, measuring the change in OH^- concn., due to hydrolysis of CrO_4^{II} . The method can therefore be used only in solutions of the same as K_2CrO_4 .

J. S. A.

Inclusion of rarer metals in elementary qualitative analysis. I. Inclusion of tungsten and molybdenum in groups I and II. L. E. PORTER (Ind. Eng. Chem. [Anal.], 1934, 6, 138—139).—A suitable scheme is recommended.

E. S. H.

Volumetric determination of uranium in highly ferriferous ores.—See B., 1934, 325.

Detection of bismuth with alkali thiocyanates. E. TOMMILA (Suomen Kem., 1934, 7, B, 79; cf. A., 1923, i, 1076).—A slightly acid solution (I) of < 5 mg. Bi per litre gives a visible yellow colour with KCNS. The same reaction occurs in glycerol or glycol. HNO_3 affects the reaction, but not org. acids. (I) is decolorised by EtOAc and amyl alcohol, but not by Et₂O (in which the corresponding Fe compound is sol.). Molybdates produce similar colours, but the (I) is decolorised by Et₂O.

J. L. D.

Detection of bismuth with sulphur-containing organic reagents. I. Dimercaptothiodiazole. J. V. DUBSKÝ and A. OKAČ (Z. anal. Chem., 1934, 96, 267—270).—Dimercaptothiodiazole (prep. given) gives with acid and alkaline Bi solutions an intense red ppt. $[\text{Bi}(\text{C}_5\text{HNS}_2)_3]$ if pptd. from alkaline solution]. Other metals of the sulphide group give white to yellow ppts., except Hg (black). Bi may be first separated as $\text{Bi}(\text{OH})_3$. The limit is 1.2×10^{-6} g. Bi. The test is not suited to spotting on filter-paper.

J. S. A.

Determination of traces of bismuth in presence of other metals. L. A. HADDOCK (Analyst, 1934, 59, 163—168; cf. A., 1932, 1103; 1933, 1064).—Bi is extracted with a solution of diphenylthiocarbazonone in CHCl_3 , and is determined colorimetrically as iodobismuthous acid in amyl alcohol. 0.005—0.1 mg. of Bi in 1 g. of material can be determined, the only

elements which interfere being Pb and Th, and these only in amounts > 0.5 mg. E. C. S.

Detection of small amounts of tantalum and niobium. W. R. SCHOELLER (*Z. anal. Chem.*, 1934, 96, 252—257; cf. this vol., 50).—The tannin (I) test is more sensitive than those of Rienacker and Schiff. 0.05 mg. of Ta_2O_5 gives a yellow ppt. with (I) in presence of NH_4Cl . 0.02 mg. Nb_2O_5 gives a red ppt. (II), as does Ti. In presence of Ti the $NaHSO_4$ melt is dissolved in aq. $(NH_4)_2C_2O_4$, and (I) is added, giving (II) with Nb only. Mixtures containing Nb, Ta, Ti, and Zr are fused with $NaHSO_4$ and pptd. with (I). The ppt. is treated with $HNO_3 + H_2SO_4$. Ti is detected with H_2O_2 , Zr with Na_2HPO_4 . The residue is fused with $NaHSO_4$, taken up in $(NH_4)_2C_2O_4$, and pptd. with (I). This ppt. P_1 is re-fused and re-pptd., giving a lighter orange ppt. P_2 if Ta is present. Nb gives a red ppt. when NH_4OAc and (I) are added to the filtrate. With small amounts of Ta, P_2 may be only slightly lighter than P_1 . J. S. A.

Amalgamation assay of platinum.—See B., 1934, 325.

Thermostat for temperatures between 5° and 20° . L. M. PIDGEON (*Canad. J. Res.*, 1934, 10, 252). J. L. D.

Equalisation of temperature in electric ovens. F. G. H. TATE (*Analyst*, 1934, 59, 168—170).—A fan mounted in the door maintains temp. equality to within 1° in an oven which otherwise has temp. inequalities of 20° . E. C. S.

Electrical combustion furnace. G. B. CRIPPA and M. GALLOTTI (*Annali Chim. Appl.*, 1934, 24, 82—86).—Eleven U-shaped heating elements, arranged side by side and separately controllable, form the bed in which the combustion tube lies. T. H. P.

Calorimetry. Method of electrical compensation. Microcalorimetry. A. TIAN (*J. Chim. phys.*, 1933, 30, 665—708).—Full details are given for the construction and manipulation of a microcalorimeter operating on the principle that the heat evolved during an exothermal change is absorbed by means of the Peltier effect and the heat absorbed by an endothermal change is replaced by means of the Joule effect. Heat changes of < 0.7 g.-cal. per hr. lasting for 10—20 hr. are determined, and the method, applied ballistically, is satisfactory for heat changes of < 100 sec. duration. Data are recorded. J. G. A. G.

Examination of opaque objects with the aid of polarised light. O. FEUSSNER (*Z. Metallk.*, 1933, 25, 313—314, 314). M. VON SCHWARZ (*Ibid.*, 314).—Polemical (cf. A., 1932, 606, 908). A. R. P.

Degree of precision in measurement of the refractive index of samples of small dimensions. A. BRÖT (*Ann. Soc. Sci. Bruxelles*, 1934, B, 54, 5—13).—The min. deviation, grazing incidence, and interference methods of determining n should each require certain min. vols. of the sample to ensure definite degrees of accuracy, about 10^{-3} c.c. and 0.5 c.c., respectively, for accuracies of 1×10^{-4} and 1×10^{-5} . The last method shows slight advantages for small samples. The theory is applied to the study of n for lenses. J. W. S.

Nickel salts as light filters. W. V. BHAGWAT (*J. Indian Chem. Soc.*, 1934, 11, 5—11).—The absorption and % transmission of solutions of $NiCl_2$, $Ni(NO_3)_2$, and $(NH_4)_2SO_4 \cdot NiSO_4$, have been determined. Combinations of Ni salts with Co salts transmit only in the ultra-violet. R. S.

Absolute colorimeter. R. GUELKE (*J. Soc. Dyers and Col.*, 1934, 50, 77—80).—A Leitz abs. colorimeter (dipping spectrophotometer), which combines the simplicity of the ordinary colorimeter with the accuracy of the spectrophotometer, and is suitable for the determination of dyes in solution or on the fibre (including vat dyes), is described. A. J. H.

Colorimetry. J. GUILD (*J. Sci. Instr.*, 1934, 11, 69—78).—General principles are discussed. C. W. G.

Interferometer microscope. C. DUNBAR (*J. Sci. Instr.*, 1934, 11, 85—89).—Small displacements of the stage are measured by means of an interferometer system. Applications to the determination of the sizes of small particles are described. C. W. G.

Spectrometer. S. J. DULY (*J. Sci. Instr.*, 1934, 11, 92—94).—The instrument is intended principally for measuring n , crystal angles, and visual spectra. C. W. G.

Industrial microscopy. IV. Crystals. C. H. BUTCHER (*Ind. Chem.*, 1934, 10, 105—108).—The method of identification of crystals by determining n with polarised light is discussed. C. A. K.

Constant ultra-violet output from quartz mercury arc lamps. W. T. ANDERSON, jun. (*Rev. Sci. Instr.*, 1934, [ii], 5, 127—129).—A method of intensity control, using the Weston "Photronic" light-sensitive cell for measuring the ultra-violet emission from quartz Hg arcs, is described. N. M. B.

Mercury-sealed, water-cooled, rotating X-ray target. W. T. ASTBURY and R. D. PRESTON (*Nature*, 1934, 133, 460—461). L. S. T.

Universal chamber for measuring X-ray doses without the use of lead sulphide. R. JAEGER (*Physikal. Z.*, 1934, 35, 184—187).—The apparatus, which is considerably smaller than the usual blende chamber, is described. A spectral range of 2—0.15 Å. can be covered without changing the window. A. J. M.

Focalisation method for X-ray crystal analysis. A. ROCOZINSKI (*Compt. rend.*, 1934, 198, 953—955).—The substance is arranged in the form of a hoop, the plane of which is perpendicular to the beam of X-rays, the centre lying in that beam. A small Pb screen prevents direct incidence of the beam on the photographic film. The method greatly reduces the period of exposure. C. A. S.

Optical osmometer. C. H. DWIGHT and H. KERSTEN (*Rev. Sci. Instr.*, 1934, [ii], 5, 130—131).—The instrument makes use of an optical lever for measuring rapid changes in vol. of a solution in osmosis, and gives magnified readings at a distance. N. M. B.

Photographic intensity measurement with moving electron beams. F. C. POULTNEY and R.

WHIDDINGTON (Proc. Leeds Phil. Soc., 1934, 2, 492—494).—Electron streams of very different intensity may be compared by measuring the effects produced by the streams on photographic films moving at different speeds. H. S. P.

Photo-electric spectrophotometer using dual electrostatic compensation. L. A. WOODWARD (Proc. Roy. Soc., 1934, A, 144, 118—128).—The apparatus described is suitable for the measurement of extinction coeffs. of substances in solution, especially in the ultra-violet region. The method used is purely electrical. It is tested by a series of determinations of the mol. extinction coeff. of KNO_3 in dil. solution. L. L. B.

Radio relay circuit. G. B. HEISEG and D. C. GERNES (Ind. Eng. Chem. [Anal.], 1934, 6, 155—156). E. S. H.

Silver chloride electrode for use in dilute solutions. A. S. BROWN (J. Amer. Chem. Soc., 1934, 56, 646—647).—A Pt wire is plated with Ag by electrodeposition from a solution of $\text{KAg}(\text{CN})_2$, and coated with AgCl by anodic treatment for 30 min. in 0.1N-HCl. The electrodes are not sensitive to light, and are reproducible to within a few hundredths of a mv., even in very dil. solutions. E. S. H.

Comparison of vacuum and gas-filled [photo-electric] cells. G. A. BOUTRY and J. ORCEL (Compt. rend., 1934, 198, 808—810; cf. this vol., 383).—The claim to an accuracy of 0.25% for vac. cells is doubtful. The max. potential safely applicable diminishes as the flux of light increases, but should never be > 80 volts. C. A. S.

Technique of investigation of crystalline powders by means of electron scattering. F. TRENDLENBURG and O. WIELAND (Wiss. Veröff. Siemens-Konz., 1934, 13, 41—47).—An arrangement for the use of the powder method with an electron beam of 50 kv. intensity is described. A. J. M.

Sector copying process for the diminution of the diffuse background blackening in electron diffraction photographs. F. TRENDLENBURG and E. FRANZ (Wiss. Veröff. Siemens-Konz., 1934, 13, 48—54).—By means of a sector device, the intensity of illumination of the negative in taking a positive of electron diffraction photographs is varied in different parts, so eliminating the background. A. J. M.

Construction and performance of the magnetic electron microscope. E. RUSKA (Z. Physik, 1934, 87, 580—602). A. B. D. C.

Comparison of constancy of gold- and chromium-plated analytical weights. H. V. MOYER and P. K. WINTER (Ind. Eng. Chem., 1934, 26, 238).—Cr-plated weights underwent much smaller changes than did similar weights plated with Au during use for 1 year in the same laboratory. The reason is probably the greater resistance of the Cr to scratching and abrasion, since positive errors due to corrosion of the underlying brass had occurred with some of the Au-plated weights. H. F. G.

Preparation of sintered Pyrex glass filters. P. L. KIRK, R. CRAIG, and R. S. SOSENFELS (Ind.

Eng. Chem. [Anal.], 1934, 6, 154—155).—Directions are given for making filters of any desired degree of porosity. E. S. H.

Application of the automatic pipette in dispensing. R. F. ARMBRUST (Pharm. Weekblad, 1934, 71, 300—301).—An automatic pipette for measuring conc. solutions from bottles is described. S. C.

Retention of dichromate by glassware after exposure to potassium dichromate cleaning solution. E. P. LAUG (Ind. Eng. Chem. [Anal.], 1934, 6, 111—112).—The amount of $\text{Cr}_2\text{O}_7^{2-}$ retained is practically independent of the duration of contact of glass with the cleaning solution. About 50% is recovered in the wash- H_2O during the first 30 min. and about 80% within 2 hr. Little difference is observed between behaviours of Pyrex and Na-O-glass. E. S. H.

Automatic vacuum regulation. G. F. LIEBIG, jun. (Ind. Eng. Chem. [Anal.], 1934, 6, 156). E. S. H.

Preparation of microscopic glass spheres. S. SKLAREW (Ind. Eng. Chem. [Anal.], 1934, 6, 152—153).—Powdered glass is blown by an air blast through a heated chamber, in which the particles melt to spherical droplets, to a settling chamber. E. S. H.

Absorption tube. G. E. LE WORTHY (Ind. Eng. Chem. [Anal.], 1934, 6, 139).—The tube is designed for the determination of H in analysis by combustion. E. S. H.

Rapid method of dust sampling. T. HATCH and E. W. THOMPSON (J. Ind. Hygiene, 1934, 16, 92—99).—Eight samples are collected on a single slide, by a modification of the Owens counter, and matched against standards under a microscope. H. G. R.

Measurement of surface tension of liquids. A. ACHMATOV (Kolloid-Z., 1934, 66, 266—270).—Apparatus and technique for a method, in which the pressure in a conical capillary tube is measured, are described. Results for a no. of liquids compare favourably with those obtained by the capillary rise method. E. S. H.

Improved form of Sprengel tube. A. D. GARDINER (Analyst, 1934, 59, 172). E. C. S.

Objective demonstrations with rutile suspensions. A. EHRLINGHAUS (Naturwiss., 1934, 22, 149—150).—Experimental details are given for showing the increase in mean velocity of the Brownian movement with temp., the coagulation by electrolytes, and the electrophoresis of colloidal solutions of rutile. A method of showing the rotation of the plane of polarisation of linearly polarised light, making use of scattering at colloidal particles of rutile, is described. A. J. M.

Highly polymerised compounds. XCI. Ultra-centrifugal mol. wt. determinations in synthetic highly polymerised substances. R. SIGNER and H. GROSS (Helv. Chim. Acta, 1934, 17, 335—351).—Mol. wts. of polystyrene and polyanethole in CHCl_3 solution and of polyethylene oxide in $\text{C}_2\text{H}_5\text{Br}$ have been obtained by determining sedimentation equilibria with the ultra-centrifuge. The method can be applied to substances not otherwise accessible to measure-

ment. The results also make it possible to show at what concn. swelling pressures set in. By determining the friction factor from the mol. wt. and sedimentation const. and comparing with the friction factor for spherical particles of the same mass, a dissymmetry factor is obtained. There is a parallelism between the ultra-centrifugal mol. wt. determinations and Staudinger's sp. viscosity-mol. wt. relationship. M. S. B.

Mol.-wt. analysis in the centrifugal field. T. SVEDBERG (*Kolloid-Z.*, 1934, 67, 2—16).—A review of much published work, describing apparatus, technique, and results for several proteins. E. S. H.

Micromanometer. O. STALHANE (*J. Sci. Instr.*, 1934, 11, 79—82).—A bubble in a tube is brought back to its original position by tilting with a micromanometer screw. C. W. G.

Sealed α -ray bulbs in the study of chemical reactions produced by radon. E. C. TRUESDALE and C. H. SHIFLETT (*Rev. Sci. Instr.*, 1934, [ii], 5, 119).—To avoid the use of a Hg seal, a method of progressively sealing off the stem of the bulb and driving the radon ahead of the seal is employed. N. M. B.

Evaporation technique for highly refractory substances. H. M. O'BRYAN (*Rev. Sci. Instr.*,

1934, [ii], 5, 125—126).—Pt, B, Mo, SiO_2 , and other substances which would react with a W filament have been evaporated in vac. in a pure graphite crucible heated by bombardment with electrons at 4000 volts from a W filament. N. M. B.

Determination of the specific gravity of liquids with a new pycnometer. J. M. AAS (*Fettchem. Umschau*, 1934, 41, 3—4).—A 25-c.c. bottle with a narrow neck (3.5—4 mm. diameter) is graduated in divisions of 0.01 c.c., so that the vol. of the liquid can be read to 0.002 c.c.; d is determined to ± 0.0001 , if the temp. is measured to within $\pm 0.1^\circ$. E. L.

"Atmos" distillation apparatus for water. J. J. HOFMAN (*Pharm. Weekblad*, 1934, 71, 338—339).—In a continuous, all-glass distillation apparatus the condenser jacket is fitted with a const.-level device and is also connected directly with the boiling vessel. S. C.

Nomogram for solving percentage conversions of binary mixture components. T. C. PATTON (*Chem. Met. Eng.*, 1934, 41, 148—149).

Lecture experiment on gas diffusion. A VISWANATHAN (*J. Indian Chem. Soc.*, 1934, 11, 79).—The change of pressure resulting from the different rates of diffusion of gases can be demonstrated by the use of Cartesian divers. R. S.

Geochemistry.

Conductivity of natural mineral waters. I. Mineral water of Vrnjačka Banja. P. S. TUTUNDZIC (*Bull. Soc. Chim. Yougoslav.*, 1933, 4, 145—155).—The conductivity of the H_2O of various springs has been determined. R. T.

Bucharest drinking water. D. BUTESCU (*Bul. Chim. Soc. Romana Științe*, 1932, 35, 137—170).—Analytical and other data are given. R. T.

Analysis and physico-chemical data of the thermo-mineral water of the S. Calogero spring, Lipari. L. IRRERA and G. LABRUTO (*Annali Chim. Appl.*, 1934, 24, 57—70).—This H_2O , issuing at 58° , has d 1.002, p_H 7.46, residue 1.9 g. per litre, radioactivity 0, and contains mainly $\text{SO}_4^{''}$, $\text{CO}_3^{''}$, Na^+ , Ca^{++} , and Mg^{++} , in amounts $<$ in 1872 and 1907, when the temp. was higher. T. H. P.

Analysis of water from the Mangiatorella (Calabria) spring. B. RICCA (*Annali Chim. Appl.*, 1934, 24, 36—54).—Results are given of the chemical, physico-chemical, and bacteriological analysis of this H_2O , which is classed as an oligo-mineral drinking H_2O . T. H. P.

Phytoplankton in English lakes. II. Composition of the phytoplankton in relation to dissolved substances. W. H. PEARSALL (*J. Ecology*, 1932, 20, 241—262).—Diatoms occur when the H_2O is richest in NO_3^+ , $\text{PO}_4^{'''}$, and SiO_2 ; green algæ and desmids occur when NO_3^+ and $\text{PO}_4^{'''}$ are low. CH. ABS.

Origin of iodine and bromine in oil-bearing waters. A. P. VINOGRADOV (*Compt. rend. Acad.*

Sci. U.R.S.S., 1934, 1, 214—216).—It is concluded that the deep-seated H_2O of oil-bearing regions which contain large amounts of I and Br originate in fossil mud H_2O of marine bottoms. J. W. S.

Accuracy of mineralogical measurements. M. H. HEY (*Min. Mag.*, 1934, 8, 495—500).—The accuracy to be expected from the measurement of various physical consts. and in chemical analyses is reviewed. L. J. S.

Origin of helium in sylvine. O. HAHN and H. J. BORN (*Naturwiss.*, 1934, 22, 138).—The high He content of sylvine is due to the action of hot H_2O rich in Ra-D on the primary minerals, carnallite or kainite. The Ra-D content of sea- H_2O is too low to account for it. A. J. M.

Silica-glass from the Libyan desert. P. A. CLAYTON and L. J. SPENCER (*Min. Mag.*, 1934, 23, 501—508).—Wind-worn lumps, up to 10 lb., of clear, pale greenish-yellow SiO_2 -glass, suitable for cutting as gemstones, have been found in large amount on the surface of the desert 500 miles S.W. of Cairo. Analysis [by M. H. HEY] gave SiO_2 97.58, TiO_2 0.21, Al_2O_3 1.54, Fe_2O_3 0.11, FeO 0.23, CaO 0.38, Na_2O 0.34, H_2O 0.10, NiO , MnO , MgO traces, total 100.49; d 2.206, n_D 1.4624. The material is compared with tektites, but its origin is obscure. L. J. S.

Metasomatism in flint nodules in the Scawt Hill contact-zone. C. E. TILLEY and A. R. ALDERMAN (*Min. Mag.*, 1934, 23, 513—518).—Flint nodules in the chalk of Co. Antrim have been altered by the

intrusion of dolerite, showing a progressive change from granular quartz to an assemblage of wollastonite, melilite, and alkali-pyroxene with pectolite and xonotlite, but without any change in the vol. and shape of the nodules. Analyses are given of the material at the various stages, and the nature and origin of the solutions that effected the change are discussed.

L. J. S.

Zeolites. VI. Edingtonite. M. H. HEY [with F. A. BANNISTER] (*Min. Mag.*, 1934, 23, 483—494).—Analysis of edingtonite from Böhlet, Sweden, gave SiO_2 35.35, Al_2O_3 19.98, BaO 38.83, CaO 0.10, Na_2O 0.04, K_2O 0.65, H_2O 13.11 = 100.06, d 2.777, and the orthorhombic unit cell, a 9.56, b 9.68, c 6.53 Å., contains $\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{40}\cdot 8\text{H}_2\text{O}$. The rarer edingtonite from Old Kilpatrick, Scotland, is apparently tetragonal with a 9.585, b 9.585, c 6.53 Å., but the two minerals appear to be essentially identical, the difference shown by them being due to an appreciable amount of Ca in the Scottish mineral. Optical data and v.-p. curves are given for the Böhlet mineral. By base-exchange Ti^{IV} and Ag edingtonites were prepared. The K and Na base-exchange products (pseudo-edingtonites) have a unit cell about eight times as large as that of edingtonite.

L. J. S.

Geochemistry of strontium [and barium]. W. NOLL (*Chem. Erde*, 1934, 8, 507—600).—Full details are given (cf. A., 1933, 1030). Many determinations were made of the minute amounts of Sr present in a variety of minerals and in igneous and sedimentary rocks. The average amount of both SrO and BaO in igneous rocks is about 0.05%, but Sr has a preference for alkali-rocks, whilst Ba occurs more in granitic rocks. In the minerals of sedimentary rocks Sr is associated with Ca, but more in aragonite and anhydrite than in calcite, gypsum, and dolomite.

L. J. S.

Contact-metamorphic limestones in Spessart. R. MOSEBACH (*Chem. Erde*, 1934, 8, 622—662).—Calc-silicate rocks and their minerals (phlogopite, chondrodite, etc.) are described. An analysis of a mineral related to picrosminine occurring as veins in the rock is given.

L. J. S.

Ball sandstone in Thuringia. H. JUNG (*Chem. Erde*, 1934, 8, 601—612).—Spherical concretions 2.5—3 cm. in diameter occur in the Middle Bunter sandstone at Kahla. Analysis of the balls and of the matrix show an addition of 33.03% $(\text{Ca}, \text{Mg}, \text{Fe})\text{CO}_3$ in the balls.

L. J. S.

Origin of sulphur deposits. F. AHLFELD (*Chem. Erde*, 1934, 8, 613—621).— SO_4^{2-} in mineral oils may give H_2S and CO_2 , and the H_2S coming to the surface in contact with O_2 deposits S.

L. J. S.

Origin of volcanic sulphur from observations of the craters of volcanoes in S. Italy. O. VON DEINES (*Naturwiss.*, 1934, 22, 129—134).—Three reactions are supposed to give rise to the S found in volcanic districts: (i) $\text{SO}_2 + \text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$. The kinetics of this reaction are examined. It is also necessary to take into account the thermal dissociation of the H_2S , and the action of SO_2 on the H_2 thus produced. In a gas consisting of H_2O , H_2S , SO_2 , S_2 , and H_2 , SO_2 remains const., H_2S dis-

appears, and H_2 increases if the temp. is raised from 700° to 1000°. The action of H_2 on the sulphide magma (FeS_2 or FeS) is also considered. (ii) Hydrolysis of S can occur at $> 100^\circ$, forming H_2S and H_2SO_3 , from which polythionic acids and their decomp. products (S , H_2S , H_2SO_4 , etc.) are produced. (iii) The decomp. of H_2SO_4 at high pressures: $3\text{H}_2\text{SO}_4 - 2\text{H}_2\text{SO}_4 + \text{S} + \text{H}_2\text{O}$. All the above reactions may occur at various depths.

A. J. M.

Eruptive rocks of the Trias of Wezzan (Morocco). J. BOURCART and G. CHOUVERT (*Compt. rend.*, 1934, 198, 960—963).—In addition to sericite schists, red sandstones, marbles, clays with fossil limestones and gypsum, dolomites, and grey limestone, there are associated with the Triassic rocks a large variety of granites (including syenites, monzonites, diorites, and gabbros), gneisses (with leptynites, and orthoamphibolites), and episyenites (with ophites and a hauyne phonolite), exhibiting two metamorphoses separated by crushing.

C. A. S.

Basic rocks, intrusive and metamorphic, of the Kasai (Belgian Congo). M. E. DENAEYER (*Compt. rend.*, 1934, 198, 956—958).—These include hypersthene-gabbros, dolerites passing into basalts, with spessartite and ariegites, all apparently derived from the same magma; associated with them are amphibolites, much diopside, and an orthoamphibolite containing zoisite. Mt. Musungu consists of a dark red rock made up of red garnet, magnetite, and hypersthene, with vein quartz.

C. A. S.

Alteration of feldspars in granite sands of the Vosges. A. S. MIHARA (*Compt. rend.*, 1934, 198, 955—956).—The white altered feldspars of the sands, etc. formed from the granite of Hohwald (Vosges) consist of 55% soda-lime feldspar, 36 phyllite (28 sericite + 8 kaolinite) and 9 free SiO_2 . Analyses of granite in which the feldspar was sericitised, but had not disintegrated, compared with one of the granite sand show insufficient Al_2O_3 in the former for kaolinite to be present there as such; it must therefore result from sub-aerial action accompanying disintegration.

C. A. S.

Chemical modifications of clay in typical Yugoslavian red earth and podsol. S. NIKOLIĆ (*Bull. Soc. Chim. Yougoslav.*, 1933, 4, 157—167).—Various clays (I) are capable, in contradistinction to kaolin, of combining with both acids and alkalis. The combining power of (I) diminishes with the depth from which the sample is taken.

R. T.

Separation of constituents of clays. P. URBAIN (*Compt. rend.*, 1934, 198, 964—967).—Electrolytes are removed by suspension in H_2O and thrice centrifuging. The solids are then suspended in H_2O in an inverted cylindrical vessel closed by a cap, and subjected to a vertical electric field of approx. 100 volts per cm.; positive below. The negative colloids are subsequently separated from the cryst. solids (with which they have settled to the bottom) by a similar method, whilst the positive colloids remain in suspension. All trace of electrolytes is finally removed by electrodialysis, and four fractions are obtained: cryst. solids, positive colloids (metallic hydroxides), negative colloids (Al silicates), and a saline solution.

C. A. S.

Metallogenetics of the Caucasus. L. A. VAR-DANJANTZ (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1145—1162).—Four geological epochs are distinguished in connexion with the origin of various Caucasian ores.

R. T.

Mineralogy of cassiterite and of certain other pegmatitic and pneumatolytic minerals. B. N. ARTEMIEV (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1125—1144).—Crystallographic, analytical, and other data are recorded for samples of cassiterite, wolframite, beryl, columbite, tantalite, and monazite from various localities of the U.S.S.R.

R. T.

Viscosity of basalt glass at high temperatures. II. K. KANI (Proc. Imp. Acad. Tokyo, 1934, 10, 79—82; cf. this vol., 385).—The viscosities of four glasses have been determined between 1150° and 1400°.

C. W. G.

Thermal expansion of olivine. S. KÔZU, J. UEDA, and S. TSURUMI (Proc. Imp. Acad. Tokyo, 1934, 10, 83—86).—Analyses and thermal expansions of an Egyptian olivine are recorded.

$\text{Mg}_2\text{SiO}_4 : (\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{Mn})_2\text{SiO}_4$ —89.92 : 10.08.

C. W. G.

Thermal expansion of augite. S. KÔZU and J. UEDA (Proc. Imp. Acad. Tokyo, 1934, 10, 87—90).—Vals. for specimens from Japan, Bohemia, and Rhineland are given.

C. W. G.

Radio-geological survey of Czechoslovakia. W. SANTHOLZER and F. ULRICH (Nature, 1934, 133, 461).—The radioactivity of the springs of the Krkonose (Riesengebirge), Jizera Mts., has been systematically determined. The H_2O of the strongest springs

contains 10^{-11} g. Ra per litre. Chemical and mineralogical analyses of the neighbouring rocks have also been made. At Zaly (Heidelberg on Benecko), waters become radioactive through their long contact with phyllite (8.3×10^{-12} g. Ra per g.) and orthogneisses (4 to 7×10^{-12} g. Ra per g.).

L. S. T.

Soil mapping. E. OSTENDORFF (Z. Pflanz. Düng., 1934, B, 13, 119—124).—The practical val. of soil classification and mapping is discussed.

A. G. P.

Paleo-soils in quaternary deposits in the Saar valley. ERHART (Compt. rend., 1934, 198, 959—960).—Three old soils are described. The lowest, 1 m. thick, is a steppe soil; the two upper, each 1.8—2 m. thick, are forest soils.

C. A. S.

Transformation of petroleum in nature. D. C. BARTON (J. Inst. Petroleum Tech., 1934, 20, 206—213).— CH_4 and petroleum may be formed simultaneously, the former from a wide range of material, the latter from a limited range.

C. W. G.

Chemical evidence for the low-temperature history of petroleum. B. T. BROOKS (J. Inst. Petroleum Tech., 1934, 20, 177—205).—A review and discussion.

C. W. G.

Peaty lignites and anthracitic coals. C. MAHADEVAN (Indian J. Physics, 1933, 8, 259—268).—The cellulose : lignin ratio decreases during the early stages of coal development, but increases again in later stages, indicating that lignin is the more resistant initially, but cellulose later. The ratio provides an index of the stage of coal development.

J. W. S.

Organic Chemistry.

Pyrolysis of the lower paraffins. V. Conversion of the gaseous paraffins into aromatics in baffled metal tubes and the chemical composition of the products. A. CAMBRON and C. H. BAYLEY (Canad. J. Res., 1934, 10, 145—163; cf. B., 1934, 308).—"Recycling" of C_3H_8 in baffled steel tubes (Cr 18%, Ni 8%) affords some liquid (I), but the deposit of C diminishes the utility of the tubes. The catalytic activity (II) of the alloy does not decrease on prolonged use, is variable, and depends on (II) of a surface oxide film. When 28% Cr (Ni-free) baffles are used, more (I) and a higher light oil/tar ratio result. In steel tubes (Cr 28%, Ni 0%) C is not deposited; 20% of (I) is formed at 850° under the best conditions of flow, and increase of pressure up to 1 atm. increases the yield of (I) without increasing C deposition. Pyrolysis of C_3H_8 affords a product separated into olefines (mostly C_3H_4), butadiene, light oil containing C_6H_6 (64%), PhMe (14%), styrene (7.8%), xylene and cyclopentadiene in traces, and a tar which contains C_{10}H_8 (5%), anthracene (12.5%), also $\text{C}_{10}\text{H}_7\text{Me}$, $\text{C}_{10}\text{H}_6\text{Me}_2$, and phenanthrene.

J. L. D.

Neopentyl deuteride. F. C. WHITMORE, G. H. FLEMING, D. H. RANK, E. R. BORDNER, and K. D. LARSON (J. Amer. Chem. Soc., 1934, 56, 749).—Mg neopentyl chloride (I) and distilled H_2O give neo-

pentane (II), m.p. -21° to -20° . (I) and H_2O (d 1.0735) afford a mixture (A), m.p. -22° to -21° , of (II) and neopentyl deuteride (III); the presence of (III) is shown by the Raman spectrum (appearance of a line at approx. $\Delta\tau=2150$ cm^{-1} shift from the exciting line; due to the C-H^2 vibration). (A) and (II) show differences in b.p. and n .

H. B.

Catalytic micro-hydrogenation of organic compounds. R. KUHN and E. F. MÖLLER (Angew. Chem., 1934, 47, 145—149).—Apparatus and technique for a differential manometric method of determining double linkings by catalytic hydrogenation are described. The accuracy is $\pm 0.5\%$ on a sample of 1—5 mg.

E. S. H.

Oxidation with organic peracids. J. BÖESEKEN (Chem. Weekblad, 1934, 31, 166—170).—An account of the reactions of org. compounds with AcO_2H (I) and BzO_2H . The following are recorded for the first time: the rate of reaction of (I) with ethylenic compounds depends on the no. of H atoms attached to the unsaturated C atoms, the rates for the isomeric heptenes being $\text{CH}_3\text{CH}:\text{CH}:\text{C}_5\text{H}_{11} < \text{CHMe}:\text{CHBu}^a$, $\text{CH}_3:\text{CMeBu}^a < \text{CHMe}:\text{CET}_2$. Isoprene and 1 mol. of (I) gives an unsaturated acetate of a cis-diol (isopropylidene derivative with COMe_2), containing a tert. OH. Oxidation of $\cdot\text{C}:\text{C}\cdot$ linkings is much less

rapid than that of $>C:C<$ and takes place by way of the $\alpha\beta$ -diketone and the corresponding dicarboxylic acid. Aromatic amines and dil. solutions of (I) give azo- and azoxy-compounds with very small amounts of NO-compounds, but with a large excess of conc. (I) NO₂-compounds are obtained. The primary oxidation product is a labile amine oxide, $R\cdot NH_2\cdot O$. Conc. solutions of (I) do not explode spontaneously below 40° in the absence of catalysts (H_2SO_4).

S. C.

Laboratory preparation of pure ethylene and propylene. P. K. SAKMIN (Ber., 1934, 67, [B], 392—393).—96—98% C_2H_4 is obtained by passing EtOH over unglazed porcelain contained in a Cu tube heated at 400—450°. C_3H_6 is obtained similarly at 300°.

H. W.

Condensation of carbonyl chloride with ethylene. S. L. VARSCHAVSKI and E. A. DOROGANJEVSKAJA (Gazzetta, 1934, 64, 53—59).—Under the conditions described by Pace (A., 1929, 1419) the authors did not obtain $CH_2Cl\cdot CH_2\cdot CO_2H$ from $COCl_2$ and C_2H_4 ; reaction products result from the PhMe used.

E. W. W.

Thermal decomposition of organic compounds from the viewpoint of free radicals. VII. Ethylidene radical. F. O. RICE and A. L. GLASEBROOK (J. Amer. Chem. Soc., 1934, 56, 741—743).—When diazoethane (I) is passed through a quartz tube at 600—650° at about 0.5 mm., the Paneth effect with Sb mirrors is not shown (even at 1000°). Slow passage of (I) at 650°/2—3 mm. results in complete decomp.; the only condensable gas formed is C_2H_4 , indicating that CHMe rearranges easily to C_2H_5 . Decomp. of (I) in presence of CO (method; Staudinger and Kupfer, A., 1912, i, 245) gives no CHMe:CO. Thermal decomp. of acetaldazine gives (from about 60%) $N_2 + C_2H_4$ (2 mols.); the remainder affords a non-volatile oil, some HCN, and (probably) CH_4 . The Paneth effect is shown with Sb mirrors at $>700^\circ$; this is attributed to the formation of Me.

H. B.

Action of nitrogen trioxide on allylene and dimethylbutadiene (disopropenyl). N. J. DEMJANOV and A. A. IVANOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 318—323).—Interaction of allylene and N_2O_3 in cold Et_2O affords a nitrosite, $C_3H_4O_3N_2$, m.p. 89° (decomp.), and an unstable oil, reduced to an unstable amine, which is converted into an aldehyde and acid. Similarly, dimethylbutadiene affords a compound, $C_6H_{10}O_3N_2$, m.p. 104—105° (reduced to an amine and hydrolysed by conc. HCl to an oil which reacts with $NHPh\cdot NH_2$), and an oil, reduced (Zn—HCl) to a diamine, $C_6H_{10}(NH_2)_2$, b.p. about 195° [dihydrochloride (I); platinichloride; Bz_2 , derivative, m.p. 241—242°]. (I) affords a pyrrole when heated.

J. L. D.

Action of magnesium on polyhalogenated hydrocarbons in ethereal solution. IV. Action of magnesium on ethylene dibromide. C. L. TSENG and F. M. FAM (Sci. Quart. Nat. Univ. Peking, 1934, 4, 1—7).— $(CH_2Br)_2$ and Mg in dry Et_2O give C_2H_4 and $MgBr_2\cdot 2Et_2O$ with, at most, a trace of the Grignard compound.

R. S. C.

Peroxide effect in addition of reagents to unsaturated compounds. IV. Addition of halogen acids to vinyl chloride. M. S. KHARASCH and C. W. HANNUM (J. Amer. Chem. Soc., 1934, 56, 712—714).—Addition of HBr to $CH_2:CHCl$ (I) [which is more sensitive to "peroxides" than $CH_3\cdot CHBr$ or $CH_2\cdot CH\cdot CH_2Cl(Br)$ (cf. A., 1933, 805)] in a vac. or in presence of air, Bz_2O_2 , or ascaridole in the dark at room temp. gives 73—87% of $CH_2Br\cdot CH_2Cl$ (II) (the "abnormal" product); the peroxide effect is destroyed by addition of anhyd. $FeCl_3$, and $CHMeClBr$ (III) (the "normal" product) is then obtained. (III) also results in presence of good antioxidants (IV) in the dark. The effect of (IV) is almost completely destroyed and the velocity of the "abnormal" reaction is increased enormously by sunlight or artificial light at 0°—room temp.; addition occurs more rapidly and the amount of (III) is decreased at 76° in the dark. Addition in presence of $PhNO_2$ and $s-C_6H_3Me_3$ in a vac. in the dark gives products containing 29 and 95%, respectively, of (III); the % of (III) is increased (in AcOH also) by addition of (IV), but in presence of air and no (IV), (II) is practically the sole product. Addition of HCl to (I) occurs only in presence of a catalyst such as $FeCl_3$; $CHMeCl_2$ is the sole product (cf. Wibaut and van Dalfsen, A., 1932, 819). Addition of HI occurs rapidly in presence or absence of "peroxides" and gives $CHMeClI$; the "peroxide" is destroyed by the HI.

H. B.

Preparation of chloropicrin from methane. N. DANAILA and A. G. SOARE (Bul. Chim. Soc. Romana Stiinta, 1932, 35, 53—75).—Attempts to prepare $MeNO_2$ from CH_4 were unsuccessful. Max. utilisation (13%) of Cl_2 for production of liquid products is obtained when CH_4 and Cl_2 are passed through a SiO_2 tube at 400—420°; in presence of C activated with Fe_2O_3 40.5% of the Cl_2 is so utilised at 355°. Using 1:3 mixtures of CH_4 and Cl_2 , passed at a rate of 0.24 litre per min. over a pumice— $CuCl_2$ catalyst at 360—370°, 41% utilisation of Cl_2 is achieved, to yield a product containing 63% of $CHCl_3$ and 30% of CCl_4 . CCl_4 is readily reduced by the ordinary methods, to yield 70% of $CHCl_3$, and 30% of products of further reduction. 58% yields of $CCl_3\cdot NO_2$ are obtained by heating $CHCl_3$ with HNO_3 (d 1.52) at 140—150° during 2 hr.

R. T.

Determination of hydroxyl groups in alcohols and phenols by benzylation in tetrahydronaphthalene at high temperatures. T. M. MEIJER (Rec. trav. chim., 1934, 53, 387—397).—The OH-compound is heated with $BzCl$ or, better, $p-NO_2\cdot C_6H_4\cdot COCl$ (I), in boiling tetrahydronaphthalene and the HCl produced swept out by dry air or H_2 (for readily oxidisable substances) and absorbed in H_2O . In most cases, $>90\%$ of the theoretical amount of HCl is evolved; exceptions are glycerol (48.2%) and $C_6H_4(OH)_2$ (62%) (using $BzCl$), and $o-C_6H_4(OH)_2$ (74%) [with (I)]. With $BzCl$ and $p-OMe\cdot C_6H_4\cdot NH_2$, $p-OEt\cdot C_6H_4\cdot NH_2$, $p-C_6H_4Br\cdot NH_2$, and $p-C_6H_4Cl\cdot NH_2$, the amounts of HCl evolved are 17.7, 22.5, 74, and 84%, respectively. The following are described: benz-*p*-aniside, m.p. 158—162° (lit. 154.5°), *p*-phenetidine, m.p. 174.5—175.5° (lit.

173°), and *p*-chloroanilide, m.p. 193—194.5° (lit. 187—187.5°); *Ph*, m.p. 127°, *benzyl*, m.p. 83.5—84°, and *cyclohexyl*, m.p. 42—43°, *p*-nitrobenzoates; *resorcinol di-p-nitrobenzoate*, m.p. 175°; *pyrocatechol di-m-nitrobenzoate*, m.p. 144°. H. B.

Yacarol, a secretion of the glands of alligators. G. FESTER and F. BERTUZZI (Ber., 1934, 67, [B], 365—370).—The liquid wax, which constitutes about 35—63% of the gland, yields when hydrolysed small amounts of volatile fatty acids, chiefly unsaturated acids with one double linking, palmitic and myristic acids. P is present in small amount, but lecithin cannot be detected with CdCl₂. The non-saponifiable material contains small amounts of volatile and non-volatile nitrogenous bases, glycerol, cholesterol, cetyl alcohol, and *yacarol* (I), to which the odour of musk is due. (I), b.p. 234° (corr.)/757 mm., f.p. -10°, appears to be a primary alcohol of simple structure, possibly identical with βζ-dimethyl-Δ⁸-hepten-α-ol. It is not directly related to muscone or zibetone. H. W.

Butane-βγ-diol and its derivatives. I. Halogenhydrins of ψ-butylene. M. V. LICHOSCHERSTOV and S. V. ALEXEEV (J. Gen. Chem. Russ., 1933, 3, 927—932).—Solutions of NH₂·CO·NHCl containing 5% of AcOH react with gaseous or liquid ψ-butylene (I) at 15° (CuCl₂ catalyst) to afford a 4:1 mixture of β-chlorobutan-γ-ol (*Ac*, b.p. 152—156°, and *Bz* derivative, b.p. 263—265.5°) and βγ-dichlorobutane (II); the proportion of (II) increases with the acidity of the reaction mixture. 80% yields of β-bromobutan-γ-ol, b.p. 152—154° (*Ac* derivative, b.p. 165—167°), and βγ-dibromobutane (20%) are obtained from (I) and aq. NHBrAc containing 3% of AcOH. β-Iodobutan-γ-ol, an oil, decomposing at 65° to yield COMeEt, is prepared from the oxide of (I) and HI. R. T.

Synthesis of acetopropyl alcohol. I. L. KNU-
NIANZ, G. B. TSHELINTSEV, and E. D. OSITROVA
(Compt. rend. Acad. Sci. U.R.S.S., 1934, 1,
312—314; cf. A., 1901, i, 538).—Interaction of Et
sodioacetoacetate with (CH₃)₂O in EtOH at 0° during
24 hr. affords α-aceto-γ-butyrolactone, b.p. 142—
143°/30 mm., hydrolysed by warm 5% HCl in 2 hr.
to δ-keto-*n*-amyl alcohol, b.p. 115—116°/30 mm.

J. L. D.

Reaction between primary aliphatic alcohols and sulphuric acid. C. M. SUTER and E. OBERG (J. Amer. Chem. Soc., 1934, 56, 677—679).—The figures quoted after the following alcohols are the amounts (%) of ester (RHSO₄) formed at equilibrium from approx. equimol. amounts of ROH and 96.7% H₂SO₄ and 5.2, 22.6, and 31.98% oleum, respectively, at 25°: MeOH, 61.2, 66, 70.5, 73.2; EtOH, 52.6, 59.8, 65.1, 67.7; CH₂Cl·CH₂OH, 55, 59.8, 66.7, 70; PrⁿOH, 56.8, 61.9, 67.3, 70.6; BuⁿOH, 58.8, 63.9, 68.1, 71.5; BuⁱOH, 60.8, 65.7, —, —; *n*-amyl alcohol, 59.2, 64.4, —, —; *n*-hexyl alcohol, 58.3, 63.3, —, —. Appreciable quantities of coloured by-products are formed in the last three cases with the more conc. oleums. In general the val. of the equilibrium const. (highest for MeOH and lowest for EtOH) increases with decrease in the concn. of H₂O in the reaction mixture. H. B.

Relative mobilities of the propyl and isopropyl groups and their mono- and di-chloro-derivatives. P. CARRE and J. PASCHE (Compt. rend., 1934, 198, 939—940).—Substitution by Cl decreases successively the mobility of the Pr^α and Pr^β groups, the effect being greater with a Me than with a CH₂ group. Pr^α, *γ*-chloro-, b.p. 111—112°/21 mm., and βγ-dichloro-propyl chlorosulphite, b.p. 110—111°/3 mm., partial decomp. at 15 mm., obtained from SOCl₂ and the appropriate alcohol, decompose at 34—35°, 51°, and 61°, respectively. CH₂Cl·CHMe·OH or CH(CH₂Cl)₂·OH with SOCl₂ and C₅H₅N affords di-β-chloroisopropyl, b.p. 155—158°/37 mm., or di-ββ'-dichloroisopropyl sulphite, b.p. 215°/30 mm., which with SOCl₂ yield β-chloro- (I), b.p. 86—88°/20 mm., and ββ'-dichloro-isopropyl chlorosulphite (II), b.p. 120°/20 mm. SOCl₂·OPr^β, (I), and (II) decompose at 24°, 39°, and 70°, respectively. R. S. C.

Systematics and nomenclature of the phosphatides. R. ROSENBUSCH (Z. Unters. Lebensm., 1934, 67, 258—268; cf. B., 1933, 330, 651).

E. C. S.

Halides of vinyl sulphides. S. M. KLIGER (J. Gen. Chem. Russ., 1933, 3, 904—908).—(CH₂Cl·CHCl)₂SO (I) is reduced to (CH₂Cl·CHCl)₂S (II) by HBr in AcOH, and (CHCl·CH)₂S (III) is obtained by distilling (II) under reduced pressure; the corresponding Br derivatives are prepared analogously. (I), on treating with PCl₅, yields the compound CHCl₂·CHCl·S·CHCl·CH₂Cl, which on distillation under reduced pressure affords the compound CHCl₂·CHCl·S·CH·CHCl, b.p. 95—97°/5 mm.

R. T.

Direct synthesis of acid fluorides from acids and preparation of formyl fluoride. A. N. NESMEJANOV and E. J. KAHN (Ber., 1934, 67, [B], 370—373).—AcF is obtained in very good yield by inter-action of AcCl and KF in Ac₂O or AcOH. AcF is also obtained exclusively when a higher acyl chloride is substituted for AcCl owing to the change R·COCl + AcOH = R·CO₂H + AcCl and the greater volatility of AcF. On this principle, numerous examples are quoted of the conversion of an acid, R·CO₂H, which dissolves KF into R·COF by the action of BzCl. CPhCl₂ may replace BzCl. Formyl fluoride, b.p. about -26°/750 mm., is obtained from BzCl, KF, and HCO₂H. H. W.

Organic catalysts. VIII. Esterase model. W. LANGENBECK and J. BALTES (Ber., 1934, 67, [B], 387—391; cf. A., 1933, 22).—In the case of polymeric vinyl acetate in quinoline and KOAc in PrⁿOH at 160°, alkyl interchange is accelerated by CH₂Ph·OH, α-C₁₀H₇·CH₂·OH, CH₂Bz·OH (I), and, notably, by glycollanilide (II). Hydrolysis of PrⁿCO₂Me is hastened 4—5-fold by (II) and 6—7-fold by (I). Similar results are recorded for olive oil partly dissolved by Na deoxycholate. Addition of PrⁿOH causes retardation. The possibility that esterase is an activated alcohol is expressed.

H. W.

Catalytic hydrogenation of unsaturated compounds. II. Step-wise reduction of conjugated acids. E. H. FARMER and L. A. HUGHES (J.C.S., 1934, 304—307).—Re-examination of the 50% hydro-

genation of sorbic acid (I) using a small amount of $\text{PtO}_2 \cdot \text{H}_2\text{O}$ in EtOH has confirmed the results previously obtained (A., 1932, 365; 1933, 257, 935); the dihydro-derivatives formed are determined by isolation (as such or simple derivatives) and direct weighing. Dihydro-derivatives are also obtained from muconic acid (II) (as Na salt in H_2O); *trans*- Δ^6 -dihydromuconic acid has been obtained for the first time in the homogeneous condition. The failure of Ingold and Shah (A., 1933, 935) to detect the presence of dihydro-derivatives in the reduction products from (I), the Et ester of (II), and β -vinylacrylic acid is probably due to the use of an unsuitable analytical procedure. Much more complete reduction of (I) and (II) to dihydro-derivatives has been found using a Ni catalyst. H. B.

Hydrogenation of ricinoleic acid by hydrazine hydrate. J. VORISEK (Chem. Listy, 1934, 28, 57—58).— $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and ricinoleic acid at room temp. yield λ -hydroxystearic acid (*Me*, m.p. 57—58°, *Et*, m.p. 52.5—53°, *Pr*, m.p. 50—51°, *Pr* ^{β} , m.p. 47—47.5°, *Bu* ^{β} , m.p. 40°, and isoamyl, m.p. 35°, ester). R. T.

Examination of hydroxy-acids produced by oxidising paraffin with air. P. P. SCHORIGIN and A. P. KRESCHKOV (J. Gen. Chem. Russ., 1933, 3, 825—830).—The products obtained by passing air through paraffin at 52° consists of a mixture of hydrocarbons, fatty acids and OH-acids, and their anhydrides, lactones, and lactides, amongst which the acids $\text{C}_{13-17}\text{H}_{26-34}(\text{OH}) \cdot \text{CO}_2\text{H}$ and $\text{C}_{35}\text{H}_{69}(\text{OH}) \cdot \text{CO}_2\text{H}$ (I) [as lactone, m.p. 58—59.4°, obtained by hydrolysing the *Me* ester, m.p. 46—48°, of (I)] are identified. R. T.

Determination of acetyl values of lipins applicable to hydroxylated fatty acids. E. S. WEST, C. L. HOAGLAND, and G. H. CURTIS (J. Biol. Chem., 1934, 104, 627—634).—The sample is acetylated with a mixture of Ac_2O and $\text{C}_5\text{H}_5\text{N}$ (hot or cold), excess of Ac_2O is decomposed with hot H_2O , BuOH added to give a homogeneous solution, and the mixture titrated with alcoholic alkali with phenolphthalein as indicator. Another sample, treated with $\text{C}_5\text{H}_5\text{N}$ only, is similarly titrated and the difference subtracted from a blank on the Ac_2O - $\text{C}_5\text{H}_5\text{N}$ mixture. A new definition of Ac val. is proposed: mg. of Ac taken up per g. of substance. W. O. K.

Moderated oxidation of bixin. V. VIEBÖCK (Ber., 1934, 67, [B], 377—383).—Methylbixin (I) rapidly absorbs 20 when treated with $\text{Mn}(\text{OAc})_3$ in AcOH, whereas subsequent oxidation proceeds very slowly. The product is a mixture of hydroxytriacetox- and dihydroxydiacetox-compounds, whereas *hydroxytrihydroxytetrahydromethylbixin* (II) is obtained if Ac_2O is added to the mixture. OH is *tert.*, since further acetylation appears impossible. Bixin and norbixin behave similarly, but yield less definite compounds owing to partial production of lactone or lactide. The yellow compounds very readily lose AcOH. Thus, treatment of (II) with boiling AcOH gives a red product poorer than (II) by 1 AcOH, but retaining OH, a similar change appearing to be induced by alkaline hydrolysis, whereby a ketodihydroxy-acid is produced. Hydrogenation of the

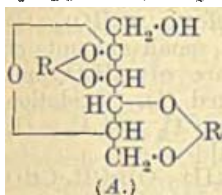
triacetate from bixin followed by alkaline hydrolysis and immediate treatment with Me_2SO_4 leads to *keto-dihydroxyperhydromethylbixin* (III). Treatment of (III) with $\text{Pb}(\text{OAc})_4$ in AcOH gives in poor yield an *ester-aldehyde* (IV), $\text{C}_{13}\text{H}_{24}\text{O}_3$, which readily gives a peroxide when exposed to air, and hence is converted during repeated distillation into an ester-acid (*Ag* salt), also obtained by oxidation with CrO_3 ; this appears homogeneous. In the production of (IV) the original mol. is halved, but rupture appears also to occur at other points of the mol. Treatment of (I) with $\text{Mn}(\text{OAc})_3$ in CHCl_3 causes addition of 1 OH and 1 OAc. H. W.

Enolates of carbonyl compounds. I. Dienolate of ethyl dibenzoylsuccinate. H. LOHAUS (Annalen, 1934, 509, 130—137).—Et $\alpha\alpha'$ -dibenzoylsuccinate (I) (mainly the β -ester, m.p. 128°; cf. Knorr, A., 1897, i, 63) and EtOH-KOEt give the *K*₂ salt (II) of a dienolic form. (II) and BzCl in Et_2O afford (mainly) a *dibenzoate*, m.p. 121—122°, and a little of the *dibenzoate* (III), m.p. 203°, described by Paal and Hartel (A., 1897, i, 598). (II) and Et_2O -I yield Et dibenzoylfumarate, whilst acidification (dil. H_2SO_4 , Et_2O at 0°) gives a liquid enol (blood-red colour with FeCl_3) which changes fairly rapidly to (I). (II) does not possess the same configuration as the Na salt of (I); this with Et_2O -I gives Et dibenzoylmaleate, whilst acidification yields a stable enol (bluish-violet colour with FeCl_3), and with BzCl , (III) results. Et $\alpha\alpha'$ -diacetylsuccinate (IV) and EtOH-KOEt give a solid *K*₂ salt (cf. Willstätter and Clarke, A., 1914, i, 286), which with Et_2O -I yields a little Et diacetylfumarate, and with Et_2O - BzCl affords a little of the *dibenzoate* (V), m.p. 108°, described by Paal and Hartel (*loc. cit.*), and much oil. (IV) and EtOH-NaOEt in Et_2O give a *Na*₂ salt (+EtOH), which with Et_2O - BzCl yields varying amounts of (V). H. B.

Reductic acid, a strongly reducing degradation product from carbohydrates. II. T. REICHSTEIN and R. OPPENAUER (Helv. Chim. Acta, 1934, 17, 390—396).—Reductic acid (I) (A., 1933, 1299) is oxidised by EtOH-I (+ $\text{AgCl} + \text{Ag}_2\text{CO}_3$) to 1:2:3-triketocyclopentane (as hydrate), which with $\text{NHPh} \cdot \text{NH}_2$ gives a 1:3-diphenylhydrazone, m.p. 248° (corr., decomp.) (*loc. cit.*), and, at 145°, a triphenylhydrazone, m.p. 207—208° (corr., decomp.). Oxidation of (I) with Ag_2CO_3 at 10° gives $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$. With Ac_2O - AcCl (I) gives a *Ac*₂ derivative, b.p. 112°/0.2 mm., reduced (PtO_2 - H_2 in AcOH) to a separable mixture of cyclopentyl acetate and the *Ac*₂ derivative of *cis*-cyclopentane-1:2-diol. The structure (3-keto- Δ^1 -cyclopentene-1:2-diol) assigned to (I) is thus confirmed, the 1-OH group most probably being the acidic one. J. W. B.

Glucoreductone for standardisation of 2:6-dichlorophenol-indophenol solutions for determination of ascorbic acid. Z. I. KERTESZ (J. Biol. Chem., 1934, 104, 483—485).—A solution of reductone, obtained by warming glucose with NaOH under standard conditions and addition of HCl, is used for the standardisation of indophenol solutions. H. D.

Synthesis of l-ascorbic acid (vitamin-C). T. REICHSTEIN and A. GRUSSNER (Helv. Chim. Acta, 1934, 17, 311—328).—With the appropriate ketone and H_2SO_4 or anhyd. CuSO_4 , l-sorbose (I) affords its mono-, b.p. $135^\circ/0.3$ mm., m.p. 93° , $[\alpha]_D^{20} +7.02^\circ$ in H_2O , and di-, m.p. $77-78^\circ$, $[\alpha]_D^{20} -18.1^\circ$ in COMe_2 , isopropylidene, dimethylene, b.p. $132^\circ/0.2$ mm., m.p. $77-78^\circ$, $[\alpha]_D^{20} -45.7^\circ$ in H_2O , and di-(α -methyl-n-propylidene), b.p. $140^\circ/0.6$ mm., m.p. $96-99^\circ$, $[\alpha]_D^{20} -16.6^\circ$ in COMeEt , derivatives, all of type A, oxidised by KMnO_4 - KOH to diisopropylidene- + H_2O (II), m.p. $98-99^\circ$ (decomp.) (*K* salt $[\alpha]_D^{18} -13.8^\circ$ in H_2O), dimethylene-, m.p. $129-130^\circ$, $[\alpha]_D^{18} -43.25^\circ$ in H_2O , di-(α -methyl-n-propylidene)- + H_2O



m.p. $95-100^\circ$, and dibenzylidene-, m.p. $202-204^\circ$ (corr.) [from the corresponding syrupy derivative of (I)], α -keto-l-gulonic acid. When hydrolysed by boiling H_2O , (II) affords α -keto-l-gulonic acid (III), m.p. 121° (corr., decomp.), $[\alpha]_D^{18} -48.0^\circ$ in H_2O (Et ester, $[\alpha]_D^{20} -145^\circ$ in EtOH) [(IV) in mother-liquor]. When (III) is heated with CO_2 -saturated H_2O , or better its Me ester, m.p. $155-157^\circ$, $[\alpha]_D^{18} -25.0^\circ$ in MeOH, is heated with NaOMe-MeOH , in CO_2 or N_2 , l-ascorbic acid (IV), chemically and physiologically identical with the natural product, is obtained, the overall yield being 25—30 g. of (IV) from 100 g. of (I). J. W. B.

Synthesis of hexuronic acids. V. **Synthesis of l-mannuronic acid from l-mannosaccharic acid.** C. NIEMANN, R. J. MCCUBBIN, and K. P. LINK. VI. **Synthesis of l-galacturonic acid from l-galactose.** C. NIEMANN and K. P. LINK (J. Biol. Chem., 1934, 104, 737—741, 743—746; cf. this vol., 280).—V. l-Arabinose by HCN-Ba(OH)_2 gives γ -d-mannonolactone, m.p. $149-150^\circ$, $[\alpha]_D^{20} -52^\circ$, oxidised to l-mannosaccharic acid, m.p. $183-185^\circ$, $[\alpha]_D^{20} -202.5^\circ$, whence, by the authors' standard methods, are obtained Ba, $[\alpha]_D^{20} +4 \pm 1^\circ$ in H_2O (containing 30% of an unidentified, inactive, non-reducing substance) (p-bromophenylhydrazone), and brucine d-mannuronate, m.p. $155.5-156.5^\circ$ (decomp.), $[\alpha]_D^{20} -22 \pm 2^\circ$ in H_2O , and l-mannuronolactone (I), m.p. $143-144^\circ$ (decomp.), $[\alpha]_D^{20} -92 \pm 2^\circ$ in H_2O (max.). (I) and its salts give characteristic aldehyde reactions. l- and d-(I), when mixed, sinter at $138-140^\circ$ and melt at 155° with decomp., probably owing to formation of a racemate.

VI. The mixture of l-galactose and d-xylose obtained from flax-seed mucilage was converted into the diisopropylidene compounds, b.p. $140-150^\circ/0.018$ mm., $[\alpha]_D^{20} +34^\circ$, which are oxidised by KMnO_4 to diisopropylidene-l-galacturonic acid, m.p. $152-154^\circ$, $[\alpha]_D^{20} +80 \pm 3^\circ$ in CHCl_3 (*K* salt, $+0.5\text{H}_2\text{O}$), hydrolysed by hot H_2O to l-galacturonic acid, + H_2O , m.p. $162-163^\circ$ (decomp.) after sintering at $112-113^\circ$ [oximehydroxylamine salt of this and of the d-isomeride, + H_2O , m.p. $151-152^\circ$ (decomp.)]. R. S. C.

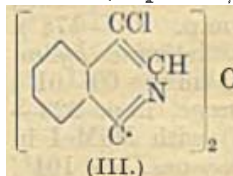
Catalytic preparation of aldehydes and ketones from monohalides of hydrocarbons. P. SCHORIGIN and I. LOSEV (J. Gen. Chem. Russ., 1933, 3, 821—824).—The products obtained by passing various halides over a V_2O_5 catalyst in presence of air and

H_2O at $360-400^\circ$ were: iso- $\text{C}_6\text{H}_{11}\text{Br}$, Bu^iCHO (I) 25, $\text{Bu}^i\text{CO}_2\text{H}$ (II) 6—10, isoamylenes (III) (as dibromides) 13—20%; iso- $\text{C}_8\text{H}_{17}\text{Cl}$, (I) 2—3, (II) 5—7, (III) 15—20%; Pr^iBr and Pr^iCl , respectively, COMe_2 4 and 10, AcOH 3 and 2, HCO_2H 1.5 and 0.5, C_3H_6 25 and 21%; $\text{CH}_2\text{Ph-CH}_2\text{Cl}$, PhCHO 35, BzOH 52, $\text{CH}_2\text{Ph-CHO}$ 6, CHPh-CH_2 3%; cyclohexyl chloride, cyclohexanone 48%. The chief products of reaction in the absence of air and H_2O are unsaturated hydrocarbons.

R. T.

Synthesis of aldehydes. E. B. HERSHBERG (Helv. Chim. Acta, 1934, 17, 351—358).— MgPhBr and $\text{CH}_2\text{:CH-CH}_2\text{Br}$ (I) afford $\text{CH}_2\text{:CH-CH}_2\text{Ph}$ (80% yield), which reacts with the AgI(OBz)_2 complex of Prévost (A., 1933, 711), formed *in situ*, to give the Bz_2 derivative, m.p. $74-75^\circ$ (85% yield), of γ -phenyl-n-propane- $\alpha\beta$ -diol, b.p. $163-165^\circ/15$ mm., which is obtained (84% yield) by hydrolysis with KOH-MeOH , and is oxidised by Pb(OAc)_4 - AcOH to $\text{CH}_2\text{Ph-CHO}$ (72% yield) and CH_2O . Similarly MgBu^iBr and (I) give Δ^i -n-heptene, b.p. $90.5-90.8^\circ/725$ mm. (59% yield), the Br_2 additive compound, b.p. $100-101^\circ/15$ mm. (96% yield), of which is hydrolysed by KOAc-EtOH at $130-140^\circ$ to n-heptane- $\alpha\beta$ -diol, b.p. $127.5-128.5^\circ/15$ mm. (86% yield), oxidised to n-hexaldehyde, isolated as its dimedon compound, m.p. $109-109.5^\circ$. J. W. B.

Reduction of chloral hydrate and chloral acyl chlorides [$\alpha\beta\beta\beta$ -tetrachloroethyl acylates]. G. W. DEODHAR (J. Indian Chem. Soc., 1934, 11, 83—86).— $\text{CCl}_3\text{-CH(OH)}_2$ is reduced (Al-Hg , H_2O) to $\text{CHCl}_2\text{-CHO}$ (mainly as hydrate), which with $\text{CH}_2(\text{CO}_2\text{H})_2$ and $\text{C}_5\text{H}_5\text{N}$ gives $\gamma\gamma$ -dichlorocrotonic acid (I), m.p. $100-101^\circ$, and a Cl-containing acid, m.p. $117-118^\circ$. $\alpha\beta\beta\beta$ -Tetrachloroethyl acetate (from $\text{CCl}_3\text{-CHO}$, AcCl , and a little conc. H_2SO_4) and $\text{CCl}_3\text{-CH(OAc)}_2$ are reduced (Zn dust, AcOH) to $\beta\beta$ -dichlorovinyl acetate (II), b.p. $148-149^\circ$ (dibromide, b.p. $127^\circ/40$ mm.), and not $\text{CH}_2\text{Cl-CHCl-OAc}$ (Curie and Millet, A., 1877, i, 188). (II) and dry NH_3 in CHCl_3 containing anhyd. Na_2SO_4 give $\beta\beta$ -dichlorovinylamine, m.p. 109° , which with BzCl and aq. NaOH affords the compound (III), m.p. 199° (decomp.). (II) with



$\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$, NHPh-NH_2 , and $\text{NH}_2\text{-CO-NH-NH}_2$ affords (I), $(\text{-CH}_2\text{N-NHPh})_2$, and $(\text{-CH}_2\text{N-NH-CO-NH}_2)_2$, respectively. $\alpha\beta\beta\beta$ -Tetrachloroethyl propionate, b.p. $120^\circ/40$ mm., and n-butyrate, b.p. $128^\circ/36$ mm., are similarly reduced to $\beta\beta$ -dichlorovinyl propionate, b.p. $90-92^\circ$ (dibromide, b.p. $145-146^\circ/39$ mm.), and n-butyrate, b.p. $100-101^\circ/36$ mm. (dibromide, b.p. $162-164^\circ/40$ mm.), respectively. $\beta\beta$ -Dichlorovinyl cinnamate, m.p. 70° (tetrabromide, m.p. $87-88^\circ$), and benzoate, m.p. $34-35^\circ$, are described. H. B.

α -Substituted ketones. (MME.) BRUZAN (Ann. Chim., 1934, [xi], 1, 257—358).—Interaction of the Na derivative of COPr^iBu^i (I) with MeI affords a mixture of (I) with di-tert-butyl ketone, b.p. $70^\circ/43$ mm., separated by its inability to form an oxime. $\gamma\gamma\epsilon\epsilon$ -Tetraethylheptan- δ -one, similarly prepared, has m.p. 44° . COPr^i (II) (Na derivative) with excess

of allyl iodide affords $\delta\delta\zeta\zeta$ -tetramethyl- Δ^9 -nonadien- α -one, b.p. 95–96°/16 mm. Improved preps. of many similar ketones are described; purification is effected by hydrolysis of the pure oxime or semicarbazone. Ph α -dimethylamyl ketone (oxime, m.p. 135–136°) is converted into α -dimethylhexyl alcohol, which with CrO_3 affords the aldehyde (semicarbazone, m.p. 134–135°). Substitution of H adjacent to CO in (II) by alkyl displaces the absorption curve towards the visible spectrum and increases max. absorption. At the same time CO reactivity is diminished. 4-Methyl- (semicarbazone, m.p. 168–169°) and 4-methoxy-deoxybenzoin [oxime, m.p. 118–119° (lit. 111°); semicarbazone, m.p. 148–149°] amongst other deoxybenzoin are described and their absorption spectra measured. Interaction of $\text{CHPhMe}\cdot\text{CO}\cdot\text{NH}_2$ (III) with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ in PhMe affords 4-methyl-meso-methyldeoxybenzoin, b.p. 188–190°/19 mm. Interaction of $\text{CPhMe}_2\cdot\text{CO}\cdot\text{NH}_2$ and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{MgBr}$ in xylene followed by HBr affords the *ketimine hydrobromide*, m.p. 205–206°, of 4-methoxy-meso-dimethylbenzoin, hydrolysed to the ketone, m.p. 100–101° (oxime, m.p. 193–194°; semicarbazone, m.p. 210–211°). Further methylation of meso-methyldeoxybenzoin through the Na derivative (prepared with sodamide) is established. $\text{CHPhMe}\cdot\text{COCl}$ (IV) (prep. described) with PhOMe in boiling CS_2 containing AlCl_3 during 3 hr. affords 4-methoxy- (V), m.p. 58–60° (*dl*-form; semicarbazone, m.p. 125–126°) and 78–80° (*d*- or *l*-form), together with 4-hydroxy-meso-methyldeoxybenzoin, m.p. 134–135°. Similarly, (IV) with PhMe affords 4-methyl-meso-methyldeoxybenzoin (VI), b.p. 190–191°/16 mm. [semicarbazone, m.p. 150–151°; oxime, m.p. 123–124°, which is hydrolysed to (VI), m.p. 46–47°]. (V) and (VI), examined spectroscopically, show traces of impurities, probably ethylenic compounds. Interaction of $\text{CPhMe}_2\cdot\text{CN}$ (VII) with MgPhBr affords the *ketimine hydrochloride*, m.p. 240–241°, hydrolysed to meso-dimethyldeoxybenzoin, m.p. 46–47° (oxime, m.p. 192–193°; semicarbazone, m.p. 176–178°). 4-Methyl-meso-dimethyldeoxybenzoin *ketimine hydrochloride*, m.p. 246–247° (ketone, m.p. 60–61°; oxime, m.p. 205–206°; semicarbazone, m.p. 223–224°), is prepared similarly. (VII) with MgMeI in PhMe affords β -phenyl- β -methylbutan- γ -one, b.p. 104°/17 mm. (semicarbazone, m.p. 185–186°). Similarly prepared, β -phenylbutan- γ -one has b.p. 93–94°/15 mm. (semicarbazone, m.p. 172–173°). PhMe (and PhOMe) with BzCl in presence of AlCl_3 affords Ph *p*-tolyl (semicarbazone, m.p. 121–122°) and Ph *p*-anisyl ketone [semicarbazone, m.p. 179–180° and 151–152° (*syn*- and *anti*-forms)], respectively. Absorption (VIII) spectra measurements of these compounds show that (a) (VIII) varies with the solvent; (b) deoxybenzoin are not enolised in EtOH or hexane; (c) the extent of (VIII) varies with the degree of substitution of the meso-C atom. J. L. D.

Oxidation of glucose by Fehling's solution at room temperature. H. WUNSCHENDORF and P. VALIER (Bull. Soc. Chim. biol., 1934, 16, 64–67, 73).—The rate of oxidation of glucose by Fehling's solution (I) at room temp. is dependent on, and the amount of oxidation independent of, the concn. of

Cu salt. The products give no further ppt. with (I) on boiling, nor do they react with $\text{NHPh}\cdot\text{NH}_2$. Among the products of the reaction are found MeCHO , lactic, glucuronic, tartaric, and gluconic acids.

A. I.

Oxidative degradation of carbohydrates with lead tetra-acetate. I. P. KARRER and K. PRAEHLER (Helv. Chim. Acta, 1934, 17, 363–368).—Oxidation of α -methylglucoside (I) (1 mol.) with 1 or 2 mols. of $\text{Pb}(\text{OAc})_4$ in AcOH affords $(\cdot\text{CHO})_2$ (II) (0.66 and 0.33 mol., respectively), small amounts of $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (III), only a trace of CH_2O , unidentified products, and unchanged (I). Oxidation probably occurs by fission between C_2 and C_3 : (I) $\rightarrow \text{OH}\cdot\text{CH}(\text{OMe})\cdot\text{CHO}$ \rightarrow (II) + $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}$ \rightarrow (III); and (IV) $\rightarrow \text{CH}_2\text{O} + \text{OH}\cdot\text{CH}(\text{CHO})$.

J. W. B.

Halogenoses of the β -series and their application to synthesis. VIII. Crystalline β - γ -ethylgalactoside (galactofuranoside). H. H. SCHLUBACH and K. MEISENHEIMER (Ber., 1934, 67, [B], 429–430).— γ -Galactose penta-acetate in transformed by anhyd. HCl at 20° into β -acetochlorogalactose, converted directly by Ag_2CO_3 in moist COMe , into galactose tetra-acetate (I) in 40% yield. (I), Ag_2O , and boiling EtI afford β -ethylgalactofuranoside tetra-acetate, m.p. 59° (corr.), $[\alpha]_D^{20} -50.5^\circ$ in CHCl_3 , hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to β -ethylgalactofuranoside, m.p. 86° (corr.), $[\alpha]_D^{20} -97.2^\circ$ in H_2O . H. W.

Condensation of α -methylmannoside with benzaldehyde. G. J. ROBERTSON (J.C.S., 1934, 330–332).— α -Methylmannoside and PhCHO at 150–155°/about 330 mm. give 4:6-benzylidene- α -methylmannoside (I), m.p. 146–147°, $[\alpha]_D^{20} +71.7^\circ$ in CHCl_3 [the benzylidene derivative, m.p. 110°, of van Ekenstein and Blanksma (A., 1906, i, 511) is probably a mixture of (I) and (III) (below)], a dibenzylidene- α -methylmannoside (II), m.p. 181–182° (cf. *loc. cit.*), and an isomeric dibenzylidene- α -methylmannoside (III), m.p. 97–98°, $[\alpha]_D^{20} -61.3^\circ$ in CHCl_3 . Methylation (MeI , Ag_2O , COMe_2) of (I) affords the 2:3- Me_2 derivative, b.p. 185–190°/0.47 mm., $[\alpha]_D^{20} +62.7^\circ$ in CHCl_3 , hydrolysed ($N\text{-HCl}$ in aq. COMe_2) to 2:3-dimethyl- α -methylmannoside, $[\alpha]_D^{20} +43.5^\circ$ in CHCl_3 (6- CPh_3 derivative, m.p. 172–173°; 4:6-dibenzoate, m.p. 121°, $[\alpha]_D^{20} +52.9^\circ$ in CHCl_3), which is then hydrolysed (8% HCl) to 2:3-dimethylmannose, $[\alpha]_D^{20} +10.6^\circ$ in EtOH, -4.3° in CHCl_3 (oxime, m.p. 112–114°). The two CHPh groups of (II) are hydrolysed (CHCl_3 -EtOH containing 0.3% dry HCl) simultaneously at the same rate. H. B.

Reactions of carbohydrates in liquid ammonia.

I. E. MUSKAT (J. Amer. Chem. Soc., 1934, 56, 693–695).— α -Methylmannoside (0.02 mol.) and K (0.08 mol.) in liquid NH_3 give a K_4 derivative, which with MeI (>0.08 mol.) and AcCl (>0.08 mol.), respectively, affords tetramethyl- α -methylmannoside (92% yield), m.p. 40°, and α -methylmannoside tetra-acetate (almost quant. yield), m.p. 65°. *iso*Propylidene- and diisopropylidene-glucose are similarly methylated to the 3:5:6- Me_3 (95% yield), b.p. 90–95°/0.05 mm., and 3-Me (96% yield), b.p. 105°/0.3 mm., derivatives, respectively. No change in ring structure

occurs when isopropylidene- γ -methylrhamnoside is similarly methylated. The method can be used for arylation and introduction of P (with POCl_3) or S (with SOCl_2 or S_2Cl_2). Glucose and liquid NH_3 give 1-aminoglucose, m.p. 121° . H. B.

Anhydro- β -methylhexoside from triacetyl- p -toluenesulphonyl- β -methylglucoside. A. MULLER (Ber., 1934, 67, [B], 421—424).—The anhydro- β -methylhexoside (I) of Helferich and Muller (A., 1930, 1411) is converted by Ag_2O and MeI in boiling COMe_2 into the Me_2 (II) derivative, m.p. $83\text{--}84^\circ$, $[\alpha]_D^{20} -148.2^\circ$ in CHCl_3 , or, if reaction is suitably interrupted, into the Me_1 compound, m.p. 121° , $[\alpha]_D^{20} -141.6^\circ$ in H_2O . The presence of $\cdot\text{CH}_2\cdot\text{OH}$ in (I) is established by the isolation of 6-triphenylmethyl-anhydro- β -methylhexoside acetate, m.p. $180.5\text{--}181.5^\circ$ after softening at 178° , $[\alpha]_D^{20} -91.8^\circ$ in CHCl_3 . Treatment of (I) with $2N\text{-HCl}$ at 100° and of the product (III) with Ac_2O and NaOAc at 100° leads to chloro- β -hexose tetra-acetate, m.p. 126° , $[\alpha]_D^{20} -21.17^\circ$ in CHCl_3 . (III) yields a sparingly sol. phenylosazone which resinifies completely during attempted purification. (II) and $N\text{-HCl}$ at 100° afford chlorodimethyl- α -hexose, m.p. (indef.) $135\text{--}137^\circ$, $[\alpha]_D^{20} -53.7^\circ$ to -67.6° in H_2O , which reduces warm Fehling's solution and retains Cl firmly. (II) is converted by the successive action of $2N\text{-HCl}$ at 100° and $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH-NH}_2$ into an osazone which could not be purified. Treatment of the acetoanhydro-bromoglucose of Reichel *et al.* (A., 1932, 1237) with abs. MeOH and anhyd. Ag_2CO_3 leads to a non-cryst. product, apparently not identical with anhydro- β -methylhexoside diacetate (*loc. cit.*). H. W.

Analysis of γ -methylfructoside mixtures by means of invertase. I. II. Isolation of a new crystalline methylfructoside. C. B. PURVES and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 702—707, 708—711).—I. The hydrolysis of " γ -methylfructoside" (I) by invertase (II) at 20° is followed polarimetrically and by the Cu reducing power of the hydrolysate. (I) is thus shown to contain a (II)-hydrolysable constituent (III), $[\alpha]_D^{20} -52 \pm 2^\circ$ in H_2O , assumed to be a true methylfructoside. The optical changes suggest that (III) is a derivative of γ -fructose and possesses the β -configuration. (I) also contains a fraction (IV), $[\alpha]_D^{20} +50^\circ$ (approx.) in H_2O , which is stable to (II). Fermentation of (I) with yeast removes (III) [and any unchanged fructose (V)] and leaves (IV). When the condensation of (V) with MeOH-HCl is stopped at the point of max. dextro-rotation, the resultant non-reducing product contains about 45% of (III) and 55% of (IV); wide variations in the conditions of condensation do not alter these proportions, but the amount of uncondensed (V) varies considerably. The non-reducing product obtained by prolonged condensation of (V) and MeOH-HCl contains only 10—20% of (III); the remainder is strongly laevorotatory (owing to the production of is fructoside of the normal ring type). Sucrose is hydrolysed 13.5 times as rapidly as (III) by (II) under comparable conditions; neither reaction is strictly unimol.

II. The material left after fermentation of a methylfructoside" (A) containing (V) (3%), (III)

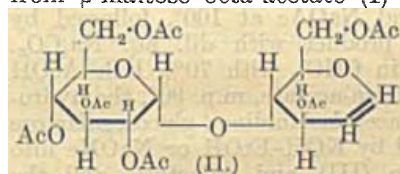
(42%), and (IV) (55%) is separated (pptn. with EtOAc from the aq. MeOH-solution; less sol. portion extracted twice with *n*-amyl alcohol) into (i) more sol. and (ii) less sol. fractions, and thence into (i) a γ -methylfructoside (VI) [about 10% of (A)], m.p. 69° , $[\alpha]_D^{20} +93.05^\circ$ in H_2O , and liquid γ -Me derivatives (21.7%), $[\alpha]_D^{20} +51^\circ$ in H_2O , and (ii) liquid γ -Me derivatives (19.8%), $[\alpha]_D^{20} +25.2^\circ$, and a residue of normal ring type [about 7.5%; determined by hydrolysis ($N\text{-HCl}$ at 20°) and subsequent fermentation]. (A) thus contains at least three γ -fructose derivatives. (VI) is hydrolysed more rapidly than sucrose by dil. acid. (A) does not give Raybin's diazouracil test (A., 1933, 811), which is considered to be more sp. for the sucrose linking than the action of (II).

H. B.

Reduction of W. C. Austin's α - d -glucoheptulose. (MME.) Y. KHOUVINE (Compt. rend., 1934, 198, 985—987).— α - d -Glucoheptose with saturated aq. Ca(OH)_2 at 35° gives α - d -glucoheptulose (I), m.p. 173° , $[\alpha]_D^{20} +61^\circ$, which with 2.5% Na-Hg and dil. H_2SO_4 gives α -glucoheptitol, m.p. 129° , $\alpha 0^\circ$, and α - d -glucoheptulitol (II), m.p. 130° (block), $[\alpha]_D^{20} +2.1^\circ$ in H_2O , an isomeride of the alcohol formed by biosynthesis. (II) is oxidised by *Acetobacter xylinum* to (I).

R. S. C.

Maltal and 4- α -glucosidomannose. W. N. HAWORTH, E. L. HIRST, and R. J. W. REYNOLDS (J.C.S., 1934, 302—303).—Treatment of the product from β -maltose octa-acetate (I) and HBr in AcOH



with Zn dust in cold aq. AcOH gives maltal hexa-acetate (II), m.p. $131\text{--}133^\circ$, $[\alpha]_D^{20} +68^\circ$ in CHCl_3 , which when boiled

with 0.5% aq. AcOH passes into ψ -maltal penta-acetate (III), m.p. 129° , $[\alpha]_D^{20} +162^\circ$ in CHCl_3 . (II) does not reduce Fehling's solution, but (III) does so; (III) does not decolorise Br in CHCl_3 . Maltal (in H_2O) [obtained by de-acetylation (MeOH-NH_3) of (II)] and BzO_2H (in Et_2O) give 4- α -glucosido- β -mannose (IV), m.p. $215\text{--}216^\circ$ (decomp.), $[\alpha]_D^{20} +97^\circ \rightarrow +115^\circ$ (in H_2O) [α -octa-acetate (V), m.p. 157° , $[\alpha]_D^{20} +117^\circ$ in CHCl_3]. The "epimeric difference" between the mol. rotation of β -maltose and (IV) is 7300; (I) and (V) show a difference of only 4000, thus affording further confirmation of the unreliability of epimeric differences as a means of assigning ring structures to carbohydrate derivatives. The maltal penta- and hexa-acetate hydrates of Bergmann and Kobel (A., 1924, i, 265) are maltose hepta- and octa-acetates, respectively.

H. B.

Flavanoneglucoside in *Glycyrrhiza glabra*, L., var. *glandulifera*, Regel et Herder. J. SHINODA and S. UEEDA (Ber., 1934, 67, [B], 434—440).—Extraction of liquorice root with MeOH leads to the isolation of liquiritin (I), $\text{C}_{21}\text{H}_{22}\text{O}_{11}$, m.p. 212° (also $+1\text{H}_2\text{O}$), hydrolysed by dil. H_2SO_4 to glucose and liquiritigenin (II), $\text{C}_{15}\text{H}_{12}\text{O}_4$, m.p. 207° (also $+1\text{H}_2\text{O}$). (II) gives an oxime, m.p. 178° , a diacetate, m.p. 186° , and a non-cryst. Me derivative. (II) is converted by 50% KOH at $170\text{--}180^\circ$ into resaceto-

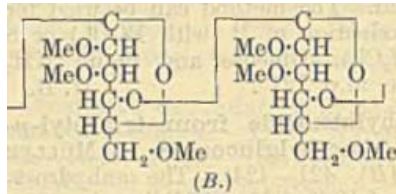
phenone (III) and $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (IV). Treatment of (I) with aq. $\text{Ba}(\text{OH})_2$ gives only (III) and unchanged (I). Treatment of (I) with anhyd. K_2CO_3 and MeI in boiling COMe_2 followed by hydrolysis leads to pæonol and (IV). (II) is therefore 4':7-dihydroxyflavanone (V). Treatment of $p\text{-CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COCl}$ with $m\text{-C}_6\text{H}_4(\text{OH})_2$ and AlCl_3 in PhNO_2 and of the product with KOH affords 2:4:4'-trihydroxychalcone and (V), m.p. 207° , identical with (II) [Tambor (A., 1916, i, 831) records m.p. $182\text{--}183^\circ$]. H. W.

Reactions of digitoxin, digitalin, and digitonin. L. EKKERT (Pharm. Zentr., 1934, 75, 228—229).—Colour reactions are described with phenols, naphthols, and aldehydes in the presence of acids, the colour changes depending on the condensation of pentoses or hexoses with these reagents. S. C.

Constitution of the solanines *t* and *s*. G. ODDO and G. CARONNA (Ber., 1934, 67, [B], 446—458; cf. Oddo *et al.*, A., 1905, i, 455; 1906, i, 527, 980; 1911, i, 671; 1929, 299; Colombano, A., 1908, i, 99; 1912, i, 798; Zemplen *et al.*, A., 1929, 51).—Treatment of *Solanine tuberosum* (I) with Ac_2O and NaOAc (Zemplen) gives a product, m.p. $204\text{--}205^\circ$ after incipient decomp. at 190° ; contrary to Zemplen, it regenerates (I) when treated with $\text{KOH}\text{--EtOH}$ or NaOMe , and is the acetate of *trideca-acetylsolanine-t* (II), $\text{C}_{71}\text{H}_{105}\text{O}_{33}$. Solanine trideca-acetate is obtained from (I), Ac_2O , and NaOAc at 100° , followed by treatment of the product with dil. aq. Na_2CO_3 . Treatment of (II) in CHCl_3 with 70% $\text{HBr}\text{--AcOH}$ leads to rhamnose tetra-acetate, m.p. 90° , the hydrobromide of nona-acetylsolanidine-*t*-glucosegalactose ($-\text{H}_2\text{O}$) converted by $\text{KOH}\text{--EtOH}$ or NaOMe into solanidine-*t*-glucoside (III) and galactose, and the hydrobromide of penta-acetylsolanidine-*t* ($-\text{H}_2\text{O}$) hydrolysed to (III). The sequence in (I) is therefore solanidine-*t*-*d*-glucose-*d*-galactose-*d*-rhamnose. Acetylation of *S. sodomaeum* (Zemplen) yields solanine-*s*-deca-acetate, m.p. $135\text{--}138^\circ$, obtained previously. Hydrolysis with 70% $\text{HBr}\text{--AcOH}$ leads to rhamnose diacetate (IV), m.p. 75° (slight decomp.), *hepta-acetylsolanidine-s*-glucosegalactose ($-\text{H}_2\text{O}$) (II), m.p. 170° after becoming yellow at 140° (hydrolysed by $\text{KOH}\text{--EtOH}$ or NaOMe to solanidine-*s*-glucoside and galactose), and *acetobromosolanidine-s* (VI), m.p. 135° after becoming yellow at 110° . The use of 30% $\text{HBr}\text{--AcOH}$ leads to (IV) and (V), the hydrobromide of *acetylsolanidinerhamnose*, $\text{C}_{18}\text{H}_{31}\text{ON}\cdot\text{C}_6\text{H}_{12}\text{O}_5\text{Ac}\cdot\text{HBr}$, m.p. 132° (decomp.) [hydrolysed to (IV) and (VI)], and (VI). The sequence in the glucoside is therefore solanidine-*s*-*d*-glucose-*d*-galactose-*d*-rhamnose-solanidine-*s*. H. W.

Ivory-nut mannans. I. Constitution of mannan-A. F. KLAGE (Annalen, 1934, 509, 159—181).—Extraction of ivory-nut shavings with H_2O and COMe_2 , subsequent treatment with ClO_2 (cf. Schmidt *et al.*, A., 1931, 1101) for 5 days, extraction of the residue with 5% NaOH , and acidification of the extract with AcOH gives mannan-A (I), $[\alpha]_D^{20} -44.7^\circ$ in $\text{A}\cdot\text{NaOH}$, which is methylated (Me_2SO , aq. NaOH , 6 6) *trimethylmannan* (II). Complete hydrolysis

(dil. HCl) of (II) gives 2:3:6-trimethylmannose (about 80%) [indicating the presence of the unit (B) in (II)] and 1.15—1.4% of 2:3:4:6-tetra-methylmannose (III) (arising from



the end grouping). Partial hydrolysis of (II) affords a mixture (C) of oligosaccharides; methylation (MeI , Ag_2O) and fractionation gives non-homogeneous octa-methylmannobiose and hendecamethylmannotriose, which on further hydrolysis yield (III). Oxidation of (C) by Honig and Ruzicka's method (A., 1930, 1166) and methylation (MeI , Ag_2O) of the resulting lactones gives non-homogeneous heptamethylmannobionolactone and decamethylmannotriolactone. Hydrolysis (0.01—0.1N- HCl at 98°) of (II) is not unimol., and marked retardation occurs after about 50% hydrolysis; probable reasons are discussed and the course of the hydrolysis is considered to be similar to that of cellulose (Freudenberg *et al.*, A., 1930, 1025). The amount of (III) obtained by complete hydrolysis of (II) indicates that (II) contains 71—86 C_6 units; oxidation with hypiodite indicates about 68 units. In agreement with Hess *et al.* (A., 1930, 1416), the "I vals." of non-methylated sugars [e.g., (I) and glucose] increase with continued action of the hypiodite. H. B.

Enzymic amyolysis. III. Crystalline hexaose from starch. See this vol., 449.

Starch. VI. Iodomethyl-di-*p*-toluenesulphonylmethylglucoside from starch tri-*p*-toluenesulphonate. K. HESS and O. LITTMANN (Ber., 1934, 67, [B], 465—466; cf. A., 1933, 1279).—Methylglucoside tri-*p*-toluenesulphonate acetate is transformed by NaI in COMe_2 at 125° into *iodomethylglucoside di-*p*-toluenesulphonate acetate*, m.p. $129\text{--}130^\circ$, $[\alpha]_D^{20} +13.16^\circ$ in CHCl_3 , -16.18° in C_6H_6 , -8.59° in COMe_2 , not identical with the corresponding compound from iodostarch di-*p*-toluenesulphonate (*loc. cit.*). H. W.

Chain length of lichenin of native composition. E. SCHMIDT, R. SCHNEGG, and E. WURZNER (Naturwiss., 1934, 22, 172).—After repeated treatment with ClO_2 and Na_2SO_3 , lichenin (I) is dissolved from *Cetraria islandica* by $\text{Cu}(\text{OH})_2\text{--NH}_3$, pptd. by EtOH from the acidified solution, electro dialysed, extracted with MeOH and Et_2O , and dried. It then contains 0.1% of ash and is free from pentosans. Conductometric titration shows the presence of 0.563% CO_2H (calc. as CO_2), indicating a chain of 47 glucose residues and 1 residue containing CO_2H . Acetylxylen, (I), and cellulose contain therefore 2×16 , 3×16 , and 6×16 individual links, respectively, in the chain. H. W.

Highly-polymerised compounds. LXXXIX. Polyoxy-methylenes as model of cellulose. H. STAUDINGER. XC. Cellopentaose acetate and the constitution of cellulose. H. STAUDINGER and E. O. LEUPOLD (Ber., 1934, 67, [B], 475—479, 479—486).—LXXXIX. Mainly a reply to Hess *et al.* (this vol., 493).

XC. Measurements with oligosaccharide derivatives show that the sp. viscosity of a glucose residue diminished regularly from glucose penta-acetate (I) to cellobiose octa-acetate (II), tending towards the final val. found for complex cellulose acetates. Examination of the cellobiose octa-acetate of Zechmeister and Toth along these lines indicates it to be a cellobiose octa-acetate. This view is confirmed by determinations of mol. wt. in camphor in which (I), cellobiose octa-acetate, cellobiose acetate, and (II) behave normally. The η_{sp} val. for a glucose residue in cellobiose hepta-acetate stearate, m.p. 130—132°, is identical with that in the pentaose acetate and complex cellulose acetates, whereas that of the corresponding nonoate, m.p. 116—118°, is somewhat greater.

H. W.

Assumed non-identity of cotton and wood cellulose. J. BARSHA and H. HIBBERT (J. Amer. Chem. Soc., 1934, 56, 748).—Rayon pulps from spruce, beech, and maple do not contain a "resistant portion" (to methylation) (cf. Bell, A., 1932, 934).

H. B.

Reactions relating to carbohydrates and polysaccharides. XLVI. Structure of the cellulose synthesised by the action of *Acetobacter xylinus* on fructose and glycerol. J. BARSHA and H. HIBBERT (Canad. J. Res., 1934, 10, 170—179).—Fructose and glycerol are converted into bacterial celluloses [(I) and (II), respectively] (cf. A., 1931, 826) ($C_6H_{10}O_5$)_n. (I) and (II) with Ac_2O in $AcOH$ containing $SOCl_2$ afford Ac_3 derivatives, $[\alpha]^{25}_D$ —21.0° (III) and —21.8° (IV) in $CHCl_3$, respectively, hydrolysed by 2*N*- $NaOH$ - $MeOH$ at room temp. in 24 hr. to celluloses ($C_6H_{10}O_5$)_n. (III) or (IV) with $MeOH$ - HCl (0.9%) at 125° during 60 hr. affords a mixture, $[\alpha]^{25}_D$ +105.9°, of α - and β -methylglucoside, which gives the α -form, m.p. 163.5°, $[\alpha]^{25}_D$ +156.6°, when fractionally crystallised. Hydrolysis of (I) or (II) with $ZnCl_2$ - HCl (cf. A., 1930, 1561) affords a product with $[\alpha]^{25}_D$ nearly identical with that of glucose. (III) and (IV) with Me_2SO_4 in warm $NaOH$ afford trimethylcellulose, m.p. 227—230°, $[\alpha]^{25}_D$ —14.2° in C_6H_6 , and m.p. 232—234°, $[\alpha]^{25}_D$ —15.2° in C_6H_6 , respectively; either is hydrolysed by 1% $MeOH$ - HCl at 100° during 50 hr. to 2:3:6-trimethylmethylglucoside, b.p. 110—113°/25 mm., hydrolysed further to 2:3:6-trimethylglucose, m.p. 104—106°. (I) or (II) with Ac_2O containing conc. H_2SO_4 at 50° during 19 days affords cellobiose octacetate, m.p. 222—223°, identical with the product obtained when bacterial cellulose prepared from glucose is acetylated. The identity of these celluloses is supported by X-ray analysis.

J. L. D.

Carbon double linkings and carbon-nitrogen linkings. XII. Decomposition of quaternary ammonium compounds with sodium amalgam. H. EMDE and H. KULL (Arch. Pharm., 1934, 272, 469—481).—A summary of quaternary NH_4 salt degradations by the ordinary Hofmann reaction and by Na - Hg reduction classified according as to whether the two reactions do, or do not, follow similar courses.

J. W. B.

Quaternary ammonium salts of possible therapeutic value. C. CUTOLO (L'Ind. Chimica,

M M

1934, 9, 322—325).—These salts may be prepared by dissolving the Na salt of the org. acid in aq. $EtOH$, treating the solution with one of NMe_4Cl or NEt_4Cl in $EtOH$ of definite concn., and adding a little HCl . Practically all the $NaCl$ is thus pptd., whilst the NMe_4 salt remains dissolved. Details are given for the prep. of HCO_2NMe_4 .

T. H. P.

Quaternary ammonium salts from dialkyl-bromopropylamines. IV. Formation of four-membered rings. C. F. GIBBS and C. S. MARVEL (J. Amer. Chem. Soc., 1934, 56, 725—727).—Diethyl- γ -bromopropylamine, b.p. 52—54°/5 mm. (platinichloride, m.p. 150—153°) (A., 1927, 1064) [from diethyl- γ -phenoxypropylamine, b.p. 118—120°/5 mm. (platinichloride, m.p. 134—135°)], passes when kept at 0—100° into diethyltrimethyleneammonium bromide, $(CH_2)_3N^+Et_2Br^-$, m.p. 175—178°, and not into a linear polymeric [as does $NMe_2(CH_2)_3Br$ (A., 1933, 381)]. Di-*n*-propyl-, m.p. 52—59°, and di-*n*-butyl-, m.p. 120—121°, trimethyleneammonium bromides are similarly obtained from di-*n*-propyl-, b.p. 77—78°/4 mm. (platinichloride, m.p. 194—196°), and di-*n*-butyl-, b.p. 96—98°/6 mm. (auribromide, m.p. 130°), γ -bromopropylamine, respectively, which are prepared (method; A., 1930, 349; 1933, 812) from di-*n*-propyl-, b.p. 137—139°/6 mm., and di-*n*-butyl-, b.p. 148—150°/5 mm., γ -phenoxypropylamine, respectively. Diethylallylamine hydrobromide has m.p. 189—190°. The mol. wts. (f.p. in H_2O) of the above bromides are of the same order (50%) as those of NBu_4I and $NEt_4Bu^+I^-$.

H. B.

Glucosyl-alkylamines. E. VOTOCEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1934, 6, 77—96).—The following 1-derivatives are prepared by interaction of the appropriate sugar and amine in H_2O or $MeOH$: arabinose-methyl- (+2 H_2O), m.p. 101°, and -heptyl-imine (+3 H_2O); fucose-methyl-, m.p. 125° (+1 H_2O), -*n*-propyl-, m.p. 124—125° (decomp.), -*n*-butyl- (+0.5 H_2O), m.p. 88—89°, -*n*-amyl- (+1 H_2O), m.p. 95° (sinters 75°), -*n*-hexyl-, m.p. 109—110°, and -*n*-heptyl-imine (+0.5 H_2O), m.p. 84—85°; glucose-methyl- (+1 H_2O), m.p. 78—80°, decomp. 100—115°, -*n*-butyl- (+1 H_2O), m.p. 97—98°, -*n*-amyl- (+1 H_2O), m.p. 96—97°, -*n*-hexyl- (+1 H_2O), m.p. 79—80°, and -*n*-heptyl-imine (+1 H_2O), m.p. 97°; rhamnose-methyl- (+1 $MeOH$), m.p. 126—127°, -ethyl- (+0.5 H_2O), m.p. 141—142°, -*n*-propyl-, m.p. 145°, -*n*-butyl- (+1 $MeOH$), m.p. 136—137° (decomp.), -*n*-amyl-, m.p. 139—140°, -*n*-hexyl-, m.p. 132—133°, and -*n*-heptyl-imine, m.p. 138°; galactose-*n*-propyl-, m.p. 127—128° (decomp.), -*n*-butyl- (+1 H_2O), m.p. 82—83°, -*n*-amyl- (+1 H_2O), m.p. 110° (anhyd.), and -*n*-heptyl-imine (+1 H_2O), m.p. 99—100° (sinters 80°); xylose-*n*-butyl- (+1 H_2O), m.p. 81—82°, and -*n*-hexyl-imine (+1 H_2O), m.p. 87°; and mannose-*n*-butyl- (+1 H_2O), m.p. 71—72°, -*n*-amyl- (+0.5 H_2O), m.p. 70—71°, -*n*-hexyl- (+0.5 H_2O), m.p. 75°, and -*n*-heptyl-imine (+0.5 H_2O). All show mutarotation in H_2O .

H. A. P.

Oxidation of amino-acids by silver oxide. R. M. HERBST and H. T. CLARKE (J. Biol. Chem., 1934, 104, 769—788).— α - NH_2 -acids, $NRR'COR''R'''CO_2H$, are oxidised by Ag_2O (excess) in boiling H_2O (not in acid or alkaline solution) quantitatively, but with varying velocity, to $NHRR'$, $COR''R'''$, and

CO₂. Aldehydes, if formed, may be further oxidised to acids. Acylation of the NH₂, including peptide formation, slows down or entirely inhibits oxidation, depending on the rate of hydrolysis of the N·CO linking which must precede oxidation. Alkylation of NH₂ increases the rate of oxidation, but betaines are completely stable. Oxidation is thus associated with primary loss of H from the N atom of NHR·CR₂·CO₂, and is thus not a dehydrogenation in the sense of Wieland's theory. With NMe₂·CMe₂·CO₂H (I) NHMe₂ is liberated more rapidly than CO₂, but OH·CMe₂·CO₂H is not the primary reaction product, since this compound is oxidised more slowly than (I) (although CO₂ is quantitatively formed). NH₂·CMe₂·CO₂H (II) is excreted largely unchanged by dogs, and the Ag₂O-oxidation thus bears no relation to the metabolic reactions of NH₂-acids. Curves are given for the rate of evolution of CO₂ and NH₃; the results are summarised as follows, the reaction products isolated being given in parentheses: (a) very rapidly oxidised: sarcosine (CO₂, NH Me), NMe₂·CH₂·CO₂H (CO₂, NHMe₂), NHMe·CHMe·CO₂H and NMe₂·CHMe·CO₂H (CO₂, NH₂Me or NHMe₂, MeCHO, AcOH), (I) (CO₂, NHMe₂, COMe₂); (b) rapidly oxidised: glycine [CO₂, NH₃, CO(NH₂)₂ (III) (trace), N₂ (10%)], alanine [CO₂, NH₃, MeCHO, AcOH, (III)], (II) (CO₂, NH₃, COMe₂), leucine (CO₂, NH₃, isovaleraldehyde and isovaleric acid), NH₂·CHPh·CO₂H (CO₂, NH₃, PhCHO, BzOH), CH₃·Ph·CH(NH₂)·CO₂H (CO₂, NH₃, PhCHO, BzOH, CH₂Ph·CHO, CH₂Ph·CO₂H), glutamic acid [CO₂, NH₃, (-CH₂·CO₂H)], proline, NHPh·CH₂·CO₂H [CO₂, NH₃Ph, (NPh)₂], NHPh·CHMe·CO₂H [CO₂, NH₃Ph, (NPh)₂, AcOH], NHPh·CMe₂·CO₂H [CO₂, NH₃Ph, (NPh)₂, COMe₂], NH₂·CPhEt·CO₂H (CO₂, NH₃, CPhEt), NHAc·CH₂·CO₂H (CO₂, NH₃, hippuric acid (CO₂, NH₂Bz), NH₂Bz·CHPh·CO₂H (CO₂, PhCHO), PhSO₂·NH·CH₂·CO₂H (CO₂, NH₂·SO₂Ph), NH₂·CO·NH·CHMe·CO₂H [CO₂, NH₃, (III), MeCHO, AcOH], NHPh·CO·NH·CHMe·CO₂H (NH₂Ph), 5-methyl- [CO₂, NH₃, (III), AcOH, NHAc·CO·NH₂] and 3-phenyl-5-methyl-hydantoin (NH₂Ph), creatine; (c) slowly oxidised: glycyl-, alanyl- (CO₂, NH₃, AcOH), *p*-toluenesulphonyl-, and benzenesulphonyl-phenyl-alanine (CH₃Ph·CHO), alanylglycine, PhSO₂·NH·CMe₂·CO₂H, benzenesulphonyl-leucine (isovaleric acid), PhSO₂·NH·CHPh·CO₂H (PhCHO); (d) not oxidised: betaine, NH₂·CH₂·CH₂·CO₂H, NHBz·CHMe·CO₂H, *d*-*o*-C₆H₄(CO₂)₂·N·CHMe·CO₂H, NHBz·CMe₂·CO₂H, NHBz·CPhMe·CO₂H, 5:5-dimethyl- and 3-phenyl-5:5-dimethyl-hydantoin.

R. S. C.

Reactions of betaine. L. EKKERT (Pharm. Zentr., 1934, 75, 209—210).—Betaine and KOH give OH·CH₂·CO₂H, which affords CH₂O on treatment with H₂SO₄, identified by the colour reactions with guaiacolsulphonic acid, codeine, and resorcinol.

S. C.

Synthesis of serine. M. S. DUNN, C. E. REDEMANN, and N. L. SMITH (J. Biol. Chem., 1934, 104, 511—517).—OEt·CH₂·CH₂·OH is oxidised with Na₂Cr₂O₇-aq. H₂SO₄ and the fraction, b.p. 70—95°, of the distillate treated successively with 7*N*·NH₃-MeOH, anhyd. HCN, and 40% HBr, neutralised

with PbCO₃, filtered, boiled, treated with Pb(NO₃)₂, filtered, treated with H₂S, and evaporated. A 64% yield of crude, and a 40% of pure, *dl*-serine (photomicrograph) is obtained.

R. S. C.

Preparation of polypeptides containing glycine and I(+)-alanine alternately linked, and their behaviour towards enzymes. E. ABDERHALDEN and A. NEUMANN (Fermentforsch., 1934, 14, 133—142).—The following polypeptides and precursors were prepared by Fischer's methods: glycyl-*l*-alanine, [α]_D²⁰ —50° in H₂O, from chloroacetyl-*l*-alanine, [α]_D²⁰ —45° (NH₄ salt, [α]_D²⁰ —21·4° in H₂O, not —60°; cf. A., 1931, 767); *l*-alanylglycyl-*l*-alanine (I), m.p. 207°, [α]_D²⁰ —19·5° in H₂O, from *l*-bromopropionyl-glycyl-*l*-alanine, m.p. 103°, [α]_D²⁰ —19·2° in H₂O; glycyl-*l*-alanylglycyl-*l*-alanine, [α]_D²⁰ —24·6° in H₂O, purified through Cu salt from chloroacetyl-*l*-alanylglycyl-*l*-alanine. The following were prepared by the method of Bergmann and Zervas (A., 1932, 935): glycyl-glycyl-*dl*-leucine by catalytic hydrogenation of *N*-benzylcarbonatoglycylglycyl-*dl*-leucine, m.p. 175°; *l*-alanylglycyl-*dl*-leucine (II), m.p. 224°, [α]_D²⁰ +44·4° in H₂O, from *N*-benzylcarbonato-*l*-alanylglycyl-*dl*-leucine, m.p. 103°, [α]_D²⁰ —5·5° in EtOH; glycyl-*l*-alanine, [α]_D²⁰ —46·5° in H₂O, from *N*-benzylcarbonatoglycyl-*l*-alanine, m.p. 155—156°, [α]_D²⁰ —4·7° in EtOH, prepared from *l*-alanine and *N*-benzylcarbonatoglycyl chloride (III). *N*-Benzylcarbonato-*l*-alanylglycyl chloride (IV), a yellow oil, crystallises in ice-salt, and is rapidly converted by atm. H₂O into a substance C₄H₅O₃N, probably $\begin{matrix} \text{CHMe} \cdot \text{CO} \\ | \\ \text{NH} - \text{CO} \end{matrix} > \text{O}$ [(III) is also partly converted into an analogous substance, C₃H₅O₃N]. An attempt to couple (IV) with glycyl-*l*-alanine (V) failed. (V), (I), and (II) are hydrolysed by crepsin.

A. E. O.

Reactions of nitrous acid with cystine and related sulphur-containing compounds. S. A. LOUGH and H. B. LEWIS (J. Biol. Chem., 1934, 104, 601—610).—Cystine (I) and HNO, slowly give up to 85% of the theoretical amount of H₂SO₄. Substitution of the SH or NH, or oxidation of the SH to SO₃H, prevents formation of H₂SO₄. SH·CH₂·CO₂H (II), SH·CHMe·CO₂H, and dithiodiacetic acid give H₂SO₄; the gas obtained from (II) is shown spectrographically to be N₂. The high val. in the Van Slyke determination of (I) is thus due to oxidation of SH to H₂SO₄ and evolution of "extra" N₂.

R. S. C.

δ-Ethoxybutylcarbamide. E. WERTHEIM (J. Amer. Chem. Soc., 1934, 56, 735—736).—γ-Ethoxybutyronitrile, b.p. 175°/716 mm. (from the bromide and aq. EtOH-KCN), is reduced (Na, MeOH) to δ-ethoxybutylamine, b.p. 155—156°/730 mm. (lit. 153—154°/746 mm.), which with KCNO and dil. H₂SO₄ gives δ-ethoxybutylcarbamide, m.p. 68—69°, slight bitter taste. The sweet taste of dulcin [*p*-OEt·C₆H₄·NH·CO·NH₂] depends on the presence of the C₆H₆ ring. *o*-OH·C₆H₄·NH·CO·NH₂ is very sweet, whilst OH·CH₂·CH₂·NH·CO·NH₂ is practically tasteless.

H. B.

Electrolytic preparation of semicarbazide hydrochloride. T. Y. CHANG and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 157—165).—Electrolytic reduction of NH₂·CO·NH·NO, in

18% HCl with a Cu cathode and a graphite anode, c.d. 0.05 amp. per sq. cm., gives a yield of 53–55% of semicarbazide, isolated by concentrating in vac.

F. R. S.

Electrolysis of ether solutions of the Grignard compound. Isolation, identification, and determination of anodic products. W. V. EVANS and F. H. LEE (J. Amer. Chem. Soc., 1934, 56, 654–657).—Electrolysis (stirrer between Pt electrodes) of 1.22–3.53*M*-solutions of MgEtCl(Br, I) in Et₂O gives C₂H₆ (47.7–53.3%), C₂H₄ (45.6–51.4%), and H₂ (0.8–1.3%). The main reaction is considered

to be: $2\text{Et} \longrightarrow 2\text{Et} \longrightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$; $2\text{Et} \longrightarrow 2\text{C}_2\text{H}_4 + \text{H}_2$ is probably a secondary change. MgPrBr (1.34–1.36*M*) affords C₃H₈ (50.1–50.9%), C₃H₆ (48–49%), and H₂ (0.9–1.1%), whilst an equimol. mixture of MgEtBr and MgPrBr gives C₂H₆ (30.3%), C₃H₈ (24.2%), C₂H₄ (22.6%), C₃H₆ (22%), and H₂ (0.7%). With low concns. (1.09–1.45*M*) of MgMeBr, the products are CH₄ (66.7–79.3%), C₂H₆ (0–23.8%), C₂H₄ (3.5–5.3%), and isobutene (8.1–17.2%); the corresponding % for 1.65–2.08 and 2.83*M* solutions are 21.2–41, 48.2–71.5, 2.1–3.9, 5.2–6.9, and 0, 100, 0, 0, respectively. The following reactions probably occur: $4\text{Me} \longrightarrow \text{C}_2\text{H}_4 + 2\text{CH}_4$; $8\text{Me} \longrightarrow \text{C}_4\text{H}_{10} + 4\text{CH}_4$; $2\text{Me} \longrightarrow \text{C}_2\text{H}_6$; in concn. solution the change $\text{Me} + \text{Me} \longrightarrow \text{C}_2\text{H}_6 + e$ may take place. In general, the yield of gaseous hydrocarbon is $\text{Cl} > \text{Br} > \text{I}$. With an equimol. mixture of MgPhBr and MgEtBr, 0.8–0.85 mol. of gaseous hydrocarbon per faraday is obtained, indicating the production of Et only. Gas evolution does not occur with an Al anode, but Al is consumed; Al⁺⁺⁺ is probably formed which then reacts with, e.g., 3Et[–] to give AlEt₃. Electrolysis experiments favour the structure R₂Mg·MgX₂ for the Grignard reagent. H. B.

Sulphoacetato-salts of complex hexammine-, pentammine-, and tetrammine-cobaltic salts. J. V. DUBSKY, H. J. BACKER, K. J. KEUNING, and J. TRTILEK (Rec. trav. chim., 1934, 53, 380–386).—Successive treatment of hexamminecobaltic chloride with AgOH and SO₃H·CH₃·CO₂H (I) gives *hexamminecobaltic sulphoacetate*, [Co(NH₃)₆]₂($\text{SO}_3\text{CH}_2\text{CO}_2$), 2H₂O,

orange-yellow; 1 : 6-dinitrotetramminecobaltic chloride similarly affords 1 : 6-dinitrotetramminecobaltic *H* sulphoacetate, [(NH₃)₄Co(NO₂)₂]₂(SO₃·CH₂·CO₂H), ochre, and some 1 : 6-nitroaquotetramminecobaltic sulphoacetate, [(NH₃)₄Co(NO₂)(H₂O)]₂($\text{SO}_3\text{CH}_2\text{CO}_2$), brownish-yellow; octamminediolcobaltic chloride similarly yields diaquotetramminecobaltic sulphoacetate,

[(NH₃)₄Co(H₂O)₂]₂($\text{SO}_3\text{CH}_2\text{CO}_2$) + 2H₂O (violet-red) and +4H₂O (red), and sulphoacetatotetramminecobaltic NH₄ sulphoacetate, pale violet-red,

[(NH₃)₄Co($\text{SO}_3\text{CH}_2\text{CO}_2$)]₂ + 2H₂O; 1 : 2-dichlorodiethylenediaminecobaltic chloride similarly furnishes 1 : 6-dichlorodiethylenediaminecobaltic *H* sulphoacetate, [en₂CoCl₂]₂(SO₃·CH₂·CO₂H), green. Successive treatment of carbonatotetramminecobaltic sulphate with BaCO₃ and (I) gives sulphoacetatotetramminecobaltic *H* sulphoacetate,

[(NH₃)₄Co($\text{SO}_3\text{CH}_2\text{CO}_2$)]₂SO₃·CH₂·CO₂H·2H₂O, pale

violet-red, whilst carbonatotetramminecobaltic carbonate (containing some tetrammine derivative) and (I) afford *aquopentamminecobaltic sulphoacetate*,

[(NH₃)₅Co(H₂O)]($\text{SO}_3\text{CH}_2\text{CO}_2$)SO₃·CH₂·CO₂H + 0.5H₂O, and anhyd., red, which when dried passes into sulphoacetatotetramminecobaltic sulphoacetate,

[(NH₃)₅CoSO₃]($\text{SO}_3\text{CH}_2\text{CO}_2$), pale violet-red.

H. B.

Tricyclohexylmethane series. O. NEUNHOEFFER (Annalen, 1934, 509, 115–130).—Reduction (H₂, PtO₂, Pr^oOH) of CHPh₃ gives *tricyclohexylmethane* (I), b.p. 180°/12 mm., m.p. 61° (cf. A., 1927, 457); *cyclohexyldiphenylmethane*, m.p. 56°, can be isolated as an intermediate. Reduction (H₂, PtO₂, AcOH) of COPh₂ affords 25% of *dicyclohexylmethane* and 75% of *dicyclohexylcarbinol* (II), b.p. 154°/12 mm., m.p. 66° (lit. 56°) (*phenylcarbamate*, m.p. 157°; *H* phthalate, m.p. 136°). (II), also prepared from Mg *cyclohexyl* chloride (III) and HCO₂Me, is oxidised (CrO₃, AcOH) to *dicyclohexyl ketone* (IV), b.p. 138°/13 mm., m.p. 11° (the *oxime*, m.p. 161°, and *semicarbazone*, m.p. 208°, are formed very slowly). The Et and Pr^o esters of hexahydrobenzoic acid with (III) in Et₂O give (IV) (about 70%), some *dicyclohexyl*, and about 7% of *tricyclohexylcarbinol*, m.p. 93° (lit. 81.5°) [*bromide* (V), m.p. 136°, prepared in 65.5% yield using AcBr in Et₂O]. MgPhBr and (IV) afford *dicyclohexylphenylcarbinol*, m.p. 83° [*bromide* (VI), m.p. 127° (decomp.) (lit. 104–105°)]. (V) and quinoline at 150° (short time) and then at room temp. (12 hr.) give *dicyclohexylcyclohexyldienemethane*, b.p. 175°/10 mm., m.p. 52°, whilst (VI) similarly affords *cyclohexylphenylcyclohexyldienemethane*, b.p. 178°/11 mm., m.p. 45°, which is reduced (H₂, PtO₂, EtOH) to *dicyclohexylphenylmethane*, m.p. 36.5°, and thence to (I). When a solution of (V) in C₆H₆ is kept for 1 month, HBr is eliminated and (probably) *dicyclohexyl-Δ¹-cyclohexenylmethane*, m.p. 41°, is produced. Diphenylcyclohexyldienemethane is reduced (H₂, PtO₂, Pr^oOH) to the *-cyclohexylmethane* and thence to (I).

H. B.

Constitution of polymerides of cyclopentadiene. K. ALDER and G. STEIN (Ber., 1934, 67, [B], 373–375).—The method of Pirsch (this vol., 285) is considered inadequate for elucidation of structural and configurative problems in the series of polymeric-homologous *cyclopentadienes*. H. W.

Plant colouring matters. LIX. New oxidation products from α-carotene and physalien. α-Carotene di-iodide. P. KARRER, U. SOLMSEN, and O. WALKER (Helv. Chim. Acta, 1934, 17, 417–419).—Oxidation of α-carotene (di-iodide C₄₀H₅₆I₂, 20 × 10^{–6} g. per diem causes 0.9 g. daily growth) with CrO₃ (= 2 O) gives α-hydroxycarotene, m.p. 183° (absorption max. 502, 471, and 440 mμ in CS₂), and α-carotone C₄₀H₅₆O₅, m.p. 148°, [α]_D²⁵ +341° in C₆H₆. Similar oxidation of physalien (zeaxanthin dipalmitate) gives a diketone *physalienone* (absorption max. 538, 503 mμ in CS₂) (formula suggested) and a tetraketone, not yet isolated. J. W. B.

Carotene. VII. Physical properties of carotenes from different plant sources.—See this vol., 458.

[Light]-sensitivity of aromatic nitro-compounds. N. N. VOROSHCHEV (Helv. Chim. Acta, 1934, 17, 286).—A reply to the priority claim of Steiger (this vol., 63). J. W. B.

Chloro- and bromo-derivatives of diphenyl. F. L. W. VAN ROOSMALEN (Rec. trav. chim., 1934, 53, 359—379).—Diacetylbenzidine and Cl_2 (rapid stream) in boiling AcOH give the NN'- Ac_2 derivative (I), m.p. 350°, of 3:5:3':5'-tetrachlorobenzidine (II), m.p. 226°. (II) is de-aminated (usual method) to 3:5:3':5'-tetrachlorodiphenyl (III), m.p. 162°, also prepared from 3:5:1- $\text{C}_6\text{H}_3\text{Cl}_4\text{I}$ and Cu powder. (III) and abs. HNO_3 at 0° give the 2:2'-(IV), m.p. 172°, and 4:4'-(V), m.p. > 360°, $-(\text{NO}_2)_2$ derivatives. (V) is also prepared from (II) by way of its tetrazonium dinitrate (cf. Korner and Contardi, A., 1917, i, 85). 2:2'-Dinitrobenzidine and Cl_2 in warm dil. HCl afford 3:5:3':5'-tetrachloro-2:2'-dinitrobenzidine, m.p. 251°, also obtained by hydrolysis (conc. H_2SO_4) of its Ac_2 derivative, m.p. 290° [from (I), abs. HNO_3 , and conc. H_2SO_4 at 0°], which is de-aminated to (IV). Short treatment of diacetylbenzidine with Cl_2 (rapid stream) in boiling AcOH gives the Ac_2 derivative of 3:3'-dichlorobenzidine. The latter is converted into 3:4:3':4'-tetrachlorodiphenyl, m.p. 171°, which with abs. HNO_3 at 0° gives the 6:6'-(NO_2)₂-derivative, m.p. 186°. This is reduced (Fe powder, AcOH) to the $(\text{NH}_2)_2$ -derivative, m.p. 167°, which with 15% HCl at 200° affords 2:3:6:7-tetrachlorocarbazole, m.p. 267°. Reduction (Zn dust, aq. EtOH-NaOH) of 3:5- $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$ gives 3:5:3':5'-tetrachloro-azobenzene, m.p. 195°, reduced (Zn dust, AcOH) to the -hydrazobenzene, m.p. 129°; this is converted by conc. H_2SO_4 - H_2O (2:1 by vol.) into 2:6:2':6'-tetrachlorobenzidine (VI), m.p. 212° (Ac_2 derivative, m.p. 312°), which is de-aminated to 2:6:2':6'-tetrachlorodiphenyl, m.p. 198°. 3:5:3':5'-Tetrabromobenzidine (VII) [Ac_2 derivative (VIII), chars at 340°] is de-aminated to 3:5:3':5'-tetrabromodiphenyl, m.p. 186°, nitration of which affords non-homogeneous products. (VII) is converted [as (II)] into 3:5:3':5'-tetrabromo-4:4'-dinitrodiphenyl, m.p. > 360°. 2:2'-Dinitrobenzidine and Br-H₂O in dil. HCl give 3:5:3':5'-tetrabromo-2:2'-dinitrobenzidine, m.p. 272° [Ac_2 derivative, m.p. 266° (slight decomp.), from (VIII), abs. HNO_3 , and conc. H_2SO_4 at 0°—room temp.], de-aminated to a little 3:5:3':5'-tetrabromo-2:2'-dinitrodiphenyl, m.p. 192°, and (largely) a condensation product, m.p. > 300°. 3:4:3':4'-Tetrabromodiphenyl, m.p. 169°, is prepared from 3:3'-dibromobenzidine. 3:4:5:3':4':5'-Hexachloro-, m.p. 198° [2:2'-(NO_2)₂-derivative, m.p. 209°], and -hexabromo-, m.p. 248° [2:2'-(NO_2)₂-derivative, m.p. 287—288°], -diphenyl are obtained (Sandmeyer) from (II) and (VII), respectively. (VI) and Cl_2 in dil. HCl give octachlorobenzidine, m.p. 289°, de-aminated to 2:3:5:6:2':3':5':6'-octachlorodiphenyl, m.p. 161° and converted (Sandmeyer) into decachlorodiphenyl, m.p. 310° (Maquenne block). 2:4:6:2':4':6'-Hexachlorodiphenyl, m.p. 112°, is prepared from (VI). H. B.

Application of electronic theory to organic compounds. IV. Naphthalenemonosulphonic acids. A. M. BERKENHEIM and M. G. TSCHENTSOVA (J. Gen. Chem. Russ., 1933, 3, 933—946; cf. this vol., 176, 289).— $\beta\text{-C}_{10}\text{H}_7\cdot\text{O}\cdot\text{SOCl}$ (I), m.p. 72—75°, obtained from $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (II) and SOCl_2 in Et₂O at 0°, readily decomposes, with elimination of SOCl_2 to afford a product, m.p. 200°, from which $(\text{C}_{10}\text{H}_7)_2\text{SO}_3$ (III) is obtained on dissolving in EtOH and adding H₂O. Attempts at preparing $\beta\text{-C}_{10}\text{H}_7\cdot\text{H}$ sulphite (IV) by hydrolysis of (I) were unsuccessful, the final product being in all cases (III). The salts of (IV) are, however, more stable; thus the Na salt, obtained by shaking an Et₂O solution of (I) with H₂O, and neutralising the aq. layer with NaOH, differs from that of 2- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$ in being readily decomposed by dil. aq. NaOH to yield Na_2SO_3 and (II). An interpretation of the above results from the point of view of the electronic theory leads to the conclusion that the first product of sulphonation of C_{10}H_8 is 1- $\text{C}_{10}\text{H}_7\cdot\text{SO}_3\text{H}$, the SO_3H of which then migrates to the third C atom. During the process of fusion with NaOH the SO_3H undergoes electronic rearrangement, with conversion into the sulphite radical, which again migrates to the second C atom to afford (IV), which is converted as above into (II). R. T.

Metallo-ammino-complexes of nitro-naphthalene- and -benzene-sulphonic acids. N. N. VOROSHCHEV and V. V. KOZLOV (J. Gen. Chem. Russ., 1933, 3, 917—926).—Salts of the type $\text{Cu}(\text{NH}_3)_4\text{R}_2$ and $\text{Ni}(\text{NH}_3)_6\text{R}_2$, where R represents 1:2-, 1:5-, 1:6-, 1:7-, and 1:8- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$, and 1:4- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, are obtained by adding salts of the appropriate metal to aq. NH_3 solutions of the sulphonic acids (I). The above salts are, in contrast to those of 2- $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{H}$, very sparingly sol. in H₂O. Double salts of the type $\text{NH}_4\text{X}\cdot\text{CuR}_2$ are obtained by adding salts of NH_4^+ to solutions of (I) containing CuSO_4 . R. T.

Synthesis of 1-methyl-2-ethyl- and 2-methyl-1-ethyl-naphthalene. O. BRUNNER and F. GROF (Monatsh., 1934, 64, 76—79).— $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ (I) condenses with $\text{CH}(\text{Et})(\text{CO}_2\text{Et})_2$ (Na in PhMe) to give Et β -phenylethylethylmalonate, b.p. 186—187°/11 mm., hydrolysed and decarboxylated to γ -phenyl- α -ethyl-n-butyric acid, b.p. 172—173°/11 mm., cyclised (conc. H_2SO_4 at 100°) to 1-keto-2-ethyl-1:2:3:4-tetrahydro-, b.p. 140—145°/11 mm., converted by MgMeI into 1-methyl-2-ethyl-3:4-dihydro-, b.p. 135—145°/11 mm., dehydrogenated (S) to 1-methyl-2-ethyl-, b.p. 140—145°/11 mm. (picrate, m.p. 97°; styphnate, m.p. 140°), -naphthalene. Similarly with $\text{CHMe}(\text{CO}_2\text{Et})_2$ (I) affords successively the malonic ester, b.p. 175—185°/11 mm., γ -phenyl- α -methyl-n-butyric acid, b.p. 155—165°/11 mm., 1-keto-2-methyl-1:2:3:4-tetrahydro-, b.p. 140—150°/11 mm., and through the H_2 -compound, b.p. 130—140°/11 mm., 2-methyl-1-ethyl-, b.p. 135—145°/11 mm. (picrate, m.p. 110—111°; styphnate, m.p. 141°), -naphthalene. Most b.p. are bath temp. J. W. B.

Synthesis of 6- and 7-methyl-1-ethylnaphthalene. O. BRUNNER and F. GROF (Monatsh., 1934, 64, 28—34).— $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COEt}$ condenses with Zn and $\text{CH}_2\text{Br}\cdot\text{Br}\cdot\text{CO}_2\text{Et}$ to give the OH-ester, converted by PBr_3 and NPhMe_2 into the unsaturated ester, b.p.

153—155°/11 mm., reduced (Na-EtOH) to γ -p-tolyl-n-pentan- α -ol, b.p. 134—136°/11 mm. This is converted through the bromide, b.p. 133°/12 mm., and nitrile into γ -p-tolyl-n-hexoic acid, b.p. 189°/13 mm., the chloride, b.p. 141°/11 mm., of which is cyclised (AlCl₃) to 4-keto-6-methyl-1-ethyl-1:2:3:4-tetrahydronaphthalene, b.p. 159°/11 mm. (semicarbazone, m.p. 156°), reduced (Clemmensen) to the tetrahydro-derivative, b.p. 126°/10 mm., of 6-methyl-1-ethylnaphthalene, b.p. 135—138°/12 mm. (I) (picrate, m.p. 81.5°; styphnate, m.p. 90°), which is obtained by dehydrogenation (S) at 250—280°. Similarly 1-keto-7-methyl-1:2:3:4-tetrahydronaphthalene with MgEtBr affords 7-methyl-1-ethyl-3:4-dihydro-, b.p. 135°/11 mm., dehydrogenated to 7-methyl-1-ethyl-, b.p. 128°/11 mm. (II) (picrate, m.p. 106°; styphnate, m.p. 142—143°), -naphthalene. Neither (I) nor (II) is identical with the hydrocarbon C₁₃H₁₄ obtained by dehydrogenation of amber. J. W. B.

Action of bromine on naphthalene-1-sulphonic acid. J. S. SALKIND, L. VEISBRUT, and M. ALEXEEVA (J. Gen. Chem. Russ., 1933, 3, 892—895).—The products of bromination are 1:5-C₁₀H₆Br·SO₃H, and 1:4- and 1:5-C₁₀H₆Br₂, and not the 1:7-isomeride, as supposed by Forsling (cf. A., 1889, 718). R. T.

α -Sulphonic derivatives of naphthalene. W. M. CUMMING and G. D. MUIR (J. Roy. Tech. Coll., 1934, 3, 223—230).—Naphthionic acid (I) {NH₂Ph + 3H₂O, β - + 3H₂O [converted by distillation into NH(C₁₀H₇ β)₂], and α - + 4H₂O, -naphthylamine salts} heated with excess of NH₂Ph gives only NHPh·C₁₀H₇ α . Diazotisation of (I) (addition of aq. NaNO₂ to dil. HCl suspension at room temp.) followed by a Sandmeyer reaction gives 1:4-C₁₀H₆Cl·SO₃H (anilide, m.p. 143°; o-toluidide, m.p. 151°, p-nitroanilide, m.p. 188°; α -naphthylamide, m.p. 142°; Na + H₂O and K salts), and a modified Gattermann reaction affords a 17% yield of the K salt of 1:4-C₁₀H₆I·SO₃H (amide, m.p. 202°; anilide, m.p. 133°; o-toluidide, m.p. 138°), and 1-C₁₀H₇·SO₃H (II) [anilide, m.p. 152° (lit. 112°); o-toluidide, m.p. 134°; p-nitroanilide, m.p. 205°] is isolated from the mother-liquor. With boiling HI diazotised 1:8-NH₂·C₁₀H₆·SO₃H gives only the 1:8-sultone, and with KI and Cu powder (II) is obtained, but Cu₂Cl₂·HCl gives 1:8-C₁₀H₆Cl·SO₃H. J. W. B.

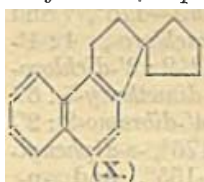
Syntheses of phenanthrene, chrysene, and picene. L. RUZICKA and H. HOSLI, and (in part) A. CASSINA, K. DOLD, H. FRICKER, and F. MOSTERTS (Helv. Chim. Acta, 1934, 17, 470—474).—Mg β -phenylethyl bromide with 1-ketotetrahydronaphthalene (I) gives, after dehydration of the product with 2-C₁₀H₇·SO₃H, 1-(β -phenylethyl)-3:4-dihydronaphthalene, b.p. 165—168°/12 mm., converted by AlCl₃ in CS₂ into chrysene. Similarly Mg β -1-naphthylethyl chloride and (I) give 1-(β -1-naphthylethyl)-3:4-dihydronaphthalene (II), b.p. 225—227°/1 mm., converted by distillation with P₂O₅ into (·CH₂·C₁₀H₇-I)₂ (III). With AlCl₃ (II) or (III) affords picene. Dibenzyl is similarly partly converted into phenanthrene. J. W. B.

Synthesis of compounds related to sterols, bile acids, and oestrus-producing hormones. II. Formation of tetracyclic hydroaromatic hydrocarbons. J. W. COOK and C. L. HEWETT (J.C.S., 1934, 365—377).—The compound previously

described (A., 1933, 1042) as *trans*-1:2-cyclopentano-1:2:3:4-tetrahydrophenanthrene is now considered to be 7:8-dihydrophenalyl-7-spirocyclopentane (I). (I) is oxidised (dil. HNO₃ at 175—180°) to 4-nitrohemimellitic acid (Me ester, m.p. 143—144°), also obtained similarly from 4-nitronaphthalic acid, 1-(β -1'-Naphthylethyl)cyclohexanone (II), b.p. 220°/7 mm., m.p. 60—70° (from cyclohexanone and 1-C₁₀H₇·CH₂·CH₂·MgCl), is dehydrated (KHSO₄ at 160°) to 1-(β -1'-naphthylethyl)- Δ^1 -cyclohexene, b.p. 167—168°/3—4 mm., which is converted by AlCl₃ in CS₂ at 0° into 7:8-dihydrophenalyl-7-spirocyclohexane (III), b.p. 176—177°/5 mm., m.p. 55—56° (picrate, m.p. 141—142°), *cis*(?)-as-octahydrochrysene (IV), m.p. 78—79° (picrate, 2C₁₈H₂₀C₆H₃O₇N₃, m.p. 106—106.5°), and *trans*(?)-as-octahydrochrysene (V), m.p. 114—114.5°. (IV) and (V) are dehydrogenated (Se at 300—310°) to chrysene (VI), whilst (III) and Se at 320—340° give (by ring fission and loss of 2C) some pyrene (VII). (I) is similarly converted into 1-methylpyrene (VIII) and not an indene (cf. *loc. cit.*). The absorption curves of (VII) and (VIII) are very similar. Treatment of (II) with AcOH-conc. H₂SO₄ at 100° and subsequent dehydrogenation (Se at 310—330°) gives (VI) and unchanged (III). The dihydrophenalene of Mayer and Sieglitz (A., 1922, i, 740) could not be prepared from β -1-naphthylpropionyl chloride and AlCl₃; the free acid and anhyd. SnCl₄ at 120° afford 9-phenalene, m.p. 153—154° [which has marked basic properties and is the "pyrene ketone" of Bamberger and Philip (A., 1887, 271)], and a little of a ketone, C₁₃H₁₀O (either 7:8-dihydro-9-phenalene or 4:5-benz-1-hydrindone), m.p. 120—121° [oxime, m.p. 226—227° (slight decomposition)]. 4-Keto-1:2:3:4-tetrahydrophenanthrene, CH₂Br·CO₂Et, and Zn filings (activated with I) in C₆H₆ give [after hydrolysis (MeOH-KOH)] 1:2-dihydrophenanthryl-4-acetic acid, m.p. 173—174°, cyclised by 85% H₂SO₄ at 100° (bath) to 5-keto-1:2:4:5-tetrahydropyrene, m.p. 130—130.5°, which when reduced (Na, amyl alcohol) and then dehydrogenated (Se at 330—340°) affords (VII). The crude carbinol from 1-keto-1:2:3:4-tetrahydronaphthalene and CH₂Ph·CH₂·MgCl is dehydrated (KHSO₄ at 160°) to 1-(β -phenylethyl)-3:4-dihydronaphthalene, b.p. 209—212°/16 mm., which is converted by AlCl₃ in CS₂ at 0° into 1-(β -phenylethyl)naphthalene, b.p. 175°/5 mm. (dipicrate, m.p. 116—117°) (also prepared by Clemmensen reduction of 1-C₁₀H₇·CO·CH₂Ph); cyclisation to hexahydrochrysene does not occur.



The compound C₁₇H₁₂, described by Kon (A., 1933, 1153) as an indene, is now shown to be chrysosfluorene (1:2-benzfluorene) (IX). α -Hydrindone and CH₂Ph·CH₂·MgCl give (after dehydration) 3- β -phenylethylindene, b.p. 186°/9 mm., converted by AlCl₃ in CS₂ at 0° or AcOH-conc. H₂SO₄ at 100° into a little tetrahydrochrysosfluorene, b.p. 176°/8 mm., which is dehydrogenated (Se at 300—340°) to (IX). (IX) is probably formed by rearrangement of the spiran (X), which is considered to be present in the crude mixture of tetra-



cyclic hydrocarbons obtained from 1-(β -1'-naphthylethyl)- Δ^1 -cyclopentene. There is no evidence that dehydrogenation (Se) of a five-membered ring can occur. The 5'-methyl-1:2-cyclopentadienophenanthrene of Kon (*loc. cit.*) is (probably) 1:2-dimethylpyrene.

2- β -Phenylethyl-trans-decahydro- β -naphthol, b.p. 193—194°/5—6 mm., m.p. 54—59°, is dehydrated (KHSO₄ at 170—180°) to 2- β -phenylethyl- $\Delta^{2:3}$ -octahydronaphthalene (XI), b.p. 155°/3—4 mm., converted by AlCl₃ in CS₂ at 0° into dodecahydro-1:2-benzanthracene (XII), m.p. 71—72°, and a mixture of stereoisomerides (A) of (XII). Dehydrogenation (Se at 320—330°) of (XII) gives 1:2-benzanthracene, also formed together with 5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 89—90° (picrate, m.p. 155°) [also prepared by Wolff-Kishner reduction of its 5-CO-derivative (Haworth and Mavin, A., 1933, 1043)], by similar dehydrogenation of (A). C₁₀H₈, CH₂Ph·COCl, and AlCl₃ in CS₂ at 0° give (cf. Gräbe and Bungener, A., 1879, 807) a mixture, m.p. 55—58°, of about 80% of 1-phenylacetyl- (XIII), m.p. 66—67° (picrate, m.p. 99—100°; semicarbazone, m.p. 162—163°), and about 20% of 2-phenylacetylnaphthalene (XIV), m.p. 99—100° [picrate, m.p. 143—144°; semicarbazone (XV), m.p. 203—205°], separable through the picrates. These results show that the conclusion (A., 1931, 1157) that (XIII) is converted into (XIV) by heat is unjustified, since a mixture was used. 2- β -Phenylethyl-naphthalene, m.p. 99—100°, is prepared from (XV) and EtOH-NaOEt at 180—190° or by dehydrogenation (Se) of (XI). The hydrocarbon "C₁₈H₁₆" (A., 1928, 169) is not 1:2-cyclopentenophenanthrene. H. B.

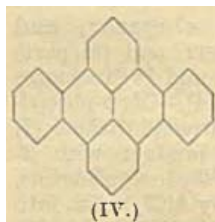
Thiocarbamide formation under different conditions. L. C. RAIFORD and G. M. McNULTY (J. Amer. Chem. Soc., 1934, 56, 680—681).—s-Diarylthiocarbamides (I) could not be obtained from 3-nitro-, 3:5-dichloro-, and 3:4- and 3:5-dibromo-anilines, CS₂, and a little S in EtOH; they can be prepared by Fry's method (A., 1913, i, 1174) (reaction is accelerated by stirring). Satisfactory yields of (I) are usually obtained from NH₂Ar, CS₂, and a little powdered NaOH in EtOH. Snedker's method (J.S.C.I., 1925, 44, 486t) is not generally satisfactory when solid NH₂Ar is used. o- and p-NO₂-derivatives do not give (I) by any method tried. The following are described: 6-acetamido-m-toluidine, m.p. 129—130° (lit. 143°); 2-bromo-, m.p. 129—130°, 3-bromo-, m.p. 210—211°, and 3:5-dibromo-, m.p. 244—245°, 4-acetamidylaniline; 4-chloro-2'-aminodiphenyl, m.p. 52°; 6-bromo-4-methoxy-m-toluidine, m.p. 96° (Ac derivative, m.p. 122—123°, prepared by bromination of 3-acetamido-p-tolyl Me ether); 3:4:3':4', m.p. 100—103°, and 3:5:3':5', m.p. 134—135°, tetrabromo-, 2:4:2':4', m.p. 184—185°, 2:5:2':5', m.p. 175—176°, and 3:5:3':5', m.p. 156—157°, tetrachloro-, 4:4'-dichloro-2:2'-dibromo-, m.p. 206—207°, 2:2'-dichloro-4:4'-dibromo-, m.p. 159—160°, 2:2'-dimethoxy-5:5'-dimethyl-, m.p. 143—144°, and 4:4'-dibromo-2:2'-dimethoxy-5:5'-dimethyl-, m.p. 175—176°, s-diphenylthiocarbamides; s-di-o-, m.p. 154—155°, and -p-, m.p. 230°, -diphenylthiocarbamides: s-di-4'-chloro-o-

m.p. 193—194°, and -p-, m.p. 219—220°, -diphenylthiocarbamides. H. B.

Nitration of ethyl 2:4-dimethyloxanilate. G. TIERIE (Rec. trav. chim., 1934, 53, 355—358).—Et 2:4-dimethyloxanilate (I), m.p. 56° (obtained together with a little ox-m-4-xylylide from approx. equimol. amounts of Et₂C₂O₄ and m-4-xylylene), and HNO₃ (d 1.48) at 0° give the 5:6-(NO₂)₂-derivative, m.p. 172°, hydrolysed (conc. H₂SO₄) to 5:6-dinitro-m-4-xylylene. With HNO₃ (d 1.42) at 0°, Et 6-nitro-2:4-dimethyloxanilate, m.p. 97°, results. (I) and N₂H₄·H₂O in EtOH give 2:4-dimethyloxanilhydrazide, m.p. 160° (benzylidene, m.p. 208°, and isopropylidene, m.p. 140°, derivatives). H. B.

Manufacture of o-aminoarylalkylsulphones, o-aminoarylaralkylsulphones, and azo dyes therefrom.—See B., 1934, 267.

Formation of cyclic compounds from diphenyl derivatives. II. Formation of 4:5:9:10-dibenzopyrene and 4:5-diphenyldiphenylene oxide from 6:6'-diphenyldiphenyl-2:2'-bisdiazonium sulphate. S. SAKO (Bull. Chem. Soc. Japan, 1934, 9, 55—74).—2-Acetamidodiphenyl (easily obtained by use of Ac₂O if AcOH formed is removed) is nitrated by HNO₃ in Ac₂O-AcOH to 3-nitro-2-acetamidodiphenyl (I), m.p. 188—188.5°. From this 3-nitro-2-aminodiphenyl (II), m.p. 44—45°, b.p. 194—196°/6 mm., 2:3-diaminodiphenyl dihydrochloride (red diaminophenazine with FeCl₃), and, using NaOAc and phenanthraquinone, 5-phenyl-2:3-(oo'-diphenylene)quinoxaline, m.p. 221°, are successively obtained. With (I), 5-nitro-2-acetamidodiphenyl (A., 1928, 1367) is formed, hydrolysed and reduced to 2:5-diaminodiphenyl dihydrochloride (violet ppt. with FeCl₃). Diazotised (II) yields (KI) 2-iodo-3-nitrodiphenyl, m.p. 90—91°, b.p. 178°/4 mm., converted (Cu) into 2:2'-dinitro-, m.p. 201—202°, and thence into 2:2'-diamino-6:6'-diphenyldiphenyl (III), m.p. 163—164° (hydrochloride, sulphate); attempts to resolve (III), with a view of showing that lack of optical activity in Ph₂ compounds containing a 2:2':5- or 6-membered ring is not due to racemisation, were unsuccessful. Heating (III) with 2N-HCl at 200° leads to 4:5-diphenylcarbazole, m.p. 145—146°, and diazotisation and decomp. to products varying with temp. The main product at any temp. is 4:5:9:10-dibenzopyrene (IV), m.p. 353—355°. Decomp. at 100°, without Cu, yields in addition 4:5-diphenyldiphenylene oxide, m.p. 154—155°, with some 2:2'-dihydroxy-6:6'-diphenyldiphenyl, m.p. 145—147°. Decomp. of diazotised 6:6'-diamino-2:2'-dimethyldiphenyl yields 6:6'-dihydroxy-2:2'-dimethyldiphenyl, m.p. 161—162.5°. E. W. W.



Preparation of 3:3'-diamino- and -dihydroxyazobenzene and analogous compounds. P. RUGGLI and M. HINOVKER (Helv. Chim. Acta, 1934, 17, 396—412).—The best methods for the prep. and purification of these substances are described. 3:3'-Diaminoazobenzene (I) (Bz₂ derivative, m.p. 247°; lit. 272°) is obtained in 85% yield by electrolytic

reduction of $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (II) with a c.d. of 4.7 amp., for 23.2 amp.-hr. With conc. H_2SO_4 at $50\text{--}80^\circ$ (I) gives mainly 3 : 3'-diamino-4-hydroxyazobenzene (Ac_3 , m.p. 214° , and Bz_3 , m.p. 289° , derivatives) and a brown powder, m.p. 182° . Similar reduction of (II) for 31 amp.-hr. gives 3 : 3'-diaminoazobenzene (III) (75% yield), best purified by crystallisation from xylene with addition of PbO_2 which oxidises any hydrazo-compound present. Longer reduction gives a 90% yield of 3 : 3'-diaminohydrazobenzene (IV), m.p. 169° (lit. 153°) (Bz_3 , m.p. 198° , and Ac_1 , m.p. 90° , derivatives). When heated alone or in PhNO_2 or $\text{C}_6\text{H}_5\text{Cl}_3$, (IV) gives (III) and $\text{C}_6\text{H}_4(\text{NH}_2)_2$ which resinifies. With warm 10% HCl followed by rapid cooling (IV) gives its hydrochloride, but when heated, or with conc. H_2SO_4 at $115\text{--}120^\circ$, rearrangement to 2 : 4 : 2' : 4'-tetra-aminodiphenyl occurs. 3 : 3'-Dihydroxyazoxybenzene (Bz_2 , m.p. 175° , and Ac_2 , m.p. 102° , derivatives) is obtained in 65% yield by reduction of $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ with Zn —30% KOH at $< 20^\circ$, a similar reduction at the b.p. giving the corresponding azo-compound [Bz_2 , m.p. 180° (lit., 129°), and Ac_2 , m.p. 144° (lit., 137°), derivatives], which is obtained only in 38% yield by diazotisation of (III). J. W. B.

Rearrangements of phenyl ethers. Course of the reaction in presence of foreign aromatic compounds. R. A. SMITH (J. Amer. Chem. Soc., 1934, 56, 717—718).— PhOPr^β is converted by AlCl_3 at room temp. into a mixture (65% yield) of *o*- and *p*- $\text{C}_6\text{H}_4\text{Pr}^\beta\cdot\text{OH}$, $\text{C}_6\text{H}_5\text{Pr}^\beta\cdot\text{OH}$, and a little material of higher b.p.; in presence of an equimol. amount of Ph_2O , a 30% yield of the same products with PhOH (33%) and *o*-, b.p. 263.4° , and *p*-, b.p. 288.9° , -isopropylidiphenyl ethers are formed. *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OPr}^\beta$ and AlCl_3 give 70% of 3-isopropyl-*p*-cresol (I); in presence of C_6H_6 (3 vols.), *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OH}$ (II) and cumene (about 60%) are the main products, whilst in Ph_2O (excess), (I) (8—10%), (II) (50%), and isopropylidiphenyl ether (about 40%) are formed. PhOBu^β and AlCl_3 afford *p*- $\text{C}_6\text{H}_4\text{Bu}^\beta\cdot\text{OH}$ (III); in presence of C_6H_6 (excess), 5—6% of (III) is obtained, whilst 70% is converted into mono- (mainly), di-, and tri-*tert*-.butylbenzene. These rearrangements appear to be inter- and not intra-mol. H. B.

Behaviour of nitrophenols with *p*-toluenesulphonyl chloride. IV. S. S. JOSHI (J. Indian Chem. Soc., 1933, 10, 677—678; cf. A., 1925, i, 134; 1928, 1130).—Iodination of 4 : 6-dinitro-*m*-cresol in presence of HgO gives the 2-*I*-derivative, m.p. 93° , the *p*-toluenesulphonate of which, m.p. $136\text{--}137^\circ$, is converted by NH_3 in EtOH into 2-iodo-4 : 6-dinitro-*m*-toluidine, m.p. 97° , and by NH_2Ph into 2-iodo-4 : 6-dinitro-3-methyldiphenylamine, m.p. $143\text{--}144^\circ$. 3 : 2 : 4- $\text{C}_6\text{H}_3\text{MeClBr}(\text{NO}_2)_2$ is similarly converted by NH_3 into 2-bromo-4 : 6-dinitro-*m*-toluidine, m.p. 80° , and by NH_2Ph and NaOAc into 2-bromo-4 : 6-dinitro-3-methyldiphenylamine, m.p. 128° . 2-Bromo-4 : 6-dinitro-*m*-tolyl *p*-toluenesulphonate has m.p. 141° .

Fluorescence of a new organic substance. S. SCHLIVIC and S. LEBEDEV (Bull. Soc. Chim. Yougoslav., 1933, 4, 133—136).—Carvacrol and malic acid react with conc. H_2SO_4 to yield a yellow, resinous

product, the dil. aq. alkaline solutions of which are colourless, and exhibit an intense blue fluorescence on ultra-violet irradiation. R. T.

Action of sodium ethoxide on phenyl thiocyanate. J. ROSS (J. Amer. Chem. Soc., 1934, 56, 727—729).—The main reaction between PhSCN and $\text{EtOH}\cdot\text{NaOEt}$ is $\text{PhSCN} + \text{NaOEt} \rightarrow \text{PhSNa} + \text{EtOCN}$ [$\rightarrow \text{EtNCO} \rightarrow \text{NHEt}\cdot\text{CO}_2\text{Et}$ (isolable)]; a secondary reaction (20%) gives Ph_2S_2 and PhEtS , probably thus : $\text{PhSCN} + \text{NaOEt} \rightarrow \text{NaCN} + \text{PhS}\cdot\text{OEt}^{2\text{PhSH}}$ (I); $\text{PhS}\cdot\text{OEt} \rightarrow \text{PhEtS}\cdot\text{O} \rightarrow \text{Ph}_2\text{S}_2 + \text{PhEtS} + \text{H}_2\text{O}$. PhSH and $\text{PhEtS}\cdot\text{O}$ in EtOH containing a little NaOEt give Ph_2S_2 and PhEtS ; similarly, PhSH and *Et benzenesulphenate* (I), b.p. $100^\circ/4$ mm. [prepared by Lecher's method (A., 1925, i, 390)], react vigorously to give Ph_2S_2 . PhSH and KCNO in boiling EtOH afford 15% of Ph_2S_2 . PhSCN and EtOH -free NaOEt in Et_2O or C_6H_6 give a quant. yield of Ph_2S_2 . H. B.

Oestrogenic activity of condensed-ring systems.—See this vol., 457.

5-Nitrosopyrocatechol-4-sulphonic acid and derivatives. J. ŽIKA (Coll. Czech. Chem. Comm., 1934, 6, 60—68).—Action of HNO_2 (2 equiv.) on *Na* pyrocatechol-4-sulphonate (cf. A., 1933, 947) gives 5-nitrosopyrocatechol-4-sulphonic acid [as *Na* salt (+ $3\text{H}_2\text{O}$): *K* salt (+ $1\text{H}_2\text{O}$); Me_2 ether [*Na* salt (+ $1\text{H}_2\text{O}$); *K* salt; sulphonyl chloride, m.p. 132° ; amide, m.p. $198\text{--}201^\circ$; anilide]} which is reduced by Sn and HCl to the 5- NH_2 -acid. Reduction of (I) similarly gives 5-aminoveratrole-4-sulphonic acid (cf. J.C.S., 1917, 111, 952). Action of HNO_3 (*d* 1.41) on (I) at 100° gives 4 : 5-dinitroveratrole, m.p. 128° .

H. A. P.

Preparation of di- β -naphthol by oxidising β -naphthol with oxides of metals. I. S. TRAVKIN (Anilinokras. Prom., 1934, 4, 13—17).—2 : 2'-Dihydroxy-1 : 1'-dinaphthyl is obtained in 70% yield by heating $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ (I) during 7 hr. at 260° with $\text{Fe}(\text{OH})_3$ (II), CuO , or MnO_2 , and 92% yield by adding colloidal (II) to boiling aq. solutions of (I). R. T.

Optically active *cis*- and *trans*-1-methylcyclohexan-3-ol. M. GODCHOT and (Mlle.) G. CAUQUIL (Compt. rend., 1934, 198, 663—665).—3-Methylcyclohexanone (I) with Na in moist Et_2O affords only *l*-*trans*-1-methylcyclohexan-3-ol (II), b.p. $76\text{--}77^\circ/16$ mm. (*phenylurethane*, m.p. $117\text{--}117.5^\circ$; *p*-nitrobenzoate, m.p. $45\text{--}45.5^\circ$; *H phthalate*, m.p. $92\text{--}93^\circ$), but with H_2 — Pt gives the *l*-*cis*-form (III), b.p. $67\text{--}68^\circ/16$ mm. (cf. A., 1926, 1032) (*phenylurethane*, m.p. 90° ; *p*-nitrobenzoate, m.p. $78\text{--}79^\circ$; *H phthalate*, an oil), and (I), separated by fractional crystallisation of their *p*-nitrobenzoates. Oxidation ($\text{H}_2\text{SO}_4\text{--K}_2\text{Cr}_2\text{O}_7$) of (II) and (III) affords optically active (I).

J. L. D.

Hydrogenation of optically active compounds over nickel and copper-chromium oxide. E. BOWDEN and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 689—691).—Hydrogenation (H_2 at $150\text{--}200$ atm.; $\text{Cu}\text{--}\text{Cr}$ oxide catalyst; 250° except where stated otherwise) of *Et* α -phenylpropionate, + 22.9° (all rotations are $[\alpha]_D$), gives PhPr^β (33%) and β -phenyl-*n*-propyl alcohol (16%), + 2.5° , whilst a specimen of

+65.1° affords PhPr^β (80%). Similarly, Bu lactate, +4.9°, yields (at 225°) 81% of propane-α-β-diol, 0°; menthyl β-phenylbutyrate, -90.3°, furnishes γ-phenylbutyl alcohol (61–73%), -26° to -31.4°, whilst a specimen, -40.9°, gives γ-phenylbutyl alcohol (33–61%), +12.2° to +15.7°; menthyl α-phenylbutyrate, m.p. 58°, -82°, affords sec.-BuPh (26%), +0.4°, and β-phenylbutyl alcohol (17%), -3.7°; Et α-phenylbutyrate, -6° and -2.3°, yields β-phenylbutyl alcohol (50 and 61%), < -0.5° and -0.1°, respectively, and (in the former case) 24% of sec.-BuPh, 0°; Et α-methylbutyrate, +3.04° and -8.3°, furnishes β-methylbutyl alcohol (80 and 97%), 0° and +1.2°, respectively; Et β-methylvalerate, +1.79°, gives 90% of γ-methylamyl alcohol, +1.8°; Et α-ethylnonoate, b.p. 131°/23 mm., -0.65°, affords 50% of β-ethyl-n-nonyl alcohol, b.p. 126°/19–20 mm., -0.2°; Et δ-phenyl-α-ethylvalerate, b.p. 162–165°/23–25 mm., +0.26°, yields 47% of ε-phenyl-β-ethyl-n-amyl alcohol, b.p. 150–153°/18–20 mm., +0.26°; in the above reductions, varying amounts of ester are recovered and in some cases much racemisation has occurred. Camphor, +46.5°, gives (at 150°) a borneol, m.p. 197°, -9.2°; at 120°, α-isoborneol, m.p. 208–209°, -22.3°. The "menthol" recovered from the hydrogenation of menthyl esters has [α]_D -17° and is an isomeride or mixture of isomerides. Reduction (Raney Ni catalyst at 200°) of β-, -2.4°, and γ-, +14°, -phenylbutyl alcohols affords β-, b.p. 119–121°/18 mm., -1.22°, and γ-, b.p. 130°/18–20 mm., +4.02°, -cyclohexylbutyl alcohol, respectively. dl-α-Ethylnonoic acid, b.p. 117–118°/5–6 mm., and dl-δ-phenyl-α-ethylvaleric acid, b.p. 141–143°/5–6 mm., are prepared by way of C₆H₁₃·CH₂·CET(CO₂Et)₂ and CH₂Ph·CH₂·CH₂·CET(CO₂Et)₂, respectively. H. B.

Marine products. III. Ostreasterol. W. BERGMANN (J. Biol. Chem., 1934, 104, 553–557; cf. this vol., 404).—Hydrogenation (Pd-black-PtO₂) of the acetate (I) of ostreasterol (II) gives ostreastanyl acetate, identical with sitostanyl acetate and giving sitostanol and sitostanone (ostreastanone). (II) is, therefore, C₂₈H₄₈O (lit. C₂₇H₄₄O), isomeric with stigmasterol. (I) gives a Br₄-derivative, m.p. 150.5°, reduced to (I) by Zn and AcOH. R. S. C.

Constitution of œstrin. J. F. DANIELLI (J. Amer. Chem. Soc., 1934, 56, 746–747).—The work of Butenandt *et al.* (A., 1933, 540), in conjunction with the results (*ibid.*, 605) obtained with unimol. films of derivatives of œstrin, proves that the five-membered ring is in the same position as in the sterols.

H. B.

Resolution of trans-cycloheptane-1 : 2-diol. M. GODCHOT and M. MOUSSERON (Compt. rend., 1934, 198, 837–838).—dl-cycloheptane-1 : 2-diol (I) is converted by H₂SO₄ at -5° into its di(H sulphate) the strychnine salt of which (prep. through the Ba salt) is resolved by crystallisation from EtOH at 90° into a more sol. strychnine salt +2.5H₂O, [α]_D²⁰ -33.40°, and a less sol. strychnine salt +2.5H₂O, [α]_D²⁰ -23.50°, the latter giving 1-cycloheptane-1 : 2-diol, b.p. 138–139°/15 mm., [α]_D²⁰ -44.25° (phenylurethane, m.p. 275°). (I) is therefore the trans-diol.

J. W. B.

Configuration of polyalcohols deduced from their effect on the conductivity of boric acid. J. BOESEKEN (Bull. Soc. chim., 1933, [iv], 53, 1334–1357).—A lecture.

Decarboxylation of 1-phenylcycloparaffin-1-carboxylic acids. F. H. CASE (J. Amer. Chem. Soc., 1934, 56, 715–717).—1-Phenyl-cyclopropane-, m.p. 86–87°, -cyclobutane-, m.p. 106–107°, -cyclopentane-, m.p. 158–159° (amide, m.p. 157–158°), and -cyclohexane-, m.p. 121° (amide, m.p. 95–96°), -1-carboxylic acids are prepared in 14.5–46% yield from CHNaPh·CN and (CH₂)_nBr₂ in Et₂O and subsequent hydrolysis (EtOH-KOH). 2-Phenyl-hydrindene-2-carboxylic acid, m.p. 194–195°, is similarly obtained in 8% yield from o-C₆H₄(CH₂Br)₂. 1-Phenylcycloheptane-1-carboxylic acid could not be prepared by this method. Phenyl-cyclopropane (I), b.p. 79–80°/37 mm., 171°/771 mm., -cyclobutane, b.p. 101–102°/41 mm., 190–191°/755 mm., -cyclopentane, b.p. 116–117°/37 mm., 216°/755 mm., and -cyclohexane, b.p. 127–128°/30 mm., 238°/759 mm., are obtained when the appropriate Ba salt (1 mol.) is heated with dry NaOMe (3 mols.) at 40 mm.; ketones are removed by fractionation. The unsaturated material accompanying (I) is removed with 1% KMnO₄ at 0°. H. B.

Crystalline forms of N-substituted 3-nitrophthalimides. P. P. T. SAH and T. S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 147–149).—Photographs of the N-substituted 3-nitrophthalimides previously described are reproduced (A., 1932, 1231).

F. R. S.

Preparation of γ-p-aminophenylbutyric and ε-p-aminophenylhexoic acids. J. VAN DER SCHEER (J. Amer. Chem. Soc., 1934, 56, 744–745).—γ-Phenylbutyric acid and HNO₃ (d 1.42) at 20–25° give the p-NO₂-derivative (I), m.p. 92–93°, reduced (Zn dust, N-HCl) to γ-p-aminophenylbutyric acid, m.p. 130–131°. ε-Phenylhexoic acid, b.p. 192–196°/20–22 mm. (lit. 180–190°/17 mm.), prepared by way of Et δ-phenylbutylmalonate, b.p. 212–215°/20–22 mm., similarly gives p-NO₂- (II), m.p. 64–65°, and p-NH₂-derivatives, m.p. 108–109°. (I) and (II) are oxidised (dil. HNO₃ at 200°) to p-NO₂·C₆H₄·CO₂H. H. B.

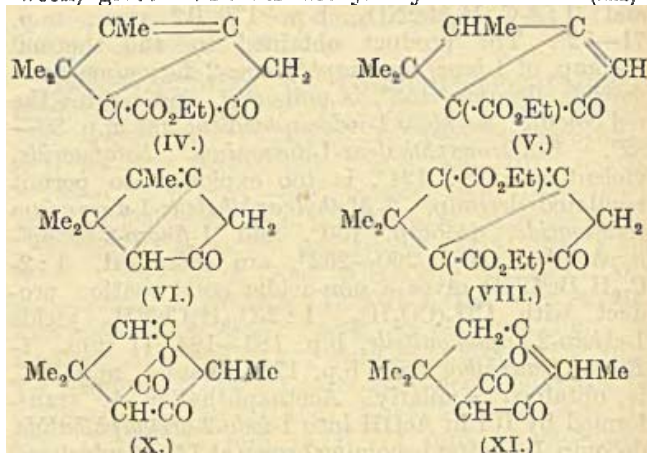
ortho-Effects. II. Naphthalene series. H. WILLSTAEDT and G. SCHEIBER (Ber., 1934, 67, [B], 466–474; cf. A., 1932, 55).—Condensation of CH₂(CO₂H)₂ with α- and β-C₁₀H₇·CHO in AcOH at 100° leads to 1- (I), m.p. 214–215°, and 2-, m.p. 193° after incipient decomp. at 184°, -naphthylidene-malonic acids, respectively. (I) is converted into β-1-naphthylacrylic acid (II), m.p. 129–130°, which adds Br in CHCl₃ at about the same rate as does o-C₆H₄F·CH·CH·CO₂H with production of αβ-dibromo-β-1-naphthylpropionic acid, m.p. 189° (decomp.). The following observations were made during attempts to prepare (II) with substituents at 2 or 8. 1 : 2-NO₂·C₁₀H₆·NH₂ (III) is diazotised and converted through the diazonium borofluoride, decomp. 181°, into 2-fluoro-1-nitronaphthalene, b.p. 120–124°/12–15 mm., m.p. 49–50°. (III) is diazotised and transformed by KI into 2 : 1-C₁₀H₆I·NO₂, b.p. 172.5°/

Reactions of γ -ketonic acids. I. Ketonic β -lactones. E. P. KOHLER and R. H. KIMBALL (*J. Amer. Chem. Soc.*, 1934, **56**, 729—731).— β -Bromo- β -benzoyl- α -phenylpropionic acid (I) (less fusible form ;

A., 1927, 262) and cold 1% NaHCO_3 give β -benzoyl- α -phenyl- β -propiolactone (II) (about 90%), m.p. 95° , a β -hydroxy- β -benzoyl- α -phenylpropionic acid (III), m.p. 132° [*Me* ester, m.p. 89° , using CH_3N ; also obtained from (II) and $\text{MeOH-H}_2\text{SO}_4$], and an isomeric β -OH-acid (*loc. cit.*). (II) is converted by 50% HBr and MeOH-40\% HBr into (I) and the *Me* ester [also obtained from (III) and MeOH-HBr] of (I), respectively. (II) in Et_2O and aq. 5% NaOH give $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{COPh}$ (IV), benzyl α -hydroxybenzyl ketone (phenylacetylphenylcarbinol), m.p. 115° [also prepared by hydrolysis (H_2O) of $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CHPhBr}$], *Ph* α -hydroxy- β -phenylethyl ketone (benzoylbenzylcarbinol), m.p. 66° [also obtained by hydrolysis (aq. NaHCO_3) of *Ph* α -bromo- β -phenylethyl ketone, m.p. $56\text{--}57^\circ$ (from $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COPh}$ and Br in Et_2O)], and α -hydroxy- α - β -diphenylpropionic acid [from (IV) by the "benzilic acid" change]; the mechanism of formation of these compounds is discussed. (I) and $\text{C}_5\text{H}_5\text{N}$ give *cis*- β -benzoyl- α -phenylacrylic acid (V). Extraction of (I) from Et_2O with dil. aq. $\text{C}_5\text{H}_5\text{N}$ affords a $\text{C}_5\text{H}_5\text{N}$ salt, $\text{C}_{21}\text{H}_{18}\text{O}_3\text{NBr}$, m.p. 135° (decomp.). (II) is polymerised by traces of $\text{C}_5\text{H}_5\text{N}$ (or KOAc) in MeOH or COMe_2 ; the polymeride (mixture) and (II) are converted by $\text{C}_5\text{H}_5\text{N}$ into (V). H. B.

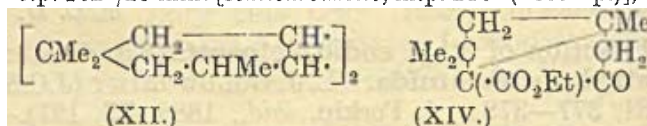
Bridge formation. III. Influence of the methyl and carbethoxy-groups in the internal dehydration of gem-disubstituted dihydroresorcinol esters. IV. Tautomerism of isophorone. P. S. MAYURANATHAN (J. Indian Inst. Sci., 1933, 16A, 113—122, 123—127; cf. A., 1933, 503).—III. Presence of a third *Me* group facilitates dehydration of dihydroresorcinol derivatives; this occurs most readily with the di- but also with the mono-carbethoxy-derivatives, but neither substituent is essential. Reversible wandering of a *Me* group during dehydration is considered improbable. *Et* 1:1-dimethylcyclohexane-3:5-dione-2-carboxylate (A) with cold 25% KOH-EtOH or 60% H_2SO_4 gives a small amount of the ketone (I), m.p. 176° (*loc. cit.*), a trace of which is also obtained from dimethyldihydroresorcinol and P_2O_5 in xylene at $100\text{--}120^\circ$. *Et* sodiomethylacetoacetate condenses with *Et*, isopropylidenemalonate in hot EtOH with loss of a CO_2Et group to form *Et* 1:1:2-trimethylcyclohexane-3:5-dione-6-carboxylate (II), b.p. $187^\circ/21\text{ mm.}$ [disemicarbazone, m.p. 225° (decomp.)], also obtained from methylmesityl oxide and $\text{CH}_2(\text{CO}_2\text{Et})_2$. (II) with hot, conc. aq. Ba(OH)_2 gives 1:1:2-trimethyldihydroresorcinol (III); with cold 20% KOH-EtOH (2 days) or 50% H_2SO_4 it affords the ester (IV), or, less probably, (V), b.p. $145\text{--}147^\circ/20\text{ mm.}$ [semicarbazone, m.p. 205° (decomp.)], which gives (III) with hot Ba(OH)_2 , but with cold 20% KOH-EtOH after 1 week the ketone (VI), b.p. $105^\circ/20\text{ mm.}$ (semicarbazone, m.p. 186°), is obtained. With hot 10% KOH-EtOH (VI) gives (III). *Et* 1:1-dimethylcyclohexane-3:5-dione-2:6-dicarboxylate (VII) and cold 20% KOH-EtOH (2 days) or 50% H_2SO_4 give the ester (VIII), b.p. $195^\circ/20\text{ mm.}$ [semicarbazone, m.p. 232° (decomp.)], hydrolysed to (I) by hot 60% H_2SO_4 . The *N*-derivative of (A) or (VII) with *MeI* yields 1:1:4-trimethylcyclohexane-3:5-dione-2-carboxylate, m.p. 108° , b.p. $165^\circ/5\text{ mm.}$ [disemicarbazone, m.p. 236°

(decomp.)], which with cold 20% KOH-EtOH (1 week) gives 1:1:4-trimethyldihydroresorcinol (IX)



and with hot or cold 60% H_2SO_4 affords the lactone (X) or (XI), $+0.5\text{H}_2\text{O}$, m.p. 79° [semicarbazone, m.p. 188° (decomp.)], hydrolysed to (IX) by hot 10% KOH-EtOH .

IV. Clemmensen reduction of isophorone gives a small amount of hydrocarbon, $\text{C}_{18}\text{H}_{32}$, b.p. $102^\circ/5\text{ mm.}$, which does not give caronic acid on oxidation and is thus probably (XII). Mesityl oxide (XIII) and *Et* sodioacetoacetate in EtOH at 0° give the ester (XIV), b.p. $162^\circ/20\text{ mm.}$ [semicarbazone, m.p. 218° (decomp.)],



or, if heated, isophorone. (XIV) with NaOEt and MeI at 100° give *Et* 1:1:2:5-tetramethyl- Δ^4 -cyclohexen-3-one-2-carboxylate (XV), b.p. $175^\circ/20\text{ mm.}$ [semicarbazone, m.p. 235° (decomp.)]. (XIII) and *Et* sodiomethylacetoacetate in EtOH give *Et* 5-hydroxy-1:1:2:5-tetramethylcyclohexan-3-one-2-carboxylate, b.p. $196^\circ/20\text{ mm.}$, some 1:1:2:5-tetramethyl- Δ^4 -cyclohexen-3-one, b.p. $143^\circ/20\text{ mm.}$, and (XV).

R. S. C.

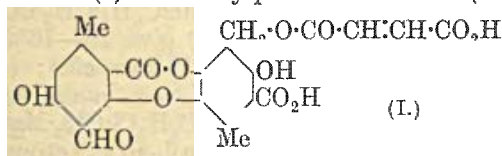
4:5-Dimethoxy-2-benzoylbenzoic acid and its derivatives. A. OLIVERIO (Gazzetta, 1934, 64, 139—148).—*m*-Hemipinic acid reacts with C_6H_5 (AlCl_3) to give 4:5-dimethoxy-2-benzoylbenzoic acid (I), m.p. $199\text{--}200^\circ$ (*Me* ester, m.p. $110\text{--}111^\circ$), together with the partly demethylated 4(or 5)-hydroxy-5(or 4)-methoxy-2-benzoylbenzoic acid. (I) reacts with $\text{NHPh}\cdot\text{NH}_2$, giving a compound, m.p. 212° , and is reduced by Zn-NaOH to 5:6-dimethoxy-3-phenylphthalide, m.p. $156\text{--}157^\circ$, and by Zn-AcOH to 4:5-dimethoxy-2-benzoylbenzoic acid (II), m.p. 217° . In H_2SO_4 (II) condenses to 2:3-dimethoxy-9-anthrone (III), m.p. $135\text{--}137^\circ$ (*Ac* derivative, m.p. 174°), whilst with glycerol and H_2SO_4 (III) yields 2:3-dimethoxy-1:10-benz-9-anthrone, m.p. $276\text{--}277^\circ$; (III) is also obtained by reduction of 2:3-dimethoxyanthraquinone. $\alpha\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$ and veratrole combine to form 2-3':4'-dimethoxybenzoylbenzoic acid (IV) (*Me* ester, m.p. $109\text{--}110^\circ$; $\text{NHPh}\cdot\text{NH}_2$ derivative, new m.p. $197\text{--}197.5^\circ$). Reduction of (IV) by Zn-NaOH yields 3-3':4'-dimethoxyphenylphthalide (A., 1920, i, 437) (5'-*Br*-derivative, m.p. 122°), whilst the

product of reduction by Al-Hg in aq. NH_3 or by Zn-Cu in NaOH is 2:3':4'-dimethoxybenzylbenzoic acid, m.p. 118° (Me ester, b.p. $235^\circ/15$ mm.), which is converted by H_2SO_4 into (III). E. W. W.

Structure of ethyl dibenzhydrylmalonate. A. C. COPE (J. Amer. Chem. Soc., 1934, 56, 721—725).—Et dibenzhydrylmalonate (I), dimorphous, m.p. $136\text{—}136.5^\circ$ (lit. 132°) and $176\text{—}177^\circ$ (stable), is prepared by Kohler's method (A., 1905, i, 700) and from the Na enolate of $\text{CHPh}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ and CHPh_2Br in C_6H_6 . Et *p*-methylbenzylidenemalonate (II), m.p. $50\text{—}51^\circ$ (lit. $46\text{—}47^\circ$), and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ (III) in Et_2O give Et 4:4'-dimethylbenzhydrylmalonate (IV), b.p. $192\text{—}196^\circ/1$ mm., m.p. $71\text{—}71.5^\circ$ [free acid, m.p. 184° (decomp.)], undergoes thermal decomp. to $\beta\beta$ -di-*p*-tolylpropionic acid, m.p. $187\text{—}188^\circ$, the Na enolate of which with 4:4'-dimethylbenzhydryl chloride (V) in C_6H_6 affords Et di-(4:4'-dimethylbenzhydryl)malonate (VI), m.p. $148\text{—}149^\circ$, also obtained by the successive action of (III) and (V) on (II). Successive treatment of $\text{CHPh}_2\text{C}(\text{CO}_2\text{Et})_2$ (VII) with MgPhBr and (V) gives Et 4:4'-dimethyldibenzhydrylmalonate (VIII), m.p. $122\text{—}123^\circ$, also prepared from the Na enolate of $\text{CHPh}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ and (V) in C_6H_6 . The successive action of (III) and CHPh_2Br on (II) affords (I) (7%), (VI) (12%), and (VIII) (4%). These methods of prep. of (VIII) indicate that (I) is $\text{CR}_2(\text{CO}_2\text{Et})_2$ and not $\text{CO}_2\text{Et}\cdot\text{CR}:\text{C}(\text{OEt})\cdot\text{OR}$ (Kohler, *loc. cit.*). Hydrolysis of (I) and $\text{CN}\cdot\text{CR}_2\cdot\text{CO}_2\text{Et}$ ($\text{R}=\text{CHPh}_2$) (Kohler and Reimer, *ibid.*, 347) causes scission of a CHPh_2 group. Similar scission is found with (VI) and $\text{CO}_2\text{Et}\cdot\text{C}(\text{CHPh}_2):\text{C}(\text{OEt})\cdot\text{OMgBr}$ [from (VII) and MgPhBr], whereby (VIII) results in 39% yield; no exchange occurs with the corresponding Na enolate. H. B.

Some molybdo- and tungsto-quinates. G. SARTORI (Gazzetta, 1934, 64, 17—20).—K molybdoquininate, $(\text{KC}_7\text{H}_{11}\text{O}_6)_2\text{MoO}_3\cdot 4\text{H}_2\text{O}$ (cf. A., 1914, i, 1124), and the corresponding *K*, *Na*, *Pb*, and *Ba* tungstoquinates are prepared, and their loss of H_2O at 98° and 120° is studied. E. W. W.

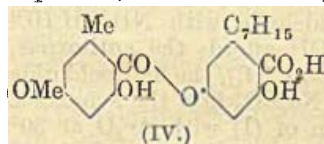
Lichen substances. XXXVI. Fumarprotocetraric acid. Y. ASAHINA and Y. TANASE. XXXVII. Constitution of sphærophorin. Y. ASAHINA and A. HASHIMOTO (Ber., 1934, 67, [B], 411—416, 416—420; cf. A., 1933, 1161).—XXXVI. Marked analogies are traced between fumarprotocetraric acid (I) and acetylprotocetraric acid (II) as a



result of which, combined with fresh analyses, the above constitution is assigned to (I). Extraction of *Cetraria islandica* with COMe_2 affords (I), $\text{C}_{22}\text{H}_{16}\text{O}_{12}$, decomp. $250\text{—}260^\circ$ after darkening at about 230° , which yields an anil, $\text{C}_{22}\text{H}_{16}\text{O}_{11}\cdot\text{NPh}$, decomp. about 250° , and is hydrogenated (Pd-C in AcOH) to hypoprotocetraric acid, m.p. $240\text{—}241^\circ$ (decomp.), and succinic acid. With Ac_2O containing a little conc. H_2SO_4 (I) affords tetra-acetylfumarprotocetraric acid, m.p. 155° (decomp.) after softening at about

130° or $(+3\text{H}_2\text{O})$ m.p. $130\text{—}131^\circ$, hydrogenated (Pd-C) to the H_2 -derivative, m.p. $107\text{—}108^\circ$ (also $+2\text{H}_2\text{O}$), whereas (II) absorbs 3H_2 with formation of hypoprotocetraric acid. Protocetraric acid (—capraric acid from *Parmelia caperata*) and its Ac_1 derivative are transformed by Ac_2O containing conc. H_2SO_4 into penta-acetylprotocetraric acid $(+ \text{H}_2\text{O})$, m.p. $112\text{—}113^\circ$, which does not absorb H (Pd-C), also obtained similarly from cetraric acid (III) and its Me ether. Treatment of (II) with boiling EtOH yields (III).

XXXVII. Extraction of the thalli of *Sphærophorus melanocarpus*, DC, with Et_2O yields (?) fragilin and sphærophorin (IV), $\text{C}_{23}\text{H}_{28}\text{O}_7$ (instead of $\text{C}_{23}\text{H}_{30}\text{O}_8$), m.p. 140° , which does not give a colour with CaOCl_2 and is sol. in NaHCO_3 . (IV) gives a Ac_2 derivative, m.p. $133\text{—}134^\circ$, and a Me_3 compound, m.p. $85\text{—}86^\circ$. (IV) is hydrolysed by KOH-



EtOH to evernic acid, m.p. 170° (decomp.) (Me ester, m.p. 68°), and sphærophorol [5-*n*-heptylresorcinol] (V), m.p. 51° or $(+ \text{H}_2\text{O})$ m.p. $57\text{—}58^\circ$, oxidised by KMnO_4 to *n*-octoic acid (anilide, m.p. $49\text{—}50^\circ$). (V) is obtained synthetically by condensation of Et *n*-decoate with Et acetonedicarboxylate in presence of Na and treatment of the product with KOH at 250° . Extraction of *S. globosus*, Wain, *f. mecophorus*, A. Zahlbr., yields (IV) in 0.025% yield and isosquamatic acid, possibly identical with Zopf's sphærophoric acid. H. W.

Electro-organic oxidations in concentrated aqueous organic salt solutions.—See this vol., 496.

Highly activated carbonyl group. Mesitylglyoxal. A. R. GRAY and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 739—741).—Acetomesitylene is oxidised (SeO_2 , dioxan, little H_2O) to mesitylglyoxal (I), b.p. $105\text{—}106^\circ/4$ mm., $118\text{—}119^\circ/12$ mm. (oxime, m.p. $138.5\text{—}139^\circ$; phenylhydrazone, m.p. $145.5\text{—}146^\circ$; semicarbazone, m.p. $207\text{—}208^\circ$), which contains a highly activated CO group since it forms a stable hydrate (II), m.p. $100\text{—}100.5^\circ$; the keto-group does not react. (II) and 5:5-dimethyldihydroresorcinol in EtOH give a methone, $\text{C}_{27}\text{H}_{24}\text{O}_5$, m.p. $194.5\text{—}195^\circ$. Mesitylglycollic acid, m.p. $152\text{—}153^\circ$, is obtained from (II) and aq. $\text{Ca}(\text{OH})_2$ or KOH. (I) and MgPhBr give 2:4:6-trimethylbenzil, m.p. $136\text{—}137^\circ$ (semicarbazone, m.p. $203\text{—}204^\circ$), which could not be caused to undergo the benzilic acid rearrangement. (I) and 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{MgBr}$ afford 2:4:6:2':4':6'-hexamethylbenzil, m.p. $120\text{—}121^\circ$ (also prepared, together with a compound, $\text{C}_{30}\text{H}_{33}\text{O}_3$, m.p. $231\text{—}232^\circ$, from 2:4:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{COCl}$ and Mg in Et_2O containing a little MgMeI), and $\alpha\beta$ -dihydroxy- $\alpha\beta$ -di-2:4:6-trimethylbenzoylthane (III), m.p. $160.5\text{—}161.5^\circ$ (diacetate, m.p. $185\text{—}185.5^\circ$). (III), also prepared by reduction of (I) with $\text{Mg}+\text{MgI}_2$ in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ (cf. A., 1927, 245), is reduced (red P, I, AcOH) to $\alpha\beta$ -di-2:4:6-trimethylbenzoylthane. (III) is also formed from (I) and MgPr^+Br ; $2\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CHO}+\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CHR}\cdot\text{OMgBr}\rightarrow\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{COR}+\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CH}(\text{OMgBr})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Me}_3$.

H. B.

5-Chloro-3:4-dimethoxybenzylidene-di-amides. R. M. HANN (J. Washington Acad. Sci., 1934, 24, 124—126; cf. A., 1933, 1039).—5-Chlorovanillin in warm NaOH with Me_2SO_4 affords 5-chloro-3:4-dimethoxybenzaldehyde, m.p. 57°, which when heated with NH_2Ac and a little AcOH at 140° during 15 hr. affords 5-chloro-3:4-dimethoxybenzylidenediacetamide, m.p. 244—245°. The following are prepared similarly: 5-chloro-3:4-dimethoxybenzylidenedi-propionamide, m.p. 235°; -n-butyramide, m.p. 204—205°; -n-hexamide, m.p. 172—173°; -benzamide, m.p. 217°.

J. L. D.

Isomeric oximes of ethylvanillin. R. M. HANN (J. Washington Acad. Sci., 1934, 24, 126—128).—3-Methoxy-4-ethoxybenzaldehyde with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and NaHCO_3 in 95% EtOH affords the anti-oxime, m.p. 102° (Ac derivative, m.p. 69°), the hydrochloride of which is converted by Na_2CO_3 into the syn-oxime (I), m.p. 98°. Interaction of (I) with Ac_2O at 30° affords 3-methoxy-4-ethoxybenzonitrile, hydrolysed by NaOH to 3-methoxy-4-ethoxybenzoic acid.

J. L. D.

Condensation of piperonal with hippuric acid. G. LABRUTO and L. IRRERA (Gazzetta, 1934, 64, 136—138).—These substances condense (Ac_2O) to give compounds (I), m.p. 195°, and (II), m.p. 228° (K salt), for which the formulæ $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{C} \begin{smallmatrix} \text{N Bz} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix}$ (I) and $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{NHBz}$ (II) are proposed; (I) adds 2Br to form a compound, m.p. 92°, and (II) is converted by AcCl into (I).

E. W. W.

Acetophenone derivatives.—See this vol., 445.

Synthesis of *p*-iodoacetophenone according to Friedel-Crafts and ω -bromo-*p*-iodoacetophenone. W. KIMURA (Ber., 1934, 67, [B], 394—395; cf. Judefind *et al.*, A., 1920 i, 480).— $p\text{-C}_6\text{H}_4\text{I}\cdot\text{COMe}$ (I) is obtained in 80—95% yield when PhI and AcCl are added immediately to AlCl_3 in CS_2 and the mixture is at once heated to gentle boiling. Addition of Br to (I) in AcOH at $\geq 70^\circ$ gives a nearly theoretical yield of $p\text{-C}_6\text{H}_4\text{I}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$.

H. W.

Organo-magnesium derivative of pentamethylbenzene. H. CLEMENT (Compt. rend., 1934, 198, 665—667).—Interaction of equimol. quantities of C_6BrMe_5 and EtBr in boiling Et_2O with Mg (25% excess) affords Mg pentamethylphenyl bromide (I) in 1.5 hr., converted by CO_2 into pentamethylbenzoic acid. (I) with PhCHO affords pentamethylbenzhydrol, $\text{C}_6\text{Me}_5\cdot\text{CHPh}\cdot\text{OH}$, m.p. 107.5°, and with EtOAc affords pentamethylphenyl Me ketone, m.p. 241.7° (oxime, m.p. 190.6°; semicarbazone, m.p. 241.7°).

J. L. D.

ω -Derivatives of tetrahydronaphthyl methyl ketone. I. RABCEWICZ-ZUBKOWSKI (Rocz. Chem., 1934, 14, 160—164).—1:2:3:4-Tetrahydronaphthalene and $\text{CH}_2\text{Cl}\cdot\text{COCl}$ in CS_2 afford with AlCl_3 6-tetrahydronaphthyl CH_2Cl ketone (I), m.p. 65—66°, which with NaI or NaCNS in boiling EtOH yields the CH_2I (II), m.p. 62.5°, and $\text{CH}_2\cdot\text{CNS}$, m.p. 79.5—80 ketone. 6-Tetrahydronaphthyl Me ketone (III) with Cl_2 yields (I), and with Br the CH_2Br ketone, m.p. 68.5—69°, which yields (II) with NaI. The CHCl_2 ketone, m.p. 42—42.5°, is prepared analogously

from $\text{CHCl}_2\cdot\text{COCl}$, or by chlorinating (III), the CHBr ketone, m.p. 54.5—55°, by brominating (III), and the CHClBr ketone, m.p. 50.5°, from (I) and Br in CS_2 .

R. T.

Reversible addition of aromatic compounds to phenyl styryl ketones. J. T. EATON, D. B. BLACK, and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 687—688).— $\text{C}_6\text{H}_5\text{R}\cdot\text{CH}:\text{CH}\cdot\text{COPh}$ ($\text{R}=\text{o}$ -, *m*-, and *p*-Cl, *m*- and *p*-Br, and *p*-Me), C_6H_6 (saturated with HCl), and AlCl_3 give $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{COPh}$ (I). Ph $\beta\beta$ -di-*p*-chlorophenylethyl ketone (II), m.p. 120—121° [oxidised (KMnO_4 , NaOH, aq. $\text{C}_5\text{H}_5\text{N}$) to $\text{CO}(\text{C}_6\text{H}_4\text{Cl-}p)_2$], is similarly obtained using PhCl and $\text{R}=\text{o}$ - and *p*-Cl and *m*-Br. (II), C_6H_6 , HCl, and AlCl_3 give (I). The results agree with the view (cf. A., 1933, 1170) that addition of aromatic compounds to $\alpha\beta$ -unsaturated CO- (and similarly constituted) compounds is reversible.

H. B.

Use of P_2O_5 in preparation of *p*-benzoyldiphenyl and 4-benzoylacenaphthene. A. C. DE DEGIORGI (Anal. Assoc. Quím. Argentina, 1933, 21, 135—141).—The satisfactory prep. of $\text{C}_{10}\text{H}_7\text{Bz}$ from BzCl and C_{10}H_8 with P_2O_5 as catalyst (A., 1913, i, 1166) is confirmed. *o*-Benzoyldiphenyl is prepared analogously, but more of a by-product, m.p. 86—89°, is obtained than with AlCl_3 . 4-Benzoylacenaphthene is obtained analogously in increased yield. $\text{o-C}_6\text{H}_4\text{Ph}\cdot\text{CO}_2\text{H}$ and SO_2Cl_2 at 70—90° for 2 hr. yield fluorenone; the chloride is obtained only at lower temp.

R. K. C.

Action of phosphorus pentachloride on dimethylmethone. N. J. TOIVONEN and A. KAYSER (Suomen Kem., 1934, 7, B, 79—80).—Interaction of 2:2:5:5-tetramethylcyclohexane-1:3-dione [dimethylmethone] (I) with warm PCl_5 (2 mols.) during 30 hr. affords 4-chloro-2:2:5:5-tetramethylcyclohexane-1:3-dione, m.p. 129°, converted into (I) by Zn in AcOH, and into an acid, $\text{C}_{10}\text{H}_{16}\text{O}_3$, m.p. 87—89°, with aq. NaOH. (I) with excess of PCl_5 also affords a Cl_2 -derivative, m.p. 142—144°. (I) (1 mol.) with Br (2 mols.) in AcOH affords a compound, $\text{C}_{10}\text{H}_{14}\text{O}_2\text{Br}_2$, m.p. 145°.

J. L. D.

Grignard reaction in synthesis of ketones. IV. Preparation of unsymmetrical benzoin. S. S. JENKINS (J. Amer. Chem. Soc., 1934, 56, 682—684).—Ph *p*-methoxybenzyl ketone, m.p. 96.5° (all m.p. are corr.) (A., 1932, 516) is obtained in 30% yield from MgPhBr and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$. Anisamide and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ (I) give 70—76% yield of anisyl benzyl ketone, m.p. 77° (*loc. cit.*); (I) and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ afford 77% of *p*-chlorophenyl benzyl ketone, m.p. 107.5°; $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{MgCl}$ and NH_2Bz yield 70% of Ph *p*-chlorobenzyl ketone, m.p. 138°. These are brominated in CCl_4 and intense light to the α -Br-derivatives, m.p. 93—94°, 72.5—73.5°, 67.5—68.5°, and 62—62.5°, respectively, which are converted by EtOH-NaOEt and subsequent hydrolysis (cold dil. HCl) into benzoylanisyl-, m.p. 90°, anisoylphenyl-, m.p. 106.5°, *p*-chlorobenzoylphenyl- (II), m.p. 90—91°, and benzoyl-*p*-chlorophenyl- (III), m.p. 116—117°, -carbinol, respectively. For the prep. of these benzoin, the intermediate Br-derivatives need not be isolated. (II) is also prepared

from mandelamide and p -C₆H₄Cl-MgBr, whilst (III) is obtained from MgPhBr and p -chloromandelamide.

H. B.

Action of organo-magnesium derivatives on ω -cyanoacetophenone. A. MAVRODIN (Bul. Soc. Chim. Romania, 1933, 15, 99—106).—CN·CH₂·COPh (I) and an excess of MgEtI in Et₂O or, better, PhMe give benzoylpropionylmethane, b.p. 276—277°, hydrolysed (aq. 25% KOH) to COMeEt, COPhMe, BzOH, and EtCO₂H; the following reactions probably occur: (I)+MgEtI \rightarrow C₆H₅+CN·CH·CPh·OMgI \rightarrow IMg·N·CEt·CH·CPh·OMgI \rightarrow COEt·CH·CPh·OH \rightarrow COEt·CH₂·COPh. Similarly, (I) and MgPhBr afford CH₂Bz₂.

H. B.

Isomerisation of 2 : 2-disubstituted derivatives of indandione. G. GHEORGHIU (Compt. rend., 1934, 198, 755—758).—Me and Et 2-methylindan-1 : 3-dione-2-acetate with Na alkoxide undergo transformation into naphthalene derivatives less readily than the 2-Ph derivative (cf. A., 1927, 243). 2-Phenyl- and less readily 2-methyl-2-acetylindan-1 : 3-dione and 2-phenyl- (I) (but not -methyl-) -2-allylindan-1 : 3-dione give C₁₀H₈ derivatives. That from (I) is an oil and from the Me compounds definite products cannot be isolated. 2-Phenyl-2-benzylindan-1 : 3-dione gives α -carboxyphenyl $\alpha\beta$ -diphenyl-ethyl ketone.

R. S. C.

Tautomerism of p -benzoquinoneoxime- p -nitrosophenol systems. L. C. ANDERSON and R. L. YANKE (J. Amer. Chem. Soc., 1934, 56, 732—735; cf. A., 1932, 1026).—Absorption spectra indicate that the equilibrium mixture of p -benzoquinoneoxime (I) and p -NO·C₆H₄·OH in dioxan, CHCl₃, EtOH, and aq. acid consists mainly of (I). The curve for 3-chloro- p -benzoquinone-4-oxime (II) is very similar to that of its Me ether, but the curve for 3-chloro-4-nitrosophenol (III) differs from that of its Me ether and (II); the difference is not due to ionisation or association of (III). The spectrum of 2-chloro-4-nitrosophenol (Hodgson, A., 1932, 509) resembles those of the quinoneoxime Me ethers rather than the nitrosoanisoles. Absorption of alkaline solutions of the quinoneoximes is independent of the metal hydroxide used and is due to a highly ionised form (probably the ion of the quinonoid form). The absorption spectra are independent of [H⁺] at p_H < 3 and > 7, but are very sensitive to changes between p_H 3 and 7.

H. B.

Optical method for the study of reversible organic oxidation-reduction systems. II. Halogenated benzoquinones. III. Preparation and use of a new optically active standard. D. E. KVALNES (J. Amer. Chem. Soc., 1934, 56, 667—670, 670—672).—II. The relative oxidation potentials of the following halogenbenzoquinones, determined polarimetrically in C₆H₆ using d -camphor-10-sulphonyl-2 : 5-dimethylquinol (cf. A., 1932, 947), are: benzoquinone, 0.711 volt (assigned arbitrarily); chloro-, 0.734; bromo-, 0.737; iodo-, 0.737; 2 : 3-, 0.750, 2 : 5-, 0.746, and 2 : 6-, 0.740, -dichloro-, 2 : 5-, 0.768, and 2 : 6-, 0.744, -dibromo-, 2 : 6-di-iodo-, 0.746; trichloro-, 0.755; tribromo-, 0.763; tetrachloro-, 0.742; tetrabromo-, 0.746. The vals. are compared

with those determined electrometrically in aq. and EtOH-solution.

3-Iodo-4- p -sulphobenzeneazophenol is reduced (Na₂S₂O₄) to 3-iodo-4-aminophenol, m.p. 140° (char- ring; darkens at 135°), oxidised (Na₂Cr₂O₇, 25% H₂SO₄) to iodobenzoquinone, m.p. 62°. This is reduced (SnCl₂) to iodoquinol, m.p. 115—116° (diacetate, m.p. 86—87°).

III. Reduction (SnCl₂, HCl) of the product from α -naphthaquinone and d -camphor-10-sulphinic acid (from Zn salt) gives d -camphor-10-sulphonyl- α -naphthaquinol (I), m.p. 159—160°, [α]_D²⁵ +44.7° in C₆H₆, oxidised (FeCl₃, EtOH) to the α -naphthaquinone (II), m.p. 131°, [α]_D²⁵ +355° in C₆H₆ (cf. loc. cit.). p -Toluenesulphonyl- α -naphthaquinol, m.p. 181°, and -quinone, m.p. 172—173°, and p -bromobenzenesulphonyl- α -naphthaquinol, m.p. 221—222° (decomp.), and -quinone, m.p. 175—176°, are similarly prepared.

The relative oxidation potentials of 17 quinones are determined polarimetrically in C₆H₆ using the system (I)–(II). Introduction of Me into benzoquinone causes a marked decrease in potential; a second Me (position of no importance) has not quite such a pronounced effect. The decrease due to one OMe is > twice that due to a second. The effect of the following groups in decreasing the potential is OH OMe > Me > OPh. Increase in size of the alkyl group has little effect.

H. B.

Action of alkali on dibromodianilinobenzoquinone. M. M. SPRUNG (J. Amer. Chem. Soc., 1934, 56, 691—693).—3 : 6-Dibromo-2 : 5-dianilino- p -benzoquinone, m.p. 261° (decomp.) (from bromanil or 3 : 6-dibromo-2 : 5-diphenoxy- p -benzoquinone and EtOH-NH₂Ph), with aq. EtOH-NaOH gives NH₂Ph, 2 : 5-dianilino-3 : 6-dihydroxy- p -benzoquinone (I), m.p. 206—207° (decomp.), and the anil (II), m.p. 139—141° (decomp.), of (I). (II) is hydrolysed (2N-HCl) to (I) and is prepared from (I) and NH₂Ph in aq. NaOH.

H. B.

Application of electronic theory to organic compounds. V. Anthraquinonedisulphonic acids. A. M. BERKENHEIM and L. G. TSCHENTSOVA (J. Gen. Chem. Russ., 1933, 3, 947—957; cf. this vol., 518).—In anthraquinone-2 : 6-disulphonic acid one SO₃H is attached to a negative, and one to a positive, C atom; the latter group should therefore be a sulphite one, and should, on reduction, be replaceable by H. This postulate was realised experimentally by reduction with 2% Na-Hg at 0°, when 50% yields of anthraquinone-2-sulphonic acid were obtained.

R. T.

Preparation of 1 : 4-di- p -toluidinoanthraquinone. M. GALLOTTI (Annali Chim. Appl., 1934, 24, 32—34).—Quinizarin is reduced in alkaline solution with Na₂S₂O₄ and, without being separated, the leucoquinizarin is condensed with p -C₆H₄Me·NH₂ in presence of H₃BO₃ to give an almost theoretical yield of di- (free from mono-) p -toluidinoanthraquinone, yielding Alizarin Brilliant Green G on sulphonation. The dye obtained is free from 1-hydroxy-4- p -toluidinoanthraquinone- m -sulphonic acid (Alizarin Irisol), which, even in small proportion, lowers the brilliancy.

T. H. P.

Anthracene derivatives.—See B., 1934, 355.

1-Nitroanthraquinone-2-carboxyl chloride and its reaction with cholesterol. P. P. T. SAN and T. S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 143—145).—1-Nitroanthraquinone-2-carboxyl chloride, m.p. 243—244°, with cholesterol gives cholesteryl 1-nitroanthraquinone-2-carboxylate, m.p. 227—229°.

F. R. S.

Atractyligenin. III. Functions of oxygen atoms. T. AJELLO (Gazzetta, 1934, 64, 59—65; cf. A., 1933, 612, 829).—Atractyligenin, $C_{14}H_{22}O_4$, m.p. 168°, $[\alpha]_D^{20}$ —143°, the product of alkaline hydrolysis of K attractylate (*loc. cit.*), is a dihydroxymonocarboxylic acid, which combines with $PhNCO$ to form the compound $C_{14}H_{20}O_4(CO \cdot NPh)_2$, and has no ethylenic linkings.

E. W. W.

Asteric acid.—See this vol., 544.

Chlorinated derivatives of cineole. II. A. GANDINI (Gazzetta, 1934, 64, 118—135).—When cineole is treated as before (A., 1933, 830), but with $2Cl_2$, the products include 3-chlorocineole, b.p. 110—112°/50 mm., oxidised by $KMnO_4$ to cineolic acid; 2-chlorocineole (*loc. cit.*), b.p. 126°/50 mm., 2:3-dichlorocineole, b.p. 109—110°/3 mm., also oxidised to cineolic acid; 2:6-dichlorocineole, b.p. 126—127°/3 mm., oxidised to terpenylic, terebic, and teracemic acids; and 2:3:6(?)-trichlorocineole, b.p. 143°/3 mm. The action of Na and of KOH on these compounds is described.

E. W. W.

Piperitone. XII. Two varieties of piperitol. J. READ and J. WALKER (J.C.S., 1934, 308—313).—*d*-Neopiperitol, formed from *l*-piperityltrimethylammonium iodide and Ag_2O , has $[\alpha]_D^{20}$ +50.8° in EtOH, and on keeping for a short time eliminates H_2O giving *d*- α -phellandrene: it has probably the *trans*-H configuration. Reduction of *l*-piperitone with Pr^iOH and $Al(OPr^i)_3$ affords *l*-piperitol, b.p. 98.5—100.5°/13 mm., $[\alpha]_D^{20}$ —24.5° in EtOH (3:5-dinitrobenzoate, m.p. 84—85°, $[\alpha]_D^{20}$ —30° in $CHCl_3$), which is stable. Piperitylamine contains a stable substance, $C_{10}H_{21}ON$, m.p. 89—90.5°, $[\alpha]_D^{20}$ +7.24° in $CHCl_3$. In an attempt to purify crude *d*-piperitylamine, the *Ac*, m.p. 101—102°, $[\alpha]_D^{20}$ +159° in $CHCl_3$, *Bz*, m.p. 102—103°, $[\alpha]_D^{20}$ +175°, and *p*-dimethylaminobenzylidene derivatives, m.p. 127—128.5°, $[\alpha]_D^{20}$ +1°, have been prepared. *l*-Piperitylamine is methylated to the *N*-Me compound, b.p. 95—99°/16 mm., $[\alpha]_D^{20}$ —355°, and is hydrogenated to a mixture of *l*-iso- and *l*-menthylamine, indicating *cis*-H configuration. *l*-Piperitone and NH_3 form the piperitoneimine, b.p. 105°/10 mm., which on reduction passes into a mixture of menthylamines, and the ketone and NH_2Me yield piperitonemethylamine, b.p. 103.5—105°/13 mm., reduced to *N*-methylmenthylamine, b.p. 96.5—98°/16.5 mm.

F. R. S.

Menthone series. XII. Isolation and characterisation of the neoisomenthols. J. READ and W. J. GRUBB (J.C.S., 1934, 313—317).—By reduction of *dl*-isomenthone with Pr^iOH and $Al(OPr^i)_3$ and esterification with 0.5 mol. of *p*- $NO_2 \cdot C_6H_4 \cdot COCl$, *dl*-neoisomenthol, m.p. 14°, b.p. 81°/6 mm. (*p*-nitrobenzoate, m.p. 63—64°), purified through the 3:5-dinitrobenzoate, m.p. 13.73.5°, has been obtained. Hydrogenation of *l*-piperitone and purification by successive

treatment with phthalic anhydride and H_3PO_4 gives *d*-neoisomentholphosphoric acid, decomposed to *d*-neoisomenthol, b.p. 84.2°/7.5 mm., m.p. —8°, $[\alpha]_D^{20}$ +2.2° in EtOH (*p*-nitrobenzoate, m.p. 72.5—73°, $[\alpha]_D^{20}$ —5.3° in $CHCl_3$); 3:5-dinitrobenzoate, m.p. 100.5—101°, —9.5° in $CHCl_3$; *d*-, m.p. 69—70°, $[\alpha]_D^{20}$ +17.3° in $CHCl_3$, and 1-camphor-10-sulphonate, m.p. 84—86°, $[\alpha]_D^{20}$ —41° in $CHCl_3$; *d*-, $[\alpha]_D^{20}$ +43.6°, and 1-menthoxyacetate, $[\alpha]_D^{20}$ —71.6°).

F. R. S.

Phosphoric acid compounds of menthols and other alcohols. J. W. BLAGDEN and W. E. HUGGETT (J.C.S., 1934, 317—318).—With H_3PO_4 menthols form cryst. derivatives $3C_{10}H_{20}O \cdot H_3PO_4$, used in separating and purifying the stereoisomeric menthols. The process is possible with nearly all terpene and hydroaromatic alcohols and with some aliphatic alcohols.

F. R. S.

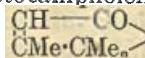
Rearrangement of acetylenic carbinols. *d*-isoMenthone and *l*-menthone. H. RUPE and A. GASSMANN (Helv. Chim. Acta, 1934, 17, 283—285).—Since catalytic reduction of pulegone gives a mixture of *d*-isomenthone and *l*-menthone (Read *et al.*, A., 1926, 1147), one of these ketones, and not *d*-menthone (as in A., 1929, 314), must give rise (through the acetylenic carbinol) to *d*-3-methyl-6-isopropylcyclohexylideneacetaldehyde (I) (cryst. data shows homogeneity of oxime). The ketone, b.p. 85—87°/11 mm., $[\alpha]_D^{20}$ +20.25°, obtained by rearrangement of (I) gives a semicarbazone, m.p. 184° (not 181°), $[\alpha]_D^{20}$ —37.82° in C_6H_6 , and is therefore *l*-menthone.

J. W. B.

β -Pinene oxide in Grignard's reaction. N. PRILESHAIEV and N. PROKOPTSCHUK (J. Gen. Chem. Russ., 1933, 3, 865—868).— β -Pinene oxide yields with $MgMeI$ (I) $\Delta^1:6$ -menthen-7-ol (II), b.p. 130—132°/30 mm., converted by $K_2Cr_2O_7$ into an aldehyde, b.p. 122—125°/32 mm. (semicarbazone, m.p. 201°), isomeric with phellandral. Using $MgEtBr$ in place of (I) the product is a mixture of (II) and an alcohol, which on oxidation yields an aldehyde (III), b.p. 134—136°/28 mm. (semicarbazone, m.p. 173°).

R. T.

Action of carbon dioxide and sodium on 2:5-diketocamphane. Y. ASAHINA and M. ISHIDATE (Ber., 1934, 67, [B], 440—446).—2:5-Diketocamphane (I) is converted by Na and CO_2 in boiling xylene into 2:5-dihydroxycamphane, m.p. 233°, and a mixture of acids (II) which, on treatment with C_6H_6 , yields 2:5-diketocamphane-6-carboxylic acid (III), m.p. 210—211° (loss of CO_2), $[\alpha]_D^{20}$ +94.4° in EtOH. (III) and its alkali salts lose CO_2 slowly in cold H_2O , immediately in boiling solution, with production of (I). Similarly, (III) and $NH_2 \cdot CO \cdot NH \cdot NH_2 \cdot AcOH$ in cold EtOH afford 2:5-diketocamphanedisemicarbazone. Treatment of (III) with Br in AcOH leads to 6-bromo-2:5-diketocamphane-6-carboxylic acid, m.p. 185—186° (decomp.), which does not give a coloration with $FeCl_3$ and is converted by warm $NaHCO_3$ into 6-bromo-2:5-diketocamphane (IV), m.p. 145°. Warm 10% KOH transforms (IV) into ketocampholenic acid, m.p. 124—125°, shown to be



by its oxidation to α -ketoisocamphoronic acid, m.p.

185—186° (decomp.). The residue obtained after removal of (III) from (II) is neutralised and pptd. with quinine hydrochloride. The quinine salt is extracted with boiling COMe_2 . The filtered extract deposits the *quinine* salt, m.p. 165—166° (decomp.), of *acid* B (V), $\text{C}_{11}\text{H}_{16}\text{O}_4$, m.p. 133—134° (decomp.) [*Me* ester, m.p. 87°]. (V) is very unstable, immediately decolorises KMnO_4 , is optically inactive, and in EtOH gives a wine-red colour with FeCl_3 . When its Na salt is heated in H_2O it yields a neutral, unstable *product* (VI), m.p. (indef.) 112°, which resinifies on exposure to air. (V) or (VI) is transformed by Br in EtOH into the substance $\text{C}_{10}\text{H}_{15}\text{O}_2\text{Br}$, m.p. 91—92°, by Ac_2O at 130° into the *Ac* derivative (VIII), $\text{C}_{12}\text{H}_{18}\text{O}_3$, m.p. 65—66°, stable to KMnO_4 and giving no coloration with FeCl_3 , and by NH_2OH into the *oxime* $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}$, m.p. 165° (decomp.). The *semicarbazone* $\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_3$, m.p. 215° (decomp.), is derived solely from (VII). Reduction of (V) by Na—Hg leads to a neutral *product* (VIII), $\text{C}_{10}\text{H}_{20}\text{O}_2$, m.p. 92—93°, stable towards KMnO_4 , and two *acids*, $\text{C}_{11}\text{H}_{18}\text{O}_4$, m.p. 125—126°, and $\text{C}_{11}\text{H}_{20}\text{O}_4$, m.p. 188—189°, which yields a neutral oil, b.p. 200°/31 mm., when heated with Ac_2O . Similar reduction of (VI) gives (VIII) and a volatile substance of camphoraceous odour, (?) $\text{C}_{10}\text{H}_{18}\text{O}$, m.p. 125°, which gives a *semicarbazone* $\text{C}_{11}\text{H}_{21}\text{ON}_3$, m.p. 225—226°. The quinine salt insol. in COMe_2 (see above) yields *acid* C, $\text{C}_{11}\text{H}_{16}\text{O}_4$, m.p. 145·5°, $[\alpha]_D^{25}$ —64·81° in EtOH [*quinine* salt, m.p. 133—134° (decomp.)]; *Me* ester, m.p. 98—99°, which is unaffected by boiling 10% HCl or AcCl and does not yield an oxime or semicarbazone. H. W.

Lipoid-soluble compound of polonium. M. SERVIGNE (Compt. rend., 1934, 198, 731—733).—The prep. is described of *Po camphorcarboxylate*, sol. in C_6H_6 , CHCl_3 , and olive oil, and partly in aq. camphorcarboxylic acid. R. S. C.

Optical superposition. I. H. RUPE, F. BURKI, and H. WERDENBERG (Helv. Chim. Acta, 1934, 17, 271—282).—By action of the Na derivative of *d*-, *l*-, or *dl*-hydroxymethylenecamphor (I) on the chloride of *d*-, *l*-, or *dl*-bornylenecarboxylic acid (II) (prep. described) in dry C_6H_6 the eight stereoisomeric *hydroxymethylenecamphor bornylenecarboxylates*, respectively, *d-d* (III), m.p. 125°, $[\alpha]_D^{20} +209\cdot07^\circ$; *d-l* (IV), m.p. 134°, $[\alpha]_D^{20} +47\cdot87^\circ$; *d-dl* (V), m.p. 132°, $[\alpha]_D^{20} +97\cdot36^\circ$; *l-l* (VI), m.p. 125°, $[\alpha]_D^{20} -209\cdot12^\circ$; *l-d* (VII), m.p. 134°, $[\alpha]_D^{20} -48\cdot09^\circ$; *l-dl*, m.p. 132°, $[\alpha]_D^{20} -97\cdot28^\circ$; *dl-d*, m.p. 128°, $[\alpha]_D^{20} +74\cdot99^\circ$; *dl-l*, m.p. 128°, $[\alpha]_D^{20} -75\cdot01^\circ$; and *dl-dl*, m.p. 135°, are prepared. The $[\text{M}]_D^{20}$ vals. of these are different from those calc. by direct summation of the components, therefore in esterification of an optically active alcohol with an active acid a polar factor is superimposed on the optical. If *A* and *B*=mol. rotation of the (I) and (II) residues, respectively, $A+B=[\text{M}]_D^{20}$ of (III)=715·51°, and $A-B=[\text{M}]_D^{20}$ of (IV)=163·83°, whence $A=439\cdot67^\circ$ and $B=275\cdot84^\circ$. Since $[\text{M}]_D^{20}$ of (V)=332·31°, the polar influence of (II) or (I) is 106·46°, and that of (I) or (II) is 19·20°, the same vals. being similarly obtained from (VI) and (VII). When this polar factor is taken into account, the principle of optical superposition holds throughout. *Me d*-, b.p. 106°/11 mm., $[\alpha]_D^{20} +122\cdot94^\circ$, and

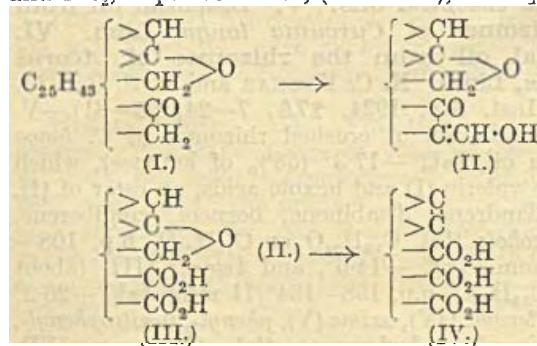
Me l-, b.p. 106°/11 mm., $[\alpha]_D^{20} -123\cdot02^\circ$, -bornylenecarboxylate are described. J. W. B.

Indian essential oils. V. Essential oil from the rhizomes of *Curcuma longa*, Linn. VI. Essential oil from the rhizomes of *Acorus calamus*, Linn. N. C. KELKAR and B. S. RAO (J. Indian Inst. Sci., 1934, 17A, 7—24, 25—31).—V. Steam-distillation of crushed rhizomes of *C. longa* gives an oil, $[\alpha]_D^{20} -17\cdot3^\circ$ (58% of ketones), which contains valeric (I) and hexoic acids, an ester of (I), *d*- α -phellandrene, *d*-sabinene, borneol, zingiberene, tert. alcohols (II), $\text{C}_{15}\text{H}_{24}\text{O}$ or $\text{C}_{15}\text{H}_{22}\text{O}$, b.p. 108—110°/3 mm., $[\alpha]_D^{20} -14\cdot6^\circ$, and ketones (III) (about 50%), $\text{C}_{15}\text{H}_{22}\text{O}$, b.p. 158—164°/11 mm., $[\alpha]_D^{20} +26\cdot2^\circ$ [*semicarbazone* (IV), *oxime* (V), *phenyl*-, *p*-nitrophenyl-, and *dinitrophenyl-hydrazones*, oils]. Curcumone (VI), b.p. 112—115°/7 mm., was obtained from (II) and (III) by 30% KOH—EtOH and partly by hydrolysis of (IV) by $\text{H}_2\text{C}_2\text{O}_4$. (VI) and $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{MgBr}$ give δ -hydroxy- ζ -*p*-tolyl- $\delta\zeta$ -dimethyl- Δ^4 -hexene, b.p. 140—145°/7 mm., partly decomposed by distillation at atm. pressure to (VI), giving an *acid*, m.p. 39—42°, with 4% aq. KMnO_4 at 0—5°, but stable to KOH. (III) with Na—EtOH give sec. alcohols, $\text{C}_{15}\text{H}_{28}\text{O}$, b.p. 135—140°/10 mm. (V) is a mixture; the Et_2O -sol. portion with Na—EtOH gives a base, $\text{NH}_2\cdot\text{C}_{15}\text{H}_{21}$, an oil (*oxalate*, m.p. 130°); the CHCl_3 -sol. portion gives a base, b.p. 85—95°/? mm. (III) with HNO_3 (1:2) at 85—95° gives a weak *acid*, m.p. >400°, $\text{p-C}_6\text{H}_4(\text{CO}_2\text{H})_2$, $\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$, and $\text{H}_2\text{C}_2\text{O}_4$, but with KMnO_4 (best in COMe_2) the main product is curcumatic acid. (II) and (III) give oily mixtures with S and Se.

VI. Steam-distillation of the rhizomes of Indian *A. calamus* gives an oil (2·8%), containing palmitic (VII) and heptonic acids, esters of (VII) and $\text{Pr}\cdot\text{CO}_2\text{H}$, α -pinene, camphene, asaraldehyde, eugenol (0·3%) and its *Me* ether (1%), asarone (82%), calamene (4%), *calamenenol*, $\text{C}_{15}\text{H}_{23}\cdot\text{OH}$ (5%), b.p. 140—146°/8 mm., $[\alpha]_D^{20} +1\cdot8^\circ$, and a ketone, *calameone*, $\text{C}_{15}\text{H}_{26}\text{O}_2$ (1%), m.p. 167—168°. The characteristic odour is due to unidentified constituents in the fraction of b.p. 125—135°/11 mm. R. S. C.

Polyterpenes and polyterpenoids. LXXXVII. Dehydrogenation of betulin. Degradation of allobetulin and dihydrobetulin derivatives. Contents of birch bark. L. RUZICKA, G. F. FRAME, H. M. LEICESTER, M. LIGUORI, and H. BRUNGER (Helv. Chim. Acta, 1934, 17, 426—442).—*alloBetulone* (I) with *isoamyl* formate and NaOEt in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ gives a *hydroxymethylene* derivative (II), m.p. 258—259°, oxidised by $\text{CrO}_3\text{-AcOH}$ to an *anhydride-acid* $\text{C}_{30}\text{H}_{44(46)}\text{O}_5$, m.p. 293° (sparingly sol. in AcOH) [*Me* ester, m.p. 290—292°, by CH_2N_2 ; *Me*₃ ester (as IV), m.p. 253—256°, by MeI-NaOMe], which gives no m.p. depression with oxyallobetulinic acid (A., 1932, 749; *oxime*, m.p. 215°), but does not form an oxime, and an *acid* (III), m.p. (indef.) 180—210°, giving a *Me*₂ ester, $\text{C}_{32}\text{H}_{52}\text{O}_5$, m.p. 155—156°. Oxidation of the ketone $\text{C}_{29}\text{H}_{44}\text{O}_3$ from oxyallobetulinic acid (Dischendorfer *et al.*, A., 1929, 449, modified) with $\text{CrO}_3\text{-AcOH}$ gives an *acid*, which is difficult to purify, but at 360—370° gives an *anhydride*, $\text{C}_{28}\text{H}_{40}\text{O}_5$, m.p. 385° (decomp.) [*Me*, m.p. 270° by instantaneous

heating, resolidifying and m.p. 384°, *Et*, sinters 220°, m.p. 231—232°, resolidifying and m.p. 384°, and *Me*₂, m.p. 265—266°, (no oxime), esters].



Dihydrobetulonic acid (*loc. cit.*, improved prep. and purification through its semicarbazone or Na salt: oxime, m.p. 285—295°) with NaOH-*Me*₂SO₄ gives its *Me* ester, m.p. 191—192° [oxime, m.p. 252—253° (decomp.)], which gives only an indefinite hydroxymethylene derivative from which no cryst. products could be obtained on oxidation. From the high-b.p. fraction of Se dehydrogenation products of betulin (V) (A., 1933, 69) a second hydrocarbon C₂₅H₂₀, sinters 315°, m.p. 324°, is obtained. Dehydrogenation of (V) with Pd-C at 340—360° gives similar products, 1:2:3:4-C₆H₄Me₄, sapotalin, 1:2:5:6-C₁₀H₄Me₄ [compound with C₆H₃(NO₂)₃, m.p. 178.5—179°], and fractions difficult to purify. From the EtOH-extract of birch bark are also isolated a paraffin hydrocarbon C₂₅H₅₂, m.p. 53—54°, and acetyloleanolic acid, identical with a specimen prepared by Winterstein *et al.* (A., 1931, 1159).

J. W. B.

Polyterpenes and polyterpenoids. LXXXVIII. Dehydrogenation of hederagenin, oleanolic acid, and sumaresinolic acid with selenium and palladium. L. RUZICKA, H. HOSLI, and L. EHMANN (Helv. Chim. Acta, 1934, 17, 442—455).—Reinvestigation (cf. A., 1932, 517; 1933, 69) of the Se and Pd-C dehydrogenation products of various triterpenes has led to the isolation of further products. The combined results are summarised thus, the numerals referring to the dehydrogenation products: 1:2:3:4-C₆H₄Me₄ (I), 2:7-C₁₀H₆Me₂ (II), 1:2:7-C₁₀H₃Me₃ (sapotalin) (III); oxysapotalin (IV), 1:2:5:6-C₁₀H₄Me₄ (V), a phenanthrene hydrocarbon C₁₈H₁₈ (VI), m.p. 126—127° [picrate, m.p. 165°; styphnate, m.p. 174—175°; and compound with C₆H₃(NO₂)₃, m.p. 174—175°, all decomposing into their components by recrystallisation; oxidised by CrO₃-AcOH to the quinone, m.p. 203—104° (quinoxaline, m.p. 178—179°)], a picene hydrocarbon C₂₅H₂₀ (VII), m.p. 305°, and a dinaphthyl hydrocarbon C₂₆H₂₄ (VIII), m.p. 143°. Hederagenin+Se [(I)—(IV), (VI), and (VII)], +Pd [same products except (VI)]; oleanolic acid (IX)+Se [(I)—(V), and (VII)], +Pd [same products except (V)]; sumaresinolic acid (X)+Se [(I)—(V), (VII), and (VIII)], +Pd [(I)—(IV), and (VII)]. The absorption spectra of (VII) from (IV) (chief absorption max. 3.421 1/λ) and from (X) (1/λ=3.425) closely resemble that of tar picene (1/λ=3.496), confirming the view that (VII) is a picene homologue.

J. W. B.

Orientation in furan nucleus. VIII. 3-Acylamidofurans. R. R. BURTNER (J. Amer. Chem. Soc., 1934, 56, 666—667).—3-Furohydrazide, m.p. 124—124.5° (from the Et ester and N₂H₄·H₂O), is converted into the azide and thence (in boiling C₆H₆) into 3-furylcarbimide (not isolated owing to its offensive properties), which with MgPhBr gives 3-benzamidofuran, m.p. 142°. 2-Methyl-3-furohydrazide, m.p. 148°, and 3-benzamido-, m.p. 135° (cf. Blomquist and Stevenson, this vol., 300), and 3-acetamido-, m.p. 148°, -2-methylfurans are similarly prepared.

H. B.

Anomalous Friedel Crafts reactions with furans. H. GILMAN, M. McCORKLE, and N. O. CALLOWAY (J. Amer. Chem. Soc., 1934, 56, 745).—2-Furoic acid, C₆H₆, and AlCl₃ give α-C₁₀H₇·CO₂H (probably through an endoxy-derivative) and not 3-phenyl-2:3-dihydro-2-furoic acid (King, A., 1927, 358). In the reaction between furfuraldehyde, Pr^βCl, and AlCl₃ in CS₂ (A., 1933, 1300), Pr^β is introduced into the 3- or 4-position; bromination of the corresponding acid gives 5-bromo-3(or 4)-isopropyl-2-furoic acid (Et ester, formed from Et 5-bromo-2-furoate, Pr^βCl, and AlCl₃), also obtained by oxidation of the product from o-bromofurfuraldehyde, Pr^βCl, and AlCl₃.

H. B.

Bases of the type of fast-violet B, with a furoyl radical in place of benzoyl. N. KISHNER and V. KRASOVA (Anilinokras. Prom., 1933, 3, 430—433).—5-Nitro-4-methoxy-*o*-toluidine and furoyl chloride give, on keeping 24 hr. at room temp. in presence of NaOAc, quant. yields of *o*-nitro-2-furamido-4-methoxytoluene, m.p. 175°, which with Zn and HCl gives the corresponding 5-amino-derivative, m.p. 134°. The analogous products from 6-nitro-4-methoxy-*m*-toluidine are 6-nitro-, m.p. 170°, and 6-amino-3-furamido-4-methoxytoluene, m.p. 169°, and from 3-chloro-4-nitro-6-methoxyaniline 3-chloro-4-nitro-1-furamido-6-methoxybenzene, m.p. 194.5°, and 3-chloro-1-furamido-4-amino-6-methoxybenzene, m.p. 181.5°. The above amines yield, on diazotising and coupling, dyes similar to those containing Bz in place of furoyl.

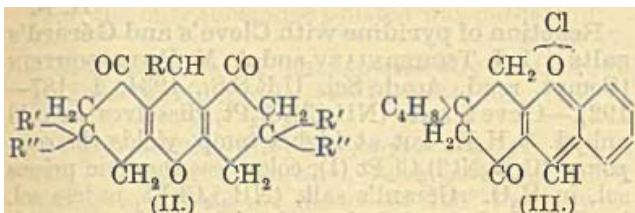
R. T.

[Preparation of] xanthone. M. SPEKTOR (Khim. Farm. Prom., 1933, 195—196).—Acetylsalicylic acid is distilled at 120—170° until all the AcOH has passed over; the temp. is then raised in 4 hr. to 350—355°/40 mm., and xanthone crystallises. Yield (from EtOH) 70%.

CH. ABS.

Dihydroresorcinols. II. Condensation of aldehydes with cyclopentanespirocyclohexane-3:5-dione and dimethyldihydroresorcinol. R. D. DESAI (J. Indian Chem. Soc., 1933, 10, 663—671; cf. Vorlander and Kalkow, A., 1900, i, 99).—The alkyl- (or arylidenebis) derivatives of dimethyldihydroresorcinol (I) and similar compounds are best formed in presence of piperidine and are dehydrated by HCl (except for *o*-OH-compounds), AcOH, or Ac₂O to the corresponding octahydroxanthens (II), which are formed direct in presence of HCl, AcOH, etc. Condensation of *o*-OH·C₆H₄·CHO with cyclopentanespirocyclohexane-3:5-dione in presence of HCl, however, gives 4-keto-2-spirocyclopentanotetrahydrobenzopyrylium chloride (III), decomp. 300° (cf. A., 1932, 279); this

resists hydrolysis with KOH in EtOH, giving only the corresponding base, m.p. $> 300^\circ$. The following



are described: *methylene-*, m.p. 165° , *benzylidene-*, m.p. 167° , and *salicylidenebiscyclopentanespirocyclohexane-3:5-dione*, m.p. $208-209^\circ$ [*Ac* derivative, m.p. $180-184^\circ$, from *o*- $\text{AcO}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (IV); converted by Ac_2O or AcOH into (V) (below)]; 1:8-*diketo*-3:6-*bis*spirocyclopentaneoctahydroxanthene [(II): $\text{R}=\text{H}$, $\text{R}'\text{R}''=\text{C}_4\text{H}_8$], m.p. $180-181^\circ$, and its 9-*Ph* ($\text{R}=\text{Ph}$), m.p. $185-186^\circ$, and 9-*salicyl* derivative, m.p. 191° [*Ac* (V), m.p. $181-182^\circ$, and *Bz*, m.p. 137° , derivatives]; and 1:8-*diketo*-9-*phenyl*-3:3:6:6-*tetramethyloctahydroxanthene*(mono)*phenylhydrazone*, m.p. $266-267^\circ$ (decomp.). The compound, m.p. $209-210^\circ$ (*loc. cit.*) from (I) and *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ in aq. KOH appears to be the corresponding xanthene [(II): $\text{R}=\text{O}\cdot\text{OH}\cdot\text{C}_6\text{H}_4$, $\text{R}'=\text{R}''=\text{Me}$] (*Bz* derivative, m.p. $154-155^\circ$; *phenylhydrazone*, m.p. 235°), as it is formed by heating *salicylidenebisdimethyldihydroresorcinol*, m.p. 184° [*Ac* derivative (VI), m.p. $200-201^\circ$ [from (IV)]; *Me* ether (VII), m.p. 184° (from *o*- $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$)], with glacial AcOH , whilst its *Ac* derivative, m.p. $190-191^\circ$, and *Me* ether, m.p. 180° , are similarly formed from (VI) and (VII), respectively. H. A. P.

Chemical constituents of tobacco. III. Colouring matter of tobacco blossoms. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1933, 9, 137-139).—An anthocyanidin present as a monoglucoside and a flavone glucoside have been isolated in small yield.

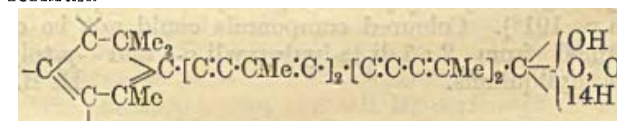
R. K. C.
[Vegetable] tannins and their behaviour towards proteins. K. FREUDENBERG (J. Soc. Leather Trades Chem., 1934, 18, 152-155).—The intermol. forces which cause PhOH and N compounds to combine also cause tannins to interact with proteins. Opposite electrical charges may also assist the reaction. The formation of this mol. compound, which is reversible, is followed by a partly reversible permeation process and condensation and oxidation of the tannins in the mol. compound. D. W.

Quebracho tannin. K. FREUDENBERG and P. MATTLAND (J. Soc. Leather Trades Chem., 1934, 18, 156-159).—Quebracho catechin (I) is synthesised from fisetinidin chloride and possesses the properties of catechin. It gave the same type of condensation without the elimination of H_2O as did the natural quebracho tannin and the same degradation products. The presence of a pyran OH group is unnecessary for phlobaphen formation (cf. A., 1931, 964). The evidence confirms Freudenberg's formula for (I) (cf. B., 1925, 369; A., 1926, 73). D. W.

Action of alkalis on substituted benzodioxins. F. D. CHATTAWAY and H. IRVING (J.C.S., 1934, 325-330).—When the 6-position of a substituted 2:4-bis-trichloromethyl-1:3-benzodioxin contains an electron-

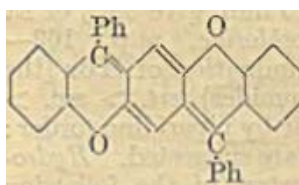
attracting group the heterocyclic ring is ruptured by $\text{KOH}\cdot\text{EtOH}$, and the group also facilitates elimination of HCl from $\text{CH}\cdot\text{CCl}_3$ in position 4 under milder alkaline conditions. If the group is electron-donating the ring is unaffected, but the action is modified by the presence of groups in the heterocyclic ring. 6-Nitro-2-trichloromethyl-4-dichloromethylene-1:3-benzodioxin, prepared by elimination of HCl , is oxidised to 6-nitro-4-keto-2-trichloromethyl-1:3-benzodioxin, m.p. $172-5^\circ$, which with $\text{NaOH}\cdot\text{EtOH}$ gives CHCl_3 and 5-nitrosalicylic acid, whilst the corresponding 7-*Me* compound, m.p. 149° , prepared from 6-nitro-2-trichloromethyl-4-dichloromethylene-7-methyl-1:3-benzodioxin, m.p. $120-121^\circ$, similarly affords CHCl_3 and 5-nitro-2-hydroxy-4-methylbenzoic acid. 6:8-Dinitro-2-trichloromethyl-4-dichloromethylene-1:3-benzodioxin and $\text{EtOH}\cdot\text{KOH}$ give ω -dichloro-3:5-dinitro-2-ethoxyacetophenone. 6:8-Dinitro-1:3-benzodioxin and 1% NaOH yield CH_2O and 3:5-dinitrosaligenin, m.p. $104-104.5^\circ$ (diacetate, m.p. $81.5-82^\circ$). F. R. S.

Plant colouring matters. LVIII. New occurrence of astacin: its constitution. P. KARRER and F. BENZ (Helv. Chim. Acta, 1934, 17, 412-416).—Isolation (after hydrolysis) of astacin (I) $\text{C}_{30}\text{H}_{56}\text{O}_3$ (from new analytical data), identical with that obtained by Kuhn (A., 1933, 509), from *Ophidiaster ophidianus* is described. Oxidation of (I) with KMnO_4 in aq. C_6H_6 at room temp. gives $\text{CMe}_2(\text{CO}_2\text{H})_2$; (I) therefore contains the carotene ring and the partial formula



is suggested. Catalytic reduction ($\text{Pt}\cdot\text{H}_2$) gives perhydroastacin, $\text{C}_{30}\text{H}_{56}\text{O}_3$, which is no longer sol. in alkali. The OH is therefore enolic. J. W. B.

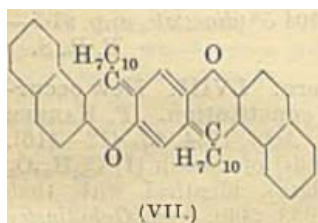
Transformations of 2:5-di-(α -hydroxydiaryl-methyl)quinols. H. LIEBERMANN and J. BARROLIER (Annalen, 1934, 509, 38-50).—Et 2:5-dihydroxyterephthalate (I) and MgPhBr in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ give 2:5-di-(α -hydroxybenzhydryl)quinol (II), m.p. 220° (red at 150°), which when heated in PhNO_2 passes into 5:12-diphenyl-5:12-dehydrochromoxanthene (*chromanorufen*) (III), red with metallic green reflex, m.p. about 400° . (II) and HCl in COMe_2 afford 2:5-di-(α -chlorobenzhydryl)quinol (IV), m.p. about 250° (red at 180°), and (mainly) 2:5-di-(α -acetonylbenzhydryl)quinol, becomes red at about 250° . (IV) heated in PhNO_2 gives (III). 2:5-Di-(α -anilinobenzhydryl)quinol, sinters at about 255° to a dark red melt, is prepared from (IV) and NH_2Ph in C_6H_6 . (II) and boiling Ac_2O give 2-hydroxy-9-phenyl-3-



α -hydroxybenzhydrylxanthene, m.p. 165° [which when heated in O_2 passes into (III)], and (III). (III) is reduced ($\text{HI}\cdot\text{AcOH}$) to 5:12-diphenylchromoxanthene (*chromanorufan*), colourless, m.p. $> 270^\circ$ (red at 220°), and oxidised ($\text{CrO}_3\cdot\text{AcOH}$; Br ; HNO_3 —

AcOH) to a peroxide, $C_{32}H_{22}O_4$, m.p. 270° [regenerating (III)]. Reduction (Zn dust, AcOH) of (II) gives 2:5-dibenzhydrylquinol (V) (diacetate, m.p. 235° ; dibenzoate, m.p. 286°), oxidised (CrO_3 , AcOH) to 2:5-dibenzhydryl-p-benzoquinone (tetraphenylphlorone), m.p. 250° (previous reddening), which when heated to about 270° passes into (III). (II) is oxidised (CrO_3 , AcOH) to 2:5-di-(α -hydroxybenzhydryl)-p-benzoquinone, which also gives (III) when heated at 270° in H_2 or CO_2 . (V) is unaltered at 270° in CO_2 , but in air (III) results. 1:4-Dimethoxy-2:5-di-(α -hydroxybenzhydryl)benzene, m.p. 240° , from $MgPhBr$ and Me 2:5-dimethoxyterephthalate, m.p. 140° , shows no tendency to pass into a coloured compound.

(I) and α - $C_{10}H_7$ -MgBr give 2:5-di(hydroxydi- α -naphthylmethyl)quinol (VI), m.p. $> 400^\circ$ (violet at 140°), which when heated in $PhNO_2$ passes into 5:12-di- α -naphthyl-5:12-dehydro-3:4-benzchroman-10:11-benzxanthen (chromanoviolon) (VII), violet



with bronze reflex, m.p. $> 400^\circ$, reduced (HI-AcOH) to chromanoviolon, colourless, turns violet at 240° , and oxidised (CrO_3 , AcOH) to a peroxide, $C_{48}H_{30}O_8$, m.p. 212° (loss of O_2 to a deep

violet melt). (VI) is reduced (Zn dust, AcOH) to 2:5-di(di- α -naphthylmethyl)quinol. Me 3:6-dihydroxyphthalate and $MgPhBr$ give 3:6-dihydroxy- α -diphenylphthalide, m.p. 296° (diacetate, m.p. 191°). Coloured compounds could not be obtained from 2:5-di-(α -hydroxydi-*o*- and -*p*-tolylmethyl)quinols.

H. B.

Reaction of organic halides with piperidine.

IV. Bromo-esters. W. V. DRAKE and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 697—700).—The rates of reaction of 1 mol. of $CHBrR \cdot CO_2Et$ ($R=H$, Me, Et), $CBrMe \cdot CO_2Et$, $Br[CH_2]_n \cdot CO_2Et$ ($n=2-4$), $CH_2Br \cdot CHMe \cdot CO_2Et$, and $CHBrMe \cdot [CH_2]_n \cdot CO_2Et$ ($n=1-5$) with piperidine (I) (2 mols.) are determined at 90° , essentially as previously described (A., 1931, 494). With certain exceptions, the order of reactivity, as determined by the amount of (I) hydrobromide produced in a given time, is (as bromides) primary $>$ sec. $>$ tert.; CO_2Et has a general activating effect. The β -Br-esters are the most reactive; in these cases, piperidino-ester formation involves elimination of HBr and subsequent addition of (I). $CH_2 \cdot CH \cdot CO_2Et$ and (I) in light petroleum at 90° for 15 min. give 95% of Et β -piperidinopropionate (hydrochloride, m.p. $163-164^\circ$). Mechanisms for the elimination of HBr [the order of this is usually (as bromides) tert. $>$ sec. $>$ primary] and replacement of Br by piperidino (order: usually primary $>$ sec. $>$ tert.) are suggested. Hydrochlorides, m.p. quoted after ester, of the following are described: Et piperidinoacetate, m.p. $130-131^\circ$, α -piperidino-propionate, m.p. $131-132^\circ$, and -butyrate, m.p. $113-114^\circ$, β -piperidino-butylate, m.p. $177-178^\circ$, and -isobutylate, m.p. $134-135^\circ$, γ -piperidino-butylate, m.p. $128-129^\circ$, and -valerate, m.p. $128-129^\circ$, δ -piperidino-valerate, m.p. $154-155^\circ$, and

-hexoate, m.p. $135-136^\circ$, ϵ -piperidinoheptate, m.p. $121-122^\circ$, and ζ -piperidino-octate, m.p. $116-117^\circ$.

H. B.

Reaction of pyridine with Cleve's and Gerard's salts. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 187—192).—Cleve's salt, $(NH_3Cl)_2Cl_2Pt$, dissolves in cold anhyd. C_5H_5N , but at higher temp. yields the compound $(C_5H_5NCl)_2Cl_2Pt$ (I), colourless rhombic prisms sol. in H_2O . Gerard's salt, $(NH_3)_2Cl_4Pt$, is less sol. in C_5H_5N , but when heated with the latter yields the compound $(NH_3)_2(C_5H_5NCl)_2PtCl_2 \cdot 4H_2O$ (II), which is readily sol. in an excess of C_5H_5N in H_2O , whereas (I) is insol. (II) reacts with $H_2C_2O_4$ to form the compound $(NH_3)_2(C_5H_5NCl)_2Pt(CO_2 \cdot CO_2H)_2 \cdot 2H_2O$ (III), with Na_2PtCl_6 to form the compound $(NH_3)_2(C_5H_5NCl)_2Pt(PtCl_6)$, and on reduction with $N_2H_4 \cdot 2HCl$ gives $(NH_3)_2Cl_2Pt$. Oxidation of $(NH_3)_2(C_5H_5N)_2PtCl_2$ with Cl_2 yields the trans-diammine-trans-dipyridine trans-dichloro-compound $(NH_3)_2(C_5H_5N)_2Cl_2PtCl_2 \cdot 4H_2O$ (IV), isomeric with (II) but less sol., yielding with $H_2C_2O_4$ an oxalate similar to (III) but less sol. and losing H_2O only at 110° , whereas (III) also loses C_5H_5N . With K_2PtCl_4 (IV) gives the chocolate-coloured compound $(NH_3)_2(C_5H_5N)_2Cl_2Pt \cdot PtCl_4$, with K_2PtCl_6 the yellow compound $(NH_3)_2(C_5H_5N)_2Cl_2Pt \cdot PtCl_6 \cdot 3H_2O$, and with $N_2H_4 \cdot 2HCl$, $(NH_3)_2Cl_2Pt$ and $(C_5H_5N)_2Cl_2Pt$. After reduction, K_2PtCl_4 ppts. the compound $(NH_3)_2(C_5H_5N)_2Pt \cdot PtCl_4$. Addition of C_5H_5N to Peirone's salt $(NH_3Cl)_2Pt$ and oxidation of the resulting tetrammine with Cl_2 yields the compound $(NH_3C_5H_5N)_2Cl_2PtCl_2$, isomeric with (II) and (IV), colourless, sol. in H_2O , and sparingly sol. in EtOH. It gives no ppt. with $H_2C_2O_4$ or with $PtCl_6^{--}$ and with excess of K_2PtCl_4 gives Magnus' salt $(NH_3 \cdot C_5H_5N)_2Pt \cdot PtCl_4$; reduction with $N_2H_4 \cdot 2HCl$ gives the compounds $(NH_3 \cdot C_5H_5N)_2PtCl_2$ and $C_5H_5N \cdot NH_3Cl_2Pt$.

J. W. S.

6-Bromo-2-methylpyridine. H. D. T. WILLINK, jun. and J. P. WIBAUT (Rec. trav. chim., 1934, 53, 417—420).—6-Hydroxy-2-methylpyridine (I) (A., 1923, i, 600) and $POBr_3$ at 160° give 6-bromo-2-methylpyridine (II), b.p. $205.5-207^\circ/772$ mm. (picrate, m.p. $115-116^\circ$), also formed from 6-amino-2-methylpyridine (III) and $NaNO_2$ in aq. $AcOH-KBr$. (III) and $NaNO_2$ in 48% HBr afford (II) and 3(?) : 5(?) : dibromo-6-hydroxy-2-methylpyridine (IV), m.p. $250.5-251^\circ$. (I) and a large excess of PBr_5 at 160° give (II) and 3(?) : 5(?) : 6-tribromo-2-methylpyridine, m.p. $75-76^\circ$, also obtained from (IV) and $POBr_3$, which is oxidised (alkaline $KMnO_4$) to a little 3(?) : 5(?) : 6-tribromopyridine-2-carboxylic acid, m.p. $144.5-145^\circ$. Attempts to prepare a tribromopyridine from this were unsuccessful.

H. B.

Amino-derivatives of pyridine. G. B. CRIPPA and M. LONG [with E. DE MARTINI] (Gazzetta, 1934, 64, 83—91).—2-Aminopyridine yields 2-phthalimidopyridine, m.p. 224° . 2:6-Diaminopyridine, obtained from lutidine by way of dipicolinic acid and its Ag salt, Et ester (m.p. 28°), and amide, similarly yields 2:6-diphthalimidopyridine, m.p. above 340° , and with PhN_2Cl forms 2:6-diamino-3-benzeneazopyridine, m.p.

135°. When the *diphthalimido*-compound, m.p. 223°, was prepared from the last, and reduced and dehydrated, the only substance isolated was phthalanil.

E. W. W.

Manufacture of therapeutically active substances [pyridones].—See B., 1934, 301.

4-*p*-Dialkylaminophenylpyridines. E. KOENIGS and E. RUPPELT (Annalen, 1934, 509, 142—158).—C-H₅N and BzCl are heated at 100° (bath) with a little naturkupfer *C* until most of this dissolves; addition of NPhMe, to the cooled mixture and subsequent heating at 100° for 5 hr. gives 67% of 4-*p*-dimethylaminophenylpyridine (I), m.p. 234° [hydrochloride, m.p. 220°; dihydrochloride, m.p. 205°; picrate, m.p. 246° (decomp.)]; quaternary salt (II) (+2H₂O), orange-red, m.p. 265° (yellow at 145°), with 1 mol. of CH₂PhCl, also obtained in very poor yield from C₅H₅N and *p*-NMe₂-C₆H₄-N₂Cl. The mechanism of formation of (I) is considered to be: 1-benzoylpyridinium chloride → 4-chloro-1-benzoyl-1:4-dihydropyridine → 1-benzoyl-4-*p*-dimethylaminophenyl-1:4-dihydropyridine → (I) + PhCHO (which is isolable from the reaction mixture). (I) dyes wool and tanned cotton a shade similar to auramine; (II) is a better dye than (I). (I) is oxidised (KMnO₄, dil. H₂SO₄) to isonicotinic acid. (I), 64% HNO₃, and a little NaNO₂ give (probably) the 3:3':5'-(NO₂)₃-derivative, m.p. 129° [crude nitrate, m.p. 195—197°; quaternary salt, m.p. 165° (decomp.)], with CH₂PhCl (and a little of a substance, m.p. 241°), which is reduced (SnCl₂, conc. HCl) to (probably) the 3:3'-(NH₂)₂-derivative, m.p. 176° (trihydrochloride, decomp. 364°). (I) and hot HNO₃ (*d* 1.52) afford a trinitro-4-*p*-methylaminophenylpyridine, m.p. 160° [nitrate, m.p. 211° (decomp.)], similarly reduced to a diamino-4-*p*-methylaminophenylpyridine, m.p. 174°. (I) and Br in hot AcOH-HBr give (probably) 4:3':5'-dibromo-4'-aminophenylpyridine, m.p. 136° [quaternary salts, m.p. 185° (previous sintering) and 395°, with CH₂PhCl and amyl bromide, respectively], which when diazotised and coupled with NPhMe₂ affords the corresponding 4'-*p*-dimethylamino-benzeneazo-derivative, m.p. 212°. 4-*p*-Diethylaminophenylpyridine, m.p. 157° [picrate, m.p. 211°; quaternary salt, m.p. 283°, with CH₂PhCl; (NO₂)₃-derivative, m.p. 115° (nitrate, m.p. 208°), reduced to a (NH₂)₂-derivative, decomp. 250°], and HNO₃ (*d* 1.52) give a trinitro-4-*p*-ethylaminophenylpyridine, m.p. 143° [nitrate, m.p. 208—210° (decomp.)]; picrate, m.p. 223—225° (decomp.)], reduced to a diamino-4-*p*-ethylaminophenylpyridine, m.p. 139—140°. *o*- and *p*-C₆H₄Me-NMe₂ do not react (as above), whilst *m*-C₆H₄Me-NMe₂, C₅H₅N, and BzCl give a compound, C₂₁H₂₀ON₂, m.p. 94° (hydrochloride, m.p. 176°).

The following are prepared [as (I)] from the appropriate NPhRR': 4-*p*-methylethyl-, m.p. 154° (picrate, m.p. 216°), 4-*p*-methyl-*n*-propyl-, m.p. 123° [picrate, m.p. 200° (decomp.)], 4-*p*-methyl-*n*-butyl-, m.p. 92° (hydrochloride, m.p. 184°), 4-*p*-methylisoamyl-, m.p. 120°, 4-*p*-benzylmethyl-, m.p. 122° [hydrochloride, m.p. 237°; picrate, m.p. 185° (previous sintering); quaternary salt (+xH₂O), m.p. 103°, m.p. (anhyd.) 215° (not sharp), with CH₂PhCl], 4-*p*-ethyl-*n*-propyl-, m.p. 49°, 4-*p*-ethyl-*n*-butyl-, m.p. 41°, 4-*p*-di-*n*-propyl-, m.p. 108° [picrate, m.p. 212° (decomp.)], and 4-*p*-di-*n*-butyl-,

m.p. 156—157° (hydrochloride, m.p. 149°; picrate, m.p. 186—187°), -aminophenylpyridines. H. B.

Nitration of β-phenylethylpyridines and related compounds. II. E. A. WAGSTAFF (J.C.S., 1934, 276—278).—4'-Methyl-2-stilbazole nitrate, m.p. 147°, with HNO₃ gives 3'-nitro-4'-methyl-2-stilbazole, m.p. 137° (65%), no other product being isolated, and it is concluded that ·CH:CHR (R is electron-attracting) exerts an *-I+T* effect. 2', 3', and 4'-Nitro-4-stilbazole, m.p. 171° (lit. 119°), have been prepared by heating the appropriate NO₂-C₆H₄-CHO with the bases obtained from mono- and di-methylpyridines with PhCHO and ZnCl₂. 2:5-Di-2', m.p. 140°, -3', m.p. 216°, and -4'-nitrostyrylpyridine, m.p. 258°, were obtained in the same reaction. 4-Stilbazole nitrate, m.p. 160°, on nitration indicates an *o/p* ratio of 1.05. 4-β-Phenylethylpyridine is nitrated to the 4'-NO₂-compound, m.p. 85°; 2-β-4'-nitrophenylethylpyridine affords the 2':4'-(NO₂)₂-derivative, m.p. 78° [nitrate, m.p. 160° (decomp.)]; methiodide, m.p. 210°].

F. R. S.

Mercurated substitution products of di-*p*-hydroxyphenylisatin. S. E. HARRIS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 108—113).—Acetoxymercuri- or diacetoxymercuri-derivatives (all decomp. without melting) of 3:3'-dibromo-, m.p. 144—145°, 3:3':5:5'-tetrabromo-, 3:3'-dinitro-, m.p. 225° (decomp.), 3:3'-diphenyl-, m.p. 183—185°, 3:3'-diphenyl-5:5'-dibromo-, m.p. 115°, 3:3'-diphenyl-5:5'-dinitro-, m.p. 148°, 3:3'-dimethyl-5:5'-dibromo-, m.p. 250° (decomp.), and 3:3'-dinitro-5:5'-dimethyl-4:4'-dihydroxydiphenylisatin, m.p. 238—240°. Diresorcinolisatin [di-(2':4'-dihydroxydiphenyl)isatin] and its 3:3'-Br₂-compound, m.p. 250—255° (decomp.), and the OH·Hg-derivative of 3:3'-dinitrodiresorcinolisatin, decomp. at 220°, are described. The highest dilutions killing *B. typhosus* in 5 min. range from 1—500 to 1—30,000. E. H. S.

Comparison of the dimethylquinoline from aniline, isobutaldehyde, and methylal with 2:3-dimethylquinoline and the relationship of 2:3-dimethylquinoline to benzil. G. RONDE (Ber., 1934, 67, [B], 431—434).—Direct comparison of the dimethylquinoline from NH₂Ph, CH₂(OMe)₂, and isobutaldehyde with 2:3-dimethylquinoline (I) and of their picrates, platinichlorides, and aurichlorides shows them to be chemically and crystallographically identical. A substance, C₁₅H₂₁O₂N, m.p. 145—146°, is the primary product of the interaction of (I) and benzil (II) at 100°, and is transformed by warm conc. H₂SO₄ into the substance C₂₅H₁₉ON, needles or prisms, m.p. 180—181°, which when heated above its m.p. passes into a yellow isomeride, m.p. 246—247°. (I) and (II) at 180° afford CO₂, H₂O, and a compound (?) C₉H₆NMe·CH₂·CHPh₂, m.p. 121—122°. 2-Methylquinoline (III) and (II) similarly yield the compounds, C₂₄H₁₉ON₂, m.p. 134—135°, and C₂₄H₁₇ON, m.p. 189—189.5°. (III) and (II) at 180° afford a substance (?) (C₉H₆N·CH:CHPh)₂, m.p. 245—246°. H. W.

2-Hydroxy-6-methoxy-4-methylquinoline. O. G. BACKEBERG and W. O. KERMACK (J.C.S., 1934, 377).—The m.p. of 2-hydroxy-6-methoxy-4-methyl-

quinoline is 272° (uncorr.) and the specimens of other workers contain some impurities. F. R. S.

Action of halogens on polycyclic indole derivatives. IV. Some reactions of 1-keto-1:2:3:4-tetrahydrocarbazole. A. J. MEARS, S. H. OAKESHOTT, and S. G. P. PLANT (J.C.S., 1934, 272—276).—*cycloHexane-1:2-dionemono-p-bromophenylhydrazine*, m.p. 176°, obtained by Coffey's method (A., 1923, i, 803), with AcOH-HCl gives 6-bromo-1-keto-1:2:3:4-tetrahydrocarbazole (I), m.p. 222—224° (9-Ac derivative, m.p. 154—155°). The corresponding *o-bromophenylhydrazine*, m.p. 172—174°, does not undergo Fischer's reaction, whilst the *m*-compound yields a mixture of 5(or 7)-, m.p. 233—235° (9-Ac derivative, m.p. 135°), and 7(or 5)-bromo-1-ketotetracarbazole, m.p. 163° (9-Ac derivative, m.p. 186—188°). 6-Nitro-1-ketotetracarbazole (II), m.p. 259° (lit. 212°), is similarly prepared. Bromination and nitration, respectively, of 1-ketotetrahydrocarbazole gives (I) and (II), and not the additive compounds. *cycloHexane-1:2-dionemono-o-tolylhydrazine*, m.p. 95—96°, yields 1-keto-8-methyltetrahydrocarbazole, m.p. 167°, whilst the 5-bromo-, m.p. 95—97°, and 5-nitro-hydrazones, m.p. 155—157°, give the corresponding 6-bromo-, m.p. 229—230°, and 6-nitro-tetrahydrocarbazoles, m.p. 294°, also obtained by direct bromination or nitration. *cycloHexane-1:2-dionemono-3-bromo-p-tolylhydrazine*, m.p. 79—82°, gives 8-bromo-1-keto-6-methyltetrahydrocarbazole, m.p. 164°, and the corresponding 2-derivative forms a mixture of 5(or 7)-, m.p. 253—254°, and 7(or 5)-bromo-1-keto-6-methyltetrahydrocarbazole, m.p. 197°. The 3-NO₂-compound yields 8-nitro-1-keto-6-methyltetrahydrocarbazole, m.p. 199—201°, and the 2-NO₂-compound, m.p. 141—142°, gives a mixture of 5(or 7)-, m.p. 253—255°, and 7(or 5)-nitro-1-keto-6-methyltetrahydrocarbazole, m.p. 207—208°. Bromination or nitration of 1-keto-6-methyltetrahydrocarbazole affords the 7(or 5)-Br- or -NO₂-compounds. Reduction of 1-ketotetrahydrocarbazole with P-HI gives tetrahydrocarbazole and with Sn-HCl yields *cis*-hexahydrocarbazole. F. R. S.

Catalytic dehydrogenation of cyclic bases. II. M. EHRENSTEIN and I. MARGGRAFF (Ber., 1934, 67, [B], 486—491).—Passage of tropine over Pd-asbestos at 280—290° occurs without evolution of H₂ and yields a *sec.* base isolated as the *Bz* derivative, C₁₅H₁₉ON, m.p. 94—96.5°. Hexamethyleneimine in presence of Pt- or Pd-asbestos suffers slow dehydrogenation and ring contraction, affording 2-methylpyridine and unidentified pyrrole derivatives. H. W.

Optically active allantoin. R. FOSSE, P. E. THOMAS, and P. DE GRÈVE (Compt. rend., 1934, 198, 689—672).—Allantoinase from soya-bean at 40° destroys *d*-allantoin (I) preferentially, giving a mixture whence was isolated the 1-form of (I), [α]_D²⁰ -92.4° in H₂O. The classical formula is thus upheld. R. S. C.

Synthesis of ethyl 5-benzylidene-N-3-methylhydantoin-N-1-acetate and its derivatives. A. LITZINGER (J. Amer. Chem. Soc., 1934, 56, 673—677).

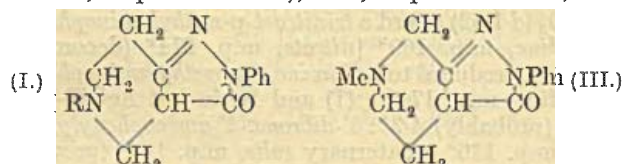
The Na derivative of 5-benzylidene-3-methylhydantoin and CH₂Cl·CO₂Et in EtOH give *Et* 5-benzylidene-3-methylhydantoin-1-acetate (I), b.p. 215—216°/5.5 mm., m.p. 50.5—51.5°, converted by HCl in EtOH

into an *isomeride* (II), m.p. 121—122° (corresponding *Me* ester, m.p. 115.5—116°). (I) is hydrolysed (EtOH-NaOH) to 5-benzylidene-3-methylhydantoin-1-acetic acid (III), m.p. 160—161° (*Na* salt, decomp. 294—295°), whilst (II) similarly gives an isomeric acid (IV), m.p. 222—223° [*Na*, m.p. 299—300° (decomp.)], *K* (+EtOH), m.p. 235—237° (decomp.), and *Pb* (+4H₂O), m.p. 241—242° (decomp.), salts]. (I)—(IV) are reduced [red P, HI (*d* 1.7)] to 5-benzyl-3-methylhydantoin-1-acetic acid, m.p. 150—151° [*Na* salt (+2EtOH), m.p. 275—276° (decomp.)], and *Et* ester, m.p. 49.5—51°, both hydrolysed [ac. Ba(OH)₂] to phenylalanine-*N*-acetic acid (A., 1933, 166). (I) or (II) and Br in CCl₄ give (probably) *Et* 5- α -bromobenzylidene-3-methylhydantoin-1-acetate, m.p. 113—113.5°, decomp. 195—200°. H. B.

Formation of histamine by irradiation of histidine. P. HOLTZ (Arch. exp. Path. Pharm., 1934, 175, 97—103).—Ultra-violet irradiation of histidine, especially at an alkaline reaction and in N₂, yields histamine. F. O. H.

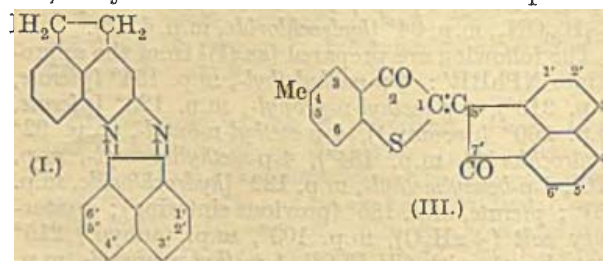
Reactivity of deoxybenzoin. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1934, 64, 100—102).—2:3-Diphenyl- $\alpha\beta$ -naphthoquinoxaline is prepared by the interaction of deoxybenzoin and benzeneazo- β -naphthylamine at 205—210°. E. W. W.

Pyrazolones derived from carbethoxypiperidones. S. M. E. ENGLERT and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 700—702).—Pyrazolones (I), where R is Me (II) (*hydrochloride*, m.p. 224—225°), Et (*hydrochloride*, m.p. 187—188°), Pr^a (*hydrochloride*, m.p. 191—192°), Bu^a, m.p. 117—118°, and



isoamyl, m.p. 125—126° (accompanied by a substance, m.p. 117—118°, possibly isomeric), are obtained from the requisite Et 1-alkyl-4-piperidone-3-carboxylate *hydrochloride*, NHPH·NH₂·HCl, and a little conc. HCl at 110—150°; the free bases could not be used. Et 1-methyl-3-piperidone-4-carboxylate similarly affords the pyrazolone (III) (*hydrochloride*, m.p. 191—193°). (II) could not be methylated to an antipyrine. H. B.

Dyes derived from acenaphthenequinone. IV. Azines and indigoid vat dyes. S. K. GUHA (J. Indian Chem. Soc., 1933, 10, 679—683; cf. A., 1933, 167).—By condensation of 2:3-diaminoacenaphthene



with acenaphthenequinone and its substitution products in AcOH 2:3:7':8'-diacenaphthazine (I), m.p.

> 315°, and its 3'-chloro-, m.p. > 315°, 3'-bromo-, m.p. > 315°, 1'-methoxy-, m.p. 293°, and 3':4'-dinitro- (II), sublimes > 315°, -derivatives are formed. These dye wool in yellow to chocolate (II) shades from an acid bath. 1-Methoxyacenaphthaphenazine has m.p. 187—188° (lit. 182—183°). Similarly, with 3-hydroxy-4-methylthionaphthen 4-methyl-2:8'-thionaphthenacenaphthyndigo (III), m.p. 265—266°, its 3'-chloro-, m.p. 284—285° (sinters 281°), 3'-bromo-, m.p. 282°, and 1'-methoxy-, m.p. 279—280°, -derivatives, are formed. These dye cotton scarlet from a Na₂S₂O₄ vat, and dye wool from an acid bath (? suspension). H. A. P.

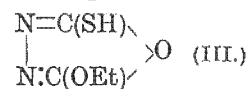
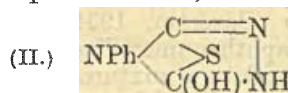
Acetyl derivatives of diphenylthiosemicarbazide. M. BUSCH and W. RENNER (Ber., 1934, 67, [B], 384—387).—The compound obtained by the action of AcCl on 1:4-diphenylthiosemicarbazide (I) cannot have the structure NPh·NH·C(NHPh)·S·Cl·Ac ascribed to it by McKee (J.C.S., 1915, 107, 1133), since analysis shows it to contain 1 H₂O < is thereby required. Since hydrolysis by hot H₂O is accompanied by intermediate production of the carbinol

base $\text{N}=\text{C}(\text{NHPh})\text{S}^-\text{NPh}\cdot\text{CMe}(\text{OH})$, m.p. 173°, it is regarded as $\text{N}^+\text{C}(\text{NHPh})\text{S}^-\text{NPh}\cdot\text{CMeCl}$ the possible triazole formula being excluded, as desulphurisation is not effected by HgO. McKee's "anhydride" is identified as 1:4-diphenyl-5-methyl-3:5-endothiotriazole (II), also obtained by the action of Ac₂O on (I), whereby a thermally unstable form, m.p. about 233°, is immediately produced. Treatment of 2:4-diphenylthiosemicarbazide with Ac₂O gives, in addition to 1-acetyl-2:4-diphenylthiosemicarbazide, m.p. 133° (McKee, loc. cit.), (I) and thence (II). McKee's "4-acetyl-1:4-diphenylthiosemicarbazide," m.p. 161° (decomp.), is probably $\text{N}=\text{C}(\text{NHPh})\text{S}^-\text{NPh}\cdot\text{C}(\text{NHPh})\text{Me}$ H. W.

N-Aminotriazoles of higher fatty acids. J. VOŘÍŠEK (Coll. Czech. Chem. Comm., 1934, 6, 69—76).—Prolonged heating of the higher aliphatic acids with N₂H₄·H₂O gives, in addition to the hydrazides, aminotriazole derivatives. The following are described: 1-amino-3:5-bis-λ-hydroxyheptadecyltriazole, m.p. 139.5—140.5°. [Ac₃ (an oil) and Ac₂ derivatives; hydrochloride, m.p. 105—106° (decomp.); sulphate, m.p. 106.5—107.5°]; 1-amino-3:5-bisheptadecyltriazole, m.p. 135.5—136° (hydrochloride; 1-Ac derivative, m.p. 87—88°). H. A. P.

Formation of heterocyclic compounds from derivatives of ethyl carbazinate. D. N. MAJUMDAR and P. C. GUHA (J. Indian Chem. Soc., 1933, 10, 685—692).—Et carbazinate (I) (prep. improved) adds PhNCS to form Et 4-phenylthiosemicarbazide-1-carboxylate, m.p. 141—142° (cf. A., 1923, i, 858); this with boiling 2N-aq. KOH loses 1EtOH and gives a compound, m.p. 283—284° (decomp.), which is not desulphurised by HgO and is therefore regarded as 3-hydroxy-4-anilo-3:5-endothio-2:3-dihydro-1:3:4-triazole (II), and with conc. HCl loses NH₂Ph to form 2-ethoxy-5-thiol-1:3:4-oxdiazole (III), m.p. 274—275° (decomp.) With PhNCO (I) gives Et 4-phenylthiosemicarbazide-1-carboxylate, m.p. 154—155°, and with

CS₂ and KOH it gives a K salt converted by MeI into Me carbethoxydithiocarbazinate, CO₂Et·NH·NH·CS₂Me, m.p. 80—91°, which is also formed from ClCO₂Me and Me dithiocarbazinate. (I) forms normal hydrazones with mono- and dialdehydes, and normal acyl derivatives with dicarboxylic chlorides. The o-nitrobenzylidene, m.p. 130—131°, salicylidene, m.p. 129—130°, p-tolylidene, m.p. 116—118°, cinnamylidene, m.p. 196—197°,



piperonylidene, m.p. 123—124.5°, furfurylidene, m.p. 132.5—133.5°, vanillylidene, m.p. 152.5—153.5°, glyoxylidenebis-, m.p. 305—306° (decomp.), carbonylbis-, m.p. 119—120°, oxalylbis-, m.p. 182—183° (decomp.), and o-phthalylbis-, m.p. 166—167°, -derivatives, camphorquinone-, m.p. 199.5—200°, and phenanthrenequinone-monocarbethoxyhydrazone, m.p. > 320° (sinters 275°), acetophenonecarbethoxyhydrazone, m.p. 119.6—120.6°, and Et₂ hydrazinedicarboxylate, m.p. 131.5—132.5° (ClCO₂Et), are described.

H. A. P.

Chlorophyll-A. H. FISCHER (J.C.S., 1934, 245—256).—A lecture. 1:3:5:8-Tetramethyl-2:4-diethyl-6-carboxyporphin-7-propionic acid has been synthesised and found to be identical with natural rhodoporphyrin, which on loss of the 6-CO₂ group yields pyrrroporphyrin (I), also obtained by direct synthesis. Ethylation of (I) leads to phylloporphyrin (II), showing that the unsubstituted group is at position 6. (I), (CH₂Cl)₂O, and HBr give bromomethylpyrrroporphyrin (haemin). γ-Methylpyrrroporphyrin (1:3:5:8-tetramethyl-2:4-diethyl-γ-methylporphyrin-7-propionic acid) is identical with natural (II). Reduction (HI-AcOH) of phaeophorbide yields phaeoporphyrins and of chlorin-e, chloroporphyrins; the constitution of these is discussed. Reduction with HI in the cold of chlorophyll, the phorbides, purpurins, and chlorins gives ketoporphyrins ("oxo-reaction"), but porphyrins and their leuco-compounds do not undergo the reaction. The "oxo-reaction" is due to the presence of a :CH₂ group which gives rise to ·CHO. The relationship between chlorophyll and haemin is discussed (cf. this vol., 420).

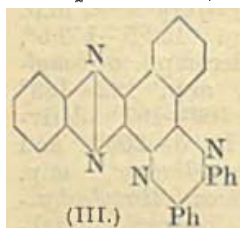
F. R. S.

Chlorophyll. VII. Oximes of phaeophorbide-b. A. STOLL and E. WIEDEMANN (Helv. Chim. Acta, 1934, 17, 456—470; cf. A., 1932, 1265; this vol., 308).—Methylphaeophorbide-b with cold C₂H₅N and NH₂OH·HCl gives its monoxime I, m.p. 280° (corr.), which is phase-positive, hydrolysed by HCl-Et₂O successively to phaeophorbide-b monoxime I (II) and phaeophorbide-b (III), which with NH₂OH gives (II); hydrolysis of (II) with MeOH-KOH-C₂H₅N gives rhodin-g oxime (IV), hydrolysed (HCl) to rhodin-g, which with NH₂OH gives (IV). Longer treatment at 100° converts (I) into a dioxime (V), not melting at 280° (corr.), which is phase-negative and is hydrolysed (HCl-Et₂O) to phaeophorbide-b dioxime [absorption spectrum identical with that of (V)], and then to phaeophorbide-b monoxime II (phase-negative), which gives 60% of (III) with 24% aq. HCl-Et₂O at 50°, but some decarboxylation (C₁₁)

also occurs giving, probably, pyrophosphoribide-*b*. The monoxime *I* in which the (rhodin) CO-*I* group is oximated, and the dioxime, give *a*-type absorption spectra, whereas monoxime *II* gives the *b*-type, and Fischer's hypothesis of a second CO group (CO-*II*) in chlorophyll-*b* is accepted, but it is not considered that CO-*I* can be in the propionyl side-chain.

J. W. B.

Oxidation of naphthoquinoxalines. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1934, 64, 91—99).—2 : 3-Diphenyl- $\alpha\beta$ -naphthoquinoxaline (I) is oxidised by CrO₃ in AcOH-Ac₂O to a mixture of its 5 : 6-quinone (II), m.p. 267°, which condenses with *o*-C₆H₄(NH₂)₂ giving the phenazine (III), m.p. above 300°, with 2 : 3-diphenyl-6-*o*-carboxyphenylpyrazine-5-carboxylic acid (IV), m.p. 148° (decomp.), also formed by action of KMnO₄ on (I). Heating (IV) with CaO furnishes 2 : 3 : 5-triphenylpyrazine (?), m.p. 143°. The action of H₂O₂-AcOH



on (I) and (IV) gives the respective 1(or 4)-oxides, m.p. 252° and 224°, which are reduced by SnCl₂ to (I) and to (IV). 3-Phenyl-naphthoquinoxaline (A., 1931, 1169) similarly yields a 1(or 4)-oxide, m.p. 236°, further oxidised to the quinone. E. W. W.

Violacein, the violet pigment of *Bacillus violaceus*. I. F. WREDE and A. ROTHHAAS (Z. physiol. Chem., 1934, 223, 113—118).—The cryst. pigment violacein (I), C₄₂H₃₅O₆N₅ or C₅₀H₄₂O₈N₆, decomp. > 350° (hydrochloride, sulphate, decomp. > 300°), is a monacid base, which on hydrogenation takes up 14 or 16 H. With Ac₂O-NaOAc, (I) yields a Ac₅ (or Ac₆) derivative, decomp. > 300°.

J. H. B.

Synthesis with $\beta\beta'$ -dichlorodiethyl ether. Morpholine derivatives. W. N. AXE and C. FREEMAN (J. Amer. Chem. Soc., 1934, 56, 478—479).—(CH₂Cl-CH₂)₂O (1 mol.), NPh-NH₂ (1 mol.), and 40% KOH (2 mols.) give *N*-anilinomorpholine, m.p. 107.5°, in 20—30% yield. *p*-Phenylene- (I), m.p. 196°, and diphenyl-4 : 4', m.p. 228.5°, -NN'-dimorpholines are similarly prepared from *p*-C₆H₄(NH₂)₂ and benzidine, respectively. (I) forms coloured additive compounds with various acids and heavy metal salts.

H. B.

1 : 3 : 4-Oxdiazines. W. J. HOPPENBROUWERS (Rec. trav. chim., 1934, 53, 325—354; cf. van Alphen, A., 1928, 780, 1386; 1929, 334, 707).— β -Aroyl(acyl)- α -chloroacetyl- α -phenylhydrazines are converted by anhyd. K₂CO₃ (NaOEt, NH₂Me, NHMe₂, or conc. aq. NH₃) in COMe₂ into Δ^2 -5-keto-4-phenyl-2-aryl(alkyl)-1 : 3 : 4-oxdiazines. The following compounds are new : β -benzoyl- α -*p*-bromophenylhydrazine, m.p. 156° (α -chloroacetyl derivative, m.p. 180°); β -*o*-, m.p. 171—172°, -*m*-, m.p. 156°, and -*p*-, m.p. 200°, -bromobenzoyl- α -phenylhydrazines (α -chloroacetyl derivatives, m.p. 163—164°, 162°, and 142°, respectively); β -*p*-bromobenzoyl- α -*p*-bromophenylhydrazine, m.p. 201° (α -chloroacetyl derivative, m.p. 191°); β -*p*-nitrobenzoyl- α -*p*-nitrophenylhydrazine, m.p. 265—268°; β -phenylacetyl- α -chloroacetyl- α -phenylhydrazine, m.p. 85°; β -acetyl- α -chloroacetyl- α -*p*-bromophenylhydrazine, m.p.

130°; β -benzoyl-, m.p. 150—151°, and β -acetyl-, m.p. 207°, - α -chloroacetyl- α -*p*-nitrophenylhydrazines; β -*o*-, m.p. 204°, -*m*-, m.p. 164°, and -*p*-, m.p. 188°, -nitrobenzoyl- α -chloroacetyl- α -phenylhydrazines; substituted 5-keto-1 : 3 : 4-oxdiazines : 4-phenyl-2-benzyl-, b.p. 180—188°/0.5—1 mm., 4-*p*-bromophenyl-2-methyl-, m.p. 58—59°, 2-phenyl-4-*p*-bromophenyl-, m.p. 136°, 4-phenyl-2-*o*-, m.p. 112—113°, -*m*-, m.p. 119°, and -*p*-, m.p. 137°, -bromophenyl-, 2 : 4-di-*p*-bromophenyl-, m.p. 164°, 4-*p*-nitrophenyl-2-methyl-, m.p. 97—98°, 2-phenyl-4-*p*-nitrophenyl- (I), m.p. 175°, 4-phenyl-2-*o*-, m.p. 148°, -*m*-, m.p. 156°, and -*p*-, m.p. 146° (II), -nitrophenyl-. The oxdiazines containing Ph (or substituted Ph) in the 2- and 4-positions are not hydrolysed [except with (I)] by 10% H₂SO₄; partial hydrolysis occurs with 15% H₂SO₄ in some cases. (II) is reduced (EtOH-NH₄HS) to Δ^2 -5-keto-4-phenyl-2-*p*-aminophenyl-1 : 3 : 4-oxdiazine, m.p. 143° (Ac derivative, m.p. 213—215°). Attempts to benzoylate or methylate the enolic form of Δ^2 -5-keto-2 : 4-diphenyl-1 : 3 : 4-oxdiazine were unsuccessful.

Δ^2 -5 : 6-Diketo-4-phenyl-2-aryl(alkyl)-1 : 3 : 4-oxdiazines are obtained from β -aroyl(acyl)- α -phenylhydrazines and (COCl)₂ in C₆H₆. Thus, β -phenylacetyl- α -phenylhydrazine (III) and 2 equivs. of (COCl)₂ give Δ^2 -5 : 6-diketo-4-phenyl-2-benzyl-1 : 3 : 4-oxdiazine (IV), m.p. 102—103° [use of 1 equiv. of (COCl)₂ affords a compound, m.p. 214—215°, which may be $\beta\beta'$ -di(phenylacetyl)- $\alpha\alpha'$ -diphenyloxalhydrazide, (CO-NPh-NH-CO-CH₂Ph)₂, and which is not hydrolysed by H₂O, dil. acid, or dil. alkali]. (IV) is hydrolysed by H₂O to (III), by H₂O-Et₂O to a substance, m.p. 138°, and by EtOH to β -phenylacetyl- α -ethoxyoxalyl- α -phenylhydrazine, CO₂Et-CO-NPh-NH-CO-CH₂Ph, m.p. 104—105° [also prepared from (III) and CO₂Et-COCl in C₆H₆]. (IV) and conc. aq. NH₃ in EtOH give oxamide; with NH₃Ph and NPh-NH₂, ox-anilide and -phenylhydrazide, respectively, are formed. The following substituted 5 : 6-diketo-1 : 3 : 4-oxdiazines are described : 4-*p*-bromophenyl-2-methyl-, m.p. 178°, 2-phenyl-4-*p*-bromophenyl-, m.p. 206°, 4-phenyl-2-*o*-, m.p. 138—140°, -*m*-, m.p. 245°, and -*p*-, m.p. 183—185°, -bromophenyl-, 2 : 4-di-*p*-bromophenyl-, m.p. 314°, 2-phenyl-4-*p*-nitrophenyl-, m.p. 212°, and 4-phenyl-2-*o*-, m.p. 183.5°, -*m*-, m.p. 179°, and -*p*-, m.p. 212—213°, -nitrophenyl- [the last three are also accompanied by $\beta\beta'$ -di-*o*-, m.p. 254°, -*m*-, m.p. 254°, and -*p*-, m.p. 275°, -nitrobenzoyl- $\alpha\alpha'$ -diphenyloxalhydrazide (CO-NPh-NH-CO-C₆H₄NO₂)₂]. These are hydrolysed (EtOH) to β -acetyl- α -*p*-bromophenyl-, m.p. 96°, β -benzoyl- α -*p*-bromophenyl-, m.p. 178°, β -*o*-, m.p. 118°. -*m*-, m.p. 110°, and -*p*-, m.p. 138.5°. -bromobenzoyl- α -phenyl-, β -*p*-bromobenzoyl- α -*p*-bromophenyl-, m.p. 138°, β -benzoyl- α -*p*-nitrophenyl-, m.p. 130°, and β -*o*-, m.p. 161°, -*m*-, m.p. 151.5°, and -*p*-, m.p. 159°, -nitrobenzoyl- α -phenyl- α -ethoxyoxalylhydrazine, respectively. β -Acetyl- α -*p*-nitrophenylhydrazine and (COCl)₂ give a substance, m.p. about 70°.

β -Phenylacetyl- α -chloroacetyl- α -phenylhydrazine and the requisite NH₂Ar at 100° give β -phenylacetyl- α -anilinoacetyl- (V), m.p. 154°, - α -*p*-bromoanilinoacetyl-, m.p. 186°, and - α -*o*-, m.p. 165°, -*m*-, m.p. 129—130°, and -*p*-, m.p. 163°, -toluidinoacetyl- α -phenylhydrazines. β -Acetyl-, m.p. 201°, and β -benz-

oyl, m.p. 167°, α -p-bromophenyl-, β -acetyl- α -p-nitrophenyl-, m.p. 202°, β -o-, m.p. 174—175°, and -p-, m.p. 179—180°, -bromo- and β -o-, m.p. 222°, and -m-, m.p. 193·5°, -nitro-benzoyl- α -phenyl-, and β -p-bromobenzoyl- α -p-bromophenyl-, m.p. 183°, α -anilinoacetylhydrazines are also prepared. (V) is hydrolysed (20% H_2SO_4 , EtOH) to α -anilinoacetyl- α -phenylhydrazine, m.p. 157° (anisylidene, m.p. 175—176°, and piperonylidene, m.p. 190°, derivatives). β -Acetyl- α -p-bromoanilinoacetyl- α -phenylhydrazine, m.p. 189—190°, is similarly hydrolysed to α -p-bromoanilinoacetyl- α -phenylhydrazine, m.p. 194° (benzylidene, m.p. 224°, anisylidene, m.p. 205°, and piperonylidene, m.p. 218°, derivatives). H. B.

Toxoflavin, the yellow poison from Bongkrek. A. G. VAN VEEN and W. K. MERTENS (Rec. trav. chim., 1934, 53, 398—404).—The yellow pigment previously described (A., 1933, 1207; this vol., 454) is now termed *toxoflavin* (I), probably $\text{C}_6\text{H}_5\text{O}_2\text{N}_4$, m.p. 172°, containing a $>\text{NMe}$ group. (I) dialyses rapidly through parchment and is stable towards H_2O_2 , HNO_3 , and $\text{Br}-\text{H}_2\text{O}$; reduction (SO_2 in slightly acidic or alkaline solution gives a colourless compound, which is re-oxidisable (air; H_2O_2 ; $\text{Br}-\text{H}_2\text{O}$) to (I). (I) gives an additive compound with NaHSO_3 , does not afford $\text{CO}(\text{NH}_2)_2$ on hydrolysis [$\text{Ba}(\text{OH})_2$], has no acidic properties, and is decolorised by aq. NH_3 and very dil. alkali (the colour is restored only by immediate neutralisation). Careful treatment of (I) with $\text{N}-\text{HCl}$ gives a colourless compound, $\text{C}_6\text{H}_8\text{O}_3\text{N}_4$, m.p. 250° (decomp.), sublimes at 230°, which is unaffected by conc. HCl at 100° and dissolves in alkali to an intense yellow solution. Oxidation (KClO_3 , HCl) of (I) affords NH_3 , NH_4Me , and alloxan (or methylalloxan). Reduction (H_2 , PtO_2 , AcOH) results in the uptake of 3 mols. of H_2 per mol. of (I) (about 1 mol. is absorbed using Pt-black and EtOAc); aeration of the resultant solutions restores the original colour. Evidence is given to show that (I) is probably formed in combination with some complex. H. B.

Derivatives of benzoyl- and furoyl-thiocarbimides and their use in synthesising heterocyclic compounds. I. B. DOUGLAS and F. B. DAINS (J. Amer. Chem. Soc., 1934, 56, 719—721).— BzNCS (I) (from NH_4SCN and BzCl in COMe_2) and $\text{NHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ give $\text{N-benzoyl-N'-phenyl-N'-}\beta$ -hydroxyethylthiocarbimide (II), m.p. 154°, converted (cold 80% H_2SO_4 or 48% HBr) into 2-benzoylimino-3-phenylthiazolidine, m.p. 122°, which is hydrolysed to 2-keto-3-phenylthiazolidine, and converted by $\text{EtOH}-\text{NaOH}$ into a compound (III), m.p. 173—174°. (II) and yellow HgO in C_6H_6 afford 2-benzoylimino-3-phenyloxazolidine, m.p. 117°. $\text{N-Benzoyl-N'-}\beta$ -hydroxyethyl-, m.p. 128°, and - N'-o- , m.p. 141°, and -p-, m.p. 136°, -tolyl- $\text{N'-}\beta$ -hydroxyethyl-thiocarbimides are similarly prepared and converted into 2-benzoylimino-, m.p. 168°, and 2-benzoylimino-3-o-, m.p. 137—138°, and -p-, m.p. 154°, -tolyl-thiazolidine, respectively. 2-Benzoylimino-3-o- and -n-tolyloxazolidines have m.p. 103° and 134°, respectively. $\text{NHPh}\cdot\text{CHET}\cdot\text{OH}$ [$\text{NHPh}\cdot(\text{CH}_2)_3\cdot\text{OH}$] and (I) give $\text{N-benzoyl-N'-phenyl-N'-}\gamma$ -hydroxypropylthiocarbimide, m.p. 94°, convertible (H_2SO_4) into 2-benzoylimino-3-phenylthiazan, m.p. 137°. $\text{N-Benzoyl-N'-phenyl-N'-carbethoxymethyl-}$, m.p.

165° [from (I) and $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$], or the -carboxymethyl-, m.p. 166—167°, -thiocarbimide similarly gives 3-benzoyl-1-phenyl-2-thio-4-glyoxalone, m.p. 163°. *o-Benzoylthiocarbamidobenzoic acid* (IV), m.p. 159—160° (decomp.), re-solidifying with m.p. 190—200° [from (I) and $\text{o-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$], and H_2SO_4 afford 4-keto-2-thio-3-benzoyl-1:2:3:4-tetrahydroquinazoline, m.p. 157—158°; this and (IV) are hydrolysed (NaOH) to 4-keto-2-thio-1:2:3:4-tetrahydroquinazoline (V), m.p. 305—310°. (IV) heated at 160—175° gives H_2S and a S-free compound, m.p. 207—208°. (V) is methylated [Me_2SO_4 ; aq. NaOH (min. amount)] to 4-keto-2-methylthiol-3:4-dihydroquinazoline, m.p. 219°; excess of the reagents gives 2:4-diketo-3-methyl-1:2:3:4-tetrahydroquinazoline, m.p. 236°. *S-Methylphenylthiocarbimide* and (I) afford a methylthiol-1:1'-di-phenyl-2-thiodihydrotriazine, m.p. 211°. The following substituted thiocarbimides are prepared from furoylthiocarbimide and the appropriate amine: *N-furoyl-*, m.p. 183°; *N-furoyl-N'-methyl-*, m.p. 142°, -*N'-ethyl-*, m.p. 101—102°, -*N'-benzyl-*, m.p. 122°, -*N'-phenyl-*, m.p. 116°, -*N'-o-*, m.p. 115—116°, -m-, m.p. 99°, and -p-, m.p. 130°, -tolyl-, -*N'-\alpha-*, m.p. 186°, and - β -, m.p. 139—140°, -naphthyl-, -*N'-phenyl-N'-methyl-*, m.p. 98—99°, -*N'-phenyl-N'-benzyl-*, m.p. 124°, -*N'-N'-diphenyl-*, m.p. 139—140°, and -*N'-phenyl-N'-hydroxyethyl-* (VI), m.p. 111°. 2-Furoylimino-3-phenylthiazolidine, m.p. 123° [from (VI) and 80% H_2SO_4], is hydrolysed (alkali) to (III). H. B.

Reactions of aldehydes and ketones. Synthesis of thiodiazolines from aldehydes. H. WUYTS and (MLLE.) A. LACOURT (Bull. Acad. roy. Belg., 1934, [v], 20, 156—167).—The appropriate aldehyde and thioacetylhydrazine in EtOH with a little HCl give the following substituted 2:3-dihydro-1:3:4-thiodiazoles (thiodiazolines) (I) (cf. A., 1933, 839): 3:5-diphenyl-2-o-, m.p. 120°, -m-, m.p. 139°, and -p-nitrophenyl, m.p. 129°; 3:5-diphenyl-p-dimethylaminophenyl, m.p. 144°; 3-phenyl-2-p-anisyl-5- α -naphthyl, m.p. 101°; 3-phenyl-2-piperonyl-5- α -naphthyl, m.p. 131°; 5-phenyl-3-p-bromophenyl-, m.p. 128°, and -3- α -naphthyl-2-(1-furyl), m.p. 118°; 3-phenyl-2-tolyl-5- α -naphthyl, m.p. 150°; 3-phenyl-2:5-di- α -naphthyl, m.p. 196°; 3-phenyl-o- α -naphthyl-2- β -naphthyl (II), m.p. 197·5° (picrate, m.p. 202°). The m.p. quoted are the temp. at which the substance melts within 20 sec. when suddenly immersed. The m.p., similarly determined, of other derivatives of (I) are 1—3° > previously quoted (*loc. cit.*), and those of thiobenzoyl-, thiobenzoylbromo-, and α -naphthoyl-phenylhydrazine are 92°, 132°, and 164°, respectively. 3-Phenyl-5-methyl- and -5-benzyl- and 3:5-diphenyl-thiodiazoline give picrates, m.p. 147·5°, 145°, and 176°, respectively. (II) forms a compound with 1 mol. of AgNO_3 and the other derivatives slowly reduce AgNO_3 . R. S. C.

Optical analysis and rotatory power of glycothiodiazolines. H. WUYTS and R. VERSTRAETEN (Bull. Acad. roy. Belg., 1934, [v], 20, 168—177).—The glycothiodiazolines from glucose, mannose, and galactose (A., 1933, 810) are mixtures of dextro- and laevo-rotatory isomerides, the max. $[\alpha]_{\text{D}}^{20}$ observed being -406·6° and +697°; -233·6° and +1203° -568·2° and +1974°, respectively. R. S. C.

Isolation of hepaflavin. P. KARRER, H. SALOMON, and K. SCHÖPP (Helv. Chim. Acta, 1934, 17, 419—425).—A detailed scheme for the isolation of cryst., hepaflavin (I) $C_{17}H_{20}O_6N_4$, m.p. about 280°, from liver extract is given. The composition, m.p., cryst. form, and absorption spectra of (I) are identical with those of lactoflavin. J. W. B.

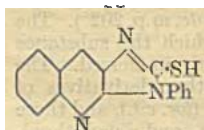
Influence of attached rings on formation and stability of heterocyclic compounds. II. T. N. GHOSH (J. Indian Chem. Soc., 1934, 11, 23—32; cf. this vol., 307).— $NH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$ (I) with *o*- and *p*- $C_6H_4Me \cdot NCS$ in aq. EtOH gives β -*o*-, m.p. 144—145° (decomp.), and β -*p*-, m.p. 151—152° (decomp.), -*tolylthiocarbamidopropionic acid*, respectively, which could not be hydrolysed (conc. HCl). $NH_2 \cdot CHPh \cdot CH_2 \cdot CO_2H$ and $PhNCS$ in EtOH afford β -*phenylthiocarbamido*- β -*phenylpropionic acid* (II), m.p. 145—146° (decomp.), converted by Ac_2O into 2-*anilino*-6-*keto*-4-*phenyl*-1:3-*thiazine*,

$CH_2 \cdot \begin{array}{c} CHPh \cdot N \\ \diagup \quad \diagdown \\ CO \quad S \end{array} \cdot C \cdot NHPh$, m.p. 232—233° (decomp.),

which is not desulphurised by HgO and is readily hydrolysed (cold *N*-KOH) to (II). β -*o*-*Tolylthiocarbamido*- β -*phenylpropionic acid*, m.p. 154—155° (decomp.), similarly gives 2-*o*-*toluidino*-6-*keto*-4-*phenyl*-1:3-*thiazine*, m.p. 169°. 2:4-Diketo-1:2:3:4-tetrahydroquinazoline [1:3-Et₂ derivative, m.p. 108° (lit. 105—106°)] is not hydrolysed by EtOH-KOH,

whereas $CH_2 \cdot \begin{array}{c} CH_2 \cdot NH \\ \diagup \quad \diagdown \\ CO \quad NH \end{array} \cdot CO$ similarly gives (I). *o*- $NHPh \cdot CO \cdot NH \cdot C_6H_4 \cdot CO_2H$ and Ac_2O give the oxazine, *o*- $C_6H_4 \cdot \begin{array}{c} N \cdot NHPh \\ \diagup \quad \diagdown \\ CO \quad O \end{array}$ m.p. 124—125°, whilst β -*phenylcarbamido*- β -*phenylpropionic acid*, m.p. 168—169° (decomp.), similarly affords 2-*anilino*-6-*keto*-4-*phenyl*-1:3-*oxazine*, $CH_2 \cdot \begin{array}{c} CHPh \cdot N \\ \diagup \quad \diagdown \\ CO \quad O \end{array} \cdot C \cdot NHPh$ m.p.

221—222°; these oxazines are hydrolysed very rapidly by hot 0.1*N*-alkali. *Salicylideneanthranilic acid*, m.p. 188—190°, and Ac_2O give the lactone, *o*- $C_6H_4 \cdot \begin{array}{c} CH \cdot N \\ \diagup \quad \diagdown \\ O \quad CO \end{array} \cdot C_6H_4 \cdot o$, m.p. 156—157°, which is relatively stable (owing to the presence of the two C_6 rings) to cold alkali. $NH_2 \cdot CH_2 \cdot CO_2H$ with *o*- and *p*- $C_6H_4Me \cdot NCS$ in aq. EtOH affords 4-*keto*-2-*thion*-3-*o*-, m.p. 230° (darkens and decomp. at 105°) (5-*benzylidene* derivative, m.p. 180—181°), -*tolyl*-1:3-*diazole*, m.p. 229—146°, and -3-*p*-, m.p. 229—146°, and -3-*p*-, m.p. 229—146°.



(III.)

230° (darkens and decomp. at 105°) (5-*benzylidene* derivative, m.p. 180—181°), -*tolyl*-1:3-*diazole*, m.p. 229—146°, and -3-*p*-, m.p. 229—146°. *ole*, $\begin{array}{c} NH \cdot CS \\ \diagup \quad \diagdown \\ CH_2 \cdot CO \end{array} \cdot N \cdot C_6H_4Me$, respectively, hydrolysed (EtOH-KOH) to *o*-, m.p. 141—142° (decomp.), and *p*-, m.p. 147—148° (decomp.) [*K* salt, m.p. 240° (decomp.)], -*tolylthiocarbamidoacetic acid*, respectively. The 5-*o*-*nitrobenzylidene* derivative, m.p. 216—218°, of 4-*keto*-2-*thion*-3-*phenyl*-1:3-*diazole* (5-*benzylidene* derivative, m.p. 196—197°), is reduced (Sn, conc. HCl) to the *quinoline* (III), m.p. 186°. H. B.

Ergot alkaloids. II. Degradation of ergotinine with alkali. Lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1934, 104, 547—551; cf. A., 1932, 1147).—When ergotinine is dis-

solved in *N*-KOH-McOH, the McOH removed, and the resinous residue treated with 8% aq. KOH, there are formed *lysergic acid*, $C_{14}H_{12}N(NMe) \cdot CO_2H$, m.p. 238° (decomp.), $[\alpha]_D^{25} +40^\circ$ in C_6H_5N (*Me* ester, m.p. 168°), $Pr^{\beta} \cdot CO \cdot CO_2H$ [NH_4 salt, m.p. 175° (sublimation); phenylhydrazone, m.p. 152°], and NH_3 . Similar treatment of ergine gives a different acid. R. S. C.

Amidation with sodium and potassium amides in the alkaloid series. I. α -Aminoanabasine. M. M. KATZNELSON and M. J. KABATSKNIK (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 406—411).—With $NaNH_2$ in various solvents (best in NMe_2Ph at 120—150°) anabasine (Orékhov *et al.*, A., 1931, 498) gives an α - NH_2 -derivative (2- or 6-), m.p. 105—106° [*picrate*, m.p. 233—233.5° (decomp.)]; *platinichloride*, m.p. 225°]. J. W. B.

Action of hydriodic acid on lupanine. G. R. CLEMO and R. RAFFER (Ber., 1934, 67, [B], 463—464; cf. Winterfeld *et al.*, A., 1931, 371, 1433; Cremo, *ibid.*, 1931, 970).—Treatment of lupanine (I) with very conc. HI and red P at 150—260° does not appear to afford β -lupinane unless lupinine (II) is present in the initial material, which is probably the case in the absence of special purification. Winterfeld's results would require the presence of $\leq 10\%$ of (II) in (I) which would cause a very profound depression of the m.p. H. W.

Stereochemistry of 2:2'-disubstituted diphenyls. IV. Diphenates of the cinchona alkaloids. (Miss) M. S. LESSLIE and E. E. TURNER (J.C.S., 1934, 347—350).—*Quinine diphenate alcoholate* (I) (1EtOH), m.p. 217—218°, and *acetone* (1COMe₂), m.p. 217—218°, *quinidine* (+2EtOH), *cinchonine* (1EtOH), *cinchonidine* (1EtOH), and *dihydroquinine diphenate* (+3EtOH) are strongly dextrorotatory and show slight mutarotation. A possibility is that in solution the alkaloid diphenate undergoes a very rapid process of asymmetric induction, only the last stages being detectable. The optical rotation of (I) in a series of EtOH-H₂O mixtures shows that the extent of the induction process varies inversely as the dissociation; induction is greater in conc. than in dil. EtOH solution. *Quinine phthalate alcoholate* is levorotatory and does not show mutarotation. F. R. S.

Microchemistry of quinine carbonate (Aristochine). M. WAGENAAR (Pharm. Weekblad, 1934, 71, 316—319).—Quinine carbonate (I) dissolved in dil. mineral acids fails to give all the reactions of quinine, particularly the formation of the sparingly sol. iodosulphate. (I) reacts with KI-I solution and $H_2C_2O_4$ giving the *iodo-oxalate* (characteristic dichroic needles), which differentiates it from equinine. (I) forms a sparingly sol. nitrate, but this compound is unsuitable for microchemical identification. Directions are given for carrying out microchemically the colour reaction produced by Cl_2 and NH_3 on quinine alkaloids. S. C.

Alkaloids of *Alstonia* barks. I. *A. constricta*. F. Muell. T. M. SHARP (J.C.S., 1934, 287—291).—The bark of *A. constricta* contains at least 4 alkaloids, one of which is *cryst.* and appears to be *alstonine*,

$C_{21}H_{20}O_3N_2 \cdot 4H_2O$, sinters 77° , transparent 130° (from EtOH, containing $1.25H_2O$) (Hesse, Ber., 1878, 11, 1546). It forms a *sulphate*, m.p. 209° , $[\alpha]_D +118.6^\circ$ in H_2O ; *acid sulphate*, m.p. $246-248^\circ$ (decomp.), $[\alpha]_D +113.1^\circ$ in H_2O ; *hydrochloride*, m.p. 286° (decomp.), $[\alpha]_D +131.9^\circ$ in H_2O ; *acid oxalate*, m.p. 239° (decomp.); *nitrate*, m.p. $262-263^\circ$ (decomp.); *picrate*, m.p. $194-195^\circ$; *hydriodide*, m.p. 291° (decomp.); and *monomethiodide*, m.p. 246° . Preliminary experiments on the constitution are described.

F. R. S.

Strychnos alkaloids. LXXIX. Nature of the acidic products of the oxidation of benzylidene- and 11-hydroxy-dihydrostrychnine. H. LEUCHS and H. BEYER (Ber., 1934, 67, [B], 459-463).—Contrary to Kotake *et al.* (A., 1933, 1061), the acid (I) obtained by oxidising benzylidenedihydrostrychnine with $KMnO_4$ in $COMe_2$ is $C_{21}H_{22}O_5N_2$; it is frequently mixed with a *hydrate*, whereas the *perchlorate* gives consistent analytical results. Hydrolysis of (I) with $Ba(OH)_2 \cdot H_2O$ at 95° gives BaC_2O_4 and a substance isolated as the *perchlorate* $C_{19}H_{24}O_3N_2 \cdot 2HClO_4$, $[\alpha]_D^{25} -84.4^\circ/d$. Bromination of (I) affords the compound $C_{21}H_{21}O_5N_2Br$, m.p. $237-239^\circ$ (decomp.), $-63.8^\circ/d$ in NaOH, hydrolysed by $Ba(OH)_2$ at 100° to BaC_2O_4 and the substance $C_{19}H_{23}O_3N_2Br$ (*diperchlorate*, $[\alpha]_D^{25} -103.5^\circ/d$).

H. W.

Narcotine.—See this vol., 476.

Recent syntheses of alkaloids. E. SPATH (Bull. Soc. chim., 1933, [iv], 53, 1358-1387).—A lecture.

Diarsyls. VII. 4 : 4''-Dihydroxy- and 3 : 3' : 3'' : 3'''-tetrahydroxy-tetraphenyldiarsyl. Reaction between p-hydroxy- and p-aminophenylarsine and tetraphenylarsyl oxide. F. F. BLICKE and J. F. ONETO (J. Amer. Chem. Soc., 1934, 56, 685-687).—*p*-Nitrodiphenylarsinic acid, m.p. $177-179^\circ$ [prepared by Sakellarios' method (A., 1924, i, 1247)], is reduced ($FeSO_4$, aq. NaOH) to the NH_2 -acid, m.p. $215-216^\circ$, convertible into *p*-hydroxydiphenylarsinic acid, m.p. $202-203^\circ$. This is reduced (H_3PO_2 , little HI, AcOH) to 4 : 4''-dihydroxy-tetraphenyldiarsyl, m.p. $161-163^\circ$ (sealed tube in N_2). 3 : 3'-Dihydroxydiphenylarsinic acid (I), darkens about 202° (Me_2 ether, m.p. $151-153^\circ$), prepared from the $(NH_2)_2$ -acid, is similarly reduced (in EtOH) to 3 : 3' : 3'' : 3'''-tetrahydroxytetraphenyldiarsyl, m.p. $207-208^\circ$ (sealed tube in N_2), also obtained [with $(AsPh_2)_2$ (II)] from $AsHPh_2$ and $[3 : 3'-(OH)_2C_6H_4 \cdot As]_2O$. 3 : 3'-Dihydroxydiphenylbromo-, m.p. $131-133^\circ$, and -iodo-, m.p. $130-131^\circ$, -arsines are prepared from (I) by the usual methods. The above diarsyls absorb O_2 readily. $(AsPh_2)_2O$ and *p*-OH-C₆H₄·AsH₂ in C_6H_6 give (II) and (*p*-OH-C₆H₄·As.)₂; *p*-NH₂-C₆H₄·AsH₂ similarly affords (II) and (*p*-NH₂-C₆H₄·As.)₂.

H. B.

Hexa-alkyltriaminotriphenyl-phosphines and -phosphine oxides. E. KOENIGS and H. FRIEDRICH (Annalen, 1934, 509, 138-141).— $NPhMe_2$, C_3H_5N , and $POCl_3$ at 140° give *pp'p''*-hexamethyltriaminotriphenylphosphine oxide, m.p. 290° (lit. $149-152^\circ$ and $319-320^\circ$); $NPhEt_2$ similarly affords *pp'p''*-hexaethyltriaminotriphenylphosphine oxide, m.p. 239° .

pp'p''-Hexamethyl-, m.p. 308° (lit. 262° and 273°), and *pp'p''*-hexaethyl-, m.p. 274° , -triaminotriphenylphosphines are similarly prepared using PCl_3 .

H. B.

Organic selenium compounds. III. Decomposition of selenium phenyl halides. D. G. FOSTER (Rec. trav. chim., 1934, 53, 405-416).— $SePhCl_3$ (A., 1933, 407) heated at $110-115^\circ$ (bath) gives *Se p-chlorophenyl chloride* (I), b.p. $103-104^\circ/4$ mm.; $SePhCl_3 \rightarrow SePhCl + Cl_2 \rightarrow HCl + p-C_6H_4Cl \cdot SeCl$. $SePhBr_3$ (*loc. cit.*) similarly affords *Se p-bromophenyl bromide* (II), b.p. $127-129^\circ/4$ mm. When (I) and (II) are kept, crystals of *pp'-dichloro-* (III), b.p. $192^\circ/1$ mm., m.p. 89° , and *pp'-dibromo-* (IV), m.p. $114-115^\circ$, -diphenyl diselenide, respectively, are deposited. *p*-Chloroselenophenol, m.p. 57° (from *p*-C₆H₄Cl·MgBr and Se followed by decomp. with dil. HCl), EtBr, and aq. EtOH-NaOH give *p-chlorophenyl Et selenide*, b.p. $85^\circ/1$ mm., $90^\circ/3$ mm.; the *dichloride*, m.p. $84-85^\circ$ (decomp.), of this decomposes when heated to EtCl and (I) [and (III)]. *p*-Bromoselenophenol, m.p. 84° , similarly affords *p-bromophenyl Et selenide*, b.p. $146^\circ/18$ mm.; the *dibromide*, m.p. $123-124^\circ$ (decomp.), of this decomposes to EtBr and (II) [and (IV)]. *Se p-chlorophenyl trichloride* (V), m.p. 184° (decomp.) [from (III) or *Se Ph chloride* (VI), b.p. $92^\circ/5$ mm., m.p. $64-65^\circ$ (prep.; *loc. cit.*), and Cl_2 in Et_2O], decomposes at $>160^\circ$: $3p-C_6H_4Cl \cdot SeCl_3 \rightarrow 3p-C_6H_4Cl_2 + SeCl_4 + Se_2Cl_2$. *Se p-bromophenyl tribromide* (VII), m.p. 132° (decomp.) [from (IV) and Br in light petroleum], decomposes at 135° to (II) and Br. (I) is hydrolysed (H_2O) to (III) and *p-chlorophenylseleninic acid* (VIII), m.p. $183-184^\circ$; (II) similarly gives (IV) and *p-bromophenylseleninic acid* (IX), m.p. 187° (decomp.), whilst (VI) and $SePhBr$ afford $(SePh)_2$ and $PhSeO_2H$. It is considered that Se aryl monohalides are normally equilibrium mixtures: $3SeArX \rightleftharpoons SeArX_3 + (SeAr)_2$. (VIII) and (IX) are also prepared by hydrolysis (H_2O) of (V) and (VII), respectively, and by oxidation (HNO_3 ; Pyman, J.C.S., 1919, 115, 166) of (III) and (IV), respectively.

H. B.

Action of thioglycollanilide and of thiophenol on arylstibinic acids. G. SCHUSTER (J. Pharm. Chim., 1934, [viii], 19, 264-265).—Thioglycollanilide (I) with $SbPhCl_2$ (II) and with $SbPh_2Cl$ (III) gives only dithioglycollanilide. (I) reacts neither with *p*-SbO·C₆H₄·NO₂ (IV) nor with *p*-SbO·C₆H₄·OEt (V). $PhSH$ (VI) gives with (II) an unstable substance, m.p. 65° approx., which could not be purified, and with (III) in C_6H_6 a white, cryst., unstable substance, m.p. 83° , M 377 ($SbPh_2 \cdot SPh = 383$), which readily hydrolyses with regeneration of (VI). (IV) and (V) gave products with (VI) which could not be purified.

W. S.

Spectroscopic identification of phenylalanine in protein material. W. F. ROSS (J. Biol. Chem., 1934, 104, 531-534).—Phenylalanine (I) shows at 2680, 2640, 2585, 2525, and 2480 Å. absorption bands suitable for identifying (I) in proteins, e.g., gelatin and lucerne proteins, or their hydrolysates after removal of tryptophan and tyrosine.

C. G. A.

Sericin fractions of silk. H. MOSHER (Canad. Text. J., 1934, 51, 31-32).—Silk sericin is separable

by fermentation and microscopic methods into three fractions (*A* and *B* form an outer layer of the fibre, and *C* an inner layer). *A*, sol. in hot H_2O , is readily attacked by enzymes, and acid and alkali gives peptones and proteoses. Its aq. solution disperses acid alizarin dyes, but is not generally a good peptising agent. *B*, sparingly H_2O -sol., resists proteolysis by enzymes; it is dispersed by H_2O at 105° under pressure and is then an efficient dispersing agent for fats, oils, and waxes. The high dispersing power of boiled-off liquor is due to its content of *B*. *B* is converted into *A* by atm. influences or by acid or alkali treatment so that the H_2O -sol. content of silk increases during storage. *C* is insol. in all common solvents and resists enzyme attack; it resembles fibroin. The decomp. products (acid; alkali) differ from those obtained from *A* and *B*. Most of the yellow silk pigment lies between the inner (*C*) and outer (*A* and *B*) sericin layers. A. J. H.

Use of sulphuric, hydrochloric, phosphoric, and nitric acids, and of alkalis for catalytic fission of ovalbumin. V. S. SADIKOV, V. A. VADOVA, and R. G. KRISTALLINSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 411—415).—Hydrolysis of ovalbumin with 2–4% solutions of H_2SO_4 , HCl , H_3PO_4 (I), and HNO_3 (II) at 180° for 3–6 hr. brings 81.5–88.4% of the total N (*A*) into solution, mainly as *cyclopeptides*, since only 25.4–29% of (*A*) is NH_2-N (*B*). (I) causes rather more deep-seated fission, and (II) forms basic products. With 2% Na_2CO_3 under similar conditions 86.4% of (*A*) goes into solution, only 13% being (*B*). With 0.1% $NaOH$ (*B*) is 30–35%. J. W. B.

Preparation of dipeptidephosphoric acid from caseinogen. G. SCHMIDT (Z. physiol. Chem., 1934, 223, 86–88).—A dipeptidephosphoric acid consisting of serine, glutamic acid, and H_3PO_4 is obtained from caseinogen (cf. Levene and Hill, A., 1933, 1062) by tryptic digestion, pptn. by Pb acetate, regeneration by H_2S , and pptn. of the *Ba* salt ($C_8H_{10}O_9N_2P_2Ba$), by $EtOH$. J. H. B.

Gelatin-tannin reaction. F. C. THOMPSON (J. Soc. Leather Trades Chem., 1934, 18, 175–178).—Vegetable tannin (*T*) combines with gelatin (*G*) in the same way as does HCl . Evidence is adduced to show that *T* displaces the HCl from a *G*- HCl compound in accordance with the theory of addition of strong acids to weak ones. D. W.

Quantitative organic semi-micro-methods of combustion. B. L. MANJUNATH and S. SIDDAPPA (J. Mysore Univ., 1932, 6, 123–139).—Methods and apparatus based on existing micro-technique have been developed for the determination of C, H, and N, using 20–30 mg. of substance and an ordinary balance. Unlike micro-technique proper, the new methods are claimed to be practicable for general adoption. W. S.

Recent improvements introduced by ter Meulen into his methods of analysis. (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1934, 43, 73–92).

The ter Meulen methods for the determination of C, H, O, N, S, Cl, Br, I, As, Hg, Cd, and Zn are described in detail and experimental results for

numerous substances are quoted. The following modifications in procedure have been introduced. In the determination of O, asbestos is dispensed with, owing to the difficulty of drying it thoroughly, and reduced Ni containing about 10% ThO_2 is used as catalyst. If halogens are present, pure Ni must be used. In the determination of N as NH_3 , asbestos impregnated with the same catalyst is used. This method is of more general application than the ordinary oxidation method in which the N is measured as N_2 . A red-hot Pt spiral is used to ensure completion of the combustion in the determination of C and H and of the reduction in the determination of S as H_2S . Where the reduction of S compounds presents exceptional difficulty, asbestos may be used. If N is present in addition to S, $(CN)_2$ is formed during the reduction and aq. KOH therefore cannot be used for the absorption of the H_2S . A mixture of equal vols. of 10% aq. $ZnSO_4$ and 10% aq. $NaOAc$ acidified with one drop of $AcOH$ should be employed. Certain improvements in the apparatus used are also described. D. R. D.

Volumetric determination of formaldehyde in presence of sulphites. J. EURY (J. Pharm. Chim., 1934, [viii], 19, 261–264).—The CH_2O (I) is made to reduce standard $HgCl_2$ (II) in presence of Na_2SO_3 , the resulting Hg is removed, and the amount of (I) is calc. from the excess of (II) determined in a convenient manner in the filtrate. The accuracy of the method is checked by an assay of $CH_3O-KHSO_3$. W. S.

Styphnic acid. III. Use as a reagent for the identification of aromatic compounds containing benzene nuclei. T. S. MA, C. T. HSIA, P. P. T. SAH. IV. Use as a reagent for the identification of heterocyclic nitrogen compounds. V. Hoo, T. S. MA, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 151–156, 191–199).—III. Additive compounds of styphnic acid with the following compounds have been prepared and the acid determined with $NaOH$: $C_{10}H_8$, m.p. 168–169° (lit. 165.6°), 1- $C_{10}H_7Cl$, m.p. 126–128° (lit. 109.8°), 1- $C_{10}H_7Br$, m.p. 116–118° (lit. 101.2° and 107.8°), α -, m.p. 183–184°, and β - $C_{10}H_7OH$, m.p. 169–170°, α -, m.p. 181–182°, and β - $C_{10}H_7NH_2$, m.p. 194–195°, anthracene, m.p. 180–181° (lit. 176.3°), and phenanthrene, m.p. 138–139° (lit. 132.7° and 125.6°).

IV. The following *styphnates* have been prepared as above: C_5H_5N , m.p. 184.5–185.5°, α -, m.p. 179.5–180.5°, and β -picoline, m.p. 153–154°, piperidine, m.p. 231–232°, quinoline, m.p. 207–208°, 8-hydroxyquinoline, m.p. 193–194°, *p*-nitro-, m.p. 189.5–190.5°, *p*-amino-, m.p. 239–240°, *o*-, m.p. 218–219°, and *p*-tolu-quinoline, m.p. 201–202°, quinaldine, m.p. 213–214°, *p*-toluquinaldine, m.p. 199–200°, carbazole, m.p. 178.5–179.5°, and phenyl-acridine, m.p. 209–210°. F. R. S.

Determination of saturated and unsaturated sterols, dihydrocholesterol, coprosterol, and cholesterol. H. DAM (Biochem. Z., 1934, 268, 297–303).—A crit. review of existing methods.

P. W. C.
Determination of furfural[dehyde] at 0° with bromine. E. E. HUGHES and S. F. ACREE (Ind.

Eng. Chem. [Anal.], 1934, 6, 123—124).—Furfuraldehyde is converted quantitatively into the dibromide when treated for 5 min. at 0° with excess of 0.1N-KBrO₃-KBr solution in 3% HCl; the free Br is determined with KI and 0.1N-Na₂S₂O₃ solutions. The temp. is very important, since the secondary reaction (formation of tetrabromide) has a high temp. coeff.

S. C.

Application of the ter Meulen methods for the determination of sulphur and nitrogen to the analysis of the thiodiazolines. (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1934, 43, 93—99).—Analytical results are given for 27 substituted thiodiazolines with practical details of the methods used.

D. R. D.

Biochemistry.

Excitation metabolism of red blood-cells. I. Increase in respiration during faradic stimulation. II. Mechanism of the increase in respiration during faradic stimulation. I. VON HATTINGBERG (Z. Biol., 1934, 95, 44—54, 55—63).—I. Faradisation (I) produces an increase in the respiration (II) (the O₂ consumption increasing up to 170%) of erythrocytes (III) (pigeon, goose, rabbit, man, frog) which is proportional to the applied current and is not due to the rise in temp.

II. The above phenomenon is not related to the salts present in the suspension medium (Ringer-NaHCO₃, aq. PO₄-NaCl, and serum) nor to any change in [H⁺]. (I), which increases anaerobic acid-formation by (III), increases the (II) of hæmolysed (III), but not the oxidation of H₂C₂O₄ in presence of C. F. O. H.

Red cell diameter and red cell volume measurements [in blood]. J. M. VAUGHAN and H. M. GODDARD (Lancet, 1934, 226, 513—517).—Mean corpuscular vol., diameter, corpuscular hæmoglobin and its concn. have been determined in various samples of human blood.

L. S. T.

Regulation of the hæmoglobin level in poultry. S. F. COOK and I. W. HARMON (Amer. J. Physiol., 1933, 105, 407—417).—The hæmoglobin val. (I) of normal hens' blood shows great individual variations (5—19 mg. per 100 c.c.), varying inversely with the rate of egg production (II). During broodiness (I) rises, falling again with resumption of laying. (I) in normal hens and chicks on a standard normal diet increases when additional Fe (FeSO₄) is fed. The spleen (III) of the chick contains practically no stored Fe. During growth (III) size increases greatly and the Fe concn. rises to double the initial val., after which it remains const. In the adult, (III) size and Fe content cannot be correlated with (I) or (II). The hen has not a store of reserve Fe for hæmatopoiesis and depends on the current intake of dietary Fe. Since this probably varies widely, it may account for the great fluctuations in (I) in normal hens.

NUTR. ABS. (m)

Proportion of cystine yielded by hæmoglobins of the horse, dog, and sheep. H. B. VICKERY and A. WHITE (Proc. Soc. Exp. Biol. Med., 1933, 31,

Action of mercurous chloride on alkaloid salts and its significance for toxicological investigation. J. J. L. ZWIKKER (Pharm. Weekblad, 1934, 71, 22—29).—Reduction of Hg₂Cl₂ (I) to Hg is not sp. for cocaine, novocaine, and pilocarpine hydrochloride, being also obtained with cotarnine, narcotine, quinine, narceine, and thebaine hydrochloride in solvents (EtOH, EtOH-CHCl₃) in which the solubility is > 1:4. Alkaloid hydrochlorides (II) react with (I) in highly conc. solutions forming complexes (III) of the type [HgCl₄]²⁻B₂ and Hg. (III) are stable only in conc. solutions and revert on dilution to sparingly sol. mercurichlorides of the type HgCl₂.2B. Colloidal Hg, obtained by the action of NH₃ or (II) on (I), will not amalgamate with Au.

S. C.

6—7).—By the Cu^I mercaptide method, hydrolysed hæmoglobin of the horse, sheep, and dog yielded, respectively, 0.41, 0.6, and 1.16% of cystine.

CH. ABS.

Equilibria between native and denatured hæmoglobin in salicylate solutions and the theoretical consequences of the equilibrium between native and denatured protein. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1934, 17, 399—408).—Denaturation of hæmoglobin (I) by salicylate (II) in neutral solution is completely reversed by removal of (II) by dialysis or on dilution with H₂O. Amounts of (II) not conc. enough to denature (I) completely produce an equilibrium mixture of native and denatured (I) as shown by a study of the absorption of monochromatic green light. The higher the (II) concn., the higher is the % denaturation.

A. L.

Light absorption of hæmatoprosthetic, its reduced form, carbonyl compound, and its ammonia hæmochromogen. A. HERZOG (Biochem. Z., 1934, 268, 260—264).—The absorption curves for hæmatoprosthetic (I) show a max. at 608 and a min. at 566 mμ, and for its NH₃-hæmochromogen max. at 553 and 524 mμ and min. at 536 mμ, the curve thus corresponding with those for the analogous modifications of hæmin. The curve for reduced (I) shows two flat max. at 573 and 562 mμ with a min. at 566 mμ and for CO-(I) max. at 560 and 530 mμ and a min. at 543 mμ.

P. W. C.

Protein content of blood and coelomic liquid of invertebrates. M. FLORKIN and H. F. BLUM (Bull. Acad. roy. Belg., 1934, [v], 20, 239—252).—The blood-protein is as follows: Bivalves 0.1%, *Cirripedia* 0.2%, *Decapoda* 4%, *Polychæta* 2%. The coelomic liquid is practically protein-free.

H. G. R.

Colloid-osmotic (oncotic) pressure. XXX. Albumin and globulin fractions. A. GRONWALL (Arch. exp. Path. Pharm., 1934, 174, 544—554; cf. this vol., 201).—Solutions of pure albumin (I) and globulin (II) can be prepared from human serum by cataphoresis (III). The colloidal particles of aq. (I) thus prepared do not exhibit a uniform rate of

cataphoretic migration (IV) and can be further divided by (III) into fractions varying both in (IV) and in the colloid-osmotic pressure/% albumin ratio (V). The aq. (II), however, does not yield fractions of different (V). F. O. H.

Physical properties of blood-serum. M. DOLADILHE (Compt. rend., 1934, 198, 1189—1191).—Each of the individual proteins of serum exerts a flocculating or protective action on a colloidal hydro-sol, the flocculating zone of the euglobulin being wider than that of the other proteins. The protective and dispersive power of whole serum results from the dispersive action of the albumins counterbalanced by the flocculating effect of the euglobulins. Sharp differences exist in the protective zones of normal and syphilitic sera. P. G. M.

Blood volume regulation and blood composition in experimental hydræmia. I. Regulation of blood volume. D. B. CALVIN, A. H. SMITH, and L. B. MENDEL (Amer. J. Physiol., 1933, 105, 135—145).—Tests on female dogs receiving intravenous injections of 0.95% NaCl at the rate of 250 c.c. per min. until amounts equal to the calc. blood vol. are injected, show that there is a 16% increase in blood vol. after 45 min. and 5% after 235 min.

NUTR. ABS. (m)

Maintenance of salt content of the fresh-water crab (*Potamobius*). E. HUF (Pflüger's Arch., 1933, 232, 559—573).—The blood-Cl (I) of *P. astacus* kept for 2 weeks under almost natural conditions varies by $\pm 10\%$, averaging 6.5 mg. per g. of blood. The variations are less on longer keeping in fresh H₂O, indicating adaptation. After 4—5 weeks there is an average fall of 6—7%. A diet of pond mussels does not suffice to maintain (I) at a level $>$ in starving crabs, in which, however, the dry wt. of the blood is less. (I) of crabs kept in distilled H₂O falls by 30—35% in 8 days and death ensues. Return to natural fresh H₂O or dil. artificial sea-H₂O (II) causes rapid recovery, although (I) remains low. (II) without either Ca or K, but of the usual osmotic pressure, suffices to maintain the mineral content of the blood at normal level.

NUTR. ABS. (m)

Regulation of the salt content of the hæmolymph of some Crustacea and their adaptation to changes in salinity. A. DRILHON-COURTOIS (Compt. rend., 1934, 198, 1079—1081).—The Na, K, and Ca content of the hæmolymph of *Carcinus maenas* and *Potamobius astacus* increases, whilst that of the sol. phosphates and proteins decreases, with increasing salinity of the H₂O in which the animals are placed. R. S. C.

Alkali reserve in the pigeon. H. SCHARNKE (Compt. rend. Soc. Biol., 1933, 113, 1169—1170).—For normal adults on normal diet determinations average 53.2 c.c. of total CO₂ per 100 c.c. of plasma; for normal fasting adults they vary from 36.7 to 43.4. Similar figures are obtained for cock, duck, and goose. In birds made to inspire air rich in CO₂ for 60—70 min., the alkali reserve (I) rises from 43.3—50.2 to 49.2—74.8. These results are analogous to those obtained under like conditions in mammals; hence a similar mechanism for adjustment of (I) probably exists.

NUTR. ABS. (m)

Acid-base balance of blood. I. Micro-technique for determination of the acid-base balance of blood. N. W. SHOCK and A. B. HASTINGS. II. Nomogram for calculation of acid-base data of blood. A. B. HASTINGS and N. W. SHOCK. III. Variation in acid-base balance of blood in normal individuals. N. W. SHOCK and A. B. HASTINGS (J. Biol. Chem., 1934, 104, 565—573, 575—584, 585—600).—I. Apparatus and technique are described for the determination of percentage cells (I), of the serum (II), and total CO₂ (III) on the same 0.1-c.c. sample of blood, the accuracy being $\pm 1.0\%$ for (I), $\pm 0.02 p_H$ for (II), and $\pm 1.0\%$ for (III).

II. The construction and use of a nomogram for the solution of the various forms of the Henderson-Hasselbalch equation are described.

III. The normal variations in acid-base balance between males may be from p_H 7.35 to 7.45; serum-HCO₃' 23.0 to 30.0 millimol. per litre; CO₂-tension of blood 40.0 to 50.0 mm. of Hg, and for females 7.37—7.47, 22.0—28.0, and 36.5—46.0, respectively. Normal individuals differ from one another and some show large daily variations. During the day there is no characteristic change in the acid-base balance of an individual. C. G. A.

Micro-determination of sodium in serum and plasma. A. D. MARENZI and R. GERSCHMAN (Compt. rend. Soc. Biol., 1933, 114, 1212—1214).—The Na of the CCl₃·CO₂H filtrate of serum or plasma is pptd. as U Zn Na acetate. The washed ppt. is dissolved in AcOH, treated with K₄Fe(CN)₆, and compared colorimetrically with a standard solution of UO₂(OAc)₂ (of known equivalence to Na) similarly treated.

NUTR. ABS. (b)

Determination of chloride, potassium, and calcium in blood. F. RAPPAPORT (Klin. Woch., 1933, 12, 1774—1775).—Modifications of Rusznyak's and the Kramer and Tisdall methods are described.

NUTR. ABS. (m)

Micro-determination of calcium in blood-serum. P. WENGER, C. CIMERMAN, and P. BORGEAUD (Mikrochem., 1934, 14, 141—158).—2 c.c. of serum are evaporated and ashed in a Pt capsule over a free flame, dissolved in HCl, and brought to 5 (Me-red), CaC₂O₄ is pptd. at 100°, dissolved in H₂SO₄, and titrated at 70° with 0.01N-KMnO₄. J. S. A.

Microcrystallographic determination of phosphates in blood-serum. E. A. PRIBRAM (Arch. Path., 1933, 16, 520—521).—Equal quantities of serum are diluted with increasing amounts of 2.5% NaCl and Dowd's (NH₄)₂SO₄-MgSO₄ reagent is added. The last tube in which crystals are formed after 45 min. contains 3 mg. of P per 100 c.c. The method is sensitive to 0.5 mg. of P.

NUTR. ABS. (m)

Inorganic phosphate contents of serum, fluoride-plasma, and native plasma. H. L. WHITE and B. MONAGHAN (Proc. Soc. Exp. Biol. Med., 1933, 31, 1—5).—Colour production in the Benedict-Thois method for inorg. PO₄''' is not affected by the use, as an anticoagulant, of NaF in a concn. of 0.3%, but is inhibited at 1%. The inorg. P content of serum is the same as that of native plasma.

NUTR. ABS. (m)

Blood-bromine. F. HOLTZ and C. ROGGENBAU (Klin. Woch., 1933, 12, 1410—1411; Chem. Zentr., 1933, ii, 2567).—Zondek's method for the micro-determination of blood-Br (A., 1933, 739) is untrustworthy.

H. J. E.

[**Blood-bromine.**] H. ZONDEK (Klin. Woch., 1933, 12, 1411—1412; Chem. Zentr., 1933, ii, 2567; cf. preceding abstract).—A reply, reaffirming the correctness of the method.

H. J. E.

[**Blood-bromine.**] L. PINCUSSEN (Klin. Woch., 1933, 12, 1412; Chem. Zentr., 1933, ii, 2567; cf. preceding abstracts).—Some unknown factor is responsible for the occasional failure of Zondek's method.

H. J. E.

Determination of blood-bilirubin. G. FERRARI (Diagnostica Tec., 1933, 4, 696—716).—A crit. review of methods of determination in serum and other org. liquids of both total bilirubin (I), and of CHCl_3 -sol. and H_2O -sol. (I) separately.

R. N. C.

Creatine and creatinine metabolism. I. Creatinine determination in urine and blood. H. LIEB and M. K. ZACHERL (Z. physiol. Chem., 1934, 223, 169—179).—Creatinine is determined following Folin's method, but using the Pulfrich photometer in place of the colorimeter.

J. H. B.

Micro-determination of urea in blood. P. WENGER, C. CIMERMAN, and A. MAULBETSCH (Mikrochem., 1934, 14, 132—140).—Minor modifications of the methods of Nicloux and Welter (gravimetric) (A., 1922, ii, 170) and of Allen and Luck (volumetric) (A., 1929, 962) are described.

J. S. A.

Blood-chemistry of pigs. I. Blood changes following ingestion of glucose. D. F. EVELETH (J. Biol. Chem., 1934, 104, 559—563).—Ingestion of glucose by pigs evokes an increase in NH_4 -acid-N, urea-N, and serum-Ca and a fall in inorg. P, the peaks of the curves occurring approx. 30 min. after the peak of the blood-sugar curve which occurs 30—60 min. after administration.

C. G. A.

Influence of the carotid sinus on the blood-sugar. F. BRAUCH (Arch. exp. Path. Pharm., 1934, 175, 104—112).—"Pernocton" narcosis in rabbits is not accompanied by a rise in blood-sugar (I) nor by a change in the hyperglycemic response to adrenaline or urethane. During and after elimination of the influence of the carotid sinus (by clamping the common carotids), (I) is unchanged, a result not influenced by section of the adrenal nerves. Section of the two depressor nerves produces an immediate rise in (I) lasting for several hr. No correlation appears to exist between the pressor-receptor centres and carbohydrate metabolism.

F. O. H.

Determination of blood-sugar by the picric acid reaction. E. KAUFMANN (Z. ges. exp. Med., 1933, 92, 480—489).—Improvements are suggested so that the method can be easily used to give approx. results where there are no adequate laboratory facilities.

NUTR. ABS. (m)

Effect of anticoagulants and antiglycolitics on determination of blood-sugar. R. C. FORMIGUERA and E. BIETO (Compt. rend. Soc. Biol., 1933, 114, 116—118).—The addition of 0.2% of NaF lowers

the apparent blood-sugar level by 6.8 mg. per 100 c.c., whilst the addition of 0.2% of $\text{Na}_2\text{C}_2\text{O}_4$ causes an apparent decrease of 7.9 mg.

NUTR. ABS. (m)

Determination of fibrinogen in blood. G. BOEHM (Diagnostica Tec., 1933, 4, 683—687).—A syringe rinsed with 20% aq. K oxalate was used to draw blood. The greatest dilution of the plasma which when treated with a drop of 10% CaCl_2 solution coagulated in $\frac{1}{2}$ —1 hr. was considered to be the fibrinogenic unit. Normal human blood contained 40—60 units per c.c.

R. N. C.

Determination of phosphatides in blood. B. NORBERG (Biochem. Z., 1934, 269, 1—3; cf. A., 1933, 1183).—Phosphatide (I)-P is colorimetrically determined in 0.2—0.5 c.c. of blood after dilution with 3 c.c. of H_2O , pptn. of (I) with 3.5 c.c. of 10% aq. $\text{CCl}_3\text{-CO}_2\text{H}$ (II), extraction of the ppt. with EtOH-CHCl_3 (3 : 1) after washing with 1—2% aq. (II), evaporation to dryness of the extract, and treatment of the residue with H_2SO_4 and HNO_3 at 250° .

W. McC.

Chemistry of the lipin involved in the coagulation of blood. A. FISCHER and E. HECHT (Biochem. Z., 1934, 269, 115—132).—The coagulating power (I) of kephalin (II) decreases as its purity increases. The active substance (III) which accompanies (II) is optically inactive, non-sp., thermostable, sol. in EtOH , and probably complex. Increase in the activity of (III) is accompanied by parallel increase in power to absorb ultra-violet light. Lipins (lecithin, cerebro-sides), cholesterol, and simple degradation products of these (glycerophosphoric acid, triolein, stearic and oleic acids, etc.) have no (I).

W. McC.

Hæmolysis and the solar spectrum. W. W. LEPESCHKIN and G. E. DAVIS (Protoplasma, 1933, 20, 189—194).—Decreased resistance and hæmolysis of corpuscles produced by light is due to a chemical change in the hæmoglobin.

A. G. P.

Nature and physical properties of an antibody; electrophoresis of hæmolytic sera. P. GIRARD and M. LOURAU (Compt. rend., 1934, 198, 1081—1083).—Hæmolysin undergoes cataphoresis; the velocity of movement is much slower than that of proteins or Cl' . It behaves as an ion with isoelectric point at p_{H} 6.2.

R. S. C.

Reducing substances of living tissue. R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1934, 223, 136—143).—Jensen sarcoma of the rat contains vitamin-C (I) (cf. Boyland, A., 1933, 851). In the separation of glutathione (II) from other reducing substances with Ag lactate, a yellow pigment, probably vitamin- B_2 (III), is pptd. Liver-tissue probably contains, besides (I), (II), and (III), a fourth reducing substance, mainly in the oxidised condition. (II) is present in living tissue almost entirely in the reduced form. Activation of enzymes depends not so much on the presence of reduced (II) as on that of a heavy metal complex.

J. H. B.

Reducing substance in brain tissue. F. G. YOUNG and M. MITOLO (Nature, 1934, 133, 572).—Brains of the mouse, rat, guinea-pig, and ox contain a substance (I) which reduces AgNO_3 in neutral or AcOH solution, but not in cold aq. NH_3 solution.

Extracts from brain tissue containing (I) reduce phenol-2 : 6-dichloroindophenol under the conditions laid down for determining ascorbic acid (II) in tissues. The chemical and physiological properties of (I) are different from those of (II), and thus the determination of (II) by the indophenol titration method is untrustworthy. The activity of solutions of (I) is destroyed in acid and alkaline solutions. A cryst. semicarbazone, m.p. 251—252° (uncorr.), has been isolated from active extracts, but this may or may not be a derivative of (I). L. S. T.

Asteric acid, a carotenoid acid from starfish. H. VON EULER and H. HELLSTROM (Z. physiol. Chem., 1934, 223, 89—97).—The pigments from various species of starfish were examined spectroscopically. The H₂O-sol. blue pigment of *Asterias rubens* (C 55.2, H 7.75, N 11.1, S 2.3%) contains a carotenoid *asteric acid*, C₂₈H₄₀O₄, m.p. 185°.

Occurrence of flavins in animal tissues. H. VON EULER and E. ADLER (Z. physiol. Chem., 1934, 223, 105—112).—Examination of a large no. of animal organs and tissues shows that those richest in vitamin-B₂, viz., liver and kidney, are also richest in flavin (I). The retina of fish contains about the same amount of (I) in dialysable form. Corpus luteum contains, in addition to (I), a blue fluorescent substance, which may be a derivative of (I).

Lyochromes: a new group of animal pigments. P. ELLINGER and W. KOSCHARA (Nature, 1934, 133, 553—556).—A summary.

Lyochrome in the pigmented epithelium of the eye. H. VON EULER and E. ADLER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 21, 4 pp.).—Extraction with COMc₂ of the pigmented epithelium (I), but not of the retina (II), of eyes (III) of oxen yields a green-fluorescing solution which on evaporation and treatment with H₂O and Et₂O yields an aq. layer containing lyochrome (IV) and an Et₂O layer containing carotene. Aq. alum used for fixation of (III) also contains (IV), which can be separated by acidification with HCl, adsorption on fuller's earth, and elution with H₂O-C₆H₅N-MeOH. Fish-(III) contain varying amounts of (IV), the purified (IV) of shellfish (III) having an absorption max. at 447 mμ corresponding with lactoflavin (this vol., 227). The irises of pike's (III) yield an unstable COMc₂-sol. colouring matter which, in light petroleum, has absorption max. at 470 and 441 mμ; after keeping in the dark for 3 weeks the max. are at 493 and 457 mμ.

Visual purple. H. VON EULER and E. ADLER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 20, 6 pp.).—Extraction of ox-retina (I) (hardened with MgSO₄, alum, or CH₂O) with 2—3% aq. digitonin yields a clear violet solution from which digitonin is removed by dialysis. Heating yields a dark yellow solution from which 95% EtOH (1 vol.) ppt. the colouring matter. Extraction of the dry residue with MeOH gives a yellow solution containing a lyochrome and having absorption max. at 490 and 460 mμ. The aq. Na cholate or AcOH extract of visual purple from nsh-eyes gives a ppt. with cholic acid. COMc₂-followed by Et₂O-extraction of unhardened (I)

yields carotene (II), 20 (I) yielding 95×10⁻⁶ g. and twenty pigmented epithelial layers 240×10⁻⁶ g. Vitamin-A also appears to be present. (II) occurs in the retina of a few fishes.

F. O. H.

Free and bound cholesterol content of different parts of the brain of normal and polyneuritic animals. H. G. K. WESTENBRINK (Arch. Néerland. Physiol., 1934, 19, 122—131).—The bound is much < the free cholesterol (I) in all parts of the brain. The (I) contents decrease in the order medulla oblongata, mid-brain, cerebellum, and cerebrum in both rats and pigeons. There is no difference in the (I) contents of the brains of normal and polyneuritic animals.

C. G. A.

Details of muscle structure revealed by salt extraction. H. N. BAKER, H. C. MCPHEE, and P. E. HOWE (J. Agric. Res., 1933, 47, 1009—1014).—Ox muscle tissue is extracted for 1.5 hr. at 15° with either 1.25M-NaCl or a 0.225M-mixture of KH₂PO₄ and K₂HPO₄ (pH 7.0—7.4). This removes sol. proteins without materially damaging the remaining structures. The fibrils are completely removed by NaCl-extraction, the fibres appearing as short tubes. Characteristic swelling of the fibre membrane occurs.

P. G. M.

Are oxalylmethylguanidine (creatone), methylguanidine, and oxalic acid normal constituents of muscular tissue? T. MANN (Biochem. Z., 1934, 268, 339—344).—The oxalylmethylguanidine (I) isolated from muscle by Gulewitsch (A., 1933, 735) is an artefact arising from creatinine during manipulation, and since (I) readily gives methylguanidine and H₂C₂O₄ on hydrolysis, it appears probable that these also are artefacts.

P. W. C.

Linking of purine bases in the unfertilised sea-urchin's egg. G. SCHMIDT (Z. physiol. Chem., 1934, 223, 81—88).—The unfertilised ripe egg has high total purine (I), but only traces of acid-sol. (I). All (I) compounds are extracted by 0.03N-NH₃. About 70% of the total (I) is contained in the proteins pptd. by AcOH. The nucleic acid components contain the thymonucleic acid group.

J. H. B.

Osmotic pressures in the hen's egg. E. J. BALDES (Proc. Roy. Soc., 1934, B, 114, 436—440).—There is a difference of osmotic pressure (I) between the yolk (II) and the white in the hen's egg and a gradient of (I) in (II). There is very little difference in (I) across the vitelline membrane.

H. G. R.

Vapour-pressure isotherm of muscle. J. BROOKS (Proc. Roy. Soc., 1934, B, 114, 258—272).—The vals. obtained for bound H₂O in muscle are of similar magnitude to those for protein and H₂O only. In rigor, probably only a small fraction of H₂O is bound. Drying over P₂O₅ does not produce any change in the H₂O-binding capacity.

H. G. R.

Coagulation of muscle-plasma. II. Solubility of myosin. E. C. SMITH (Proc. Roy. Soc., 1934, B, 114, 494—505).—Not more than 10% of the myosin (I) in rabbit muscle is in the form of a sol. Coagulation of muscle-plasma is due to the pptn. of (I) from a sol formed by previous addition of salt.

Data for the effect of salt concn., p_H , and total protein concn. on the solubility of (I) in KCl are given.

C. G. A.

Distribution of calcium and magnesium in the organs of the dog. BARTHELEMY and R. WOLFF (Compt. rend., 1934, 198, 1370—1372).—The Ca and Mg content varies, but they are present in definite proportions which are characteristic for each organ. The total mol. concn. of Ca and Mg (1.08—1.72) is approx. const. in kidney, lungs, pancreas, spleen, and muscle.

H. G. R.

Distribution of inorganic salts in the tissues of birds. III. A. BERNARDI and M. A. SCHWARZ (Biochem. Z., 1934, 268, 369—371).—Two tables give the H_2O , P, Ca, Mg, and Cl contents of certain tissues of the hen and of *Perdix coturnix*.

P. W. C.

Factors affecting determination of the ash content of the tibiae of chicks. R. M. BETHKE and P. R. RECORD (Poultry Sci., 1934, 13, 29—33).—Differences in the technique for determining ash contents are examined. The preliminary extraction of the bones with 95% EtOH is as effective as with EtOH followed by Et₂O. Removal of proximal cartilage causes a significant increase in the ash val. recorded. Extracted bones absorb sufficient H_2O to cause a significant change in results. Ash vals. are preferably calc. on a fat-free, H_2O -free basis.

A. G. P.

Nature of "preformed water." J. P. PETERS and P. H. LAVIETTES (J. Clin. Invest., 1933, 12, 695—712).—There is little evidence that H_2O is chemically or physically held by protein, fat, or carbohydrate in the body, but the proportion of H_2O to solutes tends to remain const. within wide limits. There is little support for the hypothesis that the proportion of protein or protein+glycogen to H_2O in the cells remains const. There appears to be a physiological distinction between intracellular (I) and extracellular (II) H_2O , and separate movements of the two seem to occur. Since "preformed H_2O " must be regarded as (I), which cannot be distinguished from (II) by purely metabolic methods, there is no valid reason for retaining it in Newburgh and Johnston's calculations.

NUTR. ABS. (m)

Storage in the kidney cortex. R. KELLER (Biochem. Z., 1934, 268, 336—338).—The cortex stores pigmented colloids, sugar, urea, K, and Mg salts, and $PO_4^{'''}$.

P. W. C.

State of potassium in the central nervous system and its dependence on the degree of stimulation. E. PICHLER (Arch. exp. Path. Pharm., 1934, 175, 85—91).—Extraction of the brain and spinal cord of normal (or strychninised) frogs by 96% EtOH and 0.01N-HCl in 96% EtOH yields, respectively, 52.3 and 87.4% of the total K, whilst with frogs narcotised by urethane, respectively, 67.9 and 98.5% are extracted. With normal frogs, abs. EtOH or Et₂O extracts from the dried tissue an average of 17.2%. The nature of the K fractions sol. and insol. in lipin-solvents and their variations with narcotisation are discussed.

F. O. H.

Iodine content of the thyroids and other organs of Argentine cattle. G. DUFF (Folia biol., 1933, 1,

131—132).—The thyroids contained 357—410 mg. I per 100 g. (dry); vals. are independent of age or sex, but are lower in summer than in winter. Other vals are: spleen 10.3, adrenals 5.5, testicles 3.8, ovaries 1.2, pancreas 1.0, placenta 0.7, mammary glands 0.2, liver 0.2, anterior pituitary lobe (I) 0.4—0.6, posterior (I) 0.16—0.34.

CH. ABS.

Diffuse vital staining of certain flagellates and the chemical affinity of the cytoplasm and its constituents. P. GAVAUDAN (Compt. rend., 1934, 198, 848—850).—Vital staining by cresol-blue of the cytoplasm of a no. of flagellates is described and the chemical mechanism of the process discussed.

A. G. P.

Relationship between chloride content and blood-:cerebrospinal fluid-bromide ratio. W. MALAMUND, B. M. MULLINS, and J. R. BROWN (Proc. Soc. Exp. Biol. Med., 1933, 30, 1084—1087).—Br added to H_2O , blood-serum, or cerebrospinal fluid from which Cl had been removed was recovered quantitatively. Recovery of 100 mg. of Br' in presence of 0.2, 0.3, and 0.6% NaCl was, respectively, 86.5, 78.0, and 73.7 mg. per 100 c.c.

CH. ABS.

Effect of gastric secretion on circulation rate, oxygen utilisation, and sugar and chloride content of arterial and venous blood. D. F. OKUNEV and M. S. SOLNZEVA-RJASANOVA (Arch. Verdauungs-Krankh., 1933, 54, 78—96).—During gastric secretion (I) in man the circulation rate, as measured by the arterial-venous difference (II) in O_2 concn., is increased, and is partly related to the acidity of the gastric juice. The Boas-Ewald meal produced a general fall in the circulating sugar, EtOH a rise, changes which appeared to be connected with tissue metabolism and insular activity. The resting Cl' (II) in the normal was on the average 5.5% in favour of arterial blood (III); in anacidity 3.4, and in hyperacidity, 7.1%. (I) caused the Cl' in the (III) to be increased, in venous blood diminished, so that these differences at the height of secretion were 14.2, 7.2, and 19%, respectively.

NUTR. ABS. (b)

Occurrence of glycogen and fat in liquor folliculi and uterine secretion in *Loris lydekkerianus*. Cabr. C. R. N. RAO (J. Mysore Univ., 1932, 6, 140—170).

Constants of normal human milk. M. TALENTI (Ann. Ig., 1933, 43, 876—882).—Six samples of normal human milk contained: total solids, 10.8—15.8, ash 0.24—0.38, fat 3.0—4.7, lactose 4.6—7.8, protein 2.2—3.0%. The ratios fat:lactose, fat:protein, and fat:ash were approx. const. In milk from pathological cases, the vals. varied considerably.

NUTR. ABS. (m)

Caseinogen. M. RONSE (Compt. rend. Soc. Biol., 1933, 114, 1380—1381).—By the reverse of Demanez's technique the author has confirmed his findings as to the specificity of the caseinogen (I) of human milk. Benzoylated (I) behaves in the same way as (I) itself. (I) of milks is distinguished from the proteins of serum by its stability towards physical and chemical agents.

NUTR. ABS. (m)

Phosphopeptone obtained in the early stages of digestion of caseinogen by activated tryptase.

P. GRABAR (Compt. rend. Soc. Biol., 1933, **114**, 13—15).—The substance gives a ppt. with $\text{CCl}_3\text{CO}_2\text{H}$, picric acid, and Cu acetate, but not with phosphotungstic acid. It contains traces of tyrosine, but no tryptophan. Only 1 in 14 of its N atoms is free $\text{NH}_2\text{-N}$.
NUTR. ABS. (m)

H_2O content of the water of milk. H. ERLMAYER and H. GARTNER (Helv. Chim. Acta, 1934, **17**, 334).—By improving the method previously employed (this vol., 262) 8 litres of pure H_2O gave 20 c.c. of d 1.00087. H_2O from cows' milk under similar treatment gave H_2O of d 1.00083, thus showing, within the limits of experimental error, that no change in the H_2O content of milk had taken place in the animal organism.
M. S. B.

Effect of different planes of protein intake on milk productions. II. Further comparisons of 16, 20, and 24% mixtures. E. S. HARRISON, E. S. SAVAGE, and S. H. WORK (Cornell Univ. Agric. Exp. Sta. Bull., 1933, No. 578, 12 pp.).—No significant improvement in milk yield was produced by raising the protein level of the ration to > 16%.
A. G. P.

Effect of feeding on the fat content of cow's milk. E. J. SHEEHY (J. Dept. Agric. Irish Free State, 1933, **32**, 18—29).—Short-period feeding experiments show that, apart from cod-liver oil, vegetable, animal, or fish oils or oilcakes have no sp. quant. effects on the % of fat in milk. The amount of fat necessary in a cow's ration is small. Introduction of sugar-beet pulp, mangolds, beet, treacle, wet grains, rice meal, or fresh grass in the ration does not affect the % of fat, if the milk yield is unaltered; but if it alters there may be a temporary lag in the total fat. Alteration in the plane of nutrition of the cow does not alter the % of fat. Feeding of separated or whole milk (I) powder does not influence the % of fat. The possible effect of (I) or cream in raising the fat is to be attributed to some substance or substances rather than to the fat *per se*.
NUTR. ABS. (m)

Yacarol, a secretion of glands of alligators. —See this vol., 509.

Secretion of phosphorus and sulphur in the sweat. G. A. TALBERT, F. STINCHFIELD, and H. STAFF (Amer. J. Physiol., 1933, **105**, Proc. 94).—Sweat contains appreciable, although variable, amounts of inorg. P and S, S being generally in excess of P. The amount of P secreted depends on the P content of the diet.
NUTR. ABS. (m)

Blood and urine of colts. W. W. DEMOCK and D. J. HEALY (J. Amer. Vet. Med. Assoc., 1933, **36**, 806—809).—Blood-serum of normal and over-fed fillies contained (mg. per 100 c.c.), respectively: Ca 12.0, 12.5; K 15.4, 18.5; P 4.9, 5.0; non-protein-N 28.1, 19.9; $\text{SO}_4\text{-S}$ 13.4, 10.0; sugar 106, 123. Urine from the same animals had d 1034, 1038, p_{H} 7.4, 6.6, and contained albumin 0, 0; NH_3 50.0, 100.0; Ca 128.5, 184.9; $\text{SO}_4\text{-S}$ 81.9, 63.1.
CH. ABS.

Determination of albumin in urine. D. GANASINI (Arch. Biochim. Ital., 1934, **6**, 3—12).—Albumin (I) in urine (II) is determined rapidly by observing at the same temp. the sp. gr. of (II) both

before and after coagulation of the (I) by heat, the sp. gr. of coagulated (I) being taken as 1.315 (const., experimental val.).
R. N. C.

Micro-determination of uric acid in urine. P. WENGER, C. CHERMAN, and A. MAULBETSCH (Mikrochem., 1934, **14**, 129—131).—Uric acid in 2 c.c. of urine is pptd. as NH_4 urate (I) by addition of aq. $\text{NH}_3 + \text{NH}_4\text{Cl}$. (I) is redissolved in AcOH, the solution made alkaline with borax, and titrated with 0.01N-I.
J. S. A.

Influence of parenteral administration of amino-acids, sodium chloride, and glucose on the urinary quotients. A. ROEHDER (Biochem. Z., 1934, **268**, 265—271).—A single subcutaneous injection into male white rats of the NH_2 -acid mixture obtained by hydrolysis of proteins (particularly vegetable) or of pure glutamic acid causes on the day of injection a considerable increase of urinary C:N, vacate-O:N, and vacate-O:C, the extent of the increase diminishing on repeating the injection daily. A single injection of 15% NaCl also does, but of 7—16% glucose does not, affect the quotient.
P. W. C.

Application of Benedict's solution to the micro-detection of sugar in urine and other liquids. H. TAUBER (Mikrochem., 1934, **14**, 169—170).—0.1% of glucose may be detected in a drop of urine by Benedict's solution (I) (A., 1909, ii, 442). Urates, if present, also give a turbidity. Bioses also reduce (I).
J. S. A.

Acetone and acetoacetic acid in urine. P. FISCHER (Pharm. Zentr., 1934, **75**, 189—191).—Lange's nitroprusside test (I) is a sensitive one for $\text{CH}_3\text{Ac-CO}_2\text{H}$. If (I) is negative, COME_2 may be recognised by the CHI_3 reaction.
R. K. C.

Excretion of inorganic phosphate by the aglomerular kidney. E. K. MARSHALL, jun., and A. L. GRAFFLIN (Proc. Soc. Exp. Biol. Med., 1933, **31**, 44—46).—Urine of the angler fish (*Lophius piscatorius*) contained 0.0007—0.045 mol. of inorg. PO_4 per litre; the plasma contained 0.0042—0.0077 mol. per litre. Intramuscularly injected inorg. PO_4 was not excreted in the urine.
CH. ABS.

Dependence of acidity ratio of urine on diet. E. HELMS (Z. ges. exp. Med., 1933, **89**, 631—640).—The acidity ratio (I) of the urine represents the % ratio of acid PO_4 to total PO_4 . After a meal (I) falls, reaching the min. in about 4 hr. The fall is greatest after the chief meal of the day, and if this is taken < 4 hr. after the preceding meal, the fall continues. When the diet is vegetarian the acidity curve is shifted towards the alkaline side, but is otherwise similar to that found on mixed diet.
NUTR. ABS. (m)

Nitrogenous compounds of the excrement from the caecum of the fowl. K. SUZUKI and A. KAWABATA (J. Agric. Chem. Soc. Japan, 1933, **9**, 1095—1103).—The excrement contained H_2O 78.80, crude protein 9.86, pure protein 6.25, crude fat 1.36, crude fibre 0.79, ash 3.83, sol. N-free matter 5.36, and $\text{NH}_3\text{-N}$ 0.099%. The protein is > in ordinary faeces. The distribution of N in the dry material was: total N 6.584, protein-N 5.225, H_2O -sol. N 2.153, N pptd. by $\text{Pb}(\text{OAc})_2$ 0.648, N pptd. by

phosphotungstic acid 0.840%. Tyrosine and valine, but not $(\text{NH}_2)_2$ -acids, were isolated. CH. ABS.

Mechanism of sodium depletion in Addison's disease. R. F. LOEB, D. W. ATCHLEY, E. B. GUTMAN, and R. JILLSON (Proc. Soc. Exp. Biol. Med., 1933, 31, 130—133).—The loss of Na is not dependent on the excretion of unusual quantities of acid as determined by the excretion of NH_3 and titratable acid. The Na regulatory mechanism is disturbed. The clinical condition parallels the blood-Na and depends on the amount of Na ingested. CH. ABS.

Non-protein-iron of the blood. J. F. MCINTOSH (J. Clin. Invest., 1933, 12, 967).—The non-protein-Fe (I) of whole blood, determined on the $\text{CCl}_3\cdot\text{CO}_2\text{H}$ filtrate, averages 1.02 mg. per 100 c.c. in health. In various anæmias it varies directly with the severity of the anæmia. The greater part of (I) is in the red cells. NUTR. ABS. (m)

Tissue metabolism in secondary anæmia. H. H. RIECKER (J. Clin. Invest., 1933, 12, 986—987).—Tissues from anæmic rabbits use only half as much O_2 [determined by mixing with defibrinated rabbits' blood of known O_2 content (I) and measuring (I) after 1 hr.] as do those from normal rabbits. Anæmia affects all the tissues, probably because of Fe starvation. NUTR. ABS. (m)

Value of cod-liver oil in the treatment of anæmia. A. D. HOLMES, M. G. PIGOTT, and L. P. BOWSER (New Engl. J. Med., 1933, 209, 839—842).—Cod-liver oil (I) alone does not regenerate blood in anæmic rats. Rats given 0.5 mg. Fe and 0.05 mg. Cu daily with (I) show more rapid blood-regeneration than rats receiving Fe and Cu but not (I). However, when the Fe administered is 1.5, 2.5, or 3 mg. the rate of hæmoglobin increase is normal. Similar results were obtained with peanut oil free from vitamin-A. CH. ABS.

Anti-anæmic principle in stomach tissue. J. F. WILKINSON (Proc. Roy. Soc. Med., 1933, 26, 1341—1350).—Carnivore stomach (silver fox) is active, but ruminant stomach (ox and sheep) is inactive. The active principle (I) is destroyed by temp. $> 45^\circ$, by autolysis, and by digestion with pepsin (II) or trypsin. Press juice of pig's stomach (III) is active in doses of 150 c.c. daily. EtOH treatment yields a ppt. which contains all the (I) and (II). The ppt. is efficient in daily doses of 5 g., equiv. to 50 g. of fresh (III). Further fractionation by isoelectric pptn. separates (II) from (I). The active fraction has a high P content, and is practically free from Cu, Mn, and Fe. NUTR. ABS. (m)

Muscular dystrophy and atrophy. Clinical and biochemical results following oral administration of amino-acids. C. J. TRIPOLI and H. H. BEARD (Arch. Int. Med., 1934, 53, 435—452).—The administration of glycine or glutamic acid in cases of muscular dystrophy or atrophy results in an increase in the excretion of creatine and, to a smaller extent, of creatinine in the urine. W. O. K.

Mineral metabolism in bursitis calcarea. T. AOKI (Tôhoku J. Exp. Med., 1933, 21, 556—591).—Ca, Mg, and P metabolism, urinary uric acid excre-

tion, serum-proteins and blood viscosity, and the renal function were normal. NUTR. ABS.

Hormonal control of tumour growth and metabolism. M. REISS, H. DRUCKREY, and A. HOCHWALD (Z. ges. exp. Med., 1933, 90, 408—420, and Klin. Woch., 1933, 12, 1049—1050).—Removal of the pituitary gland from rats in which Jensen sarcoma is growing rapidly causes an immediate cessation of growth (I) and rapid appearance of degeneration of the tumour accompanied by reduction of O_2 consumption (II). Administration of the pituitary growth hormone leads to reappearance of (I) with increase in (II). The sexual hormone of the pituitary favours (I) independently of the presence of the sex glands which seem to hinder (I) independently of the pituitary growth factor. Regressive changes in the tumour, however produced, are always accompanied by reduction in (II). The old view of the autonomous growth of tumour tissue seems to be erroneous. NUTR. ABS. (m)

Effect of the ingestion of aluminium on cancer. G. BERTRAND and P. SERBESCU (Compt. rend., 1934, 198, 1100—1103).—Ingestion of 20 mg. of Al per kg. body-wt. per day in the rabbit for 6 months has no harmful effect on the alimentary canal. It does not increase the incidence of cancer due to the application of a carcinogenic tar. P. G. M.

Effect of a dinitrophenol on tumour metabolism. E. C. DODDS and G. D. GREVILLE (Lancet, 1934, 226, 398—399).—Respiration of Jensen rat sarcoma is increased by $10^{-5}M$ -4:6-dinitro-*o*-cresol in the presence of glucose, lactate, and pyruvate, but not in the absence of added substrate. Simultaneously, the aerobic glycolysis is increased. L. S. T.

Balance of phosphatase in the carcinomatous organism. F. KOHLER (Z. physiol. Chem., 1934, 223, 98—104).—Considerable differences are shown in the activation of phosphatase (I) by MgCl_2 in the organs of normal (II) and carcinomatous rats (III). The auto-activated (I) of tumour, muscle (IV), and kidney (V) decreases as the tumour ages, although (V) shows increased (I)-action in (III). (V)-(I) of immune Wistar rats is much $>$ the normal val. The (I) of (IV) and (V) of (II) are fully active, but in (V) of (III) only 30% active, although the tumour-(I) is highly active. In the blood, which shows increased (I) in (III), the auto-activity is doubled. J. H. B.

Gelatinisation of serum by organic acids. W. KORACZEWSKI (Compt. rend., 1934, 198, 1271—1273).—With lactic acid, or, more slowly, AcOH or HCO_2H , serum sets to a transparent gel, which only slowly aggregates. In cancer and, possibly, syphilis, the gelatinisation is accelerated. R. S. C.

Prevention of tar cancer by barium salts. J. MAISIN and J. DETROUX (Compt. rend. Soc. Biol., 1933, 113, 926—928).—Very small repeated doses of Ba saccharate in saccharic acid reduce the incidence of tar tumours in mice. NUTR. ABS. (m)

Importance of the anion and of dosage in the prevention of tar cancer by barium salts. J. DETROUX (Compt. rend. Soc. Biol., 1933, 113, 928—930).—The effect of Ba salts on the growth (I) of tar

tumours in mice depends partly on the anion. Small doses of BaCl_2 retard, larger doses accelerate (I), and large doses of Ba gluconate inhibit (I).

NUTR. ABS. (m)

Chemical composition of saliva and blood-serum of children in relation to dental caries. R. B. HUBBELL (Amer. J. Physiol., 1933, 105, 436—442).—Children (I) with active caries show a moderate or high *B. acidophilus* count, whilst those (II) free from caries are negative or nearly so. The chemistry of the blood and of the saliva shows no great variation in either group except as regards CO_2 capacity (III) and titratable alkalinity (IV) of the saliva. In (I) (III) is 44% and (IV) 24% < in (II).

NUTR. ABS. (m)

Etiology and pathogenesis of darmous (spontaneous fluorosis of phosphate zones). H. VELU (Bull. Soc. Path. exot., 1933, 26, 616—621).—The favourable effect of $\text{Ca}_3(\text{PO}_4)_2$ on sheep receiving rations containing CaF_2 indicates that a lack of mineral balance may be a contributory cause of darmous, and that the severity of the F intoxication may depend on the $\text{PO}_4^{'''}$ content of the ration. F is regarded as interfering with fixation of Ca to a degree depending on the form in which it is present. Although both plants and bone powder contain as much F as certain waters and natural phosphates, they are not toxic. Apparently F loses its toxicity when fixed by the vegetable or animal organism.

NUTR. ABS.

Diabetes mellitus and pregnancy. E. SKIPPER (Quart. J. Med., 1933, 2, 353—380).—Insulin exerts a beneficial effect on the fertility of diabetics (I), lowering the maternal mortality (II) during pregnancy (III) and the puerperium (IV), but leading to no reduction in foetal (II). (I) usually lose tolerance during the later months of (III), and regain it after childbirth, so that hypoglycaemia is common during (IV). With adequate treatment (III) is not harmful to (I). There is a marked tendency to ketosis in pregnant (I).

NUTR. ABS. (m)

Relationship of excretion of water, anions, and cations to glycosuria in diabetes mellitus. H. KEILHACK (Z. ges. exp. Med., 1933, 89, 159—172).—In diabetes the vol. and sp. gr. of single specimens of urine are related to the amount and concn. of the glucose, and in about half the specimens examined the output of Cl, SO_4 , and P_2O_5 is in inverse proportion to the glycosuria (I), no such relationship being found with Na, K, and Ca. No difference is noted relative to the severity of the diabetes. In renal (I) no similar correlation is observed.

NUTR. ABS. (m)

Insulin ketonuria in children. N. SICK and M. WEICHSEL (Monatsschr. Kinderheilk., 1933, 58, 383—387).—Healthy, normally fed children, given 15 units of insulin in the morning, fasting, show no COMe_2 in the urine 5 hr. after the injection. Diabetic children given twice that dose with their usual food, or the same dose fasting, if the urine is sugar-free, show no COMe_2 in 5 hr.

NUTR. ABS. (m)

Mineral threshold in young epileptics. R. ENGEL, I. McQUARRIE, and M. ZIEGLER (Arch exp Path. Pharm., 1934, 174, 555—574; cf. A., 1933,

1337).—The balance of H_2O , Cl, Na, K, Ca, Mg, N, S, and P was determined in young epileptics under normal conditions and following treatment with luminal, NH_4Br , pituitary preps., etc., and the results were correlated with the incidence of epileptic convulsions.

F. O. H.

Alimentary lipaemia of man in fever. W. RAAB (Z. ges. exp. Med., 1933, 89, 616—621).—The blood-fat (petrol extract) curve after 100 c.c. of olive oil is flatter in patients with fever. This is attributed to increased storage of circulating fat in the liver, an effect similar to that of lipoitrin which apparently takes part in the chemical regulation of temp.

NUTR. ABS. (m)

Urinary excretion of iodine. G. M. CURTIS and F. J. PHILLIPS (J. Clin. Invest., 1933, 12, 963).—The urinary excretion (I) of I by patients with non-toxic goitre is not > that of those without thyroid disease. Administration of I to subjects with diffuse hyperplastic goitre is followed by slow (I), which rises parallel with clinical improvement. During the early stage of menstruation blood-I and (I) of I increase.

NUTR. ABS. (m)

Pathology of toxicosis in infants. Acid-base balance in parenteral infections. J. CSAPO and E. KERPEL-FRONIUS (Monatsschr. Kinderheilk., 1933, 59, 18—23).—Acidosis in all cases is due to increase in org. acids. Increases in P and Cl are not observed. HCO_3' of blood is much reduced.

NUTR. ABS. (m)

Blood-brain barrier in infectious diseases; its permeability to toxins in relation to their electrical charges. U. FRIEDEMANN and A. ELKELES (Lancet, 1934, 226, 719—724).—Lambdysentery toxin and cobra venom pass, but toxins of tetanus, diphtheria, and botulinus do not pass, the selective mechanism which regulates the exchange of substances between blood and brain.

L. S. T.

Composition of pus. R. VARA-LOPEZ and K. THORBECK (Zentr. inn. Med., 1933, 54, 913—917; Chem. Zentr., 1933, ii, 3151).—The p_n and sugar, K, Ca, Mg, albumin, and globulin content of pus from different sources have been examined.

H. J. E.

Phosphatase. IV. Serum-phosphatase of non-osseous origin. Significance of variations of serum-phosphatase in jaundice. A. BODANSKY and H. L. JAFFE (Proc. Soc. Exp. Biol. Med., 1933, 31, 107—109).—Serum-phosphatase was decreased by prolonged fasting and increased by administration of dextrin or in jaundice of hepatic origin, but not in that associated with anaemia.

CH. ABS.

Phosphatase. VII. Phosphatase of blood, spleen, liver, and kidney in acute lymphatic leucæmia. R. IWATSURU and Y. MINAMI (Biochem. Z., 1934, 268, 394—398).—The phosphatase content of the blood in chronic myelitic leucæmia (I) increases considerably, but in acute lymphatic leucæmia (II) shows scarcely any change. The phosphatase content of liver, spleen, and kidney in (II) gives vals. < in (I).

P. W. C.

Blood-proteins during experimental liver-impairment by Eck fistulae. R. JURGENS and F.

GEBHARDT (Arch. exp. Path. Pharm., 1934, 174, 532—543).—In dogs with Eck fistulae, ingestion of large amounts of horse-flesh produces a marked increase in the blood-fibrinogen and -globulin. The extent of the increase indicates an extra-hepatic source of blood-proteins, probably the reticulo-endothelial system.

F. O. H.

Proteinuria in chronic nephritis. P. M. T. KERRIDGE (Lancet, 1934, 226, 675—678).—Proteins have been separated from the urine of cases of chronic nephritis by dialysis against NaCl solution. When injected intravenously into anaesthetised cats they were not excreted.

L. S. T.

Effect of renal insufficiency on plasma-magnesium and magnesium excretion after ingestion of magnesium sulphate. A. D. HIRSCHFELDER (J. Biol. Chem., 1934, 104, 647—653).—In normal animals and man about 42% of MgSO_4 administered orally is excreted by the kidneys in 24 hr. Little rise of plasma-Mg takes place, but in animals with excised or injured kidneys a marked rise in plasma-Mg is found which frequently exceeds 16.0—17.0 mg. per 100 c.c. and results in coma. The rate of excretion of Mg by injured kidneys is similar to that of phenolsulphonephthalein rather than that of xylose, so that it is probably excreted by the tubules.

W. O. K.

Role of the kidney in experimental acidosis in healthy subjects. W. MARKERT (Compt. rend. Soc. Biol., 1933, 113, 957—959).—In man administration of 10—13 g. of NH_4Cl daily for 5—8 days causes the alkali reserve of the plasma to fall to 20 vol.-%. The urinary output increases by 27—171% on the second day, then decreases to nearly normal. NH_3 excretion increases up to sixfold and urea and Cl^- excretion rise. The p_{H} of the urine falls to 4.7.

NUTR. ABS. (m)

Role of the kidney in experimental acidosis. Site of production of ammonia. W. MARKERT (Compt. rend. Soc. Biol., 1933, 113, 962—964).—The NH_3 content of the blood in the healthy subject under NH_4Cl acidosis and with free NH_3 excretion is 12—18 mg. per 100 c.c. In uræmic acidosis, when NH_3 excretion is low, the val. is 23 mg. The glomerular system of the kidney is the site of NH_3 production.

NUTR. ABS. (m)

Role of the kidney in experimental acidosis in Bright's disease. W. MARKERT (Compt. rend. Soc. Biol., 1933, 113, 959—961).—In chronic nephritis daily administration for 5—8 days of 10—13 g. of NH_4Cl causes a rapid fall in the alkali reserve of the blood and an increase in blood-urea. Urinary excretion of NH_3 increases slightly.

NUTR. ABS. (m)

Relation of plasma-cholesterol to obesity and to some of the complicating degenerative diseases (diabetes mellitus, essential hypertension, osteo-arthritis, and arterio-sclerosis). B. BRUGER and C. A. POINDEXTER (Arch. Int. Med., 1934, 53, 423—434).—Simple obesity in man is not associated with hypercholesterolaemia (I), but obese subjects suffering from degenerative diseases frequently develop (I).

W. O. K.

Blood in normal pregnancy. III. Haemoglobin and cell volume coefficients; erythrocyte volume, haemoglobin content and concentration; colour, volume, and saturation indexes. IV. Percentages and grams per kilogram of serum-protein and fibrin and variations in total amount of each. W. J. DIECKMANN and C. R. WEGNER (Arch. Int. Med., 1934, 53, 345—352, 353—366).—III. In normal human pregnancy (I) from the 26th to the 35th week, the erythrocytes are slightly larger and contain more haemoglobin than normally, becoming normal at term. The individual variation of the various indexes is large.

IV. During (I) a slight fall occurs in the concn. of serum-protein (II), which is at a min. a few days *post partum*. The amount of (II) per kg. of body-wt. remains approx. const. The concn. of fibrin in the plasma and the amount per kg. of body-wt. increase during (I).

W. O. K.

Acid-base balance of the minerals retained during human pregnancy. C. M. COONS, R. R. COONS, and A. T. SCHIEFELBUSCH (J. Biol. Chem., 1934, 104, 757—768).—A preponderance of the base-forming elements was retained, usually in amounts exceeding the foetal requirements. The mean daily retentions in g. were: Ca 0.28, Mg 0.06, Na 1.26, K 0.51, Cl 0.89, S 0.0, P 0.30.

H. G. R.

Effect of a calcium-deficient diet on pregnant ewes. A. H. H. FRASER, W. GODDEN, and W. THOMSON (Vet. J., 1933, 89, 408—411).—Serum-Ca was lower on a Ca-deficient diet.

NUTR. ABS.

Cholesterol balance in pregnancy and the puerperium. Pregnancy hypercholesterolaemia. C. KAUFMANN and O. MUHLBOCK (Z. ges. exp. Med., 1933, 89, 200—210).—During pregnancy (two primiparae) the output of cholesterol (I) was > the intake, although serum-(I) was high and (I) was being stored in the foetus. In one case, over 36 days, the negative balance was 8 g., which is about the same as that for non-pregnant women. In one patient, from the tenth to the forty-first day of the puerperium, the output [milk (5.8 g.) and excreta] was > the intake by 15.3 g., so that during lactation the organism must synthesise large amounts of (I).

NUTR. ABS. (b)

Phosphorus and rickets. III. Inhibition of bone calcification of rachitic rats by metallic carbonates and phosphates. R. LECOQ and H. VILLETTE (J. Pharm. Chim., 1934, [viii], 19, 201—206).— MgCO_3 and SrCO_3 inhibit the calcifying effect of Na_2HPO_4 on rats rendered rachitic by the Randoim-Lecoq diet (A., 1928, 556). Mg and Sr phosphates exert a calcifying effect. Fe and Mn carbonates and phosphates all inhibit calcification. Bi and Ca carbonates cause only slight inhibition, whilst the phosphates are strongly inhibitory. Thus the anti-rachitic activity of phosphates is affected both by the metal itself and by the basicity of the salt.

C. G. A.

Treatment of tetany. I. SNAPPER (Lancet, 1934, 226, 728—731).—Oral administration of small amounts of the oil-sol. fraction of irradiated ergosterol in tetany restores blood-Ca to the normal level.

L. S. T.

Diet of tuberculous and non-tuberculous children. Effect of increased supply of vitamin-B concentrate and minerals. P. D. CRIMM, I. J. RAPHAEL, and L. F. SCHNUTE (Amer. J. Dis. Children, 1933, 46, 751—756).—Children receiving a cereal mixture supplying Ca, P, Fe, Cu, and vitamins-B₁, -B₂, and -E showed greater increases in wt. and in blood-haemoglobin than those receiving regular diets or diets containing added vitamin-B or minerals. Serum-Ca and -P also increased. CH. ABS.

Lipins and lipin diseases. III. Lipin content of tissues in Schuller-Christian's disease (xanthomatosis) and lipin content of human tissues. D. M. COWIE and M. C. MAGEE (Arch. Int. Med., 1934, 53, 391—399).—In a case of Schuller-Christian's disease, no significant change in the tissue lipins (I) was found except that the xanthomatous masses had a high content of (I), about 50% of which was cholesterol. W. O. K.

Blood-calcium and -potassium in totally gastrectomised dogs. L. BOUISSET and G. DUCLOS (Compt. rend. Soc. Biol., 1933, 113, 1360—1362).—The alkali reserve, total blood-Ca, plasma-Ca, total blood- and plasma-K are all lowered in the dog after gastrectomy. All return to normal levels in time, the Ca levels last. The absence of the stomach does not affect the assimilation of the Ca and K in the diet. NUTR. ABS. (m)

Water and sodium chloride balance in patients before and after surgical operations. J. D. STEWART, J. H. TALBOTT, and E. D. CHURCHILL (J. Clin. Invest., 1933, 12, 978).—After herniotomy there is a slight, and after thoracoplasty a marked, decrease of serum-Cl (I), but no significant change in NaCl retention. After partial gastrectomy there is a slight fall in (I) and a marked negative balance of NaCl. NUTR. ABS. (m)

Glutathione and irradiated yeast. C. T. BAUMANN and J. VON DESCHWANDEN (Mitt. Lebensm. Hyg., 1933, 54, 281—302; Chem. Zentr., 1933, ii, 3445).—Statistics are given correlating the glutathione (I) content of the blood with frequency of illness. The average content of (I) was 25.32 mg. per 100 c.c., the val. undergoing seasonal fluctuations. H. J. E.

Co-ordination of the reproductive processes. A. S. PARKES (Lancet, 1934, 226, 557—563).—A lecture. L. S. T.

Respiration of *Arbacia* eggs. R. W. GERARD and B. B. RUBINSTEIN (J. Gen. Physiol., 1934, 17, 375—381).—Discrepancies in the results obtained by Tang and Gerard (A., 1933, 87) and Whitaker (A., 1933, 304) with preps. of *Arbacia* eggs for respiration studies are due to errors of measurement of egg vols. by centrifuging. The respiration rate of unfertilised eggs of *A. punctulata* at 21° is 0.9 cu. mm. O₂ per hr. per 10 cu. mm. of eggs. A. L.

Biochemistry and biophysics of the developing hen's egg. II. Influence of composition of air. A. L. ROMANOFF and A. J. ROMANOFF (Cornell Univ. Agric. Exp. Sta. Mem., 1933, No. 150, 36 pp.).—During the first few days of incubation a moderate proportion (<1%) of CO₂ in the atm. tended to

stimulate and higher proportions (>1%) to retard the growth of the embryo. Very low and very high CO₂ contents increased mortality during early incubation. The [H⁺] of ovalbumin was directly related to the [CO₂], of the incubator atm. during the first week of incubation, and affords a measure of the trustworthiness of the incubator and the efficiency of hatching. A. G. P.

Germ layer origin and mitotic potentiality of regenerating tissues in *Clymenella torquata*. F. S. HAMMETT (Protoplasma, 1933, 20, 161—168).—Mitotic activity in all three chief germ-layer derivatives of regenerating *C. torquata* was favoured by SH and retarded by its suboxidised products. The extent of the effects differed in the three types of growing tissue. A. G. P.

Metabolism and anaerobiosis of tissue cultures. H. LASER (Biochem. Z., 1934, 268, 451—456).—Cultures of heart tissue live anaerobically for a long time, retaining pulsation for > 3 days. Connective tissue cultures can also live and grow for a long time both in N₂ and after respiration is inhibited by HCN. The respiration insensitive to HCN possessed a relatively greater action on fermentation than on total respiration. Addition of lactoflavin to these cultures increases the activity of respiration on fermentation. P. W. C.

Oxidation-reduction properties of "evolved carbohydrates" in absence of oxygen. N. MAYER-REICH (J. Chim. phys., 1934, 31, 9—42).—By "evolved carbohydrates" is understood the active substance described by Wurmser and Geloso (A., 1929, 719). The lack of agreement between potentiometric titration curves for oxidation and subsequent reduction is due to instability of the oxidised form, leading to formation of CO₂. Apart from this phase of the reaction, evidence is adduced in favour of the reversibility of the oxidation-reduction. When an inert electrode is placed in the solution in absence of an oxidising agent, a definite p.d. is set up, which is a function of the temp. and the activity of H⁺. E. S. H.

Oxidation-reduction processes in muscular work. I. Potential of Ringer's solution after perfusion through an isolated frog's heart. II. Potential of blood and urine in muscular work. A. J. CHARIT and I. I. FEDEROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 68—73, 130—135).—I. The E_H of Ringer's solution (I) perfused through a beating frog's heart falls sharply to a min. after 30 min., and then gradually rises. On adding KCN (0.0002M) to (I) the E_H rises during perfusion, whilst if (I) is saturated with CO the E_H rises during the first 30 min., and then falls.

II. The E_H of femoral arterial and venous blood-filtrates falls to a min. 15 min. after prolonged clonic contraction of a dog's gastrocnemius; that of the urine is at a min. after 1 hr. R. T.

Chemical changes accompanying muscular activity and hyperthermia. I. Analytical methods. T. CAHN, J. HOUGET, and R. JACQUOT (Ann. Physiol. Physico-chim. biol., 1933, 9, 205—245).—Methods are described for the determination

in muscle, blood, and liver of H_2O , total reducing carbohydrates, lactic acid, total P and P fractions, total fat, fatty acids, unsaponifiable matter, urea, NH_3 , creatine, creatinine, Na, K, and Ca. Results are accurate to within 3%.
NUTR. ABS. (m)

Post-mortem breakdown of glycogen and accumulation of lactic acid in fish muscle. I. J. G. SHARP (Proc. Roy. Soc., 1934, B, 114, 506—512).—The rates of breakdown of glycogen (I) and accumulation of lactic acid (II) decrease with fall of temp. from 15° to 0° . At -2° the rates are as great as at 15° , but fall to approx. zero at -10° . If excess of (I) is present, no further change of concn. of (I) or (II) occurs when the concn. of (II) reaches 0.40 g.-%, $\frac{1}{2}$ to $\frac{2}{3}$ of (I) being recovered as (II). With insufficient (I), all of it disappears, giving (II) quantitatively.
C. G. A.

Electric potentials determined in the striped muscle of the frog. J. W. LANGELAAN (Arch. Neerland. Physiol., 1934, 19, 58—77).—Two potential levels, +0.360 volt and -0.340 volt at p_H 7.4, are determined by the O and H electrodes, respectively. They correspond with the reactions $AcCO_2H$ (I) \rightarrow lactic acid and glycogen \rightarrow (I).
C. G. A.

Influence of sympathetic nerves on the metabolism of striped muscle of the frog. J. W. LANGELAAN (Arch. Neerland. Physiol., 1934, 19, 78—87).—Section of the sympathetic nerves raises the lower (H electrode) potential corresponding with a 7% decrease of free energy in the reaction glycogen \rightarrow lactic acid, but has no effect on the higher (O electrode) potential.
C. G. A.

The amphibian organiser. J. NEEDHAM, C. H. WADDINGTON, and D. M. NEEDHAM (Proc. Roy. Soc., 1934, B, 114, 393—422).—Induction of a secondary embryonic axis in gastrulae can be accomplished by (a) cell-free and (b) Et_2O and petrol- Et_2O extracts of the neurula and by adult amphibian tissues and Et_2O extracts of adult viscera.
H. G. R.

Glutathione concentration and hereditary body size. II. Glutathione concentration in non-nursed young of six populations of rabbits differing in genetic constitution for adult size. P. W. GREGORY and H. GOSS (J. Exp. Zool., 1933, 66, 155—173).—In races of rabbits differing in genetic constitution for adult size, the concn. of glutathione (possibly with other SH-compounds) in the unnursed young at birth increases in proportion to potential adult size from the smallest to the largest.
NUTR. ABS. (m)

Biochemistry of Magaki (*Ostrea gigas*, Thunberg). II. Seasonal variation in chemical composition. B. MASUMOTO, M. MASUMOTO, and HIBINO (J. Sci. Hiroshima Univ., 1934, A, 4, 47—56).—During the period of fattening of the oyster (autumn and winter) and the early part of the period of gonad ripening (early spring) the ratio (I) of dry meat to shell rapidly increases, glycogen (II) and fat (III) accumulate [(III) being probably derived from (II)], and the H_2O content (IV) falls to a min. In late spring and summer (period of discharge of sexual products), (I), (II), and (III) diminish rapidly,

and (IV) rises to a max. Total N and ash contents (V) change in harmony with the total amount of meat, reaching a max. in June. There is an intimate correlation between growth of shell and (V).
A. E. O.

Relation between toxicity, resistance, and time of survival and related phenomena. L. REINER (J. Gen. Physiol., 1934, 17, 409—444).—The equation (I) $t = -a \log_2(h-r) + k$, where a and k are const., t is time of survival, r the resistance, and h toxicity, is derived. If vals. proportional to r are calc. with (I) and the % mortality is plotted against them, symmetrical curves are obtained, even although the corresponding mortality-time curves are asymmetrical. Assuming that r varies according to probability rules, theoretical mortality-time curves can be constructed from (I) which are similar to the experimental curves. Variation of temp. affects mainly the const. a . (I) is tested in four different combinations of the variables, concn., r , t , and temp., and the agreement with experimental vals. is satisfactory. Any noxious agent acting on a unicellular organism may be characterised by three consts.: r , which is the threshold val. at which the agent is still fatally toxic for the organism; a , the time corresponding with a difference of 1 between h and r ; and the const. γ of the function representing the relation between h and the concn.
A. L.

Possible cause of old age. I. W. D. HACKH and E. H. WESTLING (Science, 1934, 79, 231).—The increase in the proportion of H_2O in the body-fluids may account for the increasing inhibitory action of the protoplasm during senility.
L. S. T.

Physico-chemical factors in the ecology of mosquito larvae in Tong-king. II. H. G. S. MORIN and H. BADER (Ann. Inst. Pasteur, 1934, 52, 332—351).—The constituents of the earth (e.g., SiO_2 , clay) participate in the liberation of CO_2 from $CaCO_3$, whilst NaCl and KCl modify the solubilities of $CaCO_3$ and $MgCO_3$ in H_2O containing CO_2 . The bearing of these factors, together with that of the permeability, adsorption, etc. of the various strata of the soil, on the development of mosquito larvae is discussed.
F. O. H.

Chemistry of embryonic growth. IV. Copper requirement of the pig embryo. V. A. WILKERSON (J. Biol. Chem., 1934, 104, 541—546).—There is a const. increase in Cu throughout the embryonic period. In embryos 10—20 mm. long the liver (I) constitutes 14% of the wt. and contains approx. 100% of the total Cu. The (I) of embryos 160 mm. long constitutes 4% of the wt. and contains about 65% of the Cu. The blue colour of the ash in the early stages is due to its higher Cu content.
C. G. A.

Sodium chloride requirement and its relation to mineral metabolism. H. GLATZEL (Z. ges. exp. Med., 1933, 90, 59—77).—In an adult male on potato diet there was an increase of p_H , org. acids, and vol. of urine with reduction of NH_3 , Ca, P, and Cl (alkalotic); on rice there was increase of NH_3 , Ca, P, and org. acids, decrease of vol., and no change or decrease of p_H (acidotic). The increased intake of K delayed the reduction in Na output.

There was little change in the composition of the serum, but the CO_2 dissociation curve was shifted to the alkaline side, especially with roasted potatoes. It is incorrect that vegetarian diets (I), with the exception of rice, require addition of NaCl because of the large intake of K : the NaCl prevents the alkalotic action of (I) and is unnecessary with rice which has an acidotic tendency. NUTR. ABS. (m)

Mineral balance with (a) calcium chloride acidosis, (b) sodium hydrogen carbonate alkalosis. G. JOOS and W. MECKE (Arch. exp. Path. Pharm., 1934, 174, 676—686, 687—694).—(a) Ingestion (I) of CaCl_2 by man produces an increase in serum- Cl and a fall in $-\text{HCO}_3^-$ and -org. acids (II); subsequently $[\text{HCO}_3^-]$ further diminishes, whilst (II) increase. The urine- p_{H} decreases from 5.9 to 4.9, the excretion of NH_3 , Ca , and Cl markedly increasing. The balances (III) (i.e., differences between ingested and excreted amounts) of Na , Mg , and P before (I) are positive, whilst those of K , Ca , and Cl are approx. zero. During (I), (III) of Na , Ca , Cl , and P increase, whilst after (I) (when a compensatory alkalosis occurs) those of Na and Cl attain high negative and that of K high positive vals. The presence in the urine of significant amounts of unknown bases is not confirmed (cf. A., 1929, 343).

(b) (I) of NaHCO_3 produces a marked rise in serum- Na and a respectively gradual and sudden fall in the Mg and Ca levels, whilst the Cl and inorg. P decrease slightly. The (III) of Na , K , and Cl decrease to zero or negative vals., those of Mg and P decrease slightly, but remain positive, whilst that of Ca markedly increases. Other changes in the cations and anions of the blood and urine are described and compared with those due to CaCl_2 acidosis. F. O. H.

Relations between serum-calcium and basal metabolism. L. LENGYEL (Biochem. Z., 1934, 269, 133—149).—Single injections of Ca gluconate temporarily increase the Ca content (I) of the blood-serum in healthy rats (II), but continued daily injections of large doses, although they raise and maintain (I) in rats (III) suffering from chronic rickets, do not affect (I) in (II). Low (I) is always accompanied by increase in O_2 consumption (IV), and when (I) is increased by giving Ca , or in (III) also by giving vitamin- D , (IV) decreases in parallel, although it afterwards increases, whilst (I) remains normal. Prolonged giving of Ca to (II) increases (IV).

W. McC.

Relative utilisation of calcium from calcium carbonate and calcium gluconate by chickens. J. E. HUNTER, R. A. DUTCHER, and H. C. KNANDEL (Proc. Soc. Exp. Biol. Med., 1933, 31, 70—75).—Equiv. amounts of Ca as carbonate and gluconate were fed to laying hens receiving sub-optimal amounts of vitamin- D . The average shell-wt., % of shell-ash, and Ca content of the eggs were greater in the group receiving gluconate. NUTR. ABS. (b)

Absorption and storage of ingested calcium by rabbits. O. RIESSER and K. SALOMON [with L. KARBE] (Arch. exp. Path. Pharm., 1934, 175, 38—61).—Ingestion of 0.22—0.5 g. of Ca malonate (I), gluconate, or phosphate increases the serum- Ca (II)

by approx. 20% and the ultrafilterable (II) by approx. 40%. A small but definite increase also occurs in the Ca content of the skeletal muscle (III), heart (IV), liver, and brain (V); the lung- Ca is unchanged. Continuous intravenous injection of isotonic aq. CaCl_2 increases the Ca level of (III) and (IV), but not that of (V). Similar results are obtained with rats by feeding (I). F. O. H.

Soya-bean flour in infant feeding. Relation of the comparative intakes of nitrogen, calcium, and phosphorus to the excretion and retention of these elements by infants. G. STEARNS, M. J. OELKE, J. B. MCKINLEY, and E. A. GORF (Amer. J. Dis. Children, 1933, 46, 7—16).—In children receiving diets containing adequate vitamin supplies high intakes of N and Ca relative to P cause high urinary Ca and low P , and a shift in the mode of excretion of other bases from urine to faeces. Addition of $\text{Ca}_2(\text{HPO}_4)_2$ to the soya-bean food instead of CaCO_3 improves retention of N , Ca , and P . The relative amounts of these elements in the diet of infants are of greater importance than their abs. amounts; the proportions in cow's milk may be used as a guide. NUTR. ABS. (m)

Diffusion of inorganic phosphate into and out of the skeletal muscles and bones of the frog. M. G. EGGLETON (J. Physiol., 1933, 79, 31—48).—Only interspace H_2O is involved in phosphate (I) interchange in living muscle, the cell membranes being impermeable to (I). The results are correlated with the slight increase in inorg. (I) in the blood after exercise to exhaustion. NUTR. ABS. (m)

Bromine metabolism in hibernation. P. SUOMALAINEN (Suomen Kem., 1934, 7, B, 82).—The posterior brain of hibernating (I) and non-hibernating (II) hedgehogs contains, respectively, 0.386 and 0.193 mg. Br per g. of fresh wt. The remainder of the brain of (I) and (II) contains 0.023 and 0.022 mg. per g. of fresh wt., the blood 0.65 and 1.67 mg. Br per 100 c.c., respectively. J. L. D.

Biological significance of sterols. H. DAM (Nyt nordisk Forlag, København, Thesis, 1933, pp. 162).—In part a review. Chicks, from hatching to 2 months of age, synthesise sterol. Administration of cholesterol (I) for 3 days to a lactating goat gave no increase in milk-(I).

Chicks on a diet of casein, sol. starch, salt mixture, marmite, and filter-paper showed hæmorrhages resembling those of scurvy. These were not prevented by addition of lemon juice in presumably adequate quantities, by substituting yeast or wheat germ (II) for marmite (III), by altering the composition of the mineral mixture, or by feeding moderate amounts of gallstone-(I), cod-liver oil or fractions of it, or linseed oil, or by irradiation. Substitution of (II) for (III) caused "pellagrous" symptoms. NUTR. ABS. (b)

Origin, metabolism, and elimination of cholesterol in the animal organism. S. MINOVICI, M. VANGHELOVICI, and G. MARZA (Bul. Soc. Chim. Romania, 1933, 15, 137—152).—Dogs, mice, and cockroaches synthesise cholesterol from oleic acid, but not from stearic or margaric acid. The liver and spleen are active. C. G. A.

Distribution in the organism of fats absorbed from the intestine. G. PERETTI (Riv. Patol. sperim., 1933, 11, 47—56).—After administration of iodised fat to rabbits, by stomach tube, the blood-fat rose until the twentieth hr., fell to a min. at the forty-fourth hr., and again rose to a val. much > the initial. A similar sequence was observed in the lungs, spleen, pancreas, bone marrow, and muscles. In the liver, however, the fat val. was much > in the blood and rose steadily until the seventy-second hr. The liver plays the chief part in the fixation of fat, for which, as the role of the spleen is unimportant, the reticulo-endothelial system is probably not responsible.

NUTR. ABS. (b)

Distribution in the organism of fats introduced directly into the circulation. G. PERETTI, L. REALE, and L. CIOGLIA (Riv. Patol. sperim., 1933, 11, 73—98).—After the intravenous injection of iodised fat emulsions into dogs, there was at first a rapid disappearance of the fat from the blood, with an increased concn. in the liver, the spleen, and, to a smaller extent, the bone marrow. Later the blood val. rose, whilst the others fell. Variable amounts were found in the lungs.

NUTR. ABS. (b)

Fat-splitting in the lungs. L. JANKOVICH (Beitr. path. Anat., 1933, 92, 110—118).—Fat embolism can be detected morphologically in human lung up to about 14 days. Absorption of fat does not occur in lung by cellular activity. The decrease of fat droplets accompanying various lung processes previously observed in lower animals, and now in man, may be due to either lung- or blood-lipase.

NUTR. ABS. (b)

Fat metabolism in the lung. G. HOPPE (Z. ges. exp. Med., 1933, 89, 97—104).—The total Et₂O-sol. fraction of blood from the right auricle and femoral artery in dogs and rabbits showed little difference in seventeen cases, an increase of 18% in femoral artery blood in five cases, and a decrease of 9.5% in eight cases. There was no apparent correlation between these changes and the val. of the blood-fat. The lungs are probably not of special significance in the metabolism of fat.

NUTR. ABS. (b)

High-carbohydrate and high-fat diets. Variations in blood with dieting. E. M. GREISHEIMER, E. GOLDSWORTHY, and G. THOMAS (Proc. Soc. Exp. Biol. Med., 1933, 30, 1426—1428).—After a high-fat diet, the sugar-tolerance curve for a normal individual was of the mild diabetic type—blood-sugar 0.201% at 120 min. Urea-N was increased slightly, relative to the protein intake. Total non-protein-N was 29.5—47.7 mg. per 100 c.c.

NUTR. ABS. (b)

Alimentary metabolic reactions. V. Metabolic reactions after fat, glucose, and meat feeding. S. LEITES, V. JUSSIN, and M. VODINSKI. **VI. Metabolic reactions after glucose and fat feeding in splenectomised animals.** S. LEITES, V. JUSSIN, M. VODINSKI, and A. KOSLOVA (Z. ges. exp. Med., 1933, 90, 378—395, 396—407).—V. Administration of linseed oil (I) or butter (II) to dogs produces, within 7 hr., no increase of blood-fat (III), and ingestion of hempseed oil (IV) causes only a slight rise; in man a corresponding amount of (II) causes hyperlipæmia. These fats cause an

increase in blood-ketones (V) and cholesterol (VI) and frequently a fall in non-protein-N (VII) and sugar. Prolonged ingestion (one month) of (I) or (IV) causes a reduction of (III) and (V) and a smaller increase of (VI). Ingestion of glucose leads to reduction of (III) and (V) parallel with the hyperglycæmia (VIII). Ingestion of meat causes increase in (VII) and (VI) (slight) and decrease in (V). A meal of fat and peptones (or meat) lessens the increase in lipæmia, (V), and (VII), whilst glucose with fat reduces the hyperketonæmia. Glucose tolerance is decreased by previous ingestion of oil or meat. Adrenaline (VIII) is increased and insulin hypoglycæmia (IX) decreased when fat is administered. After long-continued administration of oil the action of insulin is increased in normal and decreased in splenectomised dogs (X).

VI. In (X) the blood-sugar curve after glucose is more prolonged and > in normal for the first month after operation: thereafter it is reduced. (IX) is more pronounced. (I) or (II) ingestion produces little increase of (III) and (V) and occasionally a reduction. After long-continued administration, oil causes a greater increase of (V). After prolonged feeding with unsaturated fats the fat content of the liver and omentum is greatly increased with rise of the I val. which is greater in (X); in the normal dog there is a very large increase in the fat of the spleen with a fall in the I val.

NUTR. ABS. (m)

Sexual variation in carbohydrate metabolism.

III. Comparative glycogen and fat content of liver and muscles of rats and guinea-pigs. H. J. DEUEL, jun., M. GULICK, C. F. GRUNEWALD, and C. H. CUTLER (J. Biol. Chem., 1934, 104, 519—530; cf. A., 1933, 631).—The liver-glycogen (I) of fasting male rats was > that in females after administration of glucose; after 96—120 hr. a sharp rise in (I) occurred in the females, producing a (I) > that of the males. The liver-fat of the females was > that of the males. After a high-carbohydrate diet with no fasting (I) was the same in males and females. The (I) of female guinea-pigs after 48 hr. fasting was > that of males.

H. D.

Magnesium and carbohydrate metabolism.

H. FRANKE (Arch. exp. Path. Pharm., 1934, 174, 727—741).—The liver-glycogen (I) of rabbits is increased by 300—400% by continuous (1 hr.) intravenous injection (II) or by ingestion of aq. MgCl₂ (but not MgSO₄) and, to a greater extent, of MgCl₂+Mg gluconate; the muscle-glycogen (III) remains const. or is slightly increased. Both (I) and (III) are markedly diminished by (II) of adrenaline, the action of which on (III), but not on (I), is inhibited by simultaneous (II) of Mg salts. Ingestion of Ca salts has no influence on (I) or (III).

F. O. H.

Nutritive value of alfalfa leaves and stems. J. SOTOLA (J. Agric. Res., 1933, 47, 919—945).—The protein (I) content of stems (II) of lucerne hay is approx. 8%, and of leaves (III) 19%, on the basis of 10% H₂O content. The ash, crude fat, N, and P in (III) are all > those in (II). The Ca : P ratio is approx. 16 : 1 in (III) of the first and third cuttings, but only 8 : 1 (owing to increase of P) in (III) of the

second cutting. The urinary vol. of lambs fed on (III) was 3.3 times that of lambs fed on (II) alone, and the urine was richer in N, whilst the faeces contained less H_2O . (III) are 3.5 times as efficient as (II) in providing digestible (I), and the biological val. of (I) of (III) is higher. In spite of the high Ca : P ratio in (III), these are an important source of Ca and P, since the ratio of Ca retained to P retained is approx. 3.3 : 1. P. G. M.

Effect of ripening of cheese on the nutritive value of milk-curd protein. J. R. BEADLES, J. H. QUITENBERRY, F. I. NAKAMURA, and H. H. MITCHELL (J. Agric. Res., 1933, 47, 947—965).—American Cheddar, Swiss (I), and Roquefort, but not Limburger (II), cheese are superior to rennet milk curd (III) as a source of protein for rats. (III) has a somewhat higher coeff. of digestibility (89.65) than any of the cheeses [(II), 87.22]. The biological val. of (III) (73.1) is essentially the same as that of (I) (73.3), whilst that of (II) is approx. 6% lower, since the ripening process in (II) involves destruction of cystine. P. G. M.

Long-period metabolism investigations on healthy infants. Breast-milk, cow's milk with alkali salts of plant acids. G. KRAUSE (Arch. Kinderheilk., 1933, 99, 228—243).—The N retention (I) was determined in four healthy infants kept for periods of 6 weeks on breast-milk (II) and cow's milk (III) and 12 days on (III) with "Basika" (a mixture of alkaline salts derived from vegetables). On (II) the (I) was 58—114 mg. per kg. per day; the absorption was 69.5—78% of the intake. On (III) (I) was increased only for the first few days; thereafter it was practically the same as on (II). Although the intake was nearly three times greater, the absorption was 86—88%. There is thus no evidence of excessive (I) in the bottle-fed infant. When "Basika" was added to (III) the urine became alkaline, the NH_3 output was decreased, and the (I) was raised (101—123 mg. per kg. per day). This supports Berg's view that, for an optimum utilisation of protein, an excess of alkali is necessary.

NUTR. ABS. (b)

Proteins causing alimentary unbalance. R. LECOQ (Compt. rend., 1934, 198, 1269—1271).—The peptone of ovalbumin, or, less so, of muscle, causes alimentary unbalance in pigeons. R. S. C.

Nutritive value of the silkworm pupa produced in Manchuria. I. Protein from the pupa of *Bombyx mori* and *Antheraea pernyi*. II. Vitamin-A, -B, and -D in the pupa of *B. mori* and *A. pernyi*. S. IZUME, Y. YOSHIMARU, and K. YOSHIMARU (J. Agric. Chem. Soc. Japan, 1933, 9, 922—931, 932—939).—I. The proteins are similar to muscle-protein in respect of the $(NH_2)_2$ -acid, cystine, tryptophan, and tyrosine contents. The nutritive val. of *B. mori* protein is equal to, and of *A. pernyi* protein <, that of beef protein.

II. The pupa oil is rich in vitamin-A, but poor in -D. Vitamin- B_1 and - B_2 contents of the pupa are high if the pupa is separated from fresh cocoons.

CH ABS

Cystine deficiency of soya-bean protein at various levels in a purified ration and as a sup-

plement to maize. C. L. SHREWSBURY and J. W. BRATZLER (J. Agric. Res., 1933, 47, 889—895).—Additions of cystine to rations containing 10% of soya-bean meal (I) improved the live-wt. increases in rats except when the ration included yellow maize. With 15% of (I) in the ration the benefit of cystine was less marked. A. G. P.

Specific dynamic action of intravenous injection of amino-acids : its relation to basal metabolism. A. SZAKALL (Biochem. Z., 1934, 269, 196—204).—In resting dogs the basal metabolism (I) fluctuates during 8—14-hr. periods. The extent of sp. dynamic action (II) produced by giving NH_2 -acids (III) [glycine, alanine (IV), glutamic acid (V)] is independent of the nature and amount of (III), but is influenced by the capability of the organism to react to their stimulating effects. (IV) always increases (I), (V), which causes decrease in body temp., sometimes produces no (II). W. McC.

Tryptophan metabolism. V. Growth on tryptophan-deficient diets supplemented with β -3-indolylacrylic, α -oximino- β -3-indolylpropionic, and *l*- and *dl*- β -3-indolyl-lactic acids. VI. Production of kynurenic acid from indole derivatives. L. C. BAUGUES and C. P. BERG (J. Biol. Chem., 1934, 104, 675—689, 691—699).—V. β -3-Indolylacrylic acid (I), m.p. 195—196°, was synthesised from indole-3-aldehyde by condensation with malonic acid and elimination of CO_2 , α -oximino- β -3-indolylpropionic acid (II), m.p. > 175°, from β -3-indolylpyruvic acid (III) and NH_2OH . Of the three acids tested, only *dl*- β -3-indolyl-lactic acid (IV) could replace tryptophan in the diet. There were indications that the *d*-acid was particularly effective.

VI. (III) and (IV) were the only indole derivatives converted into kynurenic acid by the rabbit. (II), (I), and (IV) were partly recovered from the urine after administration. Following the administration of (IV) *dl*- and *l*-(IV) were obtained. No appreciable amount of (III) was recoverable. H. G. R.

Renal excretion of creatinine. I. Functional relation between rate of output and concentration in plasma. R. DOMINGUEZ and E. POMERENE (J. Biol. Chem., 1934, 104, 449—471).—The urinary excretion (I) and plasma concn. (II) of creatinine are exponential functions of *t*, after an initial disturbance due to its ingestion, approaching asymptotically the endogenous levels. The average rates of decrease of these functions are equal. The plot of (I) against (II) is a straight line not passing through the origin, so that the ratio of (I) to (II) is not a const. and variations found by Rehberg (A., 1926, 858) are accounted for on this basis together with errors of observation which may produce variations up to 28%. H. D.

Origin of urinary ammonia. H. FASOLD (Z. ges. exp. Med., 1933, 90, 502—507).—Kids fed on goat's milk excreted large amounts of NH_4^+ when they were given HCl. Adult goats and rabbits excrete only minimal amounts of NH_4^+ . Slices of kidney from kids, goats, and rabbits produce very little NH_4^+ from *dl*-alanine in contradistinction to the kidney of rats and other carnivora. All NH_2 -acids cannot, therefore, be precursors of NH_4^+ . NUTR. ABS. (b)

Uricolysis. W. SCHULER (Klin. Woch., 1933, 12, 1253—1254).—Oxidation of uric acid to allantoin takes place in three stages, viz., oxidation, hydrolysis, and decarboxylation. NUTR. ABS.

Chemistry of mitogenetic radiation. IV. Specificity of mitogenetic spectra of oxidation reactions and the atomic basis of mitogenetic radiation. A. E. BRAUNSTEIN and A. POTOZKY (Biochem. Z., 1934, 268, 422—443).—The phenomenon of mitogenetic radiation is regarded as an ultra-violet oligoluminescence (I). Using various inorg. and org. systems, it is shown that the spectra of cathodic (I) are sp. for the reduction processes occurring at the cathode and independent of the current strength and tension. The oxidation-reduction spectra with inorg. cation oxidation in H_2O depend only on the electron acceptor, and not on the electron donor. The spectra of the chemical and electrochemical reductions of the same electron acceptor are identical. P. W. C.

Effect of mitogenetic rays on eggs of *Drosophila melanogaster*. L. K. WOLFF and G. RAS (Nature, 1934, 133, 499).—Irradiation by Gurwitsch rays from a culture of *Staphylococcus pyogenes aureus* increases the no. of eggs hatched by 16—47%.

L. S. T.

Effect of temperature of an odorous gas on the olfactory sensation. H. WOERDEMAN (Arch. Neerland. Physiol., 1934, 19, 88—93).—*iso*Amyl acetate at 50° has a more powerful olfactory effect than at 20°.

C. G. A.

Chemotropic response of a chironomid fly to petroleum oils. T. AHMAD (Nature, 1934, 133, 462—463).—*Forcipomyia* sp. is attracted in large nos. to petroleum oils, oils containing hydrocarbons with low b.p. being the least attractive. L. S. T.

Variations in the amount of yellow pigment (xanthophyll) in certain fishes, and of the possible effects upon this of coloured backgrounds. F. B. SUMNER and D. L. FOX (J. Exp. Zool., 1933, 66, 263—301).—When *Fundulus parvipinnis* (I), *Gillichthys mirabilis*, and *Girella nigricans* (II) were kept in aquaria with red, yellow, or white backgrounds, their colour varied with expansion or contraction of the xanthophores, but there was no evidence that the xanthophyll (III) increased or decreased in response to environmental change except with (II) which showed a slow decrease, particularly on a white background. In (I) the (III) content was maintained, although the food contained chiefly carotene. NUTR. ABS. (b)

Adsorption of optical isomerides by nerve tissue. G. H. RICHTER and R. C. DOSSER (Biochem. Z., 1934, 268, 399—405).—Optical isomerides are usually adsorbed to differing extents on optically active substrates and nervous tissue, but to the same extent on optically inactive substrates, e.g., animal charcoal. P. W. C.

Influence of $[H^+]$ on nerve chronaxie. L. DELIUS (Z. Biol., 1934, 95, 27—43).—With frog nerve-muscle preps., increase of $[H^+]$ produces a rise in the rheobase (I) and a disproportionate fall in the chronaxie (II). In weakly and strongly alkaline buffers (when steady vals. are not attained) (I), respectively, de-

creases and increases, (II) slightly increasing in each case. These effects are reversible even after long exposure to acid or alkaline media. F. O. H.

Tissue reactions in immunity. XIV. Specific reacting capacities of different tissues of an immunised animal. R. L. KAHN (Science, 1934, 79, 172—175).—The degree of immunity of different tissues in a protein-immunised rabbit is determined by establishing quantitatively the capacities of the tissues to react with sp. antigen. The skin has a sp. reacting capacity for antigen > ten times those of muscle, brain, and *in-vivo* plasma. L. S. T.

Biochemistry of anaesthesia. F. F. NORD (Science, 1934, 79, 159).—Critical (cf. A., 1932, 550). L. S. T.

Pharmacological action of the whole secretion and of extracts of male accessory sex glands. U. S. VON EULER (Arch. exp. Path. Pharm., 1934, 175, 78—84).—The secretions of prostate gland (man, dog, rabbit) and seminal vesicles (sheep, pig, ox) contain a substance (I) which has a depressor action (not affected by atropine) and stimulates the isolated intestine (rabbit). (I), which is pptd. by phosphotungstic acid and $HgCl_2$ and migrates to the cathode on electro-dialysis, resembles or is identical with the substance isolated by Euler and Gaddum (J. Physiol., 1931, 72, 74). F. O. H.

Chemistry and pharmacology of the kola nut. W. GEHLEN (Arch. exp. Path. Pharm., 1934, 174, 695—714).—Digestion of the fresh nuts with $EtOH-HCO_2H$ and subsequent treatment with org. solvents yields colocatechin (I) (0.4%), m.p. 170—175°, caffeine (II), and cola-red (III). Admixture of (I) (1 mol.) in $EtOH$ and (II) (2 mols.) in $CHCl_3$ affords caffeine-catechin (IV), m.p. 137—139° (cf. A., 1930, 1223; 1931, 96). (I) and (IV) do not agglutinate red blood-corpuscles, whilst (III) behaves as a tannin, producing tonic contraction of the frog's heart. (I), which has a slight toxic action, has no influence on the diuresis or isolated intestine (rabbit), but inhibits the action of (II) on the latter. Concns. of (I) of 1:500 stop the frog's heart in diastole. The action of (IV) mainly resembles that of (II). F. O. H.

Effect of phenylethanolamine and ephedrine on nasal membranes. T. B. GRAVE and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 35—36).— $OH-CHPh-CH_2-NH_2$ as the hydrochloride in H_2O or as oleate in mineral oil has the same effect on nasal membranes as corresponding ephedrine solutions. C. G. A.

Percutaneous absorption of salicylic acid and its derivatives. C. A. ROJAHN and E. WIRTH (Arch. exp. Path. Pharm., 1934, 175, 26—37).—Free salicylic acid (I), its alkali salts, and, to a smaller extent, its esters are absorbed by the rabbit's skin from ointments and fluid media. The presence of (I) or of skin irritants markedly increases the absorption. F. O. H.

Pharmacological actions of acetylsalicylic acid and strontium acetylsalicylate. I. SIMON (Arch. Farm. sperim., 1934, 57, 53—67).—Acetylsalicylic acid (I) and its Sr salt (II) are similar in their pharmacological actions, but (II) is less toxic than (I), and shows

less hæmolytic power, but more coagulative activity on the blood-proteins; unlike (I), it does not cause hæmoglobinuria *in vivo*. The beat of the isolated heart of the frog, inhibited by (I), can be restored temporarily by (II). The actions of (I) and (II) on the isolated blood-vessels, their behaviour in the animal organism when administered *per os*, and their augmentative effects on uric acid excretion are similar.

R. N. C.

Diuresis and metabolism. J. AMAR (Compt. rend., 1934, 198, 1179—1181).—The diuretic action of H₂O, beer, asparagus, cherries, and strawberries is a nutritive as opposed to a nervous effect. Urinary secretion is modified in proportion to metabolism.

P. G. M.

Excretion of aloes. G. F. HALL and W. M. KEIGHTLEY (Analyst, 1934, 59, 152—155; cf. A., 1933, 1198).—A small amount of aloes, hydrolysed (I) and unhydrolysed (II), is excreted in the urine, (I)+(II) up to 10 hr., (II) up to 60 hr., after ingestion of (II). The modified Schoutelen reaction for (II) is more delicate and distinctive than the Borntrager reaction for (I).

E. C. S.

Influence of ammonium carbonate and atophan on blood-uric acid and urate excretion with various diets. W. VON MORACZEWSKI, S. GRZYCKI, H. JANOWSKI, and R. SŁAWINSKI (Arch. exp. Path. Pharm., 1934, 174, 575—588).—The influence of substances which form uric acid (I) or increase its excretion is modified by the diet. Thus with a fat or sugar diet, nucleins and atophan significantly increase the blood- and urine-(I), respectively, but with a protein diet the effects are less marked. When a change of diet produces retention of H₂O by the body, there also occurs a retention of (I) and other urinary constituents which produces excretion of org. acids, a diminution in the alkali reserve of the blood, and liver impairment. Other metabolic disturbances accompanying diuresis are discussed.

F. O. H.

Phloridzin. II. Relation between phloridzin diabetes and glycosuria in normal rabbits and in rabbits with disturbance of liver function. III. Glutathione content of the tissues of phloridzinised rabbits. T. ONODERA (Sci-i-kwai Med. J., 1932, 51, No. 8, 17—29, 30—37).—II. In liver injury the disappearance of glycosuria (I) is slower than normal.

III. Average reduced glutathione contents of tissues of normal rabbits are: liver 0.2424, kidney 0.0823, adrenals 0.0193, muscle 0.0424, spleen 0.1249, testicles 0.0696, lungs 0.058, heart 0.0329%. The effect of max. phloridzin (I) is given by, respectively: —11, —1.0, +495.4, —2.4, +21, +60.8, +22.0, —4.0%.

CH. ABS.

Organoleptic bioassays. J. C. MUNCH, G. E. BYERS, and H. J. PRATT (J. Amer. Pharm. Assoc., 1934, 23, 24—25).—The bioassay of capsicum and ginger is possible by comparison with the threshold consens. (20 mg. and 400 mg. per litre, respectively) required to detect pungency in the throat.

C. G. A.

Bioassay of picrotoxin and *Cocculus indicus* preparations. J. C. MUNCH and A. M. PONCE (J. Amer. Pharm. Assoc., 1934, 23, 98—104).—Although

individual animals show large variations in their reactions to picrotoxin (I) and its preps. an assay based on the simultaneous injection of a standard amount of (I) (5 mg.) and the drug into similar groups of mice has been evolved.

E. H. S.

Detection and determination of novocaine. H. WILLSTAEDT (Biochem. Z., 1934, 269, 182—186).—The most sensitive reagent for detection of novocaine (I) (< 0.005 mg. per c.c.) is Reinecke's salt, although the test is not sp. For determination [if necessary after extraction (II) from biological material with Et₂O] of (I) it is diazotised and coupled with Na 8-amino- α -naphthol-3 : 6-disulphonate. The red colour produced is then compared with that of a standard. (II) is inapplicable if the amounts of (I) are small.

W. McC.

Combined [pharmacological] action of Solanaceæ alkaloids. H. YAMADA (Folia Pharmacol. Japon., 1933, 16, No. 3, 351—360).—The combined action of *l*-hyoscyamine, *l*-scopolamine, and *l*-homatropine on the parasympathetic fibres of the rabbit intestine and isolated frog heart is > that of any one in removing the effect of acetylcholine.

CH. ABS.

Pharmacology and chemistry of curine. F. HAUSCHILD (Arch. exp. Path. Pharm., 1934, 174, 742—754).—Curine (I) has a marked action on the heart, but has not the effect on the circulation characteristic of curare preps. (I) resembles caffeine in the paralyzing action of high consens. on striped muscle. The pharmacological properties of (I) confirm its identity with *l*-bebeerine (A., 1928, 1265) [or *l*- α -chondodendrine (A., 1922, i, 569)]. A quant. distinction between amorphous and cryst. (I) could not be detected.

F. O. H.

Preparation of highly-active calabash-curarine. F. HAUSCHILD (Arch. exp. Path. Pharm., 1934, 175, 14—16).—The min. lethal dose (I) of curarine for rats is 15—20% > that for rabbits (II). The purification and crystallisation of tube-curarine claimed by Zanelli (Arch. Ital. Sci. Farm., 1932, 1, No. 3) could only partly be confirmed; the prep. of Boehm (A., 1898, i, 283) appears therefore to be of max. purity. Calabash-curarine (III) is purified 200—300% by repeated pptn. with HgCl₂, but not by ultrafiltration, a (I) of 0.1 mg. per kg. for (II) being attained. Hence the purity of the (III) of Boehm (*loc. cit.*) is doubtful.

F. O. H.

Application of the mouse-tail phenomenon to the assay of morphine and scopolamine preparations. W. KEIL and A. KLUGE (Arch. exp. Path. Pharm., 1934, 174, 493—501).—The determination of morphine (I) (up to 0.013 mg. with an accuracy of $\pm 5\%$) and (I) derivatives by means of the mouse-tail reaction (II) (A., 1912, ii, 611) is described. The analgesic action of (I) and its derivatives is generally \propto the strength of (II). Scopolamine and genoscolamine diminish and, in sufficiently large doses, inhibit the (II) of (I); on this inhibition is based a method for their determination (up to 0.0005 mg. with an accuracy of approx. $\pm 15\%$). Atropine has no influence on the (II) due to (I).

F. O. H.

Distribution of nicotine in cigarette smoke. A. WENUSCH (Chem.-Ztg., 1934, 58, 206—207).—40—50% of the nicotine content (I) of the tobacco is

retained in the "secondary stream" smoke (II) of a freely glowing cigarette, 14% of the (I) in the (II) of a normally smoked cigarette, 25% being in the "main stream" smoke (III). In the smoke of a rapidly continuously drawn cigarette 3% of the (I) is in the (II) and 80% in the (III). The remaining (I) is decomposed.

C. G. A.

Tobacco smoke. IV. E. WASER and M. STAHLI (Z. Unters. Lebensm., 1934, 67, 280—284).—The HCN content (I) of cigarette (II) smoke (0.020—0.034% of the wt. of dry tobacco) is too small to be dangerous. Under const. conditions of smoking, (I) is const. for any one type of (II). It is independent of the nicotine content, but increases with increasing rate of smoking. Injection of H_2O or Bonicot into (II) has no effect on (I).

E. C. S.

Effects of cigarette smoking on the blood-sugar. H. W. HAGGARD and L. A. GREENBERG (Science, 1934, 79, 165—166).—Smoking produces a temporary increase in blood-sugar (I) and a corresponding increase in the rate of sugar combustion in the body. These effects are due to nicotine, and arise from its action on the adrenal glands. Smoking has no appreciable effect until the R.Q. and (I) have fallen below the respective vals. of 0.85 and 0.13%. By inducing a hyperglycæmia smoking may temporarily delay the development of hunger.

L. S. T.

Biochemistry of sleep and stimulation and the significance of cations. M. CLOETTA, H. FISCHER, and M. R. VAN DER LOEFF (Arch. exp. Path. Pharm., 1934, 174, 589—675).—Methods for the determination of Ca, K, and Mg in plasma (2—4 c.c.) or tissue (0.1—0.2 g.) are given. With men, dogs (I), and rabbits (II) sleep [normal or induced by narcotics (III)] is accompanied by a decrease in the plasma-Ca and -K (averaging 9.9, 16.6; 7.9, 15.3; 5.9, 12.9%, respectively) whilst the Mg level is not significantly changed. With cats (IV), in which (III) produce a stupor, the plasma-cations are approx. unchanged. With (I), (II), and (IV), psychomotor stimulation by administration of β -tetrahydronaphthalene produces corresponding increases in the Ca and K levels. Intracerebral injection of Ca into (I), (II), and (IV) induces a condition of sleep which, like that produced by (III), is accompanied by a fall of plasma-Ca and -K. The brains of (I) awake and asleep have Ca, K, and Mg contents of, respectively, 5.51, 350, 14.42, and 5.73, 358, 14.39 mg. per 100 g. Greater differences (which appear to be quantitatively related to the degree of sleep), although < those of the plasma, occur in the Ca content of the infundibular region (V) (cf. A., 1931, 386). Corresponding decreases occur in the brain on stimulation. Infundibular injection of KCl acts like that of stimulants, increasing the plasma-Ca and -K and lowering the Ca level of (V), whilst that of Ca-saponin does not induce sleep, indicating that the effect is not ionic, but due to a "dispersive" action of Ca. That injection of KCN into (V) induces sleep indicates that an increased [Ca] in (V) acts by inhibiting local oxidation processes. With (I), (II), and (IV), faradic stimulation lowers the Ca and K levels of striped muscle, indicating that the increase in plasma-Ca and -K due to stimulants is of peripheral origin; this is confirmed by the diminished action of

narcotics in lowering the Ca and K levels after curarisation.

F. O. H.

Biology of heavy water. G. N. LEWIS (Science, 1934, 79, 151—153).— H_2O is not highly toxic to tobacco seeds, yeast, flatworms, and mice and is tolerated in high concns. by lower organisms. The rate of the vital processes appears to be approx. \propto the fraction of H^1 in the total H, and when all H^1 is replaced by H^2 growth is extremely slow, if not completely inhibited.

L. S. T.

Diplogen and fish. G. VON HEVESY and E. HOFER (Nature, 1934, 133, 495—496).—Goldfish behave normally in H_2O containing 0.5 mol.-% H_2O . Using H_2O as indicator of the movement of the total H_2O in fish, nearly all the H_2O mols. leave the body of the fish within a few hr. and are replaced by H_2O mols. from the surrounding H_2O .

L. S. T.

Effect of fluorine in the nutrition of the chick. C. H. KICK, R. M. BETHKE, and P. R. RECORD (Poultry Sci., 1933, 12, 382—387).—CaF₂ is tolerated better than rock phosphate or NaF, with which > 0.036% F in the food proportionally decreased growth and food consumption. Blood-clotting time decreased with increase in ration-F. F ingestion did not affect Ca₃(PO₄)₂ in the tibiae at 8 weeks.

CH. ABS.

Effects of inhalation of hydrogen fluoride. I. Response following exposure to high concentrations. W. MACHLE, F. THAMANN, K. KITZMILLER, and J. CHOLAK (J. Ind. Hygiene, 1934, 16, 129—145).—The toxicity of HF to rabbits and guinea-pigs appears to be of the same order as that of HCl and SO₂.

H. G. R.

Halogen storage in eggs and their therapeutic value. L. BERKESSY and K. GONCZI (Magyar Orvosi Arch., 1933, 34, 402—409).—Hens were injected intravenously with 0.13—0.18 g. of NaI during 3 weeks. The eggs then contained 700—800 $\times 10^{-6}$ g. I per 100 g. After discontinuing the NaI the I content of the eggs fell to normal within a week. Feeding eggs with a high I content proved to be beneficial in Graves' disease.

NUTR. ABS. (b)

Absorption of iodine in relation to the organism as a whole. A. STURM and H. SCHULTZE (Z. ges. exp. Med., 1933, 90, 173—207).—After one cutaneous application of I-containing substances (0.08—0.4 g. of I) 1—11.6% appeared in the urine, most of it 4—6 hr. after inunction. Only insignificant amounts appeared in the faeces and sweat. The I concn. of the blood ran parallel with that of the urine. A considerable amount appeared in the saliva and gastric juice. The I content of the body was at times enriched by 50%. Alteration of cutaneous blood-flow by heat, ultra-violet light, or local stimuli, or changing the NaCl content of the diet, had no effect on the urinary excretion of I, which was diminished during great perspiration. The amount retained appears to depend on the state of the thyroid gland; during periods of hyperthyroidism greater amounts appeared in the urine. In a patient with advanced pulmonary tuberculosis large amounts were retained.

NUTR. ABS. (b)

Fate of iodide injected into frogs. O. EICHLER (Arch. exp. Path. Pharm., 1934, 175, 67—77).—In-

jection of aq. NaI into frogs is followed by its rapid passage by means of the lymph-stream from the site of injection (abdominal lymph and peritoneal cavities) into the blood and other tissues, finally returning to the main lymph circulation, where a high concn. of NaI is attained. The skin (through which a slight excretion of NaI occurs) functions as a reservoir for NaI.

F. O. H.

Mercury-laden air; toxic concentration, proportion absorbed, and urinary excretion. A. M. FRASER, K. I. MELVILLE, and R. H. STEHLE (J. Ind. Hygiene, 1934, 16, 77—91).—To produce chronic toxic effects in dogs the min. concn. of vapour inhaled for 8 hr. daily for 40 days is 3.05 mg. per cu.m. Under these circumstances, the average daily excretion is 0.5 mg. With a concn. of 2.91—26.18 mg. Hg per cu.m., 24.16% is absorbed on inhalation.

H. G. R.

Formation of cadmio-lipin complexes in the organism. A. CIRIMINNA (Arch. Farm. sperim., 1934, 57, 68—77).—Intravenous injection of CdCl_2 in the dog results in formation of cadmio-lipin complexes (I) in the liver. The Cd in (I) is linked to the fatty acids, the linking being stable to saponification with cold KOH. The formation of (I) takes place very slowly, larger quantities being found in more prolonged cases of Cd poisoning.

R. N. C.

Substance in *Tribulus* plants which produces methæmoglobinæmia. C. RIMINGTON and J. J. QUIN (Biochem. Z., 1934, 269, 4—13).—*Tribulus* plants (S. Africa) contain inorg. NO_3^- , chiefly as KNO_3 (up to 7% of dry wt.). It is this, reduced to NO_2^- by an oxidoreduction system, which rapidly poisons animals (sheep), converting hæmo- into methæmo-globin intracellularly.

W. McC.

Substances of higher plants and yeast which protect against uranium poisoning. M. JACOBY and G. EISNER (Biochem. Z., 1934, 268, 322—325).—The active substances of plants and yeast are possibly identical, are sol. in 90%, but not in abs. EtOH, and cannot be fractionated with Et₂O, light petroleum, and COMe₂. Vitamin-B₂ probably also belongs to this group of substances.

P. W. C.

Localisation of uranium in the organs of rabbits during uranium intoxication determined by the magneto-optic method. H. D. JONES, R. GOSLIN, K. D. CRANE, and G. B. JOHNSTON (Amer. J. Physiol., 1933, 105, 693—696).—The sensitivity of the method is 0.663×10^{-12} g. U per c.c. After injection of 0.5 mg. per kg. body-wt. of U nitrate U is found in the blood, urine, and urinary system, kidney, spleen, and liver, but not in the bile or gall-bladder. On an average 20% of the total U is found in the liver and 23% in the kidney (I). The U is excreted through (I) during the first 24 hr. and not through the bile.

NUTR. ABS. (m)

Determination of enzyme dissociation constants. H. LINEWEAVER and D. BURK (J. Amer. Chem. Soc., 1934, 56, 658—666).—Graphical methods involving const. slopes and straight-line extrapolations are developed for testing and interpreting kinetic data and for determining dissociation (and related) consts. of enzyme-substrate and enzyme-inhibitor

compounds [when the data (lit.) are found to be consistent with an assigned mechanism]. Representative analyses are given for invertase (I), raffinase (II), amylase (III), citric acid dehydrogenase (IV), catalase (V), oxygenase, esterase (VI), and lipase, involving substrate activation and inhibition, general competitive and non-competitive inhibition, steady states, and reactions of various orders. In the simplest cases [(I)—(III)], plotting of $1/v$ (v =observed velocity) against $1/S$ (S =substrate concn.) gives a straight line, the slope of which is K_s/V_{max} . (K_s =Michaelis dissociation const.; V_{max} =theoretical max. velocity) and the ordinate intercept is $1/V_{\text{max}}$. In presence of competitive inhibitors, the slope is increased but the intercept is unchanged; with non-competitive inhibitors, the intercept is raised also. When the active intermediate contains n mols. of substrate, a straight line is obtained by plotting $1/v$ against $1/S^n$ [as with (IV)]. Occurrence of a steady state before the formation of the active intermediate results in a curve with two limiting slopes. When the curve of v against S passes through a max. and then approaches a zero val., the existence of an additional inactive intermediate [as with (V)] is indicated; approach to a const. val. indicates two or more active intermediates [(—)-Et mandelate-(VI)]. The methods described are applicable to general chemical catalysis (homogeneous or heterogeneous).

H. B.

Detection of enzymes by spot tests. B. N. SASTRI and M. SREENIVASAYA (Mikrochem., 1934, 14, 159—160).—Enzymes may either alter the colour or the p_H of the substrate, or liberate reducing sugars. Spot tests for the more common enzymes, based on these principles, are described.

J. S. A.

Mechanism of oxidation processes. XXXIX. Dehydrogenation by yeast in presence of methylene-blue and benzoquinone. H. WIELAND and O. B. CLAREN [with P. COUCEIRO] (Annalen, 1934, 509, 182—200).—The course of reaction between methylene-blue (I) and "impoverished" yeast (II) (A., 1932, 303) with EtOH is determined by the velocity of diffusion of (I). (I) also exerts an irreversible retarding action with (II). The aerobic dehydrogenation of AcOH is retarded, probably owing to partial inactivation of the active enzyme surface by (I). Aerobic dehydrogenation of EtOH is greatly retarded by HCN (0.001—0.004M); a gradual diminution in retardation occurs, probably owing to the formation of $\text{OH}\cdot\text{CHMe}\cdot\text{CN}$. HCN also causes a retardation when dehydrogenation is carried out using (I) in absence or presence of O_2 . Dehydrogenation [O_2 or (I)] of EtOH is also retarded by CO; $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ ($M/600$) has no effect. Lactic acid with (I)+(II) gives MeCHO , EtOH, and AcOH (part formed by direct dehydrogenation of MeCHO); (I) or its leuco-compound suppresses (partly) the Cannizzaro reaction with MeCHO . Decolorisation of (I) with AcCO_2H occurs very slowly. Dehydrogenation of EtOH (to AcOH) with (II)+benzoquinone (III) (0.01M) occurs rapidly at first and then ceases owing to destruction of the enzyme. There is little difference in the rate of disappearance of (III) (0.05M) in absence or presence of EtOH; (III) is

reduced by (II). Aerobic dehydrogenation of AcOH in presence of (II) is retarded by (III) to about the same extent as with HCN. (III) also retards the aerobic dehydrogenation of EtOH, but quinol has no effect. HCN has a slight retarding action on the dehydrogenation of EtOH by (III). The ability of (II) to ferment *d*-glucose is completely destroyed by 0.005*M*-(III). H. B.

Oxidation-reduction by yeast dehydrogenase. H. VON EULER and C. MARTIUS (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 22, 6 pp.).—Yeast apozymase preps., free from cozymase, in PO_4''' buffer at p_H 7 dehydrogenate lactic acid (I) (as indicated by the decolorisation of methylene-blue or 2:6-dichlorophenol-indophenol) to AcCO_2H , the action being totally inhibited by CuSO_4 and partly by NH_3 or AcCO_2Na . The dehydrogenation (II) of lactylglycine (probably to $\text{Ac}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$) or of EtOH is almost as rapid as that of (I); that of Et lactate, alanine, or glycine is much slower. The correlation between (II) of (I) and the resynthesis of glycogen in muscle is discussed. F. O. H.

Enzymes. H. VON EULER and E. KLUSMANN (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 23, 6 pp.).—Apozymase preps. from bottom yeast, in presence of cozymase, PO_4''' buffer at p_H 6.8–8.0, and hexose monophosphate (Robison), decolorise methylene-blue (I); the reaction, which is not appreciably inhibited by NaF or lyochrome (ovoflavin), is much slower when the ester is replaced by glucose or xylose. Certain aq. dehydrogenase preps. have absorption max. at 265 μ , indicating the presence of cytoflavin or Warburg's yellow enzyme (A., 1932, 1285). Extract of rat's muscle decolorises (I), the action being accelerated by cozymase or pyruvate, but not by lactate or ovoflavin. Corpus luteum, ovarian tissue, and anterior pituitary gland resemble muscle, whilst posterior pituitary gland and liquor folliculi have a less marked action. F. O. H.

Potential of the yellow oxido-reduction pigment. R. BIERICH and A. LANG (Z. physiol. Chem., 1934, 223, 180–184).—The normal potential (I) of the oxidation pigment at p_H 7 is –208 mv. at 20° with reference to the normal electrode. The (I) of the pigment not denatured by NaOH at p_H 1.17–6.45 is about 15 mv. more positive than the CHCl_3 -sol. pigment. J. H. B.

Hæmatin content of horse-radish peroxidase. K. A. C. ELLIOT and D. KEILIN (Proc. Roy. Soc., 1934, B, 114, 210–222).—Hæmatin (I) is determined microspectrographically after transformation into a $\text{C}_5\text{H}_5\text{N}$ -hæmochromogen. The parallelism between (I) content and enzyme (II) activity was not observed in highly active preps., and the whole (I) was present as acid (I). Complete combination of free (I) with nitrogenous substances is obtained only above p_H 10.5 when (II) is nearly inactive. Willstätter's method of purification of peroxidase is inapplicable to uncultivated English horse-radish. H. G. R.

Specificity of fumarase. K. P. JACOBSON (Fermentforsch., 1934, 14, 175–181).—Neither Et_2 (I) nor Et H fumarate (II) is hydrated by liver

fumarase. (I) was partly hydrolysed to (II), which was recovered unchanged. A. E. O.

Enzymes of *Bombyx mori*, L. III. Tyrosinase and catalase of the blood of the silkworm. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1933, 9, 172–177, and J. Agric. Chem. Soc. Japan, 1933, 9, 940–948).—The blood-tyrosinase (I) of the silkworm has optimum p_H 6.6 and optimum temp. 37°; it has greater activity in males than in females, but is independent of growth. The activity is high in the larval stage, falls during spinning and in the pupal stage, and rises to a max. in the moth. The blood-catalase (II) has optimum 6.6, optimum temp. 23°, greater activity in males and in well-grown than in females and poorly grown specimens. Activity increases at spinning, and is a max. in the early pupal stage, then falls, to rise again in the moth. Chinese and Japanese strains have greater (I) and (II) activity than European strains. C. G. A.

Purification and properties of malt amylase. H. C. SHERMAN, M. L. CALDWELL, and S. E. DOEBELING (J. Biol. Chem., 1934, 104, 501–509; cf., A., 1930, 1316).—Amylase preps. with activities of 3800–4500 are obtained by fractional pptn. of extracts of barley malt by $(\text{NH}_4)_2\text{SO}_4$, dissolution of the most active fraction, dialysis in a min. of H_2O to remove SO_4'' , repeating until no increase in activity results, fractional pptn. with EtOH, and finally pptn. with EtOH and Et_2O . The preps. contain approx. 16% N, are denatured on prolonged contact with EtOH, thereby losing their activity, and behave generally like typical protein. H. D.

Action of certain alkaloids on invertase. G. MEZZADROLI and A. AMATI (Atti R. Accad. Lincei, 1933, [vi], 18, 226–231).—0.05% of strychnine nitrate, caffeine, or quinine sulphate reduces the activity (velocity coeff.) of invertase to 29.9, 97.3, and 96.1%, respectively; for 0.1% the corresponding figures are 20.8, 95.2, and 87.7; for 0.2%, 14.9, 95.2, and 79.9 and for 0.3%, 13.0, 95.2, and 79.9. T. H. P.

Oxynitrilese of emulsin. II. Kinetics of the synthesis of *d*-mandelonitrile accelerated by emulsin. H. ALBERS and K. HAMANN. III. Effect on this synthesis of hydrogen-ion concentration. H. ALBERS, K. HAMANN, and H. ALBRECHT. IV. Absorption of ultra-violet light by the system emulsin-benzaldehyde. H. ALBERS, I. MEYER, and K. MEYER. V. Intermediate products in the synthesis. H. ALBERS and H. ALBRECHT (Biochem. Z., 1934, 269, 14–25, 26–34, 35–42, 43–62; cf. A., 1933, 93).—II. The asymmetric enzymic synthesis is a reaction of the second order; it is inhibited by PhOH. The initial reaction velocity, which is \propto the amount of enzyme (I), gives a measure of the amount of active (I), this amount being independent of the degree of purity of (I).

III. The kinetics of the reaction and the effect of $[\text{H}^+]$ are not affected by accompanying impurities. The dissociation of the enzyme-substrate compounds is independent of $[\text{H}^+]$ and of the concn. of the substrates (II). The curve showing relation between p_H and activity of (I) exhibits max. at p_H 5.4, 5.85, and 6.5. Only one (I), however (oxynitrilese), is involved;

it reacts with (II) under different conditions. (I) is purified by dialysis.

IV. The $[H^+]$ (p_H 5.3, 6.0, 6.5) at which the ultra-violet light absorption curves (III) of PhCHO in 50% aq. EtOH indicate the presence of max. amounts of unchanged carbonyl form (IV) are identical with those at which (I) exhibits max. activity, the amounts of (IV) varying with varying p_H . The (III) of emulsin and these results indicate that PhCHO forms an intermediate compound (V) with (I). (V) is decomposed into its constituents only with difficulty.

V. (Cf. A., 1933, 862.) (V) consists of PhCHO + one mol. of (I) but other compounds containing, in addition, 2PhCHO, loosely bound, also exist and, further, a corresponding compound of (I) with HCN as well as $[(I) + 2HCN] + 2HCN$, loosely bound, $[(I) + 2PhCHO] + 2HCN$, loosely bound, and $[(I) + 2HCN] + 2PhCHO$, loosely bound. (I) has a greater affinity for PhCHO than for HCN. Possibly (I) contains $2NH_2$.

W. McC.

Activation of glycolysis by copper. F. LIP-MANN (Biochem. Z., 1934, 268, 314—316).—Cu (10^{-5} — 10^{-4} mol. per litre) increases by 100% and 10^{-4} — 10^{-3} mol. per litre decreases glycolysis in Meyerhof's muscle extract. Fe^{++} also inhibits. The action of Cu is independent of the presence of O_2 .

P. W. C.

Function of phosphoric acid in the glycolytic fission of carbohydrates. R. NILSSON (Svensk Kem. Tidskr., 1934, 46, 24—39).—The glycolytic fission of carbohydrates and the correlated phenomena of yeast fermentation and lactic acid production in muscle are discussed. The formation of a labile 6-hexosemonophosphoric acid (which can yield a stable mixture of glucose- and fructose-monophosphoric acids) as intermediary in both processes is emphasised. This compound, on oxido-reduction, affords glyceraldehyde- γ -phosphoric acid [giving hexosediphosphoric acid by condensation of 2 mols. and, as a secondary product, phosphoglyceric acid (A., 1930, 641)] and a non-phosphorylated compound, $C_3H_6O_3$ (probably hydrated AcCHO) which yields EtOH and CO_2 with yeast and lactic acid with muscle.

F. O. H.

Detection of triosephosphoric acid as intermediate product in the enzymic fission of carbohydrates. O. MEYERHOF and K. LOHMANN (Naturwiss., 1934, 22, 134—135).—When hexose diphosphate (I) is added in low concn. to co-enzyme-free muscle juice, or to yeast maceration juice, up to 60% is changed in a few min. into triosephosphoric acid (II), as shown by its ready hydrolysis by 0.5N-NaOH to H_2PO_4 and lactic acid and by acid hydrolysis to H_2PO_4 and AcCHO. From the action of dil. dialysed rabbit-muscle extracts on (I) at room temp., (II) was isolated as Ba salt and agreed in most of its properties with the synthetic glyceraldehyde- γ -phosphoric acid of Fischer (A., 1932, 364, 834) but differed in its low uptake of Br or I. It is probably largely dihydroxy-acetonephosphoric acid, the small optical activity ($[\alpha]_D +0.8^\circ$) being due to impurity.

W. O. K.

Influence of α - and β -glucosides on the phosphorylation of glucose. E. ABDERHALDEN and G. EFFKEMANN (Biochem. Z., 1934, 268, 461—468).—

Parenterally administered amygdalin (I) is only partly recovered in the urine. (I), arbutin (II), salicin (III), phenol- α - and - β -glucosides and -galactosides inhibit phosphorylation in muscle extracts containing NaF, β -glucosides being more active than α -glucosides. (I) and (II) inhibit the reabsorption of glucose in the kidney tubules, and (I), (II), and (III) inhibit its absorption from the intestine.

P. W. C.

Phosphatase hydrolysis of diphospho-*l*-glyceric acid. O. BODANSKY and H. BAKWIN (J. Biol. Chem., 1934, 104, 747—755).—Diphospho-*l*-glyceric acid resides entirely in the org. acid-sol. fraction of blood-P, not hydrolysable by bone-phosphatase at p_H 9.0 and 4% $CCl_3 \cdot CO_2H$ concn.

H. G. R.

Phosphatase. VI. Non-osseous origins of serum-phosphatase. Its increase after ingestion of carbohydrates. A. BODANSKY (J. Biol. Chem., 1934, 104, 473—482).—The serum-phosphatase of fasting dogs made hyperglycaemic by the administration of dextrin or glucose increases, whilst the serum-inorg. P decreases; meat ingestion under the same conditions produces the reverse effects.

H. D.

Serum-phosphatase in the domestic fowl. R. H. COMMON (Nature, 1934, 133, 572; cf. A., 1933, 1326).—Serum-phosphatase determinations on birds at different stages of the reproductive cycle give vals. for cockerels and sexually-immature pullets which are comparable, those for laying and moulting birds being higher.

L. S. T.

Phosphatase. VII. Inorganic phosphorus and serum-phosphatase in new-born puppies. A. BODANSKY (J. Biol. Chem., 1934, 104, 717—726).—Serum-phosphatase (I) averaged about 40 units per 100 c.c. at birth, rapidly increased, and then decreased to 20 units. Highest (I) was found in well-nourished animals, and was associated with a fall of inorg. serum-P and evidence of lipæmia.

H. G. R.

Glucosulphatase. IX. Specificity of the enzyme. T. SODA (Bull. Chem. Soc. Japan, 1934, 9, 83—88; cf. A., 1933, 749).—The enzyme is most active on glucose sulphate. It also hydrolyses, with decreasing activity, mannose sulphate (Ba salt; brucine salt, $[\alpha]_{5461} -14.26^\circ$) and disulphate (brucine salt); α -methylglucoside sulphate; invert sucrose sulphate; galactose tetrasulphate and disulphate (brucine salt); and maltose sulphate (Ba salt, $[\alpha]_{5461} +97.0^\circ$). Sucrose and diisopropylidene-glucose sulphates are still less readily attacked, whilst the enzyme has little or no action on mannitol tetrasulphate, starch disulphate, fructose trisulphate (K_3 salt, $[\alpha]_{5461} -5.4^\circ$), chondroitinsulphuric acid, or Et_2SO_4 .

E. W. W.

Cerace of the larva of *Galleria mellonella*. H. KRAUT, H. BURGER, and W. VON PANTSCHENKO-JUREWICZ (Biochem. Z., 1934, 269, 205—210; cf. Sieber and Metalnikov, Pflüger's Arch., 1904, 102, 269).—Although glycerol extracts of freshly killed larvæ are rich in lipase, there is no evidence that they contain a cerase capable of hydrolysing myricyl palmitate. Pertzoff (A., 1928, 1054) failed to take account of acid not derived from the wax, hence his results are untrustworthy.

W. McC.

Determination of pancreatic lipase. H. STEUDEL (Biochem. Z., 1934, 269, 175—176; cf. A., 1933, 981).—Waldschmidt-Leitz (this vol., 450) overlooks the author's finding that Willstatter's method is applicable only when the degree of hydrolysis is 10—24%, but confirms the inapplicability for certain purposes. W. McC.

[Determination of] ester formation and hydrolysis by the dilatometric method. R. AMMON and K. BARTSCH (Biochem. Z., 1934, 268, 331—335).—A new dilatometer is tested using the system PrCO_2Bu^a and powdered pig's pancreas. The synthesis of 1 mol. of ester corresponds with a vol. increase of 4.12 c.c. Hydrolysis is accompanied by a decrease in vol., but the results are not quant. P. W. C.

Limits of specific formation of defence enzymes and their origin. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 215—240).—Parenteral injection of the various plasma-proteins into rabbits (I) gives rise to proteinases (II) with sp. action only on the single protein injected, but alterations in the nature of the diet of (I) could not be sharply differentiated by this method. Removal of the spleen (III) or blockage of the reticulo-endothelial system has no effect on the production or specificity of (II). (III)-protein injected into splenectomised (I) gives rise to sp. (II) in the urine. A. E. O.

Activation of 'papain' by vitamin-C-iron and its inhibition by vitamin-C (ascorbic acid). E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1934, 223, 127—135).—The hydrolysis of gelatin by papain, which is inhibited by vitamin-C (I) alone, is accelerated by (I) + Fe. Fe cannot be replaced by Mn or Cu; indeed, traces of Cu neutralise the activation. The hydrolysis in presence of (I) + Fe is at first slower than with no addition, acceleration occurring only after some hr. J. H. B.

Action of rennin on the complex calcium caseinogenate-phosphate. C. C. CHRISTEN and E. VIRASORO (Anal. Inst. invest. cient. tecn., 1931, 2, 59—69).—The complex is prepared by treating milk-caseinogen with $\text{Ca}(\text{OH})_2$ suspension and neutralising (p_{H} 6.5, temp. 10—20°) with H_3PO_4 . For the process of coagulation by rennin (I) the product of time and (I) concn. increases slowly as the latter is decreased, whereas for the coagulation of milk the product decreases. H. F. G.

Crystalline pepsin. VI. Inactivation by β - and γ -rays from radium and by ultra-violet light. J. H. NORTHROP (J. Gen. Physiol., 1934, 17, 359—363).—The loss in activity towards haemoglobin of cryst. pepsin when exposed to β - and γ -rays from Ra or to ultra-violet light (I) is accompanied by a corresponding decrease in pepsin-protein. The rate of inactivation by (I) depends on the p_{H} and is a max. about p_{H} 2.0. A. L.

Trypsin of cold- and warm-blooded animals; its optimum temperature and heat-resistance. C. S. KOSCHTOJANZ and P. A. KORJUEV (Fermentforsch., 1934, 14, 202—214).—The chief difference between trypsin (I) of cold- and warm-blooded animals lies not in the temp. optimum, but in the heat-resistance (II), which is greater for the latter. The (II) of (I) of arctic fish is < that of fresh-water fish.

A. E. O.

Equilibrium between active native trypsin and inactive denatured trypsin. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1934, 17, 393—398).—The mobile equilibrium between native and denatured trypsin depends on the concn. of acid, alkali, and EtOH and on the temp. The heat of denaturation in 0.01N-HCl calc. from the effect of temp. on the equilibrium const. is —67,600 g.-cal. per mol. A. L.

Tryptic digestion of collagen. M. BERGMANN and G. POJARLIEFF (Biochem. Z., 1934, 269, 77—79; cf. A., 1932, 1064; B., 1927, 342, 636).—Until it reaches > 20%, degradation of collagen by pancreatin proceeds proportionally to time. W. McC.

Tyndallometric method for determination of trypsin. E. HERZFELD (Mikrochem., 1934, 14, 245—250; cf. A., 1933, 1064).—By progressive dilution with 1% NaHCO_3 , the min. amount of material to halve the Tyndall effect of a serum-albumin solution after 2 hr. incubation is determined. The limit corresponds with $3\text{—}4 \times 10^{-9}$ g. of trypsin. J. S. A.

Effect of parenteral injection of polypeptides on the content of certain polypeptidases in blood-plasma or -serum. H. HANSON (Fermentforsch., 1934, 14, 189—201).—Repeated parenteral injection of glycyl-*dl*-leucylglycine and *dl*-leucylglycine produces a definite and persistent increase in the hydrolytic power of plasma (I) towards these peptides. The acylase action of (I) is also increased. Injection of triglycylglycine or liver-protein has no marked action on (I)-polypeptidase. An acylase active against chloroacetyl-*l*-tyrosine could not be developed. A. E. O.

Determination of peptidase action of urine of man and animals. S. BUADZE (Fermentforsch., 1934, 14, 143—174).—The poly- (I) and di-peptidase (II) activities of urines can be accurately measured at p_{H} 7.8 (optimum), the respective substrates being peptone and *dl*-leucylglycine. No preliminary concn. of the enzymes is usually necessary. (I) is usually more active than (II). H_2S inhibits (I). A. E. O.

Enzymic histochemistry. VII. K. LINDERSTROM-LANG and H. HOLTER. a. Peptidase in the eggs of *Psammecinus miliaris*. T. PHILIPSON. b. Division of the mitochondria of the egg on centrifuging (Z. physiol. Chem., 1934, 223, 119—125, 125—126; cf. this vol., 338).—a. When the unfertilised eggs of *P. miliaris* are centrifuged they divide into two fragments, the lighter of which is about five times the size of the heavier (I), but both have the same abs. peptidase action.

b. When the eggs are first treated with Janus green, the stained constituents, at first evenly distributed, collect after centrifuging mainly in (I). J. H. B.

Digestion in insectivorous plants. J. DE ZEEUW (Biochem. Z., 1934, 269, 187—195; cf. Stern and Stern, A., 1932, 1064).—Opened (I) and unopened traps from the plants (varieties of *Nepenthes*) contain a catheptic (but not a tryptic) enzyme which acts in acid media only. The tryptic action of the contents of (I) is due to bacteria (*B. fluorescens liquefaciens*, *B. prodi-*

giosum, and two others). As a result of chemical (not mechanical) stimulation the glands secrete acid.

W. McC.

Specific effects of buffers on urease activity. S. F. HOWELL and J. B. SUMNER (J. Biol. Chem., 1934, 104, 619—626).—At 20° the optimum p_H for recryst. Jack bean urease (I) acting on 2.5% urea (II) depends on the buffer, being 6.4 for OAc', 6.5 for citrate, and 6.9 for PO_4''' , whilst with 0.1% (II) the corresponding figures are 6.7, 6.7, and 7.6, respectively. In PO_4''' buffer, (I) is active from p_H 5 to 9, in citrate buffer from 4.0 to 8.5 and in OAc' buffer from < 3.0 to 7.5. At a given p_H with any buffer a max. rate is reached as the concn. of (II) is increased, higher concns. being inhibitory. The concn. corresponding with max. rate decreases with increase of p_H . The concn. of buffer also influences the rate of the reaction. The max. activity occurs in presence of 1.0% (II) and 0.125*M*-citrate buffer at p_H 6.5.

W. O. K.

Pigments of a red yeast. H. FINK and E. ZENGER (Woch. Brau., 1934, 51, 89—93).—Two pigments have been isolated from a red yeast obtained from the air and cultivated on unhopped wort. Pigment I was neutral; it appeared to be a hydrocarbon having some properties in common with carotene and lycopene, but was distinguished from these by crystallographic and spectroscopic examination, and by colour tests with conc. H_2SO_4 , with $AsCl_3$, and with $SbCl_3$. Pigment II exceeded I in amount; it was acidic and appeared to be an ester of a polycarboxylic acid. It was distinguished from bixin and α - and β -crocin crystallographically and spectroscopically, and by colour tests.

I. A. P.

Yeast autolysis. H. HAEHN and H. LEOPOLD (Woch. Brau., 1934, 51, 97—100).—Autolysis in alkaline solution reduces the yield of NH_2 -acids although the total acid production is increased.

C. G. A.

Conversion of the alcoholic fermentation of sugar by yeast into a lactic acid fermentation. II. E. AUHAGEN and T. AUHAGEN (Biochem. Z., 1934, 268, 247—252).—Under the author's conditions (A., 1933, 1204), AcCHO is present as such, and is not formed in some secondary reaction on adding 2:4-dinitrophenylhydrazine.

P. W. C.

Formation of malic acid from asparagine by fermentation at different p_H . E. GLIMM and M. NITZSCHE (Biochem. Z., 1934, 268, 444—450).—A study of the fermentation at various p_H shows that more acid reaction tends to the conversion by way of the half amide of oxalacetic acid into malic acid, and more alkaline to the conversion by way of aspartic acid probably into oxalacetic acid and MeCHO.

P. W. C.

Action of oxygenated yeast on the system amino-acid-aldehyde. F. LIEBEN and V. GETREUER (Biochem. Z., 1934, 269, 69—76; cf. A., 1923, i, 424; 1932, 1114).—The interaction of glycine (I) and MeCHO in presence of yeast and O_2 leads to increased CO_2 production (II) [as compared with the action when only (I) is absent] and increased growth (III) of dry material of yeast [as compared with the action when only MeCHO is absent]. (II)

is derived from the MeCHO. Similar results are obtained with *d*-alanine, *dl*-phenylalanine, and sarcosine, but not with *dl*-alanine and proline. (II) and (III) are probably interrelated.

W. McC.

Bios. IX. So-called bios I and II. Y. HAMAMURA and M. CHIKAMATSU. **X. Distribution of bios in animals.** Y. HAMAMURA and K. OBATA (J. Agric. Chem. Soc. Japan, 1933, 9, 1018—1021, 1090—1094).—IX. Bios II has only a growth-promoting action on yeast; addition of bios I or inositol does not increase its action. There are probably two kinds of bios, one stable and the other unstable to $Ba(OH)_2$.

X. Bios is present in abundance in the leaves of plants and in the organs of the fowl, especially the pancreas and liver.

CH. ABS.

Oxygen as an accelerator in the growth of *Empusa* on flies. W. A. HIESTAND (Science, 1934, 79, 160).— O_2 accelerates the growth of *Empusa* on house-flies.

L. S. T.

Biochemistry of moulds. III. Metabolic product of *Aspergillus melleus*. Yukawa. 2. E. NISHIKAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 1059—1063).—Mellein (I) contains no OMe; monoacetylmellein, m.p. 126°, does not give the $FeCl_3$ reaction. Dinitromellein, m.p. 160°, has $[\alpha]_D^{25} -508.68^\circ$. When fused with KOH at 200° (I) affords (monobasic) melleic acid (II), $C_{10}H_{10}O_3$, m.p. 170° (Ac derivative, m.p. 110°; H_2 -derivative, m.p. 116°; Me ester, m.p. 59°). (I) with KOH at 300° affords 3-hydroxy-*o*-toluic acid. (II) is 2:6-OH·(C_3H_5) C_6H_3 · CO_2H and (I) is the lactone of 6- α - (or β)-hydroxypropylsalicylic acid.

CH. ABS.

Deuterium oxide and *Aspergillus*. S. L. MEYER (Science, 1934, 79, 210—211).—Small concns. of H_2 stimulate the vegetative growth and development of *Aspergillus* sp.

L. S. T.

Nutritional interrelationships between bacteria and moulds. H. BUCHERER (Zentr. Bakt. Par., 1933, II, 89, 273—283).—In N-free media, *Penicillium glaucum* and *Aspergillus niger* can utilise N fixed by *Azotobacter* (I) and liberated on the death of the bacterial cell. Carbohydrates which are not attacked by (I) in pure culture may be utilised in the presence of the above moulds.

A. G. P.

Influence of the temperature and water content of soil on the life processes of soil bacteria. D. FEHER (Arch. Mikrobiol., 1933, 4, 447—486).—Organisms concerned in the N cycle and in the decomp. of cellulose in soil are examined. In general, the relationship between bacterial growth and the product of soil temp. ($^\circ C$) and H_2O content (wt.-%) may be expressed as a parabolic function.

A. G. P.

Influence of the tension of oxygen on the respiration of *Rhizobia*. C. E. GEORGI and P. W. WILSON (Arch. Mikrobiol., 1933, 4, 543—564).—With *R. trifolii*, *R. leguminosarum*, and *R. meliloti* the glucose (I) consumed, the CO_2 produced from (I), and the rate of respiration increased with increasing partial pressure of O_2 (II). Approx. 60—80% of the (I) used reappeared as CO_2 , the balance being largely utilised in gum formation. The R.Q. of these

cultures was approx. 1, and was independent of (II). With *R. japonicum*, O₂ consumption and CO₂ production were < the above and the (I) consumed increased with decreasing (II). The conversion of (I) into CO₂ was maintained at a high level with small (5%) vals. of (II) if the abs. quantity of O₂ available was sufficient for requirements. A. G. P.

Stimulative action of yeast extract in the respiration of *Rhizobium*. R. H. WALKER (Science, 1934, 79, 160—161; cf. A., 1933, 1080).—Yeast extract (I) stimulates O₂ consumption and hence respiration (II) to an extent > any of the N compounds used. The extent of (II) is approx. \propto the amount of (I) present in the medium. L. S. T.

Influence of iodine on physiological activities of micro-organisms. A. ITANO and A. MATSUURA (Ber. Ohara Inst. landw. Forsch., 1933, 6, 73—81).—In small amounts I stimulated certain micro-organisms. Larger proportions were harmful. The optimum I content of media for *Azotobacter chroococcum* (I), *B. subtilis* (II), and *Sacc. cerevisiae* (III) was 0.007%. Lethal doses were 2% for (I) and (II) and 0.5% for (III). A. G. P.

Growth of *Bacillus megatherium* in relation to the oxidation-reduction potential and the oxygen content of the medium. G. KNAYSI and S. R. DUTKY (J. Bact., 1934, 27, 109—119).—The factor limiting growth under reduced pressure (> 10 mm.) is the O₂ content, and not the oxidation-reduction potential of the medium. A. G. P.

Negative oxidation-reduction system of *B. coli*. L. H. STICKLAND and D. E. GREEN (Nature, 1934, 133, 573).—The catalytic reduction of methylene-blue by H₂ due to an enzyme in *B. coli* (I) (A., 1931, 525) closely resembles the H electrode (II). Examination of the reversibility of this reaction of (I) using 4:4'-dimethyldipyridyl gives observed potentials in agreement with those calc. for (II) under identical conditions. This reversible hydrogenase system of (I) is the most negative oxidation-reduction system known in living cells. L. S. T.

Bacterial cell metabolism under anaerobic conditions. H. H. WALKER, C. E. A. WINSLOW, and M. G. MOONEY (J. Gen. Physiol., 1934, 17, 349—357).—A peptone-H₂O medium saturated continuously with N₂ to produce an aerobic conditions greatly inhibits growth and metabolic activity of *Escherichia coli*. Addition of glucose to the medium under these conditions has no effect during the first hr., but after the second hr. growth is rapid, and at the end of the fifth hr. the no. of organisms increases from 11×10^6 to 142×10^6 . This growth is accompanied by increased CO₂ production (211×10^{-11} mg. per cell per hr.) amounting to nearly double the max. vals. obtained under aerobic conditions. A. L.

Acetic acid bacteria produced in Formosa. III. S. TANAKA (J. Agric. Chem. Soc. Japan, 1933, 9, 1104—1116).—Five varieties of *B. xylinum*, Brown, were isolated. The membrane produced gave the cellulose reaction. Acid production was 4.4—5.4%. The bacteria assimilated the AcOH produced. CH. ABS.

Development and structure of acetic acid bacteria. A. A. BATSHINSKAJA (Bull. Acad. Sci. U.R.S.S., 1933, 7, 1189—1204).—Variations in the shape, dimensions, and internal structure of *B. acetii*, Hansen, with relation to the temp., p_H , and composition of the culture medium are recorded. R. T.

Unknown factor stimulating the formation of butyl alcohol by certain butyric acid bacteria. E. L. TATUM, W. H. PETERSON, and E. B. FRED (J. Bact., 1934, 27, 207—217).—A substance stimulating the decomp. by bacteria of starch and the production of BuOH (but not of other solvents formed simultaneously) occurs in a no. of plant materials, notably lettuce, cabbage, and orange. The prep. of active extracts is described. The latter are free from protein, glucose, or carbohydrates hydrolysable to glucose. A. G. P.

Hitherto unknown activators for the growth of lactic acid bacteria. S. ORLA-JENSEN (J.S.C.I., 1933, 52, 374—379T).—In the course of sterilisation by heat of carbohydrate substrates substances are formed which activate the growth of lactic acid bacteria. The activation is stronger if the source of N (I) (e.g., yeast extract) is sterilised together with sugars, or with AcCHO (II). *Thermobacterium acidophilum* will scarcely ferment sucrose (III) even when (III) and (I) have been sterilised together, but when (I) has been sterilised with (II), (III) is strongly fermented. Furfuraldehyde (IV) is nearly as effective as (II). (IV) is formed from pentoses (V) during sterilisation, but since 0.05% of xylose is as effective as 0.04% of (I) and only a very small part of (V) is converted into (IV) during sterilisation, (V), *per se*, must be able to form activating substances. The latter are probably similar in nature to cozymase. E. C. S.

***Lactobacillus acidophilus*. III. Composition of phosphatide fraction.** J. A. CROWDER and R. J. ANDERSON (J. Biol. Chem., 1934, 104, 487—495; cf. this vol., 453).—Acid hydrolysis of the phosphatide gave glycerophosphoric acid, choline, a cryst. non-reducing polysaccharide, m.p. 160—170°, $[\alpha]_D +72^\circ$, hydrolysing to *D*-galactose, glucose, and fructose, and a mixture of fatty acids containing palmitic (I) and stearic (II) acids and unsaturated acids which on hydrogenation yielded (I) and (II). H. D.

Biological occurrence of hydrogen persulphide. M. BERGMANN (Naturwiss., 1934, 22, 135—136).—The persulphide observed in S bacteria is probably produced from cystine (or glutathione) by elimination of H₂S₂. W. O. K.

Violacein, the violet pigment of *Bacillus violaceus*.—See this vol., 536.

Bacterial proteins, with special consideration of gonococcus and meningococcus. A. K. BOOR and C. P. MILLER (J. Exp. Med., 1933, 59, 63—74).—The toxic action of gonococcus and meningococcus is probably due, chiefly or entirely, to some constituent of the nucleoprotein fraction. Extraction with COMe₂ and Et₂O in the cold did not appreciably reduce the toxicity of these organisms and their nucleoproteins, and did not alter their immunological behaviour. Cross-precipitin reactions are discussed. CH. ABS.

Carbohydrates of gonococcus and meningococcus. I. Alcohol-precipitable fraction. C. P. MILLER and A. K. BOOR (J. Exp. Med., 1933, 59, 75—82).—The EtOH-insol. polysaccharides of gonococcus and meningococcus contain, respectively, 4.2 and 3.7% N; they give no protein reaction and reduce Fehling-Benedict solution only after hydrolysis. They are non-toxic to rabbits and mice, and fail to produce antibodies in rabbits. Both carbohydrates react in high dilution with antipneumococcus serum type III.

CH. ABS.

Dissociation of certain paratyphoid bacilli. Rôle of variants in the precipitation of calcium sulphite. M. E. CALDWELL (J. Bact., 1934, 27, 121—161).—Variant cells appear to have the property of pptg. CaSO_4 .

A. G. P.

Effect of meat-curing solutions on anaerobic bacteria. II. Sodium nitrate. F. W. TANNER and F. L. EVANS (Zentr. Bakt. Par., 1933, II, 89, 48—54).—In concns. up to 2.21% NaNO_3 did not inhibit *Clostridium botulinum* (types A and B), *C. putrificum*, or *C. sporogenes* on pork infusion or egg-meat media. Higher amounts (to 4.43%) produced irregular inhibitory effects.

A. G. P.

Effect of chlorides of bases on bacterial growth. J. P. TODD and I. M. SILLAR (Pharm. J., 1934, 132, 333—334).—Quinine and strychnine hydrochlorides inhibit the growth of non-sporing organisms and of anaerobes and slightly retard that of spore-bearing anaerobes. The effect is not due to the Cl'.

C. G. A.

Soluble specific substance in spirochaetes. E. HINDLE and P. B. WHITE (Proc. Roy. Soc., 1934, B, 114, 523—529).—A highly sp. sol. hapten (I) is obtained from cultures of *Spirochaeta biflexa* by pptn. from acid solution with COMe_2 . (I) ppts. homologous antisera only at a dilution of 1 in 10^5 , gives a positive Molisch test and a negative biuret reaction. (I) inhibits antibody formation in rabbits subsequently injected with large doses of *S. biflexa*.

C. G. A.

Influence of the mol. wt. of the antigen on the proportion of antibody to antigen in precipitates. W. C. BOYD and S. B. HOOKER (J. Gen. Physiol., 1934, 17, 341—348).—The antibody-antigen ratios of pneumococcus S III hapten, ovalbumin, haemoglobin, pseudoglobulin, and L-haemocyanin, calc. on the assumption that at the equivalence point in sp. precipitin reactions the antigen mol. is completely covered with a single layer of antibody-globulin mols., agree fairly well with the observed vals.

A. L.

Utilisation of carbohydrates and salts of organic acids by *C. diphtheriae* in the production of toxin of high *Lf* value. G. F. LEONARD and A. HOLM (Amer. J. Pharm., 1934, 106, 97—101).—The addition of maltose (0.45%) and NaOAc (0.75%) to a medium containing lactate, glucose, and peptone ensures the regular production of a uniform toxin with min. lethal dose 0.001 c.c., *L*+ 0.04 c.c., and *Lf* val.

32—34 units per c.c. Na succinate , replacing NaOAc , gives inferior results.

A. E. O.

Recovered diphtheria anatoxin. N. N. SPASSKY and T. ODRINA (Ann. Inst. Pasteur, 1934, 52, 308—315).—The anatoxin is treated with diphtheria serum

to max. pptn., centrifuged, and the ppt. washed with 0.35% aq. NaCl and finally dissolved in aq. HCl at p_H 6.2. Heating at 82° for 20 min. to destroy any antitoxin present yields solutions which, unlike toxin + antitoxin preps., do not inhibit the growth or carbohydrate metabolism of embryonic chick's heart, and are effective in the immunisation of children.

F. O. H.

Antigenic power of a lecithin-diphtheria anatoxin complex. C. E. PICO and F. MODERN (Folia biol., 1933, 1, 132—143).—Lecithin (I) decreases the toxicity of diphtheria toxin. A precipitin for (I) is present in the blood of rabbits given injections of (I).

CH. ABS.

Lecithin in fractionation of antitoxic sera and transformation of pseudo- into eu-globulin. I. PIROSKY and F. MODERN (Anal. Asoc. Quím. Argentina, 1933, 21, 142—148).—Addition of varying amounts of lecithin to antidiphtheria sera does not alter the proportion of activity pptd. by certain amounts of Na_2SO_4 . Anaphylaxis experiments with guinea-pigs show no difference in the antigenic properties of pseudo-globulin mixed with lecithin and no indication of conversion into euglobulin.

R. K. C.

Protein fractions of the human strain (H-37) of tubercle bacillus. M. HEIDELBERGER and A. E. O. MENZEL (J. Biol. Chem., 1934, 104, 655—665).—From the proteins of the defatted strain a no. of fractions, nucleoprotein in nature, have been obtained, the immunological reactions of which indicate the presence of < two distinct protein antigens.

W. O. K.

Tubercle bacilli. I. Extraction and fractionation of the lipins of heat-killed bacilli. M. MACHEBEUF, G. LEVY, and N. FETHKE [with J. DIERYCK and A. BONNEFOI] (Ann. Inst. Pasteur, 1934, 52, 277—307).—A mixture of heat-killed human and bovine bacilli was washed with H_2O and 1 kg. was successively extracted with COMe_2 (fraction A), warm 96% EtOH [yielding on cooling insol. (C) and sol. (B)], Et_2O (D), and CHCl_3 (E). A (11.0 g.) contained 67.3% of fatty acids and yellow pigments, but no reducing substances, cholesterol, and haptens (I). B (7.1 g.) yielded on further fractionation a wax-like mixture (P, 2.1%), m.p. 105—107°, a (I)-rich mixture, m.p. 145° (P 4.9, N 1.9%, fatty acids 67%, reducing sugars 6.25%; a non-sp. antibody), a mixture of esters of glycerol and other alcohols the purified glycerides (m.p. 30—32°) of which were free from P. C (5.4 g.) contained two non-acid-resisting fractions, m.p. 220—225° and 41—42°, 1.9 and 1.37% P, respectively, and two acid-resisting fractions (II), m.p. 50—55° and 45—52°, 0.27 and 0.45% P, respectively. Treatment of (II) with C_6H_6 followed by EtOH-HCl, etc., afforded a waxy substance, m.p. 57—58° (85.6% fatty acids; 10.8% unsaponifiable). D (5.2 g.) on dissolution in C_6H_6 and pptn. by EtOH yielded a fraction, m.p. 243—244°, mol. wt. 4—5 $\times 10^3$ (12% fatty acids; 40% unsaponifiable), and a mixture, m.p. 45° (12% fatty acids; 73% unsaponifiable). E (1.8 g.) treated with EtOH, Et_2O , and CHCl_3 gave a fraction, m.p. 204°, P 0.77%, which on alkaline hydrolysis in C_6H_6 -EtOH yielded a pentose (xylose?), but no glycerol.

F. O. H.

Peptone water as diluent in bacteriological investigation. E. L. K. DAGNEAUX (Chem. Weekblad, 1934, 31, 155—156).—Peptone solution can be used as diluent in the determination of the bacterial count (I) of milk. The tubes are incubated at 37° and (I) is determined by Erlich's indole-titre method. In 98% of the cases examined (I) is a measure of *B. coli*. S. C.

Bacteriophage. F. HODER (Arch. Mikrobiol., 1933, 4, 589—635).—A review with extensive bibliography. A. G. P.

[Are the viruses] enzymes or organisms? H. BECHHOLD (Kolloid-Z., 1934, 66, 329—340; 67, 66—79).—Determination of the size of subvisible viruses by ultra-violet photomicrography, ultrafiltration, and centrifuging indicates that they are organisms.

E. S. H.

Differentiation of hormones by the Reid Hunt reaction, the Aschheim-Zondek reaction, and the œstrus reaction, especially in ovarian cyst liquids. H. O. KLEINE and H. PAAL (Arch. Gynakol., 1933, 154, 147—160; Chem. Zentr., 1933, ii, 2546—2547).—Pituitrin (I), adrenaline (II), and œstrin (III) give a positive Reid Hunt reaction (IV), but they do not activate the thyroid. (II) lacks the protective action of (I), (III), and thyroxine. After several hrs. heating in an O₂ stream, (I) no longer gives (IV), but (II) and (III) do so. H. J. E.

Production by the stomach of a hormone stimulating the alimentary canal of birds. P. NOLF (Bull. Acad. roy. Belg., 1934, [v], 20, 204—206).—On stimulation of the vagus nerve, the stomach secretes a hormone which increases the muscular tonus of the intestine. H. G. R.

Mode of action of thymocrescin. H. BACHMANN (Biochem. Z., 1934, 268, 272—284).—Thymocrescin (I) after repeated pptn. with (NH₄)₂SO₄ still possesses a powerful growth-promoting action, the effect being greater on the sexual than on the total organs. (I) is not identical with vitamin-B₂, but does increase the growth-promoting action of the pituitary hormone. P. W. C.

Metabolic effects of intravenous injection of callicrein. R. W. NEFFLEN and A. SZAKALL (Biochem. Z., 1934, 269, 80—91).—In dogs, the injection (I) causes decrease to zero, followed by increased urinary excretion of P, increase followed by decrease in diuresis, and a parallel variation in urinary N excretion. These changes do not affect the daily P and N balances. The min. dose of callicrein (II) required to produce general metabolic changes (III) is 7 units. After repeated (I) of large doses acquired tolerance is exhibited. Pancreatectomy is without effect on (III) caused by (II). There are great individual differences as regards magnitude of dose required to produce (III). The kind of food consumed is immaterial. W. McC.

Morphological changes produced by intravenous injection of callicrein as cause of metabolic changes. A. SZAKALL (Biochem. Z., 1934, 269, 92—114).—Administration (I) of large doses of callicrein (II) to dogs causes rigor accompanied by decrease in the leucocyte content of peripheral blood, rise in body temp., followed by a fall and long-continued

leucocytosis. Small doses also cause typical changes in the blood, but no rigor. The inorg. P content of the blood first falls and then rises. These and other changes result from the increased permeability of the capillary vessels (III) which is the primary consequence of (I). (II) is probably a normal constituent of the organism, in which it acts as a regulator of the state of (II). W. McC.

Action of parathormone on basal metabolism. G. VON LUDANY and L. LENGYEL (Biochem. Z., 1934, 269, 150—157).—In normal (I) rats and in those (II) suffering from chronic rickets injection of parathormone leads to a 10—15% decrease in the O₂ consumption (III) and an increase (IV) in the Ca content (V) of the blood-serum, both lasting 8 hr. During the succeeding 10 hr. (III) rises by as much as 20%. In (II) (V) is much < in (I). The % (IV) in (I) = that in (II), but the abs. (IV) in (I) is > that in (II). The effects on the gaseous metabolism are a consequence of the increase in (V). W. McC.

Histological changes in the bone responsible for the action of parathyroid hormone on the calcium metabolism of the rat. L. I. PUGSLEY and H. SELYE (J. Physiol., 1933, 79, 113—117).—In rats 110—115 days old administration of 20 units of parathormone daily causes an immediate increase in serum- and urinary-Ca. Both vals. return to normal after 4—6 days. During the period of high Ca excretion an increased no. of osteoblasts and osteoclasts (I) appear in the bones, and the return to the normal excretory level coincides with the disappearance of (I). NUTR. ABS. (m)

Effect of parathyroid hormone and of irradiated ergosterol on the calcium content of the parotid saliva of the dog. L. ANDREYEV and L. I. PUGSLEY (J. Physiol., 1933, 80, 96—100).—The Ca content of parotid saliva (I), secreted after stimulation with meat powder, NaCl, or HCl, was three times that of the serum (II). Stimulation with pilocarpine hydrochloride produced (I) with a Ca content only a little > twice that of the (II). The rise in (II)-Ca following parathormone injection or irradiated ergosterol ingestion was in actual amount < the accompanying rise in the Ca content of the (I). NUTR. ABS. (b)

Precipitation of insulin in aqueous solution by hydrochloric acid. N. LARA (Folia biol., 1933, 1, 141—142).—The sample lost 18% of its total activity, but the purified material contained 20 units per mg. (dry) instead of 13. CH. ABS.

Carbohydrate metabolism of the rabbit. I. True blood-sugar value in convulsions due to insulin administration. L. B. DORTT (J. Biol. Chem., 1934, 104, 535—539).—The true (fermentable) sugar val. of the blood of a rabbit in convulsions is approx. zero, although the amount of non-fermentable reducing substance (I) is the same in normal blood as in blood during convulsions. (I) in rabbit blood is independent of the total reducing power, and is not affected by doses of insulin large enough to produce convulsions. C. G. A.

Hypoglycæmic action of insulin after vagotomy or atropinisation. K. WACHHOLDER (Arch. exp. Path. Pharm., 1934, 175, 62—66).—Bilateral

vagotomy in rabbits is followed by a short period during which the hypoglycaemic response (I) to insulin is somewhat diminished [probably due to the narcotic used for the operation (II)], and then by a period when (I) is normal; some days after (II), (I) is much > the normal. Large doses of atropine cause an increased (I), probably due to inhibition of convulsions.

F. O. H.

Influence of insulin and adrenaline on the blood-creatinine, -creatine, and -phosphate. L. RIGÓ and K. FREY (Arch. exp. Path. Pharm., 1934, 175, 8—13).—Injection of insulin (0.25—0.75 unit per kg.) or adrenaline (0.05—0.5 mg. per kg.) into dogs produces a fall in the total creatinine (I), creatine, and inorg. P levels of the blood, no diminution occurring in the preformed (I) or total acid-sol. P. F. O. H.

Adrenaline excitation in insulin hypoglycaemia and in Pal's vascular crises. B. KUGELMANN (Klin. Woch., 1933, 12, 1488—1489; Chem. Zentr., 1933, ii, 3445).—The hypoglycaemia following insulin (I) is accompanied by a series of vasomotor disturbances, which are a secondary effect due to increased entry of adrenaline into the blood-stream. Pal's vascular crises have the same cause. The disturbances may often be stopped by administering Gynergen simultaneously with (I). H. J. E.

Action of adrenaline on oxidations in isolated cells. A. HODEL (Biochem. Z., 1934, 268, 285—296).—The respiration of a slice of tissue in Ringer's solution is unaffected by addition of adrenaline, but is greatly increased by addition also of a little serum. The activator present in serum passes into the dialysate, and is inactivated by boiling for 5 min. The dialysate also increases the effect of Na lactate on the O₂ utilisation. P. W. C.

Cortical hormone requirement of the adrenalectomised dog, and method of assay. J. J. PFIFFNER, W. W. SWINGLE, and H. M. VARS (J. Biol. Chem., 1934, 104, 701—716).—The individual cortical requirement (I) of adrenalectomised dogs varies by approx. 100% and by about 25% for the same animal on check assays. (I) remains steady over 16 months, is not influenced by sex, but is increased by fasting. Oral administration is < 8% as efficient as subcutaneous; in the latter case the hormone is not excreted in the urine, nor is there any demonstrable storage. H. G. R.

Effects of administration of iodide and diiodotyrosine on iodine and thyroxine content of thyroid. G. L. FOSTER (J. Biol. Chem., 1934, 104, 497—500).—Thyroxine (I) was determined in the thyroids of rats treated with anterior pituitary extracts and subsequently injected with KI or diiodotyrosine (II), by a micro-adaptation of the Leland-Foster method (A., 1932, 432). There is no difference in the rates of return of total I or (I) with administration of either KI or (II). H. D.

Action of thyroxine on tissue respiration. J. A. DYE (Amer. J. Physiol., 1933, 105, 518—524).—Thyroidectomy in young pups leads to a 25% decrease in the O₂ consumption (I) of surviving muscle strips. Thyroxine (II) administration, on the other hand, leads to an increased (I) by similar tissues. In producing

this increased oxidative capacity (II) acts not directly but indirectly to increase the amount, potency, or effectiveness of the cell respiratory catalysts.

NUTR. ABS. (m)

Effect of thyroxine on the metabolism of isolated normal and malignant tissue. O. O. MEYER, C. McTIERNAN, and J. C. AUB (J. Clin. Invest., 1933, 12, 723—736).—Administration of thyroxine (I) to mice produces an increase of about 20% in the O₂ consumption (II) of liver tissue, and a definite increase in anaerobic glycolysis, but no significant change in R.Q. The (II) of transplanted sarcoma No. 180 (III) is depressed by 25% in about 80% of cases; CO₂ production and aerobic glycolysis are not significantly affected. The results with carcinoma No. 63 are similar. Denervation of kidneys makes no difference to the (I) effect on (II), so that the effect of (I) on tumour metabolism cannot be due to lack of nerve supply, but to some factor within the tumour tissue. (I) seems to inhibit slightly the growth of (III).

NUTR. ABS. (m)

Relation between the thyreotropic substance of the anterior pituitary lobe and the adrenal capsule. A. LOESER (Klin. Woch., 1933, 12, 1614; Chem. Zentr., 1933, ii, 3444).—In guinea-pigs, the thyroid (I) of which has been removed, injection of the thyreotropic hormone (II) causes no hypertrophy of the adrenal capsule (III). (II) therefore acts on (III) through (I). The hormone from (I) alone causes enlargement of (III). H. J. E.

Metabolism hormone of the anterior pituitary lobe. H. MAGISTRIS (Wien. klin. Woch., 1933, 46, 908—911; Chem. Zentr., 1933, ii, 3443).—The properties and action of the hormone (I) ("orophysin") which regulates fat metabolism are described. A rabbit unit for standardising (I) is defined.

H. J. E.

Hormones of the anterior lobe of the pituitary gland. ANON. (Nature, 1934, 133, 401—403).—A summary of the work of the University of California school. L. S. T.

Blood-fat-lowering pituitary substance "lipoitrin." W. RAAB and E. KERSCHBAUM (Z. ges. exp. Med., 1933, 90, 729—749; Chem. Zentr., 1933, ii, 3444).—The lipoitrin (I) content of a series of pituitary (II) preps. has been examined. (I) is especially abundant in "pituisan," in thyreotropic anterior (II) hormone, and in anterior (II) extract. (I) is more abundant in the anterior (II) than in the posterior (II). (I) is not identical with any known hormone from (II).

H. J. E.

Melanophore hormone. III. F. G. DIETEL (Klin. Woch., 1933, 12, 1358—1364; Chem. Zentr., 1933, ii, 2547—2548; cf. A., 1933, 869).—The melanophore hormone is not identical with any other active substance from the posterior pituitary lobe. It is less sol. in BuOH and more sol. in EtOH than the other materials, and differs from them in resistance to alkalis and in its diffusion through collodion filters. In cold-blooded animals the action is limited to the expansion of the melanophores. H. J. E.

Melanophore hormone and the eye. A. JORES (Klin. Woch., 1933, 12, 1599—1600; Chem. Zentr.,

1933, ii, 3442—3443).—An eye treated with a solution of the melanophore hormone (I) exhibits a more rapid adaptation to the dark. The increased rate of adaptation is not related to the quantity of (I). Rabbits kept in the dark show a much larger content of (I) in the blood and the eye than when kept in the light. The pituitary of a cat contains sixty times as much (I) as that of the hen, showing the amount of (I) to be related to the ability of an animal to see in the dark.

H. J. E.

Oxytocic hormone of the pituitary gland. I. B. C. GUHA and P. N. CHAKRAVORTY (Indian J. Med. Res., 1933, 21, 429—436).—The oxytocic principle is most stable (1 hr. autoclaving at 1 atm.) at p_H 3—5. It is not adsorbed by fuller's earth (p_H 1.5 or 4.5) or kieselguhr (p_H 4.5). The effects of various reagents have been investigated.

CH. ABS.

Content of oxytocic hormone in the human pituitary gland. A. JORES and E. ZSCHIMMER (Arch. exp. Path. Pharm., 1934, 174, 715—722).—The oxytocic hormone (I) of human pituitary glands (II) does not rapidly disappear after death. The content of (I) in whole (II) or in the posterior lobe (III) alone varies with age (being greatest during puberty and persisting during old age), but not with sex. The anterior lobe has a content of (I) < that of (III), the highest content being in the most anterior region. The pars intermedia probably plays no part in the formation of (I).

F. O. H.

Does an increase in oxytocic hormone occur during pregnancy? A. JORES and V. VON WITTERN (Arch. exp. Path. Pharm., 1934, 174, 723—726).—During pregnancy in rabbits the content of oxytocic hormone in the pituitary gland increases approx. tenfold. The phenomenon occurs to a smaller extent in multipara.

F. O. H.

Effect of pitressin and pitocin on oxygen consumption of excised tissue. M. H. PINCUS (Proc. Soc. Exp. Biol. Med., 1933, 30, 1171—1174).—Pitressin in low concn. increased, and in high concn. lowered, the O_2 consumption. Various tissues have different activity thresholds. Pitocin gave inconclusive results.

CH. ABS.

Action of posterior pituitary preparations on liver-glycogen. P. GOMORI and E. CSOMAY (Arch. exp. Path. Pharm., 1934, 175, 17—22).—The injection into rats of "orasthin" (a prep. of the oxytocic hormone) and "tonephin" (a prep. of the pressor substance) produces diminutions of 64 and 74%, respectively, in the liver-glycogen.

F. O. H.

Separation of the gonadotropic hormone of the anterior pituitary lobe in functional disturbances of the female sex glands. C. KAUFMANN and O. MUHLBOCK (Klin. Woch., 1933, 12, 1480—1483; Chem. Zentr., 1933, ii, 3443).—In severe functional disturbances with prolonged amenorrhœa, the separation of the gonadotropic hormone is not increased, but corresponds with the normal relations.

H. J. E.

Excretion of ovary-stimulating hormone in the urine during pregnancy. D. P. MURPHY (Surg. Gynecol. Obstet., 1933, 56, 914—917).—The amount of hormone secreted in 24 hr. in the urine of

pregnant women ranged from < 100 to 12,000 rabbit units, the amount being usually < 2000 units. The individual daily excretion is relatively const.

CH. ABS.

Female sexual hormone. XI. Determination of the constitution of the follicular hormone. II. Degree of saturation and aromatic character. A. BUTENANDT and U. WESTPHAL (Z. physiol. Chem., 1934, 223, 147—168; cf. A., 1933, 870).—Follicular hormone (I), solubility in H_2O , 0.00021%, forms with quinoline a cryst. mol. (1:1) compound, decomp. < 200°, clears 230°, readily decomposed by dil. HCl, which facilitates purification. Hydrogenation (PtO_2) of the deoxyhormone (II) gives hexahydrodeoxyhormone, $C_{18}H_{29}OH$, m.p. 110°, + H_2O , m.p. 82—85°, clears 96°, $[\alpha]_D$ -2.8° in EtOH. The hydrate of (I) yields, in addition to the hexahydrotriol (A., 1932, 781), hexahydrodeoxyhormone hydrate (III), $C_{18}H_{30}O_2$ (+0.5 H_2O), m.p. 153°, $[\alpha]_D$ -12.2° in EtOH (diacetate, m.p. 84°), and isohexahydrodeoxyhormone hydrate (IV), m.p. 162° (diacetate, m.p. 131°). By distillation with $KHSO_4$ in vac., (III) and (IV) gave hexahydrodeoxyhormone, $C_{18}H_{28}O$, and isohexahydrodeoxyhormone (semicarbazides, m.p. 262.5° and 278.5°, respectively). (II), m.p. 134°, $[\alpha]_D$ +89° in EtOH (Me ether, m.p. 76.5°, $[\alpha]_D$ +85° in EtOH), obtained (Wolff-Kishner) from (I), was identical with that obtained by Clemmensen reduction (cf. lit.). Determinations of sp. exaltations of mol. refraction indicate that (I) has only three double linkings. Therefore (I) has a benzene ring (with OH) and three reduced rings, the saturated hydrocarbon on which it is based being a 4-ring system $C_{18}H_{30}$. The dissociation consts. for (I) and its hydrate are 0.44 and 0.77×10^{-9} , respectively.

J. H. B.

Estrogenic hormone in the urine of the stallion. B. ZONDEK (Nature, 1934, 133, 494; cf. this vol., 332).—The biological reactions characteristic of the follicular hormone are exhibited by the estrogenic hormone of the urine of the stallion. The view that the metabolism of the sex hormones is, in the main, the same in both sexes, and that the male sex hormone is first synthesised and then converted into the female hormone, is advanced.

L. S. T.

Female sexual hormone (folliculin). B. ZONDEK (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 24, 5 pp.; cf. A., 1931, 878).—Stallion's urine (I) (which contains 6—8 units per litre of male sexual hormone) contains an average of 42,000 and that of non-pregnant mares < 500 mouse units of folliculin (II) per litre; the blood contains only small amounts. That the testes (III) are concerned with the formation of (II) is indicated by the low content (< 400 units per litre) of (II) in gelding's (I). Implantation of 0.05—0.10 g. of horse's (III) into spayed mice produces œstrus. Extraction with $COMe_2-C_6H_6$ of (III) yields 54,000 units of (II) per kg. Man and male animals other than the horse excrete < 200 units per litre, whilst ox (III) contain < 50 units per kg. (II) is extractable with Et_2O or C_6H_6 from stallion's (I) only after a short heating with acid.

F. O. H.

Follicular hormone content of human urine. H. BORCHARDT, E. DINGEMANSE, and E. LAQUEUR (Naturwiss., 1934, 22, 190).—The follicular hormone

content of human urine was determined in various cases by extraction with C_6H_6 of (a) neutral urine, (b) urine after acidifying to p_H 3, and (c) urine after addition of 150 c.c. of 25% HCl per litre. The hormone appears to exist in different urines in different forms. A. J. M.

Separation of the male and female sexual hormones. O. O. FELLNER (Klin. Woch., 1933, 12, 1374; Chem. Zentr., 1933, ii, 2547).—The male hormone is dissolved from a mixture of the two by conc. acids, in which the female hormone is insol. or sparingly sol. More of the male hormone is extracted from organs by acidified EtOH than by neutral EtOH, C_6H_6 , or $COMe_2$. H. J. E.

Effect of alkali on the testicular hormone. T. F. GALLAGHER and F. C. KOCH (J. Biol. Chem., 1934, 104, 611—617).—Treatment of the male hormone (I) from bull testis with boiling 3.3% KOH in EtOH results in loss of activity, but similar treatment of male (I) from human male urine produces no loss. This loss occurs with (I) from testis even in presence of urine hormone, indicating that the difference is not due to the presence in urine of a protective substance but that the two hormones are different compounds. W. O. K.

Tests on male sexual hormone with fish. E. GLASER and O. HAEMPEL (Klin. Woch., 1933, 12, 1491—1494; Chem. Zentr., 1933, ii, 3443).—Polemical against Zondek and Krohn (A., 1933, 319).

H. J. E.

Antagonism between thyroxine and vitamin-A. H. FASOLD and H. PETERS (Z. ges. exp. Med., 1933, 92, 57—62).—Hypervitaminosis-A in the rat could be prevented or cured by thyroxine (I). Conversely a solution of vitamin-A (II) in arachis oil (III), or (III) by itself, prevented the toxic action of (I) and permitted the storage in the liver of carotene and (II), but not of normal amounts of fat and glycogen.

NUTR. ABS. (b)

Biological activators and inhibitors. H. VON EULER (Arkiv Kemi, Min., Geol., 1934, 11, A, No. 12, 7 pp.).—The compensation of the loss in body-wt. due to thyroxine administration to rats on a carotene-free diet by feeding of β -carotene is confirmed (cf. A., 1932, 782). The functions of catalytic and oxidation-reduction activators and inhibitors (e.g., Cu, KCN, H_2S , ascorbic acid, glutathione) in enzyme and other systems are discussed. F. O. H.

Biological action of vitamins. H. VON EULER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 19, 6 pp.). Carotene increases the resistance of rats to an infection of *B. haemosepticum* without any concomitant increase in antibody formation in the serum. Vitamin-C produces in rats a protective action against pneumococcal infection. Other anti-infective properties of vitamins are discussed. Rats on a normal diet experience a max. growth during March and April and a min. from October to February (cf. A., 1932, 886, 1294).

F. O. H.

Vitamin-A in Indian fish-liver oils. A. R. GHOSH, P. N. CHAKRAVORTY, and B. C. GUHA (Indian J. Med. Res., 1933, 21, 441—446).—The vitamin-A potencies by the Carr-Price colorimetric technique

were for the oils of chital, shilong, kalibaus, dhain, and ar (fresh- H_2O fishes of Bengal) > for cod-liver oil.

NUTR. ABS. (b)

Canned strained vegetables as sources of vitamin-A. F. HANNING (J. Amer. Dietetic Assoc., 1933, 9, 295—305).—Vegetables canned after being cooked anaerobically for just long enough to make straining possible were tested biologically; 20 mg. of spinach, 40 mg. of carrot, and 50 mg. of tomato thus treated contained > one Sherman unit of vitamin-A; 250 mg. of green beans contained one, and 150 mg. of green peas, so cooked, < one, unit.

NUTR. ABS. (b)

Vitamin-A content of different milks and milk products. R. DEBRE and A. BUSSON (Compt. rend. Soc. Biol., 1933, 114, 1297—1299).—The vitamin-A (I) contents of various milks were compared. The (I) was extracted by the alkali digestion method. Doses corresponding with 3.5 c.c. of fresh or boiled cow's milk sufficed for slow growth in rats. Human milk was ineffective at doses corresponding with 3 c.c., but effective at 6 c.c. Doses corresponding with 6 c.c. of sweetened condensed milk, 4.5 c.c. of reconstituted dried milk, or 6 c.c. of buttermilk were ineffective.

NUTR. ABS. (b)

Yellow pigmentation of the milk of thyroid-ectomised goats. H. FASOLD and E. R. HEIDEMANN (Z. ges. exp. Med., 1933, 92, 53—56).—Goat's milk normally contains vitamin-A (I) but no carotene (II), although the diet is rich in (II). After thyroidectomy there was (II) but no (I). This was attributed to inability to transform (II) into (I) in the absence of the thyroid secretion.

NUTR. ABS. (b)

Crystalline carotene in the cow's ovary. V. DEMOLE (Arb. Ungar. biol. Forsch.-Inst. Tihany, 1933, 6, 230—231).—Cross-sections of cow's ovary fixed in formalin, lightly stained with hæmatoxylin, and mounted in glycerol, showed small red crystals in the corpora rubra and in the interstitial tissue. The crystals *in situ*, or extracted with fat solvents, gave the Carr-Price reaction. The carotene probably crystallises from the cell-fat in the process of degeneration of the corpora lutea.

NUTR. ABS. (b)

Vitamin-A required by pullets for maintenance and egg production. B. M. SHERWOOD and G. S. FRAPS (Vet. J., 1933, 89, 474—477).—The amount of vitamin-A (I) which was needed to support egg laying in hens was much > that needed for maintenance of wt. Yellow corn, ordinary lucerne meal or lucerne leaf meal, or other sun-cured green feeds did not supply sufficient (I), but green grass or green growing plants did.

NUTR. ABS. (b)

Effect of quantity and composition of diet on the course of vitamin-B₁ deficiency. H. G. K. WESTENBRINK (Arch. Neerland. Physiol., 1934, 19, 94—115).—Polyneuritis in pigeons is manifest sooner on a fat-poor, carbohydrate-rich, vitamin-B₁-free (I) diet than on a fat-rich, carbohydrate-free, (I) diet.

C. G. A.

Disappearance of vitamin-B₁ from the organs of pigeons on vitamin-B₁-free diets. Comparison of vitamin-B₁ contents of organs of rats and pigeons. H. G. K. WESTENBRINK (Arch. Neerland.

Physiol., 1934, 19, 116—121).—Vitamin- B_1 (I) disappears from all the organs of pigeons (II) in 13 days whether on carbohydrate-rich or fat-rich diets. The heart and brain of normal (II) contain less (I) than the muscle (III). In rats (III) contains < other organs. C. G. A.

Vitamin- B_2 and the pellagra-like dermatitis in rats. P. GYORGY (Nature, 1934, 133, 498—499).—The “pellagra-like” dermatitis (I) of rats is not produced by a lack of vitamin- B_2 as isolated in flavin pigment. (I) can be produced more readily, and unaccompanied by non-sp. and non-characteristic secondary symptoms, in presence of B_1 (possibly contaminated with B_4) and B_6 . It can be cured by administration of the B_1+B_2 eluate from the C adsorbate from yeast extract. This antidermatitis factor is not identical with B_4 and as a “rat-pellagra-preventive factor” it is temporarily named vitamin- B_6 . Administration of $B_1+B_4(+B_6)$ produces skin changes, but they are non-sp., mostly trivial, and never pellagra-like. They can be cured by B_2 . Vitamin- B_2 , the antidermatitis factor, has thus been separated into two components, the real vitamin- B_2 (flavin) and vitamin- B_6 . L. S. T.

Vitamin-A and -C. H. VON EULER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 18, 6 pp.).—The anterior and posterior lobes of ox-pituitary glands contain 1.0—1.5 mg. of ascorbic acid (I) (determined by 2:6-dichlorophenol-indophenol reagent) per g. of wet tissue. (I) sometimes occurs in the lens of the eye, whilst urine of pregnancy contains the same amount as normal urine. Serum (horse and pig, but not ox) contains 2 mg. per litre. Pig's bile has a reducing val. equiv. to 0.7 mg. of (I) per c.c. The corpora lutea of pig's and cow's ovaries contain 1.8 and 1.4 mg. per g., respectively. The berries of mountain ash and hawthorn have a high content of (I) (0.5 mg. per g. with the former). The presence of carotenoids in the above sources of (I) is discussed. F. O. H.

Glucoreductone for standardisation of 2:6-dichlorophenol-indophenol solutions for determination of ascorbic acid.—See this vol., 510.

Chemistry of the antirachitic vitamins. O. RYGE (Tidsskr. Kjem., 1934, 14, 26—31).—A lecture. H. F. H.

Vitamin-D. V. Determination of the antirachitic power of sunlight. A. JENDRASSIK and S. PAPP (Biochem. Z., 1934, 268, 364—368).—An apparatus which permits the irradiation of a solution of ergosterol under standardised conditions is described and tables show the biological activity in international units for varying times and with varying distance from the light source. The apparatus was used for the determination of the antirachitic power of sunlight from 1932 to 1933 in Budapest, and the results are given in the form of a graph which shows a very sharp max. in June. P. W. C.

Effect of increased vitamin-D administration on the glutathione content of the blood. (Behaviour of glutathione in the fasting condition.) H. HESSE (Biochem. Z., 1934, 268, 304—313).—Neither administration to rabbits of increased amounts of vitamin-D nor 48 hr. starvation has any effect on,

whilst toxic doses of the vitamin decrease, the blood-glutathione content. P. W. C.

Action of irradiated ergosterol on blood-calcium in chronic hypoparathyroidism. F. MATHIEU (Compt. rend. Soc. Biol., 1933, 114, 1375—1377). NUTR. ABS. (b)

Carbon assimilation by *Chlorella* in Windermere. L. LOOSE, W. H. PEARSALL, and F. M. WILLIS (Proc. Leeds Phil. Soc., 1934, 2, 519—524).—The increase of dry wt. of cultures of *C. vulgaris* in synthetic medium containing NaHCO_3 as C source suspended at varying depths in the lake was directly proportional to the intensity of light at the given depth. Photosynthesis balances respiration at approx. 10 m. deep. The rate of cell division is highest at the greatest depth. The rates of mortality and cell-growth are highest at the surface. C. G. A.

Age of plants and the photoperiodic reaction. M. C. TSCHAJLACHJAN (Compt. rend. Acad. Sci. U.R.S.S., 1933, 306—314).—The sensitivity of millet plants to variations in the duration (I) of diurnal illumination is greatest for sprouts and month-old plants. Increasing (I) to 24 hr. has only an insignificant effect, whilst diminishing (I) from 18 to 10 hr. daily leads to marked differences in the dimensions and habitus of plants of the above ages. R. T.

Chemical affinities and hybrids of *Iris*. H. COLIN and J. CARLES (Compt. rend., 1934, 198, 1257—1258).—Varieties of *Iris* differ widely in starch, fructosan, glucose, tannin, and lipin contents. R. S. C.

Growth of *Lupinus albus* seedlings in solutions of some amino-acids. D. I. MACHT (Amer. J. Bot., 1934, 21, 72—76).—The *l*-forms of leucine, cystine, alanine, valine, and aspartic acid have a greater physiological activity (inhibitory or stimulatory, according to concn.) than the *d*-forms; *r*-forms are intermediate in effect. Combinations of stereoisomeric valines produce a simple additive effect; those of leucines, cystines, and aspartic acids, a potentiation; and those of alanines an antidynamic action. A. G. P.

Germination of seeds. III. Transformation of carbohydrates during germination of soya-bean seeds. S. SASAKI (Bull. Agric. Chem. Soc. Japan, 1933, 9, 181—182).—The course of germination of the seeds is marked by an initial increase (5 days) and a subsequent decline in reducing sugar content, a steady decrease in sucrose, stachyose, and galactan, and an increase in starch, dextrin, pentosan, and crude fibre. The total carbohydrate content of the seeds did not change appreciably during the first 10 days of germination. A. G. P.

Dormancy in *Tilia* seeds. L. V. BARTON (Contr. Boyce Thompson Inst., 1934, 6, 69—89).—Germination of the seeds was accelerated by softening the seed coat by placing in moist peat or by treatment with conc. H_2SO_4 . The capacity of seeds to absorb H_2O was increased by the acid treatment. Excised embryos from H_2SO_4 -treated seed which had been exposed to low temp. (after-ripening) grew more rapidly than those softened in peat. The catalase

activity of seed increased as the after-ripening progressed. A. G. P.

Physiological and chemical changes preceding and during the after-ripening of *Symphoricarpos racemosus* seeds. F. FLEMION (Contr. Boyce Thompson Inst., 1934, 6, 91—102).—Disintegration of the seed coat by soaking in moist peat or treatment with conc. H_2SO_4 for 72 min., followed by after-ripening (A) at 25° for several weeks, induces germination. During A at 5° the catalase and peroxidase activity of seeds was markedly increased. At 25° the activity of the enzymes decreased slightly.

A. G. P.

Morphology of the seed of *Symphoricarpos racemosus* and the relation of fungal invasion of the coat to germinating capacity. N. E. PFEIFFER (Contr. Boyce Thompson Inst., 1934, 6, 103—122).—Fibre walls and the epidermis of the integument contain cellulose, pentosans, and lignins deposited in the order named. Coats of seed stored in moist peat are subject to decomp. by fungi, and become disintegrated, thus favouring germination. Reduction in fibre tissue of seed coats by treatment with H_2SO_4 is proportional to the period of treatment. If the latter is prolonged inferior germination may result from excessive growth of fungi. A. G. P.

Concentrations of inorganic ions as related to growth of excised root-tips of wheat seedlings. P. R. WHITE (Plant Physiol., 1933, 8, 489—508).—The effects of varying concns. of K, Ca, Mg, Fe, NO_3^- , NH_4^+ , SO_4^{2-} , PO_4^{3-} , CO_3^{2-} , and Cl^- on the growth of root-tips in modified Uspenski media supplemented with glucose and yeast are recorded. A. G. P.

Physiological role of boron. M. SCHKOLNIK (Compt. rend. Acad. Sci. U.R.S.S., 1934, 141—146).—Assimilation by flax and *Vicia faba* roots of PO_4^{3-} , NO_3^- , and Ca^{2+} , but not of K^+ , is greatly diminished by the presence of B compounds (I) in the nutritive mixture, whilst the growth of the seedlings is considerably enhanced. The permeability of the cell membranes is probably specifically affected by (I), in the absence of which intoxication of the cell contents by high contents of the above anions takes place. R. T.

Chemical stages in the growth of wood layers. H. HEMPEL (Cellulosechem., 1934, 15, 41—43).—The youngest layers of spruce wood contain about 10% lignin, 46% C and 2.8% OMe, the top of the stem containing more lignin than the bottom; rings one year old contain an average of 30% lignin and 50.2% C, which represent the average composition of spruce wood. Hence the cellulose skeleton built from the sap of the cambium is only very gradually lignified. Two morphologically different lignins isolated from the same wood showed practically the same C, H, and OMe contents, indicating that the lignin found in the central lamellae and the cell wall of the fibre is chemically identical. D. A. C.

Nutrient elements used by leaves and growth of apple trees. E. BURKE and H. E. MORRIS (Plant Physiol., 1933, 8, 537—544).—Of the mineral constituents of the current year's growth and leaves of apples, at the stage when full leaf size is reached, 67% of the N, 98% of the P, 100% of the K, 82% of

the Ca, and 61% of the Mg have been obtained from roots and soil. During active growth reserve N from all parts of the tree was utilised. The supply of K to all parts of trees is largely controlled by the flow of sap. Comparison is made of mineral distribution in an actually growing and a dormant tree. A. G. P.

Isotopic fractionation of water by physiological processes. E. W. WASHBURN and E. R. SMITH (Science, 1934, 79, 188—189).—During the synthesis of org. compounds by a growing willow tree an isotopic fractionation of H occurs. H^2 is preferentially selected and the sap and combined H of the woody parts of this tree both yield H_2O . No isotopic fractionation occurs during the passage of the H_2O into the tree through the root membranes. L. S. T.

Relationship between physiological phenomena and the occurrence of pigments in plants. VI. Synopsis of results obtained and their practical application. H. KOSAKA (J. Dept. Agric. Kyushu, 1934, 4, 127—160).—Not only the factors light, temp., etc., but also the functions of assimilation, growth, etc., may influence the occurrence of anthocyanins in certain plants. P. G. M.

Synthesis of proteins in plants. I. Conversion of nitrates into protein in *Helianthus annuus*. Linn. K. S. VARADACHAR (J. Indian Inst. Sci., 1933, 16, A, 129—138).—When KNO_3 is continuously injected into the N-starved plant the amount of free KNO_3 in the plant remains approx. const., the total N increasing, suggesting continuous conversion into proteins, probably through an amide stage. C. G. A.

Evolution of phospholipins of leaves during autumnal yellowing. R. ECHEVIN (Compt. rend., 1934, 198, 1254—1256).—The phospholipin content of the green leaves of five trees is the same per unit of leaf-area; it becomes 0 after autumnal yellowing. R. S. C.

Accumulation of rubber in the roots of *Tau-sagiz* as a result of its disappearance from the leaves. V. A. NOVIKOV, A. I. GRETSCHUSCHNIKOV, and J. N. BARMENKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 205—209; cf. this vol., 228).—Latex cells of *Tau-sagiz* roots play no part in formation of rubber, but are merely the channels through which it is conveyed and in which it is deposited. By checking the latex flow in some roots by ringing and comparing with unringed roots, it is shown that the disappearance of rubber from leaves on shading is due to its migration to the roots. J. W. S.

Fungi. III. *Parmelia physodes*, L. J. ZELLNER (Monatsh., 1934, 64, 6—11).—Extraction of the residue from the COMe_2 extract (14.2%) of air-dried *P. physodes* (7.77% H_2O ; ash 2.81%) with ligroin gives 1.3% of fat (hydrolysis of which gives fatty acids, m.p. $72-74^\circ$, and an unsaponifiable portion containing ergosterol and a paraffin hydrocarbon), whereas C_6H_6 extracts atranolin (0.5%) and amorphous acids (3.0%) leaving an insol. residue of capraric (6%, Et.O-insol.) and physodic (3.4%, sol.) acids. The EtOH extract of the COMe_2 -insol. residue contains the H_2O -insol. aliphatic alcohols (1.3%) *hypogymol*-I, m.p. 190° (decomp.), and -II, $\text{C}_{30}\text{H}_{62}\text{O}_9$, m.p. 218° , the H_2O -sol.

fraction containing amorphous polysaccharides (1.9%) and erythritol (< 0.1%). The H₂O-sol. portion (COMe₂- and EtOH-insol.) (20.5%) contains only lichenin and accompanying material. J. W. B.

Chemistry of the red and brown algæ. B. RUSSELL-WELLS (Nature, 1934, 133, 651).—*Corallina officinalis*, *Bostrychia scorpioides*, *Chondrus crispus*, *Rhodymenia palmata*, *Laminaria saccharina*, *L. digitata*, *Fucus serratus*, *F. vesiculosus*, *Ascophyllum nodosum*, and *Pelvetia canaliculata* contain cellulose. L. S. T.

Chemical examination of bark of *Holarrhena antidysenterica*. S. SIDDIQUI and P. P. PILLAY (J. Indian Chem. Soc., 1933, 10, 673—675).—The best method of extracting the alkaloids from the powdered bark is with Et₂O—EtOH (10%)—aq. NH₃ (2%). The Et₂O-sol. neutral products give on hydrolysis lupeol, m.p. 213—214° (benzoate, m.p. 266°), amorphous sterols, and oleic, linoleic, and linolenic acids. H. A. P.

Plant chemistry. XXV. Chemistry of barks. IX. J. BISCO and J. ZELLNER (Monatsh., 1934, 64, 12—16).—The ligroin extract of the bark of *Zizyphus vulgaris*, Lam., contains ceryl alcohol (I) and, after hydrolysis, fatty acids, m.p. 61—65°. The Et₂O extract (resin) is hydrolysed to give (I), a sterol, amorphous resin acids, and an EtOH-insol. K salt of a cryst. acid, m.p. 283° (amorphous Ac derivative). The EtOH extract contains only phlobaphens, and the H₂O extract, tannins and invert sugar (II). The ligroin extract of the ash (*Fraxinus excelsior*, L.) contains (I), and an EtOH-sol. portion containing stigmasterol, sitosterol, and a carotenoid (SbCl₃ reaction), and giving, after hydrolysis, fatty acids, m.p. 66—70°, and dihydroxystearic acid, glycerol, but no choline or H₃PO₄. The products of the EtOH extract, separated by the Pb salt method, agree with those in the lit., mannitol and (II) also being isolated. J. W. B.

Chemistry of bark substances. II. Hazel bark. O. BRUNNER and R. WOHL (Monatsh., 1934, 64, 21—27; cf. Zellner *et al.*, A., 1924, i, 814).—From the unsaponifiable portion of the EtOH extract of *Corylus avellana*, L., are isolated a hydrocarbon, b.p. 170—190°/10 mm. f.p. 16°, lignoceryl alcohol (p-methoxy-, m.p. 99° and 2:3-dimethoxy-, m.p. 93°, -phenylurethane) (Sandquist *et al.*, A., 1931, 1272), sitosterol, and betulin. The sterol, m.p. 200°, and corylols, isolated by Zellner (*loc. cit.*), could not be detected. J. W. B.

Constituents of *Cascara sagrada* extract. I. Isolation of a rhamnoglucoside of emodin. H. L. SIPPLE, C. G. KING, and G. D. BEAL (J. Amer. Pharm. Assoc., 1934, 23, 205—208).—The isolation, in 0.5% yield, of a rhamnoglucoside of emodin from an EtOH extract of the bark is described. The glucoside is relatively inactive as a cathartic. A. E. O.

Ceryl alcohol from the grass, *Agrostis*. C. E. BILLS and G. E. STEEL (Proc. Soc. Exp. Biol. Med., 1933, 31, 134—135).—The ceryl alcohol of cocksfoot and rye grass is chiefly *n*-hexacosanol (I); that of bent grass, essentially (I), had a slightly higher mean C content. CH. ABS.

Odorous substances of green tea. II. S. TAKEI, Y. SAKATO, and M. ŌNO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 11—12).—The yields of oil obtained by distillation in steam from green tea- (0.015%), mulberry- (0.0025%), acacia- (0.01%), and black radish-leaves (0.002%) vary with the age of the leaves. All these oils contain 5—6% of Δ⁸-hexenaldehyde, b.p. 138—140° (2:4-dinitro-, m.p. 144°, and p-nitro-phenylhydrazones, m.p. 137°; semicarbazone, m.p. 173°), 30—50% of Δ⁸-hexenol, and a little *n*- and iso-butaldehyde and isovaleraldehyde. The characteristic odours are due to less volatile constituents. R. S. C.

Tannin from fresh tea leaves. Y. OSHIMA and T. GOMA (J. Agric. Chem. Soc. Japan, 1933, 8, 948—952).—The fresh leaves afforded 0.2% of tannin; quercetin was also obtained. Oxidation of the tannin afforded the compound C₁₂H₁₂O₈, [α]_D²⁰—70.22°. CH. ABS.

Corms of *Arisaema triphyllum* (L.), Schott. L. MARION (Canad. J. Res., 1934, 10, 164—169).—Light petroleum removes 5% and MeOH 0.9% (I) of the dried corms. Steam-distillation of (I) affords an oil; the non-volatile part gives an acid, m.p. 183—184°, glucosazone (with NHPH·NH₂), *i*-inositol, a substance, C₆H₁₀O₆, m.p. 120° after softening at 105° (which may be a lactone), myricyl alcohol, *arisaesterol*, C₃₆H₆₄O₂, m.p. 135°, linoleic, oleic, and palmitic acids, and a phytosterol, m.p. 297°. J. L. D.

Essential oil in desert plants. IV. Oil of *Tetrademia glabrata*. M. ADAMS and G. R. ADAMS (J. Amer. Chem. Soc., 1934, 56, 991—992).—The oil (B., 1928, 106) contains α-pinene (15%), dipentene (25%), caryophyllene (8%), nonacosane (7%), aldehydes (10%), an unidentified ketone (1%) (2:4-dinitrophenylhydrazones, m.p. 132—133°), and colophonium and unidentified terpenes (34%). H. B.

Indian essential oils. V. Essential oil from the rhizomes of *Curcuma longa*, Linn. VI. Essential oil from the rhizomes of *Acorus calamus*, Linn.—See this vol., 529.

Phosphatides of wheaten meal. F. E. NOTT-BOHM and F. MAYER (Z. Unters. Lebensm., 1934, 67, 369—379).—The choline (I) content of the gluten, aq. extract, and starch fractions of wheaten meal (II) increases in the order named. (I) is present as (I)-lecithin. A method of prep. of the wheat phosphatide (III) is described. The P-L. no. (cf. B., 1934, 425) of (III) is 1.56, the carbohydrate content (as glucose) 26%. Trigonelline is absent from (II) and from the bran (IV). (II) contains less (III) than do groats. (II) contains thrice as much (III) as has hitherto been recognised, and (IV) contains even more. E. C. S.

Plant-phosphatides. E. BUREŠ and J. SCHIDLÖF (Časop. českoslov. Lek., 1933, 13, 229—235; Chem. Zentr., 1933, ii, 3144—3145).—Analysis of phosphograin (I) shows that it resembles inositolhexaphosphoric acid (28.19% P) very closely. Hydrolysis yields H₃PO₄ and optically-inactive unresolvable meso-inositol. The sample of (I) analysed contained 2.8% of phosphates, and small amounts of non-ionised combined Ca, Mg, Na, K, and Fe. H. J. E.

Distribution of methionine in food-proteins. T. TOMIYAMA and M. HANADA (J. Biochem. Japan, 1934, 19, 345—351).—Methionine was isolated from the proteins of sardine (0.52%) and whale-muscle (0.37%), silk-worm pupa (0.43%), soya bean (0.08%), and from caseinogen (0.41%). F. O. H.

Determination of amino-acids in the globulin of sunflower seeds. A. V. BLAGOVESHCHENSKI and T. A. SCHUBERT (Biochem. Z., 1934, 269, 375—378).—The globulin contains arginine 9.10, histidine 14.29, lysine 1.80, and proline 5.26% of the dry wt.

P. W. C.

Sterols from stramonium seed. O. GISVOLD (J. Amer. Pharm. Assoc., 1934, 23, 106—108).—The sterol fraction (13.21%) of the seed-oil unsaponifiable matter contains sitosterol; stigmasterol is absent.

E. H. S.

Determination of the acids of plant tissue. II. Total organic acids of tobacco leaf. G. W. PUCHER, H. B. VICKERY, and A. J. WAKEMAN (Ind. Eng. Chem. [Anal.], 1934, 6, 140—143).—Plant tissue is acidified with H_2SO_4 to p_H 1, extracted with Et_2O , and the org. acids in the extract determined by titration in presence of HNO_3 , between the limits p_H 7.8 and 2.6, using a quinhydrone electrode according to the method of Van Slyke and Palmer (A., 1920, i, 459). Under these conditions, $H_2C_2O_4$ (I) reacts as a mono-basic acid and is determined independently as CaC_2O_4 . Citric, malic, succinic, and tartaric acids titrate to approx. 90%, and therefore, after correcting for (I), a further correction of 10% is introduced in the determination of the org. acids.

S. C.

Acid secretion of the chick-pea (*Cicer arietinum*). G. R. MILNE (J. Roy. Tech. Coll., 1934, 3, 330—331).—The acid secretion from the hairs of the chick-pea consists mainly of citric, malic, and oxalic acids (0.75% of cryst. acids isolated, separated as Ca salts), and a small quantity of volatile acids of which AcOH is the chief.

J. W. B.

Iodine content of Pennsylvania potatoes. D. E. H. FREAR (J. Agric. Res., 1934, 48, 171—182).—The I content of 135 samples of potatoes (I) varied from 0.01 to 0.216 (mean, 0.0778) pts. per 10^6 pts. of dry tissue. The I content of (I) grown on marine soil was significantly high. No significant correlation was found with size or variety nor with the incidence of goitre in the various districts.

W. O. K.

Character of hemicellulose in certain fruit trees. W. E. TOTTINGHAM (Plant Physiol., 1933, 8, 559—561).—Differences in the galactose, glucose, xylose, and uronic acid fractions of the hemicellulose extract from wood of various fruit trees are recorded and discussed.

A. G. P.

Examination of starch and hemicellulose extracts from apple wood. H. OTTERSON and W. E. TOTTINGHAM (Plant Physiol., 1933, 8, 561—564).—A method for calculating starch content and hemicellulose fraction from customary analytical determinations is given.

A. G. P.

Carbohydrates in the bulbs of *Narcissus tazetta*. III. Comparison with *Lycoris radiata*. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1933, 9, 1005—1007).—*L. radiata* bulbs afforded total sol. carbo-

hydrates 75.57 (air dried), sugar sol. in hot $EtOH$ 3.74, reducing sugar 0.27, carbohydrates sol. in cold H_2O 18.28, in hot H_2O 21.95, in superheated H_2O 18.65%. The content of lower sugars is < in *N. tazetta*. The cold- H_2O extract contained fructan with 6% of glucan. The carbohydrates consist chiefly of starch.

CH. ABS.

Mannitol in olives. R. NUCCORINI (Annali Chim. Appl., 1934, 24, 20—25).—Green olives with a faint pink tinge contained, on dry matter, about 2.5% of mannitol or about 3.75% on the pericarp-free fruit. The proportion varies from year to year and diminishes as the fruit develops.

T. H. P.

Detection and determination of formaldehyde within the cell of a green plant by the Allison apparatus. A. L. SOMMER, E. R. BISHOP, and I. G. OTTO (Plant Physiol., 1933, 8, 564—567).—Allison's photometric apparatus (cf. A., 1932, 240) is adapted to the determination of CH_2O in algal cells.

A. G. P.

Pectic acid and methyl alcohol in tobacco leaves produced in Japan. III. S. MACHIDA (J. Agric. Chem. Soc. Japan, 1933, 9, 1140—1142).—Vals. were, respectively, 10—15 and 0.3—0.64%. Pectic acid was probably present as the Me or Me_2 ester.

CH. ABS.

Chemical constituents of tobacco. III. Pigments of tobacco blossoms. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1933, 9, 137—139).—Extraction of 1260 g. of dried tobacco-flower meal with $MeOH-HCl$ yielded 0.6 g. of an anthocyanin (sugar and anthocyanidin not identified). Extraction of the residue from the above with 95% $EtOH$ yielded 1.5 g. of a flavone glucoside which gave a yellow cryst. flavone on hydrolysis with 5% H_2SO_4 .

C. G. A.

Reduction of silver nitrate by chloroplasts. R. GAUTHERET (Compt. rend., 1934, 198, 1252—1254).—The reduction of $AgNO_3$ by the chloroplasts of yellow leaves is catalysed by very short exposure to light, particularly red light. The reaction takes place in the dark after previous exposure, is not affected by keeping in the dark or by anaesthesia by KCN or $NHPhCO_2Et$, but ceases with death of the leaf. The reducing substances of fresh spinach and green salad are probably tannins or hydroxyflavones.

R. S. C.

[Plant] amides. K. TAUBOCK and A. WINTERSTEIN (Handb. Pflanzenanalyse, 1933, 4, 190—221; Chem. Zentr., 1933, ii, 3321).—A review of the plant-physiological significance, properties, and determination of various NH_2 -compounds is given.

A. A. E.

Nitrogen balance. Determination of nitrogen fractions in plants. E. KEYSSNER and K. TAUBOCK (Handb. Pflanzenanalyse, 1933, 4, 1345—1402; Chem. Zentr., 1933, ii, 3321).—A review and crit. discussion.

A. A. E.

Presence of norleucine in seeds of *Ricinus communis*, L. R. NUCCORINI (Annali Chim. Appl., 1934, 24, 25—32).—The ricinin in castor seeds increases in amount as the seeds germinate. The products of hydrolysis of the seeds contain norleucine, which has not previously been found in vegetable products.

T. H. P.

Volatile base of valerian root. A. E. TSCHITSCHIBABIN and M. P. OPARINA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 119—122).—A saturated liquid pyridine base, $C_{10}H_{15}N$ (picrate, m.p. 147—148°; *platinichloride*), has been isolated. R. T.

Yohimbine Rubiaceae, *Corynanthe paniculata*, Welwitsch. RAYMOND-HAMET (J. Pharm. Chim., 1934, [viii], 19, 209—214).—Extraction of the bark by Schomer's method yields 1.60 g. of yohimbine hydrochloride per kg. By Chemnitius' method the yield is 8.4 g. of yohimbine base per kg. of bark. C. G. A.

***Thermopsis lanceolata*, K. Br.** M. VARLAKOV (Khim. Farm. Prom., 1933, 226—228).—Alkaloids (0.37%) sol. in H_2O , $CHCl_3$, and $EtOH$, but insol. in Et_2O and C_6H_6 , are present. Their physiological action is described. CH. ABS.

Bismarck-brown [as stain for] pollen-grain walls. L. A. MARGOLENA (Stain Tech., 1934, 9, 71).—Sections of buds fixed in Bouin's fluid and embedded in paraffin are stained for 6—10 min. in 0.5% aq. Bismarck-brown and dehydrated in $EtOH$. They are then counterstained with 0.3% fast-green FCF in clove oil. The sections, cleared with xylene, display a green extine and a brown intine layer of the pollen-grain wall. H. W. D.

Method for determining the purity of pollen for the preparation of pollen extracts. F. BERGER (Pharm. Zentr., 1934, 75, 239—243).—The pollen is examined in the presence of a "Fluorochrome" with a fluorescence microscope. Results on about 80 species of pollen are tabulated. S. C.

Distribution of phosphorus in wheat and flour. A. FEYTE (Ann. Agron., 1933, 3, 787—798).—The total, phytin-, and mineral P contents of a no. of samples are recorded and discussed. The proportion of the total P existing as phytin is lower in hard than in soft wheats. No direct relationship was apparent between the distribution of P in the grain and the baking val. of the flour as determined by extensimeter measurements. A. G. P.

Zinc content of green and etiolated leaves. G. BERTRAND and ANDREITCHIEVA (Ann. Inst. Pasteur, 1934, 52, 249—251).—Normal green leaves (chicory, endive, sorrel, spinach, dandelion, cress, lettuce, cabbage) have a Zn content of 0.36—8.99 mg. per kg. of dried material; that of etiolated (e.g., interior) leaves is much < that of the green leaves of the same plant. F. O. H.

Cryoscopic determination of "bound water." R. A. GORTNER and W. A. GORTNER (J. Gen. Physiol., 1934, 17, 327—339).—The criticisms by Grollman (A., 1931, 975) of the cryoscopic method for the determination of bound H_2O (I) are considered. The correction formula does not change the conclusion that winter-hardiness in plants is accompanied by (I). Using a new method of calculating the true f.p. of a solution, gum acacia (II) in aq. sucrose shows 0.6—0.7 g. (I) per g. of (II), and in aq. KCl or KBr, negative amounts of (I) indicating preferential absorption of

disease. A. V. V. IYENGAR (J. Indian Inst. Sci., 1933, 16, A, 139—152).—With the onset of spike-disease the p_H of the tissue fluids rises, then falls; the malic acid and $H_2C_2O_4$ content of the healthy sandal falls and succinic acid appears. The $PO_4^{'''}$ content of diseased tissues is higher than that of the healthy plant. A micro-sublimation apparatus is described. C. G. A.

Physiology of the virus diseases of the potato. II. Comparison of the carbohydrate metabolism of normal with that of crinkle potatoes and observations on carbohydrate metabolism in a "carrier" variety. III. Comparison of the nitrogen metabolism of normal with that of leaf-roll potatoes. E. BARTON-WRIGHT and A. McBAIRN (Ann. Appl. Biol., 1933, 20, 525—548, 549—589; cf. A., 1933, 546).—II. In the early stages of disease the process of carbohydrate formation was not significantly different in healthy and diseased leaves, although, in the latter, transport was somewhat delayed. The % of starch (I), sucrose (II), and hexoses (III) was higher in the diseased leaves, and the max. and min. points in the fluctuations were approx. 2 hr. in advance of those of healthy leaves. In both cases (II) was the sugar of transport. Later in the season (I) accumulated in diseased and (III) in healthy laminae. In the former case (II) was derived from (I) hydrolysis and in the latter by synthesis from (III) which was in turn produced by hydrolysis of (I). Transport of sugar [still as (II)] was less readily effected in diseased petioles.

III. Diurnal variations in the total N and constituent fractions indicated no marked differences in the N metabolism resulting from virus infection. A process of protein synthesis from NO_3^- , not involving NH_2 -acids as an intermediate stage, is suggested. The residual N fraction is probably an important factor in N-translocation. A. G. P.

Potato wart disease. W. SZYMANSKI (Trans. Phytopath. Sect. State Inst. Agric. Bydgoszcz, 1933, 13, 141—162).—Dry wt. is <, but ash >, normal; Fe, Mn, Cu, and N are especially high in warty tissue. CH. ABS.

Colorimetric determination of sodium in vegetation. J. G. LOUW (Onderstepoort J. Vet. Sci., 1933, 1, 425—435).—A modification of Malan and Van der Lingh's method is described. The proportion of P to Na which does not interfere with the determination is given, and it is shown that the interference of K is dependent on the abs. concn. and temp. NUTR. ABS. (b)

Standardisation of biological stains. IV. Triphenylmethane derivatives. A. R. PETERSON, H. J. CONN, and C. G. MELIN (Stain Tech., 1934, 9, 41—48).—Methods for the qual. and quant. analysis, and for biological testing, of 11 $CHPh_3$ dyes are given. Quant. analysis depends on reduction with $TiCl_3$ in the presence of a suitable buffer. H. W. D.

Differential titration of mixed strong and weak acids. Method for "free HCl" in gastric contents etc. G. M. RICHARDSON (Proc. Roy. Soc., 1934, B, 115, 170—180).—For determination of "free HCl" in acid mixtures, titration in 90% $COMe_2$ to successive end-points at p_H 3.4 and 4.0, using

Spike-disease of sandal (*Santalum album*, Linn.). XV. Role of plant-acids in health and

naphthylamine-orange, is suggested. Of other methods, the Gunzberg method or a p_H 2 titration is most satisfactory. H. G. R.

Colorimetric determination of ammonia in small amounts of material.—See this vol., 500.

Determination of mercury in air and urine.—See this vol., 502.

Colorimetric determination of magnesium in bones, by a modification of the Denis method. M. C. FRANKLIN (Univ. Cambridge, Inst. Animal Path., Rep., 1932—1933, 130—134).—2.5 g. of bone are ashed and dissolved in HCl. In one tenth of the solution the Ca is pptd. as oxalate. The Mg in the filtrate is pptd. as $MgNH_4PO_4$. The ppt. is dissolved in HCl and then in an aliquot the Mg is determined as in blood. NUTR. ABS. (b)

Adaptation of Kolthoff's colorimetric method for the determination of magnesium in biological fluids. A. D. HIRSCHFELDER and E. R. SERLES (J. Biol. Chem., 1934, 104, 635—645).—After removal of Ca from the plasma as CaC_2O_4 , 5.0 c.c. of the fluid (=0.5 c.c. plasma) are treated with 3.0 c.c. of dextrin or starch solution, 1.0 c.c. of solution of Titan- or Clayton-yellow (0.01%), and 1.0 c.c. of 0.4N-Ba(OH)₂. The colour is compared with that of a standard Mg solution, using a colour screen. A micro-method for the determination of both Ca and Mg in 0.5 c.c. blood or 0.1 c.c. of plasma is also given. For determination of Mg in urine, the Ca is first pptd. as CaC_2O_4 and PO_4''' by $UO_2(OAc)_2$. W. O. K.

Micro-incineration process and determination of calcium in organs. J. ERDOS (Magyar gyógys. Tarsas. Értes., 1933, 9, 391—396; Chem. Zentr., 1933, ii, 3166).—200—300 mg. of material are evaporated three or four times in a micro-Kjeldahl flask with fuming HNO_3 , saturated aq. NH_4NO_3 , and 30% H_2O_2 . Ca is determined by extracting the residue with dil. HCl, pptn. as CaC_2O_4 , and titration with $KMnO_4$. H. J. E.

Determination of iron in biological material by modified permanganate titration. F. H. L. TAYLOR and J. F. BROCK (Biochem. J., 1934, 28, 442—446).—Fe is determined in biological material by ashing with conc. H_2SO_4 and $HClO_4$, reduction with Zn, and titration with $KMnO_4$. H. D.

Micro-determination of phosphorus (inorganic, acid-soluble, lipin, total) in blood and excreta. F. FERRANTI and O. GIANNETTI (Diagnostica Teen., 1933, 4, 664—682).—The inorg., org., acid-sol., lipin, and total P in blood, urine, and faeces have been determined colorimetrically by a modification of the method of Bell and Doisy, consisting in adding NaOAc to remove strong acids left from the destruction of org. matter, and to bring the p_H near neutrality. The org. P vals. by this method from wts. of the same substance in the proportion 1 : 2 : 4 were in the same proportion with a max. error of 4%, whilst the inorg. P agreed with other methods. R. N. C.

Determination of total, organic, and inorganic phosphorus by the Pulfrich step-photometer. C. URBACH (Biochem. Z., 1934, 268, 457—460).—A

modification of the author's previously described (A., 1931, 1323) method is given which avoids the disadvantageous changes of colour intensity on keeping. P. W. C.

Determination of phosphoric acid by the phosphomolybdate method and its use for plant ashes.—See this vol., 500.

Determination of small amounts of bromine in body-fluids and organs. A. STOLL and B. BRENNEN (Biochem. Z., 1934, 268, 229—246).—A method is described which determines Br down to 4×10^{-6} g. in KBr and KBr-KCl mixtures with a fair degree of accuracy and is applied to its determination in rabbit blood and urine. Curves show the variation of these vals. on oral administration of Br. P. W. C.

Destruction of organic substances with chlorine. J. ERDOS and B. GROAK (Magyar gyógys. Tarsas. Értes., 1933, 9, 397—399; Chem. Zentr., 1933, ii, 3166).—The material is heated under reflux with conc. HCl and conc. saturated aq. $KClO_3$. The method is used for the determination of Pb in faeces. H. J. E.

Micro-determination of carbon in biological fluids. II. Gasometric method. I. CLAUDATUS and D. PETREA (Bul. Soc. Chim. Romania, 1933, 15, 107—110).—The C is oxidised by $KMnO_4$ in NaOH-Ba(OH)₂ solution and the CO_2 formed determined in a Van Slyke apparatus. C. G. A.

Biological determination of amino-nitrogen. G. M. RICHARDSON (Proc. Roy. Soc., 1934, B, 115, 142—169).—The Van Slyke method is recommended for coloured extracts (I), but the CH_2O (phenolphthalein) titration may be used for colourless (I). $Pb(OAc)_2$ at p_H 6.0 is recommended as a decolorant for leaf (I) in preference to norit. All EtOH and $COMe_2$ methods are discarded, since Mg and various weak acids are titrated as NH_2-N . H. G. R.

Determination of glutathione. L. BINET and G. WELLER (Compt. rend., 1934, 198, 1185—1187).—1—2 g. of tissue are minced and treated with 5 c.c. of 10% $CCl_3 \cdot CO_2H$. The extract is filtered and the extraction repeated thrice. The combined extracts are neutralised to bromothymol-blue (first appearance of blue) with NaOH and treated with 2 c.c. of 1% Cd lactate and 1 or 2 drops of 2% NaOH. The ppt. flocculates in 1—2 hr. and is collected, dissolved in 10 c.c. of 10% $CCl_3 \cdot CO_2H$, and titrated with 0.004N-I (starch indicator). A correction is required for the $CCl_3 \cdot CO_2H$ present. The method is sp. The following vals. have been found: liver, 130; suprarenals, 114; spleen, 102; pancreas, 97; cardiac muscle, 62; skeletal muscle, 27 (mg. per 100 g. of fresh tissue). P. G. M.

Determination of carnosine in biological fluids. R. KAPELLER-ADLER and F. HAAS (Biochem. Z., 1934, 269, 263—270).—Methods are given for the determination of carnosine (I) alone [hydrolysed to histidine (II) and determined colorimetrically] and in mixtures with (II) and with anserine (III). Muscle of ox, horse, and pig contains 0.238, 0.324, and 0.304% of (I), of hen 0.12% of (I) with 0.421% of (III), and of carp 0.088% of (II) with 0.059% of (I). P. W. C.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1934.

General, Physical, and Inorganic Chemistry.

Fine structure of H_a . H. KOPFERMANN (Naturwiss., 1934, 22, 218).—The fine structure of H_a is more easily observed in the spectrum of pure H^2 than in that of the isotopic mixture. A. J. M.

Fine structure analysis of H^1_a and H^2_a . R. C. WILLIAMS and R. C. GIBBS (Physical Rev., 1934, [ii], 45, 475—479).—The interval between the main components of the doublet is 0.308 for H^1_a and 0.321 cm^{-1} for H^2_a . Relative intensities of components are in approx. agreement with theory. N. M. B.

Bands in the extreme ultra-violet emission spectrum of the H^1H^2 molecule. C. R. JEPPESEN (Physical Rev., 1934, [ii], 45, 480—484).—Data for twelve bands for a 3 : 2 H^1H^2 mixture, belonging to the $2p^1\Pi_{cd}—1s^1\Sigma$ system of the H^1H^2 mol., are tabulated. Analysis gives rotational and vibrational consts. in agreement with those from the isotope effect. There is a large electronic isotope shift of 135 cm^{-1} . The apparent vibrational perturbation in the $v=3$ level of the state is 4.3, compared with 10.4 cm^{-1} for H^1H^1 . N. M. B.

Stark effect for the hydrogen isotopes. J. S. FOSTER and A. H. SNELL (Nature, 1934, 133, 568). L. S. T.

Spectrum of the HD and the D_2 molecules. G. H. DIEKE and R. W. BLUE (Nature, 1934, 133, 611—612).—The mol. spectra of samples ranging from pure H^1 to practically pure H^2 obtained under high dispersion are discussed. L. S. T.

Stark effect for the helium line 5876 Å. with high resolution. R. RITSCHL (Physikal. Z., 1934, 35, 313—316).—The Stark effect of the He line 5876 Å. has been investigated, using a special positive-ray tube, with a Fabry-Perot etalon, and a Zeiss tri-prism apparatus. The behaviour of the strong and weak components is identical. A weak component displaced towards the red occurs, which is polarised perpendicular to the direction of the field. There are also two components displaced towards the violet to an extent depending on the square of the field strength, polarised perpendicular and parallel to the field. A. J. M.

Fine structure of the He II line 1640 Å. V. M. TSCHULANOVSKI and M. P. MOCHNATKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 471—473).—The spectrum of He in the interior of a hollow C cathode has been photographed. The 1640 Å. line shows two groups of fine-structure lines, the intensities of which are not in complete agreement with theory. J. W. S.

Interferometric measurements of the absorption of helium. H. GERRITSEN (Physica, 1934, 1, 401—414).—Intensity distribution curves for the He lines $2^1P—3^1P$, $2^1P—4^1D$, $2^1P—5^1D$, and $2^1S—3^1P$ have been measured and the ratio of the Einstein absorption coeffs. is derived. H. J. E.

Anomalous dispersion near band lines of the lithium molecule. R. LADENBURG and S. LEVY (Z. Physik, 1934, 88, 449—460).—Anomalous dispersion due to Li_2 vapour at 1000° was investigated in the red, and gives the nuclear moment of Li^7 as 5/2. A. B. D. C.

Carbon bands at 2313 Å. (Possible existence of C_3 as an equilateral triangle.) T. HORI (Z. Physik, 1934, 88, 495—510).—Possible emitters of these bands are a diat., symmetrical or unsymmetrical linear triat., or an equilateral triangular mol.; the last model is preferred. A. B. D. C.

Rotation structure of the nitrogen molecule bands in the Schumann region. V. M. TSCHULANOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 473—478).—New measurements have been made of the N_2 spectrum in the far ultra-violet region and are discussed theoretically. J. W. S.

Predissociation in the first positive group of N_2 and its bearing on the electronic level diagram of the nitrogen molecule. A. VAN DER ZIEL (Physica, 1934, 1, 353—362). H. J. E.

New band system of nitrogen. A. VAN DER ZIEL (Physica, 1934, 1, 513—517).—A new band system between 2000 and 2800 Å., degraded to the violet, has been measured. The transition is probably $1^3\Sigma_g^- \rightarrow 1^3\Sigma_u^-$. H. J. E.

Anomalous dispersion of excited gases. VIII. Transition probabilities for the red-yellow neon line ($s—p$) and the half life period of the p -state. R. LADENBURG and S. LEVY (Z. Physik, 1934, 88, 461—468). A. B. D. C.

Occurrence of neon spark lines in the light from the negative glow. II. M. J. DRUYVESTEYN (Physica, 1934, 1, 427—428; cf. A., 1931, 539).—Ne III lines were observed in a glow discharge, showing electrons to be present with > 78% of the cathode fall of potential. H. J. E.

Nuclear spin of sodium. J. JOFFE (Physical Rev., 1934, [ii], 45, 468—474).—Measurements of alternations of intensities in absorption for the (0, 2) band in the $^1\Pi \leftarrow ^1\Sigma$ transition gave an average val. of 1.71, agreeing with the theoretical val. 1.67, corresponding with a nuclear spin of 3/2. N. M. B.

Intensity ratio of the lines $2P-1S$ and $2P_2-1S$ in the arc spectrum of alkali earths. F. J. CHANULEAU (Physica, 1934, 1, 518—520).—Observed and calc. vals. agree for Ca, Sr, and Ba. H. J. E.

Spectra of chlorine, Cl III, Cl IV, and Cl V. I. S. BOWEN (Physical Rev., 1934, [ii], 45, 401—404; cf. A., 1928, 210).—Full data, classifications, and term vals. for about 200, 50, and 20 new lines of Cl III, Cl IV, and Cl V, respectively, are tabulated. N. M. B.

Vibrational states of Rb_2 and Cs_2 . E. MATUYAMA (Nature, 1934, 133, 567—568).—Expressions for the frequencies of the heads of the bands of Rb and Cs are given and discussed. L. S. T.

Nuclear moment of elements. S. FRISCH and V. A. MATVEEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 460—464).—Careful study of the Ag I 3280 and 3382 Å. lines reveals no fine structure, the line breadth indicating a max. val. of 2×10^{-4} magneton for the magnetic moment of the Ag nucleus. The Mg II 2802 and 2795 Å. lines also show only slight broadening under extreme conditions. J. W. S.

Nuclear moments of the antimony isotopes. S. TOLANSKY (Nature, 1934, 133, 531—532; cf. A., 1933, 2).—Greater resolution of the lines of the Sb II spectrum shows that the nuclear mechanical spins of both Sb^{121} and Sb^{123} are $5/2$, but the nuclear magnetic moments are in the ratio 1.36 : 1, Sb^{121} having the greater val. L. S. T.

Tellurium arc spectrum. O. BARTELT (Z. Physik, 1934, 88, 522—531). A. B. D. C.

Ultra-violet resonance spectrum of iodine molecules. K. ASAGOE (Sci. Rep. Tokyo Bunrika Daigaku, 1934, A, 2, 9—16).—Data are tabulated for lines or groups of lines in the range λ 2360—1850, with I vapour weakly excited with a small transformer; they may be explained on the excitation of I_2 mols. by a resonance line of I at λ 1830.4, or by collision of the second kind with excited I atoms in the $^4P_{5/2}$ state. N. M. B.

Depolarisation of the fluorescence of iodine vapour by collision with helium atoms. S. MROZOWSKI (Bull. Acad. Polonaise, 1933, A, 346—358).—The fluorescence of I vapour has been investigated in the presence of He at 0—20 mm. pressure. The results are discussed. J. W. S.

Mean life of a spectroscopic term and width of spectral lines. I. I. AGARBICEANU (Compt. rend., 1934, 198, 1484—1486). B. W. B.

New form of discharge in mercury vapour. H. BECK (Physikal. Z., 1934, 35, 338—340).—In certain discharge tubes, with cathodes of Fe or Ni, the discharge in Hg vapour gave a no. of symmetrically placed "pearls" of light on the cathode. These are not due to impurities in the cathode. The conditions for obtaining this form of discharge are described. Liquid Hg must be present. A. J. M.

Dependence of the form of the 2537 Å. mercury line on the direction of observation of the resonance radiation. (Miss) M. MORACZEWSKA (Bull. Acad. Polonaise, 1934, A, 18—21).—The intensity distribution in the resonance line (I) depends on that

in the exciting line when (I) is viewed parallel to the direction of the exciting light, but is independent of the exciting line when viewed at right angles. H. J. E.

Resonance line 2537 and intensity increase of the mercury triplets in the presence of highly dried hydrogen. H. SCHNITGER (Z. Physik, 1934, 88, 353—354).—Collisions of the second kind of H. are particularly efficient in changing 2^3P_1 to 2^3P_0 Hg. A. B. D. C.

Intensity of the Hg spectral lines emitted from a quartz mercury-vapour lamp in the near infra-red region. M. SHODA (Japan. J. Physics, 1934, 9, 27—33; cf. *ibid.*, 1933, 8, 91).—The linear proportionality between log. intensity per unit current and log. (terminal voltage—min. voltage of Hg lamp) holds for the near infra-red regions. Complicated relationships may exist between the proportionality factor and the wave-length. J. W. S.

Proof of the axially of light emission from the Lyman line 1025 Å. R. FRERICHs and H. BONKE (Physikal. Z., 1934, 35, 349—350). A. J. M.

Long-wave infra-red radiation of high-frequency sparks. A. M. LEVITSKI (Physikal. Z., 1934, 35, 361—367).—The relative energy of metal particles in the spark was measured, and the temp. of the spark calc. The energy of the long-wave infra-red radiation was also measured under the same conditions. The infra-red rays are mainly radiated from the neighbourhood of the electrodes. It is not temp., but removal of electrons from the electrodes, which is the more important factor in the radiation of infra-red rays from high-frequency sparks. A. J. M.

"Mottled hydrogen." A. GUNTHER-SCHULZE (Z. Physik, 1934, 88, 273—274).—A reply to Gerlach (this vol., 237). A. B. D. C.

Night-sky auroral green radiation. H. GARRIGUE (Compt. rend., 1934, 198, 1398—1400).—The intensity variations of the non-polar line 5577 Å. (I) compared with the results of Cabannes and Dufay (this vol., 232) for the blue 4420 Å. line (II) indicated that the source of (I) was at a lower altitude than that of (II). (Cf. A., 1928, 1165.) B. W. B.

Dirac vector model in complex spectra. J. H. VAN VLECK (Physical Rev., 1934, [ii], 45, 405—419).—Mathematical. The use of the Dirac model in place of Slater's determinantal wave functions for calculations of at. spectral terms and in mol. spectra is examined. N. M. B.

Theory of stepped grating. G. WOLFSOHN and J. A. VREESWIJK, jun. (Physica, 1934, 1, 333—342). H. J. E.

Widths of X-ray lines from alloy targets. L. G. PARRATT (Physical Rev., 1934, [ii], 45, 364—369).—Ionisation curves of the $K\alpha$ doublet from targets of alloys of Ni, Fe, Mn, Cr, and Ti show that line widths depend on the physical or chemical state of the target. Widths for element A alloyed with B may be > or < for pure A. N. M. B.

Form of the X-ray emission bands of metals. H. JONES, N. F. MOTT, and H. W. B. SKINNER (Physical Rev., 1934, [ii], 45, 379—384).—Mathe-

matical. Variations in the optical transition probabilities for transitions from the conduction to the K and L levels are examined. An explanation of the form of the X-ray emission bands (see O'Bryan and Skinner, below) is given. N. M. B.

Measurements of K absorption limits for the elements 37 Rb to 50 Sn. E. C. INGELSTAM and B. B. RAY (Z. Physik, 1934, 88, 218—225).

A. B. D. C.

Yield of fluorescence X-rays from the K shells of thirteen elements. D. K. BERKEY (Physical Rev., 1934, [ii], 45, 437—440).—Measurements by the Compton ionisation method for the fluorescence yield are given for Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, and Tc, and show a max. of 0.79 for Mo, falling rapidly for the heavier elements.

N. M. B.

Faint lines in the L spectrum of the elements 73 Ta to 90 Th. I. S. KAUFMAN (Physical Rev., 1934, [ii], 45, 385—388).—Data for weak diagram and satellite lines in the region of the $L_{\gamma 1}$ lines of the X-ray spectra are tabulated.

N. M. B.

Characteristic X-rays from metals in the extreme ultra-violet. H. M. O'BRYAN and H. W. B. SKINNER (Physical Rev., 1934, [ii], 45, 370—378).—Identifications and transitions for soft X-ray bands in the region 50—500 Å. from Li, Be, C, Na, Mg, Al, Si, and Ba targets are obtained from photometric curves. The energy spread of the bands is calc. from the Sommerfeld theory of metals, and leads to a unique determination of the no. of conduction electrons per atom in a metal.

N. M. B.

Inner conversion in X-ray spectra. H. M. TAYLOR and E. H. S. BURHOP (Nature, 1934, 133, 531).—A criticism (cf. this vol., 341).

L. S. T.

Continuous X-ray spectrum from a thin target. W. DUKELSKY (Nature, 1934, 133, 566—567).

L. S. T.

Double refraction of X-rays. H. SEEMANN (Physikal. Z., 1934, 35, 329—336).—A comprehensive experimental investigation is described.

A. J. M.

Filter method for determination of the width of the Compton lines for scattering at solids and gases. E. O. WOLLAN (Physikal. Z., 1934, 35, 353—360).—The method uses three absorption filters, enabling the intensity of the Compton lines for scattering at solids and gases to be determined. The latter gives a measure of the electron velocity distribution in free atoms and mols.

A. J. M.

Klein-Nishina formula for X-ray scattering in the wave-length region 15—20 Å. J. READ and C. C. LAURITSEN (Physical Rev., 1934, [ii], 45, 433—436).—Measurements of the absorption coeff. per electron in C and Al of X-ray beams indicate that the Klein-Nishina formula for the scattering coeff. per electron is accurate to 1%.

N. M. B.

Scattering of X-rays by carbon. P. C. MUKHERJEE (Z. Physik, 1934, 88, 247—250).—Scattering by C obtained from combustion of C_6H_6 , camphor, and animal charcoal showed central scattering which is attributed to small C particles; these particles have

a lattice const. 3.61 Å. compared with 3.41 Å. for graphite.

A. B. D. C.

Probability of double jumps in X-ray spectra. E. G. RAMBERG (Physical Rev., 1934, [ii], 45, 389—391).—Mathematical.

N. M. B.

Compensation of electronic energy and energy of repulsion in the molecule of hydrogen. J. SAVARD (Compt. rend., 1934, 198, 1480—1482).—The relation between energy of formation and ionisation potential previously derived (cf. A., 1933, 993; this vol., 11, 347) is applied and confirmed in the case of H_2 .

B. W. B.

Doppler displacements in the spectrum of hydrogen canal rays. (Miss) A. J. MCPHERSON (Physical Rev., 1934, [ii], 45, 485—487; cf. this vol., 1).—H canal rays of uniform energy were obtained by accelerating the H ions formed in a low-voltage arc through a short electric field. The spectrum was observed at H_2 and H_+ in the direction of motion, and the Doppler displacements of the lines H_{31} , H_{21} , H_1 from atoms accelerated as H_3^+ , H_2^+ , and H_1^+ agree with calc. vals. in the range 7000—17,000 volts. A min. velocity for excitation of radiation in the neutral H atom moving in H_2 was found at about 40 volts. A He- H_2 mixture showed only the H_{21} , H_1 Doppler lines.

N. M. B.

Diffraction of electrons in the halogens. F. L. ARNOT (Proc. Roy. Soc., 1934, A, 144, 360—377).—The angular distributions of the elastically scattered electrons in the vapours of I, Br, $CHBr_3$, and CCl_4 have been measured for several energies of the incident electron beam. All the curves show diffraction effects. Those for Br and $CHBr_3$ are similar, indicating that the scattering by $CHBr_3$ is mainly due to the Br atoms. The curves for I, Br, and CCl_4 are similar to those previously obtained for Xe, Kr, and Ar, respectively (A., 1931, 1347).

L. L. B.

Polarisation of electrons by free atoms. E. RUPP (Z. Physik, 1934, 88, 242—246).—Electrons of 20—160 kv. were scattered twice through 90° by Tl vapour, and showed polarisation.

A. B. D. C.

Scattering of slow electron beams by graphite. M. KOHLER and M. VON LAUE (Naturwiss., 1934, 22, 238).—For X-ray interference the odd orders are forbidden, but this is not so for beams of slow electrons according to the dynamic theory of electron interference. The scattering of slow electrons at single crystals of graphite is taken as an example (A., 1933, 1222).

A. J. M.

Continuous electron radiation in gas discharges. W. FINKELNBURG (Z. Physik, 1934, 88, 297—310).—The continuous spectrum of high electron density discharges is radiation of electrons in the field of ions.

A. B. D. C.

Recoil of radiation scattered by free electrons. I. WALLER (Z. Physik, 1934, 88, 436—448).—Theoretical.

A. B. D. C.

Velocity distribution of diffusing electrons. F. BLANK (Z. Physik, 1934, 88, 532—535).—The

velocity distribution was measured for electrons moving through He in a homogeneous electric field.

A. B. D. C.

Negative-energy electrons. Y. NISHINA and S. TOMONAGA (Japan. J. Physics, 1934, 9, 35—40).—Theoretical.

J. W. S.

Magnetic electron and the correspondence principle of T. de Donder and J. M. Whittaker. J. GEHENIAU (Compt. rend., 1934, 198, 1580—1582).—Mathematical.

Wave-statistical theory of electron spin. K. C. KAR and K. K. MUKHERJEE (Phil. Mag., 1934, [vii], 17, 993—1003).—Mathematical.

New source of positive electrons. D. SKOBELTZYN and E. STEPANOWA (Nature, 1934, 133, 565, 646).—A weak Ra source (Ra salt) placed within a Wilson chamber in a magnetic field emits a considerable no. of positive electrons in addition to the β -particles of the natural spectrum. The observed distribution of velocities is 100—300, 300—600, 600—900 kv., 8, 16, and 6 positrons (I), respectively. The calc. no. of emitted (I) is ≤ 0.02 — 0.04 for each disintegrating atom of Ra-C. It is improbable that the observed (I) are due to the internal conversion of γ -rays, and a new mechanism, presumably connected with β -disintegration, appears to be involved in their production. Later experiments show that a large part of (I) is due to the action of the β -rays on the glass wall surrounding the radioactive source.

L. S. T.

At. wt. of uranium lead from Great Bear Lake, N.W.T., Canada, pitchblende. J. P. MARBLE (J. Amer. Chem. Soc., 1934, 56, 854—856).—The val. obtained is 206.054.

E. S. H.

New isotope of argon. P. ZEEMAN and J. DE GIER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 127—129; cf. A., 1933, 1099).—Positive-ray analysis of A shows a weak line at 38 which varies in intensity proportionally to the A 36 and 40 lines when other gases are added. Its prolongation towards the axis also suggests that it belongs to an inert gas. It is concluded that A³⁸ exists.

J. W. S.

Calcium isotope with mass 41 and the radioactive half-period of potassium. J. KENDALL, W. W. SMITH, and T. TAIT (Nature, 1934, 133, 613—614).—A correction (cf. A., 1933, 658). The calc. half-period of K⁴¹ is of the order 1×10^{11} years.

L. S. T.

Classification of atomic masses. A. JAQUEROD (Compt. rend., 1934, 198, 1478—1480).—At. nuclei are regarded as built of H atoms, and the packing divergences of isotope masses from the products mass no. \times at. wt. of H are plotted against mass no. With few exceptions, the isotopes of all elements fall successively on three straight lines in the groups Li to Zn, Zn to Xe, and Xe to U. The results are applied to calculate the isotopic ratios of K, Ca, and Cu.

B. W. B.

Action of cathode rays on mixtures. G. VON HEVESY and A. FAESSLER (Z. Physik, 1934, 88, 336—341). Radioactive indicators were used to study evaporation of PbO and Rb₂SO₄ under bombardment of cathode rays.

A B D C

Origin of the actinium series of radioactive elements. II. A. V. GROSSE (J. Physical Chem., 1934, 38, 487—494).—Aston's recent measurements (A., 1933, 762) of the mass spectra of radiogenic Pb are shown to support the actino-U theory (A., 1933, 110). Other theories contradict well-known radioactive data. The anomaly of the Great Bear Lake pitchblende is explained as due to alteration.

M. S. B.

Radioactivity of neodymium and samarium and of mixtures containing both. L. ROLLA and L. MAZZA (Atti R. Accad. Lincei, 1933, [vi], 18, 472—478).—The discrepancies in the lit. relating to the radioactivity (I) of Nd and Sm are discussed, and measurements of (I) of the oxides prepared from various fractions, obtained by different methods of separation, of a mixture containing Pr, Nd, Sm, and Gd are described. All the specimens of Sm₂O₃ exhibited approx. the same (I), irrespective of the method of prep., whilst Nd₂O₃ exhibited a small and variable (I), due probably to the presence of an extraneous metal; the vals. observed for mixtures of Sm₂O₃ and Nd₂O₃ were intermediate between those of the separate oxides. Pr₆O₁₁ was completely inert. The existence of a radioactive element 61 is improbable.

H. F. G.

Radioactive series and the classification of light elements. G. PETIAU (Compt. rend., 1934, 198, 1320—1323).—By considering transmutation of the light elements ($Z=3$ —15) series analogous to the three radioactive series are deduced. From the position corresponding with the Ac series a fork in the latter series leading to elements 85 and 87 is thought to exist. A scheme of formation of the light elements is put forward, which permits the formulation of the laws of artificial transformations by means of α -rays.

W. R. A.

Optimum frequency of collection of radium emanation. H. TELEZ-PLASENCIA (Anal. Fis. Quím., 1933, 31, 510—512).—The degree of efficiency F with which use is made of a source of Rn for radiotherapy varies as the total quantity emitted by the source during a given period and to the quantity collected at periodic intervals throughout the period. F passes through a max. when plotted against the length t of the intervals at which the Rn is collected; the calc. max occurs at approx. $t=7$ days.

H. F. G.

Distribution of radium-A, -B, and -C between the gas phase and the walls in a mixture of radon and ammonia. A. LUYCKX (Bull. Soc. chim. Belg., 1934, 43, 179—188).—A bulb with a mica window was filled with Rn-NH₃ mixture, and the α -ray activities of Ra-A, -B, and -C were measured. Covering the mica with a mica screen stopped rays from the gas phase, but the ZnS scintillations were only slightly reduced, showing that the Ra-B and -C were almost entirely ($> 97\%$) on the wall (i.e., the mica window). By calculation about 50% Ra-A remains in the gas (cf. this vol., 470).

D. R. D.

Decay constant of radium-C'. J. C. JACOBSEN (Nature, 1934, 133, 565—566).—Using Geiger counters the half-period of Ra-C' has been determined to be of the order 2×10^{-4} sec.

L. S. T.

Calculation of the ionisation produced by radon in a spherical volume. P. C. CAPRON (Bull. Soc. chim. Belg., 1934, 43, 25—34).—Theoretical.

H. F. G.

Energies of α - and γ -rays. H. A. WILSON (Proc. Roy. Soc., 1934, A, 144, 280—285).—The energies of disintegration of the radioactive atoms, calc. from the α -ray energies, may be arranged in pairs of which the sums are multiples of 3.8504×10^5 electron volts. This const. probably represents some general at. quality.

L. L. B.

Absorption of α -rays. G. MANO (Ann. Physique, 1934, [xi], 1, 407—531).—Experimental and theoretical data on the absorption of α -rays by matter are surveyed. The retardation of α -rays in gases is investigated for air, H_2 , He, Ne, and A. Results are compared with the theory based on wave mechanics. Experimental retardation curves agree with the Bethe-Bloch equation provided a suitable empirical val. is chosen for \bar{E} , the term representing the mean excitation energy. Vals. of \bar{E} for H_2 and He correspond with calc. vals., but are higher for heavier elements, and \propto the at. no.

N. M. B.

Complex radiation excited in light elements by α -particles. P. SÄVEL (Compt. rend., 1934, 198, 1404—1407).—The method previously described (A., 1933, 659) was applied to Li, N_2 , Na, and Mg excited by Po α -rays, N_2 being compressed into a brass box for examination. γ -Rays were emitted by all, and neutrons by all except N_2 . Energies of emitted particles and requisite excitation energies are tabulated. It is suggested that nuclear excitation of Li and N occurred without capture of α -particles or transmutation (process I), γ -ray emission following, and that the excitations of Na and Mg were similar to Curie and Joliot's new type (this vol., 234), the latter being attributed to process I, followed by nuclear transmutation with emission of proton or neutron and γ -rays.

B. W. B.

Theory of β -rays. I. E. FERMI (Z. Physik, 1934, 88, 161—177).—Assuming the presence of neutrinos (particles of mass \approx that of an electron, but without charge), the emission of these and β -rays is treated quantitatively by a method similar to light emission by an excited atom.

A. B. D. C.

γ -Rays on bombardment of boron with protons. L. KURTSCHATOV, G. SCHTSCHEPKIN, A. VIBE, and V. BERNASCHESKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 486—489).— γ -Rays are produced simultaneously with α -particles when B is bombarded with protons, and measurements with a screened Geiger-Müller counter indicate that every disintegration is accompanied by the emission of 1 γ -quantum of energy 2×10^6 e.v. This is in agreement with the results of Rutherford and Oliphant (A., 1933, 883).

J. W. S.

γ -Radiation of radium; number of emitted quanta; internal absorption. E. STAHEL and W. JOHNER (J. Phys. Radium., 1934, [vii], 5, 97—103).—Using an ionisation chamber filled with MeI, measurements show the emission of 1.18 quanta of γ -radiation, and 0.35 quantum of characteristic K radiation excited by internal absorption of γ -rays per

100 atoms of Ra decomposed. The coeff. of absorption of γ -rays of wave-length 0.065 Å. in Pt is 21 cm.^{-1}

N. M. B.

Induced radioactivity of the lighter elements. C. D. ELLIS and W. J. HENDERSON (Nature, 1934, 133, 530—531).—Induced radioactivity in Al, B, and Mg (this vol., 470) has been confirmed and extended. With Ra-C' α -particles reduced to 6.1 cm. range, the relative yields of positrons (I) during the entire decay from Al, B, and Mg are approx. 30, 10, and 7, respectively, and since the periods are $3\frac{1}{2}$, 14, and $2\frac{1}{2}$ min. the initial effects are in the ratio 6:0.5:2. With all materials there is an effect, due to an impurity always present, with a period of approx. 1 min. and of initial activity comparable with that of B. The probability of a 7×10^6 volt α -particle producing a radio-P atom by impact on Al is approx. 1 in 5×10^6 . The yield of (I) increases 15 times as the energy of the α -particle increases from 5.5 to 7×10^6 volts. With Th-C' α -particles measurements have been extended to 8.3×10^6 volts when the probability of excitation appears to be reaching a max. Results support the view that an α -particle colliding with an Al nucleus has a certain chance of being captured, and from this arises a phenomenon analogous to radioactive branching, the alternatives being the immediate emission of either a proton or a neutron. The latter emission produces the radioactive isotope of P which emits (I). The branching ratio is of the apparent order of 50 to 1 in favour of proton emission. There are few, if any, (I) of low energy from Al, and (I) over the range 1 to $2\frac{1}{2} \times 10^6$ volts have been detected. Some γ -radiation appears to arise from the annihilation of (I).

L. S. T.

Artificial radioelement from nitrogen. L. WERTENSTEIN (Nature, 1933, 134, 564—565).—After bombardment with α -rays (I) from Rn, Pt, Ag, Pb, Ca, and Ni show an activity decaying exponentially with a half-period of 1.2 min. The effect disappeared when the range of (I) was reduced by a few mm. of air. The effect is due to the recoil of a new radioelement produced by (I), and since it occurs only in N_2 and not in a vac., or in H_2 or O_2 , it consists in a transmutation of N_2 of the Joliot type, the probable reactions being ${}^{14}_7N + {}^4_2\alpha = {}^{17}_9F + {}^1_0n$ and ${}^{17}_9F = {}^{17}_8O + \text{positron}$. NaN_3 gives an increased effect.

L. S. T.

Artificial production of radioactive substances. C. C. LAURITSEN, H. R. CRANE, and W. W. HARPER (Science, 1934, 79, 234—235).—After deuteron bombardment (I) of targets of LiF, Be, H_3BO_3 , C, Mg, and Al examination by a Geiger counter revealed a large no. of counts during the first few min. after (I). C gave the largest effect with a half-life period of approx. 10 min., and B slightly less with a half-life period of approx. 20 min. The other substances gave appreciable effects, which may, however, be due to C contamination of the target surface. Expansion photographs showed that the activity consisted mainly of positrons and some γ -rays. The decay period and the max. energy of the positive electrons from C indicate that the active isotope in this case is the same as in the case of B bombarded by α -particles (this vol., 234), viz., N^{13} . When C is bombarded by deuterons, $\approx 1\%$

of the transformations give the radioactive N^{13} as a product, whilst the remainder give C^{13} . L. S. T.

Disintegration of the diplon. P. I. DEE (Nature, 1934, 133, 564).—The disintegration particles resulting from the bombardment (I) of "heavy" $(NH_4)_2SO_4$ with diplons show opposite pairs of tracks of approx. 14.3 cm. and 1.6 cm. range, the shorter track being due to $H^3: {}_1H^2 + {}_1H^2 \longrightarrow$ + (cf. this vol., 471). The neutrons emitted by (I) appear to constitute an approx. homogeneous group of max. energy of approx. 1.8×10^6 volts, a val. in fair agreement with the reaction ${}_1H^2 + {}_1H^2 \longrightarrow {}_2He^3 + {}_0n^1$ (*loc. cit.*). L. S. T.

Magnetic moment of the neutron. I. TAMM and S. ALTSCHULER (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 455—460).—From the hyperfine structure of at. spectra it is concluded that the most probable val. of the magnetic moment of the neutron is $-\frac{1}{2}$ nuclear magneton (cf. A., 1933, 767). J. W. S.

"Neutrino." H. BETHE and R. PRIERLS (Nature, 1934, 133, 532).—A discussion. L. S. T.

Proton emission of aluminium bombarded by highest energy α -rays. O. HAXEL (Z. Physik, 1934, 88, 346—352).—Four proton groups were observed, their range decreasing with the α -ray range. The results indicate presence of excited Si nuclei. A. B. D. C.

Path of a secondary cosmic-ray charged particle in the earth's magnetic field. I. S. BOWEN (Physical Rev., 1934, [ii], 45, 349—351).—Conclusions on decrease in ionisation in equatorial regions and on east-west dissymmetry of Geiger tube counts are reached from an analysis of secondary cosmic-ray paths. N. M. B.

Mechanism of cosmic-ray counter action. C. D. ANDERSON, R. A. MILLIKAN, S. NEDDERMEYER, and W. PICKERING (Physical Rev., 1934, [ii], 45, 352—363).—Conclusions are reached from a study of photographs obtained with Geiger-counter-controlled exposures. N. M. B.

Cosmic-ray ionisation at high altitudes. A. H. COMPTON and R. J. STEPHENSON (Physical Rev., 1934, [ii], 45, 441—450).—A criterion for the nature of cosmic rays in terms of atm. pressure and ray intensity. Graphical analysis of records made in a stratosphere balloon show the presence of two range groups corresponding with protons or possibly positrons and with neutral rays or rays having a large e/m ratio. Photons cannot constitute $>$ a negligible part of primary cosmic rays. N. M. B.

Influence of the ionisation chamber on the form of the cosmic-ray depth-ionisation curve. C. ECKART (Physical Rev., 1934, [ii], 45, 451—453).—Mathematical. The assumption of exponential absorption does not agree with observed results (see preceding abstract). N. M. B.

Highly filtered cosmic rays. W. KOLHORSTER (Z. Physik, 1934, 88, 536—549).—Absorption coeffs. were measured for radiation filtered through the equiv. of 500 m. of H_2O . A. B. D. C.

Simple method for the determination of the spin and statistics of the deuteron. T. SEXL (Naturwiss., 1934, 22, 205).—A generalisation of Mott's

theorem (A., 1930, 974) enables the spin and statistics of the deuteron and other nuclei to be determined (cf. A., 1933, 955). A. J. M.

Experimental proof of the spin maintenance law. R. DOPEL, K. GAILER, and E. WIGNER (Physikal. Z., 1934, 35, 336—337).—Many experiments, mainly concerned with ortho- and para- H_2 , are quoted, supporting the spin maintenance law. Strict accuracy of the law is not to be expected for Hg. A. J. M.

Waves and photons. II. Pauli's approximation. A. PROCA (J. Phys. Radium, 1934, [vii], 5, 121—125).—Mathematical. As a first approximation of the mechanics previously initiated (cf. this vol., 344) the photon is described by a wave function of two components only. Results satisfy Maxwell's equations and indicate that a photon corresponds with circularly polarised light. Negative energy of a particle is interpreted as an indication of sense of rotation of certain fields which are associated with the particle, and, for a light corpuscle, correspond with the Maxwell electromagnetic fields. N. M. B.

Extension of the Dirac vector model to include several configurations. R. SERBER (Physical Rev., 1934, [ii], 45, 461—467).—Mathematical. N. M. B.

Magnetic moments of atomic nuclei. H. KALLMANN and H. SCHULER (Z. Physik, 1934, 88, 210—213).—Magnetic moments of nuclei built of α -particles, even nos. of neutrons, and odd nos. of protons are accounted for. A. B. D. C.

Representation of nuclear moments of atoms by nuclear vectors. H. SCHULER (Z. Physik, 1934, 88, 323—335).—All known nuclear magnetic moments can be given by five vectors representing respectively the angular momentum of the nuclear core consisting of α -particles and an even no. of neutrons, the spin and orbital angular momentum of neutrons and of protons. The nuclei fall into two classes: those with α -particles, an even no. of neutrons, and a proton, and those with α -particles and an odd no. of neutrons. A. B. D. C.

Value of e/m . R. T. BIRGE (Nature, 1934, 133, 648). L. S. T.

Resemblance in the form of excitation functions. L. S. ORNSTEIN and J. A. SMIT (Physica, 1934, 1, 455—464).—Theoretical. Data for He, Hg, and Na are discussed. H. J. E.

Mitogenetic radiation.—See this vol., 555.

Atmospheric $O^{16}O^{18}$ bands in the solar spectrum. D. I. EROPKIN and V. N. KONDRATEEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 445—449).—The atm. absorption spectra has been studied over the region 6930—6880 Å. with the sun 3° above the horizon. From the relative intensities of the B and B' O₂ bands, the ratio $O^{16}:O^{18}$ is calc. as 595:1 (cf. A., 1931, 539). J. W. S.

Absorption spectrum of oxygen in the far ultra-violet. D. CHALONGE and E. VASSY (Compt. rend., 1934, 198, 1318—1320).—The H-tube spectrum was photographed at distances from 400 to 600 m. at Lauterbrunnen and Jungfrauoch. The continuous spectrum predicted by Herzberg was observed.

The convergence limit was determined by Birge's method, and the dissociation potential calc. as 5.09 volts. W. R. A.

Ultra-violet absorption bands of oxygen (Schumann-Runge bands). J. CURRY and G. HERZBERG (Ann. Physik, 1934, [v], 19, 800-808).—The Schumann bands of O_2 were investigated using high dispersion. The oscillation quanta of the ground state deviate considerably from the linear curve.

A. J. M.

Ultra-violet absorption of oxygen and of ozone. N. T. ZE and C. S. PIATW (Naturwiss., 1934, 22, 237).—There is similarity between the ultra-violet absorption bands of O_2 under pressure, determined by Finkelnburg and Steiner (A., 1933, 5), and the absorption bands of O_3 (A., 1927, 607; 1932, 869; 1933, 444). The absorption bands of compressed O_2 occur in triplets; for each triplet there is a single corresponding O_3 band, of which the wave-length coincides with the middle band of the O_2 triplet.

A. J. M.

Existence of O_4 in liquid oxygen. GUILLIEN (Compt. rend., 1934, 198, 1486-1488).—A const. mass of liquid O_2 was diluted up to 17.7 times with liquid N_2 (cf. Living and Dewar, A., 1895, ii, 471) and changes (I) in absorption band intensities were measured. The infra-red and red bands (due to O_2), $\lambda > 6500$, became narrower and diminished in intensity towards a finite limit on dilution. The ultra-violet and visible bands (II), $\lambda < 6500$, diminished in intensity without change of width and are attributed to O_4 , which gives quant. agreement with (I), and corresponds with a slight displacement observed in the calc. $\lambda\lambda$ of (II). The proportion of O_4 in liquid O_2 was 51% (cf. Lewis, A., 1924, ii, 811).

B. W. B.

$^1\Pi \rightarrow$ **band of NH and the corresponding ND bands.** G. H. DIEKE and R. W. BLUE (Physical Rev., 1934, [ii], 45, 395-400; cf. Pearse, this vol., 129).—A comparison and analysis of the NH^1 3240 Å. band and the corresponding NH^2 3235 Å. band are given. The zero lines are 30755.61 and 30849.00, respectively; the shift is due to the zero-point vibrational energy of half a quantum. The Λ -doubling in the NH^2 is $<$ in the NH^1 band by a factor 3.511.

N. M. B.

Band spectrum of PN and its significance. W. JEVONS (Nature, 1934, 133, 619-620). L. S. T.

Ultra-violet band system of AsN. J. W. T. SPENKS (Z. Physik, 1934, 88, 511-514).

A. B. D. C.

Band spectrum of aluminium chloride. P. C. MAHANTI (Z. Physik, 1934, 88, 550-558).—The dissociation energy of the lower state of $AlCl$ is 3.76 volts.

A. B. D. C.

Ultra-violet absorption spectrum of carbon suboxide gas. R. M. BADGER and R. C. BARTON (Proc. Nat. Acad. Sci., 1934, 20, 166-169).—Data for eighteen bands, and curves showing max., were obtained in the range $\lambda\lambda$ 3200-2500, approx. A continuum with a max. at about λ 2600 overlies the bands. The calc. separation of the rotation lines is 0.013 Å., approx.

N. M. B.

Influence of pressure on the flame spectra of hydrogen and carbon monoxide. W. A. BONE and F. G. LAMONT (Proc. Roy. Soc., 1934, A, 144, 250-256).—Using an apparatus for the maintenance of continuous flames of combustible gases in air or O_2 at high pressures, a study has been made of the effect of increasing pressure up to 100 atm. on the flame spectra of H_2 and CO and a series of $CO+H_2$ mixtures, burning in O_2 . Although in some of the spectrograms of $CO+H_2$ flames at atm. pressure the banded spectrum of burning CO underlying its continuous spectrum is faintly discernible, in those obtained at higher pressures it is swamped by the intensity of the continuous spectrum. L. L. B.

Electron-isomerism of organic compounds with multiple linkings. A. BURAWOY (Z. wiss. Phot., 1934, 32, 289-294; cf. A., 1932, 791; 1933, 228).—The author's previous work indicates that the chromophores corresponding with the different absorption bands of a compound are formed in electron-isomeric mols., and that the *R* and *K* bands correspond with a double linking in a biradical compound and conjugated system, respectively. Intensities of bands are discussed, with regard to the determination of configurations. J. L.

Absorption curves for potassium chloride and bromide on the short-wave side of their infra-red frequencies. A. MENTZEL (Z. Physik, 1934, 88, 178-196).—The transmission of KCl was observed between 20 and 45 μ , and of KBr between 16 and 53 μ . The observed extinction coeffs. decreased more rapidly with decreasing wave-length than the dispersion theory predicts; these coeffs. for KCl, KBr, and NaCl plotted against λ/λ_0 , where λ_0 is the characteristic frequency, all fall rapidly after $\lambda/\lambda_0=0.25$. Subsidiary max. were observed at 42.5, 41, and 33 μ for KCl, at 35 μ for KBr, and at 34 μ for NaCl.

A. B. D. C.

Ultra-violet absorption of [solid and dissolved] sodium chloride. R. TREHIN (Compt. rend., 1934, 198, 1492-1494; cf. A., 1932, 107).—The optical density (I) of rock-salt was $>$ that of its aq. solution and the latter was $>$ that of pure NaCl solution. For an equal concn., (I) was $>$ in glycerol than in aq. solution.

B. W. B.

Kinetics of additive colouring of alkali halides. I. S. ARZYBYSHEV (Z. Physik, 1934, 88, 260-264).—The colouring is due to electrons from halide ions that have passed into the liquid metal; this gives levels sufficiently high for the electrons to pass into the conductivity band of the crystal. A. B. D. C.

Absorption spectra of cobalt halide solutions. R. J. MACWALTER and S. BARRATT (J.C.S., 1934, 517-524).—The visible absorption spectrum of $CoCl_2$ in H_2O at concn. up to saturation at 100°, and in aq. HCl, EtOH, and C_5H_5N , and that of $CoBr_2$ and CoF_2 , has been measured. In red Co solutions the band at 5100 Å. is attributed to Co^{++} . In the blue solutions a complex band is observed at wave-lengths increasing with the wt. of the anion, attributed to complex anions. The relative amounts of the red and blue forms have been calc. Solutions

of CoCl_2 in $\text{C}_5\text{H}_5\text{N}$ are anomalous in the position of the band and the effect of H_2O . H. J. E.

Spectra and photochemical decomposition of metallic carbonyls. I. Spectral data. H. W. THOMPSON and A. P. GARRATT (J.C.S., 1934, 524—528).— $\text{Ni}(\text{CO})_4$ (I) vapour (at $p=1$ —200 mm.) and $\text{Fe}(\text{CO})_5$ (II) vapour (at $p=1$ —15 mm.) gave continuous absorption only, commencing at 3950, 4100 Å., respectively. That of (I) in C_6H_{14} or CCl_4 solution was the same. (II) in the same solvents gave a continuum at $\lambda < 5500$ Å., attributed to $\text{Fe}_2(\text{CO})_9$ present as an impurity. The photo-dissociation mechanisms operative in the region of continuous absorption are $(\text{I}) + h\nu \longrightarrow \text{Ni}(\text{CO})_3 + \text{CO}$, $\text{Ni}(\text{CO})_3 \longrightarrow \text{Ni} + 3\text{CO}$; $(\text{II}) + h\nu \longrightarrow \text{Fe}(\text{CO})_4 + \text{CO}$; $\text{Fe}(\text{CO})_4 + (\text{II}) \longrightarrow \text{Fe}_2(\text{CO})_9$. H. J. E.

Photochemistry and absorption spectrum of acetone. E. J. BOWEN and H. W. THOMPSON (Nature, 1934, 133, 571).—The absorption spectrum of COMe_2 has been examined using pressures from 0.5 to 200 mm. in columns up to 1 m. long. At pressures $>$ a few mm. a region of continuous absorption extends from approx. 3200 to 2400 Å. with a max. at approx. 2800 Å. At lower pressures this splits up into four groups, with centres at approx. 3150, 2900, 2710, and 2570 Å., each containing approx. 25 diffuse bands. The bands are 2.5 Å. wide with a uniform separation of approx. 4 Å. With increasing pressure the bands widen and the groups extend to give a continuous spectrum. This type of spectrum is similar to that found in other Y-shaped mols. The diffuseness of the bands can be attributed to an unresolved close packing of the rotation lines; there is no need to assume a process of pre-dissociation involving the splitting of C-H or C-C. L. S. T.

Absorption of ultra-violet light by some organic substances. XXXI. W. GABRYELSKI and L. MARCHLEWSKI. XXXII. L. MARCHLEWSKI and W. URBANCZYK (Bull. Acad. Polonaise, 1933, A, 397—408, 409—415; cf. A., 1933, 661).—XXXI. The absorption spectra of glucose, galactose, and maltose in 0.002—0.5N aq. NaOH have been studied between 2100 and 3600 Å. Solutions above 0.002N show strong bands near 2690 and 3100 Å., which develop slowly in the case of dil. NaOH solutions, and disappear on neutralising. The change in absorption is attributed to the formation of the aldehydic forms of the carbohydrates, which require a $p_H > 10$ for their production.

XXXII. Solutions of *l*-arabinose and rhamnose in aq. NaOH show similar results to hexoses.

J. W. S.

Absorption of ultra-violet light by some organic substances. XXXIII. L. MARCHLEWSKI and J. PIZLO. XXXIV. W. GOŚLAWSKI and L. MARCHLEWSKI. XXXV and XXXVI. (Miss) G. HERTZÓWNA and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1934, A, 22—41, 42—44, 45—59, 60—63).—XXXIII. Solutions of $\text{C}_5\text{H}_5\text{N}$ in H_2O or EtOH gave similar absorption spectra with three max., whereas in CHCl_3 or Et_2O there was only one absorption max. Salts of $\text{C}_5\text{H}_5\text{N}$ with HNO_3 , H_2SO_4 , or HCl also gave only one max. Similar variations with solvent were

found for quinoline, isoquinoline, NH_2Ph , and the toluidines.

XXXIV. The absorption spectrum of phloroglucinol (I) and its Me_3 ether in EtOH are similar, showing (I) to be present largely as $(\text{OH})_3$ -compound and not in the keto-form.

XXXV. Absorption data for the following acids are recorded and discussed: phthalic, isophthalic, terephthalic, *o*-benzoylbenzoic, phenyl-acetic and -propionic, benzoyl-, xyloyl-, mesitoyl-, and phenetoxy-acrylic, pyrogallolcarboxylic, gallic, carminic, and the Me esters of the first three.

XXXVI. In EtOH solution absorption max. occur for glucosazone at 3830, 2570 Å., for maltosazone at 3910, 2590 Å., for arabinosazone at 3835, 2560 Å., and for rhamnosazone at 3880, 2565 Å. H. J. E.

Ultra-violet absorption spectra of aromatic substances. II. A. HILLMER and P. SCHORNING (Z. physikal. Chem., 1934, 168, 81—106; cf. this vol., 345).—The change caused in the ultra-violet absorption spectra of C_6H_6 , PhOH, pyrocatechol, and their Me and methylene ethers by introduction of Pr^a or a side-chain containing a C:C linking, CO, OH, bridge O, or several of these has been studied. The spectra of some polynuclear compounds have been determined. The effect of the solvent on the spectrum of the solute has been studied with a few solutes. R. C.

Ultra-violet absorption spectrum of aniline vapour. J. SAVARD (Bull. Soc. chim., 1933, [iv], 53, 1404—1408).—220 bands from 2980 to 2632 Å. have been measured, and are represented by equations. The energy of dissociation into NHPH and H is calc. to be -108 kg.-cal. The activated mol. exists in three electronic states. F. L. U.

Continuous absorption spectra of polyatomic molecules. IV. Y. HUKUMOTO (Sci. Rep. Tôhoku, 1934, 23, 62—75; cf. A., 1933, 336).—The continuous absorption spectra in the ultra-violet have been investigated for the following compounds: $\text{C}_6\text{H}_5\text{Br}$, $\text{CH}_2\text{Cl}\cdot\text{CHCl}_2$, C_2Cl_6 , MeCN, EtCN, $\text{CH}_2\text{Cl}\cdot\text{CN}$, AcCl, AcBr, EtCOCl, and PrSH. The relationship between the dissociation energy of the C-halogen linking and the structure of the mol. is discussed and the conclusions are compared with those deduced from Raman and infra-red spectral data. M. S. B.

Optical absorption of substituted benzenes. IV. Toluene halides and relations between band displacement and dipole moment. H. CONRAD-BILLROTH (Z. physikal. Chem., 1934, B, 25, 139—150).—Absorption data for monohalogen derivatives of C_6H_6 and PhMe have been used to check the rule for the calculation of the position of the absorption bands of polysubstituted derivatives of C_6H_6 from the displacement, Q , of the band of the monosubstituted derivative relative to the spectrum of C_6H_6 (cf. A., 1933, 445). The rule fails for MeOBz and Me toluate and when $\cdot\text{CN}$ and $\cdot\text{NC}$ are present. The graph of \sqrt{Q} against the dipole moment for symmetrical substituents is a straight line not passing through the origin (cf. A., 1930, 136). R. C.

Absorption spectra of some hydrocarbons in the Schumann violet. E. P. CARR and H. STUCKLEN (Z. physikal. Chem., 1934, B, 25, 57—70).—

Hexane, heptane, Δ^{α} -heptene, Δ^{α} - and Δ^{β} -pentene, and $\text{CMe}_2\cdot\text{CHMe}$ vapours exhibit a broad dissociation band at $<1530 \text{ \AA}$. The unsaturated compounds have a second dissociation band at 1740 \AA . and groups of narrower bands nearer the red varying in position according to the position of the C:C linking in the mol. With C_6H_6 the first dissociation band is absent and the second displaced somewhat towards the red and resolved; there is also a group of intense narrow bands between 1720 and 1800 \AA . representing a deformation vibration spectrum. R. C.

Optical absorption of some carbon compounds in the Schumann ultra-violet. G. SCHEIBE and H. GRIENEISEN (Z. physikal. Chem., 1934, B, 25, 52–56).—Measurements have been made with hydrocarbons, ketones, and ethers. R. C.

Absorption spectra of chlorophylls-*a* and -*b* at room and liquid nitrogen temperatures. F. P. ZSCHEILE, jun. (Nature, 1934, 133, 569).—Absorption max. of Et_2O solutions of chlorophyll-*a* and -*b* photographed at -196° are recorded and compared with those obtained by a spectro-photoelectric method (this vol., 272) at room temp. At -196° the bands are much narrower than at room temp. and their max. are shifted. L. S. T.

Absorption in the visible spectrum of solutions of litmus and red-cabbage colouring matter. I. G. POPESCU (Bul. Soc. Romane Fiz., 1934, 36, 1–10).—Absorption curves are given for neutral, acid, and alkaline aq. solutions, and for solutions in EtOH and in Et_2O . N. M. B.

Rotation-vibration spectrum of water vapour. W. WEIZEL (Z. Physik, 1934, 88, 214–217).—The dipole moment varies appreciably only for vibrations normal to the symmetry axis, a first approximation giving no variation with vibrations parallel to this axis; this explains the absence of certain bands from the spectrum. A. B. D. C.

Temperature radiation from glowing oxides and oxide mixtures in the infra-red. G. RITZOW (Ann. Physik, 1934, [v], 19, 769–799).—The emission from electrically heated oxides and oxide mixtures has been investigated in the region 1 – 10μ , the dependence of the emission on wave-length, temp., nuclear size, and composition being determined. The emission of all white oxides (I) was relatively small, but const., at a given temp., between 1 and 5μ , but increased rapidly above this wave-length. The emission of the coloured oxides (II), CeO_2 and Cr_2O_3 , between 1 and 7μ was considerably $>$ from (I) at the same temp. and wave-length. For all oxides, the emission increased with rise of temp. For nuclear sizes between 20 and 0.5μ , the emission decreased as the nuclear size decreased for all temp. and wave-lengths. The addition of a small amount of (II) to (I) gives a mixture with a lower emission than either alone, but with larger amounts of (II) the emission is $>$ that of (I). A. J. M.

Two types of diamond. (Sir) R. ROBERTSON, J. J. FOX, and A. E. MARTIN [with W. T. GORDON, B. ROBINSON, and G. P. THOMSON] (Phil. Trans., 1934, A, 232, 463–535).—Diamonds showing a laminar structure (I) differ in certain properties from

ordinary diamonds (II). (II) have an infra-red absorption band at 8μ and are opaque to ultra-violet light $<3000 \text{ \AA}$., whilst (I) have no band at 8μ and are transparent up to 2250 \AA . With (II) the conductivity induced by light is very small, high voltages having to be applied to detect a current, whilst (I) give an appreciable current without an applied voltage. (I) are activated by light of 2300 \AA . and afterwards give a current in the dark and a large current when re-illuminated with light $>5000 \text{ \AA}$. These activated diamonds are deactivated by light of 2400 – 5000 \AA . X-Ray examination indicates that (I) have a mosaic structure; they are also more optically isotropic than (II), but the sp. gr., n , dielectric const., and Raman effect are the same for both types. It is considered that the difference between (I) and (II) is not due to impurities, but to different conditions resulting during their formation from the plastic state. H. S. P.

Application of Raman effect and infra-red absorption spectra to the distinction between the five isomeric hexanes. A. ANDANT, P. LAMBERT, and J. LECOMTE (Compt. rend., 1934, 198, 1316–1317).—Raman and infra-red frequencies for the isomerides are tabulated. W. R. A.

Raman spectrum of heavy water. R. W. WOOD (Physical Rev., 1934, [ii], 45, 392–394; cf. this vol., 129).—Excitation of 18% heavy H_2O by $\lambda 2536$ of Hg gave the usual $\Delta\nu=3445$ band and a new $\Delta\nu=2623$ band probably due to H^2OH^1 . With 80% heavy H_2O the latter band was shifted slightly to shorter wave-lengths and was stronger than the former, which was shifted slightly towards the red. From the shift it is concluded that mols. containing only one H^2 atom give bands $\Delta\nu=2623$ and 3500 , whilst H_2O mols. give a single band $\Delta\nu=2517$. N. M. B.

Raman spectra of HCl in non-ionising solvents. W. WEST and P. ARTHUR (J. Chem. Physics, 1934, 2, 215–216).—Raman data, 2797 – 2860 cm^{-1} , for 0.2 mol. fraction of HCl at -65° excited by Hg $\lambda 4047$ are given for solutions in SiCl_4 , PCl_3 , CHCl_3 , HCl , liquid SO_2 , EtBr , and AcCl , and frequency displacements are considered in relation with electric moments of the solvent and ionisation processes in HCl mols. N. M. B.

Raman effect in hydroxy-compounds. L. MEDARD (Compt. rend., 1934, 198, 1407–1409).—Purified specimens of H_2SO_4 , HNO_3 , MeOH , EtOH , $\text{Pr}^{\alpha}\text{OH}$, $\text{Pr}^{\beta}\text{OH}$, $\text{Bu}^{\alpha}\text{OH}$, and $\text{Bu}^{\gamma}\text{OH}$ all gave wide bands of varying intensity from 3000 to 3600 \AA ., with max. between 3360 and 3440 \AA ., frequently asymmetrical, attributed to OH. B. W. B.

Raman effect and constitution of molecules. VI. Raman frequencies in CH_2Cl_2 and their polarisations. Polarisation of wings of Rayleigh lines. B. TRUMPY (Z. Physik, 1934, 88, 226–234).—New displacements were observed at 898 and 1060 cm^{-1} Observed polarisations agree with Placzek and Teller's theory. A. B. D. C.

Raman spectra of cyclopentene, cyclopentenyl alcohols, cyclopentanol, and 1-cyanocyclopentene. L. PIAUX (Compt. rend., 1934, 198, 1496–

1499)—The Raman spectra of the above compounds were determined (cf. Godehot, A., 1933, 448), the alcohols being *cyclopentenyl*-substituted MeOH, EtOH, and PrOH. 1-*Cyanocyclopentene*, b.p. 58—60°, was prepared by dehydration of *cyclopentanone*-cyanohydrin with SOCl_2 and $\text{C}_5\text{H}_5\text{N}$. The effects of substitution and conjugation on the various frequencies are discussed. B. W. B.

Anomalies in the absorption spectrum of visual purple. S. HECHT and A. M. CHASE (Proc. Nat. Acad. Sci., 1934, 20, 238—243).—An initial increase of absorption occurs at the blue end of the spectrum during the bleaching, by light, of those extracts of visual purple which afford an intermediate yellow stage (I). During the bleaching of retinal extracts from spring and summer frogs only traces of (I) appear, whereas extracts from hibernating winter frogs have a pronounced (I). J. G. A. G.

Fluorescence excited by circularly polarised light of $\lambda=3131 \text{ \AA}$. S. M. MITRA (Current Sci., 1934, 2, 347).—The fluorescence of dyes in glycerol is unpolarised. C. W. G.

Polarisation of the fluorescence of dyes as a function of the wave-length of the exciting light. A. JABLONSKI (Bull. Acad. Polonaise, 1934, A, 14—17).—The % polarisation of the fluorescent light from Cellophane impregnated with tryptaflavine, euchrysine, rhoduline-yellow, or *isoquinoline*-red diminishes with decreasing wave-length of the exciting light (5000—3500 \AA). H. J. E.

Luminescence excited in calcium tungstate by an electric current. A. GÜNTHER-SCHULZE and M. GERLACH (Z. Physik, 1934, 88, 355—357).—A current of 1—10 ma. traversing a thin film of CaWO_4 gives rise to the characteristic fluorescence. Powdered ruby shows the same effect. A. B. D. C.

Effect of electric discharge on the phosphorescence of alkaline-earth sulphides. R. COUSTAL (Compt. rend., 1934, 198, 1403—1404).—A brush discharge taken from the surface of phosphorescing alkaline-earth sulphides in contact with either pole immediately, but temporarily, quenched phosphorescence (I). When (I) had been excited by light from a Hg arc, vivid luminescence appeared before extinction. B. W. B.

Fluorescence of fluorspars at low temperatures. S. KREUTZ (Bull. Acad. Polonaise, 1933, A, 573—574).—Observations relating to four fluorspars of different origin are tabulated. In three specimens the colour of the fluorescence at liquid air temp. differed from that at 20°, and in all four the intensity was much greater at the lower temp. F. L. U.

Photo-electric limit of tantalum carbide. A. ENGELMANN and H. TEICHMANN (Z. Physik, 1934, 88, 275).—The limit is 265 m μ before, and 310 after, degassing. The photo-electric effect is similar to that of heavy metals. A. B. D. C.

Photo-electric effect of crystal semiconductors. Proustite, pyrrargyrite, bournonite, and molybdenite. G. ATHANASIU (J. Phys. Radium, 1934, [vi], 5, 132—140; cf. this vol., 474).—Photo-electric curves for the four minerals are given; for

the first, second, and fourth, sensitivity max. correspond with radiations 0.580, 0.620, and 0.800—0.900 μ , respectively; for the first and second the max. photo-electric effect is produced by radiation corresponding with the region of strong optical absorption. Photo-electric and photo-conductance effects are compared. It is concluded that radiation giving max. photo-electric effect at room temp. is identical with that giving max. photo-conductance at low temp. (—100° to —150°). Among other crystals examined, a strong thermo-electric effect was found for hessite, sylvanite, and nagyagite. N. M. B.

Mechanism of the selenium electrolytic photo-cell. R. AUDUBERT and J. ROULLEAU (Compt. rend., 1934, 198, 1489—1490).—The photo-potential (I) of a Se-Pt cell was of the same order in solutions of KI in several org. liquids as in H_2O , which is therefore not necessary for the development of (I) (cf. A., 1931, 999). In aq. solutions of various electrolytes (I) was less in oxidising than in reducing media; hence it is attributed to the capture of photo-electrons by cations, a mechanism which agrees with the observed light-response functions. B. W. B.

Metallic photo-resistance in a current of water. Q. MAJORANA (Atti R. Accad. Lincei, 1933, [vi], 18, 347—352; cf. this vol., 353).—Experiments with the metal (Pt) immersed in running H_2O show that the photo-resistance effect does exist, although in absence of H_2O it is associated with thermal effects. Hysteresis (35—45°) occurs between the illumination and resistance cycles. H. F. G.

Metallic photo-resistance at high frequencies. Q. MAJORANA (Atti R. Accad. Lincei, 1933, [vi], 18, 433—437; see preceding abstract).—With increase of the frequency of interruption of the light (up to 16,000 per sec.) the effect diminishes more rapidly than does the ordinary photo-electric effect. H. F. G.

Ionisation potentials and dissociation energies of non-polar molecules. J. SAVARD (Physica, 1934, 1, 321—323).—In a mol. of the type A_2 the dissociation energy, D , $=2n(I_m - I_a)$ e.v., and in a mol. of the general type AB_p , $D=2n \times I_m -$ e.v. (I_m =ionisation potential of the mol., I_a =ionisation potential of atom A , $2n$ =no. of binding electrons of one shell and n_a =no. of electrons furnished by the atom A for this shell). In a radical such as Me or CN the ionisation potential of the free radical = that of the C atom. In a mol. of the type R-R the binding energy between the two radicals, B , $=2(I_m - I_a)$ e.v. Examples are given. H. J. E.

Electrical strength of alkali halides and the influence of mixed crystal formation and foreign substances. A. VON HIPPEL (Z. Physik, 1934, 88, 358—365).—General conditions are deduced for formation of cryst. insulators. A. B. D. C.

High-frequency resistances. W. GRAFFUNDER (Ann. Physik, 1934, [v], 19, 689—706).—The constancy of capacity of various resistances used in high-frequency work was tested against Pt resistances. The majority showed considerable variation. The capacity of liquid resistances was also investigated. A. J. M.

Absorption measurements in liquids in the range of short electric waves. II. J. MALSCH (Ann. Physik, 1934, [v], 19, 707—720; cf. A., 1932, 470).—A critique of work on this question. Recent work leads to results which cannot be explained according to any theory involving anomalous dispersion. A. J. M.

Electrical conductivity of thin cupric sulphide films. H. DEVAUX and J. CAYREL (Compt. rend., 1934, 198, 1339—1342).—Dried CuS films (100—200 Å. thick) formed on Cu^{II} salt solutions by surface H₂S attack gave $\rho=10^{-1}$ — 4×10^{-1} ohm cm. when fresh, ρ increasing with age (cf. A., 1929, 989).

B. W. B.

Conductivity of paraffin wax. W. JACKSON (Naturwiss., 1934, 22, 238—239).—The sp. conductivity of paraffin wax, m.p. 45—55°, increases to a max. at temp. from 0° to 16°, then decreases to 35°, after which it rapidly rises. The max. at 16° is connected with the dielectric after-effect.

A. J. M.

Dipole moments and physico-chemical properties. I. A. E. VAN ARKEL (Chem. Weekblad, 1934, 31, 139—141).—An outline is given of the theory, and the results of measurements with various groups of org. compounds are summarised briefly.

H. F. G.

Measurements of the dipole moments of nitrous oxide and ethyl nitrite in the vapour phase. E. CZERLINSKY (Z. Physik, 1934, 88, 515—521).—The moment of N₂O is 0.14×10^{-18} , and of EtO·NO 2.38×10^{-18} . Possible structures are discussed.

A. B. D. C.

Dielectric constant. XII. G. DEVOTO (Gazzetta, 1934, 64, 76—83; cf. A., 1933, 1230).—Dielectric const. measurements are recorded for aq. solutions of betaine, thiobetaine, NH₂·CHMe·CH₂·CO₂H, NH₂·[CH₂]₃·CH(NH₂)·CO₂H, NH₂·C₆H₄·AsO₃H₂, dimethylpyrone, pyrocatechol, resorcinol, quinol, NH₂·CO·CH(OH)·CH₂·CO·NH₂, MeOAc, CH₂Ac·CO₂Et, MeNO₂, NH₂OH, and H₃BO₃. The polar nature of some of these compounds is discussed. O. J. W.

Calculation of the dipole contribution to the cohesion energy of organic compounds. A. E. VAN ARKEL (Physica, 1934, 1, 343—352; cf. A., 1933, 888).—Theoretical. The dipole contribution to the cohesion energy in approx. spherical mols. is calc. In the C-Cl linking the centre of the dipole is < 0.4 Å. from the C atom. This distance is also small with C-Br, C-I, C-F, C-NO₂, and C-Me. In isomerides with the dipole groups attached to a different no. of C atoms, the order of the b.p. may be calc. from the vector sum of the dipoles on each C. In isomerides with the dipole groups on the same no. of C atoms (as in C₆H₆ derivatives) the mutual influence of the dipoles must be considered.

H. J. E.

Dielectric properties of acetylenic compounds. I. Symmetrical dialkylacetylenes. H. H. WENZKE and R. P. ALLARD (J. Amer. Chem. Soc., 1934, 56, 858—860).—A zero moment has been obtained for the Bu₂ compound in heptane and for the *n*-diamyl compound in C₆H₆ at 25°. The at.

polarisation is somewhat > that of the more saturated hydrocarbons of the same mol. wt. E. S. H.

Dipole moment and dielectric constants of solvents. H. MULLER (Physikal. Z., 1934, 35, 346—349).—The polarisation of CH₂Cl₂ and PhNO₂ in C₆H₁₄ and CS₂ at various temp. (−80° to 41°) has been measured. Small effects due to the solvent may lead to very erroneous vals. for the at. polarisation. Correct vals. can be obtained only when working with gases.

A. J. M.

Molecular polarisations of nitrobenzene in various solvents at 25°. H. O. JENKINS (J.C.S., 1934, 480—485; cf. this vol., 240).—The mol. electrical polarisation and apparent dipole moment (I) of PhNO₂ in C₆H₆, dekaline (II), CCl₄, *n*-C₆H₁₄, cyclohexane, CS₂, and CHCl₃ has been measured. The val. of (I) varies with the solvent. The total polarisation of the solute at infinite dilution is related linearly with the reciprocal of the dielectric const. of the solvent. This holds for non-polar (C₆H₁₄) and for polar (CHCl₃) solvents, small deviations occurring for C₆H₆, (II), and CCl₄.

H. J. E.

Dielectric polarisation of benzene, carbon disulphide, hexane, and nitrobenzene. A. PIEKARA (Bull. Acad. Polonaise, 1933, A, 305—318).—The mol. polarisation (I) of C₆H₆ has a min. val. at about the f.p. and is higher in the region of supercooling. (I) for CS₂ and C₆H₁₄ increase with rising temp., but not so rapidly as with C₆H₆. The dielectric const., ϵ , and (I) of liquid PhNO₂ show no abnormality in the region of supercooling. ϵ of solid PhNO₂ at 250 m. is much < found by Mazur (A., 1931, 148) at 800 m. This may be due to anomalous dispersion.

J. W. S.

Induction in the benzene molecule. E. NÆS-HAGEN (Z. physikal. Chem., 1934, B, 25, 157—160).—By measurement of dipole moment with mono-substituted Ph₂ derivatives induction effects in the C₆H₆ mol. have been demonstrated.

R. C.

Dielectric constants of ethyl behenate and molecular volumes of ethyl behenate and hexacosane in the liquid and solid states. R. BUCKINGHAM (Trans. Faraday Soc., 1934, 30, 377—386).—Changes of dielectric const., ϵ , and between the m.p. and room temp. show that Et behenate exists in < 4 modifications. The irreversible transition $\alpha \rightarrow \beta$ at 43° is accompanied by a sharp fall of ϵ , a sharp rise of d , and a change in the inclination of the H-C chain. Phase changes also occur at 45° (irreversible) and 30° (reversible). The ester grouping oscillates in the α modifications, but motion is largely restricted in the β forms. The transition point α —of hexacosane is 42° and the β form probably exists in two modifications.

J. G. A. G.

Dispersion of inert gases. T. LARSEN (Z. Physik, 1934, 88, 389—394).—Dispersion measurements between 5780 and 2300 Å. fit a Sellmeyer formula of three terms, two of which correspond with the resonance lines.

A. B. D. C.

Paramagnetic rotatory power and the law of magnetisation of tysonite in the direction of the optic axis. J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Physica, 1934, 1, 383—400,

and Compt. rend., 1934, 198, 1400—1403).—Measurements between 1.3° and 20.4° abs. with the Hg line 5460.7 Å. are recorded. H. J. E.

Magneto-optical Kerr effect. A. PIETZCKER (Z. Physik, 1934, 88, 311—322).—Measurements are given showing the proportionality of the Kerr effect to magnetisation of the ferromagnetic mirror.

A. B. D. C.

Isomorphism and chemical constitution: constitution of formic acid and formates. (SIR) P. C. RAY (Nature, 1934, 133, 646—647).—Sarkar now concludes that the difference between HCO_2H (I) and its higher homologues is due to the different structure of (I) in which the H attached to C is the ionisable atom. Undissociated (I) and its esters are not reducing agents. Reduction is due to the formate ion (II) owing to the presence of a lone pair of electrons in the C atom. The structure of (II) is almost identical with that of NO_2^- . *Mixed crystals* of $\text{Ba}(\text{NO}_2)_2$, $\text{Ba}(\text{CO}_2\text{H})_2$, and H_2O ; $\text{Sr}(\text{CO}_2\text{H})_2$ and $\text{Sr}(\text{NO}_2)_2$; $\text{Cd}(\text{CO}_2\text{H})_2$ and $\text{Cd}(\text{NO}_2)_2$, have been prepared. The double salts $\text{Mg}(\text{CO}_2\text{H})_2 \cdot 2(\text{CH}_2)_6\text{N}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Mn}(\text{CO}_2\text{H})_2 \cdot 2(\text{CH}_2)_6\text{N}_4 \cdot 10\text{H}_2\text{O}$, isomorphous with the corresponding nitrites, have also been prepared.

L. S. T.

Significance of the hydrides of the carbonyls of iron and cobalt. A. A. BLANCHARD and M. M. WINDSOR (J. Amer. Chem. Soc., 1934, 56, 826—827).—It is maintained that the electron pattern of $\text{Ni}(\text{CO})_4$ is repeated in all the volatile carbonyls, the addition of H furnishing the electrons required to complete the pattern.

E. S. H.

Diamagnetic susceptibility of the hydrogen molecule. K. HONDA and T. HIRONE (Z. Physik, 1934, 88, 414).—A correction (cf. A., 1933, 890).

A. B. D. C.

Magnetic properties of manganous sulphate and of certain rare earths. S. VELAYOS (Anal. Fis. Quim., 1933, 31, 597—606).—Magnetic data for MnSO_4 , $\text{Gd}_2(\text{SO}_4)_3$, Gd_2O_3 , and Dy_2O_3 are recorded; the magneton nos. are 28.99, 38.62, 38.78, and 51.73, respectively, the deviations from integral vals. being in the opposite sense to those calc. on the basis of the quantum theory.

H. F. G.

Wave mechanics and structural chemistry. N. V. SIDGWICK (Nature, 1934, 133, 530).—The conclusions of wave mechanics and of structural chemistry can be reconciled if an isomeric (tautomeric) reaction in which the atoms have nearly the same relative positions after as before has a small heat of activation and occurs with great rapidity.

L. S. T.

Lattice energies of the ammonium halides and the proton affinity of ammonia. W. E. BLEICK (J. Chem. Physics, 1934, 2, 160—163).—Lattice energies, in kg.-cal., calc. by the method of Born and Mayer (cf. A., 1932, 564) are: NH_4Cl , 161.6; NH_4Br , 154.0; NH_4I , 145.5. From these, by means of a thermal cycle the energy change at 0° abs. of the reaction $\text{NH}_3(\text{gas}) + \text{H}^+(\text{gas}) \rightarrow \text{NH}_4^+(\text{gas})$, which may be called the proton affinity of NH_3 , is -206.4 , giving 191.4 for the lattice energy of NH_4F , for which asymmetrical lattice the Born method fails. N. M. B.

Probability of the spontaneous decomposition of linear triatomic molecules. T. KONTOROVA and V. SOROKIN (J. Chem. Physics, 1934, 2, 216; cf. Rosen, this vol., 7).—Mathematical. N. M. B.

Parachors of the hexafluorides of the sulphur group. E. B. R. PRIDEAUX (Chem. and Ind., 1934, 351).—The interpretation of the parachor data for SF_6 (this vol., 477), SeF_6 , TeF_6 , and PCl_5 is considered.

D. R. D.

Parachor of esters of orthoformic acid. T. HUANG and K. SUNG (J. Chinese Chem. Soc., 1934, 2, 1—5).—The following vals. are found for the parachors of the trialkyl orthoformates: Me 249.5, Et 366.8, Pr^a 481.4, Pr^b 484.7, Bu b 598.3, Bu a 599.9, *isoamyl* 713.9, all within 1% of the vals. calc. from Sugden's consts.

D. R. D.

Confirmation of crystal wave-length measurements and determination of $h/e^{4/3}$. P. KIRKPATRICK and P. A. ROSS (Physical Rev., 1934, [ii], 45, 454—460).—The potential necessary for producing general radiation capable of reflexion from calcite at a known Bragg angle θ is $V' \sin \theta = 2035.3 \pm 0.2$ international volts, where V' is electron potential fall, using Ag $K\alpha_1$ radiation. Discrepancies of available data are discussed. Results yield $h/e^{4/3} = (1.7559 \pm 0.0002) \times 10^{-14}$, or, using recent auxiliary consts., 1.7563, and $h = (6.546 \pm 0.006) \times 10^{-27}$, assuming $e = (4.770 \pm 0.005) \times 10^{-10}$.

N. M. B.

Photometric measurement of the reflexion of X-rays. P. DE LA CIERVA and J. LOSADA (Anal. Fis. Quim., 1933, 31, 607—615).—Full details are given of the method, in which a line of the Al X-ray spectrum is employed. The results obtained with NaCl , CaCO_3 , and FeS_2 are in close agreement with those derived by the ionisation chamber method.

H. F. G.

Connexion between the thermal and mechanical rupture of atomic linkings in metals. F. REGLER (Ann. Physik, 1934, [v], 19, 637—664).—The width of X-ray interference lines for diffraction at a metal increases with the application of mechanical strains of all kinds, and also with rise of temp. The width of the radial interference lines is a measure of the potential energy of the crystal lattice. Each lattice of a metal can be associated with a certain definite amount of potential energy, the breakdown of at. linkings occurring if energy is acquired > this amount. Plasticity, hardening, and recrystallisation can be explained on the theory.

A. J. M.

Stacking of spheres. W. J. PORE (Chem. and Ind., 1934, 361—362).—There are only four regular ways of stacking spheres: (1) cubic stacking, each sphere making contact with six others; (2) body-centred cubic stacking, in which (1) is expanded so as to allow an additional sphere at the centre of each cube, each sphere making eight contacts. The void is 31.25%. The other two methods each give a void space of 25.95%. (3) Face-centred cubic stacking. (1) is expanded to allow another sphere at the centre of each cube face. This has full cubic symmetry and the variant (4) obtained by displacing triangular arrangements of cubes has hexagonal symmetry. Atoms of most cryst. metals are arranged in conformity with (3) and (4).

C. I.

Properties of substances having structural number 56. H. SPINDLER (Compt. rend., 1934, **198**, 1409—1410).—ZnS (structural no. 40; cf. A., 1933, 1229) fused at 2000° under pressure, but ZnSe and CdS (structural nos. 56) were suddenly volatilised from the furnace without melting, a behaviour attributed to structural peculiarities common to all compounds with such structural no., of which examples are given.

B. W. B.

Crystallisation of vitreous substances. P. MONDAIN-MONVAL (Compt. rend., 1934, **198**, 1413—1415).—Vitreous S and Se were shown by dilatometric and other observations to crystallise only at temp. above -29° and 32°, respectively (cf. A., 1930, 281). The transitions monoclinic \rightarrow rhombic S and red \rightarrow black Se also ceased below the same temp.

B. W. B.

Reciprocal exchange action. S. SCHUBIN and S. VONSOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, **1**, 449—454).—Interchange action in a crystal lattice is discussed mathematically.

J. W. S.

Measurement of lattice constants. V. KUNZL and J. KOPPEL (J. Phys. Radium, 1934, [vii], **5**, 145—151).—An extended account of work already noted (A., 1933, 450).

X-Ray examination of electrolytically deposited silver. G. R. LEVI and M. TABET (Atti R. Accad. Lincei, 1933, [vi], **18**, 463—467).—The particles of Ag deposited from a AgBr bath rich in Na₂S₂O₃ are isodiametrical, and growth proceeds in a direction perpendicular to the faces of the octahedra. H. F. G.

Lattice array faults in cuprous iodide. K. NAGEL and C. WAGNER (Z. physikal. Chem., 1934, **B**, **25**, 71—80).—The conductivity of CuI in I vapour at 40—300° increases with the pressure of I vapour. This is attributed to electron-deficiency conduction (cf. A., 1933, 888), which has been confirmed by thermo-e.m.f. measurements with Pt|CuI|Pt. With I v.p. of 46 mm. at 200° the partial conductivity of Cu is 1.8×10^{-4} ohm⁻¹, cm.⁻¹, or five times that of CuI in a high vac. Since both electron and Cu⁺ partial conductivity rise with the pressure of I vapour the excess of I in the lattice is interpreted by electron-deficiency points and empty positions in the Cu⁺ partial lattice. The rate of formation of a CuI film on Cu in I vapour at 200° is determined by the velocity of diffusion of the components through the film, and this diffusion is due to migration of Cu⁺ and electrons from metal towards vapour.

R. C.

Periodic structure in ice. S. C. BLACKTIN (Nature, 1934, **133**, 613).—A periodic structure formed in natural ice is described.

L. S. T.

Structure of the β -form of solid carbon monoxide. L. VEGARD (Z. Physik, 1934, **88**, 235—241).—This form of CO is very similar to that of β -N₂; it has approx. hexagonal closest spherical packing, the deviation being due to mol. rotation. A. B. D. C.

Crystal structure of 3I₂O₅·H₂O. J. GARRIDO (Anal. Fis. Quím., 1933, **31**, 616—617).—The monoclinic holohedral crystals have $a : b : c = 0.901 : 1 : 0.891$, and $\beta = 112^\circ 53'$.

H. F. G.

X-Ray studies on the hydrous oxides. IV. Titanium dioxide. H. B. WEISER and W. O. MILLIGAN (J. Physical Chem., 1934, **38**, 513—519).—X-Ray analysis and thermal dehydration isobars of hydrous TiO₂, freshly pptd. at room temp. or prepared by oxidation in air of Ti₂O₃· x H₂O, indicate that no definite hydrates have been prepared. On ageing under H₂O for some weeks, or on heating the freshly formed material at 184°, anatase crystals are obtained. The results indicate that pptd. TiO₂ consists of the anhyd. oxide (anatase modification) with adsorbed H₂O. Rutile is formed by hydrolysing TiCl₄ and Ti(NO₃)₄ at b.p. and anatase by hydrolysing Ti(SO₄)₂. By igniting the pptd. TiO₂ at 1000° the product is mainly rutile.

M. S. B.

Constitution of perovskite and related compounds. H. RHEINBOLDT (J. pr. Chem., 1934, [ii], **139**, 318—321).—A crystal structure for perovskite, CaTiO₃, is proposed, in which Ca and Ti are surrounded by 12 and 6 O, respectively, and O by 4 Ca and 2 Ti. KMgF₃ and similar compounds are similarly formulated.

R. S. C.

Guanidine *d*-tartrate. Crystallographic study. A. SWARYCZEWSKI (Bull. Acad. Polonaise, 1933, **A**, 359—365).—Guanidine *d*-tartrate, (CN₃H₅)₂(C₄H₆O₆)·1.5H₂O, crystallises in monoclinic form with $a : b : c = 0.7056 : 1 : 0.3366$ and $\beta 104^\circ 57'$. Optical data for the crystal over the wave-length range 4360—6560 Å. are given. X-Ray investigation shows the inter-planar distances to be 9.88, 14.77, and 4.78 Å. for the 100, 010, and 001 planes, respectively. Since d is 1.473 and the mol. wt. 295.4, the unit cell contains 2 mols.

J. W. S.

Investigation of the dihydrazide molecule by means of X-rays. M. WOLF (Physica, 1934, **1**, 417—424).—The long spacing (I) in compounds of the type [CH₂] _{n} (CO·NH·NH₂)₂ increases by 1.29 Å. for each C atom added to the chain, up to 24 C. In most dihydrazides with an even no. of C atoms a side spacing of 2.62 Å. was observed. In the odd dihydrazides side spacings of 3.62, 4.00 Å. were recurrent. The intensity of the different order reflexions of (I) for all members of a series is the same function of the reflecting angle. A mol. model is suggested.

H. J. E.

X-Ray study of the structure of liquid benzene, cyclohexane, and their mixtures. H. K. WARD (J. Chem. Physics, 1934, **2**, 153—159).—C₆H₆ and cyclohexane give X-ray diffraction peaks corresponding with preferred spacings of 4.68 and 5.09 Å., respectively, interpreted as the effective thickness of the respective rings. Mixtures give two independent peaks indicating emulsion-type solutions, the disperse phase being too small to show a Tyndall effect.

N. M. B.

Structure of cellulose and its derivatives. M. MATHIEU (Compt. rend., 1934, **198**, 1434—1436).—If the plane of the sugar rings in cellulose is parallel to the a and b axes (cf. Andress, A., 1929, 630; 1930, 280), the strongest X-ray interference is reflected at $11^\circ 22'$; if it is parallel to the b and c axes (cf. Astbury, A., 1931, 152), the angle is $10^\circ 50'$. By superimposing the diagram on that of NaCl, $11^\circ 19'$ is found, confirming the former view. If the distance between the planes

is calc. in accordance with this angle, it is substantially the same in cellulose and its mercerised, $(\text{NH}_2)_2$ -, Me, and perchloric acid derivatives, suggesting that the substituents are in the plane of the ring. In alkali-celluloses the distance is greater, suggesting substituents between the planes of the rings. E. W. W.

Large Barkhausen discontinuities and their propagation in Ni-Fe alloys. R. E. REINHART (Physical Rev., 1934, [ii], 45, 420—424; cf. Sixtus, A., 1933, 216).—Propagation velocity as a function of circular and longitudinal field, torsion, and tension for a 10% Ni-Fe wire is investigated. N. M. B.

Permeability of nickel and iron at very short wave-lengths, $\lambda=4$ to 10 m. J. MÜLLER (Z. Physik, 1934, 88, 143—160).—The dependence of permeability on frequency was obtained for various points on the magnetisation curve by means of a bolometer. A. B. D. C.

Equation of state and elementary carrier of magnetism in nickel. L. NEEL (J. Phys. Radium, 1934, [vii], 5, 104—120).—A model is proposed, based on Lenz's law, for a ferromagnetic substance, and allowing the calculation of the effect of mol. field fluctuations. The properties of the model are compared with those of Ni, and quantum-mechanical corrections are embodied. Results indicate that the magnetic properties of Ni are due to a variable no. of carriers having resultant spin $S=1/2$, the no. being a function of the magnetisation. At saturation and at weak magnetisation there is 0.607 and 0.867 carrier, respectively, per atom of Ni. N. M. B.

Recovery of electrical resistance and hardness of zinc, magnesium, and other low-melting metals from the effects of cold-working. G. TAMMANN and K. L. DREYER (Ann. Physik, 1934, [v], 19, 680—688).—The change of resistance of Zn wires by twisting at various temp., and the recovery from the effect, were measured. The recovery was also investigated for Tl, Pb, Sn, and Cd. The recovery of the hardness of Mg, Zn, Pb, Sn, and Cd was examined. A. J. M.

Experimental proof of the resistance change of thin layers of metals on charging. A. DEUBNER (Naturwiss., 1934, 22, 239).—The change of resistance of thin layers of Ag on charging to potentials of 1000—5000 volts has been measured. It varies linearly with the charging potential, and is of the expected order of magnitude. A. J. M.

Variation of resistance of nickel, iron, and bismuth in alternating magnetic fields of sonic frequencies. J. MÜLLER (Z. Physik, 1934, 88, 277—294).—The dependence of the resistance on the angle between the lines of force of the magnetic field and the crystal axes has been measured between 155° and 49.8 abs. At each temp. there is a field strength at which the resistance has the same val. with either of

the two mutually perpendicular shorter axes parallel to the field. This field strength decreases with falling temp. H. J. E.

Theory of optical absorption in alkali metal crystals. W. H. WATSON (Canad. J. Res., 1934, 10, 335—341). R. S.

Spontaneous variation in light transmission of thin silver foils. A. JAGERSBERGER and F. SCHMID (Z. Physik, 1934, 88, 265—269).—Variation of optical transparency of sputtered Ag films was observed up to 150 days after formation; it is attributed to structural changes, degassing, and chemical effects. A. B. D. C.

Metallic dispersion in the near infra-red. C. HURST (Proc. Roy. Soc., 1934, A, 144, 377—381).—Theoretical. The equations for the index of refraction and the coeff. of absorption of a metal in the near infra-red, developed by Kronig on a quantum-mechanical basis (A., 1929, 871), are formally identical with the dispersion equations obtained by Drude by classical methods. L. L. B.

Refractive indices [of metals] for electron waves. J. WINTER (Compt. rend., 1934, 198, 1352—1354).—Theoretical. B. W. B.

Metastability of elements and compounds as a consequence of enantiotropy or monotropy. XVIII. The lead oxide problem. E. COHEN and N. W. H. ADDINK (Z. physikal. Chem., 1934, 168, 188—201).—The red form of PbO , d_{40}^{30} 9.34₉, is stable below 488.5°, and the yellow form, d_{40}^{30} 9.63₂, m.p. 884±1°, stable above. Complications encountered by previous workers are ascribed to neglect of the effect of the solid-liquid interfacial tension in pycnometric d determinations of solids. R. C.

Allotropic transition of bismuth at 75°. S. AOYAMA and G. MONNA (Sci. Rep. Tōhoku, 1934, 23, 52—61).—Data obtained from thermal analysis, dilatometry, thermal expansion, and thermo-o.m.f. do not support the view that Bi exists in two modifications with a transition point at 75°. M. S. B.

Acoustical studies. III. Rates of excitation of vibrational energy in carbon dioxide, carbon disulphide, and sulphur dioxide. IV. Collision efficiencies of various molecules in exciting the lower vibrational states of ethylene, together with some observations concerning the excitation of rotational energy in hydrogen. W. T. RICHARDS and J. A. REID (J. Chem. Physics, 1934, 2, 193—205, 206—214; cf. this vol., 135).—III. Measurements of the velocity of sound in CO_2 , CS_2 , and SO_2 at 30° and various pressures and frequencies are tabulated, and their relation with energy terms is examined.

IV. Sound velocity data in C_2H_4 are given for various pressures, temp., and frequencies. Collisions with A, He, and N_2 have no appreciable effect on the vibrational energy of the C_2H_4 mol.; collisions with H_2 mols. are about ten times as effective as C_2H_4 - C_2H_4 collisions in producing transitions in the lower vibrational states. H₂ shows a dispersive region at ultrasonic frequencies. It is supposed that C_2H_4 - H_2 collisions are about twenty times as effective as H_2 - H_2 collisions in exciting the rotational energy of H_2 mols. N. M. B.

Rendering visible ultrasonic waves in liquids. H. R. ASBACH, C. BACHEM, and D. HIEDEMANN (Z. Physik, 1934, 88, 395—398; cf. this vol., 354).

A. B. D. C.

Heat content of gases from 0° to 1900°. G. B. TAYLOR (Ind. Eng. Chem., 1934, 26, 470).—Vals. are tabulated for the heat required to raise the temp. of 1 g.-mol. of H₂, O₂, N₂, CO, CO₂, CH₄, C₂H₂, and H₂O gases from 0° to temp. up to 1900°. They are calc. by integrating Bryant's sp. heat equation $C_p = A + BT + CT^2$.

A. G.

Thermal properties of condensed helium. R. KAISCHW and F. SIMON (Nature, 1934, 133, 460).—The heat of fusion is 6.75 g.-cal. per g.-atom at 4.0° abs. and 5.1 g.-cal. at 3.4°. d for solid He in equilibrium with the liquid phase is 0.23 at 4.0° and 0.22 at 3.6°. d and compressibility (I) of liquid He at 2.4° and 4.5° agree well with recent data (this vol., 136), but (I) falls appreciably at higher pressures. (I) for solid He is approx. 1.5×10^{-3} atm.⁻¹ at 3.7° and 115 atm. C_v for solid He between 2.7° and 3.7° at d 0.23 agrees with a Debye function $\Theta = 32.5^\circ$ which gives a zero point energy of 73 g.-cal. per g.-atom compared with a thermal energy of only 1 g.-cal. at 4°. Adiabatic expansion measurements have also been made.

L. S. T.

Behaviour of condensed helium near absolute zero. F. SIMON (Nature, 1934, 133, 529; cf. preceding abstract).—A discussion.

L. S. T.

Effect of pressure on the m.p. of *o*-, *m*-, and *p*-xylene. J. C. SWALLOW and R. O. GIBSON (J.C.S., 1934, 440—442; cf. this vol., 255).—Data are tabulated for the effect of pressures up to 2750 kg. per sq. cm. on the m.p. of *o*-, *m*-, and *p*-xylene, and on the first crystallisation temp. and eutectic temp. of a mixture of 70% *o*- and 30% *p*-xylene.

H. J. E.

Determination of specific heats of liquids. N. DE KOLOSOVSKI and V. V. UDOVENKO (Compt. rend., 1934, 198, 1394—1395; cf. A., 1933, 1006).—Mol. heats (I) and mol. entropy-temp. coeffs. (II) at 29° were determined for: PhEt, PhPr², PhBr, PhCHO, *m*-C₆H₄Me·NO₂, NPhMe₂, NPhEt₂, *m*- and *o*-C₆H₄Me·NO₂, and quinoline. With the exception of CCl₄, (II) increased with mol. complexity and (II)/(I) was approx. const. for all org. liquids so far examined.

B. W. B.

Exact measurement of the specific heats of metals at high temperatures. V. Specific heats and thermal hysteresis of beryllium. F. M. JAEGER and E. ROSENBOHM (Rec. trav. chim., 1934, 34, 451—463).—Cryst. Be when heated above 500° or 600° undergoes internal change and shows a strong retardation in the heat development (I) on cooling. The Be returns to its original condition after some months at room temp. X-Ray examination after heating shows changes in the structure which are discussed. With powdered Be (I) is normal owing probably to thin films of BeO surrounding the particles preventing internal change.

H. S. P.

Measurements of the latent heat of thallium connected with the transition, in a constant external magnetic field, from the superconduc-

tive to the non-superconductive state. W. H. KEESOM and J. A. KOK (Physica, 1934, 1, 503—512).—The latent heats at 2.11°, 1.91° abs. were 0.000276, 0.000346 g.-cal. per mol., respectively. On passing the magnetic threshold val. no irreversible entropy change occurs.

H. J. E.

Abnormal thermal effects produced by certain minerals and chemical substances. I. Measurements with the adiabatic calorimeter. W. SWIENTOSŁAWSKI and (Miss) E. BARTOSZEWICZ (Bull. Acad. Polonaise, A, 1934, 69—72).—No continuous heat evolution was observed from As₂O₃ or Bi, the method being sensitive to $1-5 \times 10^{-5}$ g.-cal. per g. hr. (cf. A., 1933, 212, 335).

H. J. E.

Physico-chemical constants of cyclic hydrocarbons. F. M. VIVALDI (Anal. Fis. Quim., 1933, 31, 645—648).—The densities, sp. deviations, parachors, and Raman spectra of 1-ethylcyclopentene and -hexene, ethylcyclopentane and -hexane are recorded. The results are in general accordance with the theoretical vals. and with those in the lit. for related compounds. The Raman lines at 1440 and 1200 cm.⁻¹ are present in each case, whilst that at 800 cm.⁻¹ is displaced in conformity with the law that the product of the no. of C atoms in the ring and the square of the frequency is const.; the line at 993 cm.⁻¹ is exhibited by the unsaturated compounds.

H. F. G.

Principle of Le Chatelier and Braun. M. PLANCK (Ann. Physik, 1934, [v], 19, 759—768).—Theoretical. The limitations of the principle are discussed, and an expression is derived to cover all cases.

A. J. M.

Determination of the fundamental pressure coefficient of helium. W. H. KEESOM, (Miss) H. VAN DER HORST, and K. W. TACONIS (Physica, 1934, 1, 324—332).—The fundamental coeff. of the normal (ice-point pressure 1000 mm.) He thermometer, $\alpha_{He} = 0.0036607_2$. The fundamental temp. coeff. of the Avogadro state, $\alpha_A = 0.0036610_7$. The temp. of the ice point on the Kelvin scale, $T_{0.c.} = 273.14_4$.

H. J. E.

Line co-ordinate charts for v.p.-temperature data. F. E. E. GERMANN and O. S. KNIGHT (Ind. Eng. Chem., 1934, 26, 467—470).—183 org. compounds give straight lines when $1/T$ is plotted against $\log p$. Nomographs are given connecting the v.p. and temp. for all these substances over the range 500—900 mm.; the v.p. are accurate to 2 mm. and the temp. to 0.25°.

A. G.

Thermodynamic relation. D. TEODORESCU (Bul. Soc. Romane Fiz., 1934, 36, 19—21).—From the linear variation, in an org. series, of temp. and max. v.p. (cf. Lucatu, this vol., 246), a relation between the latter and the Clapeyron equation is deduced, and verified by calculating the heat of vaporisation of heptane from that of hexane.

N. M. B.

Vapour pressure and mol. wt. of chromium carbonyl. M. M. WINDSOR and A. A. BLANCHARD (J. Amer. Chem. Soc., 1934, 56, 823—825).—The v.p. has been determined between room temp. and 125°. The mol. wt. by the v.d. method corresponds with the formula Cr(CO)₆.

E. S. H.

V.p. of silicobromoform. W. C. SCHUMB and F. A. BICKFORD (J. Amer. Chem. Soc., 1934, 56, 852—854).— SiHBr_3 has m.p. -73.5° , b.p. 111.8° , $\log P = -1819.5/T \times 7.6079$. E. S. H.

V.p. of solid and liquid heavy hydrogen. G. N. LEWIS and W. T. HANSON, jun. (J. Amer. Chem. Soc., 1934, 56, 1001—1002).—The triple point of H_2 is at 18.66° abs. E. S. H.

V.p. of liquid and solid dicyanous acid. G. N. LEWIS and P. W. SCHUTZ (J. Amer. Chem. Soc., 1934, 56, 1002).—There is scarcely any difference between the v.p. of H^+CN and H^2CN ; the equations lead to 259° and 261° abs., respectively, for the f.p. E. S. H.

Properties of heavy water. H. S. TAYLOR and P. W. SELWOOD (J. Amer. Chem. Soc., 1934, 56, 998—999).—The ratio of d of heavy to light H_2O at 25° is 1.1079 and the difference in n_D^{20} is -0.00462 . The f.p. of H_2O is 3.82° and the viscosity at 20° 12.6 millipoises. H_2O readily takes up H_2O from the air and from the glass walls of the apparatus. E. S. H.

Mass of the normal litre, compressibility, and deviation from Avogadro's law of propylene gas. T. BATUECAS (J. Chim. phys., 1934, 31, 165—183).—The wt. of the normal litre of C_3H_6 prepared by three different methods is 1.9149 ± 0.0001 , and from vals. at reduced pressure the deviation from Avogadro's law is given by $1 + \lambda = 1.0204$. The at. wt. of C is 12.005 from the limiting density of C_3H_6 , taking the g.-mol. vol. as 22.414 and 6H as 6.047. Parallelisms between the compressibilities of members of the hydrocarbon series are discussed. J. G. A. G.

System magnesium-antimony. G. GRUBE and R. BORNHAK (Z. Elektrochem. 1934, 40, 140—142).—The system has been studied in detail by thermal analysis. Horizontal eutectic lines occur at 629° (6% Mg) and 579° (86% Sb), without appreciable mixed crystal formation. The only compound is Mg_3Sb_2 (m.p. 1228°), for which the transformation occurs at $930^\circ \pm 2^\circ$ (40—44% Sb). The results are compared with those for the system Mg—Bi. H. F. G.

Alloys of magnesium research. I. Constitution of the magnesium-rich alloys of magnesium and nickel. J. L. HAUGHTON and R. J. M. PAYNE (Month. J. Inst. Metals, 1934, 1, 165—173).—Mg and Mg_2Ni form a simple eutectiferous system, the solubility of Ni in Mg being $< 0.1\%$ at 500° ; the eutectic is at 507° and 23.5% Ni. A careful re-determination of the m.p. of pure Mg gave $649 \pm 0.5^\circ$. A. R. P.

Solid solution of aluminium in silver. S. KOKUBO (Sci. Rep. Tôhoku, 1934, 23, 45—51).— d for a 4.5% Al—Ag alloy is $<$ that calc. from X-ray data on the basis of a simple substitution of Al atoms for those of Ag in the Ag lattice. The discrepancy is attributed to pinholes and Al_2O_3 in the alloy, and not to chemical combination between Al and Ag. M. S. B.

Transformations in the copper-palladium TAYLOR (Month. J. Inst. Metals, 1934, 1, 11—30).—Alloys with 0—55 at.-% Pd have been

examined by thermal, micrographic, and electrical resistance methods. Transformations in the solid state occur within the ranges (A) 10—30 and (B) 35—50 at.-% Pd. In A the change from random to regular orientation is preceded by a lattice distortion; the first stage occurs at a max. of 570° for the 22 at.-% Pd alloy and the second stage at a max. of 500° for the 15 at.-% Pd alloy. The min. sp. resistance (R) for the ordered state occurs at 15 at.-% Pd and the max. change in R due to transformation at 25 at.-% Pd. In B the change from a randomly oriented face-centred cubic lattice to an ordered body-centred cubic lattice is complete at 40 at.-% Pd, but only partial in alloys near this composition, although it may be rendered more complete in these alloys by heat and mechanical treatment; in no case does the change occur at const. temp., but the temp. is highest and the range smallest at 40 at.-% Pd. Min. val. of R in the ordered state occurs at 47 at.-% Pd, and the R curve of the face-centred cubic alloys shows two breaks, at 32.5 and 42 at.-% Pd, respectively. A. R. P.

Physical properties of platinum-rhodium alloys. J. S. ACKEN (Bur. Stand. J. Res., 1934, 12, 249—258).—The m.p., hardness, d , electrical resistivity, temp. coeff. of resistance, and thermo-electric force against Pt has been measured for Pt—Rh alloys containing 10—80% Rh. The microstructure of each alloy appears to be that of a solid solution. The suitability of alloys containing 20—40% Rh for use in windings of high-temp. resistance furnaces is discussed. J. W. S.

X-Ray investigation of hydrogen-charged palladium-gold alloys. H. MUNDT (Ann. Physik, 1934, [v], 19, 721—732).—These alloys are exactly similar to the Pd—Ag alloys (A., 1933, 341). A saturated solution of small H concn. is first formed, giving an expansion of the lattice. Subsequently a second solution is produced with a lattice corresponding with a higher H content. With increasing Au content the lattices of the two conjugate solutions approach each other in size, and the concn. region for co-existence diminishes, until at 45% Au the alloy becomes homogeneous. Up to 40% Au in alloys containing no H, there is a small deviation from the additive law, a contraction of the lattice being observed. A. J. M.

Heat content and specific volume of iron-carbon alloys. G. TAMMANN and G. BANDEL (Arch. Eisenhüttenw., 1933—1934, 7, 571—578).—Recent data for the heat content, sp. heat, d , and sp. vol. of Fe—C alloys at temp. up to 1600° are summarised in tables and graphs. A. R. P.

Crystal structure of the Heusler alloys. A. J. BRADLEY and J. W. RODGERS (Proc. Roy. Soc., 1934, A, 144, 340—359).—An alloy has been prepared of the composition $(\text{CuMn})_2\text{Al}_4$, in which the atoms occupy the same positions as in Cu_2Al_4 . The annealed and slowly cooled alloy is non-magnetic, but on quenching from 800° it becomes strongly ferromagnetic. The structure is now body-centred cubic, with a face-centred superlattice. A comparison of X-ray photographs of the same specimen of the ferromagnetic alloy made with radiations from Fe, Cu, and Zn anticathodes shows that the relative intensities of the weaker reflexions vary with the wave-length of the radiation.

In this way it is possible to distinguish the Mn from the Cu atoms. The ideal structure of the ferromagnetic alloy is given.

L. L. B.

Constitution of copper-iron-silicon alloys. D. HANSON and E. G. WEST (Month. J. Inst. Metals, 1934, 1, 95—116).—The system has been examined up to 8% Si and 8% Fe. Addition of Si to Fe-Cu alloys reduces the solid solubility of Fe and, with about 5% Si, causes the separation of FeSi which tends to segregate to the top of the ingot. FeSi appears to form pseudo-binary systems with the α , β , γ , δ , and ϵ phases of the Si-Cu system. In the ternary system the range of existence of the α +FeSi field decreases rapidly with fall in temp., indicating the possibility of producing pptn.-hardening effects in alloys with > 4.5% Si.

A. R. P.

Vapour pressure of potassium amalgams. H. H. VON HALBAN, jun. (Nature, 1934, 133, 463).—Dil. K amalgams show a lowering of the v.p. of the Hg > that which corresponds with Raoult's law (I), but when the surface is continually renewed by suitable movement the v.p. rises very nearly to the val. required by (I), and then returns to the lower val. soon after the motion ceases. Impurities in Hg produce the same effect. These results explain previous observations on the dependence of the sensibility and threshold of the photo-effect of K amalgams on concn.

L. S. T.

Electrical conductivity and phase diagram of binary alloys. X. System magnesium-bismuth. G. GRUBE, L. MOHR, and R. BORNHAK. XI. System lithium-magnesium. G. GRUBE, H. VON ZEPPELIN, and H. BUMM (Z. Elektrochem., 1934, 40, 143—150, 160—164).—X. The system has been studied by means of conductivity measurements and thermal analysis. Between 0 and 14.3 at.-% Bi the primary solid phase consists of γ mixed crystals; the eutectic for α and γ mixed crystals occurs at 14.3% Bi and 551°. Between 14.3 and 31.5% Bi α mixed crystals separate, and this phase undergoes a transition at 680°, β mixed crystals separating between 31.5 and 40% Bi. For the pure compound the transition temp. is 700°. The m.p. of Mg_3Bi_2 is 823° (not 715° as previously reported). β - Mg_3Bi_2 separates between 40 and 43.5% Bi, and the α form between 43.5 and 95.7% Bi. The α - Mg_3Bi_2 -Bi eutectic lies at 260° and 95.7% Bi. The results of conductivity measurements with alloys containing 30 and 35% Bi are not reproducible, but the reason is obscure; no other transition could be detected. Photomicrographs are reproduced.

XI. Between 0 and 16.3% Li mixed crystals separate, and between 16.3 and 21.8% Li mixed crystals and the eutectic (587.5°, 21.8% Li) with Li_2Mg_5 . The phase diagram passes through a very flat max. at about 592° and then falls smoothly to the m.p. of Li. Alloys containing > 15% Li exhibit only the hexagonal Mg lattice, and those containing 35—40% Li a cubic body-centred lattice; the 15—35% Li alloys exhibit both types. The lattice const. of the cubic type is const. between 20 and 31% Li, and falls abruptly between 31 and 40% Li.

H. F. G.

Interpretation of paramagnetic properties of alloys. L. NEEL (Compt. rend., 1934, 198, 1311—1313).—Theoretical. A formula is given for the

susceptibility of an alloy, in which case the straight line of the Curie-Weiss law is replaced by a curve. Where fluctuations of mol. field can be neglected the formula agrees with experiment. The results extend and confirm the views of Slater and of Stoner.

W. R. A.

Density of propionic acid solutions in water. B. N. CHUCKERBUTTI (Current Sci., 1934, 2, 340).— d_4^{25} has a max. at 51.2% acid by vol.

C. W. G.

Effect of temperature on the viscosity of binary mixtures with abnormal viscosities. L. E. SWEARINGEN and L. B. HECK (J. Physical Chem., 1934, 38, 395—400).—The viscosity-composition curves for the systems $AcOH-H_2O$ and $C_5H_5N-AcOH$ have a max. at a fixed composition even at 80°. For $PhNO_2-Bu^oOH$ the curve has a min. the composition of which depends on the temp.

M. S. B.

Dielectric polarisation of hexane-nitrobenzene mixtures. I. Behaviour of the polarisation near the separation temperature. II. Dipole moment and association of nitrobenzene. A. PIEKARA (Bull. Acad. Polonaise, 1933, A, 319—332, 333—345).—I. The dielectric consts. and d of mixtures have been measured at 0—30°, and the corresponding mol. polarisations calc. For mixtures which separate into two layers at lower temp. the dielectric const. shows an inflexion point at the crit. solution temp. and abnormal vals. just above it, where the solution is opalescent. The interpretation of these results is discussed.

II. From the mol. polarisation of solutions of $PhNO_2$ in C_6H_{14} and the mol. polarisation of $PhNO_2$ in the solid state, its dipole moment is calc. as 3.96×10^{-18} e.s.u. The inaccuracy of vals. derived from the temp. coeff. of the mol. polarisation is discussed. The degree of association of $PhNO_2$ in C_6H_{14} solutions has been deduced.

J. W. S.

Structure of alcohol solutions of lithium chloride. G. W. STEWART (J. Chem. Physics, 1934, 2, 147—152).—X-Ray diffraction measurements for conc. solutions of LiCl in EtOH, Pr^oOH , and Bu^oOH suggest that Li^+ and Cl^- react with the mols. of the solvent to form a liquid of cybotactic or quasi-cryst. structure.

N. M. B.

Vapour pressures of mixtures of light and heavy hydrogen. G. N. LEWIS and W. T. HANSON, jun. (J. Amer. Chem. Soc., 1934, 56, 1000—1001).—Preliminary determinations are in accordance with Raoult's law.

E. S. H.

Vapour pressures of nitric and sulphuric acids. J. H. PERRY and D. S. DAVIS (Chem. and Met. Eng., 1934, 41, 188—189).—The total and partial pressures for aq. HNO_3 (20—100%) and the H_2O pressure for aq. H_2SO_4 (10—95%) at different temp. are given in the form of alignment charts.

D. K. M.

Partial pressures of formic and acetic acids above some aqueous solutions, and their partial molal free energies at 1.0 molal concentration. W. A. KAYE and G. S. PARKS (J. Chem. Physics, 1934, 2, 141—142).—From measurements at 25° the partial molal free energies are calc.

N. M. B.

Liquid-vapour equilibria of mixtures of aromatic and non-aromatic hydrocarbons. M. MIZUTA

(J. Soc. Chem. Ind. Japan, 1934, 37, 60—61b).—The addition of petrol to a mixture of C_6H_6 and PhMe decreases the efficiency of separation by distillation; an azeotropic mixture contains 0.7 mol. fraction of C_6H_6 in the liquid phase. The distillation of mixtures of PhMe with petrol fractions of about the same b.p. has been studied. A. G.

Equilibrium in systems composed of sulphur dioxide and certain organic compounds. H. W. FOOTE and J. FLEISCHER (J. Amer. Chem. Soc., 1934, 56, 870—873).—V.-p. measurements are recorded for the binary systems formed by SO_2 with NH_3 , Ph, $NHPh$, $NHPhEt$, $NPhEt_2$, $NHPh$, $C_6H_5Me \cdot NH_2$, $C_{10}H_8$, Ph_2 , Ph_2O , α - and β - $C_{10}H_7 \cdot OH$, and $[CH_2 \cdot OH]_2$ between -20° and 30° . The existence of the following solid compounds is established: $NH_3 \cdot Ph \cdot SO_2$, $NHPhMe \cdot SO_2$, m.p. 31° ; $NHPhEt \cdot SO_2$, m.p. 29° ; p - $C_6H_4Me \cdot NH_2 \cdot SO_2$. E. S. H.

Ternary heteroazeotropic system ethyl alcohol-carbon disulphide-water. W. SWIENTOSLAWSKI and E. WARDZIŃSKI (Bull. Acad. Polonaise, 1933, A, 462—471; cf. A., 1932, 1226).—The heteroazeotropic mixture has b.p. 41.345° and contains CS_2 94.36, $EtOH$ 6.55, and H_2O 1.09%. F. L. U.

Classification of zeotropic and azeotropic mixtures. W. SWIENTOSLAWSKI (Bull. Acad. Polonaise, 1933, A, 472—476; cf. preceding abstract). F. L. U.

Distillation of dilute aqueous solutions of hydrochloric and nitric acids. P. JAULMES (J. Chim. phys., 1934, 31, 227—235).—A steam-distillation method shows that the concn. of acid, C , in the vapour is approx. $\propto C^2$ in solution, but the volatility increases more rapidly than C at concn. $> 1N$. The results are discussed with reference to the effect of ions on the volatility of the non-ionised acid. J. G. A. G.

Method of constructing the W , S , γ surface of binary systems. G. VAN LERBERGHE (Physica, 1934, 1, 475—480).—Theoretical. H. J. E.

Physical properties of ternary systems. Specific gravities, refractive indices, and changes in volume on dissolution of the system methyl alcohol, isobutyl alcohol, water at $60^\circ F$. D. M. SMITH (Ind. Eng. Chem., 1934, 26, 392—395).—Data are presented for the whole range of ternary mixtures, and the most accurate method of interpolating between the experimental points is described. A. G.

Velocity of gas exsorption of liquids. II. A. GUYER and B. TOBLER (Helv. Chim. Acta, 1934, 17, 550—555; cf. this vol., 483).—"Evasion coeffs.," expressing the amount of dissolved gas leaving 1 sq. cm. of the surface of a solution under standard conditions, have been determined for C_2H_2 , CO_2 , H_2S , SO_2 , and NH_3 . E. S. H.

Principles of gas exsorption. A. GUYER and B. TOBLER (Chem. Fabr., 1933, 7, 145—148).—Exsorption of gases is defined to include desorption and the degassing of a solution when the osmotic pressure of the gas in solution is $>$ its partial pressure in the gaseous phase. The rate of removal of gases which do not react with the aq. solvent (H_2 , CH_4 ,

C_2H_2) increases slightly with increasing rate of diffusion, whilst the rate of removal of gases such as SO_2 and NH_3 depends mainly on the degree of interaction with the solvent. H_2S occupies an intermediate position. E. S. H.

Mechanism of activated diffusion through silica glass. R. M. BARRER (J.C.S., 1934, 378—386).—The logarithms of the diffusion rates of He , H_2 , O_2 , N_2 , A , and air through SiO_2 glass are linearly related to $1/T$ in the range 17 — 1000° . The energies of activation, E , for diffusion vary from 5700 g.-cal. per mol. for He to approx. 48,000 for A . Owing to the formation of a new cryst. surface phase (I) with increasing time of heating, the permeability decreases and E increases for all gases except He and H_2 . The diffusing gases migrate in two ways: He , H_2 , and Ne pass through the "lattice" of the SiO_2 glass at high temp., whilst O_2 , N_2 , and A migrate mainly through slip-planes the width of which is diminished in process (I). At low temp. He , H_2 , and Ne exhibit slip-plane diffusion, and there is evidence that migration proceeds from the adsorbed layer of gas and not directly from the gas phase (cf. A., 1933, 565). The gases migrate as undissociated mols., and E arises from dynamic polarisation due to van der Waals cohesion and to exchange forces leading to gas-solid repulsions. Vals. of E calc. from the laws of interaction of H_2 , He , and A are consistent with those observed, when probable vals. of pore diameter are chosen, and indicate "lattice" migration for He and H_2 . J. G. A. G.

Solubility of sodium arsenate in 93.5% ethyl alcohol. A. WÖHLK (Dansk Tidsskr. Farm., 1934, 8, 107).—The solubility at room temp. of Na_2HAsO_4 is 0.02465%. R. P. B.

Anomalous valency effect of strong electrolytes in aqueous solutions. J. B. CHLOUPEK, V. Z. DANEŠ, and B. A. DANEŠOVÁ (Coll. Czech. Chem. Comm., 1934, 6, 116—125; cf. A., 1933, 26, 351).—The solubility of $Ca(IO_3)_2$ in presence of other salts indicates that the anomalous valency effect is shown only by ions of valency > 2 . D. R. D.

Calculation of the solubility of certain salts in water at high pressures from data obtained at low pressures. R. E. GIBSON (J. Amer. Chem. Soc., 1934, 56, 865—870).—The d and compressions of solutions of KI have been determined. Assuming that H_2O in an aq. solution behaves like H_2O under hydrostatic pressure, and that the sp. compression of a salt in solution is equal to that in the solid state, an equation expressing the properties of H_2O as a function of pressure may be adapted to the computation of the effect of pressures up to 10 kilobars on the solubility of salts, from measurements made at 1 kilobar. E. S. H.

Solubility of carbamide in water. Heat of fusion of carbamide. F. W. MILLER, jun., and H. R. DITTMAR (J. Amer. Chem. Soc., 1934, 56, 848—849).—The solubility of $CO(NH_2)_2$ in H_2O has been determined between 70° and 132.7° . The solutions are ideal when the mol. fraction of $CO(NH_2)_2$ is $>$ approx. 0.6. The calc. heat of fusion of $CO(NH_2)_2$ is 3470 g.-cal. per mol. E. S. H.

Calcium sulphate in sea-water. I. Solubilities of dihydrate and anhydrite in sea-waters of various concentrations at 0–200°. R. HARA, Y. TANAKA, and K. NAKAMURA (Tech. Rep. Tôhoku, 1934, 11, 87–109).—The solubilities have been determined interferometrically. The solubility at 60° of CaSO_4 prepared from the dihydrate at 600–650° is > the normal val. by up to 30%, and does not attain the normal val. within 13 days. Quant. data relating to the brine concn., amount of CaSO_4 which may be removed, and temp. of secondary evaporation are given for the process in which CaSO_4 is removed from brine by heating at about 200°. The transition temp. di- mono-hydrate varies between 52° and 95°, according to $[\text{Cl}]$; in aq. solution the transition temp. is 98° (lit. 107°). All the solubility curves pass through a max. at $[\text{Cl}]$ about 3.0–4.5%.

H. F. G.

Solubility in the quaternary system NH_4NO_3 – NaCl , and the effect of added ammonia. L. HACKSPILL, A. P. ROLLET, and LAUFFENBURGER (Compt. rend., 1934, 198, 1231–1233).—The system (cf. Le Chatelier, A., 1921, ii, 248; Rengade, *ibid.*, 93) is represented at 20° by a projected pyramidal space model. Addition of NH_3 increases the solubilities of NH_4Cl and NH_4NO_3 . Conditions for the separation of pure NaNO_3 and NH_4Cl are indicated.

B. W. B.

Action of alkaline copper solution on silk fibroin. VII, VIII. Dissolution phenomena in the system fibroin–copper–amine–alkali. Y. TAKAMATSU (J. Soc. Chem. Ind. Japan, 1934, 37, 107–110B).—The addition of NH_3 or $[\text{CH}_2\cdot\text{NH}_2]_2$ to the system fibroin– Cu – KOH probably does not increase the solubility of fibroin, but greatly increases its rate of dissolution. A fibroin– Cu –amine compound is first formed and subsequently converted into a fibroin– Cu – KOH compound.

A. G.

Solubility of phenols in proteins. E. A. COOPER and (Miss) TREADGOLD (J. Physical Chem., 1934, 38, 259–267).—The increase in the partition coeff. of $\text{C}_6\text{H}_5(\text{NO}_2)_3\cdot\text{OH}$ between protein and H_2O , when the protein sol or gel is coagulated by the phenol itself, is very much < previously observed for unsubstituted phenols and cresols and their halogen derivatives. Practically no change takes place in the partition coeff. of $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ on coagulation of the protein, so that the phenomenon is not common to all OH compounds. Proteins pptd. from colloidal solution by addition of a colloid of opposite electric charge, e.g., gelatin by dialysed Fe, or by formation of an insol. salt, e.g., edestin chloride, do not exhibit this increased solvent power for PhOH . Experiments with red cells and ovalbumin indicate that the increased partition coeff. is real, and not due to calculation errors as a result of the movement of H_2O from one phase to another. The imbibed H_2O may, however, diminish the solubility of PhOH in proteins, thus accounting, in the case of sols and gels, for the low partition coeff. which rises to the normal figure when H_2O is expelled on coagulation.

M. S. B.

Precipitation. I. Precipitation of silver chloride, bromide, and iodide. B. TEŽAK (Bull. Soc. Chim. Yougoslav., 1933, 4, 137–143).—The turbidity-concn. curve of the system AgNO_3 – KX ($\text{X}=\text{Cl}, \text{Br}, \text{I}$)

has two well-defined max., corresponding with certain optimum relative concns. of the substrates. It is inferred that the first stage of the process consists in the formation of particles of colloidal dimensions, which then undergo aggregation to yield micro- and macro-crystals of AgX .

R. T.

Adsorption of the vapours of certain dichloro-hydrocarbons by activated charcoal. IV. J. N. PEARCE and J. F. EVERSOLE (J. Physical Chem., 1934, 38, 383–393).—The adsorption of the vapours of $[\text{CH}_2\text{Cl}]_2$ (I), CHMeCl_2 (II), $\text{CHMeCl}\cdot\text{CH}_2\text{Cl}$ (III), and $\text{CH}_2(\text{CH}_2\text{Cl})_2$ (IV) on charcoal has been determined between 0° and 136°. Within the pressure range employed the adsorption is expressed by the simple Langmuir equation for adsorption on a plane surface. Both the natural and Langmuir isotherms have been plotted for these vapours and for the Cl-derivatives previously studied at temp. corresponding with the b.p. of the pure liquids. The Langmuir equation applies, but not the Freundlich equation. At very low pressures the amount of vapour adsorbed is greatest for the compound of greatest mol. wt., largest mol. vol., and highest b.p. Similar relations hold with increase in the no. of Cl atoms in the mol. At higher pressures the reverse is the case. The influence of the no. and position of the Cl atoms is discussed. The heats of adsorption in g.-cal. calc. from the slopes of the isosteres are (I) 11,500, (II) 10,965, (III) 13,160, and (IV) 13,700.

M. S. B.

Adsorption of ethylene, ethane, and hydrogen in relation to hydrogenation of ethylene. R. KLAR (Z. physikal. Chem., 1934, 168, 215–226).—The adsorption at about 0–200° of H_2 , C_2H_6 , C_2H_4 , and mixtures of C_2H_4 and C_2H_6 on a Ni catalyst prepared from NiC_2O_4 and therefore containing NiO and CO has been examined. In the adsorption of C_2H_4 there is both van der Waals adsorption, which is practically instantaneous, and activated adsorption, which is slower. The rate of hydrogenation of C_2H_4 on the catalyst was a max. at about 130°, the fall at higher temp. being ascribed to rapid diminution in the concn. of adsorbed C_2H_4 . The catalyst was poisoned by H_2 , probably owing to the latter being stabilised on the surface as a CO complex. With this catalyst the active-adsorbed C_2H_4 plays the chief part in the hydrogenation, and the acceleration of the activated adsorption with rise in temp. is responsible for the initial rise in reaction velocity with temp.

R. C.

Adsorption of hydrogen by copper poisoned with cyanogen. C. W. GRIFFIN (J. Amer. Chem. Soc., 1934, 56, 845–847).—Measurements at 0° show that C_2N_2 decreases the adsorption of H_2 , especially at low pressures. The effect of C_2N_2 is compared with that of CO.

E. S. H.

Adsorption of water vapour by magnesium oxide. F. ISHIKAWA and K. SANO (Sci. Rep. Tôhoku, 1934, 23, 129–138).— MgO first adsorbs H_2O vapour and the adsorption equilibrium is established before chemical combination to $\text{Mg}(\text{OH})_2$ takes place. The velocity of adsorption of H_2O vapour from air at $21.5\pm0.5^\circ$ has been determined. The adsorption isotherm at 51° may be expressed by Freundlich's formula. The relation between temp., pressure, and

amount adsorbed (*a* c.c.), for the temp. range 9–42°, is given by $\log n/aT = 2.9483 - 2179.77/T$.

M. S. B.

Sorption of vapours by alumina. II. Benzene. L. A. MUNRO and F. M. G. JOHNSON (Canad. J. Res., 1934, 10, 321–332; cf. A., 1926, 347).—The amount of C_6H_6 sorbed per g. of Al_2O_3 gel varies with the extent of dehydration of the gel. Expressed as g. sorbed per g. of "active" Al_2O_3 , a const. val. is obtained for gels of different H_2O content. The plot of $\log x/m$ against $\log p$ is a straight line and Patrick's equation (cf. A., 1920, ii, 417) holds at lower relative pressures. Comparison with the data for H_2O does not bring out any notable differences such as might be expected if chemical forces were operative. R. S.

Adsorption of wool-violet (4BN) by lead sulphate and the influence of the adsorbed dye on the speed of kinetic exchange. I. M. KOLTHOFF, W. VON FISCHER, and C. ROSENBLUM (J. Amer. Chem. Soc., 1934, 56, 832–836).—At saturation 1 ion of the dye is adsorbed by 1.5 ions of Pb^{++} when the supernatant liquid is neutral, thus permitting the sp. surface of $PbSO_4$ to be measured. In acid solution the amount of dye adsorbed increases. Adsorption is of the exchange type, and the replaced SO_4^{--} causes pptn. of some $PbSO_4$ from the supernatant liquid. When coarsely-cryst. $PbSO_4$ is shaken in 0.01*N*- HNO_3 , recrystallisation occurs; this process is prevented by adsorbed wool-violet. E. S. H.

Aminolysis and adsorption. K. WUNDERLY (Helv. Chim. Acta, 1934, 17, 523–531).—Animal C adsorbs more HCl or NaOH than sugar C and is the more powerful aminolytic agent. Adsorption isotherms of aspartic acid and alanine on animal C and sugar C and of phenylalanine, serine, leucine, and hydantoic acid on animal C have been determined. E. S. H.

Adsorption of calcium and copper from ammoniacal medium by silica gel. I. M. KOLTHOFF and V. A. STENGER (J. Physical Chem., 1934, 38, 475–486).— $Ca(OH)_2$ is much more strongly adsorbed by SiO_2 gel than NaOH or KOH, owing to the slight solubility of Ca silicate. The presence of NH_3 up to 0.3*N* increases the adsorption of $Ca(OH)_2$ because the former, by its solvent effect on the gel, widens the pores, and the NH_4 silicate formed reacts chemically with $Ca(OH)_2$ in the interior of the gel. Addition of NH_4 salts decreases the p_H and increases the solubility of Ca silicate, thus decreasing the adsorption of $Ca(OH)_2$. Cu^{++} from dil. aq. NH_3 is adsorbed as a complex ammino ion. A silicate is formed at the surface, $Cu(NH_3)_2(H_2O)_2SiO_3$, and this, on keeping, loses NH_3 and becomes $Cu(NH_3)(H_2O)_3SiO_3$. On electrodialysis this loses its last NH_3 , the gel changing colour from blue to green. NH_4Cl decreases the adsorption of the ammino ion. M. S. B.

Adsorption of alkali hydroxides by silica gel in the presence of ammonia and ammonium salts. I. M. KOLTHOFF and V. A. STENGER (J. Physical Chem., 1934, 38, 249–258).—In the adsorption of KOH and NaOH by SiO_2 gel a primary adsorption of OH^- takes place. The surface of the gel is thus ionised and a secondary adsorption of the alkali ions occurs. The adsorption of strong alkali hydroxides

cannot be determined exactly, owing to the solvent action on the gel. Since the adsorption is ionic, NH_4^+ is much less readily adsorbed than NaOH or KOH of the same concn. K salts increase the adsorption of KOH, but NH_4 salts do not affect that of NH_3 . The amount of total base adsorbed from a mixture containing NH_4^+ and K^+ is primarily a function of the OH^- concn., but the ratio in which NH_3 and KOH are adsorbed is mainly determined by the ratio of NH_4^+ to K^+ in the solution, and the secondary adsorption of NH_4^+ is actually stronger than that of K^+ .

M. S. B.

Absorption of dyes by cellulose. III. Comparison of the absorption of benzopurpurin 4B with that of sky-blue FF. J. HANSON and S. M. NEALE. **IV. Absorption of related dyes of the disazobenzidine class with reference to their molecular structure.** L. H. GRIFFITHS and S. M. NEALE (Trans. Faraday Soc., 1934, 30, 386–394, 395–403; cf. A., 1933, 1241).—III. The equilibrium wt. (*w*) of benzopurpurin 4B (I) absorbed by sheet viscose (II) rises rapidly with added NaCl, and a given increase in [NaCl] produces a rise of *w* > that effected by a proportional increase in the final concn. of dye in the bath. The rate of absorption of (I) by (II) accords with the diffusion theory, and with increasing [NaCl] the apparent diffusion coeff. rises rapidly to a max. The absorption equilibrium of sky-blue FF is attained approx. twice as rapidly as that of (I), but (I) is thrice as strongly absorbed, and in the absence of NaCl both dyes are feebly absorbed, but (I) has the stronger affinity.

IV. The absorption of the dyes by viscose is 2–3.5-fold that by bleached cotton, but the ratio is affected by the substituents. Substitution in the *o*-position of the benzidine nucleus does not greatly affect the substantivity, *S*, of the product, but a ten-fold decrease occurs with *m*-substitution. The no. and position of SO_3H groups attached to the $C_{10}H_8$ nucleus affect *S*, and in the cases examined the vals. of *S* for the dyes with four SO_3H are < for those containing only two such groups, whilst substitution of NH_2 for OH increases *S*. J. G. A. G.

Electrolytic adsorption of iron by viscose rayon and other fibres. K. TANEMURA, H. KOHNO, and K. NISHIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 89–90B).—Viscose rayon, silk, cotton, and wool behave similarly. Adsorption is a max. at p_H 2.5–3.0 for $FeCl_3$ and at p_H 4.0–5.5 for $FeSO_4$, the adsorbed ions being $[mFe_2O_3.nCl.zH_2O]FeO^+$ and $[HFeO_2.Cl.H_2O]FeO^+$, respectively. The ions Fe^{+++} and $[HFeO_2.Cl.H_2O]FeO_2^-$ and negatively-charged $Fe(OH)_3$ sol are not adsorbed. A. G.

Imbibition of liquids by porous bodies. (MILLER.) P. BERTHIER (Compt. rend., 1934, 198, 1607–1609).—The theory of Guye and Saini (Helv. phys. Acta, 1929, 2, 445), relative to the heights of ascent of liquids in porous bodies is extended to the case of descent and checked by experiments with filter-paper. B. W. B.

Adhesion tension of liquids against strongly hydrophilic solids. A series of liquids against barytes. F. E. BARTELL and H. Y. JENNINGS (J. Physical Chem., 1934, 38, 495–501).—A receding con-

tact angle method for determining adhesion tension is described, and also an improved method for preparing membranes from finely-divided powders by tamping. The adhesion tension of C_2H_5Br , $1-C_{10}H_7Br$, C_6H_6 , C_7H_{16} , and $BuOAc$ against barytes is given. Comparison of the vals. for these liquids against several hydrophilic solids shows that corresponding vals. are of nearly the same magnitude. Hence it is concluded that surfaces of strongly hydrophilic solids are covered with an adsorbed film of H_2O and, as a result, their measured free surface energy vals. are of the same order of magnitude. M. S. B.

Alteration of the surface properties of stibnite as revealed by adhesion tension studies. F. E. BARRELL and C. W. WALTON, jun. (J. Physical Chem., 1934, 38, 503—511).—Determinations of the adhesion tension of liquids against stibnite (cf. preceding abstract) show that whilst stibnite itself is hydrophobic, oxidation by heating causes it to become progressively more hydrophilic, although the appearance of the surface, the particle size of powder, and the pore radii remain unaltered. A condition may be reached in which there are no preferential wetting properties. Treatment with H_2S restores the original hydrophobic surface. Two qual. tests for studying the condition of the powders are described, viz., the "drop on powder test" and the "degree of packing on settling test." M. S. B.

Adsorption at the surface of solutions. III. Surface structure of solutions of lower aliphatic alcohols. J. A. V. BUTLER, A. WIGHTMAN, and W. H. MACLENNAN. **IV. Adsorption constants in solutions containing two solutes.** F. R. HIMSWORTH and J. A. V. BUTLER (J.C.S., 1934, 528—532, 532—535).—III. The surface tensions of aq. solutions of $MeOH$ and Pr^oOH have been determined at 25° . The Gibbs adsorption decreases at higher concn. of alcohol, and although the data for aq. $MeOH$ are consistent with a single adsorbed layer at the surface, those for aq. Pr^oOH suggest a more elaborate surface structure, e.g., a complete layer of Pr^oOH mols. which are associated with H_2O mols. in nearly the same proportion and in the same way as in the bulk of the solution.

IV. The surface tensions of ternary mixtures of H_2O containing 0—1.5 g.-mol.-% of Bu^oOH (I) with either 0.4 g.-mol.-% of $EtOH$ (II) or $EtCO_2H$ (III) have been determined at 25° . (I) and (II) do not affect each other's adsorption consts. when present together in the surface layer, but the observed vals. for H_2O —(I)—(III) are < those calc. from the consts. of the binary solutions, showing that (III) decreases the adsorption of (I) to an extent > that corresponding with the area it occupies. This is the reverse of what might be expected if ester formation occurred. J. G. A. G.

Phase boundary potentials of monolayers of long-chain fatty acids. N. W. H. ADDINK and E. K. RIDEAL (J. Chem. Physics, 1934, 2, 144).—The behaviour of the stable and metastable liquid expanded and condensed states of myristic acid has been investigated. The changes in the properties of a compressed liquid expanded film suggest a micellar structure for the film, and are interpreted on the view that during the fall of potential with time, H_2O is squeezed out from the space between the chains. N. M. B.

Electrokinetic potentials and mineral flotation. H. B. BULL, B. S. ELLEFSON, and N. W. TAYLOR (J. Physical Chem., 1934, 38, 401—406).—The cataphoretic velocity of a no. of minerals suspended in pure H_2O has been determined by the use of a micro-cell. Carbonates, Pb oxides, and $PbSO_4$ carry a positive charge. The effect of the addition of electrolytes on the electrokinetic potential (I) of galena, quartz, and sphalerite has been examined. The floatability of galena varies directly as the potential on the particles in the case of Ag^+ , Pb^{++} , Cd^{++} , Co^{++} , Ba^{++} , and Mg^{++} , and the order of toxicity of the nitrates, $Ag > Pb > Cd > Co$, is exactly that of the ability of the cation to reduce (I) of galena. This, in combination with earlier work on flotation (B., 1929, 521), shows that peptisation rather than flocculation is necessary for good flotation, when followed by the addition of suitable collecting agents. M. S. B.

Cryoscopic study of aliphatic alcohols. T. J. WEBB and C. H. LINDSLEY (J. Amer. Chem. Soc., 1934, 56, 874—878).—A fairly rapid procedure for determining f.-p. depressions of aq. non-electrolytes with an accuracy of about 0.1% is described. Data are recorded for nine aliphatic alcohols and for $CH_2Ph\cdot OH$ over the concn. range 0.01—0.2 or 0.5M. E. S. H.

Cryoscopic studies in anhydrous acetic acid. W. C. EICHELBERGER (J. Amer. Chem. Soc., 1934, 56, 799—803).—The f.-p. apparatus described gives an accuracy of 0.0001° with $AcOH$ as solvent. NH_4NO_3 (0.005—0.05M) behaves as though present in at least binary ion pairs; 0.1M- H_2SO_4 behaves as though highly associated in the Bjerrum sense. Both electrolytes deviate widely from the predictions of the Debye-Hückel limiting law. E. S. H.

Non-electrolyte solutions. G. SCATCHARD (J. Amer. Chem. Soc., 1934, 56, 995—996).—Polemical (cf. Chem. Rev., 1931, 8, 321; Hildebrand and Wood, this vol., 146). E. S. H.

Non-electrolyte solutions. J. H. HILDEBRAND (J. Amer. Chem. Soc., 1934, 56, 996).—Polemical (cf. preceding abstract). E. S. H.

Physical chemistry of amino-acids, peptides, and related substances. I. Apparent molal volume and the electrostriction of the solvent. E. J. COHN, T. L. McMECKIN, J. T. EDSALL, and M. H. BLANCHARD (J. Amer. Chem. Soc., 1934, 56, 784—794).—Analysis of the apparent mol. vols. of NH_2 -acids and peptides in terms of the internal CH_2 and $CO\cdot NH$ groups, and of the NH_2 and CO_2H groups shows that the dimensions of the internal groups are identical with those of the same groups in the liquid state. On the assumption that the smaller mol. vols. of the terminal groups are due to electrostriction, the apparent mol. vols. of the uncharged NH_2 and CO_2H have been determined from the mol. vols. of fatty acids, amides, amines, and hydantoic acid. The vals. obtained indicate that $CO(NH_2)_2$ and hydantoic acid are not zwitterions and that a large proportion of the mols. of $m\text{-}NH_2\cdot C_6H_4\cdot CO_2H$ are zwitterions. Separation of the charged groups from each other in a zwitterion increases electrostriction. E. S. H.

F.p. of aqueous solutions. V. Potassium, sodium, and lithium chlorates and perchlorates.

G. SCATCHARD, S. S. PRENTISS, and P. T. JONES (J. Amer. Chem. Soc., 1934, 56, 805—807; cf. this vol., 25).—Data are recorded for f.p. and electrical conductivity. Discussion is reserved. E. S. H.

F.p. of aqueous solutions. VI. Potassium, sodium, and lithium formates and acetates. G. SCATCHARD (J. Amer. Chem. Soc., 1934, 56, 807—811).—Data are recorded for concns. from about 0.001*M* to about 1.1*M*. Correlation of the results with those obtained for other salts shows that the polyat. anions can be divided into two classes, which deviate in opposite ways from the noble gas type ions. The deviations of OAc' and HCO_2' are explained by the concns. of the ionic charge near the surface. This effect and the presence of dipoles are unimportant factors in the case of NO_3' , ClO_4' , and ClO' .

E. S. H.

Cryoscopic determination of the total hydration of the ions of lithium chloride. F. BOURION and E. ROUYER (Compt. rend., 1934, 198, 1490—1492; cf. this vol., 361).—The hydration in 0.5*M*- and 1.0*M*-LiCl corresponds with LiCl, 15.0 aq. and LiCl, 17.8 aq., respectively. B. W. B.

Cryoscopic technique. G. SARTORI (Gazzetta, 1934, 64, 21—32).—Hovorka's method has been modified and rendered suitable for the study of more dil. solutions. Measurements with solutions of K molybdo- (I) (0.012—0.067*M*) and tungsto-quinate (II) (0.010—0.108*M*) are described. For (I) the results are closely in accordance with theory, but for (II) they are somewhat scattered. The vals. of *a* and *b* in the equation $t - a - bm^{\frac{1}{2}}$ are 5.547 and 2.318 for (I) and 5.521 and 1.781 for (II), respectively. H. F. G.

Calculation of partial molal solute quantities as functions of the volume concentration, with special reference to the apparent molal volume. F. T. GUCKER, jun. (J. Physical Chem., 1934, 38, 307—317).—A simple method of calculating the apparent molal vol., $\phi(V_2)$ as a function of *c*, is described. The ratio *c/m* is a sp. property of the individual solute depending on $\phi(V_2)$ and varying from 1 to < 0.8. A general equation has been developed for calculating any partial molal solute quantity G_2 from the corresponding apparent property $\phi(G_2)$ as a function of *c*, and also a special equation applicable when ϕ is a linear function of $c^{\frac{1}{2}}$. These equations are applied to the calculation of the partial mol. vol. of NH_4NO_3 , and the val. agrees with that of Adams and Gibson (A., 1933, 120) calc. from curves of apparent sp. vol. plotted against the square root of the wt. fraction, but the vol. concn. method is probably simpler and more in accordance with theory. M. S. B.

Computation of the partial volumes of the components in aqueous solutions. R. E. GIBSON (J. Physical Chem., 1934, 38, 319—326).—Partial vols. of NaCl, Na_2SO_4 , KCl, KI, and LiNO_3 in solution have been calc. from vol. concn. (c_2) data using Gucker's function *f* (cf. preceding abstract). Except for LiNO_3 the vals. are trustworthy to within 1%, and the use of a deviation curve gives still higher accuracy. If the plot of *f* against $\sqrt{c_2}$ is so strongly curved that higher powers of $\sqrt{c_2}$ have to be used, either wt. or vol. concn. may equally well be employed. M. S. B.

Dielectric constants of aqueous solutions of electrolytes at 30 cm. wave-length. H. STRIPS (Z. Physik, 1934, 88, 197—209).— MgSO_4 and CuSO_4 solutions obey the Debye-Falkenhagen theory at high dilution, but at higher concns. the const. appears to increase linearly with the conductivity. A. B. D. C.

Physical characterisation of dissolved ions from f.p. and conductivity of very dilute aqueous solutions of tetra-alkylammonium halides. J. LANGE (Z. physikal. Chem., 1934, 168, 147—187).—Conductivity and f.p. measurements have been made at concns. of about 0.001—0.03*N*. At the highest dilutions the Debye-Hückel equations for the conductivity coeff., $f\mu$, and the osmotic coeff., f_0 , are valid, but at lower dilutions the vals. of $(1-f_0)$ and $(1-f\mu)$ differ from the theoretical vals. by amounts which are proportional to the concn., but vary from one salt to another. These divergences cannot be accounted for either by the effect of the Debye-Hückel parameter *a* or by incomplete dissociation; some as yet unknown physical function is required for the characterisation of dissolved ions. There is some form of physical interaction of ions not covered by any of the present theories which has a dominant effect on the behaviour of certain strong electrolytes in dil. aq. solution. R. C.

Magnetic susceptibilities of the ions of uranium in aqueous solution. R. W. LAWRENCE (J. Amer. Chem. Soc., 1934, 56, 776—783).—Data are recorded for UO_2^{2+} , U^{4+} , UO^{2+} , and U^{3+} at different $[\text{H}^+]$. Derived magnetic moments in Bohr magnetons are 2.97 for U^{4+} , 2.73 for UO_2^{2+} , and 3.22 for U^{3+} . E. S. H.

Chemical and physico-chemical properties of polonium. III. Determination of diffusion coefficient of polonium in solution. Theoretical study and results. General conclusions. M. SERVIGNE (J. Chim. phys., 1934, 31, 211—226).—The diffusion coeffs. at 18° in 0.1*N*-HCl, HNO_3 , $\text{H}_2\text{C}_2\text{O}_4$, and H_2SO_4 are 0.78, 0.80, 1.06, and 0.47, respectively; it is inferred that the complex Po oxalate ion is univalent and that the complex Po chloride and nitrate ions are bivalent. (Cf. this vol., 484.) J. G. A. G.

Accelerated diffusion in dye solutions. S. LENHER and J. E. SMITH (J. Amer. Chem. Soc., 1934, 56, 999—1000).—The rate of diffusion in aq. solution of Na *p*-sulphobenzeneazobenzeneazo-6-benzamido- α -naphthol-3-sulphonate is affected greatly by $[\text{NaCl}]$ in the solution into which diffusion occurs. E. S. H.

Theory of Brownian movement. Distribution function $f(v, x, t)$ and the diffusion equation. J. A. KRUTKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 393—398).—Mathematical. W. R. A.

Linear problem in the theory of the Brownian motion. J. A. KRUTKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 479—485).—Mathematical. J. W. S.

So-called colloidal iron sulphide. J. CASARES (Anal. Fis. Quim., 1933, 31, 638—644).—When an excess of Na_2S solution is added to a solution of FeSO_4 and the mixture is oxidised by a current of air or by H_2O_2 , an intensely green solution, or, with more conc. solutions, a green ppt., is formed; on further oxid-

ation, black and then red substances are produced. The green compound is probably $\text{Na}_2\text{Fe}_2\text{S}_4$ or NaFeS_2 , substances of approx. these compositions being pptd. when NaCl is added to the green solutions. The colour of certain natural waters containing S is probably caused by the presence of such compounds in colloidal solution. H. F. G.

Specific inductive power of colloidal solutions. T. NANTY and M. VALET (Compt. rend., 1934, 198, 1308).—Particulars are given of a very sensitive null arrangement for use with feebly-conducting solutions. W. R. A.

Optical investigation of sols of cellulose derivatives. I. Light-scattering capacity of cellulose ester sols. R. SHINODA (J. Cellulose Inst. Tokyo, 1934, 10, 54—62).—The scattering of light by solutions of cellulose nitrate increases at first rapidly and then slowly with increasing concn. It increases slightly with falling temp., and considerably if H_2O is added to a COMe_2 solution. It is not affected by the N content (11.85—12.29%). A. G.

Osmotic pressure of gum acacia solutions. E. C. DODDS and R. T. M. HAINES (Biochem. J., 1934, 28, 499—503).—Aq. gum acacia solutions (2—6%) have an osmotic pressure (I) \propto the concn. The presence of NaCl (0.9%) reduces (I) for the 6% solution from 78.4 cm. H_2O to about 12.0 cm. Sterilisation by heat increases (I) by $> 50\%$, whilst saturation with thymol produces a 5% diminution. W. O. K.

Emulsions. II. Proteins and allied substances as emulsifiers for organic bases. R. M. WOODMAN (J.S.C.I., 1934, 53, 115—116r; cf. this vol., 363).—Proteins and allied substances generally yield the dual types of emulsions with the org. bases used; an aq. medium of dried egg is an exception, giving only oil-in- H_2O types, possibly because of its lecithin content. Instability and gel formation sometimes make verification of type difficult or impossible. The preponderance of the evidence in these systems (and in former experiments with protein emulsifiers and phenolic liquids) appears to indicate that the mechanism of dual emulsion formation with protein-like emulsifiers is due to the formation of protein complexes with one or both liquid phases, these complexes being able to act as alternative or opposite-type emulsifiers to other emulsifiers present (e.g., protein itself).

Coagulation of colloids. VII. Some anomalous variations of viscosity during the coagulation of ferric hydroxide and antimony sulphide sols. S. S. JOSHI and A. S. NANJAPPA (J. Indian Chem. Soc., 1934, 11, 133—143; cf. this vol., 253).—Rates of change of viscosity of $\text{Fe}(\text{OH})_3$ and Sb_2S_3 sols have been measured in the "slow" region of coagulation by various electrolytes. J. S. A.

p_H of sols after coagulation with electrolytes. S. RAYCHOUDHURY, A. SEN, and A. CHATTERJEE (J. Indian Chem. Soc., 1934, 11, 13—21).—The p_H of $\text{Fe}(\text{OH})_3$, As_2S_3 , and $\text{Al}(\text{OH})_3$ sols after coagulation depends on the nature of the added electrolyte, but bears no simple relation to its coagulating power. The same is true of $[\text{Cl}^-]$ in the case of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ sols. R. S.

Relation of the dispersion of gold sol to the intensity of reduction as influenced by p_H and a one-way effect produced in gold chloride by changes of p_H through certain ranges. (Miss) W. ASHBY (J. Physical Chem., 1934, 38, 427—447).—The effect of variation in the amount of $\text{K}_2\text{C}_2\text{O}_4$, glucose, and CH_2O on the colour of Au sol, and on the rate and temp. of reduction, has been studied. The relation of alkalinity to the formation of Au sol with CH_2O and $\text{K}_2\text{C}_2\text{O}_4$ has been determined. The use of Na_2HPO_4 instead of NaOH or Na_2CO_3 results in greater consistency in the production of Au sol by reduction processes, owing to the buffering action by which it maintains the optimum p_H val. throughout the reaction. The colour and quality of the sol do not depend on the character of the reducing agent, as generally supposed, but on the use of an amount of reducing agent near to the min. with the appropriate degree of alkalinity. There is a time lag in the rate of change of colour of AuCl_3 on making alkaline, but not on acidification. The causes of this behaviour are discussed. M. S. B.

Chromium oxychloride hydrosols. A. W. THOMAS and F. C. VON WICKLEN (J. Amer. Chem. Soc., 1934, 56, 794—798).—The change of p_H with age is attributed to the tendency of basic Cr^{+++} salts to polymerise in aq. solution. E. S. H.

Formation of organic jellies. I. S. PRAKASH (Allahabad Univ. Studies, Sci. Sec., 1933, 10, 257—283).—Published work on methods of prep. is reviewed. E. S. H.

Heat capacity measurements on gelatin gels. II. W. F. HAMPTON and J. H. MENNIE (Canad. J. Res., 1934, 10, 452—462).—Measurements of the heat capacity (c) of 9—100% gelatin gels at -180° to 25° show that freezing occurs at concn. $> 61\%$. The c-composition curves are linear at lower concn., but irregular at higher concn., which suggests that above 61% all the H_2O is bound. For the H_2O in gels of $> 70\%$ c is > 1 between 0° and 25° . This invalidates previous calculations of amounts of bound H_2O . A. G.

Constitution of lithium urate gel. H. HENSTOCK (Trans. Faraday Soc., 1934, 30, 403—406).—Li urate gel is not formed from the Li_1 salt, but by neutralising uric acid (I) with LiOH . It is suggested that in the sol the LiOH mol. reacts without loss of H by (I), which is in the more soluble enol form, but returns to the keto-form in the gel, the LiOH forming a chelate ring. At 100° the ring is ruptured with elimination of H_2O , and anhyd. Li urate is formed. J. G. A. G.

Molecular weight, molecular volume, and hydration of proteins in solution. M. KUNITZ, M. L. ANSON, and J. H. NORTHPROP (J. Gen. Physiol., 1934, 17, 365—373).—The H_2O of hydration per g. dry wt. of haemoglobin, isoelectric gelatin, and cryst. gelatin calc. (a) from osmotic pressure and diffusion measurements and (b) from viscosity measurements is (a) 0—0.14, 5.8, 0.54; (b) 0.13, 5.9, 0.49. A. L.

Refractivity of heat-denatured ovalbumin. H. A. BARKER (J. Biol. Chem., 1934, 104, 667—673).—The sp. refractive increment of ovalbumin [(n solution

—*n* solvent)/concn. (in g. per 100 c.c.)] is 0.00185 ± 0.00002 . The refractivity increases during denaturation in alkaline solution. W. O. K.

Colloid-colloid reactions. IV. **Protective effect of gum arabic and proteins.** W. PAULI, E. RUSSE, and G. SCHNEIDER (Biochem. Z., 1934, 269, 158—174; cf. A., 1932, 996).—When 90% of the ash-forming content is removed from gum arabic sol (I) by electrodialysis, (I) loses its protective power (II) towards highly purified Congo-blue and Au sols. (II) is restored by addition of MgO, ZnO, or the ash (which contains MgO), but not by neutralisation with NaOH or Ca(OH)₂. Positive colloids [night-blue, Fe(OH)₃] give colloid-colloid flocculation (III) with purest (I), exhibit (II) towards electrolytes (IV), and, in the region of nuclear aggregation, have sensitising effects (V) dependent on the charge and concn. of the sols. Neutral salts do not protect (I) against (III). With purest (I) and pure lyophobic negative colloids there is neither (V) nor (III), only (IV) being protected against pptn. W. McC.

Combination of formaldehyde with amino-acids and proteins.—See this vol., 635.

Plant colloids. XXXV. **Solution state of isohexosans.**—See this vol., 637.

Regularities of chemical structure. (MLLE.) S. VEIL (J. Phys. Radium, 1934, [vii], 5, 141—144).—Regularities in structure have been observed in the pptn. of Ag₃AsO₄, Ag₃PO₄, HgI₂, and SrCO₃ in a gelatin medium, in the electrolytic pptn. of colouring matter, and in the crystallisation by diffusion of alkali carbonates in gelatin. The regularities, as for Liesegang rings, are governed by the sq. root law (cf. A., 1932, 994). N. M. B.

Condition of silver chromate, silver iodide, and lead iodide in gelatin. B. M. NAIK, H. N. DESAI, and B. N. DESAI (J. Indian Chem. Soc., 1934, 11, 45—57).—The conductivity of the mixtures varies immediately after mixing, but does not alter with the subsequent colour change, which is attributed to the agglomeration of a highly disperse ppt. The amount of Ag₂CrO₄, PbI₂, and AgI remaining in the ionised condition has been examined. R. S.

Influence of acidity of gelatin on the Liesegang rings of silver chromate and silver iodide. B. N. DESAI and B. M. NAIK (J. Indian Chem. Soc., 1934, 11, 59—64; cf. A., 1932, 807).—The best rings of Ag₂CrO₄ were obtained in gelatin of *p*_H 5.0—5.25, but equally good rings of AgI appeared over the whole range investigated. The distance between successive rings of AgI first decreases and then increases, whilst the distances between the same successive rings vary inversely as *p*_H. R. S.

Anodic oxidation in a gelatin medium. (MLLE.) S. VEIL (Compt. rend., 1934, 198, 1396—1398).—When gelatin is subjected to a p.d. between embedded oxidisable electrodes, the anodic oxidation products (I) (e.g., of Fe with p.d. of 4 volts) migrate towards the cathode and form a sharp boundary (II) to the swollen cathode zone (cf. A., 1933, 1005). Anodes of Ag, Ni, Al, Pb, and Cu behave similarly. The positive polarity of (I) appears to be reversed by the occurrence of chemical reactions at (II). B. W. B.

Diffusion of soluble iron compounds *in vitro*. Effect of acids, bases, and electrolytes. J. F. BROCK and F. H. L. TAYLOR (Biochem. J., 1934, 28, 447—455).—The rate of diffusion of Fe^{III} NH₄ citrate through cellophane membranes is increased by H⁺ and decreased by OH⁻. H. D.

Donnan equilibrium and its application to chemical, physiological, and technical processes. T. R. BOLAM (Kolloid-Beih., 1934, 39, 139—258).—A comprehensive survey of published work. E. S. H.

Chemical energetics. F. MICHAUD (J. Chim. phys., 1934, 31, 197—210).—Theoretical. The laws and concepts of chemistry are discussed with reference to thermodynamics and certain postulates. J. G. A. G.

Activities of life and the second law of thermodynamics. F. G. DONNAN and E. A. GUGGENHEIM (Nature, 1934, 133, 530; cf. *ibid.*, 174). L. S. T.

Activities of life and the second law of thermodynamics. (SIR) J. H. JEANS (Nature, 1934, 133, 612).—A reply to criticism (cf. preceding abstract). L. S. T.

Law of displacement of chemical equilibrium. H. LE CHATELIER (Compt. rend., 1934, 198, 1329—1330; cf. A., 1933, 783).—A reply to criticism (Posthumus, this vol., 490). B. W. B.

Dissociation constant of hypochlorous acid, deduced from the potentiometric neutralisation curve. A. RIUS and V. ARNAL (Anal. Fis. Quím., 1933, 31, 497—509).—The dissociation const. of HOCl at 25° is 1.46×10^{-7} . H. F. G.

Ionisation constant of deuteracetic acid. G. N. LEWIS and P. W. SCHUTZ (J. Amer. Chem. Soc., 1934, 56, 1002—1003).—Conductivity measurements for 0.0722*M*- and 0.1444*M*-deuteracetic acid in 97% H₂O at 25° yield the val. $K = 0.59 \times 10^{-5}$. E. S. H.

Dissociation constants of chlorophenyl- and phenetyl-boric acids.—See this vol., 669.

Ionisation constant and heat of ionisation of the bisulphate ion from electromotive force measurements. W. J. HAMER (J. Amer. Chem. Soc., 1934, 56, 860—864).—The dissociation const. of HSO₄⁻, determined from e.m.f. measurements of the cells H₂|NaHSO₄(*m*₁), Na₂SO₄(*m*₂), NaCl(*m*₃)|AgCl|Ag⁺, can be calc. at any temp. between 0° and 60° with an accuracy of 1% from $\log K = -1387.6/T + 1.15612 \log T - 0.00001355T - 0.000038182T^2 + 3.27632$. Formulae are derived for calculating the heat of ionisation of HSO₄⁻ and the differences in sp. heats of the ions and undissociated HSO₄⁻. E. S. H.

Thermodynamic dissociation constant of a weak base. E. J. ROBERTS (J. Amer. Chem. Soc., 1934, 56, 878—879).—The const. for BOH may be derived from e.m.f. measurements of the cell Tl(Hg)|TlClO₄(*m*₁), BClO₄(*m*₂), BOH(*m*₃)|H₂. E. S. H.

Applicability of the Debye-Huckel theory to non-aqueous solutions. A. J. BRODSKI and F. I. TRACHTENBERG (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 490—493).—The distribution of LiCl between H₂O and isoamyl alcohol has been studied over the range 8.6—0.15 mol. per kg. aq. solution, and the

activity coeff. of LiCl in the alcohol calc. from the data. The results indicate that the Debye-Huckel theory is applicable to this class of solution.

J. W. S.

Statistical "interaction between ions and molecules" in media of small dielectric constant. O. HALPERN and P. GROSS (J. Chem. Physics, 1934, 2, 184—187).—The general theory is discussed with reference to Debye's theory of the salting-out effect. Formulae for the free energy of interaction between ions and dipoles are deduced, and applied to the ionic equilibrium in a medium of low dielectric const.

N. M. B.

Electrolytes in media of small dielectric constant. P. GROSS and O. HALPERN (J. Chem. Physics, 1934, 2, 188—192; cf. preceding abstract).—Conductivity data for tetraisoamylammonium nitrate in H₂O-dioxan mixtures can be interpreted by considering the activity coeff. arising from ion-dipole interaction.

N. M. B.

Ionic solvation and its determination. G. BABOROVSKY (Z. physikal. Chem., 1934, 168, 135—140).—After a review of the methods of determining ionic hydration nos. the val. of the method of H₂O transport as a means of determining the sum of the amount of chemically held H₂O and the more firmly bound part of the H₂O of physical hydration is reaffirmed.

R. C.

Ionic solvation and its determination. H. ULLICH (Z. physikal. Chem., 1934, 168, 141—146; cf. preceding abstract).—A definite dividing line may be drawn between chemical solvation, which is equiv. to formation of a complex ion with the solvent, and physical solvation, i.e., the longer-range effect of the ion on the solvent, diminishing asymptotically, on the basis of hydrodynamic considerations. In the electrolytic transport of H₂O the streaming due to the mechanical action of the moving ions on the H₂O mols. in their vicinity cannot be neglected.

R. C.

Hydrolysis of beryllium benzenesulphonates. V. CUPR and J. STRUČEK (Coll. Czech. Chem. Comm., 1934, 6, 97—100).—Measurements of p_H with aq. Be *o*-nitrotoluene-*p*-sulphonate by means of a quinhydrone electrode indicate that 0.25—0.1*N* solutions are slightly less acidic than those of the corresponding acids, whilst in more dil. solution the acidity is comparable with that of BeSO₄ and BeCl₂.

D. R. D.

Polyhalides. III. S. K. RAY (J. Indian Chem. Soc., 1934, 11, 115—124; cf. A., 1933, 904).—Equilibrium consts. for the formation of trihalide ions are calc. from the solubility of Br and I in solutions of Na, K, Sr, Ba, Zn, and Cd chlorides and bromides. Br gives no const. corresponding with Br₃'.

J. S. A.

Complex formation in salt solutions. I. R. W. MONEY and C. W. DAVIES (J.C.S., 1934, 400—403).—Added (NH₄)₂C₂O₄ depresses, in the normal manner, the solubility of BaC₂O₄·2H₂O at 25°; there is no tendency to form complex ions. The solubility of MnC₂O₄·2H₂O (I) in MnCl₂, K₂C₂O₄, and Na₂C₂O₄ solutions at 25° is much > that calc. from the complete dissociation theory, and the data lead to a dissociation const. of the weak salt, (I), in agreement with vals. from the conductivity. (I) affords no complex cations, but

forms a complex anion, Mn(C₂O₄)₂'', of which the instability const., [MnC₂O₄][C₂O₄'']/[Mn(C₂O₄)₂''], is 0.037.

J. G. A. G.

Application of the polarographic method to the study of complex ions. G. SARTORI (Gazzetta, 1934, 64, 3—16).—The deposition potentials at the dropping Hg cathode of Cd, Zn, Ni, and Co from solutions of the sulphates and of the pyrophosphates and oxalates in presence of alkali chlorides are recorded. The dissociation consts. of the ions of the type (MA₂)'' are very small (10⁻⁶ to 10⁻⁸ for the Cd and Zn salts, 10⁻¹⁰ and 10⁻¹⁴ for the Ni and Co salts, respectively). The influence of chloride additions is discussed.

H. F. G.

Salt effects of sulphonephthalein indicators. E. A. GUGGENHEIM and T. D. SCHINDLER (J. Physical Chem., 1934, 38, 543—556).—Indicator-buffer equilibria are discussed. $K_c = C_I \cdot C_{HA} / C_{HI} \cdot C_A$, where C_{HI} , C_I , C_{HA} , and C_A are concns. of indicator acid and base and buffer acid and base, respectively, has been determined colorimetrically for bromothymol-blue (I) and bromocresol-green (II) with acetate and phosphate buffers. It can be shown theoretically that the salt effect, which varies with K_c , is linear in phosphate buffers, but parabolic in acetate buffers, the salt effect being very pronounced at low equiv. salt concns. in the latter case. The thermodynamic const. K_{HI} for (II) is 1.03×10^{-5} with an accuracy of 1—2% and for (I) 3.58×10^{-8} with an estimated accuracy of 2—3%.

M. S. B.

Formation and dissociation of alkali metal peroxides. M. CENTNERSZWER and M. BLUMENTHAL (Bull. Acad. Polonaise, 1933, A, 499—522).—An account of work previously published (A., 1932, 228, 468).

F. L. U.

Thermal dissociation of manganese dioxide. M. BLUMENTHAL (Bull. Soc. chim., 1933, [iv], 53, 1418—1422).—The temp. corresponding with different pressures of O₂ have been determined. Pyrolusite and amorphous and cryst. preps. of MnO₂ contain active centres which cause a lowering of the temp. for previously unheated specimens. There is evidence of limited miscibility between MnO₂ and Mn₂O₃. Heats of dissociation are calc.

F. L. U.

Dissociation pressure of cobalto-cobaltic oxide. M. WATANABE (Sci. Rep. Tôhoku, 1934, 23, 89—102).—The dissociation pressure of Co₃O₄ has been determined at 855—960°. Co₃O₄ and CoO form solid solutions and below 928° two such solutions co-exist over a considerable range. At 960° the system is divariant throughout. For the reaction $\text{Co}_3\text{O}_4 = 3\text{CoO} + 0.5\text{O}_2$, $\Delta H^\circ = 38,972 - 0.75T + 0.00025T^2$; $\Delta F^\circ = 38,972 + 1.73T - 0.00025T^2 - 36.07T$; and for $3\text{Co} + 2\text{O}_2 = \text{Co}_3\text{O}_4$, $\Delta H_{298}^\circ = -20,6074 \text{ g.-cal.}$ and $\Delta F^\circ = -181,355 \text{ g.-cal.}$

M. S. B.

Dissociation of the nitrites of alkaline-earth metals. M. CENTNERSZWER and W. PIEKIELNY (Bull. Acad. Polonaise, 1933, A, 389—396).—The dissociation of the alkaline-earth nitrites corresponds with $3\text{M}(\text{NO}_2)_2 = 2\text{MO} + \text{M}(\text{NO}_3)_2 + 4\text{NO}$. The dissociation pressures of Ca(NO₂)₂, Sr(NO₂)₂, and Ba(NO₂)₂ = 760 mm. at 316°, 380°, and 362°, respectively. At higher temp. the nitrates dissociate like the corresponding nitrites.

J. W. S.

Phase equilibria in the system $\text{Na}_2\text{O}-\text{TiO}_2$. E. W. WASHBURN and E. N. BUNTING (Bur. Stand. J. Res., 1934, 12, 239).—The compounds Na_2TiO_3 (m.p. 1030°), $\text{Na}_2\text{Ti}_2\text{O}_5$ (m.p. 985°), and $\text{Na}_2\text{Ti}_3\text{O}_7$ (m.p. 1128°) have been detected in the system $\text{Na}_2\text{O}-\text{TiO}_2$. J. W. S.

System CS_2-CBr_4 . A. E. KORVEZEE (Rec. trav. chim., 1934, 53, 464—470).—The two three-phase lines have been determined for both monoclinic and cubic CBr_4 . From these measurements and the v.p. of the pure components, the fusion diagram of the system has been derived. The agreement between theory and experiment is good. H. S. P.

Combination of calcium in the systems $\text{CaO}-\text{TiO}_2$ and $\text{CaO}-\text{SiO}_2-\text{TiO}_2$. I. PARGA-PONDAL and K. BERGT (Anal. Fis. Quím., 1933, 31, 623—637).—The free and combined CaO in mixtures heated at temp. between 900° and 1400° have been determined. In the binary system CaO, TiO_2 is formed slowly at 900° , but readily at 1300° , and this yields $3\text{CaO}, 2\text{TiO}_2$ at 1400° ; at higher temp. compounds with larger proportions of CaO appear to exist. In the ternary system no titanates richer in Ca than those found in the binary system exist, but small quantities of TiO_2 favour the reaction between CaO and SiO_2 . No ternary compounds have been detected. H. F. G.

Isotherms of some ternary systems of metal perchlorates in aqueous solution at 30° . R. M. CAVEN and G. BRYCE (J.C.S., 1934, 514—517).—Contrary to Weinland and Ensgraber, the systems $\text{NH}_4(\text{Na}, \text{K})\text{ClO}_4-\text{Al}(\text{ClO}_4)_3-\text{H}_2\text{O}$ and $\text{NH}_4\text{ClO}_4-\text{Cu}(\text{ClO}_4)_2-\text{H}_2\text{O}$ at 30° afford no evidence of double-salt formation. NH_4ClO_4 crystallises from mixtures of NH_4ClO_4 , $\text{Th}(\text{ClO}_4)_4$, and H_2O at room temp. J. G. A. G.

System aluminium-aluminium oxide-aluminium carbide. E. BAUR and R. BRUNNER (Z. Elektrochem., 1934, 40, 154—158).—M.-p. observations have been made with the binary and ternary mixtures. Al and Al_2O_3 form a compound, $2\text{Al}, 3\text{Al}_2\text{O}_3$ (m.p. 2051°), the eutectic with Al_2O_3 being at 2016° . In the system $\text{Al}_2\text{O}_3-\text{Al}_4\text{C}_3$ there is a eutectic at 2007° ; in mixtures containing $> 40\%$ of Al_4C_3 there appear to be only two solid phases, viz., Al_2O_3 and, perhaps, a carbide-oxide. Al_4C_3 mixed with 25% of Al melts at 2650° ; there are at least two carbides, of which one, perhaps Al_6C_3 , has m.p. about 2500° . In the ternary system there is possibly a ternary compound. The results are discussed in relation to the reduction of Al_2O_3 by C at high temp. H. F. G.

Influence of manganese on the equilibrium diagram of the $\text{Fe}-\text{Fe}_3\text{C}-\text{FeS}$ alloys. T. SATO (Tech. Rep. Tôhoku, 1934, 11, 122—154).—Increase of the Mn content (between 0.45 and 1.9%) causes an extension, in the direction of low C and low S content, of the range over which two liquid phases co-exist. In absence of Mn the crit. point on the monotectic reaction surface lies at 1300° , 1.07% C , and 8% S , whereas when 1.9% of Mn is present it lies at about 1355° , 0.53% C , and 7.2% S . Increase of the Mn content thus raises the temp. at which the S -rich phase separates as slag, and, since separation occurs upon the austenite grains, causes increased fusion of the surface of the grains and consequently a diminution of

red-shortness. Numerous photomicrographs are reproduced. H. F. G.

Equilibrium in the thermal dissociation of salicylic acid. H. HIRSBRUNNER (Helv. Chim. Acta, 1934, 17, 477—504).—The v.p. and heats of sublimation of pyrogallol and benzoic, salicylic, gallic, and terephthalic acids have been determined. Analytical and manometric investigations over the range $200-250^\circ$ (approx.) show that thermal dissociation occurs to about $90-96\%$ and is a reaction of the first order. The heat of formation determined from the equilibrium consts. agrees with that determined calorimetrically. Attempts to prepare salicylic acid from PhOH by the action of CO_2 at $230^\circ/80$ atm. were unsuccessful. E. S. H.

Circular reaction and stationary equilibrium. E. BAUR (Helv. Chim. Acta, 1934, 17, 504—510).—A discussion of the failure to synthesise salicylic acid from PhOH and CO_2 (cf. preceding abstract). E. S. H.

Thermodynamic studies of sodium bromide and potassium bromide. F. ISHIKAWA and K. TACHIKI (Sci. Rep. Tôhoku, 1934, 23, 103—114).—The e.m.f. of the following cell has been determined for different concns. of amalgam: $\text{X}-\text{Hg}|\text{XBr}(\text{solid})|\text{saturated EtOH}-\text{XBr}|\text{AgBr}|\text{Ag}$ ($\text{X}=\text{Na}$ or K). The free energies and heats of formation in g.-cal. of XBr from the metal and liquid Br have been calc. For NaBr $\Delta G = -83,105$ and $\Delta H_{298} = -86,241$. For KBr the vals. are $-90,455$ and $-94,211$, respectively. M. S. B.

Cuprous iodide and cuprous bromide cells with reference to the potential difference between copper and its amalgam. F. ISHIKAWA, S. YAMAZAKI, and T. MUROOKA (Sci. Rep. Tôhoku, 1934, 23, 115—128).—The e.m.f. and temp. coeff. of the cell $\text{H}_2|\text{HX aq.}, \text{CuX}(\text{solid})|\text{Cu}(\text{Hg})$, where X may be Br or I , have been determined. From these data, in conjunction with Oku's results (A., 1928, 1192) for the p.d. between Cu and $\text{Cu}(\text{Hg})$, various thermodynamic vals. have been calc. M. S. B.

Latent energy in cold-worked iron and copper as estimated by determination of heats of solution. R. W. FRANCE (Trans. Faraday Soc., 1934, 30, 450—460).—The heats of dissolution of cold-worked and annealed Fe in HCl and Cu in Br solution have been determined; the rates of dissolution are also discussed. R. S. B.

Heat capacities of magnesium, zinc, lead, manganese, and iron carbonates at low temperatures. C. T. ANDERSON (J. Amer. Chem. Soc., 1934, 56, 849—851).—The heat capacities of magnesite, smithsonite, cerussite, rhodochrosite, and siderite have been determined from about 55° abs. to about 300° abs. The corresponding entropies are 15.7 , 19.7 , 31.3 , 20.5 , and 22.2 , respectively. E. S. H.

Heat capacities and entropies of potassium bromate and iodate from 15° to 300° absolute. Entropies of bromate and iodate ions. J. E. AHLBERG and W. M. LATIMER (J. Amer. Chem. Soc., 1934, 56, 856—858).—From the data recorded the calc. entropies of KBrO_3 and KIO_3 are 35.65 and

36.20 e.u., respectively, from which 37.4 ± 1.0 and 26.9 ± 1.0 e.u. are derived for the entropies of BrO_3^- and IO_3^- , respectively. E. S. H.

Thermal activity of lanthanum and of thorium minerals. A. SANIÉLÉVICI (J. Chim. phys., 1934, 31, 184—191).—The heat evolved by La_2O_3 is not of at. origin, since LaF_3 shows no thermal activity. The behaviour of La_2O_3 varies with the conditions and is attributable to hydration and adsorption of gases. J. G. A. G.

Thermochemistry of aqueous solutions of zinc, aluminium, and manganese sulphates. J. PERREU (Compt. rend., 1934, 198, 1410—1412).—Heats of dissolution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (I) have been determined at 17° , and of (I) and $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ at the transition point, 9° . Heats of dilution are also recorded. B. W. B.

Anomalous electrolytes. III. Electrolyte character of triarylammonium and tetra-arylhydrazinium compounds. P. WALDEN and E. J. BIRR (Z. physikal. Chem., 1934, 168, 107—123; cf. A., 1933, 907).—Conductivities have been measured in PhNO_2 and PhCN at dilutions up to 50,000 litres at 25° . Tri-*p*-tolylammonium perchlorate (I) and diphenyl-*p*-anisylmethyl perchlorate (II) give conductivity-dilution curves similar to those of the strongest binary tetra-alkylammonium salts and together with tetra-*p*-tolylhydrazinium perchlorate (III) obey Kohlrausch's square-root law. Judging by the conductivity ratio (I), (II), and NET_4ClO_4 at a dilution of 5000 litres are approx. equally strong, (III) is not as strong, and phenylbenzylethylaminoxide picrate and the compounds of SbCl_5 with tri-*p*-tolylamine and tetra-*p*-tolylhydrazine are weak. In solutions of (I) and (II) the coloured component migrates to the cathode. It is inferred that in these solutions coloured and practically unsolvated $\text{N}(\text{C}_7\text{H}_7)_3^+$, $\text{N}_2(\text{C}_7\text{H}_7)_4^+$, and C_6Ar_3^+ ions are present, and the approx. mobilities have been calc. $\text{N}_2(\text{C}_7\text{H}_7)_4^+$ apparently dissociates somewhat into $\text{N}(\text{C}_7\text{H}_7)_2^+$ and $\text{N}(\text{C}_7\text{H}_7)_2^{\cdot\cdot}$. R. C.

Conductivities of aluminium bromide and chloride in non-aqueous solution. E. WERTY-POROCH and A. SILBER (Z. physikal. Chem., 1934, 168, 124—134).— AlCl_3 and AlBr_3 dissolve only slightly in MeCHO and some other aliphatic aldehydes and form insol. substances. In $\text{CHMe}:\text{CH}:\text{CHO}$, PhCHO , and $\text{CHPh}:\text{CH}:\text{CHO}$ they form reddish-yellow solutions, which are supposed to contain additive compounds with conjugated double linkings. The conductivity relations indicate that the AlBr_3 compounds are salt-like. In AlCl_3 solutions in COMe_2 , COMeEt , and mesityl oxide (I) solvolysis of the conducting substance occurs on dilution and the mol. conductivity, λ , is small; the additive compounds are not salt-like. In (I) and COMe_2 the AlBr_3 solvates decompose on dilution, whereas in COMeEt and COPhMe they are salt-like. In HCO_2H both salts have a high λ and behave like normal binary electrolytes, whilst in AcOH the solvates decompose on dilution and λ falls. R. C.

Glass electrodes. P. GROSS and O. HALPERN (J. Chem. Physics, 1934, 2, 136—140).—Regarding a glass electrode as a difficultly sol. electrolyte which

absorbs H_2O and dissolved salts, a general formula is derived for the potential, the variations of which are discussed. N. M. B.

Periodic potential changes of iron in chromic-sulphuric acid solutions. M. KARSCHULIN (Z. Elektrochem., 1934, 40, 174—180).—The potential of electrolytic Fe in a mixture of aq. $\text{K}_2\text{Cr}_2\text{O}_7$ (7.5%) and H_2SO_4 varies regularly in periods of a few sec. when the concn. of H_2SO_4 is between certain limits (e.g., 5%). The frequency of the periods increases as the concn. of H_2SO_4 increases. Similar results were obtained in mixtures of 2.7% aq. CrO_3 and 3.1—4.3% H_2SO_4 . With dilution of the mixture the frequency of the periods decreases. An explanation is advanced based on the diffusion of $\text{H}_2\text{Cr}_2\text{O}_7$ through the FeSO_4 film adsorbed at the Fe surface. E. S. H.

Polarographic studies with the dropping mercury cathode. XXXVIII. Reduction of some aliphatic amines, quinoline, and saccharin. J. PECH (Coll. Czech. Chem. Comm., 1934, 6, 126—136).—Reduction potentials against Hg_2Cl_2 are: NH_4^+ —1.787, NH_4Me^+ —1.972, NH_4Me_2^+ —1.977, NHMe_3^+ —1.682, NMe_4^+ —2.6 volts. $\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$, creatine, $\text{CO}(\text{NH}_2)_2$, asparagine, caffeine, theobromine, and uric acid free from O_2 are not reducible; uric acid solution in air gives an unknown reducible substance. Quinoline and saccharin are reducible; the latter may be determined by this method; the former goes through stages which may be di- and tetra-hydroquinoline. Indole is reduced in acid solution, but its behaviour is anomalous. D. R. D.

Thermodynamics of the electrocapillary curve. II. Variation of the electrocapillary curve with composition. F. O. KOENIG (J. Physical Chem., 1934, 38, 339—363).—From the general equation previously deduced for the electrocapillary curve (I) (this vol., 258), special equations expressing the variation of (I) with the composition of the two phases in contact have been derived. The general equations for the effect of variations of the reference electrode and of the metallic phase α on (I) are relatively simple, but no simple general expression can be obtained for the more complex variations of the non-metallic phase β . The chief special cases have therefore been considered separately. The surface densities of certain components of the electrical double layer can be approx. calc. from the shift of (I) due to variations in the composition of α or β . M. S. B.

Behaviour of the surface of the solution of electrolyte against electronic impacts. Y. YAMAGUCHI and T. SHIBA (Bull. Chem. Soc. Japan, 1934, 9, 109—120).—When a glow discharge takes place between a metallic cathode and the surface of a solution, a film consisting chiefly of the oxides or hydroxides of the cations is formed. If the surface is covered with a film of oil, finely-divided metal powders are obtained. In the first case the action is considered to be due to the decomp. of H_2O by electron impacts, and in the second to the formation of an electric double layer which discharges the cations. By using a hot cathode it was found that

the dissociation of the H_2O is caused by electrons of energy 23.8 e.v., the theoretical val. being 23.1 e.v.

H. S. P.

Cells with liquid-liquid junctions. V. STANDARDS OF hydrogen-ion measurements and the second dissociation constant of phosphoric acid. E. A. GUGGENHEIM and T. D. SCHWINDLER (J. Physical Chem., 1934, 38, 533—541).—Measurements have been made at 25° on the cell $\text{Hg}|\text{HgCl}|0.1N\text{-KCl}|3.5N\text{-KCl}|\text{solution } S|\text{H}_2$, where S is a solution of varying $[\text{H}^+]$, and the equation $E = E_0 + E_D + RT/F \log C_{\text{H}^+} f_{\text{H}^+}$ has been applied in order to calculate the val. of E_0 . From this val. combined with electrometric measurements of phosphate buffers the val. of 5.97×10^{-8} has been obtained for the thermodynamic dissociation const. $K_{\text{H}_2\text{PO}_4}$ with an estimated accuracy of 2—3%. Vals. of E_0 and f_{H^+} have also been calc. at 0°, 18°, and 37°. Vals. thus obtained for f_{H^+} are in satisfactory agreement with those based on the convention of setting $f_{\text{Cl}^-} = f_{\text{KCl}}$ in 0.1M-KCl.

M. S. B.

Oxidation-reduction potentials of ascorbic acid. J. S. FRUTON (J. Biol. Chem., 1934 105, 79—85).—Ascorbic acid behaves reversibly between p_{H} 5.5 and 7.5 and at p_{H} 7.0 has a potential of -0.081 volt. The method employed obviates the use of metallic electrodes.

H. G. R.

Oxidation-reduction potentials of cytochrome-C. D. E. GREEN (Proc. Roy. Soc., 1934, B, 114, 423—435).—Cytochrome-C forms a reversible oxidation-reduction system, intermediate between methylene-blue and the indophenols. At p_{H} 7.0, E'_0 is $+0.123$ volt. The change from the reduced to the oxidised form involves a single equiv.

H. G. R.

Reduction potential of cysteine-cystine mixtures. J. C. GHOSH and S. C. GANGULI (Biochem. J., 1934, 28, 381—383).—An O_2 or oxide film (I) on the Hg surface is responsible for setting up potentials (II) in cystine-cysteine mixtures which follow the equation $E = E_0 - (RT/F)p_{\text{H}} - (RT/F) \log [\text{cysteine}]$ (J.C.S., 1923, 123, 2943). Removal of (I) by cathodic reduction gives rise to (II), which obey the thermodynamic equation.

A. E. O.

Electrochemical character of insulin. E. A. HARVEY, F. O. HOWITT, and E. B. R. PRIDEAUX (Trans. Faraday Soc., 1934, 30, 407—413).—From the electrometric titration of insulin hydrochloride with acid and alkali it appears that 6/7 of the potential acidic and basic groups are linked as peptide chains, but the curve has no inflexion at the isoelectric point. Insulin inactivated by acid-alcohol treatment affords different titration characteristics, but vals. similar to those for active insulin are obtained by restoration with alkali at p_{H} 12 and 0°.

J. G. A. G.

Formaldehyde, alcohol, and acetone titrations. Zwitterion conception.—See this vol., 634.

Influence of magnetic fields on electrolysis. M. PRASAD and N. B. CHOKSEY (Current Sci., 1934, 2, 345).—Application of a magnetic field at right angles alters the current flowing between Pt electrodes in an aq. solution of an electrolyte.

C. W. G.

Passivity XXII. W. J. MULLER (Z. Elektrochem., 1934, 40, 119—125).—The protective film

theory provides in all cases a qual., and in some cases a quant., explanation of activation and passivity phenomena. A film of which the pores do not exceed 10^{-4} sq. cm. per sq. cm. of surface, and is not itself attacked by the electrolyte, prevents spontaneous or anodic dissolution of the metal. If the pores exceed 10^{-2} sq. cm. per sq. cm., the metal becomes active. At a sufficiently high anodic potential, dissociation at a higher valency or evolution of O_2 occurs. The conditions governing the formation of films are described. Concepts such as those of the c.d. required to produce passivity, degree of passivity, activation time, etc. are regarded as superseded by the view stated above.

H. F. G.

Polarity and chemical reactions. H. B. WATSON (J.S.C.I., 1934, 53, 92—94r).—A summary of results and views previously published.

J. W. B.

Mechanism of self-propagating reactions. K. K. ANDREEV and J. B. CHARITON (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 402—406).—The initiation of a self-propagating system results from the formation of a centre or group of centres localised in time and space.

W. R. A.

Reactions between solids. A. ALBERTO (Ann. Acad. Brasil. Sci., 1933, 5, 223—229).—Published work, principally that of Tammann, is critically reviewed.

H. F. G.

Wave-mechanical effects and the reactivity of the hydrogen isotopes. C. E. H. BAWN and G. OGDEN (Trans. Faraday Soc., 1934, 30, 432—443).—The different reaction velocities of the H isotopes are due to differences in (a) zero point energy, and (b) the permeability for energy barriers; (b) alone may be sufficient to account for separation by electrolysis and diffusion. The effect of (a) on heats of reaction and equilibrium consts. is discussed.

R. S. B.

Chlorine-hydrogen reaction with heavy hydrogen. L. FARKAS and A. FARKAS (Naturwiss., 1934, 22, 218—219).— H_2^2 reacts one third as rapidly with Cl_2 as H_2 , in the photochemical $\text{Cl}_2\text{-H}_2$ reaction. During the course of the reaction, which was carried out with a mixture of H_2 and H_2^2 , the proportion of H_2^2 present increases owing to the more rapid removal of H_2 . The difference in rate occurs in the first part of the chain ($\text{Cl} + \text{H}_2 = \text{H}^2\text{Cl} + \text{H}^2$), there being no difference in rate in the second part ($\text{H}^2 + \text{Cl}_2 = \text{H}^2\text{Cl} + \text{Cl}$). The faster reaction with H_2 is due to its greater zero point energy compared with that of H_2^2 . Most of the methods for separating H_2^2 depend on this fact.

A. J. M.

Calculation of theoretical combustion temperature allowing for dissociation. H. TULGINSKY (Rev. univ. Mines, Métall., 1933, 76, 494—502; Chem. Zentr., 1933, ii, 2956).—The combustion temp. calc. for CO in the stoichiometric proportion of air is 2430°, or 2095° when corr. for dissociation of CO_2 and H_2O .

H. J. E.

Decomposition of nitrous oxide. M. VOLMER and H. BRISKE (Z. physikal. Chem., 1934, B, 25, 81—89).—The velocity equation for the complete decomp., taking into account the effect of the products of decomp., has been derived and verified from experi-

mental data. Recalculation shows the probability of deactivation per collision to be approx. 1. R. C.

Thermal decomposition of nitrous oxide at pressures up to 40 atmospheres. E. HUNTER (Proc. Roy. Soc., 1934, A, 144, 386—412).—The velocity of thermal decomp. of N_2O at $840\text{--}999^\circ/0.1\text{--}40$ atm. has been measured by observing the rate of pressure increase of the gas at const. temp. and vol. in a SiO_2 bulb. The observed reaction is the resultant of three quasi-unimol. reactions which become independent of pressure at approx. 0.08, 5, and 30 atm., respectively. The average activation energy of the reaction rises rapidly from 50,500 g.-cal. per g.-mol. at zero pressure to 6 atm. Above 6 atm. it becomes less dependent on pressure, and is practically independent above 30 atm. L. L. B.

Supposed intervention of steam in hydrocarbon combustion. W. A. BONE and J. BELL (Proc. Roy. Soc., 1934, A, 144, 257—266).—Evidence regarding the effects of P_2O_5 -drying on the slow combustion of typical hydrocarbon + O_2 mixture is discussed. New experiments with $\text{C}_2\text{H}_2 + \text{O}_2$ and $\text{C}_2\text{H}_4 + \text{O}_2$ mixtures are described, and the conclusion is reached that intensive P_2O_5 -drying increases, rather than diminishes, the reactivities of hydrocarbon + O_2 mixtures, both in slow and in explosive combustion. The oxidation is, in general, direct, and there is no intervention of steam. L. L. B.

Spontaneous ignition temperatures of hydrocarbon-air mixtures. S. COFFEY and T. BIRCHALL (Chem. and Ind., 1934, 245—247).—For petrol-air mixtures two spontaneous ignition ranges have been observed at $320\text{--}335^\circ$ and above 420° . Successive additions of antiknocks gradually narrow the lower ignition range (I), until it finally disappears. (I) is widened by proknocks and by kerosene. Results resemble those of Townend and Mandelkar (A., 1933, 1016). H. J. E.

Spontaneous ignition temperatures of hydrocarbon-air mixtures. D. T. A. TOWNEND and L. L. COHEN (Chem. and Ind., 1934, 53, 267—268).—In a 6.5 vol.-% petrol-air mixture at pressures between 1.15 and 1.45 atm. two ignition ranges have been observed. Between 1.45 and 1.6 atm. there are three ignition ranges. At pressures >1.9 atm. ignition occurs at all temp. $>284^\circ$. With "ethyl" petrol similar phenomena were observed, but at higher pressures. The "bluish" flame described by Coffey and Birchall (preceding abstract) may be due to the "cool" type of ignition. H. J. E.

Primary thermal dissociation. Velocity constants for propane, *n*-butane, and isobutane. R. E. PAUL and L. F. MAREK (Ind. Eng. Chem., 1934, 26, 454—457).—The following velocity coeffs. were obtained for the decomp. of hydrocarbons passed through heated tubes of Cu or SiO_2 : $\log_{10} k = 16.60 - 74,850/2.3RT$ (C_3H_8 at $550\text{--}650^\circ$), $17.05 - 73,900/2.3RT$ ($n\text{-C}_4\text{H}_{10}$ at $530\text{--}625^\circ$), and $14.89 - 66,040/2.3RT$ (CHMe_3 at $550\text{--}610^\circ$). The vals. of the coeff. were not affected by the nature of the surface, by the ratio of surface to vol., or by dilution with N_2 . A. G.

Thermal decomposition of gaseous ethylene iodide. T. IREDALE and L. W. O. MARTIN (J. Physical Chem., 1934, 38, 365—376).—The decomp. of $\text{C}_2\text{H}_4\text{I}_2$ at 65° and 75° in a glass vessel seems to be heterogeneous and largely autocatalytic. I adsorbed on the glass may be the catalyst. There is a short induction period which disappears when traces of I are present at the beginning of the reaction and when the catalytic surface is greatly increased. Immediately after the induction period the reaction is of zero order, then unimol. and finally bimol. A chain mechanism is possible. M. S. B.

Influence of temperature on the velocity of ionic reactions. A. VON KISS and P. VASS (Z. anorg. Chem., 1934, 217, 305—320).—The velocity of the reaction $\text{S}_2\text{O}_3^{2-} + \text{CH}_2\text{Br}\cdot\text{CO}_2' = \text{CH}_2(\text{S}_2\text{O}_3)\cdot\text{CO}_2' + \text{Br}'$ has been measured between 5° and 55° in very dil. solutions without the addition of salts, and in aq. NaNO_3 , Na_2SO_4 , $\text{Mg}(\text{NO}_3)_2$, and MgSO_4 of different concn. The Bronsted-Debye-Huckel relation is followed between 25° and 55° and for ionic strength $0.0025\text{--}0.010$. In salt concn. below $0.5N$ and in more conc. aq. Na_2SO_4 and NaNO_3 , the van 't Hoff temp. coeff. is independent of ionic strength. The temp. coeff. usually decreases with rise of temp. and for the kinetic activity coeff. the temp. coeff. is approx. 1. $\log k$ varies linearly with $1/T$, but not with the salt concn. Without salt addition the mean work of activation of the reaction for $5\text{--}55^\circ$ is 15,510 g.-cal., but diminishes a little with rise in temp. The activation work is not affected by neutral salts in dil. solution, but conc. aq. MgSO_4 and $\text{Mg}(\text{NO}_3)_2$ raise it, whilst NaNO_3 and Na_2SO_4 lower it a little. There is good agreement between calc. and experimental vals. of k . M. S. B.

Chain mechanism for autoxidation reactions. H. L. J. BACKSTROM (Naturwiss., 1934, 22, 170—171).—Autoxidation reactions can frequently be explained as a series of dehydrogenations. For the photochemical autoxidation of aldehydes, the following scheme of reactions is proposed: $\text{RCHO} + h\nu = \cdot\text{CHR}\cdot\text{O}\cdot$; $\cdot\text{CHR}\cdot\text{O}\cdot + \text{RCHO} = \cdot\text{CHR}\cdot\text{OH} + \cdot\text{CR}\cdot\text{O}\cdot$; $\cdot\text{CR}\cdot\text{O}\cdot + \text{O}_2 = \text{RCO}\cdot\text{O}\cdot\text{O}\cdot$; $\text{RCO}\cdot\text{O}\cdot\text{O}\cdot + \text{RCHO} = \text{RCO}\cdot\text{O}_2\text{H} + \cdot\text{CR}\cdot\text{O}\cdot$. The sensitising action of aromatic ketones can be similarly explained as due to dehydrogenation of the aldehyde and formation of acyl radicals: $\text{P}_2\text{CO} + h\nu = \cdot\text{CP}_2\cdot\text{O}\cdot$; $\cdot\text{CP}_2\cdot\text{O}\cdot + \text{RCHO} = \cdot\text{CP}_2\cdot\text{OH} + \cdot\text{RCO}\cdot$. In the autoxidation of sulphite solutions, the dependence of the velocity of autoxidation on p_{H} can be explained only by supposing that HSO_3' ions play a part in the reaction, and not only SO_3' ions (cf. A., 1931, 917). The mechanism is $\cdot\text{SO}_2\cdot\text{O}' + \text{O}_2 = \cdot\text{O}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}'$; $\cdot\text{O}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}' + \text{HSO}_2\cdot\text{O}' = \text{HO}_2\cdot\text{SO}_2\cdot\text{O}' + \cdot\text{SO}_2\cdot\text{O}'$. A. J. M.

Influence of pressure on organic reactions in the liquid phase. E. W. FAWCETT and R. O. GIBSON (J.C.S., 1934, 386—395).—The change in velocity of about fifty liquid org. reactions on increasing the pressure to 3000 atm. has been studied at temp. up to 180° . Reactions investigated include the condensation of anhydrides with aromatic hydrocarbons, of amines with aldehydes and ketones, of aldehydes with alcohols and ethers (acetal formation), of amines

with alkyl halides (formation of quaternary NH_4 salts), of acids with ethylenic hydrocarbons (forming saturated esters), of MeCHO with Et malonate and acetoacetate, and of PhCN with phenols, the polymerisation of aldehydes, unsaturated hydrocarbons, etc., and many miscellaneous condensation reactions. In all cases, reactions which do not occur at ordinary pressure in absence of catalysts cannot be made to proceed by increasing the pressure, but whenever a reaction does occur at 1 atm., whether in presence or absence of a catalyst, its velocity is increased considerably (usually 5–10 times) by raising the pressure to 3000 atm. The equilibrium $\gamma\delta$ -isoheptenoic acid \rightleftharpoons $\delta\delta$ -dimethyl- δ -valerolactone is displaced towards the right by an increase of pressure, as would be expected from the decrease in vol. which occurs on formation of the lactone. Whilst at 1 atm. the main product of the combination of $[\text{-CH}_2\text{Cl}]_2$ and $\text{C}_5\text{H}_5\text{N}$ is β -chloroethylpyridinium chloride, at higher pressures a second mol. of $\text{C}_5\text{H}_5\text{N}$ is added on, forming ethyldipyridinium dichloride, decomp. without melting. NHMePh and PhCHO react to form 4 : 4'-dimethylaminotriphenylmethane, m.p. 100–101°. 8 : 8'-Dichloro-5 : 5'-diquinolyl, m.p. 296°, could not be made to form any quaternary NH_4 salts.

D. R. D.

Influence of pressure on the rate of formation of cetylpyridinium halides. E. W. FAWCETT and R. O. GIBSON (J.C.S., 1934, 396–400).—The velocity of combination of $\text{C}_{16}\text{H}_{33}\text{Br}$ with $\text{C}_5\text{H}_5\text{N}$ increases with increase of pressure and rise of temp. (cf. preceding abstract). Quant. formation of $\text{C}_5\text{H}_5\text{N} \cdot \text{C}_{16}\text{H}_{33}\text{Br}$ does not occur, probably owing to a side reaction $\text{C}_{16}\text{H}_{33}\text{Br} + \text{C}_5\text{H}_5\text{N} = \text{C}_{16}\text{H}_{32} + \text{C}_5\text{H}_5\text{NHBBr}$. The yield is increased by elevation of temp., but is independent of pressure. Similar results were obtained with $\text{C}_{16}\text{H}_{33}\text{Cl}$ at 110°, but the influence of temp. was not studied. The curves obtained cannot be expressed in terms of the ordinary reaction-velocity equations.

D. R. D.

Relative reaction velocities of alcohols with phenylcarbimide. T. L. DAVIS and J. McC. FARNUM (J. Amer. Chem. Soc., 1934, 56, 883–885).— PhNCO (1 equiv.) is allowed to react with ROH (1 equiv.) + R'OH (1 equiv.) in dry C_6H_6 at 26° and the amounts of $\text{NHPh} \cdot \text{CO}_2\text{R}$ and $\text{NHPh} \cdot \text{CO}_2\text{R'}$ are determined in the resulting mixture by the f.p. method. The relative velocities are calc. from the data and are : MeOH (=1), EtOH (0.96), Pr^nOH (0.78), Bu^nOH (0.97), Bu^iOH (0.69), n -amyl alcohol (0.9), Pr^iOH (0.3), sec-BuOH (0.32), Bu^tOH (0.003), tert-amyl alcohol (0.0072).

H. B.

Relative reaction velocities of amines with phenylcarbimide. T. L. DAVIS and F. EBERSOLE (J. Amer. Chem. Soc., 1934, 56, 885–886).— PhNCO (1 equiv.) is allowed to react with NH_2R (1 equiv.) + $\text{NH}_2\text{R'}$ (1 equiv.) in dry Et_2O at 0° and the resulting mixture of $\text{NHPh} \cdot \text{CO} \cdot \text{NHR}$ and $\text{NHPh} \cdot \text{CO} \cdot \text{NHR'}$ analysed thermally. The relative velocities are : NH_3 (=1), NH_2Et (9.72), NH_2Pr^n (8.22), NH_2Bu^n (9.17), n -amylamine (9.17), NH_2Ph (0.53). The ratio, relative velocity of ROH (compared with MeOH) to relative velocity of NH_2R (as above) ($\text{R} = \text{Et}$, Pr^n , Bu^n , n -amyl), is practically const.

H. B.

Stability to acids of some high-molecular aliphatic sulphuric esters. W. SECK (Fettechem. Umschau, 1934, 41, 61–65).—The kinetics of the hydrolysis (at 100°) of the sulphuric esters ($\text{R} \cdot \text{O} \cdot \text{SO}_3\text{H} \rightleftharpoons \text{R} \cdot \text{OH} + \text{H}_2\text{SO}_4$) of (1) ricinoleic acid, (2) i -hydroxystearic acid, (3) octadecyl alcohol, and (4) octadecane- $\alpha\kappa$ -diol (di-ester) in 0.05*N* solution in presence of 0.5–2*N*- H_2SO_4 have been studied. Under these conditions the reaction is approx. unimol., and the velocity coeffs. afford a measure of the stability of the esters. Hydrolysis of esters of (2) is slower than of (1), whilst that of esters of (3) and (4) is inappreciable in 1 hr., although salting-out occurs unless aq. PrOH is used as solvent in order to maintain a homogeneous solution.

E. L.

Mechanism of precipitation processes. XIV. Kinetics of fractional precipitation. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1934, 217, 385–395; cf. A., 1933, 917).—When to a solution of two substances a reagent capable of forming an insol. compound with each is added in amount sufficient to react with only one of them, the resulting ppt. contains both compounds in a proportion depending on the rate of pptn. (I), and on the ratio (II) of their solubility products. The proportion of the less sol. compound varies inversely with (I) and directly with (II). It is also increased on keeping in contact with the liquid. These conclusions are verified for a no. of ppts. commonly encountered in analysis.

F. L. U.

Cannizzaro reaction. A. WEISSBERGER and R. HAASE (J.C.S., 1934, 535–536).—The velocity of the Cannizzaro reaction in 0.2*N*- NaOH - EtOH with PhCHO and nine derivatives increases as k for the acid increases, except that, probably owing to steric hindrance, the velocity with three o -derivatives is < that expected.

R. S. C.

Thermal decomposition of nitrogen pentoxide at low pressures. E. F. LINHORST and J. H. HODGES (J. Amer. Chem. Soc., 1934, 56, 836–841).—The reaction at 35–65° varies from a first-order reaction at about 0.05 mm. to the second order at < 0.001 mm. The glass surface of the reaction vessel has no effect at pressures > 0.005 mm., but at lower pressures increasing surface retards the reaction slightly. The mechanism is discussed.

E. S. H.

Oxidation of allyl alcohol. W. H. HATCHER and C. T. MASON (Canad. J. Res., 1934, 10, 318–320; cf. A., 1928, 249).—The velocity up to the stage of half reaction $\propto [\text{H}^+]$, but subsequently falls owing to the slow rate of oxidation of the three mols. of HCO_2H which remain.

R. S.

Thermal analysis of explosive compounds [alkali and alkaline-earth picrates]. T. TUCHOLSKI (Acta phys. polon., 1932, 1, 351–355; Chem. Zentr., 1933, ii, 2801).—Thermal analysis shows a change in the commencement of explosion with at. wt. of the cation. The temp. immediately before the explosion are always > the initial temp. (given in parentheses). For the picrates these are Li 342° (321°), Na 302.5° (331°), K 333° (331°), Rb 336° (335°), Cs 302° (301.5°), Ca 325.9° (318.3°), Sr 348.2° (343°), and Ba 342.5° (325.5°).

L. S. T.

Ionisation by explosion of solid explosives. S. KALANDYK (*Acta phys. polon.*, 1932, **1**, 295—308; *Chem. Zentr.*, 1933, ii, 2801).—The charges resulting from the explosion of K hexoate, K, Cu, Fe, and Ca picrates, and cellulose nitrate (I) are of the same order of magnitude as those from gaseous explosions ($2\text{CO} + \text{O}_2$). In the case of the picrates no dependence on the ionisation potential of the metal could be established. The charge appears to increase with the intensity of explosion. The negative charge is approx. double that of the positive. With an increase in potential the increase in charge is $>$ proportional to that of the potential. This is attributed to the irregular distribution of the flame. The duration of the current during explosion and the slow combustion of (I) have been followed. The latter does not depend on p.d. L. S. T.

Detonation of lead azide. A. MICHEL-LEVY and H. MURAOUR (*Compt. rend.*, 1934, **198**, 1499—1501).—The micro-photographic method previously described (this vol., 376) was used to study the transmission of detonation (I) around a circle of separated PbN_3 grains, about 2 mm. apart. Photographs show that (I) in each grain was initiated by the shock wave from the preceding grain, and not by flying particles or hot gases. B. W. B.

Combustion in a vacuum of compressed mercury fulminate. H. MURAOUR and W. SCHUMACHER (*Compt. rend.*, 1934, **198**, 1161—1162).—Although combustion is not propagated along a train of fine crystals of Hg fulminate (I) when touched by a red-hot wire in vac., it is propagated, but without detonation, if (I) has been compressed (d 1.4). Explosives are divisible into three classes according to their behaviour in this respect: (1) no propagation of combustion, *e.g.*, picric acid, guncotton; (2) propagation when compressed, but without detonation, *e.g.*, (I); (3) detonation, *e.g.*, PbN_3 , Ag fulminate, $m\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_3\cdot\text{ClO}_4$ (very violent), Pb trinitroresorcinol (feeble). C. A. S.

Properties of the chlorides of sulphur. VII. Changes of density on heating or irradiation. A. H. SPONG (*J.C.S.*, 1934, 485—492; cf. A., 1931, 438).—The velocity of the reaction $\text{S}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow 2\text{SCl}_2$, at 0° to 5° , which occurs after heating SCl_2 at 100° and cooling rapidly, or (more rapidly, due to production of a catalyst by the light) after irradiating with ultra-violet light at 20° and cooling, has been measured by density measurements with floats. The reaction is of the first order. With S_2Cl_2 small density changes occur under similar conditions, the reactions being $3\text{S}_2\text{Cl}_2 \rightleftharpoons \text{S}_3\text{Cl}_4 + \text{S}_3\text{Cl}_2$ and $\text{S}_3\text{Cl}_4 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{SCl}_2$. Normal S_2Cl_2 is probably a mixture of a Y-shaped mol. with a chain-form mol. H. J. E.

Rate of dissolution of marble in acids. W. JACEK (*Bull. Acad. Polonaise*, 1934, **A**, 73—80; cf. A., 1931, 1242).—The rate of dissolution in HNO_3 and HClO_4 has been measured. In each the rate has a max. val. at a concn. between 4 and 6 g.-mol. per litre, the results resembling those for HCl. H. J. E.

Velocity of dissolution of marble in acids. W. JACEK (*Bull. Acad. Polonaise*, 1933, **A**, 374—380; cf. A., 1931, 1242; 1932, 1211).—The velocity of dis-

solution of marble in HBr at low concn. is almost equal to that in HCl of equal concn., but at higher concn. is a little more rapid. The velocity is a max. with about 6.3*N*-HBr, and decreases considerably with increasing concn. above this figure. J. W. S.

Velocity of dissolution of aluminium, lanthanum, and cerium and their amalgams in hydrochloric acid. R. MULLER [with F. E. SCHWEITZER] (*Z. Elektrochem.*, 1934, **40**, 126—132).—Whereas the velocity coeff. of the dissolution of Al in HCl at 25° rises from 2.89 to 71.43 as $[\text{HCl}]$ is increased from 0.5*N* to 4*N*, that of the dissolution of Al amalgam (6% Al) falls, from 67.75 to 9.66, under the same conditions; further, the induction period is almost const. for the amalgam. In 4*N* anhyd. EtOH-HCl the coeff. for Al is 40.05. The Al thus reacts, not with undissociated HCl mols., but with $\text{HCl}\cdot\text{H}_2\text{O}$ (or $\text{HCl}\cdot\text{EtOH}$) complexes. La, and particularly Ce, react with HCl much more vigorously than does Al, yielding velocity coeffs. some 50 times as great, and exhibit the same anomalous behaviour, La amalgams behaving normally; Ce is very sparingly sol. in Hg. H. F. G.

Rate of [dis]solution of magnesium in acids. M. KILPATRICK and J. H. RUSHTON (*J. Physical Chem.*, 1934, **38**, 269—306).—Rates of dissolution of Mg in aq. acids have been determined by (1) weighing the metal, (2) measuring the vol. of H_2 evolved, (3) titrating, and (4) measuring the amount of acid required to maintain a definite $[\text{H}^+]$ as shown by an indicator. The last was used in the study of the H_2O reaction. The results were reproducible and in agreement for different samples of Mg. The general kinetic equation is $v = k_1 C_{\text{H}_2\text{O}} + k_2 C_{\text{H}_3\text{O}^+} + k_3 C_A + \dots$ etc., where A is an acid other than H_3O^+ or H_2O . For strong acids the primary reaction is with H_3O^+ . For weak acids the rate of reaction is not $\propto \text{H}^+$, but the increase in rate is \propto to the concn. of acid. The effect of surface speed of the metal and viscosity of the liquid has been investigated. Temp. coeffs. are given for the H_2O , H_3O^+ , and mol. AcOH reactions. The results have been discussed in relation to the diffusion theory and the Bronsted-Kilpatrick theory, and they are definitely not in agreement with the old diffusion theory, but may be considered in terms of a modified diffusion theory based on the extended theory of acids. Any modification must, however, account for the H_2O reaction. There is a general relationship between velocity coeff. and acid strength. M. S. B.

Dependence of inflammation temperature on size of metal particles. G. TAMMANN and W. BOEHME (*Z. anorg. Chem.*, 1934, **217**, 225—236).—The variation of inflammation temp. with cross-section has been determined for strips of electrolytic Fe, Mn, Mg, Ce, and Ce-Fe alloy. The inflammation temp. increases hyperbolically with increasing cross-section of the strips to a limiting temp. Fe particles torn off by grinding steel on a carborundum wheel have been examined microscopically and curves obtained showing the distribution of the burnt particles according to size and also of unburnt particles. The causes of the differences are discussed. The inflammation temp. of pyrophoric

particles of Fe and Ni has been determined in air and O_2 , and of Co in air. Os powder forms OsO_2 immediately on contact with air and then glows at a higher temp. (approx. 500°) forming OsO_4 . On heating an Fe wire of diameter 0.2 mm. in air with a current of 2.5 amp. thickening takes place and the wire inflames. The addition of Ni, Si, or Al to Fe diminishes the rate of thickening of the oxide skin and raises the inflammation temp. of narrow strips considerably, but of broad strips much less. Au does not affect the inflammation temp. The influence of shape and of the fusibility and volatility of the metal and its oxide is discussed. M. S. B.

Exothermic phenomenon of soft steel piece in nitric acid solution and its significance. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 17—19).—The initial rise in temp. of steel immersed in HNO_3 solution is due to surface oxidation. The larger temp. increase which follows is attributed to the heat of oxidation of H_2 liberated by dissolution of the steel. After the max. temp. is reached, the corrosion velocity decreases sharply. The temp. rise and corrosion both increase with increasing $[HNO_3]$ up to a certain limit (47% HNO_3), after which they fall rapidly. R. S.

Kinetics of the sol-gel transformation. II. Influence of sol concentration and temperature on the coagulation of inorganic jellies. H. L. DUBE (Z. anorg. Chem., 1934, 217, 284—288).—The sols examined were $FePO_4$, ZrO_2 , and Al_2O_3 . In the equation $\log S = \log R + p \log c$, p remains const. with increasing sol. concn., whilst $\log R$ gradually increases from negative to positive. Rise in temp. produces the same effect, except that in certain circumstances p may change slightly. M. S. B.

Corrosion at contact with glass. R. B. MEARS and U. R. EVANS (Trans. Faraday Soc., 1934, 30, 417—423).—The probability of corrosion of steel rods at the points of contact with glass or steel rods resting on them in 0.05N- Na_2CO_3 solution decreases with stirring, increases with the diameter of the resting rod, is approx. independent of the time after 10 min., and is greater for steel-steel than for steel-glass contacts. Differential aeration accounts for these results. R. S. B.

Influence of films on corrosion. W. MACHU [with W. J. MÜLLER] (Oesterr. Chem.-Ztg., 1934, 37, 46—50, 64—68).—A summary of published work (cf. A., 1932, 1238). E. S. H.

Active oxides and oxide hydrates. LXXXI. Dehydration of copper sulphate pentahydrate in relation to its mode of preparation and exposure to light. S. ŠKRAMOVSKÝ, R. FORSTER, and G. F. HÜTTIG (Z. physikal. Chem., 1934, B, 25, 1—26).—The rate of dehydration, v , at 70° of $CuSO_4 \cdot 5H_2O$ (I) in a current of N_2 containing H_2O vapour under 7.6 mm. partial pressure has been investigated by means of a new type of apparatus registering the change in wt. automatically. v is independent of the degree of dispersity of the (I), remains const. practically throughout each stage of the dehydration, and is proportional to the wt. of (I) and the vol. of the container. With increasing rate of gas flow v rises

and attains a const. val. (I) cryst. from H_2O gives on isothermal dehydration first $CuSO_4 \cdot 3H_2O$ (II), which after some time begins to change to $CuSO_4 \cdot H_2O$ (III). The length of the flat portion corresponding with (II) on the dehydration curve is reduced by raising the dehydration temp. or adding nuclei of (III) and is short with (I) cryst. from aq. H_2SO_4 . The flat portion is absent with (I) cryst. from EtOH. Addition of (II) accelerates the decomp. giving (II), and (III) accelerates the formation of (III). (I) cryst. from EtOH then exposed to light approximates in behaviour on dehydration to (I) cryst. from H_2O . The dehydration curves of $K_2Cu(SO_4)_2 \cdot 6H_2O$ and $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ show the existence of $M_2Cu(SO_4)_2 \cdot 2H_2O$. (I) probably exists in two isomeric forms according as it is crystallised from H_2O or EtOH. R. C.

Kinetics of reaction between silver bromide and photographic sensitizers. B. H. CARROLL and D. HUBBARD (Bur. Stand. J. Res., 1934, 12, 329—344).—The reactions of AgBr with (a) Na_2SO_3 and (b) allylthiocarbamide have been followed by determining the change in $[Br^-]$. The solubility of AgBr in (a) and (b), and the adsorption of KBr by AgBr have been measured. Reaction (a) is autocatalytic and appears to take place by decomp. of dissolved material at the surface of Ag_2S . Reaction (b) is also autocatalytic, but the mechanism is doubtful. E. S. H.

Mechanism of metallic corrosion. U. R. EVANS and T. P. HOAR (Trans. Faraday Soc., 1934, 30, 424—432).—Whether passivity or corrosion occurs at an anode (or naturally) may be determined by the formation of a solid hydroxide or a sol. salt as an anodic product. The bearing on the control of corrosion of the type of anodic and cathodic polarisation curve is discussed (cf. Whitby, this vol., 36). R. S. B.

Measurement of corrosion.—See B., 1934, 364.

Mechanism of acetylation of cellulose fibres. E. ELOD and H. SCHMID-BIELENBERG (Z. physikal. Chem., 1934, B, 25, 27—51).—The rate of acetylation of dry or air-dry natural cellulose fibres depends on the speeds of inter- and intra-micellar diffusion of the reaction mixture within the fibre. The reaction velocity in the air-dry state decreases in the order cotton > ramie > hemp and flax because the tendency to parallel orientation of the micelles increases and therefore the rate of intermicellar diffusion decreases in this order. Intermicellar swelling with H_2O or glacial AcOH increases the reaction velocity and when this swelling is a max. the differences in reactivity between the various fibres are absent, which points to equality in micellar surfaces and similarity in micellar structure. The rate of intramicellar diffusion, which seems to be the same for all the fibres, may be increased by intramicellar swelling before or during acetylation, this type of swelling being promoted by high AcOH content of the acetylating mixture. It is calc. that 40% of the OH groups are in the micelle surfaces. Lowering the temp. of acetylation or shortening the time by preliminary swelling increases the mol. wt. of the resulting acetate. Acetates obtained from the different fibres under comparable conditions are of

similar mol. wt., indicating that the principal valency chains in the micelles of the different fibres are of similar length.

R. C.

Stability of cellulose nitrates; hydrolysis and oxidation by dilute nitric acid. DESMAROUX (Compt. rend., 1934, 198, 1419—1421).—The extents of simultaneous hydrolysis, esterification, and oxidation of cellulose nitrate (I) (13.4% N) by prolonged heating with 25% aq. HNO_3 were compared. The osmotic pressure of residual (I) increased with the time of heating.

B. W. B.

Relation between the rates of some acid-catalysed reactions and the acidity function, H_0 . L. P. HAMMETT and M. A. PAUL (J. Amer. Chem. Soc., 1934, 56, 830—832).—The logarithms of the rates of hydrolysis of sucrose, EtOAc , and $\text{CN}\cdot\text{NH}_2$ in solutions of various strong acids up to 7*M* vary linearly with the acidity function.

E. S. H.

Inversion of sucrose in heavy water. E. A. MOELWYN-HUGHES and K. F. BONHOEFFER (Naturwiss., 1934, 22, 174).—The velocity of inversion of sucrose, catalysed by H_2SO_4 , in H_2O is $>$ in H_2O . The reaction proceeds according to the first-order equation, and the velocity is approx. proportional to $[\text{H}^+]$.

A. J. M.

Kinetics of catalytic hydrogenation. G. M. SCHWAB and W. BRENNKE (Z. physikal. Chem., 1934, B, 24, 393—406).—The rate of hydrogenation of Et cinnamate in EtOH solution under 200—700 mm. H_2 pressure is independent of the latter and is given by $-dc/dt = kc/(1+bc)$, where c is the ester concn., and b and k are consts. The temp. coeff. corresponds with a heat of activation of approx. 11 kg.-cal. With gradual poisoning of the catalyst the active centres are put out of action in order of decreasing activity. Cu has no catalytic action, but dissolved in Ni in amounts \approx about 33 at.-% increases its activity.

R. C.

Colloidal condition of cholesterol, cholesteryl ester, and lecithin. IX. Nature of catalysis by cholesterol. I. REMESOV (Biochem. Z., 1934, 269, 63—68; cf. this vol., 153).—HCN and $\text{UO}_2(\text{NO}_3)_2$ have no sp. effect on the catalytic action (I) of cholesterol (II). (I) is inhibited by Hg, HgCl_2 , and $\text{Hg}(\text{NO}_3)_2$ and is therefore "peroxidative." Saturated derivatives of (II) (dibromide, β -cholestanol) have no (I).

W. McC.

Mechanism of macropolymerisation reactions. W. CHALMERS (J. Amer. Chem. Soc., 1934, 56, 912—922).—Theoretical. The stepwise theory of macropolymerisation is considered in detail and rejected in favour of a "polymerisation-chain" mechanism, which comprises (i) a primary activation of the monomeric compound and (ii) a subsequent process of concatenation (made possible by the existence of free terminal linkings on all the intermediate stages). The linking of monomeric units proceeds initially at a rate which is almost instantaneous compared with that of activation; for very large chain-lengths, the rate becomes increasingly slow. Initiation and propagation of the chain are considered from the viewpoint of energetics and of the phenomenon of negative catalysis. It is suggested that in catalytic processes

the "trigger" mol. is formed by addition of the catalyst to one unsaturated atom; the resultant complex thus possesses a free linking.

H. B.

Enolisation as directed by acid and basic catalysts. II. Enolic mechanism of the haloform reaction. P. D. BARTLETT (J. Amer. Chem. Soc., 1934, 56, 967—969).—The rate-controlling factor in the reaction of COMe_2 (I) with alkaline NaOBr and NaOI at 0° is the enolisation of (I). The rate is $\propto [\text{OH}^-]$ and is the same in both cases. The rate of enolisation is several hundred times that of the reaction of (I) with alkaline NaOCl ; the latter is controlled by a bimol. reaction between $\text{CH}_3\cdot\text{CMe}\cdot\text{OH}$ and OCl^- . The halogenation of (I) is interpreted electronically.

H. B.

Autoxidation reactions. VII. Dative or coordination peroxide theory of autoxidation. N. A. MILAS (J. Physical Chem., 1934, 38, 411—418).—Further data are cited in support of the theory and in refutation of Stephens' criticism (A., 1933, 361).

M. S. B.

Autoxidation. IV. Mechanism of addition of oxygen. H. N. STEPHENS (J. Physical Chem., 1934, 38, 419—426).—A reply to Milas (cf. preceding abstract).

M. S. B.

Absorption of oxygen by linseed oil in presence of catalysts of different oxidation-reduction potentials. B. F. CHOW (J. Amer. Chem. Soc., 1934, 56, 894—898; cf. this vol., 261).—An empirical equation relating the rate of O_2 absorption of linseed oil to the potential of the catalyst [$\text{K}_3\text{Fe}(\text{CN})_6$ (I); $\text{K}_3\text{Mo}(\text{CN})_8$ (II); $\text{K}_3\text{W}(\text{CN})_8$ (III)] is developed. Inhibition of the O_2 absorption [using (I)] is found with acetoxime (IV), α -aminoisobutyric acid, *dl*-serine, arginine, histidine, cinnamic acid, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, *m*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, and *o*- and *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$; (IV) has the max. effect. NPhMe_2 is a catalyst (cf. *loc. cit.*). A "secondary" O_2 absorption is found with (II) and (III) at $p_{\text{H}} \leq 9$.

H. B.

Poisoning and activation of aluminium and cadmium when dissolving in hydrochloric acid. K. JABŁCZYŃSKI and T. PIERZCHALSKI (Z. anorg. Chem., 1934, 217, 298—304).—The action of 1.4*N*-HCl on Al, unlike that on Zn (A., 1932, 1004), is retarded by HCNS, the max. effect being obtained with 0.0005*N*-HCNS. In 0.05*N* there is no effect. This is explained by supposing that the reaction takes place in three stages, one being poisoned by HCNS and another activated. $\text{CS}(\text{NH}_2)_2$, KCN, CS_2 , KCl, K_2SO_4 , and FeCl_3 are accelerators, whilst $\text{CO}(\text{NH}_2)_2$ has no action. HCNS accelerates the dissolution of Cd in 7*N*-HCl, the effect being a max. at 0.0025*N*, the action between Cd and HCl probably taking place in two stages. $\text{CS}(\text{NH}_2)_2$ and I have also an accelerating action, but KCN and $\text{CO}(\text{NH}_2)_2$ have no effect. From these and previous results it is concluded that the dissolution process of metals in acids depends not only on diffusion, but also on special chemical reactions taking place either in the solution or at the surface of the metal.

M. S. B.

Current problems in catalysis. E. B. MAXTED (J.S.C.I., 1934, 53, 102—105*T*).—A crit. review of the

evidence relating to the heterogeneity of catalyst surfaces. R. S.

Catalytic activity and ferromagnetism. J. A. HEDWALL and E. GUSTAVSON (*Svensk Kem. Tidskr.*, 1934, 46, 64—65).—The catalytic activity of Ni for the reaction $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$ increases suddenly at the Curie point (360°). The sudden application of a magnetic field of 2000 gauss to the catalyst has no effect. R. P. B.

Activated adsorption and para-ortho-hydrogen conversion on charcoal. R. BURSTEIN and P. KASHTANOV (*Nature*, 1934, 133, 571—572).—The half-val. period of the para-ortho conversion measured at 20° decreases practically linearly when the amount of H_2 adsorbed at 500° increases. Adsorption of 0.17 c.c. of H_2 per g. of charcoal reduces the velocity nearly to zero, and further adsorption of H_2 has no effect. The change in catalytic activity produced by the activated adsorption cannot be explained merely by a decrease in the van der Waals adsorption, which is practically unaffected by a previous activated adsorption of 0.17 c.c. of H_2 . L. S. T.

Heavy hydrogen. I. A. FARKAS and L. FARKAS. II. **Ortho-para conversion.** A. FARKAS, L. FARKAS, and P. HARTECK (*Proc. Roy. Soc.*, 1934, A, 144, 467—480, 481—493).—I. The concn. of H_2^1 in a mixture of H isotopes (0.002 c.c.) is determined with an accuracy of 0.2% by a method based on their different sp. heats. The equilibrium in the mixture $\text{H}_2^1 + \text{H}_2^2$ balanced with H^1H^2 is rapidly established at the surface of a hot Ni wire. The equilibrium const. is about 4, in agreement with theory, and the establishment of the equilibrium is used to determine the mols. of H_2^1 , H_2^2 , and H^1H^2 in a sample of H_2 . H_2^1 and H_2^2 can be separated by pumping the gas at low pressures through a fine nozzle. If a H_2^1 – H_2^2 mixture diffuses through a Pd tube, the H_2^1 : H_2^2 ratio of the diffusing gas is the greater the lower is the temp., but above 300° this ratio is equal to that of the original gas.

II. The ortho-para conversion of H_2^2 , catalysed by charcoal, has been measured by thermal conductivity methods. The heterogeneous ortho-para conversion at 20.4° abs. proceeds at nearly the same rate for H^1 and H_2^2 under the experimental conditions. The reconversion of ortho- H_2^2 into normal H_2^2 by the paramagnetic mol. O_2 is that of the corresponding reaction for H_2^1 , indicating that the magnetic moment of the H^2 nucleus is about 1/5 of that of the proton. L. L. B.

Para-ortho-hydrogen transformation catalysed by ions of the iron group. Relation of magnetic ionic moment to concentration. H. SACHSSE (*Z. physikal. Chem.*, 1934, B, 24, 429—436).—The rates of transformation in 0.001–1M aq. solutions of Mn, Fe^{II} , Co, Ni, and Cu sulphates are independent of the previous history of the solutions and show that the magnetic moments of the cations are independent of the concn. over the whole concn. range. In this group of metals the order of magnetic cross-sections is the reverse of the order of Goldschmidt ionic radii. R. C.

Recombination of oxygen and hydrogen atoms on metallic surfaces. S. J. ROGINSKI and A. B.

SCHECHESTER (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 1, 310—312).—The process of recombination of atoms on metallic filaments was proved by the change of resistance of the filament and the concn. of atoms determined by the diffusion method of Wrede. Results for Pt and Pd over a temp. range 150 – 900° are given. Recombination is accompanied by a stage involving an energy of activation of 2000 g.-cal. W. R. A.

Electrical condition of hot surfaces during the adsorption of gases. V. Charging up of hot surfaces. J. C. STIMSON. VI. Gold surface catalysing the combustion of carbon monoxide. G. I. FINCH and B. W. BRADFORD (*Proc. Roy. Soc.*, 1934, A, 144, 307—320, 320—339; cf. A., 1931, 1006).—V. Measurements of the rates of attainment of steady potential by Au, Ni, Pt, C, and Cu surfaces after earthing indicate that the rate of charging up of a surface is a linear function of its instantaneous potential. The effect of temp. is very marked. The hot surface probably emits positive electricity over the temp. range investigated (up to 850°).

VI. Moist or dry $2\text{CO} + \text{O}_2$ mixtures were circulated over an electrically insulated heated Au gauze surface connected with a Lindemann quadrant electrometer. The reaction velocity, the rate of charging up, and the equilibrium potential of the surface were recorded. It is found that (i) the structure of the surface most suitable for the promotion of the combustion of dry CO differs from that required for moist CO; (ii) the reaction velocity in the moist is $>$ in the dry reacting system, but with rising temp. the differences between the rates in the two systems diminishes, until at about 550° approx. equality is reached; and (iii) that changes in the catalytic activity of the surface are paralleled by changes in the rate of electrical charging. L. L. B.

Catalytic activity of solid mercuric chloride in the reaction between hydrogen chloride and acetylene, compared with the catalytic activity of gaseous mercuric chloride. J. VAN DALFSEN and J. P. WIBAUT (*Rec. trav. chim.*, 1934, 53, 489—496).—The reaction between HCl and C_2H_2 has been investigated at temp. of 100° and 200 – 260° , in presence of HgCl_2 on SiO_2 gel (I), of cryst. HgCl_2 (II), and of HgCl_2 vapour (III). (II) shows very low catalytic activity compared with (I), whilst (III) is practically inactive. H. S. P.

Influence of various metallic oxides as catalysts in promoting oxidation of methane by means of copper oxide. A. ARNEIL (*J.S.C.I.*, 1934, 53, 89—92T; cf. Campbell and Gray, *ibid.*, 1930, 49, 477T).—A 5% CH_4 – N_2 mixture was passed at various temp. through a column of CuO impregnated with various metallic oxide catalysts, and the temp. of initial and complete oxidation were determined graphically. The optimum proportion of CoO was approx. 4 wt.-% and caused oxidation to begin at 220° and to be complete at 620° . The other catalysts and corresponding temp. were 4% CeO_2 (255° , 555°), 4% Cr_2O_3 ($< 200^\circ$, 640°), 1% Fe_2O_3 ($< 200^\circ$, 510°), 4% Fe_2O_3 (270° , 505°), 4% MoO_3 (240° , 695°), 4% U_3O_8 ($< 200^\circ$, 710°). The temp. necessary for complete oxidation with 4% Fe_2O_3 was $200^\circ <$ that

required by CuO alone. In the case of CoO and Fe_2O_3 the concn. of the catalyst had a relatively small influence on the catalytic activity.

Equilibrium studies in reactions between carbon disulphide and hydrogen. E. TERRES and E. SASSE (*Angew. Chem.*, 1934, 47, 238—243).—By using suitable catalysts the products of the reaction between CS_2 and H_2 at 500—900° can be restricted to CH_4 and H_2S . The reverse reaction proceeds reasonably rapidly over Pt; for the direct reaction Pt can be used above 800° and Mo above 600°. The same equilibrium is reached from both sides and the vals. of the const. agree reasonably with those calc. by the Nernst equation for the reaction $4\text{H}_2 + \text{CS}_2 = \text{CH}_4 + 2\text{H}_2\text{S} + 49,760 \text{ g.-cal.}$ A. G.

Catalytic vapour-phase hydration of ethylene.—See B., 1934, 392.

Determination of the value of a gas for tungsten lamps by observation of tungsten sputtering. A. P. STVOLIN (*J. Tech. Phys. U.S.S.R.*, 1932, 2, 1034—1052).—Traces of O_2 or H_2O cause oxide formation at 1400—2600°; N_2 and A catalyse the reaction. H_2O yields W_2O_5 ; O_2 yields WO_3 . Pressure increases oxide formation. CH. ABS.

Course of reactions in the solid state. W. JANDER (*Angew. Chem.*, 1934, 47, 235—238).—A review. At the temp. at which reaction begins at the interface of two solids, or at a slightly lower temp., other properties change; e.g., the catalytic effect or sorptive power is increased. When several reaction products are possible, as with CaO and SiO_2 , the same compound ($2\text{CaO} \cdot \text{SiO}_2$) is generally formed initially and this is converted into other compounds under favourable conditions. A mechanism is proposed. A. G.

Behaviour of iron catalysts with illuminating gas and similar gases between 250° and 450°.—See B., 1934, 390.

Catalytic oxidation of toluene in the vapour phase. J. K. CROWDHURY and S. C. CHOUDHURY (*J. Indian Chem. Soc.*, 1934, 11, 185—196).—The catalytic activities of NiO , V_2O_5 , Al and Sn vanadates with and without the addition of Al_2O_3 or SiO_2 gel have been compared in regard to the formation of BzOH at various temp. The efficiency of reduced NiO and of V_2O_5 or Sn vanadate can be increased by respective addition of Al_2O_3 and SiO_2 gel. F. L. U.

Catalysts for destructive hydrogenation. I. Hydrogenation of naphthalene in the presence of molybdenum sulphide. M. S. NEMTSOV and G. V. SPOVSKI (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 1, 494—500).—Almost complete reduction of MoS_3 to MoS_2 occurs during the hydrogenation of C_{10}H_8 in presence of MoS_3 . MoS_2 is a much less efficient catalyst, and the rate of decomp. of the tetrahydro-naphthalene (I) decreases considerably. To avoid reduction of MoS_3 it would be necessary to bring H_2S into the reaction at 100 atm. pressure, so the method is of little technical val. A method suggested is to hydrogenate C_{10}H_8 to (I) in presence of MoS_2 at a low temp., and then to decompose (I) at a higher temp. in absence of a catalyst. It is essential to have no catalyst present at the higher temp., since the

reduction equilibrium is reversed and there is a tendency to re-form C_{10}H_8 . J. W. S.

Aerogel catalysts. Thoria; preparation of catalyst and conversions of organic acids into ketones. S. S. KISTLER, S. SWANN, jun., and E. G. APPEL (*Ind. Eng. Chem.*, 1934, 26, 388—391).—As catalysts aerogels have the advantages of large surface, free space, and capillary diameter. ThO_2 aerogels were prepared in two ways and were more efficient catalysts for the conversion of aliphatic acids into ketones than other forms of ThO_2 and than other oxides. A. G.

Cellulose deterioration. I. Autoxidation of mannitol. D. J. SALLEY (*J. Physical Chem.*, 1934, 38, 449—463).—The oxidation of mannitol by gaseous O_2 in presence of FeCl_3 and NaOH is auto-accelerating. The effect of variation of concn. of reactants and of temp. has been investigated. The reaction is accelerated by light. The quantum yield determined by the difference between the light and the dark reaction, and the absence of inhibiting effect by known oxidation inhibitors, indicate that the oxidation has not a chain mechanism. Quinol, which normally acts as an inhibitor, is in this case an accelerator. The presence of thermally decomposing H_2O_2 accelerates the rate of absorption of O_2 from the gas phase by aq. mannitol in the dark. A comparison is drawn between the oxidation of alkali-cellulose and of alkaline mannitol solutions by atm. O_2 , and the application to the deterioration of cellulose and to bleaching processes is indicated. M. S. B.

Theory of the separation of H^1 and H^2 by electrolysis of water. R. H. FOWLER (*Proc. Roy. Soc.*, 1934, A, 144, 452—466).—The theory of the separation of H^1 and H^2 by the electrolysis of H_2O is discussed. The requirements of a steady state are applied to the various possible mechanisms of the H_2 electrode. The separation may be due to different overpotentials, as proposed by Polanyi, or to different combination rates for mol. formation on the surface; or both these factors may be operative.

L. L. B.

Electrolytic preparation of sodium perborate. II. F. KAWAMURA and H. MOHRI (*J. Electrochem. Assoc.*, 1934, 2, 10—14).—Cathodic reduction (I) in a bath containing alkali borate and carbonate is diminished by addition of KCl , H_2SiF_6 , and Na_2SiO_3 . A little Na_2CrO_4 and Turkey-red oil lessens (I). Superposition of a.c. on d.c. does not favour the formation of NaBO_3 . The optimal temp. is 10—12° and optimal c.d. 10—15 amp. per sq. dm. at 6 volts.

CH. ABS.

Electro-deposition of nickel from alkaline electrolytes. M. BALLAY (*Compt. rend.*, 1934, 198, 1494—1496).—Pptn. from ammoniacal solutions of Ni salts is prevented by citric, glycolic, and lactic acids and their alkali salts, but not by malic or tartaric acids, glucose, maltose, or glycerol. An electrolyte containing 20.8 g. Ni, 6.3 g. NH_4 , 6.0 g. Cl, and 150 g. neutral Na citrate per litre gave good deposits at p_H 3.6—9.8 and c.d. 2—10 amp. per sq. dm., at 40°. The current efficiency varied considerably with p_H , rising to 94.2% at p_H 9.6. B. W. B.

Cuprous oxide rectifier. T. ASADA (Japan. J. Physics, 1934, 9, 1—25).—The voltage-current characteristics of some Cu_2O -coated Cu plates, of which a superficial layer of the Cu_2O had been reduced to Cu, have been investigated, singly and in the form of full-wave rectifiers. An amplifying system for a microphotometer is described, in which the light beam falling on a Cs photo-cell is made intermittent, the photocurrent being amplified with valves and rectified with a full-wave Cu_2O rectifier of known characteristic.

J. W. S.

Structure of electrolytic deposits of copper formed in presence of colloids.—See B., 1934, 365.

Oxide coating of aluminium. W. C. VON GEEL and H. EMMENS (Physica, 1934, 1, 415—416).—Anodic oxidation of Al forms a cryst. oxide layer (I), using low c.d., and an amorphous oxide layer (II) with high c.d. Al covered with (II) may be oxidised a second time under conditions producing (I), which then forms under (II). The current efficiency is then 100%, whereas when (I) is formed directly in absence of (II) it is always < 100%. The ions pass through (II) in order to form (I).

H. J. E.

Alkaline storage battery. IV. Alkali zincate battery with nickel mesh cathode. 2. S. TANAKA and K. IWASA (J. Electrochem. Assoc., Japan, 1933, 1, 253—256).—A porous Fe or Ni-Fe plate prevents the formation of a deposit at the lower end of the anode. For preliminary treatment of the anode, amalgamation is most effective. The best electrolyte is 6—7*N*-KOH containing ZnO (KOH : ZnO = 12—15).

CH. ABS.

Electrolytic desensitisation. E. BAUR (Z. Elektrochem., 1934, 40, 184—188).—The desensitising action of FeSO_4 , CuSO_4 , MnSO_4 , KI, quinol, and metol on the reaction of UO_2SO_4 with HCO_2H under the influence of light is also observed when the aq. system is electrolysed in the dark. The mechanism is discussed.

E. S. H.

Theory of electrolysis of melts. P. DROSSBACH (Z. Elektrochem., 1934, 40, 180—182).—Theoretical.

E. S. H.

Conjugated systems. X. Electrolytic reduction of β -vinylacrylic acid.—See this vol., 631.

Heterogeneous chemical reactions in the silent electric discharge. VII. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1934, 9, 139—149).—The reduction of inorg. solids by H_2 in the silent electric discharge has given the following results: $\text{LiNO}_3 \rightarrow \text{LiOH}$, LiNO_2 , NH_3 , and NO_2 ; $\text{Be(NO}_3)_2 \rightarrow \text{Be(OH)}_2$, NH_4 salt, NO_2' , NO_2 , and NO ; $\text{Hg(NO}_3)_2 \rightarrow \text{HgO}$, Hg^{I} salt, NH_4 salt, NO_2' , and NO_2 ; $\text{HgNO}_3 \rightarrow \text{HgO}$, Hg , NH_4 salt, NO_2' , NO_2 , and NO ; $\text{Pb(NO}_3)_2 \rightarrow \text{Pb(OH)}_2$, NH_4 salt, NO_2' , Pb , NO_2 , and NH_3 ; $\text{Bi(NO}_3)_3 \rightarrow \text{Bi(OH)}_3$, NH_4 salt, NO_2' , Bi , NO_2 , and NO ; $\text{Al(NO}_3)_3 \rightarrow \text{Al}_2\text{O}_3$, NH_4 salt, NO_2' , and NO_2 ; $\text{NH}_4\text{NO}_3 \rightarrow \text{NO}_2'$, NH_3 , and NO .

H. S. P.

Relative reactivities of the hydrogen isotopes with chlorine. G. K. ROLLEFSON (J. Chem. Physics, 1934, 2, 144—145).—It is shown from a relation governing the reaction of mixtures of H_2 , 2_2 , and CO, illuminated by light absorbed by the

Cl_2 , that H^{I} mols. are less reactive than H_2 in the formation of HCl, since, for the former, the heat of activation is slightly higher.

N. M. B.

Destruction of nuclei by developing agents. LUPPO-CRAMER (Z. wiss. Phot., 1934, 32, 302—308).—The degree to which the latent image is removed by solutions of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ or its hydrochloride was tested on many different makes of plates. The most active concn. is generally about 1 : 1000. The weaker action of more conc. solutions is attributed to the adsorption of Br^{I} necessary for rebromination of the Ag nuclei. Chloroquinol is, unexpectedly, similar in behaviour.

J. L.

Premature image reversal. LUPPO-CRAMER (Z. wiss. Phot., 1934, 32, 295—301).—Various conditions under which reversal is obtainable before full exposure (*i.e.*, that required for D_{max}) is reached are discussed. AgI emulsions, lightly fogged, will show reversal with subsequent small exposures. If these emulsions are specially treated (nuclei removed with rhodamine), the effect occurs even without the preliminary fogging. In no case is the effect observed with physical development, which acts only on the surface of the grains.

J. L.

Blackening of photographic layers by electrons and electron-excited fluorescence. B. VON BORRIES and M. KNOLL (Physikal. Z., 1934, 35, 279—289).—A no. of results are collected and discussed. For both long (10^2 — 10^2 sec.) and short (10^{-5} — 10^{-8} sec.) exposures to electron beams the blackening follows the Bunsen-Roscoe law. The sensitivity of various emulsions towards blackening by electron beams was investigated. The blackening produced by the fluorescence of various substances under the influence of an electron beam was studied, and the substances arranged in order of intensity of blackening produced. The sensitivity of various types of emulsion was also investigated as for the electron beam itself.

A. J. M.

Theory of ideal colour-sensitivity of photographic emulsions. II. Ideal colour filter. J. E. DE LANGHE (Z. wiss. Phot., 1934, 32, 283—288; cf. A., 1933, 791).—Mathematical. The transmission of an ideal filter is calc. The results are not in agreement with those of previous workers.

J. L.

Quantum theory of the latent photographic image. T. H. JAMES (J. Chem. Physics, 1934, 2, 132—135).—The process of photographic exposure is explained as a true photochemical reaction. The apparent failure of the Einstein equivalence law for short exposures is not real, and an equation is derived, valid for red light to X-rays and for emulsions from Azo to Eastman portrait, on the assumption that absorption of one quantum by a sensitivity centre of the grain produces an activated but unstable state which renders the grain as a whole developable. A preliminary treatment of the Herschel effect is given.

N. M. B.

Photochemical oxidation and absorption spectra of solutions containing tervalent antimony. W. BRULL [with H. SCHLAGEL] (Z. anorg. Chem., 1934, 217, 401—416).—Solutions of Sb_2O_3 in HCl or tartaric acid and of SbCl_3 in saturated NaCl

are photochemically oxidisable, even by O_2 . In the solutions named the effect is produced in ordinary glass vessels in sunlight, whilst in others (e.g., Sb_2O_3 in H_2SO_4) light of shorter wave-length is required. In most cases a peroxide is formed as an intermediate stage. The oxidation has been studied in relation to the nature of the solution, concn., wave-length and intensity of light. The velocity of the "dark" reaction is very small. F. L. U.

Chain mechanism in autoxidation of sodium sulphite solutions. H. L. J. BACKSTROM (Z. physikal. Chem., 1934, B, 25, 122—138).—The rate, v , of the photochemical autoxidation is given by $v = 0.041I^{0.53}/(c + 0.005 + 0.0041I^{0.53})$, where c is the concn. of inhibitor (EtOH) and I the light intensity. In the oxidation catalysed by Cu the fall of v at high cannot be accounted for by pptn. of the Cu (cf. A., 1925, ii, 567). In the photochemical oxidation in presence of EtOH v is a max. at a p_H at which $>$ half the sulphite is present as HSO_3' . Hence in the reaction chain an active intermediate product must occur which can react with either HSO_3' or the inhibitor. In both the catalysed and photochemical oxidations the primary process is the formation of SO_3' (A., 1931, 917). The first step of the reaction with O_2 is probably $SO_3' + O_2 = SO_5'$. The SO_5' dehydrogenates the HSO_3' , re-forming SO_3' , and so on. The inhibiting action of the alcohol is connected with its induced oxidation, probably $SO_5' + R \cdot CH_2 \cdot OH = SO_4' + R \cdot CHO + H_2O$, the chain being broken by subsequent reaction of the SO_4' . R. C.

Formation of benzene by the photochemical polymerisation of acetylene at high temperatures. R. LIVINGSTON and C. H. SCHIFFLETT (J. Physical Chem., 1934, 38, 377—381).—The presence of C_6H_6 in the products of the photochemical polymerisation of C_2H_2 above 270° has been confirmed by its absorption spectrum. M. S. B.

Photochemical transformation of *trans*-stilbene. A. SMAKULA (Z. physikal. Chem., 1934, B, 25, 90—98).—The quantum yield, E , in the *trans-cis* change in light of the wave-length of the absorption band of the C:C linking is 1, whereas in light of wave-lengths causing vibrational excitation it is 30% smaller. Hence the primary process involves loosening the C:C linking by electron excitation, permitting rotation. In light corresponding with absorption bands of other linkings E is 0.4. On irradiation *cis*-stilbene changes into another substance. R. C.

Action of light on di-iodo-hydrocarbons: di-iodoethylenes. G. EMSCHWILLER (Compt. rend., 1934, 198, 1151—1154).—*as*-Di-iodoethylene, from NaOH and $CHI_2 \cdot CH_2I$, is a colourless liquid, d_{25}^{25} 2.94, b.p. $61^\circ/18$ mm., or about $165^\circ/760$ mm. with decomp. and, after a short interval, detonation. With HI it forms $CMeI_3$. Kaufmann's supposed $CH_2 \cdot Cl_2$ (cf. A., 1922, i, 213) was a mixture of $[CHI]_2$ and C_2I_2 . It is decomposed by ultra-violet light: $2CH_2 \cdot Cl_2 \longrightarrow C_2H_2 + C_2I_2 + (H, I)$; $2C_2I_2 \longrightarrow C_2 + Cl_4$ (cf. A., 1897, i, 389); $CH_2 \cdot Cl_2 + (H, I) \longrightarrow CMeI_3$; with small quantities of CH_4 and C_2H_4 . Although $[CHI]_2$ is not oxidised in ultra-violet light $CH_2 \cdot Cl_2$ is completely oxidised with formation of HCO_2H , a trace of C_2HO ,

I, and gas consisting of CO 57, CO_2 23, and C_2H_4 20% (cf. this vol., 375). C. A. S.

Chlorine-sensitised photochemical oxidation of chloroform in carbon tetrachloride solution. A. T. CHAPMAN (J. Amer. Chem. Soc., 1934, 56, 818—823).—The photochemical chlorination of $CHCl_3$ in CCl_4 is inhibited completely by O_2 ; when Cl_2 is present as a photosensitiser $COCl_2$ and HCl are formed, with an org. peroxide. The rate of oxidation for small light absorption is proportional to the light intensity and $[Cl_2]$, but independent of $[O_2]$ and $[CHCl_3]$. The yield increases 16% per 10° rise in temp. The average quantum yield using monochromatic radiation is 1.70 equiv. of acid per einstein absorbed. E. S. H.

Photokinetics of bromine substitution. IV. Bromination of naphthalene under the influence of light. V. Bromination of alkyl naphthalenes under the influence of light. J. KOZAK and F. PAZDÓR (Bull. Acad. Polonaise, 1933, A, 477—488, 489—498).—IV. The photo-reaction is unimol., with a temp. coeff. 1.57 per 10° between 5° and 30° . The velocity for a given rate of absorption of energy is greatest in blue light.

V. The velocity of photo-bromination of various Me and Et derivatives of $C_{10}H_8$ has also a max. in the blue, but with Br-substitution reactions of these substances and of PhMe there is also a secondary max. in the yellow. Br-addition reactions, e.g., with $CHPh \cdot CH \cdot CO_2H$, show only the max. in the blue.

F. L. U.

Chain mechanism in autoxidation of aldehydes. H. L. J. BACKSTROM (Z. physikal. Chem., 1934, B, 25, 99—121).—The ketone-sensitised oxidation of aldehydes responds to inhibitors in the same way as the ordinary photochemical oxidation, showing the substances propagating the chains to be the same for both. The primary photochemical process in the ketone-sensitised oxidation of alcohols seems to be the "lifting" of the C:O linking of the absorbing mol.: $X_2CO + h\nu \longrightarrow CX_2 \cdot O$. This substance is then able to dehydrogenate the alcohol, giving first a semipinacol radical, $CX_2 \cdot OH$. In the sensitised oxidation of aldehydes it dehydrogenates the aldehyde mol. to $CR \cdot O$, which propagates the chain. The ordinary photochemical autoxidation of an aldehyde may be supposed to be initiated by lifting the C:O linking in an aldehyde mol., which then reacts with an unchanged mol. This theory is supported by the observation that on irradiation of solutions of aromatic ketones in aldehydes in absence of O_2 pinacolones separate, and from pure PhCHO benzoin is formed. Bowen and Tietz' results for the rate of photochemical autoxidation of MeCHO vapour (A., 1930, 234) can be explained by the theory. The rate of photochemical autoxidation of liquid PhCHO in presence of inhibitors is proportional to a power of the light intensity varying from 0.5 to 0.9, depending on the inhibitor, and the rate at which an inhibitor is destroyed varies from one inhibitor to another.

R. C.

Oxidation of mannitol by oxygen photo-sensitised by hydrogen peroxide. D. J. SALLEY (J. Physical Chem., 1934, 38, 465—473).—The oxidation of mannitol by O_2 , photosensitised by H_2O_2 ,

has been investigated for different concns. of mannitol and H_2O_2 . At a const. initial $[\text{H}_2\text{O}_2]$ variation of the mannitol concn. causes an increase in the rate of absorption of O_2 and a simultaneous decrease in H_2O_2 decomp., but at sufficiently high mannitol concn. the rates of these two reactions become independent of the mannitol concn. A max. of 2O_2 is absorbed for each H_2O_2 disappearing, which indicates that the photosensitised oxidation is not a chain process. The results are discussed in relation to Haber and Willstätter's theory of alcohol and aldehyde oxidation. In the presence of NH_4Et , which is an inhibitor of the photolysis of H_2O_2 , the rate of decomp. of H_2O_2 in the mannitol- H_2O_2 mixture is increased, whilst absorption of O_2 apparently decreases, probably owing to the destruction of H_2O_2 with partial evolution of O_2 .

M. S. B.

Ultramicroscopic observations on light-sensitive crystals. II. G. SCHAUM and K. SCHAUM (Z. wiss. Phot., 1934, 33, 13—32; cf. A., 1932, 821).—The behaviour of crystals of AgBr during illumination, irradiation with α -, β -, and γ -rays, and treatment with developers has been studied by dark-ground illumination. Differences due to an excess of Br^+ or Ag^+ have been noted. The observations generally confirm those which have been obtained by ordinary microscopical methods.

F. L. U.

Temperature coefficient of the rate of combination of hydrogen and oxygen under α -radiation. C. H. SCHIFFLETT and S. C. LIND (J. Physical Chem., 1934, 38, 327—337).—The combination of H_2 and O_2 under α -radiation has been studied between -185° and 500° with Rn mixed with the reacting gases and with Rn in an α -ray bulb, with and without circulation of the gases. $-M/N$, the no. of mols. of H_2 and O_2 reacting per ion pair produced both in H_2 and O_2 , remains const. at 4.5 up to 25° , and then rises slowly to 20 at 400° . Between 400° and 500° the vals. are not reproducible owing to the thermal reaction, and above 500° the reaction is explosive. The temp. coeff., 1.02 — 1.05 , is of the same order as the temp. coeff. of the photochemical reaction. The results indicate that in the lower temp. range the reaction is of the stably quantised type, whilst at higher temp. there is a chain mechanism involved. H_2O vapour acts as an ionic catalyst of 100% efficiency.

M. S. B.

Decomposition of gaseous hydrogen sulphide by α -particles. W. MUND, M. SCHOUWENAARS, and K. DEVRIENDT (Bull. Soc. chim. Belg., 1934, 43, 49—72).—At low pressures (60 mm.) and low intensities of irradiation, the decomp. of H_2S by α -particle irradiation proceeds with an ionic yield, I , of about 2.12 . With increase of pressure from 60 to 1400 mm., I increases by about 30%. At high intensities I diminishes, by an amount which is apparently proportional to the square of the intensity. The presence of $>10\%$ of H_2 in the gas does not cause any marked decrease of I .

H. F. G.

Insulating films formed under electron and ion bombardment. R. L. STEWART (Physical Rev., 1934, [ii], 45, 488—490).—Minute traces of org. vapours in evacuated tubes give rise, on surfaces subjected to electron or canal-ray bombardment, to

insulating layers attributed to C compounds formed by polymerisation; they are not explained by the simple ion-deposition theory. The properties and effects of these films are discussed.

N. M. B.

Transmutations by means of electric rays. XV. Electrosynthesis of zinc diethyl. XVI. Transmutation from the viewpoint of modern atomic theory. M. Z. JOVRIĆ (Glas, 1932, Sept., 5 pp.; Chem. Zentr., 1933, ii, 2790).—XV. Under the influence of an electric discharge at reduced pressure various org. and inorg. substances yield condensation products; a loss in wt. is mainly accounted for as newly-formed O_2 . With ZnEt_2 up to 20% of the C and H disappears. The action of the electric rays is "to modify the C and H of hydrocarbons with the consequent formation of O_2 ."

XVI. Nascent H under the influence of electric rays can be changed in such a way that by loss of its electron a new substance is formed, which by combination with electronegative substances can give rise to new syntheses, e.g., $\text{H}^+ + \text{C}^{12} = \text{O}^{16}$.

L. S. T.

Reaction mechanism of oxidation-reduction processes. J. WEISS (Nature, 1934, 133, 648—649).—Theoretical. A simple mechanism for such processes in solution involving the assumption of electron transfers mainly with ions, and possibly H, with the gain or loss of electrons occurring singly, is outlined.

L. S. T.

Reactions between acids and salts. C. BERGELL (Allgem. Oel- Fett-Ztg., 1934, 31, 145—151).—A review, with special reference to fatty acids.

E. S. H.

Fruitless attempts to enrich the heavy hydrogen isotope in water. A. GUNTHER-SCHULZE and F. KELLER (Z. Elektrochem., 1934, 40, 182—183).—A negative result was obtained in attempts to concentrate H_2O by evaporation or electrolysis of H_2O under various conditions.

E. S. H.

Separation of the isotopes of hydrogen by the chemical decomposition of water. Mechanisms underlying the reducing action of dissolving metals. E. D. HUGHES, C. K. INGOLD, and C. L. WILSON (J.C.S., 1934, 493—498; cf. this vol., 375).—The isotopic composition of the H_2 evolved when various metals, alloys, and couples dissolve in aq. H_2O (containing, where necessary, added acid or alkali) has been determined. In all cases, the evolved gas contains a smaller proportion of H_2 than the original liquid. The greatest separation is given by a 50% Zn-Cu couple dissolving in dil. H_2SO_4 . According to the val. of the separation coeff., the metals are divided into three classes, for which the mechanism of the reaction is different and is probably as follows: (A) Ca, Mg, Al (when dissolving in acids), Mn, Zn, Cr, Fe, Co, etc., the electrons of which combine directly with H^+ (e.g., $\text{Ca} + 2\text{H} = \text{Ca}^{++} + \text{H}_2$); (B) K, Na, and Li, which combine directly with H_2O through its O atom, H_2 being subsequently eliminated between two combined H_2O mols. (e.g., $\text{K} + \text{H}_2\text{O} = \text{K}\cdot\text{OH}_2$, $2\text{K}\cdot\text{OH}_2 = 2\text{KOH} + \text{H}_2$); (C) Al and Si dissolving in alkali, the OH^+ combining directly with the Al or Si. The mechanism of dissolution of any given metal may vary with the p_{H} . With Cr, Fe, Ni, and Co, the isotopic separation is <

would be expected; these metals act as hydrogenation catalysts, and it is suggested that they catalyse isotopic interchange between the H_2 and the H_2O . When CaH_2 , CaC_2 , and Al_4C_3 dissolve in aq. H_2O (containing H_2SO_4 in the last instance), the evolved gas (H_2 , C_2H_2 , and CH_4 , respectively) contains less H_2 than the original H_2O . D. R. D.

Natural separation of the isotopes of hydrogen. M. DOLE (J. Amer. Chem. Soc., 1934, 56, 999).— H_2O obtained by the burning of kerosene, C_6H_6 , or honey has higher d than ordinary H_2O . E. S. H.

Interchange of hydrogen atoms between water and acetone. K. SCHWARZ and H. STEINER (Z. physikal. Chem., 1934, B, 24, 153—156; cf. A., 1933, 1242).—In a mixture of heavy H_2O and $COMe_2$ there is no detectable exchange of H atoms even on prolonged boiling, but in presence of NaOH exchange occurs, probably through repeated keto-enol and enol-keto change, and apparently all six H atoms of the $COMe_2$ are exchangeable. R. C.

Formation of hydrogen peroxide by the simultaneous action of oxygen and acids on metals. E. MULLER and H. BARCHMANN (Z. Elektrochem., 1934, 40, 188—193).— H_2O_2 is formed in small quantities when liquid amalgams of Zn react with dil. H_2SO_4 , H_3PO_4 , or $AcOH$ in presence of O_2 . Its formation is probably due to direct oxidation of H, since the yield is greater with Cd amalgam, which causes a slow conversion $2H \rightarrow H_2$. The yield of H_2O_2 is increased further by using $EtOH-H_2SO_4$ and agitating so as to remove the insol. $CdSO_4$ which is formed; a low temp. is also favourable. An apparatus, in which these features are combined, is described. E. S. H.

Reduction of sodium sulphate to sodium sulphide. P. P. BUDNIKOV (Compt. rend. acad. Sci. U.R.S.S., 1934, 1, 332—336).—Temp. at which the reduction of Na_2SO_4 commences are recorded for various charcoals. Since SO_2 can be detected, Na_2SO_4 must react with Na_2S . Na_2SO_4 cannot be reduced by CO below 850° without a catalyst. The reduction with H_2 is endothermic, and is effected without a catalyst at comparatively low temp. W. R. A.

Preparation of alkali fluophosphates. J. M. G. MARQUINA (Anal. Fis. Quím., 1933, 31, 516—523).—In the prep. of fluophosphates by heating P_2O_5 and NH_4F , the highest yield is obtained by working with a mol. ratio of 1 : 3. On treatment of the cooled melt with $EtOH$ (96%), only F_2PO_2' and part of the FPO_3'' dissolve. Details are given of the prep. of $(NH_4)_2FPO_2$; the mixture is heated first at 90° and finally at $130-140^\circ$ in a Ni crucible, and the $EtOH$ extract is neutralised with aq. NH_3 , when the fairly pure salt is pptd. The yield is 90 g. from 100 g. of NH_4F . $(NH_4)_2F_2PO_2$ (60 g.) is obtained by vac. evaporation at $35-40^\circ$ of the $EtOH$ mother-liquor. Na_2FPO_3 and K_2FPO_3 may be prepared by decomp. of the NH_4 salt with NaOH (KOH) and removing the NH_3 from the cold solution by a current of cold air; no hydrolysis occurs. The Na and K difluophosphates, however, cannot be prepared by the corresponding method, as much of the material used hydrolyses. H. F. G.

Basic copper carbonates. (MLLE.) S. HEMAR (Compt. rend., 1934, 198, 1507—1508).—The ppts. formed by mixing $CuCl_2$ and Na_2CO_3 solutions (I) were shown to be $8CuO \cdot 3CO_2 \cdot xH_2O$ or $2CuO \cdot CO_2 \cdot yH_2O$ according as the concns. of (I) were 0.025—0.05M or 0.125—1.0M, respectively. Malachite formed from the foregoing ppts. had the composition $2CuO \cdot CO_2 \cdot 1.5H_2O$, and thermal analysis gave no indication of a monohydrate. Other reported basic carbonates of Cu are discussed. B. W. B.

Action of iodine on silver oxide. M. LEMARCHANDS and (MLLE.) D. SAUNIER (Compt. rend., 1934, 198, 1501—1502).— Ag_2O decolorised a solution of I in CCl_4 , forming a green compound, Ag_2OI_2 (a), insol. in H_2O and CCl_4 . (a) was decomposed by heat (at $148-170^\circ$, leaving AgI), by aq. KOH (giving $AgOH + KIO_3 + KI$), and by HNO_3 (giving $AgIO_3 + AgI$), and oxidised As_2O_3 in acid solution. Other reactions are described. B. W. B.

Reduction of silver salts with hydroxylamine. M. L. NICHOLS (J. Amer. Chem. Soc., 1934, 56, 841—845).—The composition of the gaseous products of reaction varies with the concn. of the alkali and the temp. AgBr in presence of NaOH gives N_2O and N_2 ; $AgNO_3$ in presence of excess of NH_3 gives N_2 , but in presence of NaOH and Na_2SO_3 yields N_2O and N_2 . E. S. H.

Calcium thiosulphate. P. PETROVICI (J. Pharm. Chim., 1934, [viii], 19, 392—394).— $Ca_2S_2O_3 \cdot 6H_2O$ is stable at 18° when the H_2O v.p. is 9—12 mm. It loses $5H_2O$ when kept over 50% H_2SO_4 or heated at 30° and at $> 80^\circ$ decomp. to $CaSO_3$, S, and H_2O commences. E. H. S.

Ammoniates of double salts. III. G. SPACU, P. SPACU, and P. VOICHESCU (Z. anorg. Chem., 1934, 217, 339—345; cf. this vol., 375).—The existence of the following compounds has been established: $K_4CdCl_6 \cdot nNH_3$ ($n=2, 6, 10$); $RbCdCl_3 \cdot nNH_3$ ($n=2, 6, 10$); $Rb_2ZnCl_4 \cdot nNH_3$ ($n=1, 2, 4, 6, 10$); $Cs_2ZnCl_4 \cdot nNH_3$ ($n=1, 2, 3, 4, 6, 9$). In each case the first mol. of NH_3 is attached to the central atom more strongly than the succeeding mols. F. L. U.

Volatilisation, solubility, and oxidation of metallic mercury. A. STOCK [with F. CUCUEL, F. GERSTNER, H. KOHLE, and H. LUX] (Z. anorg. Chem., 1934, 217, 241—253).—When air or O_2 is excluded Hg dissolves in H_2O to a very small extent only. In presence of air it dissolves gradually until the concn. corresponds with the solubility of HgO . The solubility is increased in presence of KOH and to a smaller extent with KCl. From a saturated solution of HgO Hg vapour passes into the air, and also from aq. ($HgCl_2 + KCl$). Blood takes up Hg from the air quantitatively, and most org. liquids dissolve it more readily than H_2O , e.g., C_6H_6 , CS_2 , etc. Thus Hg vapour passes into the air through a layer of H_2O or org. liquid over its surface. It will also pass through layers of solid substances, e.g., S, SiO_2 gel, and P_4S_3 . Various fabrics such as wool, silk, artificial silk, and linen, also moist beet residues and active C or active C impregnated with I, absorb Hg vapour from the air. The presence of H_2S in the atm. does not greatly affect the volatility of Hg, Cl_2 reduces it considerably, and I vapour inhibits it, a layer of HgI and HgI_2 forming

over the surface. If air containing Hg vapour is passed through H₂O and aq. KCl, KOH, and H₂SO₄, the solutions, except 50% KOH, take up much > pure H₂O. Conc. H₂SO₄ takes up a large quantity. The volatility of droplets of varying size has also been investigated. In H₂, the volatility is > in air, probably due to surface oxidation in the latter. The results explain various phenomena such as the complete removal of Hg vapour from air by the lungs and the almost universal presence of Hg in rain H₂O.

M. S. B.

Mechanism of the oxidation of alkaline solutions of mercuric cyanide with hypobromites and permanganates. B. RICCA and P. MEDURI (*Gazzetta*, 1934, 64, 113—117).—The reaction between aq. alkalis and Hg(CN)₂ takes place thus: $2\text{Hg}(\text{CN})_2 + 2\text{KOH} \rightleftharpoons (\text{HgCN})_2\text{O} + 2\text{KCN} + \text{H}_2\text{O}$. The CN which remains attached to Hg is not oxidised by KMnO₄, but the CN' is oxidised to CNO'. The reaction between Hg(CN)₂ and hypobromites in alkaline solution takes place in the three stages: (1) $\text{Hg}(\text{CN})_2 + 4\text{NaBr} \rightleftharpoons \text{Na}_2\text{HgBr}_4 + 2\text{NaCN}$; (2) $2\text{NaCN} + 2\text{NaOBr} \rightleftharpoons 2\text{NaCNO} + 2\text{NaBr}$, and (3) $\text{Na}_2\text{HgBr}_4 + 2\text{NaOH} \rightleftharpoons \text{HgO} + 4\text{NaBr} + \text{H}_2\text{O}$ (cf. A., 1929, 531).

O. J. W.

Double thiocyanate of mercury and cobalt. I. S. AUGUSTI (*Gazzetta*, 1934, 64, 33—39).—The macro-analytical application of the formation of HgCo(CNS)₄ has been studied. The limiting sensitivities for Hg²⁺, Co²⁺, and CNS' are 0.10, 0.118, and 0.581 mg., respectively. In systematic analysis the test may be made on a slightly acid (HNO₃) solution containing the Hg, Pb etc. having been previously removed from the sulphide ppt., and on a solution containing Ni and Co. Org. liquids such as urine should be centrifuged and the residue treated with HNO₃. For determination the complex is dissolved in hot dil. HCl and the Hg is pptd. and weighed as HgS, whilst the Co may be separated by evaporation of the filtrate to dryness and conversion of the ignited residue into CoSO₄.

H. F. G.

Reactions of Nessler's solutions. M. L. NICHOLS and C. O. WILLITS (*J. Amer. Chem. Soc.*, 1934, 56, 769—774).—The compound formed when Nessler's solution reacts with NH₃ is NH₂Hg₂I₃, which is very insol. and tends to form negatively-charged colloid particles. When the alkalinity of the solution is 3*N*, the colour produced with NH₃ can be made more durable over a wider concn. range by adding stabilised, alkaline ash-free gelatin as a protective colloid.

E. S. H.

Boron arsenate and mixed crystals of boron arsenate and phosphate. G. R. LEVI and D. GHIRON (*Atti R. Accad. Lincei*, 1933, [vi], 18, 394—395).—When a solution of an equimol. quantity of H₃BO₃ in 80% H₃AsO₄ solution is evaporated and the product is dried at 600°, BaSO₄, *d* 3.583, is formed. The tetragonal crystals have *a* 4.46, *c* 6.797 Å., compared with *a* 4.33, *c* 6.633 for BPO₄; 2 mols. per unit cell; *d*_{calc.} 3.67. BaSO₄ may also be prepared by heating (NH₄)₂HAsO₄ with H₃BO₃. It forms a continuous series of mixed crystals with BPO₄.

H. F. G.

Decomposition of carbides by water or dilute acids. J. SCHMIDT (*Z. Elektrochem.*, 1934, 40, 170—174).—The carbides are divided into three groups: (1) Carbides of the Fe group and of Mn having the formula M₃C. In these the C atoms are separated in the crystal lattice, and the gaseous reaction product with H₂O consists mainly of CH₄. Probably CH₄ is first produced, accounting for the formation of some C₂H₄. (2) Carbides of the first and second groups of the periodic system and also Al₂C₃ and Ce₂C₃, in which the crystal lattice contains a C-C linking. These give rise to C₂H₂. (3) Mg₂C₃, which yields allylene when treated with H₂O. The crystal structure has not been determined, but probably contains the linking C-C-C.

E. S. H.

Constitution of graphitic acid and its reactions. U. HOFMANN, A. FRENZEL, and E. CSALAN (*Annalen*, 1934, 510, 1—41).—Graphitic acid (I), prepared (cf. A., 1928, 379) by oxidation (KClO₃, HNO₃, H₂SO₄) of Ceylon graphite, contains small amounts of K and S, is very hygroscopic, and cannot be dehydrated completely over P₂O₅ at 20°/vac. The H₂O (7.05—10.5%) obtained by combustion of different preps. of "dry" (I) is considered to arise from mol. bound H₂O and not from OH groups [since reduction (aq. FeCl₂; aq. H₂S) causes a diminution in the H content]. (I) does not contain C and O in stoichiometric proportion; the ratio varies from 2.9 to 3.5. Contrary to Thiele (A., 1930, 875), (I) is not reduced to graphite; aq. FeCl₂, aq. N₂H₄, H₂O, and aq. H₂S cause the removal of 68, 82, and 91%, respectively, of the combined O. The (I) of Thiele (*loc. cit.*) is considered to be impure and may be contaminated with org. solvent. Slow or rapid heating of (I) gives CO, CO₂, and graphite-like material (not completely O-free); O₂ is not produced. Crystallographic data (described fully) indicate that (I) is a graphite oxide; the O atoms lie above and below the hexagonal planes of C atoms. The v.-p. curve of the swelling of (I) at room temp. is given; a measurable v.p. is first observed when 10% of H₂O is present in the (I). The heat effect of the swelling is small. The intensities of the interference lines (002) and (004) alter appreciably during the swelling; the former reaches a max. at *p*_{H₂O} 7.9 mm. and then decreases, whilst the latter is a min. at 4.4 mm. and then increases. Röntgen investigation of the slow thermal decomp. of (I) shows that the process is not discontinuous. Prolonged interaction of (I) (obtained by washing with much H₂O in the brown form) and H₂S gives a graphite sulphide containing about 38% S; extraction with CS₂ reduces the S content to 27.5%.

H. B.

Volatility of SiO₂ in super-critical steam. C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (*Rec. trav. chim.*, 1934, 53, 476).—A reply to criticism (cf. A., 1930, 1262).

H. S. P.

Silicate research. W. WEYL (*Chem.-Ztg.*, 1934, 58, 285—287).—The difficulties peculiar to the physico-chemical investigation of silicates are discussed with particular reference to the m.-p. determination. Glasses are in an unstable state of equilibrium and only a careful study of the anomalous physical properties can discover their real constitution.

J. A. S.

Titanium sulphides. PICON (Compt. rend., 1933, 197, 1415—1417).—If TiO_2 in a graphite boat, or better mixed with 15% of graphite, is heated in H_2S action begins about 1200° ; after 2.5 hr. at 1200 — 1650° Ti_3S_4 containing about 1% C is obtained. This (or any sulphide richer in S) at 1300° in vac. passes into Ti_4S_5 , which above 1500° in vac. slowly loses S, and in a graphite boat in H_2 at 2000 — 2800° passes into a cryst. carbide, slowly sol. in moist Br; in N_2 at 2000° it forms mixed carbide and nitride, but at 2800° only TiC . Ti_3S_4 (or any sulphide) at 800° in H_2S forms Ti_3S_5 ; in vac. at 800° it loses S. Heated at 1400° in H_2S Ti_3S_4 forms Ti_2S_3 , which loses S, reverting to Ti_3S_4 after 1 hr. in vac. at 1100° . All the above sulphides are black and amorphous.

C. A. S.

Chemical properties of titanium sulphides. PICON (Compt. rend., 1934, 198, 1415—1417).—The actions of various inorg. reagents on Ti sulphides are described.

B. W. B.

Compounds of germanium and hydrogen: their reactions and derivatives. I. Preparation of monogermene. II. Sodium trihydrogermanides. C. A. KRAUS and E. S. CARNEY (J. Amer. Chem. Soc., 1934, 56, 765—768).—The prep. of GeH_4 and of NaGeH_3 is described. NaGeH_3 yields NaGe and H_2 when heated. Investigation of the system NH_3 — NaGeH_3 at -33° has shown the existence of four solid phases: $\text{NaGeH}_3 \cdot 6\text{NH}_3$, $\text{NaGeH}_3 \cdot 4.5\text{NH}_3$, $\text{NaGeH}_3 \cdot 2\text{NH}_3$, and NaGeH_3 .

E. S. H.

Neutral zirconium nitrate. H. PIED and (MLLE.) F. FALINSKI (Compt. rend., 1934, 198, 1505—1506).—The existence of $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (denied by Chauvenet and Nicolle, A., 1918, ii, 234) was established by analysis of crystals separated from a solution of ZrO_2 in aq. HNO_3 , by Schreinemakers' method.

B. W. B.

Compound of stannic chloride and ether. S. AI (J. Soc. Chem. Ind., Japan, 1934, 37, 107B).—When prepared by various methods the composition is always $\text{SnCl}_4 \cdot 2\text{Et}_2\text{O}$. This compound volatilises at room temp. and burns without explosion.

A. G.

Complex formation between cerium or tungsten and tartaric acid in alkaline media. R. RAMAN and B. L. VAISHYA (J. Indian Chem. Soc., 1934, 11, 179—184).—Indications of complex formation between 3 mols. of Na tartrate and 2 mols. of CeCl_3 , and between 2 mols. of K tartrate and 1 mol. of K_2WO_4 , have been observed by polarimetric and potentiometric methods.

F. L. U.

Oxyacids of quadrivalent cerium and thorium. A. HOFFMANN (Naturwiss., 1934, 22, 206).—The compounds BeCeO_3 and BaThO_3 have been prepared. They have the perovskite structure, a 4.377 ± 0.003 and 4.480 ± 0.003 Å., respectively.

A. J. M.

Simple and complex iodates of quadrivalent lead. P. R. RAY and H. SAHA (Z. anorg. Chem., 1934, 217, 376—380; cf. A., 1932, 1099).—The following compounds are described: $\text{Pb}(\text{IO}_3)_4$, $\text{Pb}(\text{IO}_3)_4 \cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{Pb}(\text{IO}_3)_6 \cdot 2\text{H}_2\text{O}$, $\text{M}_2\text{Pb}(\text{IO}_3)_6 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{NH}_4$).

F. L. U.

Nitrosyl borofluoride and its decomposition by alkali fluorides. G. BALZ and E. MAILANDER (Z. anorg. Chem., 1934, 217, 161—169).— NOBF_4 , d^{25}_{20} 2.185, has been prepared by the action of N_2O_3 on HBF_4 and purified by sublimation at 200 — 250° and 0.01 mm. By heating together dry NOBF_4 and NaF at 300° and about 0.01 mm. NOF is obtained; purification by fractional condensation gives a light blue liquid with a v.p. of 230 mm. at -79° . It is slowly decomposed by glass giving N_2O_3 . NOF is very reactive. Red P and B burn in it spontaneously. There is no action with S and I, but it is decomposed by Hg. It is readily attacked by H_2O forming HF and by P_2O_5 forming POF_3 . With liquid SO_2 colourless cryst. plates are formed and sublime without decomp. They are probably $\text{NOF} \cdot \text{SO}_2$ and melt at room temp. to a colourless liquid which slowly decomposes in glass. NOF does not combine with SeO_2 . With BF_3 it forms NOBF_4 .

M. S. B.

Preparation of dibromoamine and its reaction with Grignard reagents. G. H. COLEMAN, C. B. YAGER, and H. SOROOS (J. Amer. Chem. Soc., 1934, 56, 965—966).— NH_3 passed into Br in Et_2O at -50° gives NHBr_2 (I), which is stable (in Et_2O) at -72° but decomposes at 0° (more readily than NH_2Br). (I) and MgRX ($\text{R} = \text{Bu}^n$, *sec.*-Bu, Bu^i , CH_2Ph , and $\text{C}_2\text{H}_4\text{Ph}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) give (cf. A., 1933, 702) N_2 (1—9%), NH_3 (41—95%), NH_2R (2—34%), and NHR_2 (0.4—6%).

H. B.

Fused "onium" salts as acids. I. Reactions in fused ammonium nitrate. L. F. AUDRIETH and M. T. SCHMIDT (Proc. Nat. Acad. Sci., 1934, 20, 221—225).—Consistent with an extension of the Bronsted theory of acidity, dry fused NH_4NO_3 (I) is found to be an acid stable at the m.p. and a good conductor of electricity. CuO , UO_3 , MgO , CdO , PbO , CaO , NiO , HgO , BaO , and ZnO dissolve forming the metallic nitrate, NH_3 , and H_2O , but BeO , Al_2O_3 , Cr_2O_3 , Fe_3O_4 , Fe_2O_3 , ThO_2 , SnO_2 , Ta_2O_5 , Nb_2O_5 , V_2O_5 , MoO_3 , and WO_3 do not react although $\text{Th}(\text{NO}_3)_4$, $\text{Be}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$ are sol. in (I). Many metals above H in the electrochemical series, and Cu and Bi, react vigorously forming the nitrate, N_2 , NH_3 , and H_2O , but Al, Mn, Cr, Fe, and Sn do not react probably owing to the insolubility of their oxides. Cu_2O is oxidised to $\text{Cu}(\text{NO}_3)_2$, FeCl_2 to Fe_2O_3 , SnCl_2 to SnO_2 , and $\text{Cr}(\text{NO}_3)_3$ to dichromate, whilst Au dissolves if a little NH_4Cl is added to (I). As, Bi, and Sb are deposited electrolytically from (I). Dehydration of nitrates in the presence of (I) and an example of acid catalysis by (I) are discussed.

J. G. A. G.

Preparation of phosphorus nitride. H. MOUREU and A. M. DE FICQUELMONT (Compt. rend., 1934, 198, 1417—1419).—Couldridge's method (J.C.S., 1888, 53, 398) for preparing phospham by the action of NH_3 on $(\text{PNCl}_2)_3$ (I) yields a product which cannot be freed from Cl. The reaction also gives $\text{P}_3\text{N}_2\text{Cl}_4(\text{NH}_2)_2$ (II) in quantity; its properties are described. Either (I) or (II) heated to about 850° in a current of NH_3 gives P_3N_5 .

B. W. B.

New hydroxy-nitrogen compound of phosphorus. P. RENAUD (Compt. rend., 1934, 198, 1159—1161; cf. A., 1933, 1257).—When PN is

heated with H_2O for 15 days at 100° in N_2 or a sealed tube it hydrolyses with a 90% yield of PNO_2H_2 , tetragonal, a 7.60, c 7.57 Å., $6\text{PNO}_2\text{H}_2$ in the unit cell. It is sol. unchanged in H_2O to a slightly conducting solution, and has m.p. 195° ; it decomposes at 210° or on heating with aq. KOH in vac. at 50° with evolution of NH_3 . To bring all the P into solution it must be heated for 200 hr. with H_2SO_4 . It dissolves in aq. NH_3 with apparent production of new cryst. substances. C. A. S.

Behaviour of salts of arsenic, antimony, and tin in presence of potassium cyanate. J. DALIEROS (Z. anorg. Chem., 1934, 217, 381—384).— KCNO and SnCl_2 interact in aq. solution thus: $\text{SnCl}_2 + 2\text{KCNO} + 6\text{H}_2\text{O} = \text{Sn}(\text{OH})_2 + 2\text{NH}_4\text{HCO}_3 + 2\text{KCl}$. If KCNO is in large excess Sn is formed. Similarly $\text{Sb}(\text{OH})_3$ is pptd. from SbCl_3 solutions. AsCl_3 decomposes KCNO without forming a ppt. The ppts. of $\text{Sn}(\text{OH})_2$ and $\text{Sb}(\text{OH})_3$ are easy to filter and wash, and the method is suitable for quant. analysis. F. L. U.

Thioarsenites. IV. Silver compounds. V. Zinc, lead, manganese, iron, nickel, and cobalt compounds. H. WUNSCHENDORFF and (MME.) P. VALIER (Bull. Soc. chim., 1933, [iv], 53, 1525—1529, 1529—1532; cf. A., 1930, 48).—IV. The compounds AgAsS_3 , Ag_3AsS_3 , and KAg_2AsS_3 are described.

V. The compounds $\text{M}_3(\text{AsS}_3)_2$ and KMAsS_3 ($\text{M} = \text{Zn, Pb, Mn}$) are described. The corresponding salts of Fe, Co, and Ni are apparently formed, but are unstable and cannot be purified. F. L. U.

Formation of sulphuric acid and hydrogen sulphide in the decomposition of thiosulphate. F. FOERSTER and H. UMBACH (Z. anorg. Chem., 1934, 217, 175—188).—When dil. aq. $\text{Na}_2\text{S}_2\text{O}_3$ is slowly dropped into boiling HCl the reaction $\text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{S}$ takes place, but the max. yield is about 91%. The decomp. is favoured by increase of acidity and, to a smaller extent, by reduction in the rate of addition of $\text{Na}_2\text{S}_2\text{O}_3$ or by addition of a small quantity of Ag. Addition of Cu, SiO_2 , or As has no effect. It is suggested that the primary reaction is the formation of SO : $\text{H}_2\text{S}_2\text{O}_3 = 2\text{SO} + \text{H}_2\text{O}$; $2\text{SO} + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{S}$. M. S. B.

Formation of polythionates from thiosulphate and nitrous acid. A. KURTENACKER and H. SPIELHACZEK (Z. anorg. Chem., 1934, 217, 321—338).— $\text{Na}_2\text{S}_2\text{O}_3$ and HNO_2 interact in aq. solution at reactions between p_{H} 5.6 and $3N\text{-HCl}$, yielding HSO_3^+ , SO_4^{2-} , $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$, and $\text{S}_5\text{O}_6^{2-}$. $\text{S}_5\text{O}_6^{2-}$ appears only at the highest acidity, whilst S is not formed at p_{H} 5.6 or at acidities $> 1.5N\text{-HCl}$. The mean val. of n in the total $\text{S}_n\text{O}_6^{2-}$ rises with acidity. When $\text{S}_2\text{O}_3^{2-}:\text{NO}_2' = 2:1$ the gas formed is nearly pure N_2O , corresponding with $4\text{S}_2\text{O}_3^{2-} + 2\text{NO}_2' + 6\text{H}^+ = 4\text{S}_2\text{O}_3 + \text{N}_2\text{O} + 3\text{H}_2\text{O}$. F. L. U.

Action of chlorates on sulphur, selenium, and tellurium. J. AMIEL (Compt. rend., 1934, 198, 1033—1035).—A moist mixture of S and the chlorates of (with increasing ease in this order) Ba, Sr, Ca, Pb, Cu^{II} , Cr^{III} , Mg, Ni, Co, Zn, and Cd evolves ClO_2 below, and Cl_2 and O_2 above, $50\text{--}60^\circ$; with the $\text{S S}_2\text{Cl}_2$ is formed which is decomposed by H_2O , and finally

sulphate is formed. If org. matter is present inflammation may occur. Se acts similarly but more vigorously, a slightly moist mixture thereof with any chlorate, except of K, becoming incandescent. Te is attacked only by conc. aq. HClO_3 or aq. $\text{X}(\text{ClO}_3)_2$ if $\text{X} = \text{Mg, Ni, Co, Zn, or Cd}$. Chlorate ammoniates, e.g., $\text{Zn}(\text{ClO}_3)_2 \cdot 4\text{NH}_3$ or $\text{Cd}(\text{ClO}_3)_2 \cdot 6\text{NH}_3$, do not react with S or Se. A dry mixture of S and $\text{Sr}(\text{ClO}_3)_2$ may be preserved indefinitely over P_2O_5 ; addition of an alkali acetate prevents the action of any chlorate on S or Se. C. A. S.

Oxidation by oxygen of the tellurides, selenides, and sulphides of sodium in liquid ammonia. R. L. McCLEARY and W. C. FERNELIUS (J. Amer. Chem. Soc., 1934, 56, 803—804).— O_2 converts Na_2X (where $\text{X} = \text{Te, Se, or S}$) into a mixture of $\text{Na}_2\text{X}_2\text{O}_3$ and Na_2XO_4 . With Na_2X_n , free Te or Se is formed with Na_2XO_3 and Na_2XO_4 , excepting Na_2S_2 , when $\text{Na}_2\text{S}_2\text{O}_3$ is formed. Na_2S_3 , Na_2S_4 , and Na_2S_5 give $\text{Na}_2\text{S}_2\text{O}_3$ and S. Solutions of S or S_4N_4 yield small amounts of $\text{Na}_2\text{S}_2\text{O}_3$ on oxidation. E. S. H.

Reaction between potassium chromate and sodium sulphite in aqueous solution. A. SCONZO (Gazzetta, 1934, 64, 66—68).—When a solution containing K_2CrO_4 and Na_2SO_3 is kept out of contact with the air, a green flocculent ppt. begins to form after a time; when dried over CaCl_2 the ppt. has the composition $\text{Cr}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The reaction is probably $2\text{CrO}_4^{2-} + 3\text{SO}_3^{2-} + 5\text{H}_2\text{O} = 4\text{OH}^- + 3\text{SO}_4^{2-} + 2\text{Cr}(\text{OH})_3$, since the solution becomes strongly alkaline.

H. F. G.

Production of pure chromium.—See B., 1934, 365.

Influence of age and polonium content on centrifuging of polonium solutions. (MLLE.) C. CHAMIE and M. HAÏSSINSKY (Compt. rend., 1934, 198, 1229—1231; cf. A., 1931, 591, 697, 1230; 1933, 476).—From a $10^{-5}N\text{-HNO}_3$ solution of Po separation on centrifuging increases markedly with time (e.g., 35, 48, and 71% after 0, 7, and 45 days, respectively). Similar but less marked increases occur on keeping without centrifuging. With const. time of keeping and comparatively high concn. ($> 10^{-3}N$) of acid the % separation decreases rapidly with increased content of Po, tending towards equality with that occurring on keeping. With lower concn. the % first declines and then increases with increased content of Po.

C. A. S.

Manganese chromate. H. WUNSCHENDORFF and (MME.) P. VALIER (Bull. Soc. chim., 1933, [iv], 53, 1504—1507).—By the interaction of aq. K_2CrO_4 and MnCl_2 the compounds MnCr_2O_7 (red prisms) and $\text{Cr}(\text{MnO}_3)_3$ (black ppt.) have been prepared. The former is sparingly sol. in cold H_2O . Its aq. solutions undergo hydrolysis and oxidation on exposure to air.

F. L. U.

Petrographic methods in slag examination. R. GRAHAM and R. HAY (J. Roy. Tech. Coll., 1934, 3, 241—243).—Some optical properties of MnO-SiO_2 slags (this vol., 490) are given. H. S. P.

Lower valency states of rhenium. W. MANCHOT and J. DUSING (Annalen, 1934, 509, 228—240; cf. A., 1932, 133; 1933, 581).—The olive-green solution (I)

containing Re^{III} , obtained by cathodic reduction (*loc. cit.*) of K_2ReCl_6 (II) in $2N\text{-H}_2\text{SO}_4$, darkens when heated and evolves a little H_2 ; subsequent treatment with an excess of Ru^{II} causes immediate evolution of 1 equiv. of H_2 . (I) heated with conc. HCl and KCl affords 1 equiv. of H_2 : $\text{ReCl}_3 + \text{HCl} + 2\text{KCl} \longrightarrow \text{K}_2\text{ReCl}_6 + \text{H}_2$. These results disprove the view of Noddack and Noddack (this vol., 44) that (I) contains Re^{II} . (I) treated with $\text{Fe}_2(\text{SO}_4)_3$ (cf. Geilmann and Hurd, A., 1933, 479) consumes 4 equiv. of KMnO_4 . (I) also consumes 4 equiv. of Br (method: A., 1924, ii, 274), whilst (II) absorbs 3 equiv. H_2 (about 0.7 equiv.) is evolved when (I) is heated with conc. aq. K_2CO_3 or KOH ; the red ReCl_3 (III) of Geilmann and Wrigge (A., 1933, 1259) similarly gives about 0.3 equiv. Some H_2 is also evolved from (II) and conc. KOH . Reduction (Zn , H_2SO_4) of (III) affords a bluish-violet, strongly reducing solution, which when heated evolves 1 equiv. of H_2 ; contrary to Noddack and Noddack (*loc. cit.*), this does not contain Re^{I} , since treatment with $\text{HCl} + \text{KCl}$ gives 1 equiv. of H_2 and regenerates (III). (III) is sol. in Et_2O and amyl alcohol, it does not act as a reducing agent in acid medium, and it gives a little (II) (without the production of H_2) when heated with conc. HCl and KCl at 190° (no reaction at 150°). It is suggested that (III) may be $\text{Re}_2\text{Cl}_6\text{O}$. H. B.

Thermal decomposition of manganous salts. P. DUBOIS (Compt. rend., 1934, 198, 1502—1504).—Guichard's method (A., 1925, ii, 559) adapted to follow changes in wt. during heating in air up to 1000° was applied to $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (I), $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (II), $\text{MnCO}_3 \cdot y\text{H}_2\text{O}$, and $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (III). (I), (II), and (III) gave the anhyd. salt, (I) and (II) passing through intermediate monohydrates. (I) gave Mn_2O_3 directly, but all others passed successively through the stages MnO , Mn_2O_3 , to Mn_3O_4 , where z varied from 1.6 to 1.95 with different salts.

B. W. B.

Iodine pentoxide and its hydrates. II. E. MOLES and A. PARTS (Anal. Fis. Quím., 1933, 31, 618—622).—Oxidation of I with fuming HNO_3 and recrystallisation of the product (after evaporation to dryness) from 50—60% HNO_3 yields cryst. $3\text{I}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (I), but no HIO_3 . (I) on being heated loses H_2O much more slowly than does HIO_3 , and cannot be completely dehydrated without decomp. From a supersaturated solution of (I) in 30% HNO_3 , HIO_3 separates if a few crystals of HIO_3 are added. When heated, HIO_3 yields first (I) and finally I_2O_5 , without loss of I, but the first stage is not completed before the second begins. (I) has d_4^{20} 5.074, which confirms the formula given in yielding 13.0 as the mol. vol. of the H_2O in the mol. H. F. G.

Stereoisomerism of ferrous tetrapyridine dithiocyanate. G. SPACU (Z. Elektrochem., 1934, 40, 125—126).—Partly polemical against Hieber and Levy (A., 1933, 241). Further work has shown the black (β) form of $[\text{Fe}(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_2]$ (I) to contain only Fe^{II} and to be a geometrical isomeride of the yellow α form (II). In $\text{C}_5\text{H}_5\text{N}$ solution (I) is transformed into (II), whilst a ppt. of (I) is deposited from solutions of (II) in CHCl_3 . At 90° (I) loses 27.30%

of $\text{C}_5\text{H}_5\text{N}$, and (II) only 17.20%.

$\text{Fe}(\text{C}_5\text{H}_5\text{N})_3(\text{CNS})_2 \cdot 3\text{H}_2\text{O}$ does not appear to exist.

H. F. G.

Metal carbonyl hydrides. Formation of cobalt carbonyl hydride. W. HIEBER (Z. Elektrochem., 1934, 40, 158—159).—The relatively complicated process of the formation of $\text{Co}(\text{CO})_4\text{H}$, as compared with $\text{Fe}(\text{CO})_5\text{H}_2$, is due to the dimeric structure and lower stability of $\text{Co}(\text{CO})_4$. In these compounds FeH_2 and CoH behave as pseudo-Ni atoms. Physical properties change progressively in the series $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{CO})_4\text{H}_2$, $\text{Co}(\text{CO})_4\text{H}$, $\text{Ni}(\text{CO})_4$. H. F. G.

Stereochemistry of complex inorganic compounds. I. Walden inversion as exhibited by diethylenediaminocobaltic compounds. J. C. BAILLAR, jun., and R. W. AUTEN (J. Amer. Chem. Soc., 1934, 56, 774—776).—*l*-Dichlorodiethylenediaminocobaltic chloride (I) reacts with K_2CO_3 to form the *d*-carbonato-compound, but with Ag_2CO_3 to give the *l*-carbonato-compound. When $\text{K}_2\text{C}_2\text{O}_4$ or $\text{Ag}_2\text{C}_2\text{O}_4$ reacts with (I) the *d*-oxalato-salt is formed.

E. S. H.

Compounds of hexamethylenetetramine with complex cobalt salts and the nature of residual affinity. P. RAY and M. BAKSHI (J. Indian Chem. Soc., 1934, 11, 125—131).—The following compounds have been prepared, where $\text{B} = (\text{CH}_2)_6\text{N}_4$ and $\text{X} = [\text{Co}(\text{CN})_5(\text{S}_2\text{O}_3)]^{4-}$. $\text{Ba}_2\text{X} \cdot 1.5\text{B} \cdot 4.5\text{H}_2\text{O}$; $\text{Sr}_2\text{X} \cdot 2\text{B} \cdot 7\text{H}_2\text{O}$; $\text{Ca}_2\text{X} \cdot 2\text{B} \cdot \text{H}_2\text{O}$; $\text{Mg}_2\text{X} \cdot 2\text{B} \cdot 12\text{H}_2\text{O}$; $\text{Li}_4\text{X} \cdot 2\text{B} \cdot 8\text{H}_2\text{O}$; $\text{BaK}_2\text{X} \cdot 1.5\text{B} \cdot 1.5\text{H}_2\text{O}$; $\text{SrK}_2\text{X} \cdot 1.5\text{B}$; $\text{CaK}_2\text{X} \cdot \text{B} \cdot 7\text{H}_2\text{O}$; $\text{MgK}_2\text{X} \cdot 2\text{B} \cdot 2.5\text{H}_2\text{O}$; $\text{Li}_2\text{K}_2\text{X} \cdot 2\text{B}$; $\text{Ba}(\text{NH}_4)_2\text{X} \cdot 1.5\text{B} \cdot 4.5\text{H}_2\text{O}$; $\text{Sr}(\text{NH}_4)_2\text{X} \cdot 1.5\text{B} \cdot 2\text{H}_2\text{O}$; $\text{Ca}(\text{NH}_4)_2\text{X} \cdot \text{B} \cdot 7\text{H}_2\text{O}$; $\text{Mg}(\text{NH}_4)_2\text{X} \cdot 1.5\text{B} \cdot 5\text{H}_2\text{O}$.

J. S. A.

Micro-analysis. J. G. PEARSON (Chem. Eng. Min. Rev., 1934, 26, 279—283).—A brief review of published methods which have proved trustworthy.

Sensitivity of chemical analysis by X-rays. A. FAESSLER (Z. Physik, 1934, 88, 342—345).—Cathode-ray excitation has a sensitivity of $1 : 10^5$ for alloys and $1 : 2 \times 10^4$ for powder mixtures. X-Ray excitation is more efficient for short than for long wavelengths. A. B. D. C.

Radioactive methods in the service of chemical and technical problems. H. KADING and N. RIEHL (Angew. Chem., 1934, 47, 263—270).—A review of published work. E. S. H.

Critical test for the purity of gases. M. SHEPHERD (Bur. Stand. J. Res., 1934, 12, 185—191).—The method involves one approx. isothermal distillation, small initial distillate, middle and final residue fractions being collected. The pressures of these fractions are compared by a differential manometer, and indicate the presence of impurities of higher and lower b.p. than the pure substance. Accurate temp. control is not necessary, as in the method based on the constancy of pressure during isothermal processes, and the method may be extended to the testing of mixtures containing > two components and to approx. calculation of the amounts of impurities present. It is unsuitable for studying azeotropic mixtures. J. W. S.

Calorimetric analysis. II. Test of purity of organic substances.—See B., 1934, 354.

Sedimentation method for the determination of the particle size of finely-divided materials (such as hydrated lime). D. L. BISHOP (Bur. Stand. J. Res., 1934, 12, 173—183).—An apparatus for the automatic and continuous weighing of depositing sediments is described. This method is compared with the microscopical measurement method of determining the particle sizes of glass spherules. The differences in n for the mounting liquids yield up to 20% differences in the apparent diameters as measured by the latter method, but the shape of the distribution curve is similar by the two methods. The sedimentation method has been applied to the determination of the particle sizes in nine samples of hydrated CaO.

J. W. S.

Exact analysis of electrolytic hydrogen. V. V. SHISHKIN and E. P. KARNAUKH (Khimstroi, 1933, 5, 2475—2477).—An accuracy of 0.01% is attained in the combustion apparatus described.

CH. ABS.

Indicators. XX. Irreversible fading of phenolphthalein. A. THIEL and G. COCH (Z. anorg. Chem., 1934, 217, 254—256).—Besides the known reversible fading of phenolphthalein, an irreversible fading has been observed and investigated. It takes place on long keeping and is important when the indicator is used as a colour standard. The effect is attributed to the formation of a *tert.*-carbinol-carbonate ion and its subsequent reaction with OH', since the phenomenon is not observed with phenol-tetrachlorophthalein which does not form the *tert.* anion.

M. S. B.

Effect of long-chain salts on indicators; the valency-type of indicators and the protein error. G. S. HARTLEY (Trans. Faraday Soc., 1934, 30, 444—450).—Experiments show that the effect of long-chain salts of strong acids and bases on the colour of indicators depends on the charges on the micelle and on the indicator ions.

R. S. B.

Indicators. XXI. Easily prepared buffer solutions of practically constant electrolyte content. A. THIEL, G. SCHULZ, and G. COCH (Z. Elektrochem., 1934, 40, 150—154).—Four solutions are used, viz.: (1) 0.05*M*-H₂C₂O₄ and 0.2*M*-H₃BO₃; (2) 0.2*M*-H₃BO₃, 0.05*M*-succinic acid, and 0.05*M*-Na₂SO₄; (3) 0.05*M*-Na₄B₂O₇; (4) 0.05*M*-Na₂CO₃. From appropriate pairs of these, buffer solutions of approx. const. ionic concn. and of p_H ranging from 1.5 to 11.0 may be prepared. The greatest variation of the p_H of solutions varying between 2 and 0.1 times the standard concn. is 0.06. The influence of additions of NaCl and Na₂SO₄ has been examined.

H. F. G.

Series of simple basic indicators. III. Zero point of the acidity function scale. L. P. HAMMETT and M. A. PAUL (J. Amer. Chem. Soc., 1934, 56, 827—829; A., 1932, 921).—The zero point H_0 has been established by determining the ionisation in dil. HCl of some azobenzene indicators. Acidity functions for HCl and HNO₃ up to 7 and 9.5*M* have been determined.

E. S. H.

Indicators. XXII. Salt errors of indicators. A. THIEL and G. COCH (Z. anorg. Chem., 1934, 217, 353—375; cf. A., 1933, 29).—Extinction curves of

the acid and alkaline forms of Me-orange, Me-red, phenolphthalein, and cresol-red have been determined in presence of various salts. Data are recorded to show the effect of the salts (1) on the wave-length corresponding with the max. val. of the extinction coeff. (a), and (2) on the max. val. of a . These effects are sp., but show certain regularities. They give rise to what are termed "complex" salt errors. "Simple" salt errors depend on the displacement (Δ) of the p_H at which $[A']-[HA]$ (HA =indicator acid). Vals. of Δ for NaCl and Na₂SO₄ are given for all the indicators.

F. L. U.

[Error involved in] the application of "observed titre." J. MIKA (Z. anal. Chem., 1934, 96, 401—412).—The influence of indicator corrections (I) on the accuracy of volumetric determinations is discussed. The observed titre differs increasingly from the true equiv. vol., (a) the larger (I) is, (b) the more the vols. employed in standardisation and in determination differ, (c) the more dil. the standard solution is, (d) the smaller is the abs. quantity determined.

J. S. A.

Interferometer in the isotopic analysis of water. R. H. CRIST, G. M. MURPHY, and H. C. UREY (J. Chem. Physics, 1934, 2, 112—115).—The apparent difference of n of H₂O and that containing H₂O, as obtained by a Zeiss H₂O interferometer, is calibrated against the corresponding differences in d . These quantities are not proportional. The method is accurate to 0.01%.

N. M. B.

Determination of hypochlorous acid. LEMARCHANDS and (MILLER) D. SAUNIER (Bull. Soc. chim., 1933, [iv], 53, 1414—1418).—Conditions for the accurate determination of HOCl by As₂O₃ are defined. A simplified and exact method of determining HOCl in presence of aq. Cl₂ is based on the observation that in neutral solution KI is oxidised to KIO₃ by HOCl.

F. L. U.

Micro-determination of iodine. M. PATNAIK (Indian J. Med. Res., 1933, 21, 237—248).—The material is made into a paste with alkali, 7% KMnO₄ is added with stirring and heating, excess of KMnO₄ is reduced by gradual addition of EtOH, MnO₂ is removed by filtration, the filtrate is evaporated to dryness, and after addition of K₂CO₃ the residue is ignited. I is then determined by Newcomb and Sankaran's method. Best results are obtained when 0.001—0.003 mg. of I is present.

NUTR. ABS. (m)

Determination of fluorides in waters. E. ELVOVE (U.S. Pub. Health Rep., 1933, 48, 1219—1222).—A modification of the Zr-alizarin method of determining F' in H₂O is described. The highest vals. are found in districts where mottled enamel in teeth is most prevalent.

NUTR. ABS. (m)

Acidimetric determination of formaldehyde and sulphites. MALAPRADE (Compt. rend., 1934, 198, 1037—1039).—The solution of CH₂O is neutralised, excess of neutral aq. Na₂SO₃ added, and the resultant NaOH titrated: CH₂O + Na₂SO₃ = ONa·CH₂·SO₃H + NaOH. Conversely to determine SO₃" excess of neutral aq. CH₂O is added to the sample after it has been neutralised in absence of air,

and the resultant NaOH titrated (phenolphthalein). All other neutralisations should be with thymolphthalein. C. A. S.

Stability of aqueous solutions of sodium thiosulphate. I. BELLUCCI and I. DAMIANI (Gazzetta, 1934, 64, 69—76).—The titre of 0.1 and 0.01N aq. $\text{Na}_2\text{S}_2\text{O}_3$ is unchanged by bubbling through them pure CO_2 or O_2 for 2—3 hr. The slow decrease in the titre of $\text{Na}_2\text{S}_2\text{O}_3$ solutions on keeping (especially if < 0.01N) is ascribed to a slow decomp. by the H_2O : $\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{S} + \text{Na}_2\text{SO}_3$, followed by a rapid oxidation of the Na_2SO_3 by atm. O_2 . O. J. W.

Standardisation of thiosulphate solution with potassium dichromate as standard. Z. NAKAI (Bull. Fishery Exp. Sta. Gov. Gen. Chosen, 1933, D, No. 3, 1—24).—The wt. of KI and HCl should be respectively < 11× and < 51× wt. of $\text{K}_2\text{Cr}_2\text{O}_7$. The KI content should be < 0.6%, HCl > 3%, and liberated I about 0.08%. The solution should be titrated at < 30° and in diffused sunlight. CH. ABS.

Reactions of selenium and selenium oxide. E. MONTIGNIE (Bull. Soc. chim., 1933, [iv], 53, 1392—1393).—Se reduces hot aq. HgCl_2 slowly to Hg (faster in presence of HCl), FeCl_3 (slowly hot), KBrO_3 , HIO_3 (red Se rapidly, other forms slowly), $\text{K}_2\text{Cr}_2\text{O}_7$ — H_2SO_4 (slowly), NH_4 molybdate, Na tungstate, and $\text{K}_3\text{Fe}(\text{CN})_6$, but not Hg_2Cl_2 , KClO_3 , or KMnO_4 . SeO_2 reduces Hg_2Cl_2 in presence of HCl, forms *salts*, $\text{OR} \cdot \text{SeO}_2 \cdot \text{NH}_4$, in which R is *bornyl*, m.p. 80—82°, *menthyl*, m.p. about 50°, and *terpinyl*, m.p. 98—99°, and is reduced by warm, aq. gallic acid. R. S. C.

Nessler reagent. H. J. FUCHS (Z. physiol. Chem., 1934, 223, 144—146).—The use of LiI and LiOH in place of KI and KOH in the Nessler reagent prevents the formation of a ppt. in the reagent and during determinations. J. H. B.

Argentometric assay of ammonium chloride. B.P. 1932. E. J. SCHORN and J. Y. BAIRD (Pharm. J., 1934, 132, 361).—Direct titration, using K_2CrO_4 as indicator, is not accurate since aq. NH_4Cl has p_a 5, but dichlorofluorescein may be used as adsorption indicator. J. S. A.

Bromine method for determining ammonia-nitrogen.—See B., 1934, 449.

Phosphoric acid and phosphates. XI. Specific solvents and analytical separation of phosphates. A. SANFOURCHE. XII. Determination of water in superphosphate. A. SANFOURCHE and J. DUBIEF. XIII. A complex ferriphosphate. A. SANFOURCHE and B. FOCET. XIV. Reactions in the production of superphosphate. A. SANFOURCHE and A. KRAPIVINE. XV. Evolution and retrogradation of superphosphate. XVI. Constitution of superphosphate. General conclusions. A. SANFOURCHE (Bull. Soc. chim., 1933, [iv], 53, 1507—1512, 1512—1517, 1517—1522, 1573—1580, 1580—1594, 1594—1596; cf. this vol., 266).—XI. Alkaline NH_4 citrate (I) cannot be considered a sp. reagent for different Ca phosphates. The solubility of $\text{Ca}_3(\text{PO}_4)_2$ may vary, according to its physical condition, from 0 to 100%. CaHPO_4 is insol. when anhyd. In the case of superphosphate indications

afforded by the use of (I) are trustworthy, whilst in other cases they are not.

XII. Total H_2O is determined by mixing with an equal wt. of K_2HPO_4 and heating for 12 hr. at 120—125°. Under these conditions H_2O of constitution and volatile compounds other than H_2O are not lost. Free H_2O of the liquid phase is extracted by dry HCO_2Et . The H_2O thus removed is decomposed by CaH_2 and the evolved H_2 is measured.

XIII. When FePO_4 is dissolved in the liquid phase of superphosphate [$\text{CaH}_4(\text{PO}_4)_2 + \text{H}_3\text{PO}_4$], a gel is formed from which after 3 days a *cryst. substance* containing CaHPO_4 and $\text{Fe}_2\text{H}_3(\text{PO}_4)_3$ separates. The substance is white and does not give $\text{Fe}(\text{OH})_3$ with aq. NH_3 . It is regarded as a complex ferriphosphate of Ca, its composition approximating to $[\text{FeH}_2(\text{PO}_4)_2]_2\text{Ca}$. The influence of various factors on the course of its formation has been studied.

XIV. Formation of superphosphate from natural phosphates occurs in two stages, viz., (1) a rapid interaction of H_2SO_4 with part of the mineral to give H_3PO_4 , and (2) a slower reaction between the latter and the remaining unchanged $\text{Ca}_3(\text{PO}_4)_2$. If the state of division of the mineral is extremely fine, or if pptd. $\text{Ca}_3(\text{PO}_4)_2$ is used, both stages are completed so rapidly as to be analytically indistinguishable. The degree of completeness with which F is removed from apatite depends chiefly on the fineness of grinding.

XV. The changes occurring in freshly prepared superphosphate on keeping are mainly (1) a gradual completion of the second stage of reaction mentioned above, (2) hydrolysis of $\text{CaH}_4(\text{PO}_4)_2$ in the liquid phase, and (3) formation and separation of the complex ferriphosphate described in XIII. The first change increases, the two latter diminish, the proportion of H_2O -sol. phosphate. The principal physical change is a hardening due to hydration of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ at the expense of H_2O in the liquid phase.

XVI. Conclusions reached in the foregoing papers are summarised. F. L. U.

Photometric micro-analysis of drinking and service water. VIII, IX.—See B., 1934, 430.

Equilibrium between carbonate hardness and free carbon dioxide in natural waters. A. EMUNDS (Chem.-Ztg., 1934, 58, 328—329).—Excess of CO_2 can be determined by treating H_2O with CaCO_3 but the use of the equation $[\text{free CO}_2] = k[\text{Ca}^{++}][\text{combined CO}_2]^2$ to calculate the $[\text{combined CO}_2]$ is limited because the equilibrium is disturbed by the presence of other H carbonates or of Ca or Mg salts. A. G.

Determination of carbon dioxide in air.—See B., 1934, 449.

Determination of the concentration of vapour-air mixtures by an optical method. H. SCHILDWACHTER (Petroleum, 1934, 30, No. 11, 1—5).—The gas interferometer can be used to determine the composition of a binary mixture, e.g., vapour and gas, either by calibrating the instrument with a series of mixtures of known composition and plotting a calibration curve, or by determining n for each component and calculating the composition from

the measured val. of n for the mixture. Both methods have been applied to mixtures of air with the vapours of MeOH, EtOH, Et₂O, C₅H₁₂, C₆H₁₄, C₇H₁₆, C₈H₁₈, PhMe, C₆H₅Me₂, and of a series of technical benzines ($n=1.0024-1.0026$) and benzols ($n=1.00225-1.00237$). A. B. M.

Colorimetric determination of potassium. J. TISCHER (Z. Pflanz. Düng., 1934, A, 33, 335-336).—The suggested inconstancy of the Na K cobaltinitrite ppt. (Alten *et al.*, this vol., 47) is discussed. A. G. P.

Spectroscopic detection and determination of lithium, rubidium, and caesium. J. M. TOLMATSCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 464-470).—Li, Rb, and Cs are best determined with reference to intense components of the first doublet of the principal series, especially when using neocyanine-sensitised plates. For detection and approx. determination, specimens of mineral containing these metals are introduced into the electric arc, comparison being made with the spectra obtained with mixtures of glass and Al(OH)₃ of known composition. For accurate determination the alkali metals are extracted as chlorides and compared with standard solutions. J. W. S.

Rapid determination of small amounts of magnesium in presence of phosphates. F. THOMPSON (Ind. Chem., 1934, 10, 142).—The solution containing 0.02-0.04 mg. of Mg and about 2 ml. per litre of HCl is mixed with 2 ml. of starch-glycerite solution and 4 drops of 1% turmeric solution in EtOH in a 50-c.c. Nessler tube, and, after addition of 5 ml. of 5N-NaOH, the colour of the lake produced is compared with standards prepared in precisely the same way from aq. MgSO₄ and Ca₃P₂O₈ if the latter is present in the test. A. R. P.

Colorimetric determination of lead. S. FEINBERG (Z. anal. Chem., 1934, 96, 415-418).—The Pb (0.1-1.7 mg), as anodic deposit of PbO₂, is dissolved in HCl, diluted to 35-40 c.c., and pptd. from AcOH solution as PbMoO₄. The ppt. is treated with hot 10% H₂SO₄, 10 c.c. of 5% aq. KCNS and 5 c.c. of 10% SnCl₂ in HCl are added, and the orange colour is compared with that produced in a standard MoO₃ solution. Co-deposition of MnO₂ with the PbO₂ does not interfere. J. S. A.

Hydrolytic volumetric precipitation. L. von ZOMBORY and L. POLLAK (Z. anorg. Chem., 1934, 217, 237-240).—Pb⁺⁺ or C₂O₄⁼⁼ may be determined volumetrically by pptn. of PbC₂O₄ in solution using a sol. Pb salt and the oxalate of a strong base. The presence of a slight excess of the latter causes an alkaline reaction with chlorophenol-red, owing to hydrolysis, and gives a sharp end-point. CdSO₄ with Na₂HPO₄ may be similarly employed for the determination of Cd⁺⁺ or PO₄⁼⁼. M. S. B.

Separation of lead from mercury by carbonic acid in pyridine solution. A. JÍLEK and J. KOŘA (Coll. Czech. Chem. Comm., 1934, 6, 101-106; cf. this vol., 48).—Pb is pptd. quantitatively by CO₂ from a solution (>0.2 g. Pb in <100 c.c.) first made neutral to phenolphthalein with 10% aq. C₅H₅N and then treated with 15 c.c. more of 10%

aq. C₅H₅N and diluted to 100 c.c. The ppt. is washed with 100 c.c. of solution saturated with CO₂ containing 4 c.c. of 10% aq. C₅H₅N and 4 c.c. of 96% EtOH, and dried at 120°. It may be weighed as PbCO₃ or (preferably) ignited to PbO. Hg, the amount of which should not exceed that of the Pb, may be determined in the filtrate by Volhard's method. D. R. D.

Separation and determination of traces of lead in presence of traces of bismuth. II. Organic compounds. J. H. HAMENCE (Analyst, 1934, 59, 274-276).—FeSO₄ is added to the material, and the Pb, Bi, and Fe sulphides are co-pptd. Fe is removed by the CNS' method (A., 1932, 1223) and Pb determined colorimetrically (A., 1933, 923). The method of pre-treating viscera and org. compounds by wet oxidation is described. E. C. S.

Separation of thallium as bromide from its hydrobromic acid solution by means of ether. I. WADA and R. ISHII (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 20).—Tl and Au bromides can be completely separated from those of other metals by extraction of HCl or HBr solutions with Et₂O. The separation of Tl from Au has been effected. R. S.

Determination of copper, cadmium, and nickel as new complex compounds. A. TAURINŠ (Z. anal. Chem., 1934, 97, 27-36).—10% aq. K₂HgI₄, containing no excess KI, ppts. Cu quantitatively from NH₃ solution in presence of NH₄NO₃ as [Cu(NH₃)₄][HgI₃]₂, containing 4.91% Cu. The ppt. is washed with its saturated EtOH solution, Et₂O, and dried in vac. Cd, from 2N-NH₃ solution, is pptd. by 10% K₂HgI₄ containing 4% KI as [Cd(NH₃)₄][HgI₃]₂ (8.29% Cd). Ni is pptd. similarly as [Ni(NH₃)₆][HgI₃]₂ (4.43% Ni), washed and dried as above. Ni may be separated from Co by oxidation with H₂O₂ in NH₃ solution to [Co(NH₃)₅Cl]Cl₂, and pptn. of the Ni as described. J. S. A.

Use of complex ions as indicators in analysis. Indicators for metals, etc. A. R. UBBELOHDE (Analyst, 1934, 59, 339-340).—1 ml. of 10⁻⁴M aq. Ag⁺, Hg⁺, Hg⁺⁺, Cd⁺⁺, or Au⁺⁺⁺ gives a pink turbidity when added to 3 ml. of a reagent (R) made by adding solid Ni dimethylglyoxime to a mixture of equal vols. of 5% aq. KCN and EtOH, boiling, filtering, and diluting tenfold. Ni also gives a positive reaction but is distinguished by giving a pink colour with [CMe₂N.OH]₂. 3 ml. of 5×10⁻⁴M aq. CH₂O give a distinct silkiness with 1 ml. of R. The method is also adapted to the determination of Ag, Hg, and Cu. The possible extension of the principle to other complex ions is discussed. E. C. S.

Separation of metals by graded potential. A. J. LINDSEY and H. J. S. SAND (Analyst, 1934, 59, 328-335).—The vals. obtained by Lassieur (A., 1926, 1013; "Electrolyse Rapide," 1927) are not of general application owing to polarisation of the auxiliary electrode (I) and its back-resistance. Modifications of (I), and a potentiometer arrangement by means of which the correction to be applied to direct readings for any given (I) may be determined, are described. E. C. S.

Electrolytic analysis of certain alloys of antimony, copper, and tin. A. J. LINDSEY and H. J. S. SAND (*Analyst*, 1934, **55**, 335—338; cf. preceding abstract).—Modifications of Lassieur's method are described. The method gives accurate results for the determination of Cu and Sb, but errors of 2—3 mg. are obtained with 0.3 g. of Sn.

E. C. S.

Separation of copper from other metals by means of ammonium oxalate and its gravimetric determination. A. HEMMELER (*Annali Chim. Appl.*, 1934, **24**, 140—154).— $\text{Cu}(\text{C}_2\text{O}_4)_2$ pptd. from the solution of a Cu salt by excess of $\text{H}_2\text{C}_2\text{O}_4$, contains varying proportions of H_2O but always $< 0.5\text{H}_2\text{O}$. Pptn. of Cu as $\text{Cu}(\text{C}_2\text{O}_4)_2$ with NH_3 and $\text{H}_2\text{C}_2\text{O}_4$ and weighing as Cu is a good method of determining Cu and of separating it from many other metals, especially if not too little Cu is present. With solutions containing Cu as complex compound, even in small amount, pptn. as CuS , followed by reduction to Cu_2S , permits the exact determination of the Cu. Good results are also obtained by fixing the NH_4 salts present with CH_2O and pptg. the Cu from the complex by slight excess of NaOH or KOH .

T. H. P.

Separation reaction for mercury ion. M. STSCHIGOL (*Z. anal. Chem.*, 1934, **96**, 328—330).—Glycerol (I) is oxidised in alkaline solution to glyceraldehyde by Hg^{++} and Hg^+ , but by no other metals, Hg being pptd. The substance under test is treated with 10% aq. KI + 30% aq. NaOH and filtered. 1 c.c. of (I) + 2—3 c.c. of 30% NaOH are added, when Hg is pptd. on warming.

J. S. A.

Volumetric determination of mercury. M. STSCHIGOL (*Z. anal. Chem.*, 1934, **96**, 330—333; cf. preceding abstract).—Hg is pptd. by boiling with NaOH and glycerol and collected by filtration. The ppt. is dissolved in HNO_3 , and Hg determined by titration with 0.1N- NH_4CNS .

J. S. A.

Colour reactions of the rare earths with pyrogallol: cerium reactions and also reactions of thorium, lanthanum, and elements of the third analytical group with pyrogallol. F. M. SCHEMJAKIN (*Z. anorg. Chem.*, 1934, **217**, 272—276).— Ce^{III} and Ce^{IV} in aq. NH_3 both give with pyrogallol a lilac to dark blue colour, but not in neutral or acid solution. La gives a light brown ppt. which darkens on heating and Th gives a delicate rose colour. Fe, Cr, Al, Mn, Ni, Co, Zn, UO_2 , and Ti give brown or reddish-brown colours.

M. S. B.

Determination of metals with anthranilic acid. III. Simple method for determination of manganese. H. FUNK and M. DEMMEL (*Z. anal. Chem.*, 1934, **96**, 385—388; cf. A., 1933, **244**, 924).—Mn is quantitatively pptd. from fairly conc. neutral solution (> 80 c.c. for 0.1 g. Mn) by 3% aq. anthranilic acid (I). The ppt. is washed with 0.5% (I), then with EtOH , and dried at 105° . Separation from Ba, Sr, and Mg, but not Ca, is quant. The ppt. may be titrated with 0.1N- KBrO_3 .

J. S. A.

Rapid titrimetric determination of manganese in steel etc.—See B., 1934, 456.

Detection of rhenium in Noyes and Bray's system of qualitative analysis. C. H. KAO and

T. L. CHANG (*J. Chinese Chem. Soc.*, 1934, **2**, 6—12).—A detailed investigation has been made of the behaviour of Re (present initially as KReO_4) in this system of analysis. Most of the Re is found in the Te group, passing into the filtrate from the pptn. of Ir and Rh. To detect Re in this filtrate, 5 c.c. of 12N- HCl are added and the solution is evaporated to dryness. The residue is dissolved in 30 c.c. of H_2O , 12 c.c. of 12N- HCl are added, and the solution is heated to boiling. 5 c.c. of 15% aq. $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ and 5 c.c. of saturated aq. NaHSO_3 are added and boiling is continued for 5 min. The solution is filtered, acidified with 5 c.c. of 12N- HCl , and a rapid stream of H_2S is passed for 20 min. No ppt. indicates absence of Re. The ppt., if any, is washed several times with 5 c.c. of 0.1N- Na_2S . A black residue indicates Re. To confirm Re, this residue is warmed with 5 c.c. of 5% H_2O_2 on a boiling H_2O -bath for 5 min., filtered, and conc. to 1 drop. A small crystal of KMnO_4 is added, followed, when dissolved, by 1 drop of conc. aq. RbCl . The formation of bipyramidal rhombic crystals of RbReO_4 confirms Re.

D. R. D.

Benzoate method for the separation of iron, aluminium, and chromium from the other ions of the third group and the alkaline-earth ions. I. M. KOLTHOFF, V. A. STENGER, and B. MOSKOVITZ (*J. Amer. Chem. Soc.*, 1934, **56**, 812—815).—Fe, Al, and Cr are pptd. quantitatively by adding NH_4OBz to a solution in dil. AcOH , effecting a separation from other groups of cations. Two pptns. are made for precise analysis. The ppts. are washed with H_2O containing NH_4OBz to avoid peptisation.

E. S. H.

Electrographic determination of metals in alloys. Steel analysis.—See B., 1934, 455.

Spectral analysis with sensitive lines within the range of glass instruments. Spark spectrum of a high per cent. Ni-Fe-Cr-V special alloy. W. KRAEMER (*Z. anal. Chem.*, 1934, **97**, 14—18; cf. A., 1933, 1110).—Results are given for a stainless Ni-Fe-Cr-V alloy using the apparatus described previously.

J. S. A.

Potentiometric determination of nickel in steel with potassium cyanide.—See B., 1934, 406.

Behaviour of Cr in presence of acetate ions. J. DALIETOS (*Z. anorg. Chem.*, 1934, **217**, 189—192).—By the addition of NaOAc or $\text{Ca}(\text{OAc})_2$ under suitable conditions to Cr^{III} salts a ppt. of a basic Cr salt is obtained. By warming or by long keeping this forms a clear bluish-green or bluish-violet solution of a complex salt which, by long boiling with excess of aq. NH_3 , ppts. $\text{Cr}(\text{OH})_3$. Two methods are given by which disturbances in qual. analysis due to the presence of Cr^{III} and OAc' may be avoided. One is based on the removal of AcOH by boiling with conc. HCl and the oxidation of Cr^{III} to Cr^{VI} by H_2O_2 and the other on removal of OAc' by addition of excess of FeCl_3 and subsequent boiling when basic Fe^{III} acetate is pptd. and carries down with it Al and Cr.

M. S. B.

Colorimetric determination of uranium in ores poor in uranium.—See B., 1934, 407.

Volumetric determination of tin, using various reducing agents and various concentrations of acid. F. W. LOUW and W. E. SCHILZ (J.S. African Chem. Inst., 1934, 17, 3—7).—The Sn content of concentrates is determined by fusing with Na_2O_2 , dissolving in hot H_2O , neutralising with HCl, and diluting to 400 c.c. The Sn is then reduced with Al turnings, redissolved by boiling, cooled, and titrated with standard I. Reduction may also be effected with Zn dust, Ni foil, or Sb, but Al dust, Pb foil, and Mg give inferior results. Low results are obtained if the solution contains > 60% of conc. HCl, and the best proportion is 40%. A. G.

Volumetric determination of tin; use of potassium iodate. J. B. RAMSEY and J. G. BLANN (J. Amer. Chem. Soc., 1934, 56, 815—818).—Air-free solutions of Sn^{++} can be determined by direct titration with KIO_3 at acid concns. as high as 1.5—2.0*N*. With KI_3 an error of about 0.5% is obtained even when the concn. of HCl is only 0.3*N*. By adding air-free SnCl_2 to an excess of KIO_3 or KI_3 accurate results are obtained at any concn. of HCl up to 6.1*N* without excluding air. The re-dissolution of reduced Sn is hastened by adding small amounts of CoCl_2 or NiCl_2 . E. S. H.

Determination of bismuth. P. FARINI (Boll. Chim. farm., 1934, 73, 284—287).—The accuracy of various methods has been compared. Bi is best determined gravimetrically as BiPO_4 ; it may also be pptd. as basic nitrate and weighed as Bi_2O_3 , but not as Bi_2S_3 . Of the volumetric methods, pptn. as $\text{Bi}_2(\text{SeO}_3)_3$, which is determined iodometrically, gives the best results, the end-point being sharper than when the Bi is pptd. as the double iodide with isoquinoline. D. R. D.

Detection of bismuth with sulphur-containing organic reagents. II. Detection with 2-thiol-5-thio-4-phenyl-3:4-diazolone. J. DUBSKY and J. TRTILEK (Z. anal. Chem., 1934, 96, 412—415; cf. this vol., 502).— $\text{C}_8\text{H}_6\text{N}_2\text{S}_3$ (prep. described), used as an aq. solution of its K salt (Tz_2K), gives with Bi in neutral or acid solution orange to red ppts. of $\text{Bi}(\text{Tz})_3$ or $\text{Bi}(\text{Tz})_2\text{Cl}$. Other heavy metals also give yellow ppts.; limit, 0.0012 mg. Bi. J. S. A.

Analytical chemistry of tantalum and niobium. V. SCHWARZ (Angew. Chem., 1934, 47, 228—230).—A review of published work. E. S. H.

Potentiometric determinations in alkaline solution. Determination of gold by means of vanadyl sulphate. C. DEL FRESNO and E. MAIRLOT (Anal. Fis. Quím., 1933, 31, 531—536).—When a strongly alkaline solution of a Au^{III} salt is titrated with VOSO_4 solution at $\leq 50^\circ$, a large and sharp potential change occurs at the end of the reaction $\text{AuO}_2^{+} + 3\text{VO}^{++} + 8\text{OH}^{-} = \text{Au} + 3\text{VO}_3^{-} + 4\text{H}_2\text{O}$. The solution should contain $\leq 8\%$ of NaOH. At room temp. the quantity of VOSO_4 used is about 2% high, but at $50\text{--}70^\circ$ accurate results are obtained. H. F. G.

Separation of ruthenium from platinum, palladium rhodium, and iridium. R. GILCHRIST (Bur. Stand. J. Res., 1934, 12, 283—290).—The

solution in dil. H_2SO_4 containing NaBrO_3 is distilled and the RuO_4 evolved is absorbed quantitatively in dil. HCl saturated with SO_2 . The boiling solution is adjusted to p_{H} 6 by adding NaHCO_3 , after decomposing SO_3^{+} by treating with HCl, and the pptd. hydrated oxide is ignited in air and then reduced to Ru in H_2 , and weighed. E. S. H.

Separation of platinum, palladium, rhodium, and iridium from one another and their gravimetric determination. R. GILCHRIST (Bur. Stand. J. Res., 1934, 12, 291—303).—The solution is evaporated to dryness with HCl and NaCl and the residue dissolved in H_2O . 10% NaBrO_3 is added to the boiling solution at p_{H} 6, pptg. hydrated dioxides of Pd, Rh, and Ir. Two pptns. serve to isolate Pt quantitatively. Pt is pptd. as sulphide, ignited, and weighed as Pt. Pd is quantitatively pptd. from solutions in dil. HCl or dil. H_2SO_4 by dimethylglyoxime and the ppt. weighed. Rh is separated from Ir by the TiCl_2 method previously described (A., 1932, 1224). E. S. H.

Potentiometric determination of palladium by means of stannous and titanous salts, iodide, and cyanide. E. MULLER and W. STEIN (Z. Elektrochem., 1934, 40, 133—140).—Even at low [HCl], the potentiometric determination of Pd with Sn^{++} is not satisfactory; in H_2SO_4 solution the acid concn. has but little influence, but the end-point is not sharp. With Ti^{+++} in HCl solution the determination is accurate to within only about 2%, whilst in H_2SO_4 solution the curve is very flat. The potentiometric method based on the very low solubility of PdI_2 gives very accurate results, is not influenced by small quantities of HCl, and need not be carried out in absence of air. The indirect method in which an excess of KI is added to the Pd^{++} solution, and the excess of I^{-} is titrated potentiometrically with AgNO_3 , is also highly satisfactory, provided the PdI_2 is removed by filtration [after addition of $\text{Al}_2(\text{SO}_4)_3$ to the solution]. Ag^{+} and Pd^{++} cannot be determined consecutively in the same solution by the I^{-} method, although the total Ag^{+} and Pd^{++} may be so determined; neither can Ag^{+} be determined potentiometrically by Cl^{-} in presence of Pd^{++} . The reaction between Pd^{++} and $\text{Hg}(\text{CN})_2$ yields a very flat potential curve, but with KCN the formation of $\text{Pd}(\text{CN})_4$ is indicated by a sharp break, provided NaOAc is present; the results are accurate only if the Pd^{++} solution is added to the KCN. H. F. G.

Application of the polarographic method to the analysis of synthetic phosphorescents. Determination of palladium. S. HAKOMORI and T. TASHIRO (J. Electrochem. Assoc. Japan, 1934, 2, 15—18).—The method is discussed and a polarogram of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ is given. CH. ABS.

Low-temperature thermostats. K. PETERS (Chem. Fabr., 1934, 7, 47—49).—Liquid air drips into a closed jacket and on evaporation the air escapes through a valve operated by a thermostat; the valve opens when the temp. rises and thus permits a further quantity of liquid air to enter the jacket. Temp. between 0° and -185° may be maintained const. to within $\pm 0.1\text{--}0.5$. The same principle may be applied for temp. up to

400° ($\pm 1^\circ$), using hot air, and for temp. down to -200° or lower ($\pm 1^\circ$) using liquid air evaporating under reduced pressure. H. F. G.

Magneto-caloric production of extremely low temperatures. W. MEISSNER (Physikal. Z., 1934, 35, 303—310).—A review of the theory and practice of the method of adiabatic demagnetisation of rare-earth salts. A. J. M.

Absolute measurement of thermal conductivity of gases. P. VERNOTTE (Compt. rend., 1933, 197, 1395—1397).—The apparatus consists of a duralumin cylinder, *A*, of heat capacity *C*, raised to *V*°, enclosed in a second cylinder, *B*, 15 mm. thick, at temp. *W*° (approx. = *V*—15°), separated from *A* by a layer of gas ϵ (approx. = 0.5) mm. across. The coeff. of conductivity, *k*, of the intervening gas is then given by the equation $C\Delta V = kS(V-W)\Delta t/\epsilon$, where *S* is the area of thermal exchange and *t* the no. of sec. in which *A* cools by ΔV °. C. A. S.

Gas thermostat. A. J. BAILEY (Science, 1934, 79, 277).—An apparatus for controlling the temp. of ovens and liquid baths to 0.1° is described.

Exergic and endergic reactions. W. BLUM (Science, 1934, 79, 273—274; cf. this vol., 385).—These terms have previously been applied in connexion with nuclear transformations (*ibid.*, 1932, 76, 615). L. S. T.

Improvements in adiabatic calorimeter for measuring very small heat effects. W. SWIENTOSŁAWSKI (Bull. Acad. Polonaise, 1934, A, 64—68; cf. A., 1931, 593).—Modifications to eliminate spurious e.m.f. in the measuring thermocouples are described. L. S. T.

Errors of fluid-pressure thermometers and their methods of correction. W. G. BIRD (J. Sci. Instr., 1934, 10, 134—142).—A mathematical analysis is given. C_7H_{16} is suitable for aeronautical instruments. H. J. E.

Technique of sputtering sensitive thermocouples. L. HARRIS and E. A. JOHNSON (Rev. Sci. Instr., 1934, [ii], 5, 153—157).—Cathodic sputtering of Bi, Sb, and Te on thin cellulose gave couples sensitive, when used with a.c. amplification, to adiabatic heat produced in a sound field, and to small intensities of radiation. C. W. G.

Reproducibility of the ice point. J. L. THOMAS (Bur. Stand. J. Res., 1934, 12, 323—327).—Comparison of 34 ice-baths shows that with reasonable precautions the ice point is reproducible to 0.0001—0.0003°. N. M. B.

Laboratory gas-burner. J. HUDIG (Chem. Weekblad, 1934, 31, 321—323).—A small combined gas-ring (I) and support is described to replace the Bunsen burner (II) and tripod. (I) works on the non-luminous, bats-wing flame principle (Bray burner) and is more economical than (II). S. C.

Filters for producing the colour of the equal-energy stimulus. R. DAVIS and K. S. GIBSON (Bur. Stand. J. Res., 1934, 12, 263—267; cf. A., 1931, 592).—Two filters have been prepared which, when combined with an illuminant at 2848° abs., give the

colours of so-called equal energy stimulus on the bases of the O.S.A. and I.C.I. standard observers, respectively. These contain 3.134 and 2.954 g., respectively, each of $CuSO_4 \cdot 5H_2O$ and mannitol in solution A, and 31.180 and 28.440 g. of $CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and 17.154 and 17.840 g. of $CuSO_4 \cdot 5H_2O$, respectively, in solution B. Spectrophotometric and colorimetric data are given. J. W. S.

Portable ultra-violet intensity meter, consisting of a balanced amplifier, photo-electric cell, and micro-ammeter. W. W. COBLENTZ and R. STAIR (Bur. Stand. J. Res., 1934, 12, 231—237).—The construction and performance of the instrument and the method of testing the constancy of the amplifier are described. After preliminary running for 5—10 min. there is no fluctuation in the zero reading of the meter, and the response is linear within the accuracy of the micro-ammeter used. Owing to the selective wavelength response of the photo-cell, the instrument is calibrated in abs. vals. by means of the standard balanced thermopile and filter radiometer (*ibid.*, 1932, 8, 759; A., 1931, 1386). J. W. S.

Semi-automatic light-distribution photometer. G. H. WILSON and W. WEIR (J. Sci. Instr., 1934, 11, 114—115).—A spot of light controlled by a photo-electric cell moves over a rotating disc of polar curved paper. C. W. G.

Simple method for obtaining photographic records of time-settle curves with elutriation. G. GOLLNOW (J. Amer. Ceram. Soc., 1934, 17, 116).—The suspension is allowed to settle in a vertical tube and the corresponding change in level of the clear liquid in a side tube is recorded on a rotating drum. J. A. S.

Identification of crystalline substances by means of X-rays. B. E. WARREN (J. Amer. Ceram. Soc., 1934, 17, 73—77).—The theory and practical application of X-ray "powder" analysis are described. J. A. S.

Monochromator of high light intensity. H. R. SCHULZ (Z. Physik, 1934, 88, 270—272).

Photo-electric colorimeter. II. B. LANGE (Chem. Fabr., 1934, 7, 45—47).—Methods of increasing the sensitivity of the apparatus previously described (A., 1933, 44) are given. With the modified instrument $10^{-6}N\text{-KMnO}_4$ yields a deflexion of 12 scale divisions; the accuracy is very high, and if desired 0.2 c.c. of liquid can be dealt with. A photo-electric device for measuring the reflexion from a surface, and operating on the same principle as the colorimeter, is described. The MgO deposited from burning Mg is recommended as a standard and easily-renewable white surface. A. B. D. C.

Aluminium-surfaced mirrors. H. S. JONES (Nature, 1934, 133, 552—553).—The deposition and use of Al on glass for astronomical mirrors are described. L. S. T.

Principle of a spectrograph for ultra-radiation. H. ZANSTRA (Naturwiss., 1934, 22, 171—172).—The theory of an arrangement of counters so that coincidence is produced only by primary radiation is given. A. J. M.

Composite photo-cathodes. R. FLEISCHER and P. GORLICH (Physikal. Z., 1934, 35, 289—292; cf. A., 1933, 887, 999; this vol., 130).—The photo-cell with Cs-Cs₂O cathode can be improved by introducing a foreign metal into the cathode (*e.g.*, Ag). This is done by allowing atoms of the foreign metal to diffuse into the cathode from a very thin layer of the metal deposited on it. An increase in the sensitivity of the cell occurs as the diffusion process takes place.

A. J. M.

Apparatus for the transformation of light of long wave-length into light of short wave-length. G. HOLST, J. H. DE BOER, M. C. TEVES, and C. F. VEENEMANS (Physica, 1934, 1, 297—305).—A picture is projected in infra-red light on to a transparent photocathode (Cs on a very thin film of Ag) sensitive to infra-red rays. The photo-electrons emitted are brought by an electric field on to an anode, coated with a fluorescent salt (*e.g.*, CaWO₄), and the photograph is printed on paper sensitive to visible and ultra-violet rays.

H. J. E.

Determination of the space lattice of a triclinic mineral by means of the Weissenberg X-ray goniometer. G. TUNELL (Amer. Min., 1933, 18, 181—186).

CH. ABS.

Industrial and research spectrophotometer. J. H. DOWELL (J. Sci. Instr., 1934, 10, 153—156).—The instrument incorporates a system previously described (cf. A., 1932, 245).

C. W. G.

Temperature variation of the selenium barrier layer photo-cell. A. MITTMANN (Z. Physik, 1934, 88, 366—371).—Measurements between —174° and 85° show negative coeffs.

A. B. D. C.

Synchronisation mechanism for registering photometer. O. BLUH (Z. Physik, 1934, 88, 403—408).

A. B. D. C.

Simple ultra-violet monochromators for large area illumination. G. R. HARRISON (Rev. Sci. Instr., 1934, [ii], 5, 149—152).—A spherical concave mirror inclined at 30° to the horizontal in distilled H₂O gives monochromatic distorted images of a high-power horizontal Hg arc. The images can be isolated in turn by means of an exit slit, and give pure monochromatic radiation. In an improved instrument a plane mirror with one or two large fused quartz lenses is used.

N. M. B.

Statistical investigation of the uniformity of grades of 1000 Lovibond red glasses. G. K. WALKER (Bur. Stand. J. Res., 1934, 12, 269—282).—Apparatus and procedure for the calibration of Lovibond red glasses are described, and a method of expressing the val. in terms of the Priest-Gibson unit and scale has been adopted. The new val. is the effective additive val. when the glass is used in combination with a 35-yellow glass. Variations of 1 unit frequently exist among glasses of similar Lovibond no. The results are discussed with special reference to the oil industry.

E. S. H.

Two variations of the powder method of X-ray crystals. J. P. BLEWETT (J. Sci. Instr., 1934, 11, 148—150).—(1) A converging beam focussed on the circumference of a circular camera is scattered

by powder placed at a point diametrically opposite, giving greater intensity and making diffraction angles attainable at almost 0°. (2) A conen. of intensity in the diffracted beam is obtained by making the angle between it and the wide parallel incident beam nearly equal to that between the latter and the plane powder specimen.

C. W. G.

Colour correction filter for photo-electric photometry. J. S. PRESTON and L. H. McDERMOTT (J. Sci. Instr., 1934, 11, 150—157).—Considerable accuracy can be obtained by using an aq. solution of CuCl₂, CoSO₄, (NH₄)₂SO₄·6H₂O, and K₂Cr₂O₇.

C. W. G.

Measurement of blackening in the spectrum of sources of light of short duration on photographic plates. S. H. R. VISSER (Physica, 1934, 1, 497—502).—A spectrogram of the light source is made without using a sector or wedge in front of the slit, and the resulting negative is printed on photographic paper through an absorbing wedge the gradient of which is parallel to the spectral lines. The length of the lines on the print measures the blackening of the photographic plate.

H. J. E.

Metal contact photo-cell. J. H. DE BOER and W. C. VAN GEEL (Physica, 1934, 1, 449—451).—The cell has a layer of Cs separated from one of Zr by a thin film of ZrO₂. On illumination electrons pass from the Cs to the Zr. Max. sensitivity is at 5800 Å. Alternative systems are Cs-artificial resin-Ni or Ni-BaO-Ba.

H. J. E.

Measurement of high voltage of alternating current by Kerr cell. Y. YAMAGUCHI and K. MIYAMOTO (Bull. Chem. Soc. Japan, 1934, 9, 125—131).—Light of λ 5200 Å. was passed through PhNO₂ between crossed Nicols in alternating fields of 7000—25,000 volts per cm. The intensity of the light from the analyser was measured and the potential of the electric field calc. using the known Kerr const. The calc. vals. of the potentials are generally slightly < those obtained from the turn ratios of the transformer.

H. S. P.

Measurement of small a.c. voltages by means of cuprous oxide detectors. K. B. KARANDEEV (J. Tech. Phys., U.S.S.R., 1932, 2, 412—424).—Cu₂O acts as a rectifier at 10⁻⁴ volt.

CH. ABS.

Thyratron as an α-particle counter. H. TEICHMANN (Physikal. Z., 1934, 35, 299—301).—The use of an arrangement of thyratrons as an electrical relay in conjunction with a counter for counting α-particles in large nos. is described.

A. J. M.

Absolute method of determining dielectric constants of solutions of electrolytes at high frequencies. H. HELLMANN (Ann. Physik, 1934, [v], 19, 623—636).—The method depends on the measurement of the intensity of stationary waves in a Lecher system, when this is connected at one end with a trough containing the liquid under investigation.

A. J. M.

Valve-voltmeter for measurements of hydrogen-ion concentration. A. S. McFARLANE (J. Sci. Instr., 1934, 10, 142—147).—The instrument is truly direct reading, and is self-standardising and accurate to 0.01 *p*_H.

C. W. G.

Counter tube invariants. L. JANOSSY (Z. Physik, 1934, 88, 372—388).—Theoretical.

A. B. D. C.

Capillary electrometer of considerably reduced capacity. R. HAVEMANN (Z. Elektrochem., 1934, 40, 117—119).—A fine capillary tube sealed into a small H_2SO_4 reservoir is enlarged at its upper end to receive a globule of Hg, which, making contact through a Pt wire, serves as one electrode. Hg at the bottom of the reservoir forms the second electrode. The enlarged portion of the capillary is continued as a somewhat wider inverted U tube in which a Hg piston, operated by a screw device, is employed to adjust the air pressure in the tube and hence the position of the Hg in the enlargement and capillary. A vac. jacket maintains a const. temp. of the air. The quantity of Hg used is extremely small, and the capacity very low. With a glass electrode, no polarisation was apparent after 6 hr. at p_{H} between 2 and 9.

H. F. G.

Fluorine preparation cell. L. M. DENNIS and E. G. ROCHOW (J. Amer. Chem. Soc., 1934, 56, 879).—A modified apparatus (cf. A., 1931, 1248) is described.

E. S. H.

Experiments with pure metal resistance standards. J. L. THOMAS (Bur. Stand. J. Res., 1934, 12, 313—319).—Determinations of electrical resistance at the ice point indicate that standard wires of Pt, Au, or Cu show little change in a period of 20 months, whilst the performance of Ag and Sn is less satisfactory.

E. S. H.

Determination of the e.m.f. of the international Weston standard cell by the silver coulometer method. A. K. KOLOSOV (Vsesoy. Nauch.-Issledov. Inst. Metrol. Stand., 1933, No. 127, 3—17, 82—94).—The mean val. $E_{20} = 1.018254 \pm 8$ microv. was obtained.

CH. ABS.

Sensitive method for the determination of instantaneous falls of potential in X-ray equipment. H. TELLEZ-PLASENCIA (Anal. Fis. Quím., 1933, 31, 513—515).—A potentiometer is connected across the main supply, before the interruptor and coil primary, and a Ne lamp of known discharge voltage and with very small electrodes is connected across the potentiometer. By suitable adjustment of the electrical vals. in the circuit great sensitivity may be obtained.

H. F. G.

Inexpensive, efficient relay. P. T. BLACK (Science, 1934, 79, 322).—The relay described breaks 110 volts at 12 amp. (d.c.) without arcing.

L. S. T.

Preparation of thin metallic layers by cathode sputtering. O. G. KEIKO (J. Tech. Phys., U.S.S.R., 1933, 3, 653—656).—Apparatus is described.

CH. ABS.

Fractionating column with fritted glass plates. S. T. SCHICKTANZ (Bur. Stand. J. Res., 1934, 12, 259—261).—A fractionating column with sintered glass plates, which has a plate efficiency of about 98% as against about 87% for the bubble-cap type column, is described.

J. W. S.

Investigation of gas discharge by the use of a directed test. D. VON OETTINGEN (Ann. Physik,

1934, [v], 19, 513—532).—An apparatus for finding the val. of the space charge and electron temp. is described.

A. J. M.

Determination of capillary constant by means of two spherical segments. J. VERSLUYS (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 45—46).—Theoretical. The capillary const. is derived from measurements of the force required to pull apart two segments of a sphere, held together by a pendular body of liquid.

E. S. H.

Funnel with high filtration velocity. H. SCHAFER (Z. anal. Chem., 1934, 96, 305—307).

J. S. A.

Apparatus for the laboratory purification of gases. T. P. HOAR (Chem. and Ind., 1934, 244—245).—Two 10-litre aspirator vessels A, B, containing in all 12 litres of purifying liquid, are connected to allow liquid to pass from A to B. Purified gas is withdrawn from A by entry of impure gas for purification into B, and vice versa.

H. J. E.

Ultracentrifuge. J. W. BEAMS, E. G. PICKELS, and A. J. WEED (J. Chem. Physics, 1934, 2, 143).—The rotor of a centrifuge previously described (cf. this vol., 52) is redesigned to eliminate convection effects.

N. M. B.

Extractor for fluid systems. W. F. BRUCE (Science, 1934, 79, 253—254).—An apparatus for the extraction of various quantities of aq. solutions by solvents heavier or lighter than H_2O is described.

L. S. T.

Apparatus for continuous extraction in vacuum at room temperature. M. A. MACHEBŒUF and N. FETHKE (Bull. Soc. Chim. biol., 1934, 16, 229—234).—A modification of the Soxhlet apparatus is described.

A. L.

Beyond uranium with the magneto-optic method of analysis. J. PAPISH and A. C. SHUMAN (Science, 1934, 79, 297—298).—The method failed in the authors' hands.

L. S. T.

Ether-like compounds. XII. Determination of the rate of acetal hydrolysis. M. H. PALOMAA and A. SALONEN (Ber., 1934, 67, [B], 424—429; cf. this vol., 57).—A dilatometer which permits the rate of reaction to be measured by the change in vol. of the solution is described. Measurements are recorded for $\text{CHMe}(\text{OEt})_2$, $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$, $\text{CH}_3(\text{OEt})_2$, $\text{CH}_2(\text{OMe})_2$, $\text{CH}_2(\text{OMe})\cdot\text{OEt}$, and $\text{CH}_2(\text{OMe})\cdot\text{OPr}^a$.

H. W.

Examination of water from various natural sources for variations in isotopic composition. E. W. WASHBURN and E. R. SMITH (Bur. Stand. J. Res., 1934, 12, 305—311).—A differential pyknometer for determining d to 1 part in 10^6 is described. The following increases in d over that of ordinary H_2O (in p.p.m.) have been observed: H_2O from the Dead Sea and Great Salt Lake 2, H_2O of crystallisation from native $\text{Na}_2\text{B}_4\text{O}_7\cdot 4\text{H}_2\text{O}$ 7, sap H_2O from a young willow tree 2.8, H_2O produced by burning the dry wood 5.4.

E. S. H.

Significance of interfacial tension in pykno-metric determination of densities of solids. E. COHEN and N. W. H. ADDINK (Z. physikal. Chem., 1934, 168, 202—214; cf. A., 1933, 481).—If the

pyknometric liquid wets the solid only incompletely, the apparent d of a solid having a mol. lattice is influenced by the solid-liquid interfacial tension and by small amounts of impurities in the liquid which have some affinity for the solid, since both these influence the wetting. With ionic lattices the apparent d is independent of the pyknometric liquid.

R. C.

Correction of displacement errors in the calibration of sensitive manometers. J. WHITMORE (J. Sci. Instr., 1934, 10, 157).—A valve permits the making of connexions without disturbing the zero level.

C. W. G.

Oil manometer for moderately low pressures. K. HICKMAN (Rev. Sci. Instr., 1934, [ii], 5, 161—164).—A very sensitive, accurate, self-priming manometer suitable for the range 5—0.01 mm. is described.

N. M. B.

Automatic Wilson cloud chamber. A. J. DEMPSTER (Rev. Sci. Instr., 1934, [ii], 5, 158—160; cf. *ibid.*, 1933, [ii], 4, 373).—A simplified instrument, in which the piston is actuated by a spring and is momentarily held open by small electromagnets, is described.

N. M. B.

Simple siphon filter. G. SPIELMEYER (Chem.-Ztg., 1934, 58, 338).—A hard filter-paper is secured against an inverted funnel by gauze stitched at the funnel base and is immersed in the suspension to be filtered. It is connected by a siphon tube to an external capillary and the rate of flow is further regulated by a screw clip.

C. I.

Errors in gas analysis arising from loss of gas by dissolution in rubber connexions and stopcock lubricant. J. R. BRANHAM (Bur. Stand. J. Res., 1934, 12, 353—362).—Serious errors may result when high concns. of CO_2 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6 , or butane are present. A method of obtaining an approx. correction is proposed.

E. S. H.

Portable detector for radium. L. F. CURTISS (Bur. Stand. J. Res., 1934, 12, 379—382).

E. S. H.

Perkin tube. J. T. DUNN (Analyst, 1934, 59, 342—343).—The Perkin tube (J.C.S., 1884, 45, 443) is described.

E. C. S.

Valve for constant-pressure delivery. J. H. LEES (J. Sci. Instr., 1934, 11, 168—170).—Change of pressure causes movement of Hg into a float chamber, and actuates a rubber diaphragm which presses against the end of the gas delivery jet.

C. W. G.

Apparatus for distilling metals. R. V. JONES (J. Sci. Instr., 1934, 11, 167—168).—The metal is heated in vac. in a crucible or W helix, and the vapour is conc. in the desired direction by an electrostatic field.

C. W. G.

Lecture experiment for the direct evaluation of Debye-Scherrer photographs. E. HERSCHKOWITSCH (Physica, 1934, 1, 452—454).—A direct-reading scale for cubic crystals is described.

H. J. E.

Streaming method for the study of chemical intermediate products. H. SCHMID (Oesterr. Chem.-Ztg., 1934, 37, 73—75).—A lecture summarising published work.

E. S. H.

Rule for the interpretation of m.p. diagrams. R. F. NEWTON (Science, 1934, 79, 321—322).

L. S. T.

Micro-manipulator for pure culture and micro-chemical work. G. W. FITZ (Science, 1934, 79, 233—234).

L. S. T.

γ -Ray ionisation chamber for use with a direct-current amplifiers. L. F. CURTISS (Bur. Stand. J. Res., 1934, 12, 167—172).—A γ -ray ionisation chamber is described in which the source is within the central electrode and in which only an annular zone of ionisation about the source of γ -rays contributes to the measured ionisation current. With average Ra preps. the current is about 10^{-11} amp. and is amplified and read on a micro-ammeter. The results are accurately comparable with those obtained with a Au-leaf electroscope, and its advantages over the latter are discussed. It is particularly suited to routine standardisation of Ra and Rn preps.

J. W. S.

Copper age in ancient China. III. T. DONO (Bull. Chem. Soc. Japan, 1934, 9, 120—124).—An ancient Chinese spear-head and two halberds consist chiefly of Cu with 6—13% Pb and traces of Sn, whilst one halberd contains 13.7% Sn and only 0.3% Pb and may be called bronze.

H. S. P.

Geochemistry.

Presence of phosphorus in the sun. C. E. MOORE, H. D. BABCOCK, and C. C. KIESS (Science, 1934, 79, 390).—The position and intensity of five faint lines in infra-red spectrograms practically establish the presence of P in the sun.

L. S. T.

Distribution of ozone in the atmosphere. D. BARBIER (Compt. rend., 1934, 198, 1060—1062).—Theoretical. A new method of calculation is given, and Gauzit's results are criticised (cf. A., 1932, 358; this vol., 386).

C. A. S.

Concentration of atmospheric ozone at different (low) altitudes. D. CHALONGE, F. W. P. GOTZ, and E. VASSY (Compt. rend., 1934, 198, 1442,

and Naturwiss., 1934, 22, 297).—Simultaneous measurements of $[\text{O}_3]$ by absorption spectra at Jungfraujoch (3450 m.) and Lauterbrunnen (800 m.) during Aug., 1933, showed increase in $[\text{O}_3]$ with altitude.

B. W. B.

Proportion of heavy water in natural water. H. A. C. MCKAY (Nature, 1934, 133, 611).—Natural H_2O probably contains a sensibly const. concn. of H_2^{18}O .

L. S. T.

Proportion of heavy water in natural water. (SIR) R. ROBERTSON (Nature, 1934, 133, 611; cf. preceding abstract).—Density determinations indicate

that there is no marked proportion of H_2O in the H_2O of the Dead Sea. L. S. T.

Variations in the alkalinity of shore pools. A. D. DE VIRVILLE (Compt. rend., 1934, 198, 1178—1179).—The daily variation of c_H in coastal pools is dependent on the chlorophyllic assimilation by green algae under varying light conditions. P. G. M.

Radioactivity of mineral springs of Greece. M. PERTESSIS (Compt. rend., 1934, 198, 1053—1055).—The salts, temp., and radioactivity of 32, and the composition and radioactivity of the gases evolved at four, springs in Greece have been determined. The most radioactive waters are those of Kamena-Vourla (Phthiotis), 10.41 g. per kg., of salts, 32.4°, and 75.1 μC . The most radioactive gas is from the same: 414 μC per litre, the gas containing CO_2 15.1, O_2 0.5, and N_2 84.4%, with no He; the only abundant evolution is at Hypati (Phthiotis), 500 cu. m. per hr., of CO_2 94.8, O_2 0.4, N_2 4.62, and H_2S 0.18%, radioactivity only 0.29 μC . C. A. S.

Iodine content of Bohemian drinking waters. O. TOMÍČEK and R. UZEL (Časopis českoslov. Lek., 1933, 13, 193—196; Chem. Zentr., 1933, ii, 3023).—Results of colorimetric I determinations are recorded and correlated with the occurrence of goitre. The average of 15 samples was 1.3×10^{-6} g. of I per litre. H. J. E.

Titration of sea-water with hydrochloric acid, and the importance of controlling the CO_2 tension of acidified sea-water. G. TOMITA (J. Shanghai Sci. Inst., 1933, 1, 19—28).—The p_H of sea- H_2O (of excess alkaline reserve 0.0023N) after addition of HCl was measured at once and after aeration, the difference depending on the change in CO_2 content. The importance in biological experiments is discussed. R. S. B.

Presence of nitrifying bacteria in deep seas. C. L. CAREY and S. A. WAKSMAN (Science, 1934, 79, 349—350).—Samples of sea-bottom material from deep seas north of Bermuda practically all contained nitrite-forming bacteria. Nitrification in the sea is due to bacteria which are native inhabitants of the sea bottom and are not merely contaminants from land. L. S. T.

Geochemistry of oil-field water. K. KREJCI-GRAF (Petroleum, 1934, 30, No. 18, 1—18).—Waters are classified graphically in a square diagram in which the vertical sides represent % of mono- and di-basic ions and the horizontal sides % of O-containing and O-free acid ions. A diagonal divides the composition of the generality of surface waters from oil-waters. In the latter the Cl is more than equiv. to the alkali. H_2O analyses from the oil-fields of Rumania, Poland, Venezuela, and California are summarised in this way. In most cases each geological formation corresponds with a characteristic H_2O analysis. In Rumania $SO_4^{''}$ is usually low and $S^{''}$ is probably produced by reduction from $SO_4^{''}$. Apart from NaCl derived from dissolution of NaCl-bearing formations and similar cases there is little connexion between H_2O analysis and composition of the strata in the Rumanian oilfield; where I, Br, and K contents are high they are of organic origin, and

this occurs principally in the newer formations. It is concluded that after allowing for secondary changes the deeper waters of all oil-fields are essentially marine in character. Ra is present as an associate of $CaSO_4$ and Ba, but is absent in presence of $CaCO_3$. The H_2O of recent formations (rich in I etc.) is classified as a "by-product" of petroleum formation, that of older formations as infiltration H_2O . In both cases the origin of the salts is ultimately marine. C. I.

Leucite-basalt from Ryudô, Kankyô-Hokudô, Korea. T. TOMITA (J. Shanghai Sci. Inst., 1933, 1, 25—39).—Analyses are given and the origin of analcite is discussed. C. W. G.

Alteration of talc and antigorite to leuchtenbergite in the metamorphosed dolomite of the Matenrei system, North Korea. S. SATÔ (J. Shanghai Sci. Inst., 1933, 1, 17—24).—Analyses and a scheme for the formation of leuchtenbergite are given. C. W. G.

Dyke-rocks in South Manchuria. T. OGURA (Mem. Ryojun Coll. Eng., 1933, 6, 155—174).—Analyses are given and origins are discussed. C. W. G.

Salt rock from Morszyn. C. KUŹNIAK (Bull. Acad. Polonaise, 1933, A, 447—451).—The salt rock stratum consists of rock-salt (36.57%), anhydrite (5.58%), ankerite (42.75%), quartz and quartzine (12.01%), clay (1.6%), and $Fe_2O_3 \cdot H_2O$ (1.42%). The ankerite component contains $CaCO_3$ (59.29%), $MgCO_3$ (29.69%), $FeCO_3$ (12.02%), and traces of $MnCO_3$. J. W. S.

Gordonia uraninite and the upper precambrian rocks of Southern Africa. A. HOLMES (Amer. J. Sci., 1934, [v], 27, 343—353).—Analyses, including micro-analyses (cf. following abstract), are given. The Pb ratios are discussed and the age of the minerals is calc. to be 9.25×10^6 years. C. W. G.

Quantitative methods of micro-analysis with special reference to the Gordonia uraninite. F. HECHT (Amer. J. Sci., 1934, [v], 27, 321—342).—Experimental details are fully described and a scheme for the analysis of pitchblende is shown. Analyses of the uraninite are given. C. W. G.

Paulopost stilbite in the Camas Land sill, Chelan County, Washington. W. M. CHAPPELL (Amer. Min., 1933, 18, 440—444). CH. ABS.

Piedmontite from Shadow Lake, Madera County, California. A. M. SHORT (Amer. Min., 1933, 18, 493—500).—Piedmontite contains SiO_2 35.26, Al_2O_3 23.50, Fe_2O_3 4.65, MgO 0.21, CaO 22.73, H_2O 1.37, TiO_2 0.12, Mn_2O_3 12.13, total 99.97%. The formula $H(Ca, Mn, Mg)_2(Al, Mn, Fe)_3Si_3O_{13}$ is proposed. CH. ABS.

Tilleyite. E. S. LARSEN and K. C. DUNHAM (Amer. Min., 1933, 18, 469—473).—Tilleyite, from the contact zone at Crestmore, California, d 2.838, n_a 1.617, n_e 1.635, n_z 1.652, contains SiO_2 24.09, Al_2O_3 0.61, Fe_2O_3 0.12, MgO 0.43, CaO 57.75, H_2O 1.09, CO_2 15.82, total 99.91%. The formula $3CaO \cdot SiO_2 \cdot CO_2$ is suggested. CH. ABS.

Colusite. R. E. LANDON and A. H. MOGILNOV (Amer. Min., 1933, 18, 528—533).—Colusite, a mineral

of the sphalerite group, occurs in Cu veins at Butte, Montana. It is a sulphide in which Cu, Fe, Sn, Mo, and Zn are isomorphous, and As, Te, and Sb are isomorphous with S; d 4.2, H 3—4; Sn 6.64, Cu 35.82, Sb 0.58, As 2.50, Zn 0.90, Te 2.97, Mo 8.80, Fe 18.37, S 24.20, Cr and W trace; total 100.78%.

CH. ABS.

Ammoniorborite. W. T. SCHALLER (Amer. Min., 1933, 18, 480—492).—Ammoniorborite from Larderello, Italy, n_a 1.470, n_g 1.487, n_z 1.540, and larderellite are dimorphous forms of $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

CH. ABS.

Large monazite crystal from N. Carolina. W. T. SCHALLER (Amer. Min., 1933, 18, 435—439).—The crystal (58.75 lb.; ThO_2 5—7%) is described.

CH. ABS.

Artificial jarosites. Separation of potassium from caesium. J. G. FAIRCHILD (Amer. Min., 1933, 18, 543—547).—Artificial jarosites of K, Rb, Ag, and Pb were prepared by heating the respective sulphate solutions with aq. $\text{Fe}_2(\text{SO}_4)_3$ in sealed tubes at 110—180°. At 100° Rb and Co are taken up in small amount by the K jarosite mol.

CH. ABS.

Stability relations of a Colorado pisanite (cuprian melanterite). E. B. ECKEL (Amer. Min., 1933, 18, 449—454).—The mineral, $2(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}) \cdot (\text{Cu}, \text{Zn})\text{SO}_4 \cdot 7\text{H}_2\text{O}$, has n_a 1.473, n_g 1.478, n_z 1.483. The $7\text{H}_2\text{O}$ compound is stable at R.H. 80—44%; $2\text{H}_2\text{O}$ is lost at 30%, and the $5\text{H}_2\text{O}$ compound is stable to 5% R.H. Near zero humidity $4\text{H}_2\text{O}$ is lost, affording the monohydrate.

CH. ABS.

Sulphohalite and other minerals from the Otjiwalundo Salt Pan, S.W. Africa. W. F. FOSHAG (Amer. Min., 1933, 18, 431—434).—Sulphohalite, $2\text{Na}_2\text{SO}_4 \cdot \text{NaCl} \cdot \text{NaF}$, n 1.455, pirssonite, trona, and thenardite are described.

CH. ABS.

Thermal metamorphism around the Ballachulish granodiorite. A. J. HALL (Nature, 1934, 133, 651).—The contact margin of the granodiorite (I) has undergone contamination by assimilation of the country rocks. A mineralogical examination indicates that (I) has become richer in Al_2O_3 and K_2O , whilst the hornfels have received CaO and MgO .

L. S. T.

Pollucite, a new gem stone. L. J. SPENCER (Gemmologist, 1934, 3, 263—264).—Many silicate minerals would be suitable for use as gem stones if found as large well-developed crystals, clear and of a good colour. Pollucite $[\text{H}_2\text{Cs}_4\text{Al}_4(\text{SiO}_3)_9]$, the only mineral containing Cs as an essential constituent (Cs_2O 30.0—36.8%), has been mined at Newry, Maine, U.S.A., as a source of Cs and has yielded colourless gems with a brilliant lustre.

L. J. S.

Chemical analyses of some rocks from Aruba. Magmatic province of the Lesser Antilles. W. VAN TONGEREN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 162—168).—Analyses of typical rocks from Aruba are compared with those of specimens from other islands of the Lesser Antilles.

J. W. S.

Glaserite rocks from Stebnik. C. KUŹNIAR (Bull. Acad. Polonaise, 1934, A, 90—94).—The occurrence and composition are described.

H. J. E.

Incandescence of certain serpentines. (Mlle.) S. CAILLÈRE (Compt. rend., 1934, 198, 1354—1356).—Incandescence during thermal analysis is shown by a few minerals including the α -antigorites (I) distinguished by evolution of heat (II) at 750—850° (cf. A., 1933, 352). (II) was identified with the (easily visible) incandescence at 810° of both hydrous and completely dehydrated (I). A no. of specimens of (I) all showed incandescence, which is proposed as a test.

B. W. B.

Petrographic and mineralogical nature of the iron ore of Staro-Oskolsk district in Kursk Magnetic Anomaly (KMA) region. I. I. TANATAR (Domez, 1933, No. 9, 20—29).—The deposit is of hydrothermal nature, but (1) it was the Turingian schist and not the ferrous quartzite which first underwent metasomatic replacement, (2) pyritisation preceded sideritisation, (3) conversion of martite into limonite proceeded from the nucleus as well as from the periphery of the grain.

CH. ABS.

Kursk Magnetic Anomaly (KMA). A. N. POKHVISNEV (Domez, 1933, No. 9, 2—4).—The Fe deposits are described; as a potential source they are almost equal to known world deposits. Most of the ore requires preliminary magnetic separation.

CH. ABS.

Space lattice and optical orientation of chalcantite, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. T. F. W. BARTH and G. TUNELL (Amer. Min., 1933, 18, 187—194).—Procedure and calculations using the Weissenberg X-ray goniometer are given; a 6.110, b 10.673, c 5.95 Å.; α 82° 16', β 107° 26', γ 102° 40'.

CH. ABS.

Bavenite. C. J. KSANDA and H. E. MERWIN (Amer. Min., 1933, 18, 341—344).—Bavenite has $a:b:c=0.839:1:0.429$; a 9.67, b 11.53, c 4.95 Å., with 1 mol. of $9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{BeO} \cdot 4\text{CaO} \cdot \text{H}_2\text{O}$ per unit cell; $d_{\text{calc.}}$ 2.74 $\frac{1}{2}$.

CH. ABS.

Laumontite and thomsonite from Table Mountain, Colorado. E. P. HENDERSON and J. J. GLASS (Amer. Min., 1933, 18, 402—406).—Data are recorded.

CH. ABS.

Corvusite and rilandite, new minerals from the Utah-Colorado carnotite region. E. P. HENDERSON and F. L. HESS (Amer. Min., 1933, 18, 195—205).—Corvusite, d 2.82, H 2.5—3, is probably $\text{V}_2\text{O}_4 \cdot 6\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. Rilandite, H 2—3, contains 47.59% Cr_2O_3 .

CH. ABS.

Mercury in native silver. W. H. NEWHOUSE (Amer. Min., 1933, 18, 295—299).—Hg was frequently found in native Ag, which is probably of hypogene origin.

CH. ABS.

Physico-chemical properties of Japanese acid clay. VIII. Polarising microscopic studies. IX. Refractive index. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 90—96B, 96—98B).—VIII. A detailed description is given with photo micrographs of natural Japanese acid clay, clay after heating or treatment with acid or alkali, fuller's earth, Florida earth, etc. The main constituent, $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, is optically uniaxial.

IX. The n (about 1.5) and birefringence (0.0035—0.1) of a no. of clays are given.

A. G.

High concentration of radium and mesothorium I in nature and regularity of their migration. I. D. KURBATOV (J. Physical Chem., 1934, 38, 521—532).—A determination of the concn. of Ra, Th, and their radioactive isotopes in mineral springs indicates that there is no radioactive equilibrium. Concns. as high as 1.8×10^{-8} g. Ra and 2×10^{-2} g. meso-Th I (Th units) have been found in aq. NaCl associated with petroleum beds. This high concn. is not affected by the presence of SO_4^{--} . The amount of Ra-Th in natural active H_2O is found to be $<$ the amount in radioactive equilibrium with the meso-Th I present. The transference of Ra and meso-Th I by H_2O from eruptive rocks to sediment results in a thousand-fold concn. of these active substances, $\text{Mn}(\text{OH})_2$ and $\text{Fe}(\text{OH})_2$ being mainly responsible for the pptn. A method is described for the simultaneous determination of Ra, meso-Th I, Th-X, and Ra-Th. M. S. B.

Tests for mesothorium in radium from Labine Point, Great Bear Lake. G. C. LAURENCE and F. B. FRIEND (Canad. J. Res., 1934, 10, 332—334).—The meso-Th impurity was ascertained by a differential absorption method to be $< 0.0008\%$ by wt. or $< 0.2\%$ radiation equiv. Chemical analysis indicated 0.021% radiation equiv. R. S.

Concentration of rare elements in coal. V. M. GOLDSCHMIDT and C. PETERS (Nachr. Ges. Wiss. Göttingen, Math.-physik. Kl., 1933, 371—386; Chem. Zentr., 1933, ii, 2966—2967; cf. this vol., 53).—Be, B, Sc, Cr, Co, Ni, Ga, Ge, Mo, Y, Sn, Ce, Nd, Sm, Gd, Dy, Er, Yb, Ag, Au, Pd, Rh, and Pt have been detected spectrographically in the ash from coal, especially in coals of low ash. The origin is discussed. H. J. E.

Organic minerals. III. Chlorophyll and hæmin derivatives in bituminous rocks, petroleum, mineral waxes, and asphalts. Origin of petroleum. A. TREIBS (Annalen, 1934, 510, 42—62).—The mixture of porphyrins previously isolated (this vol., 387) from an oil-shale is shown to contain a little mesoporphyrin (I) and (probably) mesoætioporphyrin. The presence of porphyrin complex salts in numerous bituminous rocks, asphalts, and mineral waxes is shown by spectroscopic examination of $\text{Et}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ extracts. Removal of the metal with $\text{HBr}-\text{AcOH}$ (cf. *loc. cit.*) gives the porphyrin mixture, in which deoxophylloerythrin (II) and (mainly) deoxophylloerythroætioporphyrin (III) are usually present.

Similar examination of 29 specimens of petroleum shows the presence of porphyrins in 24 of them; (I), (II), and (III) are isolated from a Trinidad petroleum. When phæophytin is heated (slowly) in petroleum to $250-320^\circ$, phylloerythrin is formed; further heating at 360° gives (III). The probability of the genesis of petroleum from chlorophyll-containing material is discussed. H. B.

Soil classifications. S. J. SUSHKO (Pedology, 1933, 28, 499—511).—The classifications of Remezov (A., 1932, 1230) and Polynov are reviewed. A. M.

Saline peat profiles of Puerto Rico. A. P. DACHNOWSKI-STOKES and R. C. ROBERTS (J. Washington Acad. Sci., 1934, 24, 175—182).—Characteristics of three peat profiles are recorded and discussed in relation to palæontological classification, and to the formation of accumulations of coal and oil.

A. G. P.

Profile characteristics of New England forest soils. H. A. LUNT (Connecticut Agric. Exp. Sta. Bull., 1932, No. 342, 743—836).—Podsol, raw humus, humus, mild humus, and mull types of profile are distinguished. The physical properties of and biological activities in these types are described. The distribution of bases, org. matter, PO_4^{--} , and acidity in the various horizons of the profiles is examined.

A. G. P.

Thermal analysis of Tunisian soils. V. AGAFONOV and G. JOURAVSKY (Compt. rend., 1934, 198, 1356—1358).—Orcel and Caillère's method (cf. A., 1933, 1268) of differential thermal analysis was applied to the identification of kaolinite. Soil and mother-rock samples were decalcified with 10% aq. HCl and decanted from sand. Twenty-four samples from rocks of different ages and successive derived soil-beds, and also a granitic comparison, all showed the presence of kaolinite, inflexions occurring at $500-600^\circ$ and (less) at 950° . Some samples showed an evolution of heat at $380-400^\circ$ attributed to goethite.

B. W. B.

"White soils" of Lorraine, their origin, nature, and use. H. ERHART (Compt. rend., 1934, 198, 1522—1525).—The formation of these soils is discussed. In general they are deficient in Ca and PO_4^{--} , and pan formation beneath the surface restricts H_2O movement. After breaking up of the pan the soils are suited to silvicultural work, notably for beech.

A. G. P.

Organic Chemistry.

Preparation and physico-chemical properties of hexane and its isomerides. MAMAN (Compt. rend., 1934, 198, 1323—1325).—Hexane, β - and γ -methylpentane, $\beta\beta$ - and $\beta\gamma$ -dimethylbutane are prepared by standard methods and their physical consts. are recorded. J. L. D.

Synthesis of diacetylenes. T. Y. LAI (Bull. Soc. chim., 1933, [iv], 53, 1537—1543).—No reaction takes place between compounds $\text{CR}:\text{CNa}$ and $\text{CR}:\text{C-MgBr}$, even at 140° , but $\text{C}_5\text{H}_{11}:\text{C}:\text{C}:\text{CH}_2\text{Br}$ and

MgEtBr give nearly quantitatively $\text{C}_5\text{H}_{11}:\text{C}:\text{C}:\text{CP}1^a$. By reaction of the salts $\text{CR}:\text{CNa}$ (prepared by NH_2Na) and substances $\text{CR}:\text{C}:\text{CH}_2\text{Br}$ are obtained Δ^5 -*n-pentadeca-* (I) (15% yield), b.p. $134-135^\circ/4$ mm., Δ^7 -*heptadeca-* (18%), b.p. $150-155^\circ/6$ mm., Δ^8 -*hexadeca-* (20%), b.p. $169-170^\circ/15$ mm., and Δ^9 -*tricosadiene*, m.p. -12° to -10° . (I) with O_3 in CCl_4 gives $\text{CH}_3(\text{CO}_2\text{H})_2$ and *n*-hexoic acid, and, owing to the acidity of the central H atoms, gives with MgEtI 0.57 mol. of C_6H_6 at 35° and 1.32 mol. at 88° .

R. S. C.

Synthesis of symmetrical aliphatic γ -diacetylenes. T. Y. LAI (Bull. Soc. chim., 1933, [iv], 53, 1543—1548).—From $\text{CR}_2\text{C}\cdot\text{CH}_2\text{Br}$ (2 mols.) and Mg (1 atom) in Et_2O are obtained Δ^5 -hexadeca- (I) (50% yield), b.p. 157—158°/10 mm., Δ^7 -octadeca- (70%), b.p. 167—168°/7 mm., and Δ^9 -tetracosadiene (75%), m.p. 38.5—39° [also obtained (57%) from $\text{C}_9\text{H}_{19}\cdot\text{C}\cdot\text{CH}_2\text{Br}$ and Na]. (I) with O_3 in CCl_4 gives succinic acid and with NH_2Na in ligroin at 160—170° gives 0.6 mol. of NH_3 owing to isomerisation to the Δ^5 -compound. R. S. C.

Bibliography of chloropicrin, 1848—1932. R. C. ROARK (U.S. Dept. Agric., Misc. Publ. No. 176, 88 pp.).—Brief abstracts of 533 publications are given.

Enolisation as directed by acid and basic catalysts. II. Enolic mechanism of the haloform reaction.—See this vol., 607.

Preparation of methyl or ethyl iodide from iodoform. R. H. KIMBALL (J. Chem. Educ., 1933, 10, 747).—By boiling CHI_3 with 95% EtOH-KOH , removing the EtOH , acidifying, filtering, rendering the filtrate alkaline with NaOH , and heating it with Me_2SO_4 , a 78% yield of MeI can be obtained; Et_2SO_4 affords an 80% yield of EtI . CH. ABS.

Process for the addition of ethylene to hydrogen chloride and similar reactions. A. J. TULLENERS, M. C. TUYN, and H. I. WATERMAN (Rec. trav. chim., 1934, 53, 544—554).— HCl and C_2H_4 with anhyd. AlCl_3 in EtCl at $-78^\circ/760$ mm. give quantitatively EtCl . No products of high b.p. are formed. No advantage is gained by using higher pressure. EtBr can be obtained similarly in good yield by using HBr . Laboratory and semi-technical apparatus is described. R. S. C.

Addition of hydrogen bromide to Δ^5 -pentene and -heptene. M. L. SHERRILL, K. E. MAYER, and G. F. WALTER (J. Amer. Chem. Soc., 1934, 56, 926—930).—Addition of HBr to Δ^5 -pentene (I), b.p. 30.1—30.2 \pm 0.05° (from MgEtBr and allyl bromide or α -bromo- β -ethoxypropane and Zn), in cold AcOH or hexane gives *n*-amyl bromide in 60—75% yield. Δ^5 -Heptene (II), b.p. 93.5 \pm 0.05° (from MgBuBr and allyl bromide or α -bromo- β -ethoxyheptane and Zn), similarly affords *n*-heptyl bromide in 65—90% yield. With aq. HBr , (I) and (II) give β -bromo-pentane and -heptane, respectively, in 63—70% yield. The different mode of addition is believed to be due primarily to the solvent and not to the effect of peroxide. Numerous physical data are given for (I) and (II). H. B.

Action of light on di-iodo-hydrocarbons; di-iodoethylenes.—See this vol., 611.

Bromoacetylenes. T. Y. LAI (Bull. Soc. chim., 1933, [iv], 53, 1533—1537).— $\text{CEt}_2\text{C}\cdot\text{CH}_2\cdot\text{OH}$ and PBr_3 in $\text{Et}_2\text{O}-\text{C}_5\text{H}_5\text{N}$ give a 65% yield of α -bromo- Δ^8 -pentinene, b.p. 147—148°/754 mm. Similarly were prepared α -bromo- Δ^8 -octinene (55%), -noninene (55%), b.p. 112—114°/9 mm., and -dodecinene (60%), b.p. 131—132°/7 mm., and α -bromo- γ -phenyl- Δ^8 -propinene (70%). These substances give additive compounds with HgCl_2 , are hydrogenated (Pd -starch) in one

stage to saturated hydrocarbons, and contain very reactive Br. R. S. C.

Determination of methyl alcohol. W. ENDER (Angew. Chem., 1934, 47, 227—228).—Apparatus and procedure are described for determining MeOH in presence of other org. compounds by adding NaNO_2 , acidifying, collecting the evolved MeNO_2 in KI acidified with HCl , and titrating the liberated I with $\text{Na}_2\text{S}_2\text{O}_3$. E. S. H.

Fungi. III. *Parmelia physodes*, L.—See this vol., 570.

Compound of stannic chloride and ether.—See this vol., 615.

Constitution of glycerophosphates. III. F. L. PYMAN and H. A. STEVENSON (J.C.S., 1934, 448—450).—Kay and Lee's method (A., 1931, 766) for determination of α - in presence of β -glycerophosphates is trustworthy if enzyme poisons are absent, but is tedious; that of Carrara (A., 1932, 831) is unsatisfactory, whereas that of Fleury and Paris (A., 1933, 696) is recommended. By the last-named method (modified for Ca and Ba salts) it is shown that the samples of Ca α -glycerophosphate (I) obtained by King and Pyman (II) (J.C.S., 1914, 105, 1238) and by Fischer *et al.* (A., 1920, i, 807) are pure, but Bailly's specimen (A., 1915, i, 492) contains 10% of an impurity. The initially more sol. form of (I) (Charpentier *et al.*, A., 1932, 251) is a hydrate (+ H_2O), the solubility of (I) running parallel to its state of hydration. (II) gives the Na salt, + $6\text{H}_2\text{O}$ and anhyd., obtained by Charpentier (*loc. cit.*). J. W. B.

***d*-Ribitol-5-phosphoric acid.** P. A. LEVENE, S. A. HARRIS, and E. T. STILLER (J. Biol. Chem., 1934, 105, 153—156).—Ba *d*-ribose-5-phosphate (this vol., 390) with H_2 - PtO_2 in H_2O gives Ba *d*-ribitol-5-phosphate, $[\alpha]_D^{25} -8.9^\circ$ as Na salt in H_2O , $[\alpha]^{25} -6.4^\circ$ in H_2O (as Na salt in presence of $\text{Na}_2\text{B}_4\text{O}_7$). Na *d*-ribosephosphate has $[\alpha]_D +14.8^\circ$ and $+29.6^\circ$. Comparison of the sp. rotations of natural and synthetic ribose-5-phosphoric acids during glucoside formation in MeOH-HCl confirms their identity, and also the 5-position of the PO_4H_2 , since the rotations rise to a const. max., indicating the formation of a methylfuranoside only. A. A. L.

Preparation of organic sulphur compounds from olefines. A. MAIHLE (Chim. et Ind., 1934, 31, 255—261).—Interaction of C_2H_4 , C_3H_6 , Δ^1 -butene, and *iso*- C_5H_{10} in the gaseous phase with H_2S in presence of SiO_2 gel at 650—725° gives small amounts of the corresponding thiols and dialkyl sulphides, CS_2 , thiophen, and gaseous and liquid hydrocarbons (C_{10}H_8 isolated). Passage of BuSH over SiO_2 gel at 700° results in partial decomp. into H_2S , olefines, and thiophen. H. A. P.

Constitution of graphitic acid and its reactions.—See this vol., 614.

Detection of acetic acid. J. DÈUVRE (Bull. Soc. chim., 1933, [iv], 53, 1532—1533).— AcOH is detected by reduction with Mg and HCl and detection of the MeCHO formed by the Rimini-Simon reaction (A). Aeraldehyde and crotonaldehyde give a similar blue

colour in (A), but EtCHO and tigraldehyde do so only if an excess of Na nitroprusside is used. R. S. C.

Simplified preparation of butyric acid. L. A. ADAIR and E. J. SIMMONS (Field and Lab., 1933, 2, 31—32).—BuOAc is hydrolysed, and the alcohol (yield 56%) oxidised with $K_2Cr_2O_7$ and H_2SO_4 to $PrCO_2H$; the Ca salt is treated with conc. H_2SO_4 and the acid distilled. CH. ABS.

β -Methyl- α -ethylvaleric acid. M. M. KATZNELSON and M. S. KONDAKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 21—25).— $CEtNa(CO_2Et)_2$ condenses with $CHMeEtBr$ to give the *Et* ester, b.p. 240—270°, of *ethyl-sec.-butylmalonic acid*, m.p. 108—109° (*Ag* salt), which is converted by heating at 150—160° into *β -methyl- α -ethylvaleric acid*, b.p. 217—220° (*Ag* salt; *Me* ester, b.p. 168—170°/760 mm.; *chloride*, b.p. 66—72°/20 mm.; *amide*, m.p. 114—115°; *anilide*, m.p. 108—109°). J. W. B.

Conjugated systems. X. Electrolytic reduction of β -vinylacrylic acid. I. E. MUSKAT and B. H. KNAPP (J. Amer. Chem. Soc., 1934, 56, 943—945).—Electrolytic reduction (1 mol. H_2) of β -vinylacrylic acid (I) in 95% EtOH and a little aq. NaCl gives 25—30% of Δ^2 -pentenoic acid, b.p. 86—87°/10 mm. [ozonolysis products, MeCHO and $CH_2(CO_2H)_2$], thus differing from catalytic reduction (A., 1931, 719) but resembling Na-Hg reduction. (I) could not be reduced electrolytically in 0.5*M*-H⁺ or alkaline solution; reduction occurs most rapidly in neutral or slightly acid solutions. H. B.

Validity of Freudenberg's displacement rule. P. G. STEVENS (J. Amer. Chem. Soc., 1934, 56, 997—998).—The *p*-nitrophenyl ester of *l*- β -methylhexoic acid (Levene and Marker, A., 1931, 711) has b.p. 124—125°/0.15 mm., [M]_D (max.) +5.4°. One of Levene and Meyer's exceptions (this vol., 241) to Freudenberg's displacement rule is, therefore, incorrect. H. B.

Addition of hydrogen bromide to double linkings. Undecenoic acid. R. ASHTON and J. C. SMITH (J.C.S., 1934, 435—440).—The relative amounts of ν - (I) and κ - (II) -bromoundecenoic acid formed by addition of HBr to undecenoic acid (III) in various solvents and in presence or absence of O_2 or peroxides have been determined by thermal analysis. The main conclusions are: in absence of air (presence of H_2 or $NHPh_2$) addition of HBr to pure (III), m.p. 24—58°, in any solvent gives the normal product (I) in accordance with the Markownikov rule. In presence of O_2 or BzO_2H etc. the main function of the solvent is either to favour or hinder the peroxide effect, which reverses the normal addition to give (II). Thus in C_6H_{12} , ligroin, Et_2O , or AcOH, or without solvent, (I) is the main product, but in C_6H_6 or PhMe, it is (II), but the proportion of (I) increases with increase in the concn. of C_6H_6 solutions. H_2O has no influence on the normal reaction, but makes the peroxide effect possible with air where the dry solution (e.g., in ligroin) requires addition of an O_2 carrier. (III) becomes less sensitive to O_2 as the impurities are removed, since the main impurity is an O_2 carrier, possibly the compound $C_{14}H_{26}O$ (Perkin, J.C.S., 1883, 45) derived from *n*-heptaldehyde. Impure (III),

m.p. 19—21° or 23.7°, in ligroin or C_6H_{12} gives (II) in presence and (I) in absence of air. Pure (I), m.p. 35.1°, is best obtained (prep. described) from dry HBr and pure (III), and pure (II), m.p. 49.25°, from undried HBr and partly purified (III), both in ligroin. J. W. B.

Oxidation of palmitic acid with hydrogen peroxide in presence of cupric salt. I. S. MACLEAN and M. S. B. PEARCE (Biochem. J., 1934, 28, 486—494).—Palmitic acid was heated with H_2O_2 and $CuSO_4$ in neutral solution for varying periods. Volatile acids including $EtCO_2H$, AcOH, and HCO_2H , also EtCHO and MeCHO, were obtained. Succinic acid was obtained at all stages except the first. Unsaturated (OH)₂-acids and lactones (C_4 — C_7) predominate in the product. H. D.

Preparation of elæostearic acids from Chinese wood oil. A. W. THOMAS and J. C. THOMSON (J. Amer. Chem. Soc., 1934, 56, 898).—Details are given for the prep. of α -, m.p. 48°, and β -, m.p. 70.1—71°, -elæostearic acids from tung oil (I) and "wood oil butter" [from (I) and a trace of S], respectively. H. B.

Spectroscopic study of elæostearic acids from Chinese wood oil. A. DINGWALL and J. C. THOMSON (J. Amer. Chem. Soc., 1934, 56, 899—901; cf. Manecke and Volbert, B., 1927, 821).—The absorption spectra of α - (I) and β - (II) -elæostearic acids are of similar type, but differ sufficiently for identification; the composition of a mixture of (I) and (II) can be determined spectroscopically. Light from a W spark does not affect (I) in a 1 in 160,000 solution in 90% EtOH, but irradiation apparently leads to the production of a series of compounds. Irradiation of a 15% solution of (I) in 90% EtOH during 2 hr. gives (II). When (I) (in EtOH) is kept in presence of a little air at about -3°, MeCHO is produced. H. B.

Absorption of oxygen by linseed oil in presence of catalysts of different oxidation-reduction potentials.—See this vol., 607.

Preparation of keto-acids, unsaturated acids and disubstituted lactones.—See this vol., 650.

Reduction with lead-sodium alloy. V. The Tafel rearrangement. H. STENZL and F. FICHTER (Helv. Chim. Acta, 1934, 17, 669—681).—Reduction of $CH_2Ph\cdot CHAc\cdot CO_2Et$ with Pb-Na in $EtOH-H_2SO_4$ at 55° affords products similar to those obtained by electrolytic reduction (Tafel, A., 1907, i, 765), viz., $CH_2Ph\cdot CHEt\cdot CO_2H$, $OH\cdot CHMe\cdot CH(CH_2Ph)\cdot CO_2H$, and a hydrocarbon $C_{11}H_{16}$ which is not $CH_2Ph\cdot CHMeEt$ (*loc. cit.*), but is *n*-amylbenzene, b.p. 204—204.5°/750 mm., readily oxidised by CrO_3 -AcOH to $BzOH$, identical with a specimen obtained by Clemmensen reduction of $COPhBu^a$, and, contrary to Tafel, affording cryst. $\alpha\beta$ -dibromoamylbenzene, m.p. 64—65° (mixed m.p.), with Br at 160°. The various possible migrations of substituent groups in such reactions are discussed, and it is shown that the action of Na on CH_2PhBr and *iso*amyl bromide in PhMe (Schramm, A., 1883, 977) affords not *n*- but *iso*-hexylbenzene, b.p. 216.4°/735 mm. Reduction of $CH_2Ph\cdot CEt_2\cdot OH$ with HI-red P affords γ -benzyl-*n*-

pentane, b.p. 216.5—217°/735 mm. Reduction of $\text{CMe}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ with Pb-Na in $\text{EtOH-H}_2\text{SO}_4$ gives no hydrocarbon, but a mixture probably containing $\text{OH}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$.

J. W. B.

Analytical behaviour of oxalic acid. J. GROSSFELD, E. LINDEMANN, and M. SCHNETKA (Z. anal. Chem., 1934, 97, 1—14).— CaC_2O_4 is readily dissolved by $\text{HCl} > 0.2N$. Heating with 12.5% HCl causes some decomp. of $\text{H}_2\text{C}_2\text{O}_4$; evaporation of the solution causes loss of $\text{H}_2\text{C}_2\text{O}_4$ by sublimation. Pptn. as CaC_2O_4 is quant. in presence of a NH_4OAc buffer (p_H 3.3—4.0). Tartaric, citric, and malic acids interfere, being pptd. as Ca salts. Triple pptn. may be necessary for a quant. separation.

J. S. A.

Action of alkali iodides on [bromo]malonic esters. M. WEIZMANN and J. EDLITZ (Bull. Soc. chim., 1933, [iv], 53, 1495—1497).— $\text{CHBr}(\text{CO}_2\text{R})_2$ and $\text{CBr}_2(\text{CO}_2\text{R})_2$ ($\text{R}=\text{Me}$ or Et), liberate much I from NaI in COMe_2 or EtOH or from KI in EtOH , probably by formation of ethane- and ethylene-tetracarboxylates. A 40% yield of $\text{Cl}_2(\text{CO}_2\text{Me})_2$ was obtained.

R. S. C.

Monosubstituted fatty amines and halogenosuccinic acids. O. LUTZ (Ber., 1934, 67, [B], 648—653).—The interaction of primary amines and *l*-halogenosuccinic acids gives primarily malolactone, which passes into *N*-substituted β -malamic acids (I) with small amounts of *N*-substituted aspartic acids (II). (I) is separated from (II) by fractional pptn. with AgNO_3 . All compounds (I) when tested with Na molybdate are found to belong to the *d*-series, and all are transformed by hot aq. alkali into *d*-malic acid and the corresponding amine. (II) when treated with varied amounts of acid and alkali give characteristic rotation curves, and as $\alpha\text{-NH}_2$ -acids, are stable towards hot dil. alkali. The following compounds are described: *d*-mal- β -ethylamide, $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\text{Et}$, m.p. 68—70°, $[\alpha]_D^{20} +14.37^\circ$; β -propylamide, m.p. 85—86°, $[\alpha]_D^{20} 12.0^\circ$ (*Ag* salt); β -isobutylamide, m.p. 94°, $[\alpha]_D^{20} +10.2^\circ$; β -isohexylamide, m.p. 64—65°, $[\alpha]_D^{20} +11.5^\circ$ in H_2O (*Ag* salt); *d*-ethylamino-, *d*-propylamino-, *d*-isobutylamino- (*Ag* salt), and *d*-isohexylamino-succinic acid.

H. W.

Derivatives of alkyl γ -oxalocrotonates. A. B. BOESE, jun., and R. T. MAJOR (J. Amer. Chem. Soc., 1934, 56, 949—952).— $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (I), $\text{Et}_2\text{C}_2\text{O}_4$, and Na in Et_2O give *Et* γ -oxalocrotonate (II), m.p. 78—80° (the Me_2 ester, m.p. 124—126°, is similarly prepared), the Na derivative (III) of which is hydrolysed (cold 30% NaOH) to γ -oxalocrotonic acid, m.p. 212° (decomp.) (lit. 190°), oxidised (H_2O_2) to glutamic acid. In the above prep. of (II), (I) probably first rearranges to $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$. (III) and ClCO_2Et in Et_2O give *Et* α -carbomethoxyoxymuconate, b.p. 158—160°/3 mm.; *Me* α -carbomethoxyoxymuconate, b.p. 160—163°/6 mm., is similarly prepared. These are reduced (H_2 , PtO_2 , MeOH) to *Et* (IV) and *Me* adipate, respectively. *Et*, sodio-oxaloacetate and ClCO_2Et afford *Et* α -carbomethoxyethylene- $\alpha\beta$ -dicarboxylate b.p. 143—146°/4 mm., similarly reduced to $(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, whilst *Et* α -acetoxymuconate (Borsche and Manteuffel, A., 1932, 721) is similarly reduced to

(IV). *Et* α -acetoxymuconate could not be reduced, indicating that the changes $\cdot\text{CH}\cdot\text{C}\cdot\text{O}\cdot\text{COR}\rightarrow[\cdot\text{CH}_2\cdot\text{CH}\cdot\text{O}\cdot\text{COR}]\rightarrow\cdot\text{CH}\cdot\text{CH}\cdot\text{O}\cdot\text{COR}\rightarrow\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{COR}$ are improbable (cf. Roll and Adams, A., 1931, 1419; Michael and Ross, A., 1932, 254).

H. B.

Synthesis of homopilopie acids. N. A. PREOBRASHENSKI, A. M. POLJAKOVA and W. A. PREOBRASHENSKI (Ber., 1934, 67, [B], 710—714).—*r*-isopropyl chloride, b.p. 90.2°/0.05 mm., in boiling xylene containing Pd is transformed by H_2 into *r*-isopropylaldehyde, b.p. 90°/0.05 mm. (semicarbazone), reduced (Al-Hg in moist Et_2O) to *r*-isopropyl alcohol (I), b.p. 116—117°/0.07 mm. (I) and PBr_3 in CHCl_3 afford *r*-isopropyl bromide, b.p. 91°/0.06 mm., whence the corresponding iodide, b.p. 94°/13 mm., which yields the nitrile (II), b.p. 112—118°/0.3 mm. (II) is converted by $\text{EtOH-H}_2\text{SO}_4$ into *Et r*-homoisopropate, b.p. 98°/0.05 mm., hydrolysed by 15% HCl to *r*-homoisopropic acid, $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H}$, m.p. 74.2°.

H. W.

Polyterpenes and polyterpenoids. LXXXIX. **Synthesis of heptane- $\beta\epsilon\zeta$ -tricarboxylic acid, a degradation product of santonin.** L. RUZICKA, A. STEINER, and (in part) W. ZANKL and O. MATTER (Helv. Chim. Acta, 1934, 17, 614—621).— $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ condenses with the Na derivative of *Et* 5-methylcyclopentanone-2-carboxylate to give *Et* 5-methylcyclopentanone-2-carboxylate-2- α -propionate, b.p. 114°/0.2 mm., hydrolysed by NaOEt-EtOH to the *Et* ester, b.p. 148—149°/0.5 mm., of *n*-heptane- $\beta\epsilon\zeta$ -tricarboxylic acid (3 forms), m.p. 136—137°, m.p. 100—110°, and m.p. 127—128° [anhydride, m.p. 145—146°, and its chloride, b.p. 150°/0.1 mm.; *di*-*p*-bromoanilide, m.p. 180—183°; *di*-*p*-anisidide (probably mixture of stereoisomerides), m.p. 182—185°; α -naphthylimide, m.p. 147—147.5°], which is obtained by KOH-EtOH hydrolysis and is identical in all properties with the acid obtained by KMnO_4 oxidation of santonin (Angeli *et al.*, A., 1908, i, 543), thus confirming the position of the inter-ring Me in Clemo's formula.

J. W. B.

Dilactylic acids and their anhydrides. P. VIELES (Compt. rend., 1934, 198, 1044—1046).—*dl*-Dilactylic acid (I) with Ac_2O or when distilled at 20 mm. gives the anhydride (II), b.p. 108°/20 mm., m.p. 36°. The *l*-acid, $[\alpha]_D^{20} -126.8^\circ$, with Ac_2O gives the *d*-anhydride, $[\alpha]_D^{20} +18.7^\circ$. (I) and SOCl_2 give (II) and the dichloride, b.p. 85°/20 mm. The meso-acid (III) does not react with Ac_2O or SOCl_2 and is largely unchanged by distillation at 20 mm. When distilled at 760 mm., (I) or (III) affords H_2O , MeCHO , and CO_2 .

R. S. C.

Polarimetric study of tartaric acid. Optical method of determination. G. BUOGO (Giorn. Chim. Ind. Appl., 1934, 16, 120—122).—The solution to be tested is neutralised with KOH (phenolphthalein). An excess of saturated NH_4 molybdate solution is added, e.g., 3 vols. to 1 vol. of a 40% solution of tartaric acid (I) (less with more dil. solutions). α is then observed and the concn. of (I) calc., taking $[\alpha] = 550^\circ$. Oxalates depress $[\alpha]$, but H_3BO_3 , glycerol, HNO_3 , H_2SO_4 , and Ca^{++} do not interfere.

NaOH should not be used in place of KOH, since it gives rise to a smaller rotation. The solutions may be decolorised by means of C, which does not adsorb (I).
D. R. D.

Preparation of lactones from phenylhydrazides of acids of sugar group. R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 957—958).— α -Galaheptono- and mannono-lactones are obtained in good yield when the respective phenylhydrazides are heated with aq. CuSO_4 and a little octyl alcohol (to prevent frothing); Cu is removed as CuS and SO_4 as BaSO_4 . β -Galaheptonic acid syrups are similarly obtained from β -galaheptonophenylhydrazide.
H. B.

Lead and strontium *d*-xylonates and *d*-threose triacetate. R. C. HOCKETT (J. Amer. Chem. Soc., 1934, 56, 994—995).—Pb (+5 H_2O), m.p. 58—59°, $[\alpha]_D^{20}$ —6.8° in H_2O (cf. Hasenfratz, A., 1933, 376), and Sr (+5 H_2O) (I), m.p. 65—75°, $[\alpha]_D^{20}$ +13.2° in H_2O , *d*-xylonates are described. *d*-Threose triacetate, m.p. 113—114°, $[\alpha]_D^{20}$ +35.5° in CHCl_3 , has been prepared by degradation of (I).
H. B.

Iron compound of gluconic acid. A. PROSKOURIAKOFF and R. J. TITHERINGTON (J. Amer. Chem. Soc., 1934, 56, 996—997).—A compound, $\text{C}_6\text{H}_{13}\text{O}_9\text{Fe}$, probably a basic ferrigluconic acid, is obtained from Ca gluconate (3 mols.) and $\text{Fe}_2(\text{SO}_4)_3$ (1 mol.) in H_2O .
H. B.

Structure of glucuronic acid monobenzoate. A. J. QUICK (Biochem. J., 1934, 28, 403—405).—The compound resulting from the conjugation of glucuronic acid (I) with BzOH exhibits mutarotation, reacts directly with NaCN without previous hydrolysis, and is therefore not benzoylglucuronic acid (cf. A., 1933, 1035) but a monobenzoate of (I).
A. E. O.

***d*-Galacturonic acid. II. Transformation into *l*- δ -ketogalactonic acid.** F. EHRLICH and R. GUTTMANN (Ber., 1934, 67, [B], 573—589; cf. A., 1932, 367).—Treatment of α -*d*-galacturonic acid with a small excess of $\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ at 15—20° results in the separation of basic Ca *l*- δ -ketogalactonate (I), $\text{C}_6\text{H}_9\text{O}_7 \cdot \text{Ca} \cdot \text{OH} \cdot 2\text{H}_2\text{O}$, $[\alpha]_D^{20}$ —6.6° in 5% HCl (yellow anhyd. salt, $[\alpha]_D^{20}$ —7.3° in 5% HCl). Treatment of (I) with $\text{H}_2\text{C}_2\text{O}_4$ gives *l*- δ -ketogalactonic acid (II), m.p. 108° (decomp.) after softening at 107°, $[\alpha]_D^{20}$ —22.0° to —12.3° in H_2O . (II) is approx. as strong as α -*d*-galacturonic acid (III). When gently heated it evolves furfuraldehyde and CO_2 . It gives a red basic Pb salt; that obtained from (III) (*loc. cit.*) is probably derived from (II). The normal *Na*, *Ca*, $[\alpha]_D^{20}$ —15.25° in H_2O , and *Cd* salts could not be obtained cryst. The *brucine* salt has m.p. 149° (decomp.) after softening at 148°, $[\alpha]_D^{20}$ —25.3° in H_2O . (II) reduces cold Fehling's solution, $\text{Cu}(\text{OAc})_2$, and $\text{NH}_3 \cdot \text{Ag}_2\text{O}$, but not 2:6-dichlorophenol-indophenol or I in acid solution. With OI' according to Willstätter and Schudel, (II) requires about 1 I, but protracted action causes much further oxidation. In contrast to (III), (II) is not attacked by Br at 15—20°, and does not afford mucic acid when heated with HNO_3 . Protracted warming with Br causes disappearance of the typical keturonic acid reactions, but the sole isolable product of the change is a dextrorotatory acid which forms a sparingly sol., levorotatory Ca

salt (? *d*-arabotrihydroxyglutaric acid). Treatment of (II) with COMe_2 and conc. H_2SO_4 affords *diisopropylidene-l*- δ -ketogalactonic acid, m.p. 118—119° after softening at 114°, $[\alpha]_D^{20}$ +34.8° in COMe_2 (*Ba* salt, $[\alpha]_D^{20}$ —15.25° in H_2O). *d*-Diisopropylidenegalacturonic acid has m.p. 156—157°, $[\alpha]_D^{20}$ —73.1° in H_2O , $[\alpha]_D^{20}$ —69.4° in COMe_2 , $[\alpha]_D^{20}$ —88.6° in CHCl_3 .
H. W.

Methylglucosides of the naturally occurring hexuronic acids. III. Polygalacturonic acid methylglucoside derived from pectin. S. MORELL, L. BAUR, and K. P. LINK (J. Biol. Chem., 1934, 105, 1—13).—Citrus polygalacturonide (A., 1933, 595) heated with MeOH-HCl for 90 hr. gives approx. 50% of *Me* α -methyl-*d*-galacturonate, and a mixture of its polygalacturonic acids, the main fraction (I) of which contained 8—10 galacturonic acid residues, as indicated by analyses of (I), of the free acid, of the *Na* and *Ba* salts, and by the sp. viscosity and the mol. wt. The kinetics of hydrolysis of (I) with HCl indicate a pyranoid structure for the galacturonic acid residues. The structural unit of citrus pectin must contain at least 8—10 galacturonic acid residues.
A. A. L.

Synthesis of vitamin-C. F. MICHEEL and K. KRAFT (Naturwiss., 1934, 22, 205—206).—The series of reactions: sorbitol \rightarrow (*B. xylinum*) *l*-sorbitose \rightarrow *l*-sorbitosazone \rightarrow *l*-sorbitosone, and mild oxidation, yields *d*-keto-*l*-gulonic acid (*Na* salt), which is converted by alkali into a mixture of the *cis*- (I) and *trans*-isomerides of $\text{OH} \cdot \text{CH}_2 \cdot [\text{CH} \cdot \text{OH}]_2 \cdot \text{C}(\text{ONa}) \cdot \text{C}(\text{ONa}) \cdot \text{CO}_2\text{Na}$. The reaction is partly reversed by acid, but (I) yields some ascorbic acid, which can be isolated via the Pb salt.
R. K. C.

Primary product of the synthesis of ascorbic acid and its analogues. W. N. HAWORTH and E. L. HIRST (Helv. Chim. Acta, 1934, 17, 520—522; cf. following abstract).—The use of CaCl_2 in the KCN synthesis of ascorbic acid (I) and its analogues is not essential, but shortens the reaction period and slightly increases the yield. The small amount of NH_3 evolved is due to hydrolysis of the nitrile. The following observations support the cyclic imine structure previously assigned (this vol., 279) to the labile intermediate (II), $[\alpha]_D^{20}$ —145° in H_2O , —17° in 8% HCl, in the synthesis of glucoascorbic acid (III). In H_2O (II) displays simple rotatory dispersion, but in acids (suppression of enolic ionisation) it is anomalous, the consts. in the 2-term Drude equation being closely similar to those of (I). (II) reacts with I to give a base, the NH group in the oxidation product being labile and eliminated during osazone formation to give the osazone, m.p. 225°, obtained from oxidised (III). With CH_3N_2 (III) gives its 3-*Me* ether, m.p. 142° $[\alpha]_D^{20}$ —5° in H_2O , but (I) similarly gives its 3-*Me* ether, m.p. 121°, $[\alpha]_D^{20}$ +28° in H_2O , accompanied by an isomeric substance, m.p. 162°, $[\alpha]_D^{20}$ about +200° in H_2O (absorption band at 275—280 $\text{m}\mu$). The position of the OH responsible for the acidic properties of (I) cannot yet be decided, but it is probably 3.
J. W. B.

Synthesis of ascorbic acid and its analogues by the osone-hydrocyanic acid method. T. REICHSTEIN, A. GRUSSNER, and R. OPPENAUER (Helv.

Chim. Acta, 1934, 17, 510—520).—The efficacy of dil. aq. KCN in place of HCN in the synthesis of ascorbic acid (I) is confirmed, but with CaCl_2 (Baird *et al.*, this vol., 279) little or no liberation of NH_3 occurs and the intermediate product ψ -(I) is pptd. (cf. preceding abstract). From the appropriate osone (from the osazone and PhCHO) by this method are prepared *d*-, m.p. 174° (corr., decomp.), $[\alpha]_D^{25} = -17^\circ$, *l*-, m.p. 170° (corr., decomp.), $[\alpha]_D^{25} = +17^\circ$, and *dl*-, m.p. (?), arabo-, *d*-gluco- $+\text{H}_2\text{O}$, m.p. (indef.) 101 — 105° (decomp.), resolidifying and remelting 192° (corr., decomp.), $[\alpha]_D^{25} = -37.8^\circ$ (as anhyd. substance), *d*-galacto-, m.p. 100° , resolidifying and remelting 134 — 135° (decomp.), $[\alpha]_D^{25} = -5.8^\circ$, and *l*-gulo-, m.p. 183 — 184° (decomp.), $[\alpha]_D^{25} = -19.0^\circ$, -ascorbic acid. With CH_2N_2 in MeOH at -10° *l*-(I) gives its 3-*Me* ether, m.p. 120 — 122° , $[\alpha]_D^{25} = +42^\circ$ in MeOH [isopropylidene derivative, m.p. 88 — 90° , $[\alpha]_D^{25} = +20^\circ$ in MeOH, by methylation of the isopropylidene derivative of *l*-(I)], giving, with FeCl_3 , a violet colour and a trace of an inactive substance $\text{C}_7\text{H}_{10}\text{O}_8$, m.p. 150 — 152° (corr.). All $[\alpha]_D^{25}$ vals. are in 0.01*N*-HCl. J. W. B.

***d*-Glucosaccharosonic acid. II. Constitution of glucosaccharosonic acid and its compound with *o*-phenylenediamine.** H. ERLBACH and H. OHLE (Ber., 1934, 67, [B], 555—563; cf. this vol., 392).—Glucosaccharosonic acid (I) is smoothly and almost quantitatively dehydrogenated by $p\text{-O}:\text{C}_6\text{H}_4:\text{O}$ in H_2O or EtOH yielding $\alpha\beta$ -diketogluconolactone (II), which is readily hydrolysed, and loses CO, almost

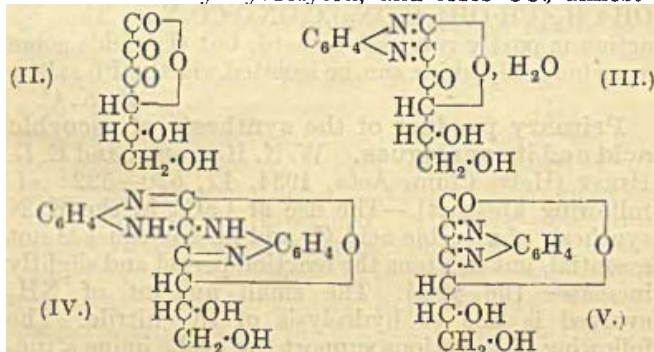
(V) affords a well-crystallised diacetate (VII), m.p. 185 — 186° , $[\alpha]_D^{25} = +133.5^\circ$ in CHCl_3 , and an isopropylidene derivative (VIII), m.p. 225° (decomp.), $[\alpha]_D^{25} = +109.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$. (VII) is also obtained by direct acetylation of (IV). The acid liberated by the action of mineral acid on (VI) passes into a mixture of the γ - and δ -lactone m.p. 186° after softening at 174° , $[\alpha]_D^{25} = +64.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$, -72.9° in H_2O , obtained pure by acid hydrolysis of the Na salt of (VIII). (V) does not condense with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$. It reduces Fehling's solution, possibly owing to loss of H_2O . When boiled with EtOH and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ it suffers partial loss of H_2O and the lactone produced decomposes with production of EtOAc. Dehydrogenation of the Na salt of (I) with $p\text{-O}:\text{C}_6\text{H}_4:\text{O}$ followed by addition of HCl and $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives very small amounts of (IV), which is not obtained at all by action on the neutral solution of the dehydrogenated product. It results in about 70% yield from the Na glycerylquinoxalinecarboxylate. The previous conception (*loc. cit.*) of the course of oxidation in neutral solution is therefore withdrawn. The poor yields of $\text{H}_2\text{C}_2\text{O}_4$ obtained by oxidation with OI' are not due to differing oxidations of (I), but to secondary changes in (II). It follows therefore that the condensation products obtained from (I) are actually derived from (II), and that (I) possesses the same structure as ascorbic acid. *l*-Ascorbic and *d*-glucosaccharosonic acid differ essentially in the configuration of C_5 . H. W.

Disulpho- and hydroxysulpho-glutaric acids. J. M. VAN DER ZANDEN (Rec. trav. chim., 1934, 53, 477—488).—Glutaric acid and SO_3 (3 mols.) in H_2SO_4 at 90° give a mixture of *dl*- (I) [*Pb* and *Ba* (hydrated) salts] and *meso*- $\alpha\alpha'$ -disulphoglutaric acid (tristrychnine, $+6\text{H}_2\text{O}$, and *Ba*₂ salts). (I) is resolved by the di-or, better, tri-strychnine salt, the Na salt of *d*-(I) having $[M]_D^{25} = +20.9^\circ$ in H_2O . *Meso*- and *dl*- α -dibromoglutaric acid (modified prep.) and $(\text{NH}_4)_2\text{SO}_3$ give the same α -hydroxy- α' -sulphoglutaric acid (*Pb*_{1.5}, $+5\text{H}_2\text{O}$, *Ag*₃, $+ \text{H}_2\text{O}$, and *Tl*₃, $+ \text{H}_2\text{O}$, salts). $\alpha\beta$ -Dibromoglutaric acid and KHSO_3 give glutaconic acid. R. S. C.

Polymerisation. I. Kinetic investigations of aqueous solutions of formaldehyde.—See this vol., 493.

Acidity of formaldehyde and end-point in formal titration. M. LEVY (J. Biol. Chem., 1934, 105, 157—165).—The titration curves of CH_2O against NaOH are determined electrometrically for different concns. of $[\text{CH}_2\text{O}]$, and the relation $p_{Kf} = 12.87 - 0.19[\text{CH}_2\text{O}]$ obtained. Functions corresponding with those in Roller's equation (A., 1932, 1101) for the % error in a titration of a weak acid by NaOH are deduced for the formal titration, and from the modified equation optimal conditions: $\text{CH}_2\text{O} = 6$ —9%, highest possible $[\text{NH}_2\text{-acid}]$, and the stoichiometric end-point are obtained. Phenolphthalein is a suitable indicator. H. D.

Principle of formaldehyde, alcohol, and acetone titrations. Proof and implication of the Zwitterion conception. G. M. RICHARDSON (Proc. Roy. Soc., 1934, B, 115, 121—141).—In the light of the zwitterion hypothesis the Sorensen and Foreman



quantitatively when boiled without apparently affording arabinosone. The cold solution of (II) in H_2O yields with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ a sparingly sol., unstable substance (? III), m.p. 175° (decomp.), $[\alpha]_D^{25} = -100.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$, which does not lose H_2O at 100° and is sol. in alkali. It affords a red phenylhydrazone, m.p. 203° (decomp.), $[\alpha]_D^{25} = -84.6^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and with $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ yields the substance (IV), m.p. 212° (decomp.), $[\alpha]_D^{25} = -14.54^\circ$ to -11.18° in $\text{C}_5\text{H}_5\text{N}$. (IV) is obtained almost quantitatively from (II) and 2 mols. of $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ or from (I) and $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$. The position of the substituent groups is established by the observations that mesoxalic esters yield an analogous substance and that cold, dil. mineral acids transform (IV) into 3-*d*-erythro- $\alpha\beta\gamma$ -trihydroxypropylquinoxaline-2-carboxylactone (V), m.p. 187° , $[\alpha]_D^{25} = +151^\circ$ in $\text{C}_5\text{H}_5\text{N}$. The lactonic structure of (V) follows from its conversion into a salt (VI), $\text{C}_{12}\text{H}_{14}\text{O}_5\text{N}_2\text{Na}$, m.p. 210° , $[\alpha]_D^{25} = -2.2^\circ$ in H_2O , an amide, m.p. 167° (decomp.), $[\alpha]_D^{25} = 86.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and a hydrazide, $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_4$, m.p. 171° , $[\alpha]_D^{25} = -77.96^\circ$ in $\text{C}_5\text{H}_5\text{N}$.

(Willstatter) titration determines NH_2 and the Linderström-Lang titration (A., 1928, 536) CO_2H . Comparison of Van Slyke $\text{NH}_2\text{-N}$ and Willstatter titrations for the liberations of NH_2 and acid groups during protein hydrolysis is valid. The hypothesis may be used to allocate titration consts. to titratable groups of ampholytes (cf. A., 1933, 1015). H. G. R.

Acidimetric determination of formaldehyde and sulphites.—See this vol., 618.

Combination of formaldehyde with amino-acids and proteins. H. ANDERSON (J. Soc. Leather Trades Chem., 1934, 18, 197—200).— p_{Ka} for glycine (I) is affected by acetylation and benzylation, but not by condensation with CH_2O , so that there is no combination of CH_2O with (I) at $p_{\text{H}} < 4.7$, the isoelectric point of (I). Very little CH_2O combines with gelatin at p_{H} vals. $<$ the isoelectric point of gelatin.

D. W.

[Highly polymerised compounds.] K. HESS (Ber., 1934, 67, [B], 610—612).—A reply to Staudinger (this vol., 514).

H. W.

cis-trans and synionic isomerism in crotyl derivatives. (MLLE.) B. GREDY and L. PIAUX (Compt. rend., 1934, 198, 1235—1237).—Raman spectra show that crotonaldehyde contains 99% of the *trans* and 1% of the *cis* form, Charon's $\text{CHMe}:\text{CH}:\text{CH}_2\text{OH}$ and the acetate obtained by Ac_2O contain much *trans* and a little *cis* form, the acetate obtained from buten- γ -ol (I) is free from crotyl acetate (II), HBr and (I) give at least 80% of *trans*- $\text{CHMe}:\text{CH}:\text{CH}_2\text{Br}$ (III) and 10% each of *cis*-(III) and the bromide of (I), and that the above mixture of bromides with NaOAc in AcOH yields equal amounts of (II) and the acetate of (I).

R. S. C.

isoPropylenedioxypropaldehyde. II. Preparation of d-isopropylenedioxypropaldehyde. H. O. L. FISCHER and E. BAER (Helv. Chim. Acta, 1934, 17, 622—632).—Oxidation of $\alpha\beta\epsilon\zeta$ -diisopropylidene-*d*-mannitol (Fischer *et al.*, A., 1916, i, 363; cf. Vargha, A., 1933, 1140) with $\text{Pb}(\text{OAc})_4$ affords *d*-isopropylenedioxypropaldehyde (I), b.p. $27^\circ/2$ mm., $[\alpha]_D^{20} + 64.9^\circ$ (readily polymerises), hydrolysis of which ($0.05N\text{-H}_2\text{SO}_4$ at room temp. or 12% AcOH) gives only syrupy *d*-glyceraldehyde, $[\alpha]_D^{20} + 9.6^\circ$ (dimedon compound, m.p. 199—201°; 2:4-dinitrophenylhydrazones, m.p. 155—156°). Direct treatment of (I), without isolation, with $\text{CH}(\text{OEt})_3$ gives its *Et*, *acetal*, b.p. $90\text{--}92^\circ/10$ mm., $[\alpha]_D^{19} + 28.78^\circ$, and with aq. $\text{Ba}(\text{OH})_2$ is obtained the inactive diisopropylidenehexose (A., 1930, 1164), an isopropylidenehexose, m.p. 155—157°, being obtained from the mother-liquor. From accumulated residues of COMe_2 -*dl*-glyceraldehyde condensations is isolated a *dimeride*, m.p. 74—75°, of *dl*-isopropylenedioxypropaldehyde, polymorphous with the form, m.p. 104°, previously obtained.

J. W. B.

Determination of aldehydes and ketones with hydroxylamine salt. H. SCHULTES (Angew. Chem., 1934, 47, 258—259).—Accurate results are obtained in the usual titrimetric method by using bromophenol-blue instead of Me-orange as indicator.

S. C.

Spectrophotometric determination of diacetyl. H. MOHLER and F. ALMASY (Z. anal. Chem. 1934, 96,

399—400).—Alcoholic distillates containing Ac_2 give an absorption spectrum with max. absorption at 4200 and 2870 Å., and a min. at 3420 Å. J. S. A.

Synthesis of β -diketo- ζ -dimethyl-*n*-hexadecane. P. KARRER and J. LEE (Helv. Chim. Acta, 1934, 17, 543—549).—Reduction of $\text{CHMe}(\text{CH}_2\text{CO}_2\text{Et})_2$ with Na-EtOH gives γ -methyl-*n*-pentane- $\alpha\epsilon$ -diol, converted by Na-EtI into its *Et*, ether, b.p. $109\text{--}111^\circ/20$ mm., the bromide, b.p. $92.5\text{--}93^\circ/20$ mm. (by PBr_3), of which with "mol." Na in PhMe at $> 50^\circ$ affords $\alpha\kappa$ -diethoxy- $\gamma\delta$ -dimethyl-*n*-decane, b.p. $105\text{--}106^\circ/0.3$ mm., hydrolysed by HBr-AcOH at 100° to the $\alpha\kappa$ -dibromide; condensation of this with $\text{CHNa}(\text{CO}_2\text{Et})_2$ and hydrolysis and decarboxylation of the product affords δ -dimethyl-*n*-dodecane- $\alpha\mu$ -dicarboxylic acid, b.p. $225\text{--}235^\circ/0.2$ mm., converted by the Blaise-Maire reaction into β -diketo- ζ -dimethyl-*n*-hexadecane, identical with a specimen obtained from perhydrocrocin (A., 1932, 1234).

J. W. B.

Crystalline compound of α -*l*-arabinose with calcium chloride and water. W. C. AUSTIN and J. P. WALSH (J. Amer. Chem. Soc., 1934, 56, 934—935).—*l*-Arabinose and $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ in a little hot H_2O and current of air give the compound $\alpha\text{-C}_5\text{H}_{10}\text{O}_5\cdot \text{CaCl}_2\cdot 4\text{H}_2\text{O}$, softens at $106\text{--}108^\circ$, liquefies slowly at $112\text{--}115^\circ$, decomp. $214\text{--}215^\circ$, $[\alpha]_D^{20}$ (in H_2O) $+ 36.41^\circ$ (3 min.) $\rightarrow + 47.65^\circ$ (const.), whence α -*l*-arabinose has $[\alpha]_D^{20} + 75.18^\circ$ (initial) (cf. Simon, A., 1901, i, 256; Hudson and Yanovsky, A., 1917, i, 445).

H. B.

Crystalline compounds of *d*-xylose and *l*-arabinose with calcium chloride. J. K. DALE (J. Amer. Chem. Soc., 1934, 56, 932—934).—*d*-Xylose and $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ in a little hot H_2O give the compound, $\alpha\text{-C}_5\text{H}_{10}\text{O}_5\cdot \text{CaCl}_2\cdot 3\text{H}_2\text{O}$, m.p. 126° , $[\alpha]_D^{20}$ (in H_2O) $+ 46.8^\circ \rightarrow + 9.33^\circ$. *l*-Arabinose similarly affords the compounds, $\beta\text{-C}_5\text{H}_{10}\text{O}_5\cdot \text{CaCl}_2\cdot \text{H}_2\text{O}$, decomp. 212° , $[\alpha]_D^{20}$ (in H_2O) $+ 99.59^\circ \rightarrow 56.6^\circ$, and $(\beta\text{-C}_5\text{H}_{10}\text{O}_5)_2\cdot \text{CaCl}_2\cdot 2\text{H}_2\text{O}$, darkens from 160° , $[\alpha]_D^{20}$ (in H_2O) $+ 124.6^\circ \rightarrow + 69.94^\circ$. The mutarotation curves of these compounds are similar to those of the component sugars [initial $[\alpha]$ (calc.) $+ 98.5^\circ$ and $+ 186^\circ$, respectively (cf. Hudson and Yanovsky, A., 1917, i, 445)].

H. B.

Triphenylmethyl derivatives of β -methyl-*d*-xyloside. E. L. JACKSON, R. C. HOCKETT, and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 947—949; cf. A., 1932, 146).— β -Methyl-*d*-xyloside and CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$ at 20° for 14 days give two ditriphenylmethyl- β -methyl-*d*-xylosides, m.p. $162.5\text{--}163^\circ$ (corr.), $[\alpha]_D^{20} - 22.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and m.p. $238\text{--}240^\circ$ (corr.), $[\alpha]_D^{20} - 55.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and a syrup (*A*). Acetylation (Ac_2O , $\text{C}_5\text{H}_5\text{N}$ at 0°) of *A* affords two triphenylmethyl- β -methyl-*d*-xyloside diacetates, m.p. $125\text{--}127^\circ$ (corr.), $[\alpha]_D^{20} - 49.1^\circ$ in CHCl_3 , and m.p. $169\text{--}170^\circ$ (corr.), $[\alpha]_D^{20} - 15.7^\circ$ in CHCl_3 . These results show that CPh_3Cl reacts with *sec*-OH groups.

H. B.

Action of triphenylmethyl chloride on α -methyl-*l*-fucoside. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 945—946).— α -Methyl-*l*-fucoside (which contains only *sec*-OH groups) and CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$ at room temp. for 5 days and then

at 100° for 1 hr. give a triphenylmethyl- α -methyl-l-fucoside (+EtOH), m.p. 123—126° (corr.); the EtOH-free form has m.p. 126—128° (corr.), $[\alpha]_D^{20}$ -59.5° in CHCl_3 . The view that CPh_3Cl is completely sp. in action towards primary OH is thus disproved.

H. B.

Free aldehyde form of fucose tetra-acetate. M. L. WOLFROM and J. A. ORSINO (J. Amer. Chem. Soc., 1934, 56, 985—987).—Fucose Et mercaptal is acetylated (Ac_2O , $\text{C}_5\text{H}_5\text{N}$) to the tetra-acetate, m.p. 99—100°, $[\alpha]_D^{25}$ +5° in CHCl_3 , converted by HgCl_2 in COMe_2 + CdCO_3 into aldehyde-1-fucose tetra-acetate, m.p. 166—167°, $[\alpha]_D^{25}$ +40° in $\text{C}_2\text{H}_2\text{Cl}_4$ (in MeOH the initial rotation of +22° changes to +9° in 4 days) [semicarbazone, m.p. 215° (decomp.); alcoholate, softens at 120—121°, solidifies on further heating, and then melts at 170°, $[\alpha]_D$ (in EtOH) -3.4° \rightarrow +3.4°, which when crystallised from H_2O gives the hydrate, m.p. 160—161°]. α -1-Fucose tetra-acetate has m.p. 92°, $[\alpha]_D^{25}$ -120° in CHCl_3 .

H. B.

Methylated sugars. I. Preparation of tetramethylglycose. E. S. WEST and R. F. HOLDEN (J. Amer. Chem. Soc., 1934, 56, 930—932).—Glucose (in conc. aq. solution) is methylated rapidly by treatment with Me_2SO_4 - CCl_4 followed by 60% NaOH and Me_2SO_4 ; the resulting tetramethylmethylglucoside (I), b.p. 88—90°/0.15 mm., contains 83—85% of the β -form. Hydrolysis (HCl under various conditions) of (I) gives tetramethylglucose (II), $[\alpha]_D^{25}$ +81.3° in H_2O (lit. 83.3°). α -Methylglucoside is similarly methylated to its Me_4 derivative, b.p. 89—92°/0.4 mm., also hydrolysed to (II). The effects of solvent and temp. on the rotation of (II) are investigated.

H. B.

Syntheses in the series of *p*-toluenesulphonyl (tosyl) sugars. O. LITTMANN and K. HESS (Ber., 1934, 67, [B], 519—526; cf. A., 1933, 1279).—Acetobromoglucose (improved prep.) is converted into 4 : 6-benzylidene- β -methylglucoside, m.p. 199—200°, $[\alpha]_D^{20}$ -63.12° in CHCl_3 , and thence according to Ohle *et al.* (A., 1929, 50) into 4 : 6-benzylidene- β -methylglucoside 2 : 3-di-*p*-toluenesulphonate (I), labile form, m.p. 157—159°, $[\alpha]_D^{25}$ -62.08° in CHCl_3 (*loc. cit.*), stable variety, m.p. 182—183°, $[\alpha]_D^{25}$ -62.82° in CHCl_3 . (I) is transformed by MeOH -HCl into β -methylglucoside 2 : 3-di-*p*-toluenesulphonate, $[\alpha]_D^{25}$ -1.51° in CHCl_3 , -12.99° in COMe_2 , -27.40° in C_6H_6 , converted by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$ at 30° into β -methylglucoside 2 : 3 : 4 : 6-tetra-*p*-toluenesulphonate, m.p. 181—182°, $[\alpha]_D^{25}$ 6.57° in CHCl_3 , $[\alpha]_D^{25}$ -10.40° in COMe_2 (cf. Oldham *et al.*, A., 1932, 500). Treatment of β -methylglucoside 4-acetate 2 : 3 : 6-tri-*p*-toluenesulphonate with 0.1*N*-NaOMe-MeOH at 100° is without effect, whereas use of a more conc. solution leads to a β -methylglucoside di-*p*-toluenesulphonate, $[\alpha]_D^{25}$ -57.76° in CHCl_3 , -54.82° in COMe_2 , -71.35° in C_6H_6 , which does not react with PhCHO , and hence does not contain a free 6-OH. Hydrolysis of 4 : 6-benzylidene- α -methylglucoside 2 : 3-di-*p*-toluenesulphonate, $[\alpha]_D^{25}$ +13.3° in CHCl_3 , with 18% HCl or, more readily, 1% HCl-MeOH, leads to non-cryst. α -methylglucoside 2 : 3-di-*p*-toluenesulphonate (II), $[\alpha]_D^{25}$ +58.21° in CHCl_3 , $[\alpha]_D^{25}$ +40.73° in COMe_2 . Successive treatment of (II) with CPh_3Cl in $\text{C}_5\text{H}_5\text{N}$ and Ac_2O at

55° affords 6-triphenylmethyl- α -methylglucoside 4-acetate 2 : 3-di-*p*-toluenesulphonate, m.p. 174—175°, $[\alpha]_D^{25}$ +56.03° in COMe_2 , +55.00° in CHCl_3 , transformed by HBr -AcOH into α -methylglucoside 4-acetate, 2 : 3-di-*p*-toluenesulphonate (III), m.p. 162—163°, $[\alpha]_D^{25}$ +35.28° in CHCl_3 . (III), $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, and $\text{C}_5\text{H}_5\text{N}$ do not react at 48°, and at 100° yield 6-chloro- α -methylglucoside 4-acetate 2 : 3-di-*p*-toluenesulphonate, m.p. 96°, $[\alpha]_D^{25}$ +53.42° in COMe_2 .

H. W.

Preparation of *d*-mannose. C. S. HUDSON and E. L. JACKSON (J. Amer. Chem. Soc., 1934, 56, 958—959).— α -Methyl-*d*-mannoside (prep.: A., 1928, 399) is hydrolysed (2% HCl) to *d*-mannose (70% yield).

H. B.

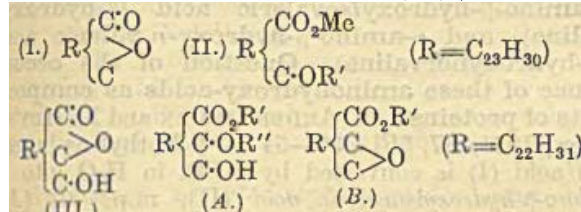
ketoFructose penta-acetate. M. L. WOLFROM and A. THOMPSON (J. Amer. Chem. Soc., 1934, 56, 880—882).—Acetylation (Ac_2O , ZnCl_2) of β -fructose tetra-acetate gives (cf. Hudson and Brauns, A., 1916, i, 118) α - (I) and β - (II) -fructose penta-acetates. (I), EtSH, and ZnCl_2 at < 0° afford *d*-fructose ethylthioacetal penta-acetate, m.p. 83°. $[\alpha]_D^{25}$ +20° in CHCl_3 , de-acetylated (MeOH - NH_3) to *d*-fructose ethylthioacetal, m.p. 65—67°, $[\alpha]_D^{25}$ +35.8° in MeOH, and converted by HgCl_2 in COMe_2 + CdCO_3 into keto-fructose penta-acetate, m.p. 69—70°, $[\alpha]_D^{25}$ +35.1° in CHCl_3 , which is identical with (I). This result confirms the work of Pacsu and Rich (A., 1933, 937). (II), EtSH, and ZnCl_2 similarly give β -ethylthiofructoside tetra-acetate, m.p. 96—98°, $[\alpha]_D^{25}$ -151.9° in CHCl_3 , de-acetylated (MeOH - NH_3) to β -ethylthiofructoside, m.p. 140°, $[\alpha]_D^{25}$ -232.9° in MeOH. The corresponding ethylthioacetal penta-acetates are similarly obtained from aldehydo-glucose and -galactose penta-acetates. This method can thus be used to distinguish between cyclic and open-chain sugar penta-acetates.

H. B.

Oxidation of sucrose to oxalic acid.—See this vol., 495.

Heart glucosides. V. Acetyldigitoxin, acetylgitoxin, and acetyldigoxin. A. STOLL and W. KREIS. VI. Nature of the oxygen atom in scillaridin A. A. STOLL, A. HOFMANN, and A. HELFENSTEIN (Helv. Chim. Acta, 1934, 17, 592—613, 641—669; cf. this vol., 59).—V. By the action of an enzyme prep. (I) from *D. lanata* (fresh leaves) digilanid C affords acetyldigoxin, $\text{C}_{43}\text{H}_{66}\text{O}_{15}$, separated (full details) into the stereoisomeric α -form, softens 222°, m.p. 230° (corr.), $[\alpha]_D^{25}$ +18.0° in $\text{C}_5\text{H}_5\text{N}$, and β -form (more sol. in MeOH and EtOH), m.p. about 170° (? loss of solvent of crystallisation), resolidifying and remelting at 258° (corr., decomp.), $[\alpha]_D^{25}$ +29.2° in $\text{C}_5\text{H}_5\text{N}$, both of which afford digoxin by hydrolysis with aq. MeOH-KOH, and have the same toxicity (cats). Similarly (I) (from dried leaves) hydrolyses digilanid A to give acetyldigitoxin, $\text{C}_{43}\text{H}_{66}\text{O}_{14}$, only the β -form, darkens about 200° (corr.), m.p. (indef.) 210—225° (corr., decomp.), $[\alpha]_D^{25}$ +16.7° in $\text{C}_5\text{H}_5\text{N}$, which affords digitoxigenin (46.6% yield) by acid ($N\text{-H}_2\text{SO}_4$), and digitoxin by alkaline (aq. MeOH-KOH), hydrolysis, being obtained cryst. Digilanid B similarly affords acetylgitoxin, also obtained only in the β -form, darkens >200°, m.p. 220—225° (corr., decomp.), $[\alpha]_D^{25}$ +15.7° in $\text{C}_5\text{H}_5\text{N}$, and affording gitoxin by alkaline hydrolysis. The contentions of Mannich (this vol., 282) are disputed.

VI. Anhydroscillaridin A (I) with cold KOH-MeOH is converted (opening of lactone ring to give a phenolic OH) into *Me anhydroscillaridate* (II, R'=H), m.p. 142—144°, $[\alpha]_D^{20} -279^\circ$ (Et ester, m.p. 125°, $[\alpha]_D^{20} -232^\circ$, similarly obtained with KOH-EtOH), reconverted into (I) by 0.1N-NaOH in 25% EtOH, and converted by MeOH-HCl into its *Me ether* (II, R'=Me), m.p. 175°, $[\alpha]_D^{20} -246^\circ$, or by *p*-NO₂-C₆H₄-COCl-C₆H₅N into its *p*-nitrobenzoyl derivative (II, R'=CO-C₆H₄-NO₂), m.p. 190—192°. (I) contains a substituted coumarin skeleton. Scillaridin A (III) with KOH-MeOH affords *Me scillaridate* (IV) (A, R'=Me;



R'=H) which passes spontaneously (—H₂O) into the *Me ester* (V) (B, R'=Me), m.p. 175°, $[\alpha]_D^{20} -301^\circ$ (Et ester, m.p. 125°, $[\alpha]_D^{20} -270^\circ$), of *isoscillaridic acid* (VI) (B, R'=H), m.p. 264°, $[\alpha]_D^{20} -292^\circ$, which is obtained by hydrolysis of (V) with aq. EtOH-NaOH, and is reconverted into (V) with CH₂N₂. Immediate treatment of (IV) with CH₂N₂ effects the isolation of its *Me ether* (VII) (A, R'=R''=Me), m.p. 177—178°, $[\alpha]_D^{20} -78.9^\circ$, hydrolysed to *methylscillaridic acid* (A, R'=H, R''=Me), m.p. 203—207°, $[\alpha]_D^{20} -79.4^\circ$, reconverted by CH₂N₂ into (VII): HCl-MeOH converts (VII) into (V). (III) contains a *tert*.-OH in addition to the lactone ring. The structural relationships of the *Strophanthus* and *Digitalis* aglucones are discussed. All m.p. are corr., and all $[\alpha]_D$ vals. in dioxan. J. W. B.

Unsaponifiable fraction of spinach fat. Glucoside of γ -spinasterol. F. W. HEYL and D. LARSEN (J. Amer. Chem. Soc., 1934, 56, 942—943).—The resin obtained by addition of H₂O to the EtOH-extract of dry spinach is freed from fat (light petroleum) and most of the pigment (Et₂O) and then extracted with EtOH. This extract contains a *phytosterolin*, m.p. 275—280° (decomp.), $[\alpha]_D^{20} -33^\circ$ in C₆H₅N [tetraacetate, m.p. 178.5—179°, $[\alpha]_D^{20} -13.4^\circ$ (this and following vals. are in CHCl₃); tetraacetate, m.p. 178—178.5°, $[\alpha]_D^{20} +21.6^\circ$], hydrolysed by Power and Salway's method (J.C.S., 1913, 103, 399) to γ -spinasterol (I), m.p. 159—160°, $[\alpha]_{5461}^{20} \pm 0^\circ$ [acetate (II), m.p. 139.5—140°, $[\alpha]_{5461}^{20} -14.1^\circ$; benzoate, m.p. 118.5—119°, $[\alpha]_{5461}^{20} -10.3^\circ$; *p*-nitrobenzoate, m.p. 200°, $[\alpha]_{5461}^{20} -8.9^\circ$; phenylcarbamate, m.p. 144—145°, $[\alpha]_{5461}^{20} -15.9^\circ$]. Reduction (H₂, PtO₂, AcOH) of (II) gives dihydro- γ -spinasterol, m.p. 105.5—106°, $[\alpha]_{5461}^{20} +24^\circ$ (as acetate, m.p. 115.5—116°, $[\alpha]_{5461}^{20} +12.4^\circ$), which appears to be identical with dihydro- α -spinasterol (A., 1932, 381). (I) appears to be an isomeride of α - (loc. cit.) and β -spinasterol (A., 1933, 989); they are all (probably) C₂₈H₄₆O (cf. loc. cit.). H. B.

Plant colloids. XXXV. Solution state of *iso*-hexosans. M. SAMEC and C. KNOP (Kolloid-Beih., 1934, 39, 259—264; cf. A., 1933, 1117).—*iso*Hexosan prepared by Pictet's method (A., 1929, 914) contains

polydisperse *isotri*- (I) and *isodi*-hexosan (II), which are stabilised by EtOH or glycerol. Diffusion experiments indicate a mean mol. wt. about 2300 for (I) and about 1700 for (II), but the val. varies greatly with the concn. E. S. H.

Carbon tetrahedron as sole ruler in all organic chemistry. R. REINICKE (Chem.-Ztg., 1934, 58, 369—371).—Mainly a re-statement of the author's views (A., 1931, 1001) and an extension of them to cellulose. H. W.

Mechanism of macropolymerisation reactions.—See this vol., 607.

Structure of cellulose and its derivatives.—See this vol., 587.

Mode of reaction of cellulose. III. Formation of intermediate compounds in the nitration of cellulose and their relation to the stability of the products of nitration. C. TROGUS and K. HESS. IV. Mechanism of denitration of cellulose nitrate. T. TOMONARI (Z. Elektrochem., 1934, 40, 193—207, 207—211; cf. A., 1933, 1280).—III. Investigation by extraction methods and by X-rays shows that nitration of cellulose to the trinitrate takes place through two intermediate stages, involving the formation of (1) an additive compound of cellulose and HNO₃, and (2) cellulose dinitrate. A nitrosulphonic ester is also formed from the dinitrate in a side reaction. The relative proportions of the reaction products depend on the concn. of H₂O in the nitration mixture.

IV. Determinations of N content, extraction by means of solvents, and X-ray investigations show that no intermediate products are formed in the denitration of cellulose trinitrate by alcoholic NH₄HS. Denitration with H₂O-rich HNO₃-H₂SO₄-H₂O mixtures is a complex process involving the formation of several intermediate products. E. S. H.

Preparation of dibromoamine and its reaction with Grignard reagents.—See this vol., 615.

Separation of dimethylamine and ammonia.—See this vol., 500.

Preparation of anhydrous ethylenediamine. J. C. BAILAR, jun. (J. Amer. Chem. Soc., 1934, 56, 955).—(CH₂-NH₂)₂ hydrate and ZnC₂O₄ give a salt, [ZnC₂H₄(NH₂)₂]₂C₂O₄, which when heated to 200° in a vac. affords anhyd. C₂H₄(NH₂)₂, b.p. 116—117°, in almost quant. yield. H. B.

Hofmann's ethylene bases. Synthesis of $\beta\beta'$ -diaminodiethylamine and of $\beta\beta'$ -diaminodiethylmethylamine. F. G. MANN (J.C.S., 1934, 461—466).—NH(C₂H₄-OH)₂ (I) with SOCl₂ in CHCl₃ gives the hydrochloride (II), m.p. 216—217°, of $\beta\beta'$ -dichlorodiethylamine (III) (benzoate, m.p. 135—136°, by decomp. of the Bz derivative during purification). With HCl-AcOH (saturated at 0°) at 100° (I) affords only the hydrochloride, m.p. 147—149°, of its *O*-Ac₂ derivative, and with boiling Ac₂O gives *aceto*- $\beta\beta'$ -diacetoxydiethylamide, b.p. 212—213°/23.5 mm., converted by saturated HBr-AcOH at 170° into NH(C₂H₄Br)₂.HBr. Crude (III) [liberated from (II) by 20% KOH at 0°] heated with *o*-C₆H₄(CO)₂NK at 145—150°, gives $\beta\beta'$ -diphthalimidodiethylamine (IV),

m.p. 178—180°, hydrolysed by boiling dil. HCl to the trihydrochloride of $\beta\beta'$ -diaminodiethylamine (*tripicrate* + 2H₂O), identical with Hofmann's "diethylenetriamine" (cf. Fargher, J.C.S., 1920, 117, 1351). Methylation of (IV) with MeI-AgO in COMe₂ gives $\beta\beta'$ -diphthalimidodiethylmethylamine, m.p. 124—126°, hydrolysed to the trihydrochloride, m.p. 239° (decomp.), of $\beta\beta'$ -diaminodiethylmethylamine [*platinichloride* + 6H₂O and anhyd.; *trioxalate*, m.p. 205° (decomp.), *tripicrate*, m.p. 203—205° (decomp.)], converted by PhSO₂Cl into the monohydrochloride, m.p. 163—164°, of di(benzenesulphonamidoethyl)methylamine.

J. W. B.

New aliphatic tetramine: tetra-aminotetramethylmethane C(CH₂·NH₂)₄. F. J. GOVAERT (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 156—162).—*Tetra-aminotetramethylmethane* (I) [*tetrahydrobromide*; *tetranitrate*, m.p. 220—222° (decomp.); *picate*, m.p. 211—212°; *diplatinichloride*] is prepared in 35% yield from C(CH₂Br)₄ and NH₃ in EtOH at 180—190°. Only a trace of (I) is obtained from Na and C(CH₂Br)₄ in liquid NH₃. Analysis of the hydrochloride of (I) suggests that it contains the spiro-compound HCl·NH₂·C₂H₄·C₂H₄·NH₂·HCl.

R. K. C.

Compounds of hexamethylenetetramine with complex cobalt salts.—See this vol., 617.

Electrometric titration of amino-acids in aqueous-alcoholic solution. A. NEUBERGER (Proc. Roy. Soc., 1934, B, 115, 180—199).—A method for the electrometric titration of H₂O-EtOH solutions of NH₂-acids against a standard calomel electrode is described. The results strongly support the zwitterion hypothesis.

H. G. R.

Hydrolytic dissociation of some readily accessible hydrochlorides of amino-acids. R. ZEYNEK and S. KIRTEL (Med. Klinik, 1933, 29, 1313—1314; Chem. Zentr., 1933, ii, 2972).—Hydrochlorides of leucine, glutamic acid, glycine, and betaine are strongly hydrolysed, and give an acid reaction in solution.

H. J. E.

Identification of amino-acids by means of 3:5-dinitrobenzoyl chloride. B. C. SAUNDERS (Biochem. J., 1934, 28, 580—586).—3:5-C₆H₃(NO₂)₂·COCl condenses in alkaline solution with many NH₂-acids (I) and may be used as a means of separation and identification. Acidic (I) are less reactive and no condensation could be effected with tyrosine. A further separation can be effected by the insolubility of some of these derivatives in dil. acid.

H. G. R.

Proteins in liquid ammonia. II. Reaction of sodium in liquid ammonia with amino-acids and related substances. C. O. MILLER and R. G. ROBERTS (J. Amer. Chem. Soc., 1934, 56, 935—937; cf. A., 1931, 1437).—Vals. of the ratio mols. H₂ evolved: mols. substances used, on treatment with a slight excess of Na in liquid NH₃ are: glycine, alanine (II) 0.48; tyrosine (III) 0.66; O-CH₂-CO₂H 0.95; L-cystine 0.54; L-leucine 0.64; 5:5-diketopiperazine (IV) 0.32; glycylglycine (V) glycyl-DL-alanine 0.51; NHAcMe 0.53; NHAcPh 0.05; a mixture of (IV) (1 mol.) and (V) (1 mol.) 0.02; a mixture of (IV) (1 mol.) and (V) (2

mols.) 0.05; a mixture of (I) (1 mol.) and (III) (1 mol.) 0.39; a mixture of (I) (53.3%), (II) (31.1%), and (III) (15.6%) 0.36. In some cases [e.g., (III), (IV)] reduction also occurs.

H. B.

Lysine reineckate. W. GRASSMANN and O. LANG (Biochem. Z., 1934, 269, 223—224).—This salt C₆H₁₄O₂N₂·2Cr(NH₃)₂(CNS)₄H₄H₂O, m.p. 230—235° decomp., obtained from the hydrochloride by pptn. with NH₄ reineckate, is sol. in EtOH. 100 c.c. of H₂O at 24° dissolve 0.74 g.

W. McC.

Synthesis of α -amino- β -hydroxy-*n*-butyric acid, α -amino- β -hydroxyisovaleric acid (β -hydroxyvaline), and α -amino- β -hydroxy-*n*-valeric acid (β -hydroxynorvaline). Question of the occurrence of these aminohydroxy-acids as components of proteins. E. ABDERHALDEN and K. HEYNS (Ber., 1934, 67, [B], 530—547).— β -Methyl- Δ^a -butenoic acid (I) is converted by HOCl in H₂O into α -chloro- β -hydroxyisovaleric acid (II), m.p. 70° [Me ester (III), b.p. 89—90°/12 mm.]. Treatment of (II) or (III) with NH₃ in H₂O, EtOH, or CHCl₃ does not give homogeneous products. (III) in MeOH does not react with NaN₃. (II) and 10% KOH-EtOH afford $\alpha\beta$ -oxido- β -methylbutyric acid (IV), which does not give homogeneous products with NH₃ in EtOH or H₂O. (II) and liquid NH₃ afford the NH₄ salt of (IV), m.p. 123—125° (decomp.) after softening at 115°. $\alpha\beta$ -Dibromoisovaleric acid, m.p. 107—108°, is converted by 30% NH₃ at 37° into α -bromo- β -methyl- Δ^a -propene, b.p. 92°/760 mm. Addition of N₂O₄ to (I) in light petroleum at 15—20° and reduction of the product by Sn and HCl leads to a mixture of α -amino- β -hydroxy- (V) and β -amino- α -hydroxyisovaleric acids, m.p. 255° (decomp.) after darkening at 240°. Crotonic acid behaves analogously. Attempts to separate the mixtures of isomerides through the Zn or Cu salts or esters were unsuccessful. Reduction (red P-HI) yields a mixture of the corresponding α - and β -NH₂-acids. *Et* α -chloro-*n*-propyl ether, b.p. 111—113°/750 mm. (from EtCHO and HCl in EtOH), condenses with Et sodiophthalimidomalonate in C₆H₆ to *Et* phthalimido- α -ethoxy-*n*-propylmalonate, hydrolysed to α -amino- β -ethoxy-*n*-valeric acid, m.p. 258°, which, with boiling HBr (*d* 1.49), affords α -amino- β -hydroxy-*n*-valeric acid (VI), m.p. 230—231° (decomp.) after darkening at 215°. *Et* crotonate is transformed by Hg(OAc)₂ in MeOH followed by KBr in H₂O into *Et* α -acetatomercuri- β -methoxy-*n*-butyrate, OMe·CHMe·CH(Hg·OAc)·CO₂Et, m.p. 78—79°, which, with Br in CHCl₃, affords *Et* α -bromo- β -methoxy-*n*-butyrate, b.p. 94—95°/12 mm. α -Bromo- β -methoxy-*n*-butyric acid, m.p. 59—60°, is converted by 25% NH₃ into α -amino- β -hydroxy-*n*-butyric acid (VII), m.p. 239° (decomp.) after becoming brown at 225°. (V), m.p. 218° (decomp.) (Cu salt), is obtained similarly but in poorer yield from OMe₂CH·CO₂Et. The constitution of the amino-hydroxy-acids is established by their transformation [HI (*d* 2.00) and red P at 140—150°] into the corresponding, known NH₂-acids and their derivatives. (VII) gives a phenylcarbimide derivative, m.p. 177—178°, and 3-phenyl-5- α -hydroxyethylhydantoin, m.p. 164—165°. The phenylcarbamide, C₁₂H₁₆O₄N₂, m.p. 182°, and 3-phenyl-5- α -hydroxyisopropylhydantoin, m.p. 125° after softening at 117°, and the phenyl-

carbamide, $C_{12}H_{16}O_4N_2$, m.p. 156° , and 3-phenyl- α -hydroxy-*n*-propylhydantoin, m.p. 154 – 155° , are derived from (V) and (VI), respectively. The phenylhydantoin of 1-hydroxyproline has m.p. 123 – 124° . Treatment of (VII) with $BzCl$ and $NaOH$ leads to α -benzamido- β -hydroxy-*n*-butyric acid, m.p. 176° , transformed by further treatment into α -benzamido- β -benzoyloxy-*n*-butyric acid, m.p. 174° , also obtained directly from (VII) by use of the reagents in large excess. α -Benzamido- β -hydroxyisovaleric acid, m.p. 153° , could not be transformed into the Bz_2 derivative. α -Benzamido- β -hydroxy-*n*-valeric acid has m.p. 170 – 171° . ON -Dibenzoyl-1-hydroxyproline, m.p. 92° , is converted by $NaOH-H_2O$ into a Bz_1 derivative, m.p. about 100° . Benzoyl-1-proline has m.p. 156° after softening at 145° . The products obtained by Schryver *et al.* and by Rimington by hydrolysis of proteins are not identical with the synthetic aminohydroxy-acids.

H. W.

Syntheses of *N*-acetyldipeptides and their azlactones and amides. R. E. STEIGER (Helv. Chim. Acta, 1934, 17, 563–573).—By either (a) the action of $Ac_2O-AcOH$ on the dipeptide or (b) interaction of the NH_2 -acid on the azlactone of the $NHAc$ -acids in $AcOH$ (details given) are obtained the *N*-Ac derivatives of *dl*- β -phenylalanyl- α -aminoisobutyric acid, m.p. 204° (corr.) (199°) [*anilide*, m.p. 200.5 – 201.5° (corr.) (197°)], *dl*- α -phenylalanyl-*dl*-alanine, m.p. 209° (corr., decomp.) (205°) [*anilide*, m.p. 202 – 203° (corr.)], and -glycine, m.p. 192° (corr.) (188°) [*anilide*, m.p. 214 – 215° (corr., decomp.) (210°)], all by (b). The azlactone, m.p. 141.0 – 141.5° (corr.), of *dl*- α -phenylalanyl- α -acetamidobutyric acid with NH_3 gives the amide, m.p. 206.5 – 207.5° (corr.) (202°). $NH_2 \cdot CMe_2 \cdot CO_2H$ with *dl*- $CHMeBr \cdot COBr$ affords *dl*- α -bromopropionyl- α -aminoisobutyric acid, sinters 197° , m.p. 199° (corr., decomp.) (195°), whence *dl*-alanyl- α -aminoisobutyric acid and its *N*-Ac derivative, sinters 182° , m.p. 183.5° (corr.) (178°) [*azlactone*, m.p. 90° (corr.)], are obtained. By (a) are obtained the *N*-Ac derivatives of *dl*-alanyl-glycine, sinters 189° , m.p. 190.5° (corr., decomp.) (184°), and -*dl*-alanine, sinters 195° , m.p. 196° (corr.) (191°), glycyl-*dl*-alanine, sinters 180° , m.p. 182° (corr., decomp.) (177°), -*dl*-valine, sinters 185.5° , m.p. 187.5° (corr., decomp.) (182°), and -*dl*-leucine, sinters 178° , m.p. 180° [corr., decomp. (175°); lit. m.p. 177° (corr.)] [*anilide* (from azlactone), m.p. 172 – 173° (corr.) (167°)]; *dl*-valyl-, sinters 223° , m.p. 224 – 225° (corr., decomp.) (220°), and *dl*-leucyl-, sinters 182° , m.p. 183.5° (corr., decomp.) (178°), -glycine. All are of type $NHAc \cdot CR_3 \cdot R_4 \cdot CO \cdot NH \cdot CR_1 \cdot R_2 \cdot CO_2H$; the temp. in parentheses are the initial bath temp. in m.p. determinations.

J. W. B.

(A) Autolysis of *N*-acyldipeptides. (B) Action of alkali on *N*-acyldipeptides. R. E. STEIGER (Helv. Chim. Acta, 1934, 17, 573–582, 583–592).—A. The % hydrolysis of *N*-Ac derivatives of the following dipeptides $X \cdot CO \cdot NH \cdot CR' \cdot R'' \cdot CO \cdot NH \cdot CRR' \cdot CO_2H$ in $0.05M$ solution by H_2O at 100° for 4 hr. (by Van Slyke determination of NH_2 -N) is given in parentheses: ($X=Me$) *dl*-alanyl- (8.8), *dl*-leucyl- (6.9), and *dl*-valyl- (6.1), -glycine; glycyl-*dl*-alanine (8.1), -leucine (6.2), and -valine (4.5); *dl*-alanyl- (I) (45), *dl*- β -

phenylalanyl- (II) (35), glycyl- (13.2), and α -aminoisobutyryl- (87) - α -aminoisobutyric acid; *dl*-alanyl-*dl*-alanine (13.7); and, in $0.025M$ solution, *N*-acetyl- α -phenylalanyl-glycine (III) (16.7), -*dl*-alanine (IV) (27), and - α -aminoisobutyric acid (V) (84) (amide suffers no hydrolysis under these conditions). Thus introduction of alkyl or aryl groups into the Me group (R or R'') reduces the velocity of hydrolysis (v), but replacement of $CH_2 \cdot H$ in *N*-acetyl-glycylglycine by alkyl increases v . The nature of X also affects v , since *dl*-alanyl- α -benzamidoisobutyric acid ($X=Ph$) is more stable than the corresponding Ac derivative (I). The *N*-benzenesulphonyl derivatives of *dl*-alanyl-, m.p. 203 – 204° (199°), and α -aminoisobutyryl-, m.p. 191 – 192° (186.5°), - α -aminoisobutyric acid are unattacked under the same conditions, and the function of the CO in permitting hydrolysis is discussed.

B. The vals of the unimol. $k \times 10^3$ (days $^{-1}$) for the hydrolysis of the above *N*-acetyldipeptides with 15 equivs. of *N*-NaOH at 25° are: (III) 16.7, (IV) 2.5, (V) 0.0, (I) 17.7, and (II) 6.0. The order of decreasing v for alkaline hydrolysis is that of increasing v for acid hydrolysis. Dil. alkali never causes rupture of the linking between an NH_2 -acid residue containing *tert*-C and the other portion of the mol., and in (I) ($R=R'=R''=Me$) and (II) ($R=R'=Me$; $R''=Ph$) it is the Ac which separates. With excess *N*-NaOH $NHAc \cdot CPhMe \cdot CO \cdot NH_2$ affords *dl*-4-phenyl-2:4-dimethyliminazol-5-one (not purified), which is not formed in acid solution. α -Benzenesulphonamidobutyric acid, sinters 143° , m.p. 145 – 146° (140.5°), is converted into its amide, sinters 201° , m.p. 202.0 – 202.5° , and methylamide, m.p. 142.5 – 143.5° , both of which are hydrolysed only very slowly with NaOH. All m.p. are corr., the figures in parentheses being initial bath temp. Mechanisms are discussed. J. W. B.

Oxidation of cystine in non-aqueous media.

III. Products of exhaustive oxygenation of cystine perchlorate in acetonitrile. IV. Course of non-hydrolytic oxygenation. G. TOENNIES and T. F. LAVINE (J. Biol. Chem., 1934, 105, 107–113, 115–121).—Cystine perchlorate at -10° in anhyd. MeCN with BzO_2H in presence or absence of $CHCl_3$ absorbs a max. of 4 O, an impure cystine tetroxide being isolated as perchlorate (I). This is hydrolysed to a mixture of cysteic acid and (?) the corresponding sulphinic acid. Oxidation to cysteic acid may be completed at any stage of the anhyd. reaction with I in presence of H_2O . Evidence is adduced that a disulphoxide is formed as an intermediate in the formation of (I).

A. A. L.

Dithiocyno-derivatives of elaidic acid. Synthesis of *p*-phenylbenzoylmethyl θ -dithiocyanostearate and some *p*-halogenbenzoylmethyl θ -dithiocyanostearates. W. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 58–60B).—The following are described (cf. A., 1933, 940): *p*-phenyl-, m.p. 92° ; *p*-iodo-, m.p. 88° , *p*-bromo-, m.p. 79° , and *p*-chlorobenzoylmethyl θ -dithiocyanostearate, m.p. 69° . The SCN groups are in the *trans*-positions, whereas in similar derivatives of oleic acid they are in *cis*-positions.

J. L. D.

Decomposition and reactions of carbamide. IV. Mechanism of the formation of ammeline

etc. J. M. DAS-GUPTA (J. Indian Chem. Soc., 1934, **11**, 207—211).—The action of heat on carbamide (I) at different temp. and for different periods has been examined and the amounts of biuret (II), cyanuric acid, ammelide (III), and unchanged (I) have been determined. (III) is not produced below 190—195°, even in presence of HCl. The decomp. point of (II) (195°) is lowered in presence of NH_2Ph . A scheme is suggested to account for the results obtained.

F. R. S.

Tautomerism of cyanocarbamide with guanyl-carbimide. J. S. BLAIR and G. E. P. SMITH, jun. (J. Amer. Chem. Soc., 1934, **56**, 907—910).—Cyanocarbamide (amidodicarbonyl acid) (I) [K , K_2 , and K_3 salts, obtained from (I) and varying amounts of KNH_2 in liquid NH_3], prepared by Hallwach's method (Annalen, 1870, **153**, 293), is hydrolysed ($6N\text{-H}_2\text{SO}_4$ at 60—65°) to biuret (II) and guanidine (III) (cf. Baumann, A., 1875, 1187). The formation of (II), and (III) cannot be explained by the structures $\text{NH}_2\text{CO}\cdot\text{NH}\cdot\text{CN}$ and $\text{NH}_2\text{C}(\text{NH})\cdot\text{NCO}$ (guanyl-carbimide) for (I). (I) may react in either of these forms or as $\text{CO}\text{--}\langle\text{NH}\rangle\text{--}\text{C}\cdot\text{NH}$. (I) should be regarded as a mixed aquo-ammonopyrocarbonic acid (A., 1926, 277). Mol. wt. determinations on diphenyldicarbimide, m.p. 175—176° (decomp.), prepared by a modification of Snape's method (J.C.S., 1886, **49**, 254), indicate that it is $\text{NPh}\text{--}\langle\text{CO}\rangle\text{--}\text{NPh}$. H. B.

Ethylenic nitriles. Δ^a -Decenonitrile. M. FONTEYN (Bull. Soc. chim. Belg., 1934, **43**, 189—192).— Δ^a -Decenonitrile is separated (Gavrilov's method, A., 1933, 1281) by fractional distillation, conversion into the amides, fractional crystallisation of these to give the trans-, m.p. 122.5—123.20°, and cis-, m.p. 64.6—65.2°, -amide, and regeneration by distillation with P_2O_5 into the trans-, b.p. 113.8—114.2°/10 mm., and cis-, b.p. 105.6—105.8°/10 mm., -nitrile. J. W. B.

Steric hindrance and steric protection. H. J. BACKER (Chem. Weekblad, 1934, **31**, 275—279).—A review. The following new data are recorded: $\alpha\gamma$ -dibromopropane and Na_3AsO_3 give propane- $\alpha\gamma$ -diarsinic acid, but $\alpha\gamma$ -dibromo- $\beta\beta$ -dimethylpropane fails to react. Methylene dialkylsulphones, $\text{CH}_2(\text{SO}_2\text{R})_2$, are readily brominated except when $\text{R}=\text{Bu}^i$. $\text{Bu}^i\text{SO}_3\text{H}$ is unique in being non-hygroscopic. S. C.

Functional exchange between magnesium compounds and halogen derivatives. E. URION (Compt. rend., 1934, **198**, 1244—1246).—Interchange of radicals between MgRBr and R'Br is shown by the following reactions. MgEtBr and cyclohexyl bromide, when kept for 1 day at room temp., give 12% of cyclohexane (I), but 40% of (I) if the liberated EtBr is removed by distillation. $p\text{-C}_6\text{H}_4\text{Br}\text{--MgBr}$ and MgEtBr give 15% of C_6H_6 and much PhBr .

R. S. C.

Resolution of co-ordinated inorganic compounds into optical isomerides. I. Resolution of triethylenediamine-cadmium chloride, bromide, iodide, and sulphate. P. NEOGI and G. K. MUKHERJEE (J. Indian Chem. Soc., 1934, **11**, 225—230). *d*-Triethylenediaminocadmium tartrate, camphorsulphonate, and bromocamphorsulphonate could

not be resolved. Crystallisation of *d*-triethylenediaminocadmium camphornitronate from H_2O has given fractions having $[\alpha]_D^{20} +133.2^\circ$, $+97.4^\circ$, and $+94.7^\circ$, respectively. The first fraction gave *d*-triethylenediaminocadmium chloride, $[\alpha]_D^{20} +113.7^\circ$ in H_2O , bromide $[\alpha]_D^{20} +105.0^\circ$ in H_2O , iodide $[\alpha]_D^{20} +90^\circ$ in H_2O , and sulphate $[\alpha]_D^{20} +83.1^\circ$, the solutions being easily racemised. F. R. S.

Copper di- and tri-ethylenediamine salts of sulphonic acids. J. V. DUBSKY and J. TRTILEK (J. pr. Chem., 1934, [ii], **140**, 47—55).—By the action of $[\text{CH}_2\cdot\text{NH}_2]_2$ (en) on the appropriate $(\text{ArSO}_3)_2\text{Cu}$ the following complex salts are obtained: $(\text{PhSO}_3)_2\text{Cu} + 6\text{H}_2\text{O}$ gives $[\text{PhSO}_3]_2\text{Cu}\cdot 2\text{en} + 5\text{H}_2\text{O}$, dissolves in H_2O of crystallisation at 100—110°, decomp. 255°, $+2\text{H}_2\text{O}$, decomp. 260°, and $+ \text{H}_2\text{O}$, m.p. 260° (decomp.); $(\text{C}_6\text{H}_5\text{Me}\cdot\text{SO}_3)_2\text{Cu} + 6\text{H}_2\text{O}$ gives $[\text{C}_6\text{H}_5\text{Me}\cdot\text{SO}_3]_2\text{Cu}\cdot 3\text{en}\cdot 6\text{H}_2\text{O}$, m.p. 95° (in H_2O of crystallisation), resolidifying, and m.p. 285° (decomp.), and $[\text{C}_6\text{H}_5\text{Me}\cdot\text{SO}_3]_2\text{Cu}\cdot 2\text{en}\cdot 2\text{H}_2\text{O}$, darkens 270°, m.p. 290—294° (decomp.); $[\text{C}_6\text{H}_5\text{Me}(\text{NO}_2)\cdot\text{SO}_3]_2\text{Cu} + 4\text{H}_2\text{O}$ gives $[\text{C}_6\text{H}_5\text{Me}(\text{NO}_2)\cdot\text{SO}_3]_2\text{Cu}\cdot 3\text{en} + 9\text{H}_2\text{O}$, decomp. 255°, and $+6\text{H}_2\text{O}$, decomp. 258°; and $[\text{C}_6\text{H}_5\text{Me}(\text{NO}_2)\cdot\text{SO}_3]_2\text{Cu}\cdot 2\text{en}\cdot 4\text{H}_2\text{O}$; and $(\text{C}_{10}\text{H}_7\cdot\text{SO}_3)_2\text{Cu} + 6\text{H}_2\text{O}$ gives $(\text{C}_{10}\text{H}_7\cdot\text{SO}_3)_2\text{Cu}\cdot 3\text{en}\cdot 4\text{H}_2\text{O}$, decomp. 260—265°, and $(\text{C}_{10}\text{H}_7\cdot\text{SO}_3)_2\text{Cu}\cdot 2\text{en}\cdot 2\text{H}_2\text{O}$, m.p. 278° (decomp.). J. W. B.

Walden inversion as exhibited by diethylenediaminocobaltic compounds.—See this vol., 617.

Organo-metallic compounds. III. Syntheses of organic compounds of lead from lead salts and carboxylic acids. K. A. KOZESCHKOV and A. P. ALEXANDROV (Ber., 1934, **67**, [B], 527—530).—*K* Et malonate, prepared by semi-hydrolysis of $\text{CH}_2(\text{CO}_2\text{Et})_2$ by KOH in abs. EtOH at 0°, is transformed by PbPh_3Cl in boiling $\text{EtOH}\text{--COMe}_2$ into *Et* triphenylplumbic malonate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}_2\text{PbPh}_3$, m.p. 159—160° (corr., decomp.), which passes at 160—165°/15 mm. into *Et* triphenylplumbiacetate, $\text{PbPh}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m.p. 59—60° (corr.). At 128—132°/25 mm., *Et* triphenylplumbic benzylmalonate, m.p. 131—132° (corr., decomp.), affords *Et* α -triphenylplumbi- β -phenylpropionate, m.p. 82—84°. H. W.

Complex metallic derivatives of polyamines. M. LESBRE and E. GARDNER (68th Congr. Soc. Savantes, 1933, 104—106).—Interaction of K_2PtCl_4 with excess of guanidine carbonate (I) in H_2O at room temp. or 40—50° gives the black, amorphous salt $[\text{Pt}(\text{CH}_5\text{N}_3\text{Cl})(\text{OH})_n]$, transformed by conc. HCl or HBr into $[\text{Pt}(\text{CH}_5\text{N}_3\text{Cl})_2]_2$ and $[\text{Pt}(\text{CH}_5\text{N}_3\text{Br})_2]_2$, respectively. Cyanurtriarnide, prep. from (I) and PhOH at 170°, similarly gives the substance $[\text{Pt}(\text{C}_3\text{N}_3(\text{NH}_2)_3\text{Cl})(\text{OH})_n]$, whereas $\text{NH}_2\cdot\text{CH}(\text{CH}_3\cdot\text{NH}_2)_2\cdot 3\text{HCl}$ affords the compounds $[\text{Pt}(\text{C}_3\text{H}_5(\text{NH}_2)_3\text{Cl})\text{Cl}]_2\cdot \text{H}_2\text{O}$ and $[\text{PdC}_3\text{H}_5(\text{NH}_2)_3\text{Cl}]_2\cdot \text{H}_2\text{O}$. H. W.

Constitution of complex metallic salts. II. Platinum derivatives of $\beta\beta'$ -diaminodiethylamine. F. G. MANN (J.C.S., 1934, 466—474).—With aq. H_2PtCl_6 $\beta\beta'$ -diaminodiethylamine trihydrochloride (I) (this vol., 637) gives tetrachloro-diaminodiethylamine monohydrochloride)platinum monohydrate $[\text{Cl}_4\text{Pt}(\text{NH}_2\cdot\text{C}_2\text{H}_4)_2\text{NH}\cdot\text{HCl}]$ (II), shrinks at 215°, m.p.

221°, decomp. 228—230° [together with a small amount of a substance, darkens at 265°, if impure (I) is used], the *platinichloride*+2H₂O of which is obtained if (I) is boiled with aq. Na₂PtCl₆. With cold conc. aq. NaBr (II) gives the corresponding *dichloro-dibromo-mono-hydrochloride*, and with aq. NH₃ or [CH₃·NH₂], an unidentified compound, and not the expected [Cl₃Pt(H₂N·C₂H₄)₂NH]Cl (III), is obtained. The N atom in the central *sec.* amine group in (II) is asymmetric, but resolution through its *mono-d.* *camphor-β-sulphonate*, [α]₅₄₆₁ +9.1° in H₂O, failed, *trichlorodiaminodiethylamineplatinum d.* *camphor-β-sulphonate*, [α]₅₄₆₁ +9.7° in H₂O (giving *trichlorodiaminodiethylamineplatinic chloride monohydrate* with cold saturated aq. CaCl₂), being obtained as a by-product. With Ag *d.* *α-bromocamphor-π-sulphonate* in hot H₂O (II) gives *trichlorodiaminodiethylamineplatinum d.* *bromocamphorsulphonate* [as (III)], but at room temp. *tetrachloro(diaminodiethylamine d.* *bromocamphorsulphonate)platinum dihydrate*, softens 120°, m.p. 205—208° (decomp.), [α]₅₄₆₁ +43.2° in H₂O, which also could not be resolved, is obtained. In an attempt to prepare similar derivatives of 4-co-ordination metals (I) was treated with hot aq. K₂PtCl₄, but from the products only *monobromo(diaminodiethylamine)platinous monobromide* [BrPt(NH₂·C₂H₄)₂NH]Br, darkens at 200°, and the corresponding *moniodo-monoiodide*, darkens at 270°, m.p. 280—281° (decomp.), were isolated, but with initial addition of N·HCl, *dichloro(diaminodiethylamine monohydrochloride)platinum platinochloride monohydrate* was obtained. With Na rhodochloride dihydrate in dil. HCl (I) gives *dichlorobis(diaminodiethylamine monohydrochloride)rhodium rhodochloride*, the filtrate with KCNS affording *oxythiocyanic acid*, m.p. 200—202° (decomp.). Similar addition of KCNS to the solution obtained from (I), aq. NaOH, and CuSO₄ gives *thiocyanato(diaminodiethylamine)cupric monothiocyanate*, m.p. 165—167° (decomp.), similar addition of saturated aq. KI affording *tris(diaminodiethylamine)dicupric tetraiodide* +2H₂O and anhyd. CO₂ into the filtrate giving *moniodo(diaminodiethylamine)cupric monoiodide*. When aquopentamminocobaltic chloride, N·NaOH, and (I) are heated together *bis(diaminodiethylamine)cobaltic tri-iodide*, unchanged at 280°, is obtained. J. W. B.

Polymerisation of cyclic hydrocarbons. VII. Energy contents of the polymeric cyclopentadienes; strain theory. K. ALDER and G. STEIN (Ber., 1934, 67, [B], 613—626).—Determination of the heats of hydrogenation of the double linkings in the *tricycloheptene* (I) and the 5-membered ring (II) of a series of *cyclopentadienes* shows those of (I) to be considerably richer in energy than those of (II) or of acyclic, semicyclic, or cyclic olefines. Extension of the measurements to *cyclohexadiene* renders doubtful whether this effect is due to strain or to the particular structure of the bridged ring. *α(endo)*-Isomerides are richer in energy than the *β(exo)*-compounds, the magnitude of the differences corresponding with those observed with stereoisomeric, alicyclic *cis-trans* compounds when the solid compounds are compared. It appears probable that the differences would be diminished or would disappear if the heats of sublim-

ation were considered. Examination of a series of *cyclopentadienes* and their H-derivatives proves that strain in the ring has a definite energy equiv., the result is confirmed by comparison of camphor with 2-ketodecahydronaphthalene and of norcamphor with 2:5-*endoethylenecyclohexanone*. H. W.

Fulvene containing a β-ionone-carbon ring. H. WILLSTAEDT (Svensk. Kem. Tidskr., 1934, 46, 61—63).—β-Ionone condenses with *cyclopentadiene* in EtOH-KOH to give 2-(γ-cyclopentadienyldiene-Δ^α-n-butenyl)-1:1:3-trimethyl-Δ²-cyclohexene, b.p. 125°/12 mm., which gives a bluish-green colour with SbCl₃. J. W. B.

Separation of carotenes by adsorption on magnesium oxide. H. H. STRAIN (Science, 1934, 79, 325—326).—MgO prepared by low-temp. decomp. of Mg(OH)₂ is preferable to CaO or Ca(OH)₂ for separating carotenes by a Tswett column. Admixture with a heat-treated siliceous earth improves filtration. Using this adsorbent, carrot-root carotene has been separated into its major constituents with a recovery of 30—40% of the β- and 40—70% of the α-carotene originally present, both of which were identical with those separated by other methods. L. S. T.

Isolation of free phenyl radicals in the reaction of sodium vapour with bromobenzene. E. HORN and M. POLANYI (Z. physikal. Chem., 1934, B, 25, 151—152).—The existence of free gaseous Ph has been demonstrated. R. C.

Compounds of aluminium bromide with toluene, nitrobenzene, and metal bromides.—See this vol., 498.

Preparation of pure mesitylene [from crude cumene]. D. TISCHTSCHENKO (Bull. Soc. chim., 1933, [iv], 53, 1428—1430).—Crude cumene (I), b.p. 163—169°, is sulphonated (95% H₂SO₄) at 80—100°; *p*-cumenesulphonic acid is removed by dilution and crystallisation (details given), and the mother-liquor containing cumenesulphonic acid is hydrolysed by HCl at 100° to pure mesitylene (II). The unsulphonated portion of (I) contains much (II). R. S. C.

Mol. wt. determinations in synthetic highly polymerised substances.—See this vol., 504.

Highly arylated aromatic compounds. II. W. DELTHEY and G. HURTIG (Ber., 1934, 67, [B], 495—496; cf. this vol., 62).—Determination of the mol. wt. of the "hexaphenylbenzene" of Durand *et al.* (A., 1931, 207) in freezing phenanthrene and boiling PhNO₂ indicates that it is a C₆H₂Ph₄. C₆HPh₅ and 1:2:3:4-C₆H₂Ph₄ give normal vals. in boiling PhNO₂. H. W.

Action of nitrosyl chloride on aromatic hydrocarbons. R. PERROT (Compt. rend., 1934, 198, 1424—1426).—In sealed tubes at 150° the following general reaction occurs: RH+2NOCl→2NO+RCl+HCl. Thus CH₂PhCl, CH₂Ph·CH₂Cl, CHPhCl, CPh₂Cl, chlorodiphenyl, 1-C₁₀H₇Cl, and 9:10-dichloroanthracene are obtained; and, from CH₂PhCl, CHPhCl₂ and CPhCl₃. In sunlight at room temp. much N₂ is formed, with oximino-compounds or nitrosochlorides. E. W. W.

Richter's supposed triarylorthosulphurous acids. D. LIBERMANN (Compt. rend., 1934, 198, 1421—1423).—These compounds (A., 1919, i, 73) are shown to be actually trihydroxytriarylsulphonium sulphates; thus the "sulphate of triphenylorthosulphurous acid" (*loc. cit.*) is tri-*p*-hydroxyphenylsulphonium sulphate, since benzoylation yields tri-*p*-benzoyloxyphenylsulphonium hydroxide (A., 1933, 389). Similarly the product from *o*-tolyl sulphite yields a Bz₄ derivative (cf. this vol., 69). The chlorides and hydroxides described by Richter are also those of the sulphonium radicals (cf. *ibid.*, 183); when treated with H₂SO₄ the hydroxides furnish Richter's sulphates.

E. W. W.

Hydrolysis of substituted sulphonanilides. II. M. PEZOLD, R. S. SCHREIBER, and R. L. SHRINER (J. Amer. Chem. Soc., 1934, 56, 696—697).—The reaction temp. and yields (%) of NH₂Ph or NHPhMe obtained from the following anilides and 80% NaOH are given in parentheses: PhSO₂NHPh (250°; 0); 2:4:6-trimethylbenzenesulphon-anilide, m.p. 108—109° (170—225°; 0), and -methylanilide, m.p. 95—96° (185—225°; 0); 2:4-dibromobenzenesulphon-anilide, m.p. 145—146.5° (210—215°; 0.8), and -methylanilide, b.p. 210—214°/4 mm. (210—215°; 0.56); 2:4:6-tribromobenzenesulphon-anilide, m.p. 118° (210—215°; 5.3), and -methylanilide, m.p. 148—148.5° (210—215°; 3.4); 2:4-dinitrobenzenesulphon-anilide (155°; 79) and -methylanilide (155°; 71). NO₂-groups are thus more effective than Br or Me in promoting cleavage (cf. this vol., 288); steric hindrance effects and the size and wt. of the group are not factors. 2:4-C₆H₃Br₂SO₂Cl, m.p. 82° (lit. 79—79.5°), and 2:4:6-C₆H₂Br₃SO₂Cl are prepared from *m*-C₆H₄Br₂ and *s*-C₆H₃Br₃, respectively, with ClSO₃H and SO₂Cl₂ at 100°. *s*-C₆H₃(NO₂)₃ could not be sulphonated. 2:4:6-(NO₂)₃C₆H₂SO₃Na and PCl₅ (varying conditions) give 2:4:6-(NO₂)₃C₆H₂Cl, which with Na₂S₂ (varying conditions) affords 2:4:6:2':4':6'-hexanitrodiphenyl sulphide, decomp. 227—228°.

H. B.

Tribenzylmethane. G. A. HILL, M. H. LITTLE, S. WRAY, jun., and R. J. TRIMBEY (J. Amer. Chem. Soc., 1934, 56, 911—912).—Reduction (red P, HI at 200°) of tribenzylcarbinol gives tribenzylmethane (I), m.p. 81.8—82° [(NO₂)₃-derivative, softens at 74°, decomp. when heated further], also obtained by similar reduction of Ph dibenzylmethyl ketone and from Ph tribenzylmethyl ketone (prep. to be reported later) and NaNH₂ in xylene at 145—150°. The hexabenzylethanes of Schmerda (A., 1909, i, 563) and Trotman (A., 1925, i, 382) are (I).

H. B.

Catalysts for destructive hydrogenation. I. Hydrogenation of naphthalene in presence of molybdenum sulphide.—See this vol., 609.

Synthesis of condensed polynuclear hydrocarbons by cyclodehydration of aromatic alcohols. II. Synthesis of ionenes. M. T. BOGERT, D. DAVIDSON, and P. M. APFELBAUM (J. Amer. Chem. Soc., 1934, 56, 959—963; cf. A., 1933, 153, 599).—Reduction (Na, amyl alcohol) of Et *m*-methyleinnamate gives *γ*-*m*-tolylpropyl alcohol, b.p. 108°/4 mm., 147°/20 mm. (bromide, b.p. 104°/4 mm., 140—145°/20 mm.; phenylcarbamate, m.p. 52—53°). Mg *γ*-*m*-tolyl-

propyl bromide and COMe₂ afford *ε*-*m*-tolyl-*β*-methylpentan-*β*-ol, b.p. 128—132°/5 mm. (phenylcarbamate, m.p. 97—98°), converted by cold conc. H₂SO₄ into 1:1:6-trimethyl-1:2:3:4-tetrahydronaphthalene (ionene), b.p. 88—91°/4 mm. (cf. this vol., 76) [(NO₂)₂, m.p. 102°, and SO₂NH₂, m.p. 158—159°, derivatives (cf. *loc. cit.*)]. Mg *γ*-phenylpropyl bromide and COMe₂ give *ε*-phenyl-*β*-methylpentan-*β*-ol (I), b.p. 120°/7 mm., 130°/10 mm. (phenylcarbamate, m.p. 101.5—102.5°), dehydrated by I to impure *ε*-phenyl-*β*-methyl-*Δ*⁸-pentene (II), b.p. 108—112°/25 mm. (ozonolysis product, CH₂Ph·CH₂·CHO). CH₂Ph·CH₂·MgBr and Pr⁸CHO afford *ε*-phenyl-*β*-methylpentan-*γ*-ol (III), b.p. 138—142°/13 mm. (I) and (III) are converted by cold conc. H₂SO₄ into 1:1-dimethyl-1:2:3:4-tetrahydronaphthalene (IV), b.p. 98°/10 mm., 220—222°/761 mm. [(NO₂)₂, m.p. 64.5°, and SO₂NH₂, m.p. 111° and 148—149°, derivatives]; reaction probably proceeds through (II) [which is converted by 90% H₂SO₄ into (IV)]. (IV) could not be dehydrogenated (S or Se); it is oxidised (alkaline KMnO₄) to o-CO₂H·C₆H₄·CMe₂·CO₂H.

H. B.

Synthesis of 1:1:2:6-tetramethyltetrahydronaphthalene and the constitution of irene. M. T. BOGERT and P. M. APFELBAUM (Science, 1934, 79, 280).—*m*-C₆H₄MeBr is condensed with (CH₂)₂O and Mg to *β*-*m*-tolyl ethyl alcohol, which yields the corresponding bromide (I) with HBr. A Grignard reaction between (I) and COMePr⁸ gives a *tert*-alcohol which, when heated with H₂SO₄, yields 1:1:2:6-tetramethyltetrahydronaphthalene (II). On heating with Se, (II) gives a C₁₀H₅Me₃ with the 1:2:6-C₁₀H₅Me₃ (Ruzicka *et al.*, A., 1933, 1296).

L. S. T.

Hydrogenation of anthracene. Attempted hydrogenation of tetra-alkyldihydroanthracenes. (MLLE.) E. MARTIN and G. HUGEL (Bull. Soc. chim., 1933, [iv], 53, 1500—1502).—9:9:10:10-Tetraisobutyldihydroanthracene is hydrogenated with difficulty (Ni, 160—188°; not Pt or at a lower temp.) to 9:9:10:10-tetraisobutyldodecahydroanthracene, m.p. 86—87°, and does not react with Br.

R. S. C.

Preparation of 9:10-dialkylanthracenes. G. HUGEL and M. LERER (Bull. Soc. chim., 1933, [iv], 53, 1497—1498).—Dialkyldihydroanthracenes (I) with *p*-O:C₆H₄:O in boiling xylene give quinhydrone and 60—80% yields of 9:10-dialkylanthracenes (II), not obtainable by Pt. The Na₂ derivatives of (II) with H₂O give (I). 9:10-Di-ethyl-, m.p. 145.5°, *n*-butyl-, m.p. 105—106°, isobutyl-, m.p. 132—133°, and isomethyl-anthracene, m.p. 134.5—135°, are prepared.

R. S. C.

Synthesis of 9:9:10:10-tetra-alkyldihydroanthracenes. G. HUGEL and M. LERER (Bull. Soc. chim., 1933, [iv], 53, 1498—1504).—The Na₂ derivatives of the appropriate 9:10-dialkylanthracenes with alkyl halides in Et₂O give 9:9:10:10-tetraisoamyl-, m.p. 168—170°, and isobutyl-dihydroanthracene, m.p. 175°, and 9:10-diisopropyl-9:10-din-butyl-dihydroanthracene, m.p. 131—133°.

R. S. C.

Alkylation of phenanthrene. G. HUGEL and M. LERER (Bull. Soc. chim., 1933, [iv], 53, 1502—1504).—The Na derivative of phenanthrene (I) with Bu⁸Cl gives some isobutyl-, b.p. 120—140°/0.02 mm., and diiso-

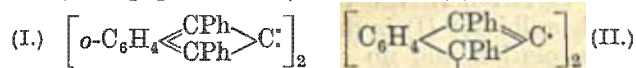
butyl-dihydrophenanthrene, b.p. 160–170°/0.02 mm., and much (I). R. S. C.

Synthesis of alkylphenanthrenes. VI. Attempts to synthesise the hydrocarbon " $C_{16}H_{14}$ " derived from strophanthidin. R. D. HAWORTH, C. R. MAYN, G. SHELDRIK, and (in part) J. MUSGRAVE (J.C.S., 1934, 454–461).—None of the following alkylphenanthrenes is identical with the hydrocarbon $C_{16}H_{14}$ obtained by Se dehydrogenation of strophanthidin (Jacobs *et al.*, A., 1932, 948). 1-Keto-2-methyl-1:2:3:4-tetrahydro- and MgMeI gives 1:2-dimethyl-3:4-dihydro-phenanthrene, m.p. 99–100° (picrate, m.p. 121–122°), dehydrogenated to 1:2-dimethylphenanthrene, m.p. 142–143° (styphnate, m.p. 153°; quinone, m.p. 213–214°; quinoxaline, m.p. 143–144°). Me β -2-naphthoylsobutyrate, m.p. 74–75°, with MgMeI gives γ -2-naphthyl- α -methyl- Δ^8 -pentenoic acid, m.p. 168–169°, reduced and cyclised to 4-keto-1:3-dimethyl-1:2:3:4-tetrahydro-, b.p. 167–169°/0.3 mm., whence 1:3-dimethyl-phenanthrene, m.p. 75–76° (styphnate, m.p. 165–166°; quinoxaline, m.p. 154–155°), is obtained. The *K* derivative of Et 5-methylcyclohexanone-2-carboxylate with α - C_6H_4 Me- CH_2 - CH_2 Br gives Et 2-(β -o-tolylethyl)-5-methylcyclohexanone-2-carboxylate (I), b.p. 170–175°/0.4 mm., converted into 1:6-dimethylphenanthrene, m.p. 87–88° (picrate, m.p. 134°; quinone, m.p. 200°; quinoxaline, m.p. 189°), also obtained from Et 2-(β -p-tolylethyl)-6-methylcyclohexanone-2-carboxylate (m), b.p. 170–175°/0.4 mm. 5-Methyl- α -naphthyl CH_2 Br ketone and $CHNa(CO_2Et)_2$ give β -(5-methyl-1-naphthyl)propionic acid, m.p. 169–170° [Me ester (II), b.p. 195–197°/0.3 mm.], reduced to γ -(5-methyl-1-naphthyl)butyric acid, m.p. 128–129°, converted successively into 1-keto-8-methyl-1:2:3:4-tetrahydro-, m.p. 164–165°, 1:8-dimethyl-3:4-dihydro-, and 1:8-dimethyl-phenanthrene (III), m.p. 191–192° (picrate, m.p. 151–152°; quinone, m.p. 190°; quinoxaline, m.p. 178°). Reduction (P–HI) of the pentenoic acid from (II) and MgMeI, and cyclisation affords 1-keto-4:8-dimethyl-1:2:3:4-tetrahydrophenanthrene (IV), m.p. 104–106°, and Et 2-(β -o-tolylethyl)-6-methylcyclohexanone-2-carboxylate (V), b.p. 170–172°/0.4 mm., is obtained in a similar manner to (I). The ultimate dehydrogenation products (m) from either (IV) or (V) are a mixture of (III) and 1:5-dimethylphenanthrene, m.p. 57–58° (picrate, m.p. 134–135°). Similar methods afford γ -(6:7-dimethyl-2-naphthyl)butyric acid, m.p. 137–139°; 4-keto-6:7-dimethyl-1:2:3:4-tetrahydro-, m.p. 112–113°, and 2:3-dimethyl-phenanthrene, m.p. 65–66° (picrate, m.p. 138–140°; styphnate, m.p. 165–167°; quinone, m.p. 234–235°; quinoxaline, m.p. 205°); 2-naphthyl β -bromoethyl ketone, m.p. 81°, 4-keto-2-methyl-1:2:3:4-tetrahydro-, m.p. 79–80°, and 2:4-dimethyl-phenanthrene, m.p. 111° (picrate, m.p. 139–140°; quinone, m.p. 169°; quinoxaline, m.p. 155–156°); 2:5-dimethylphenanthrene, b.p. 204–205°/15 mm., m.p. 46–47° (picrate, m.p. 127–129°; styphnate, m.p. 132–133°; quinone, m.p. 140–141°; quinoxaline, m.p. 166°). Reduction of β -(6-methyl-2-naphthyl)isobutyric acid and cyclisation gives 4-keto-3:7-dimethyl-1:2:3:4-tetrahydro-, b.p. 218–220° (semicarbazone, m.p. 220–221°), whence 2:6-dimethylphenanthrene, m.p. 33–34° (picrate, m.p. 135–136°;

styphnate, m.p. 148–150°; quinone, m.p. 202°; quinoxaline, m.p. 178–180°), is obtained. Similarly 4-keto-2:7-dimethyl-1:2:3:4-tetrahydro-, m.p. 133–134°, 2:7-dimethyl-, m.p. 101–102° (picrate, m.p. 152–153°; quinone, m.p. 224–225°; quinoxaline, m.p. 235°), 1-keto-2:9-dimethyl-1:2:3:4-tetrahydro-, m.p. 84–85° [from β -(4-methyl-1-naphthyl)isobutyric acid, m.p. 141–142°], 2:9-, m.p. 56–57° (picrate, m.p. 138°), 3:4-, m.p. 62–63° (picrate, m.p. 129–130°; styphnate, m.p. 142–143°; quinone, m.p. 207–208°; quinoxaline, m.p. 203–204°), and 3:6-dimethylphenanthrene, m.p. 141° (picrate, m.p. 172–173°; quinone, m.p. 212–213°; quinoxaline, m.p. 252°) [from 2- β -p-tolylethyl-5-methylcyclohexanone-2-carboxylate, b.p. 170–173°/0.4 mm.], are obtained. The appropriate MgRI and 1-keto-1:2:3:4-tetrahydrophenanthrene, and subsequent dehydration and dehydrogenation, afford 1-ethyl-, m.p. 62.5° [picrate, m.p. 108–109°; styphnate, m.p. 144°; quinone, m.p. 155°; quinoxaline, m.p. 151° (all different from *lit.*)], 1-iso-, m.p. 85–86° (picrate, m.p. 125–126°; quinone, m.p. 147–148°; quinoxaline, m.p. 142–143°), and 1-n-propylphenanthrene, m.p. 34–35° (picrate, m.p. 100–101°; quinone, m.p. 139–140°; quinoxaline, m.p. 144–145°). Similarly are obtained 4-keto-7-isopropyl-1:2:3:4-tetrahydro-, m.p. 55–56°, 2-iso-propyl-, m.p. 44–45° (picrate, m.p. 108°; quinone, m.p. 134°; quinoxaline, m.p. 172°), 2-methyl-1-ethyl-3:4-dihydro-, m.p. 77–78°, 2-methyl-1-ethyl-, m.p. 80° (picrate, m.p. 134–135°; quinone, m.p. 157–159°; quinoxaline, m.p. 146–147°), 1-keto-2-ethyl-1:2:3:4-tetrahydro-, m.p. 60–61° [from β -1-naphthyl- α -ethylpropionic acid, m.p. 112–113°], and 1-methyl-2-ethylphenanthrene, m.p. 100° (picrate, m.p. 134–135°; quinone, m.p. 163°; quinoxaline, m.p. 108°). In dehydrogenations marked (m), migration of a Me group from the 4- to the 1-position occurs, a possible mechanism being suggested. J. W. B.

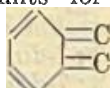
Coloured hydrocarbons of coal-tar. A. WINTERSTEIN and K. SCHÖN (Naturwiss., 1934, 22, 237–238).—1:2-Benzpyrene occurs in appreciable quantities in the fractions of higher b.p. and can be separated by fractional distillation and crystallisation. Chromatographic absorption is particularly applicable to the separation of coloured hydrocarbons occurring in small amounts in coal-tar fractions. Absorption of a C_6H_6 solution of technical anthracene (I) in a column of active Al_2O_3 gives a well-defined yellow zone from which by extraction with Et_2O and repetition of the process naphthacene (II), m.p. 337°, is isolated. The blue fluorescence of (I) is prevented by 0.00003% of (II). From a tar fraction, b.p. 425–464°, *d* 1.23, (II), (?) 1:2-benzonaphthacene, absorption max. λ 457 and 430 m μ , and (?) 1:2:2':3'-naphthanthracene, absorption max. λ 423 and 423 m μ in C_6H_6 , are similarly isolated. H. A. P.

Di-radical formula of rubrene and constitution of its dissociable peroxide. A. SCHONBERG (Ber., 1934, 67, [B], 633–638).—Rubrene (I) is considered

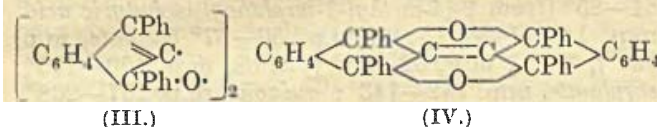


to pass under the influence of light into the activated di-radical form (II) which adds O to give the per-

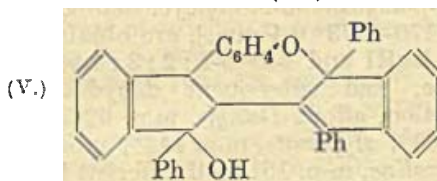
oxide (III). Structure (II) readily accounts for addition of Na and the repeated presence of



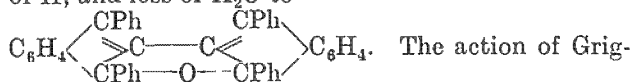
in (I) is causative of colour. A mechanism is suggested whereby (III) is transformed by MgI_2 into



(IV) and by HCl in C_6H_6 into (V). The production of "metruble" from (III), Zn, and AcOH is



explained by rupture of the $-\text{O}-\text{O}-$ bridge, addition of H, and loss of H_2O to



The action of Grignard's reagents on (III) leads partly to (IV) owing to presence of MgI_2 , and occurs partly in accordance with Gilman's scheme for the reaction with peroxides.

H. W.

Reactions of unsaturated compounds. II. Addition of arylamines to styrene. W. J. HICKINBOTTOM (J.C.S., 1934, 319—323).—Interaction of NH_2Ph in presence of its hydrochloride or hydrobromide with styrene at 220—260° gives α -anilino- α -phenylethane (*p*-toluenesulphonyl derivative, m.p. 95—96°) and *o*- (I), m.p. 58—59° (hydrochloride; Ac, m.p. 112—113°, Bz, m.p. 95—96°, derivatives), and *p*-amino-*as*-diphenylethane, (II), b.p. 176—178°/20 mm. [hydrochloride; picrate, m.p. 197—199° (decomp.); Ac, m.p. 112—113°, Bz, m.p. 127—128° (lit. 123°), and *m*-nitrobenzenesulphonyl, m.p. 122—123°, derivatives]. The constitution of (II) was confirmed by replacement of NH_2 by Br (Sandmeyer) and oxidation of the product to *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{COPh}$; this was unsuccessful with (I), which was deaminated (diazo-reaction) and the product oxidised to COPh_2 . Similarly *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ gives α -phenylethyl-*p*-toluidine, m.p. 69—70°, b.p. 183—184°/23 mm. (*p*-toluenesulphonyl, m.p. 86—87°, and *N*-*NO*-derivatives) (synthesised for comparison from *p*- $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$ and MgMeI), and α -phenyl- α -4-amino-*m*-tolylethane, b.p. 173—174°/18 mm. (hydrochloride; hydrobromide; sulphate; picrate, m.p. 162—163°; Ac, m.p. 141—142°, and *p*-toluenesulphonyl, m.p. 122—123°, derivatives), and *as*-*m*-xylidine gives α -phenyl- α -4-amino-5-*m*-xylethane (Ac derivative, m.p. 148—149°).

H. A. P.

Monophenyl nitrogen esters of biuret. J. S. BLAIR (J. Amer. Chem. Soc., 1934, 56, 904—907).—The variation in the reported m.p. (156—165°) of *as*-phenylbiuret (I) is due to its decomp. (with slow gas evolution and no charring) when heated. The phenylbiuret of Gatewood (A., 1923, i, 254) is a compound (II) of 3 mols. of (I) and 2 mols. of phenyl-

isocyanuric acid. (II) forms a continuous series of solid solutions with each component.

H. B.

Action of nitrous acid on dimethylaniline. I, II. J. C. EARL and A. W. MACKNEY (J. Proc. Roy. Soc. N.S.W., 1933, 67, 231—239, 419).—I. Equimol. amounts of $\text{NPhMe}_2\cdot\text{HCl}$ and NaNO_2 give tetramethylbenzidine and little *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ (I), whilst if small quantities of HCl are added the same products are obtained, (I) in larger yield. When excess of HNO_2 is used, the products are 3:3'-dinotrotetramethylbenzidine, *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, and a substance (II), m.p. 157—158°.

II. (II) is the nitrate of (I), since with Na_2CO_3 it gives (I) and is also formed directly from (I) and HNO_3 .

F. R. S.

Chlorination of aceto-*o*-xylidides. L. E. HINKEL, E. E. AYLING, and T. M. WALTERS (J.C.S., 1934, 283—287; cf. *ibid.*, 1923, 123, 2968).—Chlorination of aceto-*o*-3- and -4-xylidides with Cl_2 in aq. or abs. EtOH, or dichloramine-*T* in CHCl_3 , or by rearrangement of the *N*-chloroamines proceeds in the anticipated manner, the ease of direct chlorination and of rearrangement of the chloroamines being directly comparable. The following are described: 4-chloro- (I), m.p. 169°, *N*-chloro-, m.p. 94.5°, *N*:6-dichloro-, m.p. 81°, 4:6-dichloro-, m.p. 188°, 4:6:*N*-trichloro-, and 6-chloro-4-nitro-aceto-*o*-3-xylidide (6-Cl- and HNO_3 , *d* 1.5, in AcOH at 100°), m.p. 196.5°; 3-chloro- (II), m.p. 114°, *N*-chloro-, m.p. 55°, 5-chloro- (III), m.p. 157°, and *N*:5-dichloro-aceto-*o*-4-xylidide, m.p. 74°; 4:6-dichloro- (IV), m.p. 44°, and 4:5:6-trichloro-*o*-3-xylidine (V), m.p. 207°; and 3-chloro-*o*-4-xylidine, m.p. 26°. (I) was synthesised by reduction (Fe and AcOH) of 4-chloro-3-nitro-*o*-xylene, m.p. 75° (Sandmeyer, from 4:1:2:3- $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NO}_2$) and acetylation of the product. Elimination of NH_2 from (IV) (diazo-reaction) gives 1:2:3:5- $\text{C}_6\text{H}_2\text{Me}_2\text{Cl}_2$. (V) is synthesised by reduction of the corresponding NO_2 -compound, m.p. 169° (lit. 149°), (III) by reduction of 5-chloro-4-nitro-*o*-xylene, m.p. 63° (from 5:1:2:4- $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Me}_2\cdot\text{NO}_2$) and acetylation of the product, and (II) similarly from 3-chloro-4-nitro-*o*-xylene, m.p. 46°.

H. A. P.

Degradation of quaternary ammonium salts. VIII. Necessary structural conditions for migration in radicals. J. L. DUNN and T. S. STEVENS (J.C.S., 1934, 279—282).—The rearrangement $\text{COPh}\cdot\text{CH}_2\cdot\text{N}^+\text{RMe}_3\text{X} \rightarrow \text{COPh}\cdot\text{CHR}\cdot\text{NMe}_2 (+\text{HX})$ under the influence of alkali takes place when R is allyl or phenylpropargyl, but not when R is Me, Et, hexahydrobenzyl, Ph, $\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, or $[\text{CH}_2]_2\cdot\text{CH}_2\text{Ph}$. The following are prepared by interaction of $\text{COPh}\cdot\text{CH}_2\text{Br}$ and the appropriate *tert*-amine, followed by metathesis where necessary: phenacyl-allyldimethylammonium picrate (I), m.p. 78—79°; phenylpropargyldimethylammonium bromide (II), m.p. 162°; phenyldiethylammonium bromide (III), m.p. 150—152°, and hexahydrobenzyl-dimethylammonium bromide (IV), m.p. 185—187° (picrate, m.p. 123—124°). (I) is converted by 2.5*N*-NaOH at the b.p. into ω -dimethylamino- ω -allylacetophenone (picrate, m.p. 97—99°), identified by reduction of its methosulphate (Zn and H_2SO_4) to allylacetophenone. Similarly, (II) with hot 8% Na_2CO_3 gives ω -dimethylamino- ω -phenyl-

propargylacetophenone [hydrochloride, m.p. 167—168°; hydrobromide (+0.5H₂O), m.p. 182—183° (decomp., darkens 130°)], the methosulphate of which on reduction gives CH₂(CH₂Bz)₂. On the other hand, (III) with 25—30% NaOH gives BzOH, CPhMe, and NMe₃, and (IV) is either unchanged (10%) or completely decomposed (50%) by alkali. Similarly phenacyl-β-phenylethyldimethylammonium bromide with NaNH₂ gives CH₂Ph·CH₂·NMe₂, and phenacyl-γ-phenylpropyldimethylammonium bromide with boiling 25% NaOH gives CH₂Ph·[CH₂]₂·NMe₂ and a base (picrate, m.p. 103—104°) and with NaNH₂ at 130—140° gives phenacyldimethylamine (methopicate, m.p. 137—139°) and CHPh·CHMe. *o*-Hydroxyphenylbenzylidimethylammonium chloride, m.p. 115—116° [from NMe₂·C₆H₄·OH(*o*) and CH₂Ph·Cl], reacts violently with NaNH₂ at 110° to give *o*-benzyloxyphenyldimethylamine, the methiodide (+1H₂O), m.p. 157—158° (methopicate, m.p. 155°), of which is synthesised by methylation (MeI and NaOH) of *o*-aminophenyl benzyl ether. Interaction of CH₂PhCl and β-dimethylaminopropiophenone gives only (CH₂Ph)₂NMe₂Cl. Trimethyldihydroxylamine and CPh·CH₂Br give CPh·CH₂·NMe₂·HBr, m.p. 185—186°. Methylation of NH₂·CH₂·CPh₃ gives βββ-triphenylethyldimethylamine, m.p. 110—112° (hydrochloride, m.p. 207—209°). Distillation of αβγ-C₃H₅Br₃ over KOH gave β-bromoallyl bromide only (cf. *Annalen*, 1870, 154, 371); this with NHMe₂ gives β-bromoallyldimethylamine, b.p. 132—134° (picrate, m.p. 94—95°), which is either unchanged or completely decomposed by alkali. Interaction of α-dimethylaminoisobutyronitrile with MgPhBr gives phenylisopropyldimethylamine (picrate, m.p. 205°), and of dimethylaminophenylacetonitrile with MgEtBr gives α-dimethylamino-α-phenylpropane, b.p. 100—105°/22 mm. (picrate, m.p. 161—164°). β-Dimethylamino-α-phenylpropane picrate, m.p. 135—139°, and ω-piperidinoacetophenone hydrobromide, m.p. 227—228° (lit. 220°), are described. H. A. P.

Reactions of thiocarbonyl chloride. III. Structure of so-called "thiocarbonylbenzidine." G. M. DYSON and D. W. BROWNE (*J.C.S.*, 1934, 318—319).—"Thiocarbonylbenzidine" (I) is shown by ultimate analysis and synthesis to be 4:4'-bis-(4''-aminodiphenyl-4'''-thiocarbamido)diphenyl, [C₆H₄·NH·CS·NH·C₆H₄·C₆H₄·NH₂]₂, and not 4-aminodiphenyl-4'-thiocarbimide (cf. A., 1926, 1131). It is decomposed by Ac₂O (at the b.p.?) into 4-acetyldiphenyl-4'-thiocarbimide, m.p. 224°, and diphenyl-4:4'-dithiocarbimide (II), m.p. 203°. (II) is also obtained from CCl₄ and benzidine (III) in excess of 2N-HCl, and with more (III) in warm C₆H₆ gives (I). CCl₄ and (III) in AcOH give 4:4'''-diamino-4'-4''-diphenylthiocarbamide as by-product. CCl₄ and 4:4'-CH₂(C₆H₄·NH₂)₂ give 4:4'-dithiocarbimido-diphenylmethane, m.p. 196°. H. A. P.

Benzidine derivatives. S. SAKO (*Bull. Chem. Soc. Japan*, 1934, 9, 150—154).—2-Nitro- (I), m.p. 143° and dimorphous form, m.p. 117°, is reduced to 2-amino-, m.p. 134°, and dimorphous form, m.p. 50°, -benzidine, the 4:4'-Ac₂ derivative, m.p. 261—262°, of which [by HCl-SnCl₂-AcOH reduction of the Ac₂ derivative of (I)] is converted into the diazonium

iodide, decomposed by cold glacial AcOH to 2-iodo-4:4'-diacetamidodiphenyl, m.p. 310—311°, hydrolysed by EtOH-HCl to the dihydrochloride of 2-iodobenzidine (sulphate). J. W. B.

Triarylaminioethylenes. III. Interaction of sulphur and trianilinoethylene (addendum). R. SHIBATA, M. OKUYAMA, N. KOJIMA, and T. NISHI. **IV. Interaction of sulphur and tritolylaminioethylenes. V. Coloured by-products in the synthesis of triarylaminioethylenes.** R. SHIBATA and T. NISHI (*Tech. Rep. Tôhoku*, 1934, 11, 160—167, 168—183, 184—198).—III. In addition to the products already given (A., 1933, 1286), monothio-oxanilide and oxanilide [oxidation products of (NHPh·CS)₂] are isolated from the products of fusion of trianilinoethylene (I) with S, and a substance C₉H₇N, m.p. 207°, from those of the interaction of NH₂Ph and CHCl:CHCl, which condensation is investigated under a variety of conditions and with different catalysts.

IV, V. Isolated by-products of the interaction of NH₂Ph and CHCl:CCl₂ are a red substance, C₁₃H₁₀N₂, m.p. 212° [corresponding with the substance C₁₅H₁₃N₂ (II), m.p. 207°, in the *p*-tolyl series (*loc. cit.*)], and a yellow substance, C₂₂H₁₇N₃ (III), m.p. 115—117° [corresponding with the substances C₂₃H₂₃N₃, m.p. 115—116° (IV) and m.p. 141° (V), respectively, in the *o*- and *p*-tolyl series]. When heated in decalin at 160—170°, tri-*p*-tolylaminioethylene (VI) gives (V) and a trace of (II); without solvent it affords *p*-C₆H₄·Me·NH₂ (VII) and (II) at 160—170°, and (V) at 145°. Without solvent at 140—150° (V) gives a trace of (II), unchanged (V), and a trace of a colourless compound. With S at 140—150° (V) gives (VII), dithio-ox-*p*-toluidide, and tri-*p*-tolylaminiothioethylene. Reduction of (V) with either Na-Hg in 95% EtOH (CO₂) or Pd-H₂, gives an almost quant. yield of (VI), (IV) being similarly reduced to tri-*o*-tolylaminioethylene (VIII). Conversely oxidation of (VI) with PbO₂, KMnO₄, or air in NaOH-H₂O-PhMe gives (V); (VIII) gives (IV), and (I) gives (III). (III), (IV), and (V) are probably, therefore, α-anilino-αβ-di-(phenylimino)-, α-*o*-tolylamino-αβ-di-(*o*-tolylimino)-, and α-*p*-tolylamino-αβ-di-(*p*-tolylimino)-ethane, all of type NR:C(NHR)·CH:NR. With anhyd. ZnCl₂ at 140—180° (VI) gives a substance, C₁₆H₁₈ON₂, m.p. 133—134°. With 2N-HCl (V) gives a substance, m.p. 100—101° (? hydrochloride + 3H₂O). Interaction of β-C₁₀H₇·NH₂ and C₂HCl₃ in boiling 20% NaOH affords tri-β-naphthylaminioethylene, m.p. 200°. J. W. B.

Acyl diarylhydrazine series. III. Oxidation of acetylhydrazobenzene. F. O. RITTER (*J. Amer. Chem. Soc.*, 1934, 56, 975—976; cf. A., 1931, 476).—NAcPh·NHPh is oxidised (Na₂Cr₂O₇, AcOH) to *p*-benzoquinone-*p*-benzeneazodiphenylhydrazone (I). O:C₆H₄·N·NPh·C₆H₄·N·NPh, dark red with bronze reflex, m.p. 163° (corr.), which is reduced by SnCl₂ (=8H), and is converted by EtOH-KOH into *v*-anilinoazobenzene. (I), Zn dust, AcOH, and Ac₂O give *p*-NHAc·C₆H₄·NHPh, *p*-NHAc·C₆H₄·OH, and NHAcPh. It is suggested that a compound analogous to (I) may be an intermediate in the semidine rearrangement of hydrazo-compounds. NPh₂·NH₂, and EtOH-KOH give NPh₂ and NH₃. H. B.

Phosphoric acid as condensing agent. Alkylation of phenols and their ethers. A. TSCHITSCH-BABIN (Compt. rend., 1934, 198, 1239—1242).—The following are prepared by condensation with hot H_3PO_4 (d 1.85—1.87; 400 g. per mol.): 2- or 4-tert.-butyl-*m*-cresol, m.p. 23°, b.p. 121—122°/15 mm. [75—80%; from *m*-cresol and $\text{Bu}^\text{t}\text{OH}$ or $\text{Bu}^\text{t}\text{OH}$], 3-tert.-butyl-*o*- (I), m.p. 27°, b.p. 122.5°/14 mm. (78%; from *o*-cresol and $\text{Bu}^\text{t}\text{OH}$), and -*p*-cresol, m.p. 44°, b.p. 118—119°/14 mm. (73%; by $\text{Bu}^\text{t}\text{OH}$), 2- or 4-tert.-amyl-, b.p. 119—122°/10 mm., and -menthyl-*m*-cresol, b.p. 152—155°/2 mm. (by tert.-amyl alcohol or menthol), 3-benzyl-*o*-cresol, m.p. 52°, b.p. 180—186°/12 mm. (from $\text{CH}_2\text{Ph}\cdot\text{OH}$), isopropyl-, b.p. 127—130°/17 mm., and tert.-butyl-1:2:4-xyleneol, b.p. 126—128°/17 mm., tert.-butyl- (56.9%), b.p. 134—136°/1.5 mm., and ditert.-butyl-resorcinol (27.7%), m.p. 123°, the *Me* ether of (I) (65%; from $\text{Bu}^\text{t}\text{OH}$ and $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$), and hexyl-*m*-cresol, b.p. 152—154°/11 mm. (from *m*-cresol and hexene). Condensation occurs only in the *o*-position to OH. Saturated primary alcohols react only if they can isomerise to the *sec.* or *tert.* isomerides. Allyl alcohol gives polymerised products, which yield isopropylphenols and hydrocoumarans when dry-distilled. R. S. C.

Homologues of phenol. G. T. MORGAN and A. E. J. PETTET (J.C.S., 1934, 418—422).—2:3:6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{NH}_2$ gives (diazotisation) 2:3:6-trimethylphenol, m.p. 62° (*p*-xenylcarbamate, m.p. 189°). 3-Nitro-4-methylacetophenone, m.p. 62° (from *p*- $\text{C}_6\text{H}_4\text{MeAc}$), Fe, and 1% HCl give the 3- NH_2 -compound, m.p. 81°, converted (diazo-reaction) into 3-hydroxy-4-methylacetophenone, m.p. 119—120°, which is reduced (Clemmensen) to 2-methyl-5-ethylphenol, b.p. 224° (*p*-xenylcarbamate, m.p. 160°). 2-Methyl-4-ethylacetanilide (I) and fuming HNO_3 in AcOH at <40° give the 6- NO_2 -derivative, m.p. 142°, deacetylated by hot 25% HCl to 6-nitro-2-methyl-4-ethylaniline, m.p. 64°, whence were prepared successively 1-nitro-3-methyl-5-ethylbenzene (by diazotisation and EtOH), b.p. 262—264°, 3-methyl-*o*-ethylaniline (by Fe and 1% HCl), b.p. 233°, and 3-methyl-5-ethylphenol, m.p. 51°, b.p. 233° [phenylcarbamate, m.p. 151°, does not depress the m.p. of *m*-5-xylene phenylcarbamate; *p*-xenylcarbamate, m.p. 125°, and *p*-xenoate, m.p. 70°, depress the m.p. of the corresponding derivatives of *m*-5-xyleneol; *Me* ether, oxidised by hot, alkaline KMnO_4 to 5-methoxyisophthalic acid (*Me*, ester, m.p. 109°)]. (I) with H_2SO_4 - HNO_3 gives the 5- NO_2 -derivative, m.p. 143°, yielding successively 5-nitro-2-methyl-4-ethylaniline, m.p. 74°, 1-nitro-4-methyl-2-ethylbenzene, b.p. 253—263°, 4-methyl-2-ethylaniline, b.p. 230° (*Ac* derivative, m.p. 132°), and 4-methyl-2-ethylphenol (phenylcarbamate, m.p. 99°). *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, ZnCl_2 , and EtOH at 280° give a mixture containing 3-methyl-4-ethylaniline, b.p. 236° [sulphate; *Ac* derivative (II), m.p. 90°], converted into 3-methyl-4-ethylphenol, m.p. 26°, b.p. 235° (*p*-xenylcarbamate, m.p. 152°), also obtained from 4-aceto-*m*-cresol. (II) and fuming HNO_3 in AcOH at <40° give the 2-, m.p. 103°, and ?- NO_2 -derivative, m.p. 109°; the former affords successively 2-nitro-5-methyl-4-ethylaniline, m.p. 90°, 1-nitro-4-methyl-3-ethylbenzene, m.p. 23°, b.p. 271°, 4-methyl-3-ethylaniline, b.p.

234—235° (*Ac* derivative, m.p. 88°) (also obtained from 3-chloroaceto-4-methylacetanilide), and 4-methyl-3-ethylphenol, b.p. 234—235° (*p*-xenylcarbamate, m.p. 162°). R. S. C.

***o*- and *m*-4-Xylenolsulphones.** J. ZEHENTER [with O. RIEPL] (J. pr. Chem., 1934, [ii], 139, 309—317).—*o*-4-Xylenol and conc. H_2SO_4 (10:4) at 170—175° give the 3:3'- or 5:5'-sulphone, m.p. 244—245° (30—40% yield) [Na_2 salt, cryst.; Br_2 -, m.p. 227—228°, (NO_2)₂-, cryst., decomp., Ac_2 , m.p. 218°, and Bz_2 derivatives, m.p. 238°; *Me*, m.p. 184°, and *Me*₂ ether, m.p. 189°]. This with conc. H_2SO_4 at room temp. gives a sulphonic acid, +1.5 H_2O , m.p. 80—90° (*K* and *Ba* salts, cryst.), and disulphonic acid, +2.5 H_2O , m.p. 124—125° [K_2 , +2.5 H_2O , *Ba*, +2 H_2O , and basic *Ba* salt, $[\text{C}_{16}\text{H}_{15}\text{O}_4\text{S}(\text{SO}_3)_2]_2\text{Ba}_3$, +7 H_2O], whereas at 100° xylenolsulphonic acid is formed. *m*-4-Xylenol affords at 170—180° the 5:5'-sulphone, m.p. 221° (*Na* salt, +5 H_2O ; *Ac*, m.p. 199°, and *Bz* derivative, m.p. 244—245°; *Me*₂ ether, m.p. 181°), hydrolysed by H_2SO_4 to xylenolsulphonic acid. R. S. C.

2:3-Derivatives of 2-methylnaphthalene. V. VESELY and F. ŠTURSA (Coll. Czech. Chem. Comm., 1934, 6, 137—144).—The mixture of 5- and 6-bromotetralin obtained by bromination of tetralin (von Braun, A., 1924, i, 48) is converted by Mg and Me_2SO_4 in Et_2O (N_2) into a mixture of the corresponding 5- and 6-Me derivatives, from the sulphonation product of which separates the sparingly sol. *Ba* salt of 6-methyl-1:2:3:4-tetrahydronaphthalene-7-sulphonic acid, m.p. 102° [*Na* salt (I); amide, m.p. 158—159°]. Removal of the SO_3H by 55% H_3PO_4 at 165° gives 6-methyl-1:2:3:4-tetrahydronaphthalene, dehydrogenated by S at 220° to 2- $\text{C}_{10}\text{H}_7\text{Me}$. With KOH at 240—290° (I) affords 7-hydroxy-6-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 88—89° (*Me* ether, m.p. 63—64°; *p*-nitrobenzeneazo-compound, m.p. 244—245°), dehydrogenated to 3-methyl-8-naphthol, b.p. 176°/20 mm., m.p. 155—156°. This with conc. aq. NH_3 -(NH_4)₂ SO_3 at 160—170° gives 3-methyl-naphthylamine, m.p. 135—135.5° (*Ac*, m.p. 181—182°, and *Bz*, m.p. 189—191°, derivatives; *p*-nitrobenzeneazo-compound, m.p. 238—240°), converted by diazotisation and NaNO_2 -Cu-bronze into 3-nitro-2-methylnaphthalene, m.p. 117—118°. J. W. B.

Retene. III. Nitroretenols, nitrofluorenones, and related compounds. M. T. BOGERT and T. HASSELSTROM (J. Amer. Chem. Soc., 1934, 56, 983—985).—6-Acetoxyretene and HNO_3 (d 1.52) in AcOH at 15—20° give a NO_2 -derivative, m.p. 194.5—195.5° (all m.p. are corr.), reduced (SnCl_2 , EtOH-HCl) to the unstable NH_2 -compound, m.p. 215—217° (*Ac* derivative, m.p. 203.5—204.5°). Retene ketone (1-methyl-7-isopropylfluorenone) [oxime (I), m.p. 174.5°, formed only in an anhyd. medium ($\text{MeOH}+\text{BaCO}_3$)] similarly affords NO_2 -, m.p. 165.5°, and NH_2 -derivatives, m.p. 146° [*Ac* derivative, m.p. 197.5—198.5° (oxime, m.p. 254—255.5°)]. (I) and PCl_5 in Et_2O give a methylisopropylphenanthridone, m.p. 219.5—220.5°. 6-Acetoxyretenequinone is not converted by 50% KOH into a fluorenone; the resultant 6-hydroxyretenequinone gives a vat ($\text{Na}_2\text{S}_2\text{O}_4$) which dyes cotton peach-red (fugitive to light). H. B.

Manufacture of s-diarylaminophenols.—See B., 1934, 355.

Rearrangement of hydroxy-sulphones. IV. B. A. KENT and S. SMILES (J.C.S., 1934, 422—428; cf. A., 1932, 735).—The rates of change of a series of *o*-hydroxy-sulphones to ether-sulphinic acids, measured by a colorimetric method, are in agreement with the electronic considerations previously suggested. The change occurs more rapidly with a suitably placed aliphatic OH, and even with aliphatic hydroxy-sulphoxides. 4-Chloro-2-nitrophenyl 4-hydroxy-m-tolyl sulphide (I), m.p. 134° (from 4-chloro-2-nitrophenylchlorothioliol and *p*-cresol at 100°) (*Ac* derivative, m.p. 86°), and H_2O_2 -AcOH at 90° give the corresponding sulphone, m.p. 157°. *p*-Benzoquinone and $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{H}$ in H_2O give 2-nitro-2':5'-dihydroxydiphenylsulphone, m.p. 214°. $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-SCl}$ and resorcinol in CHCl_3 give *o*-nitrophenyl 2:4-dihydroxyphenyl sulphide, m.p. 157° (lit. 150—151°), the *Ac* derivative, m.p. 94° (lit. 102—103°), of which with H_2O_2 -AcOH at 90° gives 2-nitro-2':4'-diacetoxydiphenylsulphone, m.p. 125°, hydrolysed by H_2SO_4 -EtOH to the 2':4'-(OH)₂-derivative, m.p. 132°. 4-Hydroxy-m-tolylthiol (prepared from the carbonate by alkali), 3:4- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$, and NaOEt in hot EtOH give 2:4-dinitrophenyl 4-hydroxy-m-tolyl sulphide, m.p. 123° (*Na* salt), oxidised to 2:4-dinitrophenyl-4'-hydroxy-m-tolylsulphone, m.p. 139—140°. 3-Nitrophenyl disulphide (from $\text{m-NO}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl}$ and HI in 78% yield) gives the chlorothioliol, which with *p*-cresol in hot CHCl_3 yields 3-nitrophenyl 4-hydroxy-m-tolyl sulphide, m.p. 112° (*Ac* derivative, m.p. 96°), oxidised to 3-nitrophenyl-4'-hydroxy-m-tolylsulphone, m.p. 133°, which is stable to aq. NaOH. *m*-4-Xylenol and $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{Cl}$ give 2-nitro-2'-hydroxy-3':5'-dimethyldiphenyl sulphide, m.p. 123° (*Ac* derivative, m.p. 158°), and thence 2-nitro-2'-hydroxy-3':5'-dimethyldiphenylsulphone, m.p. 178°. Similarly were prepared 2-nitro-2'-hydroxy-5'-methoxy-, m.p. 135°, and 5'-chloro-2-nitro-2'-hydroxy-diphenyl sulphide, m.p. 159°, 2-nitro-2'-hydroxy-2'-methoxy- (II), m.p. 152°, and 5'-chloro-2-nitro-2'-hydroxy-diphenylsulphone, m.p. 175°, and 2-nitrobenzyl-4'-hydroxy-m-tolylsulphone (by way of an impure sulphide), m.p. 139° (not affected by 2*N*-NaOH at 180°). 2-Nitrophenyl β -hydroxyethyl sulphide gives an impure acetate, which with H_2O_2 -AcOH at 90° gives the corresponding acetyl-sulphoxide (III), m.p. 113°, hydrolysed by 2*N*- H_2SO_4 to the hydroxy-sulphoxide (IV), m.p. 157°. (III) is further oxidised to the oily *Ac* derivative of 2-nitrophenyl- β -hydroxyethylsulphone (V), m.p. 88°. Rearrangement of the appropriate hydroxysulphones and reduction of the resulting sulphinic acids by HI- SO_2 -AcOH and of the disulphides by glucose and alkali led to (a) 4-chloro-2-nitrophenyl, m.p. 137° [converted by oxidation and hydrolysis into 4-chloro-2-nitrophenyl *p*-tolyl ether, m.p. 103°, also obtained from *p*- $\text{C}_6\text{H}_4\text{Me-OK}$ and 2:5- $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$], and 2:4-dinitrophenyl-3-sulphino-*p*-tolyl ether, m.p. 117—118°, 2-nitro-4'-hydroxy-, m.p. 64°, 2-nitro-5'-hydroxy-, m.p. 107° (decomp.), 2-nitro-4-methoxy-, m.p. 122—123°, and 4'-chloro-2-nitro-, 117—118°, -2'-sulphinodiphenyl ether; (b) the following disulphides: di-(4-*p*-chloro-*o*-nitrophenoxy-m-tolyl), m.p. 133°, di-(*o*-hydroxy-2-*p*-nitrophenoxy-

phenyl), m.p. 207°, di-(2-*o*-nitrophenoxy-5-methoxyphenyl), m.p. 114°, and di-(5-chloro-2-*o*-nitrophenoxyphenyl), m.p. 159°; (c) the following sulphides: (I), 2-nitro-2':5'-dihydroxydiphenyl, m.p. 161°, and (II); (d) by more prolonged rearrangement, 3-chloro-8-methoxyphenothioxin 10-dioxide, m.p. 173°. (V) and 0.5% aq. NaOH rapidly give β -*o*-nitrophenoxyethanesulphinic acid (VI), m.p. 121° (and, under more vigorous conditions, also $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-OH}$), reduced to di-(β -*o*-nitrophenoxyethyl) disulphide (VII), m.p. 76°. (IV) with 1.5% NaOH gives a mixture of (VI) and (VII). $\text{o-NO}_2\text{-C}_6\text{H}_4\text{-SCl}$ and ψ -cumenol at 100° give ψ -cumenyl 2-nitrobenzenesulphenate, m.p. 162°, stable to hot AcOH, but slowly hydrolysed by hot 2*N*-NaOH to ($\text{o-NO}_2\text{-C}_6\text{H}_4\text{-S}$)₂. 2-Chloro-*m*-5-xylyl 2-nitrobenzenesulphenate, m.p. 190°, similarly prepared, behaves similarly. R. S. C.

isoChavibetol. I. isoChavibetol ethyl ether and its decomposition by methyl-alcoholic potassium hydroxide into isohomogenol. II. "Disochavibetol" and the stereoisomeride of isochavibetol ethyl ether. M. IMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 78—79B, 79—81B).—I. isoChavibetol Et ether (I) (prep. described) with EtNaSO₄, KOH, and a little H_2O at 157—163° under pressure during 3 hr. affords isohomogenol (II) and no isochavibetol (III).

II. (III) with EtNaSO₄ and 10% NaOH at 160° affords diisochavibetol, m.p. 179—181°, which gives (I) with Me_2SO_4 . With conc. KOH, (III) affords a stereoisomeride(?) of (I), m.p. 40—41°, converted into (I) by crystallisation from 70% EtOH, is oxidised (KMnO_4) to isovanillic acid Et ether, and affords (II) with KOH-MeOH. J. L. D.

β -Hydroxyphenylethylamines and their transformations. I. Synthesis of mezcaline. G. HAIN and H. WASSMUTH (Ber., 1934, 67, [B], 696—708).—3:4:5-(OMe)₃C₆H₂-CO₂H, prepared in 92% yield from gallic acid, Me_2SO_4 , and NaOH, is converted by conc. H_2SO_4 at 40° into 4-hydroxy-3:5-dimethoxybenzoic acid (I) (yield 83%), slowly decarboxylated at 250—295° to pyrogallol 1:3-Me, ether (II) [yield 70.7%]. Pyrogallol 1:3-Me, 2-allyl ether, b.p. 138—140°/12 mm., obtained in 91% yield from (II), $\text{C}_3\text{H}_5\text{Br}$, and K_2CO_3 in boiling COMe₂, is isomerised at 240°/75 mm. to 2:6-dimethoxy-4-allylphenol (III) in 91% yield. (I), MeOH, and HCl afford Me 4-hydroxy-3:5-dimethoxybenzoate, m.p. 107° (yield 85%), whence Me 3:5-dimethoxy-4-allyloxybenzoate, m.p. 75° (yield 93%), converted by boiling 2*N*-NaOH into (III) in 95% yield. The Na salt of (III), CaCO₃, and Me_2SO_4 in PhMe at 140° give 3:4:5-trimethoxyallylbenzene (clemicin) (IV), b.p. 152—156°/17 mm., in >79% yield. Treatment of (IV) with 1% O₃ and of the ozonide with H_2 -Pd-CaCO₃ gives 3:4:5-trimethoxyphenylacetaldehyde (V) in 75% yield (as NaHSO₃ compound), (V) gives an oxime (VI), m.p. 67°, and semicarbazone, m.p. 191°. (VI) and boiling Ac₂O afford 3:4:5-trimethoxyphenylacetonitrile, m.p. 81°, smoothly reduced to β -3:4:5-trimethoxyphenylethylamine (yield 90—95%) when gradually added in AcOH to PtO₂ suspended in AcOH containing conc. H_2SO_4 . H. W.

Diethoxydulcin, diethoxyphenacetin, and other derivatives of pyrogallol. K. FEIST, F. KLATT, and W. AWE (Arch. Pharm., 1934, 272, 221—235).—The *hydrazide*, decomp. 180°, of 2:3:4-trihydroxybenzoic acid with $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ (I) and *d*-glucose (II) gives, respectively, the 2:3:4-trihydroxybenzoylhydrazone of (I), decomp. 255°, and of (II), m.p. 161°; the 3:4:5-trihydroxybenzoylhydrazone, m.p. 246°, of (I) is similarly obtained from the hydrazide of gallic acid. The *hydrazide* (III), m.p. 116° (*hydrochloride*, m.p. 195°; *isopropylidene*, m.p. 142°, and *o*-hydroxybenzylidene, m.p. 121°, derivatives), of 3:4:5-triethoxybenzoic acid (IV) (*Me* ester, m.p. 53°) with HNO_3 gives the *azide*, m.p. 98°, converted by boiling EtOH into the *urethane*, m.p. 130°, and by boiling H_2O into *s*-di-(3:4:5-triethoxyphenyl)carbamide, m.p. 225°. With dil. $\text{EtOH}\text{--NaOH}$ (III) gives $\text{C}_6\text{H}_3(\text{OEt})_3$ and 3:4:5-triethoxybenzylidene-3':4':5'-triethoxybenzoylhydrazine, m.p. 197°, hydrolysed to 3:4:5-triethoxybenzaldehyde characterised as its *m*-nitrobenzoylhydrazone, m.p. 167°. The *acid chloride*, m.p. 68°, of (IV) with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ gives only a trace of (III), the main product being *s*-di-(3:4:5-triethoxybenzoyl)hydrazine, m.p. 193° [also by HgO oxidation of (III)], converted by heating at 250—300° into 2:5-di-(3:4:5-triethoxyphenyl)furodiazole,

$\text{O} \begin{array}{c} \text{C}[\text{C}_6\text{H}_2(\text{OEt})_3]\text{N} \\ \text{C}[\text{C}_6\text{H}_2(\text{OEt})_3]\text{N} \end{array}$, m.p. 150°. With $\text{Pb}(\text{SCN})_2$ at 200° (IV) is converted into its *nitrile*, m.p. 102°. The *amide*, m.p. 145°, of (IV) with $\text{NaOCl}\text{--NaOH}$ gives 5-amino-1:2:3-triethoxybenzene (*Ac* derivative, diethoxyphenacetin, m.p. 98°), the *hydrochloride* of which with KCNO gives 3:4:5-triethoxyphenylcarbamide (diethoxydulcin), m.p. 140°, having a bitter taste. *Me* 6-amino-2:3:4-trimethoxybenzoate (Will, A., 1888, 1089) by the Sandmeyer reaction gives the 6-chloro-compound, m.p. 67°, and [using $\text{Cu}_2(\text{CN})_2$] the *nitrile*, hydrolysed to 3:4:5-triethoxy-*o*-phthalic acid. J. W. B.

Condensation of cholesterol with aromatic amines. H. LIEB, K. WINKELMANN, and F. KOPPL (Annalen, 1934, 509, 214—228).—Cholesteryl chloride (or bromide) and boiling NH_2Ph give *cholesteryl-aniline* (I), $\text{C}_{27}\text{H}_{45}\cdot\text{NHPh}$, m.p. 189° (*Ac*, m.p. 187°, and *NO*-, m.p. 147°, derivatives). The following are similarly obtained from the appropriate NH_2Ar at 180—200°: *cholesteryl-o*-, m.p. 147°, *-m*-, m.p. 147°, and *-p*-, m.p. 171°, *-toluidine*; *-m*-4-*xylylidine*, m.p. 153°; *-α*-, m.p. 203°, and *-β*-, m.p. 201°, *-naphthylamine*; *-methylaniline*, m.p. 141·5°; *-p*-aminodimethylaniline, m.p. 154°; *-o*-, m.p. 116° (*Ac* derivative, m.p. 85°), and *-p*-, m.p. 157° (*Ac* derivative, m.p. 143°), *-anisidine*, and *-o*-, m.p. 91° (*Ac* derivative, m.p. 88°), and *-p*-, m.p. 140° (*Ac* derivative, m.p. 129°), *-phenetidine*. (I) and Br in cold AcOH afford *dibromocholestanyl-2:4-dibromoaniline*, $\text{C}_{27}\text{H}_{45}\text{Br}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Br}_2$, decomp. 147°; *dibromocholestanyl-2:4:6-tribromomethylaniline*, decomp. about 150°; *-4:6-dibromo-2-methylaniline*, decomp. 154°; *-2:6-dibromo-4-methylaniline*, decomp. 160°; and *-6-bromo-2:4-dimethylaniline*, decomp. 145—147°, are similarly prepared. (I) and HNO_3 (d 1·4) in warm AcOH give a (NO_2)₂-derivative, probably $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{NO}_2)\cdot\text{C}_{27}\text{H}_{45}$, m.p. 230°, reduced

($\text{NHPh}\cdot\text{NH}_2$ in xylene at 160—170°) to a *nitroamino*-derivative, probably $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{NH}_2)\cdot\text{C}_{27}\text{H}_{45}$, m.p. 209°, since it does not diazotise (an attempt to introduce As by the Bart reaction gave a compound, m.p. 235—237°). $p\text{-NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, NHAcPh , $\text{C}_6\text{H}_4(\text{NH}_2)_2$, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, and 1-aminoanthraquinone do not undergo the above condensation. H. B.

Comparison of the reactions of cholesterol with sulphuric, selenic, and telluric acids. E. MONTIGNIE (Bull. Soc. chim., 1933, [iv], 53, 1394).—If H_2SeO_4 (I) [not H_2TeO_4 (II)] is used instead of H_2SO_4 (III) in Libermann's test, cholesterol (IV) gives the same colours (max. after 30 min.), but the reaction is very slow with metacholesterol and stigmasterol. Substituting (I) [not (II)] for (III) in Sal-kowsky's reaction gives pink colours. With cold (I) [not (II)] (IV) gives a grey colour changing to greenish-black. (IV) reduces 45% (I) at 100° only very slowly and boiling 50% (II) not at all. (IV) (1 mol.) with *cryst.* (II) (1 mol.) at 170—180° gives Te and 10% of β -cholesterylene or cholesteryl oxide. R. S. C.

Isomerism of cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1933, [iv], 53, 1408—1409).—Cholesterol with AgOBz and I in dry Et_2O or PhMe at 100° gives some metacholesterol. R. S. C.

Action of oxides on cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1933, [iv], 53, 1411—1412).—Cholesterol does not react with BaO , ThO_2 , MoO_3 , Al_2O_3 , or ZrO_2 , gives uncrystallisable products with I_2O_5 , Sb_2O_3 , and SeO_2 , yields cholestenone with CuO at 300° or V_2O_5 at 200° (7% yield), and forms metacholesterol with CuO at 200—220°, Ni_2O_3 , MnO_2 , ZnO , Bi_2O_3 , U_3O_8 , HgO , ClO_2 , or Ag_2O . R. S. C.

Action of iodine on cholesterol. E. MONTIGNIE (Bull. Soc. chim., 1933, [iv], 53, 1412—1414).—Cholesterol (I) and I in hot C_6H_6 or CHCl_3 , not in Et_2O , $\text{C}_5\text{H}_5\text{N}$, or CS_2 , give a product behaving as a mixture of isomerides of (I), probably containing metacholesterol. R. S. C.

Dehydration of alcohols. (MILLE.) D. SONTAG (Ann. Chim., 1934, [xi], 1, 359—438).— $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$ (I) with P_2O_5 at 0° gives styrene (II), with hot acid and neutral dehydrating agents the ether (III) with or without (II), and with alkalis only (II) (quantitatively with KOH). $\text{CHPhMe}\cdot\text{OH}$ (IV) is unaffected by KOH , but gives (II) with acid reagents. Anhyd. $\text{H}_2\text{C}_2\text{O}_4$ (V) and boiling (I) give a 33% yield of $(\text{CH}_2\text{Ph}\cdot\text{CH}_2)_2\text{C}_2\text{O}_4$, m.p. 51—51·5°, obtained in 43% yield by adding (I) slowly to molten (V); by the latter method small amounts of (I) can be identified. (I), $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{OH}$, $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{OH}$, and $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{OH}$ (VI) are dehydrated by molten KOH in > 90, 43, 18—22, and 0% yield, respectively. (VI) gives PhCHO and COMe_2 . $\text{CHPh}\cdot\text{CH}\cdot\text{OAc}$ gives PhMe , whilst CH_2CPh is unaffected. (I) and NH_2Na in hot xylene give slowly only the *Me* ether. β -Phenyl-*n*-propyl *Me* ether has b.p. 84·5—85·5°/17 mm. Phenylethylene glycol and KOH at 235° give (IV) and BzOH ; ($\text{CHPh}\cdot\text{OH}$)₂ gives $\text{CH}_2\text{Ph}\cdot\text{OH}$ and (CH_2Ph)₂. $\alpha\text{-C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ and molten KOH at 30—40 mm. give $1\text{-C}_{10}\text{H}_7\cdot\text{CH}\cdot\text{CH}_2$, b.p. 115—116°/3—4 mm.

[picrate, m.p. 101—102° (decomp.) (block); styphnate, m.p. 96—97° (decomp.) (block); polymeride, m.p. about 85°]. $2\text{-C}_{10}\text{H}_7\text{Br}$ (modified prep. from $\beta\text{-C}_{10}\text{H}_7\text{OH}$ and PBr_3 at 170°), m.p. 59°, b.p. 146—147°, gives with difficulty a Grignard reagent, which with $(\text{CH}_3)_2\text{O}$ affords $\beta\text{-naphthylethyl alcohol}$, b.p. 178—188°/15 mm., m.p. 67.5—68°, dehydrated by KOH to $2\text{-vinyl-naphthalene}$, b.p. 135—137°/17—18 mm., m.p. 66° (dibromide, m.p. 84.5—85°). $2\text{-C}_{10}\text{H}_7\text{CH}_2\text{Br}$ (modified prep.), m.p. 56°, b.p. 168—172°/17 mm., readily gives a Grignard reagent, which with CH_2O forms probably $1\text{-methyl-2-hydroxymethylnaphthalene}$, b.p. 170—195°/17 mm., dehydrated by KOH to a mixture. Reduction of Et $\beta\text{-naphthylacetate}$ by Na and BuOH gives partly reduced $\beta\text{-(}\beta\text{-naphthyl)ethyl alcohol}$, b.p. 175—177°/13—14 mm., dehydrated by KOH to a substance, b.p. 130°/17—18 mm. Reduction of $\beta\text{-C}_{10}\text{H}_7\text{COMe}$ by Na—Hg and dry EtOH gives an alcohol which is partly dehydrated by distillation with NaHSO_4 in vac. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ with Br and Fe gives much *p*- and a little *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, b.p. 137—143°/15 mm., converted by KOAc in AcOH into mixed $\beta\text{-bromophenylethyl acetates}$, b.p. 148—149°/15 mm., which with KOH—EtOH give a mixture of the corresponding alcohols, b.p. 144.5—145°/15 mm. (oxidised to *p*- and *o*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$). Mixtures of the same alcohols and bromides are slowly obtained from cold (I), Br, and Fe. The alcohols, alone or mixed with the bromides, with molten KOH give a mixture of much *p*- (dibromide, m.p. 59.5°) and some *o*-bromostyrene, b.p. 88—90°/15 mm. (I) with Cl_2 and I gives a mixture of *p*- and *o*- $\beta\text{-chlorophenylethyl alcohols}$, b.p. 131—132°/11 mm., dehydrated by KOH to chlorostyrene, b.p. 71.5—72.5°/15 mm. (dibromide, m.p. 53—54°). $\gamma\text{-Phenylpropyl alcohol}$ or bromide with Br and Fe gives $\gamma\text{-bromophenylpropyl bromide}$, b.p. 161—163°/17 mm., acetate, b.p. 168—170°/17 mm., and alcohol, b.p. 157—158°/14 mm.; the last mentioned substance with KOH gives a saturated, liquid mixture containing Br. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{SH}$ (obtained from $\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Br}$ and KHS), b.p. 96—98°/15 mm., with KOH at 200—230° gives 53% of (II). CHPhMeBr similarly gives $\text{CHPhMe}\cdot\text{SH}$, b.p. 83—84°/14 mm., which with KOH gives a little (II) and much BzOH. $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SH}$ b.p. 121—122°/23 mm., similarly prepared, and KOH give much propenyl- and a little allyl-benzene, and some disulphide, b.p. 235°/21 mm. R. S. C.

Raman effect, molecular refraction, and constitution. Supposed 1-benzylcyclohexene. C. PREVOST, P. DONZELOT, and E. BALLA (Compt. rend., 1934, 198, 1041—1043).—Dehydration of phenylethylcarbinol by KHSO_4 gives only propenylbenzene, but phenylisopropylcarbinol gives 95% of $\beta\beta\text{-dimethylstyrene}$, m.p. —51°, and 5% of $\beta\text{-methylallylbenzene}$. $\text{cycloHexylphenylcarbinol}$ gives $\text{benzylidenecyclohexene}$, b.p. 116°/9 mm., m.p. —36°, oxidised to BzOH (cf. A., 1915, i, 789), the exaltations of $[R_L]$ and Raman spectra of this and similar compounds supporting this structure. R. S. C.

Stycerols. C. PREVOST and LOSSON (Compt. rend., 1934, 198, 659—661; cf. A., 1933, 711).—Cinnamyl benzoate and AgI(Obz)_2 (I) affords $\alpha\text{-styceryl tribenzoate}$ (II), m.p. 152°, and a product, m.p. about 108°, now shown to be a mixture of (II) and its β -

isomeride (III), m.p. 116.5°, hydrolysed to $\beta\text{-stycerol}$, an oil. (II) and (III) form an eutectic, m.p. 109.5° [78% (III)]. (II) has the OH groups in *cis*-positions. (I) and $^*\text{CHPh(Obz)}\cdot\text{CH}\cdot\text{CH}_2$ afford 90% of (II), which indicates that the new asymmetric C atom is sterically identical with $^*\text{C}$. J. L. D.

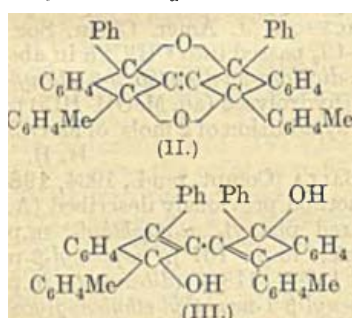
Addition of methyl hypochlorite to phenylacetylene. E. L. JACKSON (J. Amer. Chem. Soc., 1934, 56, 977—978).— Cl_2 passed into CH-CPh in abs. MeOH gives 71% of $\alpha\text{-dichloro-}\beta\text{-dimethoxy-}\beta\text{-phenylethane}$, m.p. 66—66.5° [hydrolysed (aq. MeOH—HCl) to $\text{CHCl}\cdot\text{COPh}$], formed by addition of 2 mols. of MeOCl. H. B.

Arylglycols. E. BALLA (Compt. rend., 1934, 198, 947—948).—By the method previously described (A., 1933, 711) are prepared phenyl-, $\alpha\text{-naphthyl-}$, m.p. 114.5—115° (dibenzoate, m.p. 107°), $\alpha\text{-phenyl-}\beta\text{-p-isopropylphenyl-}$, m.p. 117.5—118.5° (dibenzoate, m.p. 217.5—218°), and $\alpha\text{-phenyl-}\beta\text{-1-naphthyl-ethylene glycol}$, m.p. 95° [dibenzoate, m.p. 196.5—197° (uncorr.) and 201° (corr.)]. $\alpha\text{-Phenyl-}\beta\text{-p-isopropylphenyl-}$ (from MgPhBr and cuminaldehyde), m.p. 42—42.5°, and $\alpha\text{-1-naphthyl-}\beta\text{-phenyl-ethyl alcohol}$ (from $\text{C}_{10}\text{H}_7\text{MgBr}$ and $\text{CH}_2\text{Ph}\cdot\text{CHO}$), m.p. 78.5—79.2°, and $\omega\text{-1-naphthylstyrene}$, m.p. 72.5—73.5°, are described. R. S. C.

Synthesis of glycols, $\text{C}_6\text{H}_4(\text{CHR}\cdot\text{OH})_2$, and their derivatives. Synthesis of divinyl-, dipropenyl-, and diacetylenyl-benzenes. R. DELUCHAT (Ann. Chim., 1934, [xi], 1, 181—255).—Largely a more detailed account of work previously reviewed (A., 1930, 471, 588; 1931, 946). The following appears to be new. MgPhBr and *o*- and *m*- $\text{C}_6\text{H}_4(\text{CHO})_2$ give *o*- (I), m.p. 90° (purified through the diacetate, m.p. 106.5°), and *m*-di- $\alpha\text{-hydroxybenzyl-}$, m.p. 157°, -benzene, respectively. *o*-Di- $\alpha\text{-hydroxyethylbenzene}$ is dehydrated (dil. H_2SO_4) to dimethylphthalan , b.p. 75°/10 mm., which decomposes when kept; *o*-di- $\alpha\text{-hydroxypropylbenzene}$, m.p. 79° (lit. 70°), similarly gives diethylphthalan , b.p. 100°/11 mm., whilst (I) affords diphenylphthalan , m.p. 93° (Maquenne block) [also obtained from (I) and PBr_3 in CHCl_3 at 0°]. $\text{C}_6\text{H}_4(\text{CHEt}\cdot\text{OH})_2$ and PBr_3 (slight excess) in CHCl_3 at 0° give *o*-, m.p. 46°, *m*-, decomp. on attempted distillation, and *p*-, m.p. 70°, -di- $\alpha\text{-bromopropylbenzenes}$, which when distilled with quinoline afford *o*- (II), b.p. 108.5—109°/9 mm., m.p. —26° (tetrabromide, m.p. 85°), and *m*- (III), b.p. 117—120°/14 mm. (tetrabromide, m.p. 98—99°), -dipropenylbenzenes and *p*-dipropenylbenzene (IV), m.p. 63° [tetrabromide, m.p. 187° (lit. 168—169°)], respectively. These hydrocarbons absorb O_2 from the air at room temp. (II) is thus oxidised to (probably) *o*-propenylbenzaldehyde, b.p. 90—92°/2.5 mm. (semicarbazone, m.p. 205°), and resinous material; (III) and (IV) give aldehydes, b.p. 95°/3 mm. (semicarbazone, m.p. 226°), and b.p. 97°/3 mm. (semicarbazone, decomp. 280°), respectively. Distillation of *o*-di- $\alpha\text{-bromoethylbenzene}$ at 5 mm. gives *o*-divinylbenzene and *o*- $\alpha\text{-bromoethylvinylbenzene}$, b.p. 87.5°/3 mm., 115°/10 mm. The dibromide of *m*- $\alpha\text{-bromoethylvinylbenzene}$ has m.p. 39°. H. B.

Dissociable organic oxides. Two reducible, but not dissociable, stages of oxidation of bis-1 : 1'-*p*-tolyl-3 : 3'-diphenylrubene : bisepoxy-tetrahydro- and dihydroxydihydro-derivatives.

L. ENDERLIN (Compt. rend., 1934, **198**, 945—947).—The dissociable oxide, $C_{44}H_{32}O_2$, of bis-3 : 3'-diphenyl-1 : 1'-*p*-tolylrubene (I) with MgI_2 in Et_2O at 0° gives a mixture of much bis-3 : 3'-diphenyl-1 : 1'-di-*p*-tolyl-3 : 3'-bisepoxy-1 : 3 : 1' : 3'-tetrahydro-rubene (II), m.p. 210° (block), and some 1 : 3'-dihydroxybis-3 : 3'-di-phenyl-1 : 1'-di-*p*-tolyl-1 : 3'-dihydro-rubene (III), m.p.



(+solvent, from Et_2O , C_6H_6 , or CS_2) about 200° (decomp.) (block) and (anhyd., from ligroin) 280° (block). (II) is stable to hot $AcOH$, is not dissociable by heat, but with Fe and hot $AcOH$ affords (I). (III) loses $2H_2O$ in boiling $AcOH$ to give the

fluorescent naphthenic hydrocarbon, $C_{44}H_{30}$, loses H_2O at $275^\circ/vac.$ to give the monoxide, $C_{44}H_{32}O$, is not dissociable, and with Fe and hot $AcOH$ gives (I). Only one form of (III) is known. Analogy with tetraphenylrubene is thus complete. R. S. C.

Synthesis of adrenaline. B. CIOCCA (Boll. Chim. Farm., 1934, **73**, 241—245).—The reduction of adrenalone can be carried out very simply in 95% $EtOH$ suspension by 1.25% Na amalgam in a slow stream of H_2 . R. N. C.

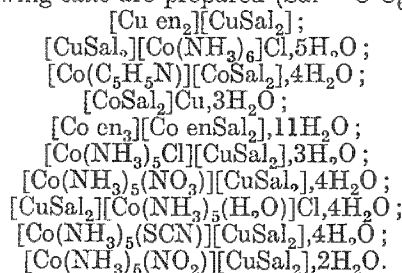
Electrolysis of benzoic and of 2 : 6-dimethyl-4-tert.-butyl benzoic acid and their salts in absolute methyl alcohol. F. FIGHTER and R. E. MEYER (Helv. Chim. Acta, 1934, **17**, 535—543).—Electrolysis of a mixture of 2 : 6-dimethyl-4-tert.-butylbenzoic acid (I) [anhydride, m.p. 140 — 141° (cryst. data by SPAENHAUER); chloride, m.p. 62° ; Me ester, b.p. $135^\circ/9$ mm., m.p. 39°] and its Na salt in $MeOH$ gives CO_2 (<20% of that required for a Kolbe synthesis), CO and O_2 , and, after hydrolysis, 5-tert.-butyl-*m*-xylene (40% ; 12%), a reduction product, $C_{26}H_{40}O_6$, b.p. 125 — $140^\circ/15$ mm. (only formed in the absence of a diaphragm), 6-methyl-4-tert.-butylphthalic acid (11% ; 21.2%) (imide, m.p. 180.5 — 181°), and amorphous products (17% ; 46.6%), the vals. in parentheses representing the proportions obtained using 0.5 and 0.3 amp. per sq. cm., respectively. $BzOH$ similarly affords a little C_6H_6 and a large amount of amorphous substances. Mechanism is briefly discussed. J. W. B.

2 : 4 : 6-Trinitrobenzoic acid. S. SECAREANU (Bull. Soc. chim., 1933, [iv], **53**, 1395—1399).— $C_6H_2(NO_2)_3CO_2H$ (I) with hot conc., aq. NH_3 gives CO_2 , $C_6H_3(NO_2)_3$, and an NH_4 salt of (I). This reaction, and the similar reactivity of 2 : 4 : 6-trinitrobenzaldehyde (A., 1932, 851), are explained on the theory of alternate polarities. R. S. C.

General reaction for preparation of keto-acids, unsaturated acids, and disubstituted lactones. G. KOMPPA and W. ROHRMANN (Annalen, 1934, **509**, 259—268).—Hexahydroisophthalic anhydride (1 mol.) and $MgMeI$ (I) (2 mols.) in $Et_2O-C_6H_6$ give α -dimethylhexahydroisophthalide, b.p. 143 — $146^\circ/18$ mm., 3-isopropylidenecyclohexane-1-carboxylic acid, b.p.

157 — $161^\circ/15$ mm. (Ag salt; Et ester, b.p. 109 — $111^\circ/8$ mm.), and 3-acetylcyclohexane-1-carboxylic acid (II) b.p. 179 — $180^\circ/7$ mm., 196 — $198^\circ/15$ mm. [Ag salt; semicarbazone, m.p. 190° (decomp.); oxime, m.p. 133° ; Et ester, b.p. 134 — $136^\circ/7$ mm. (semicarbazone, m.p. 170°)]. (II), obtained in >50% yield when 1 mol. of (I) is used, is oxidised (alkaline $NaOH$) to hexahydroisophthalic acid. Glutaric anhydride (1 mol.) and (I) (1 mol.) afford γ -acetylbutyric acid; with 2 mols. of (I), δ -methyl- δ -hexolactone, b.p. 113 — $115^\circ/13$ mm., 220 — $222^\circ/760$ mm., and δ -methyl- Δ^7 -hexenoic acid are formed. Dimethylglutaric anhydride and $MgEtBr$ (>1 mol.) give δ -keto- $\beta\beta$ -dimethylheptonic acid, b.p. $142^\circ/8$ mm. [Ag salt; semicarbazone, m.p. 140° (decomp.)], and $\beta\beta$ -dimethyl- δ -ethyl- δ -heptolactone, b.p. 117.5 — $119^\circ/17$ mm. When Ba δ -hydroxy- $\beta\beta$ -dimethyl- δ -ethylheptate (+ $2H_2O$) (corresponding Ag salt) is dried at 115° in a vac., Ba $\beta\beta$ -dimethyl- δ -ethyl- Δ^7 -heptenoate is formed. $MgPhBr$ (>1 mol.) and $(CH_2CO)_2O$ give β -benzoylpropionic acid and $(CH_2CO)_2O$; unsaturated acid and lactone are not produced. H. B.

Complex metal salicylates. G. SPAGU and M. KURAŠ (J. pr. chem., 1934, [ii], **139**, 322—328).—The following salts are prepared ($Sal = O \cdot C_6H_4 \cdot CO_2$):



R. S. C.

Organic vanadyl compounds. P. BRAUMAN (Compt. rend., 1934, **198**, 1237—1239).— o - $OEt \cdot VO \cdot C_6H_4 \cdot CO_2Me$ (I) and an excess of freshly distilled Me salicylate (II), when boiled at 200 — 210° for 10 min. in N_2 , give Me₂ vanadylsalicylate, $VO(O \cdot C_6H_4 \cdot CO_2Me)_2$ (III). (III) is slowly hydrolysed by H_2O , decomposed by $COMe_2$, and with $EtOH$ gives (I). (I), when boiled with $PhOH$ at 190° in N_2 for 5 min., gives Me phenoxyvanadylsalicylate, $OPh \cdot VO \cdot C_6H_4 \cdot CO_2Me$, with NH_4 salicylate in $EtOH$ at 98° gives $(NH_4)_2$ vanadylsalicylate, + $2H_2O$, $EtOH$ (which in air slowly gives the trihydrate), with warm (II) or Bu^iOH and o - $OH \cdot C_6H_4 \cdot CO_2H$ gives vanadyl salicylate, $(o-OH \cdot C_6H_4 \cdot CO_2)_2VO$ [gives with dil. aq. NH_3 $VO(O \cdot C_6H_4 \cdot CO_2NH_4)_2$], and with $BzOH$ affords similarly vanadyl benzoate. R. S. C.

Synthetic studies on the relationship between chemical constitution and bactericidal activity. XII. 3-Nitro- and 3-amino-4-hydroxy- and -alkyloxy-benzoic esters. T. SABALITSCHKA and K. H. TIEDGE (Arch. Pharm., 1934, **272**, 383—394). By direct esterification of the NO_2 -acid, or nitration of the *p*-alkoxy-ester are obtained Pr^a , Bu^a , b.p. 174 — $176^\circ/8$ mm., isoamyl, b.p. 177 — $179^\circ/2$ mm., m.p. 59° , and CH_3Ph , m.p. 82° , 3-nitro-4-hydroxybenzoate; Me, Et, Pr^a , b.p. 213 — $215^\circ/16$ mm., m.p. 63° , allyl, b.p. $207^\circ/11$ mm., m.p. 50° , and *n*-hexyl, b.p. 224 — $226^\circ/11$ mm., 3-nitro-*p*-anisate: Me 3-nitro-4-prop-

oxybenzoate, b.p. 144—146°/11 mm., and *Me* 3-nitro-4-benzoyloxybenzoate, m.p. 107—108°. By reduction of the NO₂-ester or coupling with diazotised *p*-NH₂·C₆H₄·SO₃H and fission of the azo-compound are obtained *Pr*^a, m.p. 105°, *Bu*^a, b.p. 230°/16 mm., m.p. 83°, isoamyl, b.p. 224—226°/3 mm., m.p. 94°, and *CH*₃·Ph, m.p. 94°, 3-amino-4-hydroxybenzoate; *Me* 3-amino-*p*-anisate, b.p. 183°/15 mm., m.p. 84°; *Me* 3-amino-*p*-ethoxy-, b.p. 202—204°/21 mm., m.p. 104°, and *Me* 3-benzylideneamino-*p*-hydroxy-, m.p. 92°, benzoate. In all cases the anti-bacterial action (against sugar fermentation by yeast) of the NO₂-derivatives is >, and that of the NH₂-compounds <, that of the parent *p*-hydroxybenzoic acid or ester.

J. W. B.

Anhydrous acetylbenzilic acid. V. K. LA MER and J. GREENSPAN (J. Amer. Chem. Soc., 1934, 56, 956).—The acetylbenzilic acid of Herzig and Schleiffer (A., 1921, i, 244; cf. Klinger and Standke, A., 1889, 885) contains approx. 1 mol. of H₂O; the anhyd. acid has m.p. 104.5—104.8° (corr.).

H. B.

Interaction of *o*-benzoylbenzoyl chloride with phenols. I. Aryl esters and α -aryloxy- α -phenylphthalides. II. Diarylphthalides. F. F. BLICKE and R. D. SWISHER (J. Amer. Chem. Soc., 1934, 56, 902—904, 923—925).—I. *o*-C₆H₄Bz·COCl (I) (from the acid or by chlorination of phenylphthalide) reacts with (a) KOAr usually in C₆H₆, (b) ArOH in C₆H₅N, and (occasionally) (cf. below) (c) ArOH in C₆H₆, to give varying amounts of hydroxydiarylphthalide and (probably) *o*-C₆H₄Bz·CO₂Ar and α -aryl-oxy- α -arylphthalide. Thus, (I) and PhOH afford [methods (a) and (b)] two isomeric compounds, C₂₀H₁₄O₃, m.p. 80—82° and 162—163°, which are hydrolysed (EtOH-NaOH) to *o*-C₆H₄Bz·CO₂H and PhOH, and are converted by conc. H₂SO₄ or AlCl₃ (in C₆H₅Cl₄) into 4'-hydroxy- α -diphenylphthalide. *p*-C₆H₄Br·OH yields (b) a compound, C₂₀H₁₃O₃Br, m.p. 92—94°, and (c) an isomeride, m.p. 170—172°. PhSH furnishes (a) a compound, C₂₀H₁₄O₂S, m.p. 112—113°, and (c) an isomeride, m.p. 117—118°. *o*-Hydroxydiphenyl gives (a) a compound, C₂₆H₁₈O₃, m.p. 103—105°, and (c) an isomeride, m.p. 195—197° [both obtained in (b)]. *p*-Hydroxydiphenyl affords (a) (b) two compounds, C₂₆H₁₈O₃, m.p. 163—165° and 117—119° [also formed in (c)]. β -C₁₀H₇·OH yields (a) a compound, C₂₄H₁₆O₃, m.p. 103—105°, also obtained (b) with an isomeride, m.p. 198—199°, whilst α -C₁₀H₇·OH furnishes (a) (b) a compound, C₂₄H₁₆O₃, m.p. 102—104°. All these compounds are hydrolysed to *o*-C₆H₄Bz·CO₂H and ArOH.

II. α -Diarylphthalides are obtained from (I) (and its 4'-OH and 4'-OMe derivatives) and ArOH or ArOMe in C₆H₆ at room temp.; the following are thus prepared: 4'-hydroxydiphenyl-, m.p. 168—170°, 4'-methoxydiphenyl- (II), m.p. 110—115° (lit. 86°), α -phenyl- α -*o*-methoxydiphenyl-, m.p. 152—154° (from *o*-C₆H₄Ph·OMe), α -phenyl- α -*p*-methoxydiphenyl-, m.p. 179—180° (from *p*-C₆H₄Ph·OH), α -phenyl- α -1-hydroxy-naphthyl-, m.p. 231—233° (from α -C₁₀H₇·OH) (*Me* *einer*, m.p. 206—207°, also prepared from α -C₁₀H₇·OMe), α -phenyl- α -2-hydroxynaphthyl-, m.p. 234—236° (from β -C₁₀H₇·OH) (*Me* *ether*, m.p. 210—212°, also obtained from β -C₁₀H₇·OMe), 4':4''-di-

hydroxydiphenyl-, m.p. 253—256°, 4'-hydroxy-4''-methoxydiphenyl-, m.p. 139—142°, and 4':4''-dimethoxydiphenyl-, m.p. 97—99° (lit. 101—102°), -phthalides. The following are obtained only in presence of AlCl₃ (1 equiv.) and C₂H₅Cl₄: 4'[5']-bromo-2'-hydroxydiphenyl- (III), m.p. 210—211° (from *p*-C₆H₄Br·OH), 3':5'-dibromo-4'-hydroxydiphenyl-, m.p. 199—200° (lit. 196—199°), α -phenyl- α -*o*-hydroxydiphenyl-, m.p. 178—180° (from *o*-C₆H₄Ph·OH), and α -phenyl- α -*p*-hydroxydiphenyl-, m.p. 220—222° (from *p*-C₆H₄Ph·OH), -phthalides. (II) is reduced (Zn dust, aq. EtOH-NaOH) to 4'-methoxytriphenylmethane-2-carboxylic acid, m.p. 146—147°, demethylated (40% HBr, AcOH) to the 4'-OH-acid. (III) is similarly reduced to 2'-hydroxytriphenylmethane-2-carboxylic acid, m.p. 194—196° (*Me* *ether*, m.p. 191—193°). *o*-Cyanodiphenylmethane [from *o*-benzylbenzoic acid and Pb(CNS)₂ at 200°] and *p*-OMe·C₆H₄·MgI give 2-*p*-methoxybenzoyldiphenylmethane, m.p. 68—70°, oxidised (dil. HNO₃) to 2-*p*-methoxybenzoylbenzophenone, m.p. 133—135° (diphenylhydrazone, m.p. 157—160°), which with N₂H₄ in AcOH affords 3-phenyl-6-anisyl-4:5-benzopyridazine, m.p. 157—159°. The colours of most of the above compounds with conc. H₂SO₄ are given.

H. B.

Halogeno- and nitro-derivatives of α -naphthoyl-*o*-benzoic acid.—See B., 1934, 394.

Ring fission of cyclohexane derivatives. G. WITTIG and G. WALTNITZKI (Ber., 1934, 67, [B], 667—675).—The action of LiPh on Et₂ *cis*- and *trans*-hexahydrophthalate, respectively, affords *cis*- (I), m.p. 204—206°, and *trans*- (II), m.p. 185—186.5°, -1:2-di(hydroxydiphenylmethyl)cyclohexane. Attempts to convert (I) and (II) by CHCl₃-MeOH into the Me₂ ethers resulted in the production of the *cis*-, m.p. 199°, and *trans*-, m.p. 221—221.5°, -anhydrides,

$\text{CH}_2\text{CH}_2\text{CH}(\text{CPh}_2)\text{CH}_2\text{CH}_2\text{CH}(\text{CPh}_2) > \text{O}$. Even in the case of (II) intramol. loss of H₂O occurs very readily, and in boiling AcOH is more rapid than with (I). The possibility that a change of configuration occurs during the formation of (I) or (II) is excluded, since Me₂ *trans*-hexahydrophthalate, [α]_D +28.7° in COMe₂, gives (—)-*trans*-1:2-di(hydroxydiphenylmethyl)cyclohexane, m.p. 184—186°, [α]_D -188° in C₆H₆, whence the *anhydride*, m.p. 259—260°, [α]_D +279° in C₆H₆. Treatment of (I) or (II) with KMe₂Ph (but not with K, which displaces only 1 H) gives the K₂ derivatives, which with MeI yield *cis*- (III), m.p. 170—172°, and *trans*- (IV), m.p. 173—175°, -1:2-di(methoxydiphenylmethyl)cyclohexane [the Me₂ *ether* of (III) has m.p. 165—167°]. Treatment of (III) and (IV) with Na-K in N₂ followed by MeOH leads to *cis*-, m.p. 174—175°, and *trans*- (V), m.p. 210—212°, -1:2-dibenzhydrylcyclohexane. Either K₂ compound under the influence of (—CMe₂Br)₂ passes into $\alpha\alpha$ 00-tetraphenyl- $\Delta^{\alpha\alpha}$ -octadiene (VI), m.p. 91—92°, identical with that obtained by the action of boiling AcOH containing a little HCl on $\alpha\alpha$ 00-tetraphenyl-octane- $\alpha\theta$ -diol, m.p. 113—115°, derived from Et suberate and LiPh. (VI) is hydrogenated (PtO₂-AcOH) to $\alpha\alpha$ 00-tetraphenylolcane (VII), m.p. 120—121.5°, and is converted by Li in dioxan or by K-Na into (VII) and (V).

H. W.

Synthetic investigation in the series of anthelmintics. K. W. ROSENMUND and D. SCHAPIRO (Arch. Pharm., 1934, **272**, 313—323).—From the appropriate phenol ether, $(\text{CH}_2\text{CO})_2\text{O}$, and AlCl_3 in PhNO_2 are obtained γ -keto- γ -p-methoxy-, m.p. 146° , γ -(4-methoxy-3-methyl)-, γ -(4-methoxy-2-methyl)-, m.p. 138° , γ -(2-methoxy-5-methyl)-, m.p. 115 — 117° , and γ -(4-methoxy-2-methyl-5-isopropyl)-, m.p. 92° , γ -phenylbutyric acid, reduced by H_2 -Pd-BaSO₄ in EtOH, respectively, to γ -p-methoxy- (I), m.p. 53 — 55° , γ -4-methoxy-3-methyl- (II), m.p. 75° , γ -4-methoxy-2-methyl- (III), m.p. 55 — 57° , γ -2-methoxy-5-methyl- (IV), m.p. 52 — 55° , and γ -4-methoxy-2-methyl-5-isopropyl- (V), m.p. 75° , γ -phenyl- γ -butyrolactone. By the method of Mayer *et al.* (A., 1924, i, 410) or Rosenmund *et al.* (A., 1928, 1010) are prepared *o*-hydroxy-, 2-hydroxy-5-methyl-, m.p. 67° , and 4-hydroxy-2-methyl-5-isopropyl-, m.p. 101° , γ -phenyl β -chloroethyl ketone, converted through the nitrile and hydrolysis, respectively, into γ -keto- γ -o-hydroxy-, m.p. 97° , γ -2-hydroxy-5-methyl-, m.p. 136 — 137° , and γ -4-hydroxy-2-methyl-5-isopropyl-, m.p. 117 — 120° , γ -phenylbutyric acid, reduced to the corresponding γ -o-hydroxy- (VI), m.p. 107 — 108° , γ -2-hydroxy-5-methyl- (VII), m.p. 110 — 112° , and γ -4-hydroxy-2-methyl-5-isopropyl- (VIII), m.p. 88 — 91° , γ -phenyl- γ -butyrolactone. The disinfectant action, on *Ascaridæ*, of (I), (II), and (VI) is much stronger than that of santonin, that of (VII) and (IV) much weaker, whereas (III), (V), and (VIII) are inactive. J. W. B.

Reactions of γ -ketonic acids. II. Hydroxy-derivatives. E. P. KOHLER and L. LEERS (J. Amer. Chem. Soc., 1934, **56**, 981—982; cf. this vol., 523).—Anisylstyryl ketone and KCN in aq. EtOH-AcOH give β -anisoyl- α -phenylpropionitrile, m.p. 68° ; the free acid, m.p. 141° (*Me* ester, m.p. 97°), is brominated to the β -Br-derivative (I), m.p. 158° , hydrolysed (boiling H_2O) to β -hydroxy- β -anisoyl- α -phenylpropionic acid (II), m.p. 159° . (I) and cold aq. NaOH (2 equivs.) or (II) and cold 1% NaOH give phenylacetylanisylcarbinol (III), m.p. 119° [also obtained from $\text{CH}_3\text{Ph}\cdot\text{MgCl}$ and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CN}$], converted by 2% NaOH at 100° (bath) into anisoylbenzylcarbinol (IV), m.p. 62° (*oximes*, m.p. 118° and 135°). (IV) is also obtained (together with an unidentified acid) from (I) or (II) and hot aq. NaOH. (III) and (IV) with $\text{NHPh}\cdot\text{NH}_2$ give the osazone of anisyl benzyl diketone. p -Methoxyphenylacetylphenylcarbinol, m.p. 126° , is prepared from $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{MgCl}$ and $\text{OH}\cdot\text{CHPh}\cdot\text{CN}$. The above results establish the mechanism of conversion of $\beta\text{-OH}\cdot\gamma\text{-CO}$ -acids into hydroxyketones previously proposed (*loc. cit.*).

H. B.

Synthesis of 5:6-dimethoxy- and methoxyhomophthalic acids. S. N. CHAKRAVARTI and M. SWAMINATHAN (J. Indian Chem. Soc., 1934, **11**, 101—105).—2-Oximino-4:5-dimethoxy- α -hydrindone (I), 40% CH_2O , and conc. HCl give 1:2-diketo-4:5-dimethoxyhydrindene (II), m.p. 150° (decomp.) [quinoxaline, m.p. 192° , from $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$]. (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ in 10% NaOH afford 2-carboxy-5:6-dimethoxyphenylacetonitrile, m.p. 175° , hydrolysed (10% NaOH) to 5:6-dimethoxyhomophthalic acid, m.p. 196° , also obtained (in poorer yield) by oxidation

(dichromate, H_2SO_4) of (II). 2-Oximino-5-methoxy- α -hydrindone, m.p. 221° (decomp.) (from the ketone, isoamyl nitrite, and conc. HCl in MeOH), is similarly converted into 2-carboxy-5-methoxyphenylacetonitrile, m.p. 177° , and thence into 5-methoxyhomophthalic acid, m.p. 222° . 1:2-Diketo-5-methoxyhydrindene (quinoxaline, m.p. 140°) has m.p. 152° . The 2-oximino-derivative, m.p. 234° (decomp.), of 6-methoxy- α -hydrindone (obtained in 20% yield from β -anisylpropionyl chloride and AlCl_3 in PhNO_2) (cf. Perkin and Robinson, J.C.S., 1907, **91**, 1081) similarly affords 2-carboxy-4-methoxyphenylacetonitrile, m.p. 140° , and 4-methoxyhomophthalic acid, m.p. 188° . 1:2-Diketo-6-methoxyhydrindene (quinoxaline, m.p. 156°) has m.p. 126° . H. B.

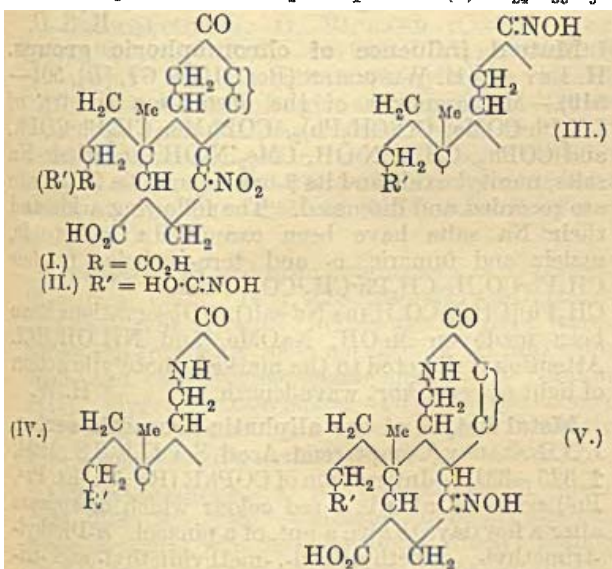
5-Carboxyhomophthalic acid, 6-nitrophthalide, and 6-nitrophthalimidine. W. BORSCHKE, K. DIACONT, and H. HANAU (Ber., 1934, **67**, [B], 675—686).—Homophthalic acid in conc. H_2SO_4 is converted by KNO_3 in H_2SO_4 at 0° into 5-nitro- (I), m.p. 215° , reduced (Sn and HCl) to 5-amino- [hydrochloride (II)], whence Ac_2O and NaOAc) 5-acetamido-, m.p. 208° , homophthalic acid. (II) is transformed by diazotisation and treatment with $\text{KCN}\cdot\text{NH}_3\cdot\text{CuSO}_4$ into 5-cyano-, m.p. 190° , hydrolysed to 5-carboxy-, m.p. 220° (decomp.), homophthalic acid [*Et*₁, m.p. 195 — 196° , and *Me*₃ (III), m.p. 95° , esters]. (I), MeOH, and H_2SO_4 yield *Me*₂ 5-nitro-, m.p. 99° , reduced (colloidal Pd) to *Me*₂ 5-amino- (hydrochloride, m.p. 235°), whence *Me* 5-cyano-, m.p. 80 — 82° , homophthalate, hydrolysed by MeOH- H_2SO_4 to (III). Phthalide is converted by KNO_3 in conc. H_2SO_4 mainly into 6- (IV), m.p. 145° , with a small proportion of 3-, m.p. 136° , nitrophthalide. The position of NO_2 in (IV) follows from its transformation by the successive action of Br in CO_2 at 175° and boiling H_2O into 5-nitro-2-aldehydobenzoic acid, m.p. 162° (phenylhydrazone, m.p. 140° , which passes in boiling MeOH or AcOH into 7-nitro-2-phenylbenzpyridazone $\text{NO}_2\cdot\text{C}_6\text{H}_3\begin{smallmatrix} \text{CH}\cdot\text{N} \\ \text{CO}\cdot\text{N}\cdot\text{Et} \end{smallmatrix}$ m.p. 171° ; 2:4-dinitrophenylhydrazone, m.p. 292°). (IV), PhCHO, and piperidine at 190 — 200° afford 6-nitro-3-benzylidenephthalide (V), m.p. 236 — 237° (corresponding 3-salicylidene, m.p. 210° ; 3-p-anisylidene, m.p. $201\cdot5^\circ$, 3-piperonylidene, m.p. 244° , and 3'-p'-dimethylaminobenzylidene, m.p. 270° , derivatives). Reduction of (V) (colloidal Pd- H_2O) leads to 6-amino-3-benzylidene-, m.p. $206\cdot5^\circ$ (Ac derivative, m.p. 258 — 259°), and thence to 6-amino-3-benzyl-, m.p. 145° (Ac derivative, m.p. 165°), phthalide. Similarly, (IV) yields 6-amino-phthalide (VI), m.p. 177 — 178° (Bz derivative, m.p. 225°), transformed by hot dil. HCl into a substance, m.p. $>300^\circ$. 6-Cyanophthalide, m.p. 188° , is obtained from (VI).

Phthalimide is transformed by spongy Sn, H_2O , and HCl and subsequently with NaNO_2 into 2-nitroso-phthalimidine (VII), m.p. 157 — 159° , readily converted (H_2 -colloidal Pd-MeOH) into phthalimidine. Nitration of (VII) affords 6-nitro-2-nitrosophthalimidine (VIII), m.p. 167° when rapidly heated, accompanied by small amounts of (?) *Me* 5-nitro-2-methoxymethylbenzoate, m.p. 102° . Boiling AcOH transforms (VIII) into 6-nitrophthalimidine (IX), m.p.

253° (decomp.), which could not be obtained from (IV) and NH_3 or $\text{CO}(\text{NH}_2)_2$. 6-Nitro-2-acetylphthalimidine has m.p. 157°. 6-Nitro-3-benzylidene-, m.p. 285° (decomp.), -3-anisylidene-, m.p. 254°, and -3-piperonylidene-, m.p. 299°, -phthalimidine are described. 6-Aminophthalimidine, m.p. 247° (decomp.) (Bz derivative, m.p. 285°), is obtained by reduction (colloidal Pd) of (IX). 2-Methyl- is nitrated to 6-nitro-2-methyl-phthalimidine, m.p. 150° (3-benzylidene derivative, m.p. 158°), reduced (Pd-C) to 6-amino-2-methylphthalimidine, m.p. 209° (Ac derivative, m.p. 246°), whereas 2-phenyl- yields solely 2-p-nitrophenylphthalimidine, m.p. 233° (decomp.). $\text{o-CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$ and $\text{p-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ at 140–180° yield 4-nitro-2'-cyanobenzylaniline, m.p. 219°, which could not be transformed into 6-nitro-2-phenylphthalimidine. 4-Nitro-2-cyanobenzyl bromide, m.p. 130°, is hydrolysed to (IV), and with NH_2Ph gives 4'-nitro-2'-cyanobenzylaniline hydrobromide, decomp. 181° after becoming discoloured at 150° and softening at 172°. $\text{o-CN}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$ and $\text{p-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ yield 2-p-tolylphthalimidine, m.p. 141°, also obtained from 2-p-tolylphthalimide, spongy Zn, and conc. HCl in MeOH. 2-Nitro-p-tolylphthalimidine has m.p. 204°.

H. W.

Bile acids. XLII. M. SCHENCK (Z. physiol. Chem., 1934, 223, 259–266; cf. this vol., 189).—With NH_2OH , the NO_2 -compound (I) $\text{C}_{24}\text{H}_{33}\text{O}_9\text{N}$



gives bilianic acid dioxime (NO_2 , NOH), and the nitroketohydroxamic acid (II), $\text{C}_{24}\text{H}_{34}\text{O}_9\text{N}_2$ (A., 1929, 558), yields a nitro-oximinohydroxamic acid (III), $\text{C}_{24}\text{H}_{35}\text{O}_9\text{N}_3$, decomp. 263°. From (III), hot 20% HCl or cold HNO_3 regenerates (II); hot conc. H_2SO_4 yields the isomeric nitrolactamhydroxamic acid (IV), decomp.

With Zn dust and AcOH, (IV) affords an oximinolactamhydroxamic acid (V), $\text{C}_{24}\text{H}_{37}\text{O}_9\text{N}_3$, decomp. from 206°. With HNO_3 , (V) gives the blue NO-compound (VI), $\text{C}_{24}\text{H}_{34}\text{O}_8\text{N}_2$, decomp. 231° (cf. A., 1928, 764).

J. H. B.

Constitution of the bile acids. H. WIELAND (Ber., 1934, 67, [A], 27–39).—A lecture. H. W.

Follicular hormone.—See this vol., 567.

Mixed halogen derivatives of toluene and benzaldehyde. F. ASINGER (J. pr. Chem., 1934, [ii], 139, 296–308).—3 : 5- $\text{C}_6\text{H}_3\text{MeCl}_2$ with Br and a little Fe gives 3 : 5-dichloro-2-bromotoluene (I), m.p. 33.5°, also obtained in 70% yield from 3 : 5-dichloro-*o*-toluidine by a diazo-reaction. 3 : 5-Dichloro-2-aminobenzaldehyde gives (diazo-reaction) a 71% yield of 3 : 5-dichloro-2-bromobenzaldehyde (II), m.p. 82° (oxime, m.p. 139–140°; phenylhydrazone, m.p. 159°). (I) and Br at 180–200° give 3 : 5-dichloro-2-bromobenzylidene bromide, m.p. 38°, b.p. 190°/16 mm., hydrolysed by conc. H_2SO_4 at 70–80 to (II). (II) gives with KMnO_4 3 : 5-dichloro-2-bromobenzoic acid, m.p. 178° (also obtained from dichloroanthranilic acid), and with HNO_3 (*d* 1.48) at 0° affords 3 : 5-dichloro-2-bromo-6-nitrobenzaldehyde, m.p. 151° [oxime, m.p. 154°; phenylhydrazone, m.p. 175–176° (decomp.)], which with NaOH and COMe_2 gives 5 : 7 : 5' : 7'-tetrachloro-4 : 4'-dibromoindigoetin, cryst. *p*-Acetotoluidide with Cl_2 in $\text{AcOH}\cdot\text{Ac}_2\text{O}$ gives the 3 : 5- Cl_2 -derivative, hydrolysed by H_2SO_4 to 3 : 5-dichloro-*p*-toluidine, b.p. 126–128°/16 mm., which gives (diazo-reaction) 3 : 5-dichloro-4-bromotoluene (III), m.p. 35–36°, b.p. 265°/763 mm., also obtained as a by-product with (I). (III) leads by similar reactions to 3 : 5-dichloro-4-bromo-benzaldehyde, m.p. 84° (oxime, m.p. 147°; phenylhydrazone, m.p. 150°), and -benzoic acid, m.p. 220° [NO_2 -derivative (IV), m.p. 217°], 3 : 5-dichloro-*o*-bromo-2-nitrobenzaldehyde, m.p. 144° [oxime, m.p. 160°; phenylhydrazone, dimorphic, m.p. about 213° (decomp.)] [oxidised to (IV)], and 5 : 7 : 5' : 7'-tetrachloro-6 : 6'-dibromoindigoetin, cryst. 3 : 5- $\text{C}_6\text{H}_3\text{MeBr}_2$ affords by Br and hydrolysis 3 : 5- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{CHO}$ (85% yield), m.p. 90°, and a little of the corresponding acid, m.p. 215°.

R. S. C.

Oxidation of organic compounds as a means of investigating their constitution. C. SANDONNINI and G. GIACOMELLO (Atti R. Accad. Lincei, 1934, [vi], 19, 43–49).—The valency of C towards O is discussed in relation to the different forms in which aldehydes may exist (cf. Fry and Payne, A., 1931, 819). The action of $1\text{H}_2\text{O}_2$ on 2PhCHO in Et_2O at 5° gives the compound, $(\text{PhCHO})_2\cdot\text{H}_2\text{O}_2$ (I), m.p. 59–60°, stable at room temp. With $1\text{H}_2\text{O}_2$ and 1PhCHO , an unstable compound, decomposing into (I), PhCHO , and H_2O_2 , is formed. Both these are regarded as additive compounds, and not as true peroxides of the aldehyde. In presence of H_2O containing either H_2SO_4 or NaOH or kept neutral, the reaction gives BzOH , PhOH , and HCO_2H . The H_2O_2 evidently acts by perhydrolysis. T. H. P.

Manufacture of aldehydes of the benzanthrone series.—See B., 1934, 356.

Reactions of maple and spruce lignins. E. E. HARRIS, E. C. SHERRARD, and R. L. MITCHELL (J. Amer. Chem. Soc., 1934, 56, 889–893).—Lignin (I) isolated in good yield by the cold H_2SO_4 method (B., 1932, 542), is free from carbohydrate (II) and contains all the OMe not accounted for in the (II) of

the wood. Hagglund and Urban's method (A., 1929, 856) gives a (I) which contains cellulose (III) and has a low OMe content, whilst the cuprammonium method affords a (I) (in low yield) also containing (III). Spruce-lignin (IV) (H_2SO_4 method) contains 17.3% OMe (i.e., 50Me in unit of 890), is methylated (Me_2SO , 1% NaOH) to a methyl-lignin (OMe 20.9%; 60Me in unit of 900), and thence in 5 and 15% NaOH to dimethyl-lignin (OMe 24.1%) and a fully methylated lignin (OMe 32.2%; 100Me in unit), respectively. Acetylation occurs slowly and gives an acetyl-lignin (OMe 14.1%, Ac 19.5%; 50Me, 5Ac). (IV) and Br in CCl_4 afford bromolignin (OMe 9.5%, Br 24.3%; 30Me, 3Br); Br- H_2O yields a bromolignin (OMe 6.4%, Br 20.6%). (IV) and Cl in CCl_4 give chlorolignin (V) (OMe 6.1%, Cl 27.5%; 20Me, 8Cl in unit of 1030), converted by 5% NaOH into CHCl_3 and a product (OMe 6.6%, Cl 15.8%; 20Me, 4Cl). The yield of (V) indicates that addition of Cl is the main reaction; loss of OMe may occur thus: $\cdot\dot{\text{C}}\text{C}\cdot\text{OMe} \rightarrow \cdot\text{CCl}\cdot\text{CCl}\cdot\text{OMe} \rightarrow \cdot\text{CCl}\cdot\text{CO}\cdot$. Maple-lignin (VI) contains 20.7% OMe (120Me in unit of 1800) and is methylated easily in 1% NaOH to the fully methylated product (OMe 32%; 200Me in unit of 1920), which with Cl_2 in CCl_4 gives a chloromethyl-lignin (OMe 14.7%, Cl 25%; 80Me and 12Cl in unit). (VI) and Cl_2 in CCl_4 afford a chlorolignin (VII) (OMe 8.7%, Cl 19.8%; 40Me and 8Cl in unit of 1440), converted by 5% NaOH into CHCl_3 , HCl, CO_2 , and a product (OMe 10.5%, Cl 11.9%; 40Me and 4Cl in unit of 1200), and by moist air into HCl and a product (OMe 8.8%, Cl 17.5%; 40Me and 7Cl in unit of 1400). Acetylation of (VI) gives an acetyl-lignin (OMe 17.4%, Ac 16.3%; 120Me and 8Ac in unit of 2130). (VI) and Br in CCl_4 afford a bromolignin (OMe 5.6%, Br 30%); Br- H_2O yields a bromolignin (OMe 2.5%, 30% Br), whilst Cl_2 - H_2O furnishes a chlorolignin (OMe 2.2%, Cl 20%; 10Me and 8Cl in unit of 1420). Chlorination and bromination cause loss of OH groups since the resulting products do not methylate or acetylate. The OH groups appear to be present as phenolic, enolic, and (at least one) as $\cdot\text{CHMe}\cdot\text{OH}$ [since (V) and (VII) afford CHCl_3 when treated with alkali; CHCl_3 is not formed when the lignins are methylated and then acted on by Cl_2 and alkali]. Evidence is given to show that lignin is combined (through OH groups) with carbohydrate in the wood.

H. B.

Mechanism of the formation of alkylcyclohexanones by the action of organomagnesium derivatives on α -chlorocyclohexanones. Indirect replacement of halogen by alkyl. M. Tiffeneau and (MLLE.) B. Tschoubar (Compt. rend., 1934, 198, 941—943).—Grignard reagents react with chloroketones at room temp. at the CO group. The OMgHal derivatives of the carbinols thus formed rearrange by migration and loss of Mg halide when warmed. Chlorocyclohexanones thus yield as final products the 2-alkylcyclohexanones and acylcyclopentanes. 2-Chlorocyclohexanone and MgMeI at room temp. give 2-chloro-1-methylcyclohexanol, b.p. 75—76°/14 mm., which with MgEtBr (1 mol.) in hot Et_2O gives C_2H_5 . 2-methylcyclohexanone (semicarbazone, m.p. 198°), and acetyl-cyclopentane (semicarbazone, m.p. 145°).

MgEtBr affords similarly 2-chloro-1-ethylcyclohexanol, b.p. 89.5—91°/14 mm., 1-ethylcyclohexanone (semicarbazone, m.p. 161—163°), and propionylcyclopentane (semicarbazone, m.p. 134—135°). 2-Chloro-5-methylcyclohexanone and MgMeI give 2-chloro-1:5-dimethylcyclohexanol, b.p. 87—89°/14—15 mm., and thence 2:5-dimethylcyclohexanone and 1-acetyl-3-methylcyclopentane [semicarbazones, m.p. 160° and 132° (lit. 155° and 122°), respectively]. R. S. C.

Molecular rearrangements in the dimethylcyclohexane series, with and without ring-diminution, by removal of halogen from chlorohydrins and isomerisation of epoxides. Tiffeneau, E. Ditz, and (MLLE.) B. Tschoubar (Compt. rend., 1934, 198, 1039—1041).—2-Chloro-4-methylcyclohexanone and MgMeI give 2-chloro-1:4-dimethylcyclohexanol, b.p. 92—94°/16—17 mm., which with MgEtBr gives C_2H_5 and an $\cdot\text{OMgI}$ derivative, which is converted at 100° into a mixture of 3-acetyl-1-methylcyclopentane (semicarbazone, m.p. 132°) and 2:4-dimethylcyclohexanone. 1:4-Dimethylcyclohexene and I-HgO give the iodohydrin and 1:2-epoxy-1:4-dimethylcyclohexane, b.p. 155°, which with kaolin at 220—230° gives 2:5-dimethylcyclohexanone and 1:3-dimethylcyclopentane-1-aldehyde (semicarbazone, m.p. 111°). The difference in the mechanism of the two reactions given in the title is thus proved.

R. S. C.

Mutual influence of chromophoric groups. H. Ley and H. Wingchen (Ber., 1934, 67, [B], 501—519).—Measurements of the absorption spectra of $\text{CH}_2\text{Ph}\cdot\text{COMe}$, $\text{CO}(\text{CH}_2\text{Ph})_2$, COPhMe , $\text{CH}_2\text{Ph}\cdot\text{COPh}$, and COPh_2 , $\text{CHMe}\cdot\text{N}\cdot\text{OH}$, $\text{CMe}_2\cdot\text{N}\cdot\text{OH}$, and their Na salts, mesityl oxide and its β -oxime, and Na fulminate are recorded and discussed. The following acids and their Na salts have been examined: α -erotic, maleic and fumaric, o- and tere-phthalic, further $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, and $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ (as Na salt). Observations have been made on MeOH, NaOMe, and $\text{NH}_2\text{OH}\cdot\text{HCl}$. Attention is directed to the marked photolytic action of light of very short wave-length. H.

Metal ketyls of the aliphatic-aromatic series. I. N. Nazarov (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 325—331).—Interaction of COPhR ($\text{R}=\text{Me}$, Et, Pr, Prⁿ) with Na affords a red colour which disappears after a few days to give a ppt. of a pinacol. ω -Diethyl-trimethyl-, -dimethylethyl-, -methyl-diethyl- and -triethyl-acetophenone afford stable cryst. ketyls under similar conditions, which indicates that branched aliphatic chains favour their formation. J. L. D.

Diphenylketazine oxide. K. von Auwers and H. Wunderling (Ber., 1934, 67, [B], 497—501).—The yellow compound (I) obtained by oxidation of $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ by $\text{K}_4\text{Fe}(\text{CN})_6$ (A., 1933, 505; Hunter *et al.*, this vol., 191) is identified as diphenylketazine oxide, $\text{CPh}_2\cdot\text{N}(\text{O})\cdot\text{N}\cdot\text{CPh}_2$. (I) is converted by SnCl_2 and HCl at 70° mainly into COPh_2 and by Zn dust and AcOH into $(\cdot\text{N}\cdot\text{CPh}_2)_2$ (II). With well-cooled PCl_5 (I) affords COPh_2 and $(\cdot\text{CPh}_2\text{Cl})_2$. A saturated solution of HCl in boiling AcOH converts (I) into COPh_2 and benzhydrol ether, m.p. 109—110°. (I) is transformed by NH_2OH in AcOH- H_2O into $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ in

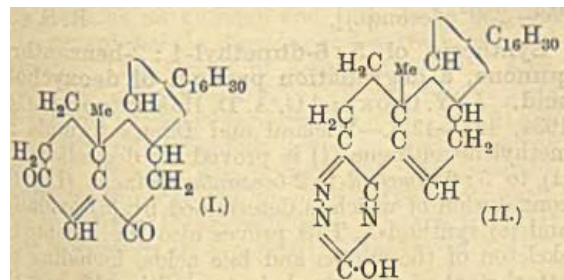
small yield, but appears unaffected by $\text{NHPh}\cdot\text{NH}_2$, whereas it gives benzophenone-*p*-nitrophenylhydrazone with $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$. With the appropriate reagent (II) affords the oxime, phenylhydrazone, and *p*-nitrophenylhydrazone of COPh_2 . (I) and cold conc. H_2SO_4 yield COPh_2 with evolution of gas; under similar conditions, no reaction appears to occur with (II), but COPh_2 is produced. (I) is mainly unchanged by boiling dil. H_2SO_4 , but yields a little COPh_2 , whereas (II) is scarcely affected. (I) and boiling HCO_2H afford COPh_2 mixed with a little oil, whereas no change is caused by AcOH at 100° . (II) and boiling HCO_2H give COPh_2 quantitatively, whilst little ketone results from the action of AcOH . With NaOH in H_2O - MeOH or H_2O - EtOH (I) yields COPh_2 and a small amount of liquid, b.p. $147\text{--}150^\circ/11\text{ mm.}$; (II) is scarcely attacked. H. W.

Abnormal reaction of potassium cyanide and an α -chloroketone. G. RICHARD (Compt. rend., 1934, 198, 943—945).—Ph α -chlorobenzyl ketone and KCN give α -cyano- $\alpha\beta$ -diphenylethylene oxide, m.p. $77\text{--}78^\circ$, which is stable to hot 5% H_2SO_4 and insol. in alkali. With NH_2OH it gives a compound, $\text{C}_{15}\text{H}_{12}\text{ON}_2$, m.p. $161\text{--}162^\circ$, whence it is not regenerated by hydrolysis, and with hot NH_2Ph (1 mol.) it gives α -cyano- β -anilino- $\alpha\beta$ -diphenylethyl alcohol (not isolated), which loses HCN to give anilinobenzoin, m.p. $97\text{--}97.5^\circ$. R. S. C.

α -Chloroketones. G. RICHARD (Compt. rend., 1934, 198, 1242—1244).— CHPhBzCl (I) and MgPhBr (2 mols.) give $\alpha\alpha\beta\beta$ -tetraphenylethyl alcohol. CHPhAcCl and MgPhBr give $\text{CHPh}_2\cdot\text{COMe}$. (I) and PhONa give phenyl α -phenoxybenzyl ketone, m.p. 85.5° , which distils unchanged in vac., but, when distilled at atm. pressure, gives 1:1:3:3-tetraphenylcyclobutanedione, m.p. $244\text{--}245^\circ$ (probably formed by way of $\text{CPh}_2\cdot\text{CO}$). R. S. C.

Cholestenone and coprostanone. H. GRASSHOF (Z. physiol. Chem., 1934, 223, 249—251).—Oxidation of ψ -cholestene (I) with CrO_3 in AcOH gives 7-keto-cholestene [probably by conversion of (I) into cholestene] and cholestenone, confirming the $\Delta^{4:5}$ -linking in (I). Hydrogenation (spongy Pd) of cholestenone in Et_2O affords coprostanone; a coprosterol derivative thus becomes readily accessible. J. H. B.

Cholestenedione. O. STANGE (Z. physiol. Chem., 1934, 223, 245—248).—Cholestenedione (I) affords a disemicarbazone, m.p. 296° (decomp.), which is reduced by NaOEt at 200° to ψ -cholestene, indicating that the double linking in (I) is between C_4 and C_5 . Hydroxy-



cholestenone yields a semicarbazone, m.p. 245° , which on reduction by NaOEt gives 3:6-dihydroxycholest-

x x

ane and an alkali-sol. product (II), $\text{C}_{28}\text{H}_{43}\text{ON}_3$, m.p. 285° (Me ester, m.p. 166°), probably a hydroxy-triazine. J. H. B.

Condensation products of hydroxymethyleneacetophenone with bases. K. VON AUVERS and H. WUNDERLING (Ber., 1934, 67, [B], 644—648).—The conversion of di- β -benzoylvinylamine (I) (Claisen's " NH_3 compound of benzoylacetaldhyde," A., 1888, 690; cf. Benary *et al.*, A., 1924, i, 872) by $\text{NHPh}\cdot\text{NH}_2$ into 1:3-diphenylpyrazole occurs through the compound $\text{NH}_2\cdot\text{NPh}\cdot\text{CH}\cdot\text{CHBz}$. $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, which reacts solely with the NH_2 group, transforms (I) into 5-phenyl-1-*p*-nitrophenylpyrazole, m.p. $116\text{--}118^\circ$. (I) is unexpectedly stable towards KMnO_4 in $\text{Na}_2\text{CO}_3\text{-COMe}_2$, although readily oxidised in presence of acid. The presence of a terminal basic group in this and allied compounds appears to mask the unsaturated linking. They are unsaturated towards Br in CHCl_3 . (I) is very resistant towards MeI at 100° and towards Ac_2O - NaOAc . β -Benzoylvinylaniline, however, readily affords an Ac derivative, m.p. 157° . Di-methyl- β -benzoylvinylamine has m.p. 92° . H. W.

Optically active mixed benzoinz derived from (+)mandelonitrile. A. McKENZIE and A. L. KELMAN (J.C.S., 1934, 412—418).—(+)-Mandelonitrile (I) and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ give (−)-*p*-toluoyl-phenylcarbinol (II), m.p. $102\text{--}103^\circ$, $[\alpha]_D^{25} -120^\circ$ in EtOH , -103.6° in COMe_2 , which with MgPhBr gives (+)-*p*-tolylhydrobenzoin (β -form) (III), m.p. $135.5\text{--}136^\circ$, $[\alpha]_D^{25} +252^\circ$ in COMe_2 . The dl-form of (II) with MgPhBr gives the dl-form of (III) (β -form), m.p. $181\text{--}182^\circ$. Similarly were prepared (−), m.p. $73\text{--}73.5^\circ$, $[\alpha]_D^{25} -122.3^\circ$ in COMe_2 , and dl-*m*-toluoyl-, m.p. $69.5\text{--}70^\circ$, (−)-propionyl-, m.p. $39\text{--}40^\circ$, $[\alpha]_D^{25} -533^\circ$ in CHCl_3 , partly racemised (−)-acetyl-, dl-cyclohexoyl-, m.p. $62\text{--}63^\circ$, and (−)-anisoyl-phenylcarbinol [(−)-benzanisoin], m.p. $102.5\text{--}103.5^\circ$, $[\alpha]_D^{25} -76.5^\circ$ in COMe_2 , and (+), m.p. $125\text{--}126^\circ$, $[\alpha]_D^{25} +244.3^\circ$ in COMe_2 , and dl-*m*-tolyl-, m.p. $123\text{--}124^\circ$, dl-cyclohexyl-, m.p. $133\text{--}134^\circ$, (+), m.p. $146\text{--}147^\circ$, $[\alpha]_D^{25} +259.7^\circ$ in COMe_2 , and dl-anisyl-hydrobenzoin, all β -forms, m.p. $155\text{--}156^\circ$. $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ and (I) give, however, Ph *o*-tolyl diketone (2-methylbenzil), m.p. $57\text{--}58^\circ$, also obtained from $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CN}$ by way of $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$. $\alpha\text{-C}_{10}\text{H}_7\cdot\text{MgBr}$ and dl-(I) give similarly Ph α -naphthyl diketone, m.p. $102.5\text{--}103^\circ$, but with (+)(I) 2:5-diphenyl-3:6-di- α -naphthylpyrazine, m.p. $260\text{--}260.5^\circ$, is obtained. The hydrobenzoinz are racemised by a few drops of KOH - EtOH , a mixture of structurally isomeric dl-compounds being obtained from the active mixed hydrobenzoinz. R. S. C.

Synthesis of substituted benzoinz and of deoxybenzoinz. R. ROGER and A. MCGREGOR (J.C.S., 1934, 442—444).— $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ (1.5 mols.) and benzil (I) in Et_2O give *m*-tolylbenzoin, m.p. $82\text{--}83^\circ$, which with KOH - EtOH gives BzOH and $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{CHPh}\cdot\text{OH}$, m.p. 52° , and with HI and red P *m*-tolyldeoxybenzoin. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ (II) (1.5 mol.), when added to (I) in Et_2O , affords an oil, b.p. $220\text{--}230^\circ$, reduced (HI-P) to *p*-tolyldeoxybenzoin; however, when (I) in Et_2O is added to (II) in Et_2O , there are formed benzoin and two substances,

$C_{28}H_{24}O$, m.p. 212—213° and 159—160°, respectively, probably pinacolins, but in a second experiment a substance, $C_{28}H_{26}O_2$, m.p. 162—163°, probably *s*-diphenyldi-*p*-tolylpinacol, was isolated. Addition of o - C_6H_4Me ·MgBr (1.25 mol.) to (I) in Et_2O gives a substance, m.p. 116—117°, probably *o*-toluoyldiphenylcarbinol, but possibly *o*-tolyldeoxybenzoin, which with KOH-EtOH gives o - C_6H_4Me ·CO₂H (III) and benzhydrol (IV) and is reduced (HI-P) to a ketone (V), $C_{21}H_{18}O$, m.p. 47.5—49°, previously (A., 1933, 611) termed *o*-tolyl CHPh₂ ketone. With KOH-EtOH (V) yields (III) and (IV). The constitution of methylbenzoin is proved reduction to CHMePhBz and alkaline fission to BzOH, *dl*-CHPhMe·OH, and (IV). It is uncertain whether the migration with *o*-tolyl derivatives occurs during the Grignard reactions or during the alkaline scission, but the former (for which a mechanism is proposed) is considered more probable. R. S. C.

Preparation and reactions of disodium stilbene $\alpha\alpha'$ -dioxide. W. E. BACHMANN (J. Amer. Chem. Soc., 1934, 56, 963—965).—Benzil (I) and 2% Na-Hg in Et_2O - C_6H_6 and N_2 at room temp. give a violet compound (1 min.) and then the orange (CPh ·ONa)₂ (II). (II) is hydrolysed (H_2O) to benzoin (III), converted by I into (I), by CO₂ into (CPh ·O·CO₂Na)₂ [which is decomposed by H_2O to CO₂ and (III)], and by ClCO₂Et into $\alpha\alpha'$ -di(carbethoxy)stilbene, m.p. 69—70° [hydrolysed (dil. alkali) to (III)]. (II) is oxidised by atm. O₂; subsequent hydrolysis (H_2O) gives BzOH and benzoic acid. The diacetate, m.p. 118°, dibenzoate, m.p. 158°, di-*p*-toluate, m.p. 199.5°, *Me*·ether, m.p. 66—67° (cf. Staudeinger and Binkert, A., 1922, i, 1016), and diallyl ether, m.p. 92—93°, of $\alpha\alpha'$ -dihydroxystilbene are prepared from (II). (II) is converted by CPh_3Cl or S into (I); with PhCHO, (III) and CH_3Ph ·OBz result. 4:4'-Diphenylbenzil, anisil, and α -naphthil similarly give analogous Na₂ derivatives, hydrolysed to 4:4'-diphenylbenzoin, anisoin, and α -naphthoin, respectively. H. B.

Synthesis of *vic*-resacetophenone. F. MAUTNER (J. pr. Chem., 1934, [ii], 139, 290—292).—2:6-Dimethoxybenzonitrile and MgMeI, best in boiling PhMe, give 2:6-dimethoxyacetophenone, m.p. 73—74°, hydrolysed by AlCl₃ in boiling PhCl to *vic*-resacetophenone, m.p. 157—158°. R. S. C.

Chalkone picrates as organic molecular compounds. T. ASAHINA (Bull. Chem. Soc. Japan, 1934, 9, 131—138).—The formation of the following compounds of various chalkones (A) and picric acid (B) (mol. ratio A:B in parentheses) is proved by thermal analysis: Ph 3:4-methylenedioxy- (I) (1:2), m.p. 128.5°, *o*- (2:3), m.p. 132°, and *p*- (1:1), m.p. 157.5°, -hydroxy-, and *p*-ethoxy- (1:1), m.p. 84.5°, -styryl ketone picrates. With β - $C_{10}H_7$ ·OH (58.2 mol.-%) (I) gives only a eutectic (71.5°) and no compound. J. W. B.

Phototropy of the semicarbazones of ethylenic ketones. II. C. V. GHEORGHIU (Bull. Soc. chim., 1933, [iv], 53, 1442—1463; cf. A., 1930, 604).—Further examples are provided of the fact that, in general, semicarbazones of ketones (A), CHAr·CH·COR, but not those of ketones (B),

CHAr·CR·COMe, are phototropic. When R=Pr³ (not Bu³), ketones (A) have diminished or no phototropy. The semicarbazone of *p*-OMe· C_6H_4 ·CH·CH·COMe, although of type (B), is phototropic, the phenomenon being reversible in this case and in that of the derivative of OMe· C_6H_4 ·CH·CH·COPr³ (colour vanishes in the dark). Phototropy is not due to structural isomerism, since it occurs only with the solid substances; it is probably caused by electronic displacements with formation of a

dipolar molecule, CHAr·CH·CH·CR·N·NH·CO·NH₂, containing triple electron links in the conjugated system. The thiosemicarbazone of CH_2O_2 · C_6H_3 ·CH·CH·COPr³ is phototropic. Semicarbazones of the following ketones are prepared, those which are phototropic being marked (*), those feebly so (†): *o*-hydroxy-, m.p. 178—179° (†), *o*-methoxy- (I), m.p. 167—178° (*), *p*-isopropyl- (II) (α -form), and 3:4-methylenedioxy-styryl Et ketone (III), α -form, m.p. 198° (*), γ -form, m.p. 198—200° (*); *o*-methoxy- (IV), m.p. 177—178°, *p*-hydroxy-, m.p. 208°, and 3:4-methylenedioxy- α -methylstyryl Me ketone, (V), m.p. 216—218° (decomp.); *p*-methoxy- α -ethylstyryl Me ketone (VI), α -form, m.p. 214—215° (reversible *); α -ethylstyryl Me ketone; styryl, *o*- (VII), m.p. 179—181° (reversible †), and *p*-methoxy-, m.p. 173—174° (†), *p*-isopropyl-, and 3:4-methylenedioxy-styryl Pr³ ketone, m.p. 188°; styryl (*) and 3:4-methylenedioxy-styryl Pr ketone (VIII), α -form (IX), m.p. 175° [† probably by change into the γ -form, which was not isolated pure, since by recrystallisation it gives (IX)]; *p*-isopropylstyryl Bu³ ketone (X), m.p. 161° (†); α -furfurylidene-methyl Et and phenyl ketone, m.p. 175—179°. The above ketones are prepared: (I) (from COMeEt, OMe· C_6H_4 ·CHO, and NaOH in cold EtOH), m.p. 30—32°, b.p. 177—178°, dimeric form, m.p. 178—179°; (II) [from cuminaldehyde (XI) and COMeEt in aq. EtOH], b.p. 170°/17 mm.; (III), m.p. 101—102°; (IV) (from OMe· C_6H_4 ·CHO, COMeEt, and HCl gas), b.p. 168—170°/20 mm.; (V) [from piperonal (XII), COMeEt, and HCl at -3°], m.p. 135—136°; (VI), b.p. 173—174°/16 mm.; (VII) (by alkaline condensation), b.p. 186—187°/20 mm.; (VIII) [from (XII), COMePr³, and NaOH in EtOH], m.p. 63°; (X) [from (XI), COMeBu³, and NaOH in aq. EtOH], b.p. 184°/14 mm. R. S. C.

Migration of the acyl group in polyhydric phenols. II. F. MAUTNER (J. pr. Chem., 1934, [ii], 139, 293—295; cf. A., 1933, 395).—Triacetylphloroglucinol and AlCl₃ in cold PhNO₂ give 2:4:6-triacetocyclohexatriene [p-nitrophenylhydrazones, m.p. 258—259° (decomp.)]. R. S. C.

Synthesis of 5:6-dimethyl-1:2-benzanthraquinone, a degradation product of deoxycholic acid. J. W. COOK and G. A. D. HASLEWOOD (J.C.S., 1934, 428—433).—Wieland and Dane's formula for methylcholanthrene (I) is proved by degradation of (I) to 5:6-dimethyl-1:2-benzanthraquinone (II), the constitution of which is determined by (a) oxidation and (b) synthesis. This proves also the accepted C skeleton of the sterols and bile acids, including the attachment of the side-chain to position 17, and the position of the CO in 12-ketocholanic acid (III) and of one OH in deoxycholic and cholic acids. (I) in C_6H_6

is carcinogenic to mice. Transformation of a product of animal metabolism into a carcinogenic substance is thus possible by reactions of a biochemical nature. Equilenin contains the same ring system as oestrin.

3:12-Diketocholanic acid (modified purification) is reduced by Zn and HCl to (III), decarboxylated at 320–345° in CO₂ to dehydronorcholene, whence by Se at 325–340° were obtained (I), m.p. 176.5–177.5° (30% yield), best purified by the *picrate*, m.p. 177–178°, and, in one experiment, a *hydrocarbon*, C₂₂H₂₆, m.p. 132–134° (*picrate*, m.p. 163–166°). (I) is rapidly oxidised by Na₂Cr₂O₇ in AcOH at room temp. to a *ketone*, m.p. 228–229° (decomp.), not isolated pure, and, when boiled, to 6-methyl-1:2-benzanthraquinonylacetic acid, m.p. variable, 250–260° (decomp.), which rapidly at 400° in CO₂ or, much better, with Cu-bronze in boiling quinoline loses CO₂ to yield (II), m.p. 229–230°. (II) with KMnO₄–H₂SO₄ affords anthraquinone-1:2:5:6-tetracarboxylic acid. Methylsuccinic anhydride, phenanthrene, and AlCl₃ in cold PhNO₂ give acids, whence after esterification (MeOH–HCl) were isolated *Me* β-2 (IV), m.p. 134.5–135.5°, and β-3-phenanthrolylisobutyrate (V), m.p. 88–89°. 2-Bromoacetylphenanthrene and CMeNa(CO₂Et)₂ led to the acid, m.p. 225–227°, corresponding with (IV). The crude bromination product of 3-acetylphenanthrene affords similarly the acid (VI), m.p. 179–180.5°, corresponding with (V). The *semicarbazone*, m.p. 193–195° (decomp.), of (VI) gives (NaOEt; 195–200°) γ-3-phenanthryl-α-methylbutyric acid, m.p. 119–121°, which with SnCl₄ at 120° yields 5-keto-6-methyl-5:6:7:8-tetrahydro-1:2-benzanthracene, m.p. 137–138.5°. This with MgMeI forms a resinous product, which is dehydrogenated (Se; 300–310°) to 5:6-dimethyl-1:2-benzanthracene, m.p. 187–188° (*picrate*, m.p. 191–193°), also obtained by reduction of (I), into which it is converted by Na₂Cr₂O₇ in AcOH. 12-Ketonorcholanic acid, m.p. 185.5–186.5°, gives a *semicarbazone*, m.p. 235° (decomp.), which is reduced (NaOEt; 170–175°) to norcholanic acid, identical with that obtained from cholanic acid.

R. S. C.

Perylene and derivatives. G. T. MORGAN and G. MITCHELL (J.C.S., 1934, 536).—Perylene, purified through its *picrate*, m.p. 223–224.5° (lit. 221°), has m.p. 273–274° (lit. 264–265°). 1:2-C₁₀H₆I·OH (I) gives by Meldola's 1:7-perylenequinone synthesis (J.C.S., 1885, 47, 525) a substance, m.p. 94.5°, which is now obtained colourless and insensitive to light. Methoxy-β-naphthol does not react. (I) in boiling C₅H₅N yields a mixture, the alkali-insol. portion of which contains no quinone and with Zn in H₂ gives C₁₀H₈, dinaphthalene dioxide, and a trace of a red substance. The Al salt of β-dinaphthol with AlCl₃ at 140–150° gives 70–80% of quinone, but the yield from the free phenol is variable and low. The Al salt of α-naphthol-3-carbanilide gives an impure, green substance forming an orange vat. Unsuccessful attempts to improve the prep. of perylenetetracarboxylic anhydride (II) are recorded. The acid from (II) and its monoimide are separated by NaCl in dil. NaOH, the imide being pptd.

R. S. C.

Atractylic acid. H. WUNSCHENDORFF and P. VALIER (Bull. Soc. Chim. biol., 1934, 16, 74–79, 80—

84).—Cryst. sec. *attractylates* of Cu, Ni, Co, Zn, Cd, Cr, Fe, Ag, and *tert. salts* of Ba, Ca, Sr, Ni, Co, Cu, Pb, Ag, Zn, Cd have been prepared. The primary salts readily decompose into *sec. salts* and free acid. With saturated aq. Ba(OH)₂, K *attractylate* gives 1 mol. of valeric acid and Ba *attractylenate* C₂₅H₄₂O₁₇S₂Ba.

A. L.

Resen of Manila-elemi resin. K. H. BAUER and H. J. STARCKE (Arch. Pharm., 1934, 272, 167–171).—Distillation of the residual resin (I) after extraction of the amylin-freed elemi resin with EtOH–NaOH and steam-distillation gives a fraction, b.p. 112–114°/5 mm., which contains elemicin (II) (Semmler, A., 1916, i, 492) since it is oxidised by KMnO₄–COMe₂ to trimethylgallic acid. Distillation of (I) with superheated steam gives (II) and elemol, and a residual resin (III) distillation of which gives fractions (a) b.p. 135–140°/7 mm. (2.52% OMe : 9.08% OH), (b) b.p. 151–152°/8 mm. (2.2% OMe), and (c) b.p. 152–200°/8 mm. The residue (OMe-free : 5.7% OH), partly purified by pptn. from solution in 98% HCO₂H by H₂O, gives a *substance*, m.p. 73° (C, 81.16; H, 10.76; OH, 1.55%; I val. 163.5), probably an autoxidation and polymerisation product of a terpene hydrocarbon.

J. W. B.

Paprika colouring matter. VII. Adsorption analysis of pigment. L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1934, 509, 269–287).—The crude pigment, obtained by hydrolysis (MeOH–KOH) of the extracted wax, is separated by adsorption on CaCO₃ [essentially Tsvett's method (A., 1907, ii, 144)] into capsanthin (I), a new violet-red polyene (termed capsorubin) (II), zeaxanthin (III), m.p. 206° (all m.p. are corr.), [α]_D²⁰ –54° in CHCl₃, and cryptoxanthin (IV) (Kuhn *et al.*, this vol., 70). Lutein (xanthophyll), m.p. 192°, [α]_D²⁰ +163° in CHCl₃, (I), and (III) are similarly obtained from a crude prep. (A., 1928, 1252) of (I). In both cases, dil. solutions in CS₂ are used. The original coloured wax (cf. A., 1931, 1066) can similarly be separated (petrol solution) into *cryst. capsanthin ester mixtures* and esters of (III) and (IV); hydrolysis (MeOH–KOH) and re-adsorption give (I), (III), (IV), and a little β-carotene [best adsorbed on Ca(OH)₂]. The previously described (A., 1931, 1066) synthetic esters of (I) are also purified by adsorption on CaCO₃, small amounts of the esters of (II) and (III) being removed: the *didecoate*, m.p. 109° [previously described (*loc. cit.*) as the *dihexaoate*], diacetate, m.p. 146.5°, and dipalmitate, m.p. 92°, are thus obtained pure. Analytical data for these esters and purified (I), m.p. 175–176° (Berl block), indicate that (I) is C₄₀H₅₈O₃ (±2H) and not C₃₅H₅₀O₃.

H. B.

Strophanthin. XXIX. Dehydrogenation of strophanthidin. R. C. ELDERFIELD and W. A. JACOBS (Science, 1934, 79, 279–280).—Dehydrogenation of strophanthidin with Se under carefully-controlled temp. conditions gave a hydrocarbon C₁₈H₁₆, m.p. 124–125° (corr.), identical with that isolated by Diels *et al.* (A., 1928, 169), which did not yield a red quinone on oxidation (cf. A., 1932, 948). The “dimethylphenanthrene” previously obtained (*loc. cit.*) appears to be due to too rapid heating of the reaction mixture. Since C₁₈H₁₆ appears to be a characteristic degradation product of the sterol skeleton, the ring

system of the cardiac aglucones appears to be built on the same general plan as that of the sterols and bile acids.

L. S. T.

Steric series of xanthophylls. R. KUHN and C. GRUNDMANN (Ber., 1934, 67, [B], 596—598).—Pure zeaxanthin, m.p. 215.5° (corr.), from *Physalis* is optically inactive, the dextrorotation of the initial material disappearing during purification. Only dextrorotatory and optically inactive xanthophylls are known, the inactive crypto-, rubi-, and zeaxanthins being related to β -, γ -, and β -carotene, respectively; although the entry of OH causes development of asymmetric C, optical activity is not observed. Lutein is related to α -carotene, but the relationships of the remaining optically active xanthophylls are obscure. Zeaxanthin dipalmitate, $C_{72}H_{116}O_4$, has m.p. 99.5°, in agreement with that of natural physalien, which is optically inactive.

H. W.

Constituents of roots of *Arctopus echinatus*.—See this vol., 709.

Spectroscopy of terpene alcohols and esters. P. BONICHON (Bull. Inst. Pin, 1933, 249—251; 1934, 1—8, 32—46).—The formates described below were obtained by Ac_2O-HCO_2H (1:1 mol.), acetates by Ac_2O and $NaOAc$ in xylene, propionates and butyrates by the acid and H_2SO_4 . Hydrogenation (PtO_2) of isopulegol (I), b.p. 96.5—98.5°/18 mm., $[\alpha]_{5461} -1.72^\circ$, and its acetate, $[\alpha]_{5461} -1.16^\circ$, and of carvone, b.p. 111°/18 mm., $[\alpha]_{5461} +64.76^\circ$, gives isopulegomenthol, b.p. 104—105°/18 mm., $[\alpha]_{5461} -16.11^\circ$ (phenylurethane, m.p. 111—112°), and its acetate, b.p. 108—109°/18 mm., $[\alpha]_{5461} -24.62^\circ$, and tetrahydrocarvone (II), b.p. 104—105°/22 mm., $[\alpha]_{5461} -23.75^\circ$ (semicarbazone, m.p. 152°). Further hydrogenation of (II) affords carvomenthol, b.p. 105—107°/18 mm., $[\alpha]_{5461} -22.3^\circ$ [phenylurethane, m.p. 88—90° (lit. 74—75°)]. Cyclisation of citronellal and its diacetate gives (I) (formate, b.p. 104—106°/24 mm.) and its acetate, b.p. 110—114°/18 mm. Reduction of pulegone with Na and EtOH gives pulegomenthol (phenylurethane, m.p. 112°) and a little pulegomenthone. Similar reduction of carvone (III) gives dihydrocarveol, b.p. 112—113°, $[\alpha]_{5461} +32.74^\circ$ (phenylurethane, m.p. 87°), and 3—4% of unchanged (III). Raman spectra are recorded for the above esters and alcohols and for menthol, its acetate, b.p. 120—122°/22 mm., $[\alpha]_{5461} -80.91^\circ$, and formate, b.p. 111—112°/18 mm., $[\alpha]_{5461} -78.88^\circ$, α -terpineol, m.p. 35°, $[\alpha]_D 0$, and its acetate, b.p. 129—132°/24 mm., borneol, its formate, b.p. 110°/20 mm., $[\alpha]_{5461} +17.25^\circ$, acetate, b.p. 97—98°/9 mm., $[\alpha]_{5461} +11.17^\circ$, propionate, b.p. 124—125°/18 mm., $[\alpha]_{5461} +18.38^\circ$, and butyrate, b.p. 140—142°/22 mm., $[\alpha]_{5461} +15.04^\circ$, and isoborneol and its formate, b.p. 110°/20 mm., $[\alpha]_D 0$, acetate, b.p. 115—117°/22 mm., propionate, b.p. 124—125°/18 mm., and butyrate, b.p. 141—143°/22 mm. (III) has a line of frequency 1.673 due to the CO and one of 1.646 due to the ethylenic linking. The lines due to the CO are materially shifted by unsaturation only if this is in the $\alpha\beta$ -position. Alcohols and their esters give very similar spectra. The isomeric menthols give distinguishable spectra, by means of which they can be detected in mixtures.

R S C

Isomerisation of α -pinene to an aliphatic terpene (alloocimene). I. Preparation and properties. II. Constitution. B. ARBUSOV (Ber., 1934, 67, [B], 563—569, 569—573; cf. A., 1933, 717).—I. The main factor in the isomerisation of α -pinene to an aliphatic terpene (I), b.p. 87—87.5°/16 mm., $[\alpha]_D \pm 0^\circ$, is the temp., reduced Cu or glass fragments being as efficient as Cr—Cu or Co—Th used previously. Production appears to occur invariably at $>300^\circ$, particularly if the products are removed rapidly from the heated zone. Exposure of (I) at 300° results in the formation of a terpene, b.p. 57—58.5°/14 mm., with, probably, di- and tri-terpenes. (I) and α -naphthaquinone give an adduct, $C_{20}H_{22}O_2$, m.p. 122°, dehydrogenated by air in presence of KOH to the dihydroanthraquinone derivative, $C_{10}H_{20}O_2$, m.p. 120—120.5°, which is oxidised by HNO_3 to an acid, m.p. 331° (decomp.). Treatment of (I) with AcOH and 50% H_2SO_4 leads to dipentene (tetrabromide, m.p. 124—125°) and, mainly, an unknown diterpene, b.p. 142—143°/4 mm., $d_4^{20} 0.8654$.

II. The identity of (I) with alloocimene is established by its comparison with the hydrocarbon of Fischer *et al.* (A., 1933, 592) and their adducts with maleic anhydride and α -naphthaquinone. γ -Methyl- Δ^8 -butenyl bromide and tiglaldehyde in Et₂O are completely resinified by Zn, but transformed by Mg into the carbinol $C_{10}H_{18}O$, b.p. 82—83°/13 mm., dehydrated by $KHSO_4$ to the hydrocarbon (II) $C_{10}H_{16}$, b.p. 160.5°/760 mm. (II) and maleic anhydride yield the substance $C_{14}H_{18}O_3$, m.p. 70—71°, from which the acid $C_{14}H_{20}O_4$, m.p. 169—170°, is derived. H. W.

Parent substance of the camphor group, dicyclo-(1:2:2)-heptane, and the stereoisomeric norborneols. G. KOMPPA and S. BECKMANN (Naturwiss., 1934, 22, 171).—Norcamphor is catalytically reduced to α -norborneol, m.p. 149—150° (phenylurethane, m.p. 158—159°). β -Norborneol (I), m.p. 123—124° (phenylurethane, m.p. 144—145°), is obtained by the Hofmann degradation of dicyclo-[1:2:2]-heptane-2-carboxylamide to norbornylamine, which is treated with HNO_2 . Conversion of (I) into the chloride and reduction with Na and EtOH leads to dicyclo-[1:2:2]-heptane (norbornylane), m.p. 86—87°, which is extraordinarily volatile. H. W.

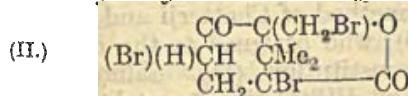
Products of the degradation of camphor and camphorquinone in the animal organism. F. REINARTZ and W. ZANKE [with O. SCHAEFERS and K. FAUST] (Ber., 1934, 67, [B], 548—553).—Camphorquinone is reduced in the animal organism to a mixture separable by MeOH—HCl into 2-hydroxyepi-camphor, identical with the synthetic product, and 3-hydroxycamphor (semicarbazone, m.p. 181—184, $[\alpha]_D^{25} -23.9^\circ$ in abs. EtOH). The authors' results with camphor confirm those of Asahina *et al.* (cf. this vol., 299). Contrary to Takeuchi *et al.* (A., 1933, 1300), diketocamphane (I) can be hydrogenated slowly and incompletely, and then yields a 5-hydroxycamphor (dinitrobenzoate, m.p. 165—171°) not identical with the biological product (dinitrobenzoate, m.p. 96—97°). (I) after being heated in light petroleum does not contain OH, is stable towards Br, and behaves like ordinary (I) when hydrogenated. The very pro-

nounced physiological action of vita-camphor" could not be confirmed. H. W.

Products of the degradation of epicamphor in the animal organism. F. REINARTZ and W. ZANKE [with O. SCHAEFERS] (Ber., 1934, 67, [B], 589—593; cf. preceding abstract).—*epi*Camphor, like camphor, is oxidised to hydroxycamphors in the cell and excreted in conjunction with glycuronic acid. The yields are poor and the *hydroxycamphor*, m.p. 206—208°, $[\alpha]_D$ —53·33° in abs. EtOH, appears to have a *tert.*-OH, since it is mainly resistant towards CrO_3 . Subsequent oxidation with KMnO_4 gives small amounts of an acid $\text{C}_{10}\text{H}_{14}\text{O}_3$, m.p. 240—242° (decomp.), apparently derived from a α -hydroxycamphor. The 3:5-dinitrobenzoate, m.p. 117—119°, of (I) and its additive compound with $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$, m.p. 201·5—205°, are described. H. W.

Synthesis of 5-hydroxycamphor. K. TAKEUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 288—296).— β -*pericyclo*Camphanone (A., 1917, i, 655) with $\text{CCl}_3\text{-CO}_2\text{H}$ and H_2SO_4 at 150—160° gave 5-trichloroacetoxycamphor, b.p. 140—145°/4 mm., $[\alpha]_D$ +9·30° in EtOH, converted by boiling KOH-EtOH into 5-hydroxycamphor, identical with one component of "campherol" isolated from the urine of dogs fed with camphor (A., 1929, 72). A. E. O.

Bromination of camphorquinone. W. C. EVANS, J. L. SIMONSEN, and (in part) M. B. BHAGVAT (J.C.S., 1934, 444—447).—The compound, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Br}_2$, obtained by Manasse and Samuel (A., 1898, i, 147; 1903, i, 45) by brominating camphorquinone has been shown to be the lactone of 1:5-dibromo-3-hydroxy-3-bromomethyl-2:2'-dimethylcyclohexan-4-one-1-carboxylic acid, reduced with Zn-AcOH to 2:2:3-trimethylcyclohexan-4-one-1-carboxylic acid or with Al-Hg to the lactone of 3-hydroxy-3-bromomethyl-2:2'-dimethylcyclohexan-4-one-1-carboxylic acid (I), m.p. 144—145°, $[\alpha]_D$ +72·25°, in CHCl_3 . (I) and NaOMe afford the lactone of the 3-*O*-*Me*-acid, m.p. 81—82°, $[\alpha]_{5461}$ +64·6° in CHCl_3 [with semicarbazide acetate, a substance, m.p. 183—184°, is formed], oxidised (HNO_3 or KMnO_4) to $\alpha\alpha$ -dimethyltricarballic acid and reduced (Pd-H_2) to the lactone of 3-hydroxy-3-methoxymethyl-2:2'-dimethylcyclohexan-4-ol-1-carboxylic acid, m.p. 48—49°, $[\alpha]_{5461}$ +14·22° in MeOH (oxidised by HIO_4 and NaOBr successively to 3-methylpentane-6 γ -tricarboxylic acid). The Br_2 -lactone of Manasse and Samuel is the lactone of 1-bromo-3-hydroxy-3-bromomethyl-2:2'-dimethyl-



cyclohexan-4-one-1-carboxylic acid. The Br_2 - and Br_3 -lactones are probably as (II). F. R. S.

Bisiminocamphor derivatives with exalted optical activity. S. M. PATEL and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 87—93).—1:4- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2\cdot 2\text{HCl}$ and $p\text{-NHAc-C}_6\text{H}_4\cdot\text{CHO}$, m.p. 154—155° (lit. 161°), in aq. EtOH-NaOAc give *di-p-acetamidobenzylidene-1:4-naphthylenediamine*, m.p. 317° hydrolysed (dil. HCl , EtOH) to the *di-p-aminobenzylidene* derivative, the *dihydrochloride* of which with camphorquinone (I) in aq. EtOH-NaOAc (general method)

affords 1:4-naphthylenebisimino-*p*-benzylideneimino-camphor, m.p. 239°, $[\text{M}]_{D}^{25} +22,050^\circ$ in $\text{C}_6\text{H}_5\text{N}$, which has a high rotatory power owing to the large no. of conjugated double linkings in the mol. (cf. Forster and Thornley, J.C.S., 1909, 95, 942). Reduction ($\text{EtOH-NH}_4\text{HS}$; aq. Na_2S ; Zn dust and AcOH ; FeSO_4 and aq. NH_3) of *di-p-nitrobenzylidene-1:4-naphthylenediamine*, m.p. 281°, gives tarry products. 4:4'-Diacetamidodiphenylcarbamide [from $p\text{-NH}_2\text{-C}_6\text{H}_4\cdot\text{NHAc}$ and $\text{CO}(\text{NH}_2)_2$; method, A., 1931, 209] is hydrolysed (conc. HCl) to the $(\text{NH}_2)_2$ -derivative, which with (I) affords *carbamidodi-p-phenylenebisiminocamphor*, m.p. 280°, $[\text{M}]_D +8911\cdot4^\circ$ in CHCl_3 , and an *isomeride*, m.p. 266°. Ox-*p*-aminoanilide (*loc. cit.*) and (I) give α -amidodi-*p*-phenylenebisiminocamphor, m.p. 183°, $[\text{M}]_D +12,095^\circ$ in $\text{C}_6\text{H}_5\text{N}$, whilst (I) (2 mols.) and $\text{CS}(\text{NH}\cdot\text{NH}_2)_2$ (1 mol.) in $\text{EtOH}+\text{anhyd. Na}_2\text{SO}_4$ afford the *thiocarbohydrazone*, $\left[\text{C}_8\text{H}_{14}\begin{array}{c} \text{C}\cdot\text{N}\cdot\text{NH}\cdot \\ \diagup \quad \diagdown \\ \text{CO} \end{array}\right]_2\text{CS}$, m.p. 226°, $[\text{M}]_D +1557^\circ$ in CHCl_3 . Introduction of $\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot$ and $\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot$ causes an increase in $[\text{M}]_D$ (compared with 4:4'-diphenylbisiminocamphor), in spite of the interruption of the conjugated system. (I) could not be condensed with 4:4'-diamino-benzophenone, azobenzene, and -diphenylazodicarbonamide, 2:2'-diaminodiphenyl, 1:2- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$, 1:4-diaminoanthraquinone, and anthraquinoned-i-*p*-aminoanil. H. B.

Polyterpenes and polyterpenoids. XC. Synthesis of the monocyclic diterpene alcohol 1-(β -cyclogeranyl)geraniol. L. RUZICKA and W. FISCHER (Helv. Chim. Acta, 1934, 17, 633—641).—Cyclisation (H_3PO_4 at 0°) of geranyl acetate and subsequent hydrolysis affords *cyclogeraniol*, converted by PCl_5 in ligroin into α -cyclogeranyl chloride $\text{CH}_2\begin{array}{c} \text{CH}=\text{CMe} \\ \diagdown \quad \diagup \\ \text{CH}_2\cdot\text{CMe}_2 \end{array}\text{CH}\cdot\text{CH}_2\text{Cl}$, condensed with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ to *Et cyclogeranylacetoacetate*, b.p. 120—127°/0·4 mm., hydrolysed by aq. $\text{Ba}(\text{OH})_2$ to dihydro- α -ionone (semicarbazone, m.p. 167—168°), identical with the product obtained by catalytic reduction ($\text{H}_2\text{-Ni}$ in EtOH at 50°) of α -ionone. The semicarbazone of dihydro- β -ionone, similarly obtained, has m.p. 153—154°. With C_2H_2 and NaNH_2 in Et_2O either dihydroionone affords the *acetylenic carbinol*, b.p. 135—138°/10 mm. (from α), b.p. 134—137°/10 mm. (from β), reduced ($\text{H}_2\text{-Ni}$ in EtOH at 50°) to ϵ -(2:6:6-trimethyl- Δ^1 -cyclohexenyl)- γ -methyl- Δ^5 -penten- γ -ol, b.p. 134—135°/10 mm. (α), b.p. 135—136°/10 mm. (β) (α - and β -cyclonerolidol), converted by PCl_5 in ligroin into the corresponding Δ^8 -pentenyl chloride (*cyclofarnesyl chloride*). Condensation of the β -product with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$ gives the substituted *aceto-acetic ester*, b.p. 165—167°/0·4 mm., hydrolysed to ζ -(2:6:6-trimethyl- Δ^1 -cyclohexenyl)-8-methyl- Δ^7 -pentenyl *Me ketone*, b.p. 116—117°/0·05 mm., similarly condensed with $\text{C}_2\text{H}_2\text{-NaNH}_2$ to the *acetylenic carbinol*, b.p. 125—126°/0·1 mm., reduced (Ni) to ι -(2:6:6-trimethyl- Δ^1 -cyclohexenyl)- $\gamma\gamma$ -dimethyl- Δ^5 -nonadien- γ -ol (1- β -cyclogeranyl-linalool), converted by anionotropic change in Ac_2O , conversion into the phthalate, and hydrolysis into the corresponding Δ^8 -n-nonadien- α -ol (1- β -cyclogeranylgeraniol), b.p. 136—138°/0·1 mm.

Preparation of α -alkyltetrahydropyrans. R. PAUL (Compt. rend., 1934, 198, 1246—1248).—Dihydropyran and anhyd. HBr at 0° give a crude 2-bromotetrahydropyran, which with Grignard reagents (excess) in Et₂O at -17° gives 75—85% yields of α -ethyl-, b.p. 128—129°/770 mm., -propyl-, b.p. 152—153°, and -phenyl-tetrahydropyran, b.p. 113°/11 mm., which with HBr at the temp. stated afford (150°) α -dibromo-heptane, b.p. 113—115°/11 mm. (90% yield), and (b.p.) -octane (80%), b.p. 127—128°/11 mm., and (90—100°) α -bromo- ϵ -phenyl- Δ^5 -pentene, b.p. 149—151°/11 mm., respectively. 2:3-Dibromotetrahydropyran at -17° gives similarly poorer yields of 2-bromo-1-ethyl-, b.p. 71—72°/12 mm., and -phenyl-tetrahydropyran, b.p. 160—162°/15 mm., m.p. 38°.

R. S. C.

Synthetical experiments in the chromone group. XI. Synthesis of isoflavone. P. C. JOSHI and K. VENKATARAMAN (J.C.S., 1934, 513—514).—*o*-Hydroxyphenyl benzyl ketone, Na, and HCO₂Et yield isoflavone, m.p. 148°. 2:4-Dihydroxyphenyl 4-nitrobenzyl ketone, m.p. 210° (2:4-dinitrophenylhydrazones, m.p. 238°; dibenzyl ether, m.p. 121°), is obtained from *p*-nitrophenylacetonitrile (I), resorcinol, and ZnCl₂, and is converted into 7-hydroxy-2-phenyl-3-*p*-nitrophenylchromone, m.p. 301°. (I), resorcinol Me ether, and ZnCl₂ afford 2-methoxy-4-hydroxy-, m.p. 149—150° (2:4-dinitrophenylhydrazones, m.p. 229°), and 2-hydroxy-4-methoxy-phenyl 4-nitrobenzyl ketone, m.p. 136° (2:4-dinitrophenylhydrazones, m.p. 232°). α -Naphthyl *p*-nitrophenylacetate, m.p. 146° and 152°, is obtained from *p*-nitrophenylacetic acid, α -C₁₀H₇-OH, and POCl.

F. R. S.

Coumarin derivatives. III. Characteristic reaction of coumarin-3-carboxylic acid. T. BOEHM and R. THEMLITZ (Arch. Pharm., 1934, 272, 406—427).—NH₂Ph coumarin-3-carboxylate (I) [from NH₂Ph, *o*-OH-C₆H₄-CHO, and CH₂(CO₂H)₂ in EtOH] is converted, by keeping in COMe₂ solution, into γ -acetyl- β -*o*-hydroxyphenylbutyranilide (II), m.p. 176° [*p*-nitrophenylhydrazones, m.p. 193—194°; Me ether, m.p. 104—105° (*p*-nitrophenylhydrazones, m.p. 178—179°)], converted by distillation in vac. into NH₂Ph and the lactone (III), b.p. 218—225°/14 mm., m.p. 65° (*p*-nitrophenylhydrazones, m.p. 141°; semicarbazone, m.p. 184°; oxime, m.p. 197—198°), of γ -acetyl- β -*o*-hydroxyphenylbutyric acid (IV), m.p. 116—118° (decomp.) (*p*-nitrophenylhydrazones, m.p. 165°; semicarbazone, m.p. 173°), which is obtained on hydrolysis, or by hydrolysis of (II). With Me₂SO₄-NaOH (IV) gives the corresponding OMe-acid, m.p. 102—104° (Et ester, b.p. 200—205°/14 mm.; *p*-nitrophenylhydrazones, m.p. 163°; semicarbazone, m.p. 199—200°), oxidised by NaOBr-NaOH to β -*o*-methoxyphenylglutaric acid, m.p. 189—190° (decomp.) (monoanilide, m.p. 182°), identical with a specimen synthesised by hydrolysis of Et β -*o*-methoxy-*n*-propane- α - γ -tetracarboxylate, m.p. 55° [from *o*-OMe-C₆H₄-CHO, CH₂(CO₂Et)₂, and NaOEt-EtOH]. With cold fuming HCl (II) affords, with loss of H₂O, the lactam of 2-anilino-2-methylchroman-4-acetic acid (V) (A, R=Ph), m.p. 126°. Similarly (III) with conc. aq. NH₃ affords the lactam of 2-amino-2-methylchroman-4-acetic acid (VI) (A, R=H), m.p. 26—27°. Heated in AcOH (IV) gives the lactone

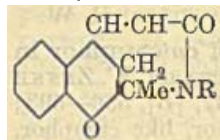
of 2-hydroxy-2-methylchroman-4-acetic acid, m.p. 148° [converted by into (VI), and hydrolysed to (IV)]. By similar methods from coumarin-3-carboxylic acid and the appropriate base in COMe₂ are obtained: the piperidine, m.p. 143—145° (*p*-nitrophenylhydrazones, m.p. 193°), of (IV), and the lactam of 2-*p*-methoxyphenyl-, m.p. 160°, 2-*p*-ethoxyphenyl-, m.p. 114—115°, 2-*p*-, m.p. 170—171°, and 2-*m*-, m.p. 132—133°, -tolyl-, and 2-*p*-chlorophenyl-, m.p. 175°, -amino-2-methylchroman-4-acetic acid [all as (A)]. By a similar reaction in COMeEt (I) affords α -acetyl- β -*o*-hydroxyphenyl-*n*-valeranalide, m.p. indefinite 200°, converted by HCl into the lactam of 2-anilino-2:3-dimethylchroman-4-acetic acid, m.p. 169—170°. The mechanisms of these reactions are given.

J. W. B.

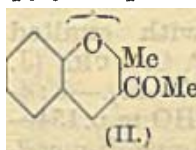
Hydroxy-carbonyl compounds. IX. Benzopyrones related to phloretin. F. E. KING and A. ROBERTSON (J.C.S., 1934, 403—405).—The Me₃ derivative of 5:7:4'-trihydroxy-3-benzyl-2-methylchromone, to which Ciamician and Silber (A., 1894, i, 471; 1895, i, 538) assigned a coumarin structure, with PhCHO-NaOEt gives 5:7:4'-trimethoxy-2-styryl-3-benzylchromone, m.p. 165°, confirming the chromone structure. CH₂Ph-CH₂-CN and phloroglucinol Me₂ ether condense (ZnCl₂-HCl) to 2-hydroxy-4:6-dimethoxy-phenylpropionophenone (I), m.p. 105°, and the ZnCl₂-imine double compound of 4-hydroxy-2:6-dimethoxy- β -phenylpropionophenone, m.p. 206—208° (decomp.), converted into the ketone hemihydrate, m.p. 73—74°, and 104—105° (anhyd.). (I) and NaOAc-Ac₂O yield 5:7-dimethoxy-3-benzyl-2-methylchromone, m.p. 168°, which with PhCHO condenses to the 2-styryl derivative, m.p. 179—181°. 7-Methoxy-2-styryl-3-benzylchromone, m.p. 174°, is obtained from the corresponding Me derivative. Phloroglucinol Me₂ ether and P₂O₅ with Et α -benzylacetoacetate form 5:7-dimethoxy-3-benzyl-4-methylcoumarin, m.p. 172—173°, and with Et α -*p*-methoxybenzylacetate, the 5:7:4'-(OMe)₃-compound, m.p. 137°, and not the 1:4-pyrones.

F. R. S.

Acid condensation of salicylaldehyde with acetylacetone, ethyl acetoacetate, and pyruvic acid. R. J. W. LE FEVRE (J.C.S., 1934, 450—454).—Salicylaldehyde (I) (2 mols.), CH₃Ac₂ (1 mol.), and HClO₄ afford 3-acetyl-2-*o*-hydroxystyrylbenzopyrylium perchlorate, m.p. 135—140°, which is obtained impure by the method of Chatterji and Ghosh (*ibid.*, 1918, 113, 446), who assigned to the corresponding chloride the constitution (II). Salicylideneacetylacetone, HCl, and HClO₄ give 3-acetyl-2-methylbenzopyrylium perchlorate (?), m.p. 145—150°, corresponding with (II). (I), CH₃Ac₂-CO₂Et, and HClO₄-HCl condense to a perchlorate C₁₈H₁₇O₇Cl (III), m.p. 300—305°, identical with the product obtained from 3-acetyl-coumarin and (I). β -Naphthol-1-aldehyde and CH₃Ac₂-CO₂Et similarly condense to a perchlorate, C₁₆H₁₅O₇Cl, m.p. above 300°. (I) and CH₃Bz-CO₂Et yield 3-benzoylcoumarin; C₆H₅Me and *o*-OAc-C₆H₄-CHO condense to 2-phenylbenzopyrylium



(A.)



(II.)

perchlorate. (I) and AcCO_2H with $\text{HClO}_4\text{--HCl}$ give 2-carboxybenzopyrylium perchlorate, m.p. 230—235° (decomp.), decarboxylated to benzopyrylium perchlorate monohydrate, m.p. 230—240°. AcCO_2H condenses with piperonal to a substance, m.p. 161—162°.

F. R. S.

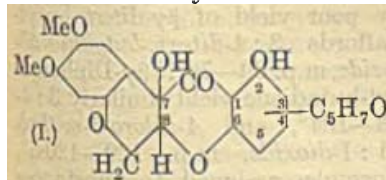
Interaction of chloroacetyl chloride with β -naphthol. K. DZIEWOŃSKI and T. DUŻYK (Bull. Acad. Polonaise, 1934, A, 81—89).—Interaction of $\beta\text{-C}_{10}\text{H}_7\text{OH}$, CH_2ClCOCl , and AlCl_3 in PhNO_2 gives dihydro- β -naphthafuran-1-one (I) (cf. A., 1921, i, 431; 1931, 737) and (if a trace of H_2O is present) its anhydrobis-derivative (II), m.p. 228—229° (picrate, m.p. 170°; Br-derivative, m.p. 267°), which is also formed from (I) by action of conc. KOH or cold conc. H_2SO_4 . Action of HNO_3 (d 1.52) in AcOH converts (I) into its 2- NO_2 -, m.p. 190° (decomp.), 2:2-(NO_2)₂ (III), m.p. 160° (decomp.), and 2:2:Bz-(NO_2)₂ (IV), m.p. 189°, -derivatives; the two former on reduction with Zn and 10% aq. KOH at 100° give 2:1-OH- $\text{C}_{10}\text{H}_6\text{CO}_2\text{H}$. (III) and (IV) are converted by dissolution in KOH and acidification of the solutions into their (di-)aci-forms, m.p. 152° (decomp.) and 202° (decomp.), respectively; the K_2 salts of these are described. With acenaphthaquinone in AcOH and Ac_2O (I) gives 2:1'-dihydro- β -naphthafuranone-acenaphtheneindigo, m.p. 287° (decomp.). (II) also gives a (NO_2)₂-derivative, m.p. 161° (decomp.), and is oxidised by PbO_2 to 5:6:5':6'-dibenzo-oxindirubin, m.p. 335°.

H. A. P.

Nitric acid oxidation of 2:5-diphenylfurans to unsaturated cis- $\alpha\delta$ -diketones. R. E. LUTZ and F. N. WILDER (J. Amer. Chem. Soc., 1934, 56, 978—979).—2:5-Diphenylfuran is oxidised by HNO_3 (d 1.42) in AcOH at 25° to cis- $\alpha\beta$ -dibenzoyl ethylene; 3:4-dichloro- and -dibromo-2:5-diphenylfurans similarly give (at 100°) cis- $\alpha\beta$ -dichloro- and -dibromo- $\alpha\beta$ -dibenzoyl ethylene, respectively. Oxidation probably involves addition of OH and NO_2 at C_2 and C_5 and subsequent elimination of HNO_2 .

H. B.

Toxicarol. V. 7-Hydroxytoxicarol and related compounds. E. P. CLARK (J. Amer. Chem. Soc., 1934, 56, 987—991).—The toxicarol and dihydrotoxicarol hydrates of Butenandt and Hilgetag



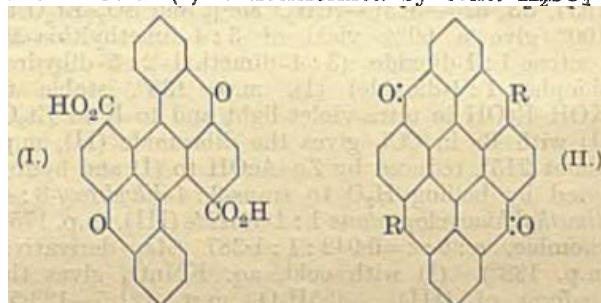
(A., 1932, 751; 1933, 1302) are 7-hydroxytoxicarol (I), m.p. 226—227°, and 7-hydroxydihydrotoxicarol (II), m.p. 222—223°, respec-

tively. The production of (I) from toxicarol (III) and EtOH-KOH (cf. loc. cit.) involves atm. oxidation. (III) and 50% KOH in $\text{C}_6\text{H}_6\text{--EtOH}$ give (I) and a little dehydrotoxicarol (IV). (I) is best prepared from (III) and 2.5% Na-Hg in $\text{C}_6\text{H}_6\text{--EtOH}$; reduction does not occur. (I) is also obtained by oxidation ($\text{CrO}_3\text{, AcOH}$) of (III); diacetyltoxicarol similarly gives 7-hydroxyacetyltoxicarol (V), m.p. 184°, hydrolysed (EtOH-KOH) to (I) and by 5% HCl to (IV). Reduction ($\text{H}_2\text{, PtO}_2\text{, EtOAc}$) of (V) affords 7-hydroxyacetyldihydrotoxicarol, m.p. 196—198° [also obtained by oxidation ($\text{KMnO}_4\text{, COMe}_2$) of diacetyldihydrotoxicarol], which is hydrolysed (EtOH-KOH) to (II). (II) is best

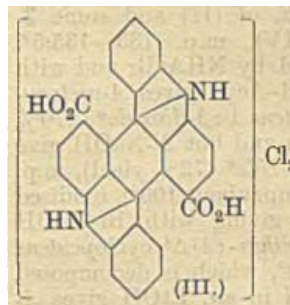
prepared from dihydrotoxicarol and Na-Hg in $\text{C}_6\text{H}_6\text{--EtOH}$; it is converted by EtOH-HCl into dehydrodihydrotoxicarol. (I), Ac_2O , and NaOAc give acetyldihydrotoxicarol, the formation of which involves acetylation of C_7OH and elimination of H_2O between C_7OH and C_8H . (IV) is produced from (I) and EtOH-HCl.

H. B.

Oxygen and sulphur analogues of antidiperidibenzocoronenequinone and attempted preparation of the nitrogen analogue, di-imidohetero-coerdianthrone. R. SCHOLL, O. BOTTGER, and L. WANKA [with, in part, H. HAHLE and H. BEHER] (Ber., 1934, 67, [B], 599—610; cf. A., 1932, 617, 731).—Treatment of 4:8-diphenoxyanthraquinone-1:5-dicarboxylic acid with $\text{Ac}_2\text{O} + \text{conc. H}_2\text{SO}_4$ gives (?) 4:8-diphenoxyanthraquinol-1:5-dicarboxylactone, whereas it is transformed by AlCl_3 or NaCl-AlCl_3 into chlorinated products, which after removal of Cl by $\text{Na}_2\text{S}_2\text{O}_4$ give heterocoerbiozene-1:5-dicarboxylic acid (I), m.p. about 350° after darkening at about 250°. (I) is transformed by conc. H_2SO_4 at



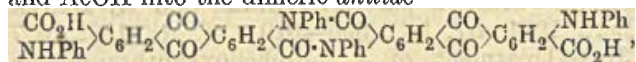
100° into 4:3'-8:3'-dioxidohetero-7':7'-coerdianthrone (II, R=O), which chars when heated and is reduced by $\text{NH}_3\text{--Na}_2\text{S}_2\text{O}_4$ to 7':7'-dihydroxy-4:3'-8:3'-dioxidoheterocoerdianthrone. Similarly, 4:8-diphenylthiolanthraquinone-1:5-dicarboxylic acid and AlCl_3 at 135—140° afford a partly chlorinated heterocoerbiothiene-1:5-dicarboxylic acid, trans-



formed by successive treatment with conc. H_2SO_4 at 100° and $\text{NaOH--Na}_2\text{S}_2\text{O}_4$ into 4:3'-8:3'-disulphidohetero-7':7'-coerdianthrone (III) (cf. II, R=S). (III) is reduced by $\text{NH}_3\text{--Na}_2\text{S}_2\text{O}_4$ to 7':7'-dihydroxy-4:3'-8:3'-disulphidoheterocoerdianthrone. 4:8-Dichloro-1:5-diamino- (IV) is converted by KOH and PhOH

at 160—170° into 4:8-diamino-1:5-diphenoxyanthraquinone, m.p. 282° after softening. 1:4:5:8-Tetraphenoxanthraquinone, m.p. 234—235°, is derived from the 4:8-dichloro-1:5-dinitro-compound, KOH, and PhOH at 150°. (IV) is transformed by boiling NH_2Ph , KOAc, and a little Cu powder into 1:5-diamino-4:8-dianilinoanthraquinone, m.p. 330°. 4:8-Dianilino-1:5-dicyanoanthraquinone, m.p. about 360°, similarly prepared from the 4:8-dichloro-1:5-dicyano-compound, is converted by 70% H_2SO_4 at 150—160° into the acridine derivative, $\text{C}_{26}\text{H}_{14}\text{N}_2$, in small yield. 4:8-Di-p-toluidino-1:5-dicyanoanthraquinone, m.p. about 365°, and the

acridine compound, $C_{28}H_{18}N_2$, are described. 1:5-Diamino- and SO_2Cl_2 in boiling C_6H_6 give 2:4:6:8-tetrachloro-1:5-diamino-anthraquinone, m.p. $<360^\circ$, whence 2:6-dichloro-1:5-diamino-4:8-dianilino- and -4:8-di-p-toluidino-anthraquinone. 2:4:6:8-Tetrachloro-1:5-dicyano-, 2:6-dichloro-4:8-dianilino-1:5-dicyano-, and 2:6-dichloro-4:8-di-p-toluidino-1:5-dicyano-anthraquinone are described. 4:8-Dianilino-anthraquinone-1:5-dicarboxyl chloride, m.p. 280—290°, from the acid (V) and PCl_5 in boiling C_6H_6 is converted by the successive action of boiling $PhNO_2$ and $AcOH$ into the dimeric anilide



m.p. 330—335° after softening. (V) and $AlCl_3$ at 145° afford 1:5-dicarboxycoerbiamidinium dichloride (VI), from which the free base is obtained by treatment with NH_3 . H. W.

Cyclic sulphones derived from butadienes.

H. J. BACKER and J. STRATING (Rec. trav. chim., 1934, 53, 525—543).— $[CH_2:CMc]_2$ and SO_2-Et_2O at 100° give a 60% yield of 3:4-dimethylthia- Δ^3 -pentene 1:1-dioxide (3:4-dimethyl-2:5-dihydrothiophen 1:1-dioxide) (I), m.p. 135°, stable to $KOH-EtOH$ in ultra-violet light and to K in Et_2O . (I) with Br in CCl_4 gives the dibromide (II), m.p. about 215°, reduced by $Zn-AcOH$ to (I) and hydrolysed by boiling H_2O to trans-3:4-dihydroxy-3:4-dimethylthiacyclopentane 1:1-dioxide (III), m.p. 175°, rhombic, $a:b:c=0.942:1:1.387$ (Ac_2 derivative, m.p. 138°). (I) with cold, aq. $KMnO_4$ gives the cis-form of (III), $+0.5H_2O$, m.p. 121.5—122.5°, monoclinic, $a:b:c=2.660:1:1.4650$, $\beta=69^\circ 34'$ (anhydride, m.p. 145°; Ac_2 derivative, $+1.5H_2O$, m.p. 92°). (I) with Cl_2-AcOH gives the 3:4- Cl_2 , m.p. 265° (decomp.), and 3-chloro-4-acetoxy-derivatives, m.p. 120—121°, the latter being also obtained by $NHAcCl$ in $AcOH$ at 100°. C_2H_4 and Cl_2-AcOH gives similarly CH_2Cl-CH_2-OAc , b.p. 143—145°. (I) and $Br-AcOH$ give 80% of (II) and some 3-bromo-4-acetoxy-derivative (IV), m.p. 133—135.5°. (IV) is obtained in 50% yield by $NHAcBr$ and with $BaCO_3-H_2O$ or $KOAc-AcOH-Ac_2O$ gives 4-acetoxy-3:4-dimethylthia- Δ^2 -cyclopentene 1:1-dioxide* (70% yield), m.p. 102—103°. (II) and hot $N-NaOH$ give 3:4-dimethylthiophen 1:1-dioxide* (72% yield), m.p. 107° ($HgCl_2$ compound, decomp. about 100°), oxidised by $KMnO_4$ to $AcOH$ and giving with $Br-AcOH$ (?)2:3-dibromo-3:4-dimethylthia-(?) Δ^4 -cyclopentene 1:1-dioxide*, m.p. 158—159°, which is decomposed by hot H_2O and with KCN in aq. $EtOH$ gives ?-hydroxy-?-cyano-3:4-dimethylthia-(?) Δ^2 -cyclopentene 1:1-dioxide, m.p. 207°. Methylthylpinacone and a little hot 20% H_2SO_4 give a 75% yield of $[CHMc:CMc]_2$, which with SO_2-Et_2O at 105° gives 2:3:4:5-tetramethylthia- Δ^3 -cyclopentene 1:1-dioxide (V), m.p. 58—59°, stable to aq. SO_2 at 150°, which with aq. HBr gives the 3:4-hydrobromide, m.p. 155° (decomp.), and with $Br-AcOH$ the 3:4-dibromide, m.p. 137° (decomp.); this is decomposed by hot H_2O , reduced by $Zn-AcOH$ to (V), and with $N-NaOH$ at 100° gives 2:3:4:5-tetramethylthiophen 1:1-dioxide*, m.p. 93—95°, unstable, which with $Br-AcOH$ gives the (?)2:3-dibromide*, m.p. 145—146° (decomp.) (?)125—126°).

Diethylpinacone and alum at 140° give $\alpha\delta$ -dimethyl- $\beta\gamma$ -diethylbutadiene (VI), b.p. 158—163°, yielding with maleic anhydride 1:4-dimethyl-2:3-diethyl- Δ^2 -tetrahydrophthalic anhydride, m.p. 90—91°, with naphthaquinone 1:4-dimethyl-2:3-diethyl-2:4:13:14-tetrahydroanthraquinone (VII), m.p. 91—92°, and 1:4-dimethyl-2:3-diethylanthraquinone, m.p. 152—153° [also obtained from (VII) by air in $KOH-EtOH$], and with SO_2-Et_2O at 100° 2:5-dimethyl-3:4-diethylthia- Δ^3 -cyclopentene 1:1-dioxide, m.p. 145° [(?)3:4-dibromide, m.p. 106° (decomp.) after softening at about 90°]. Pinacolin and $MgEtBr$ give $CMcEtBu^*OH$, b.p. 149—152°, m.p. -20° , which, when distilled with a drop of H_2SO_4 , gives impure $CHMc:CMcBu^*$; this with Br in CS_2 gives a mixture of dibromides, passing by distillation at 25 mm. into nearly pure tert.-butylbutadiene, b.p. 104—106°, whence are obtained 5-tert.-butyl- Δ^5 -tetrahydrophthalic anhydride, m.p. 123.5—124° (corresponding acid, m.p. 132—133°), 2-tert.-butylanthraquinone, m.p. 104—104.5°, and its 1:4:13:14-tetrahydro-derivative, m.p. 89.5—90°, and 3-tert.-butylthia- Δ^3 -cyclopentene 1:1-dioxide, m.p. 82—83°, which does not add Br and with $KOH-EtOH$ in ultra-violet light gives an isomeride, m.p. 96—97°. $CPhMeEtOH$ and alum at 130—140° give a 64% yield of β -phenyl- Δ^2 -butene (containing some Δ -isomeride), which with Br in CCl_4 gives the $\beta\gamma$ - (and some $\alpha\beta$ -)dibromide, which with hot $KOH-EtOH$ gives a mixture of bromo- β -phenylbutenes, decomposed at 380°/20 mm. to β -phenylbutadiene, b.p. 58—59°/9 mm. This yields 5-phenyl- Δ^5 -tetrahydrophthalic anhydride, m.p. 105—105.5° (corresponding acid, m.p. 214°), 2-phenylanthraquinone and its 1:4:13:14-tetrahydro-derivative, m.p. 142.5—143.5°, and 3-phenylthia- Δ^3 -cyclopentene 1:1-dioxide (VIII), m.p. 132.5—133.5°. (VIII) gives an isomeride, m.p. 166—167°, and, rapidly in $AcOH$ but slowly in CS_2 , the 3:4-dibromide, m.p. 147° (decomp.), decomposed by hot H_2O . (VIII) with cold $KMnO_4$ gives 3:4-dihydroxy-3-phenylthiacyclopentane 1:1-dioxide, m.p. $+0.5H_2O$, 109—110°, anhyd., 134—135°, which with Ac_2O and a drop of H_2SO_4 forms 4-acetoxy-3-phenylthia- Δ^2 -cyclopentene 1:1-dioxide, m.p. 158—159°. γ -Hydroxy- $\beta\gamma$ -ditert.-butyl- Δ^2 -butene with hot $H_2C_2O_4$ gives a very poor yield of $\beta\gamma$ -ditert.-butylbutadiene, which affords 3:4-ditert.-butylthia- Δ^3 -cyclopentene 1:1-dioxide, m.p. 69—70°. $\beta\gamma$ -Diphenyl- and β -chloro- γ -methyl-butadiene yield similarly 3:4-diphenyl-, m.p. 183—184°, and 4-chloro-3-methylthia- Δ^3 -cyclopentene 1:1-dioxide, m.p. 120—120.5°, respectively. The formulæ assigned to substances marked * above are, however, not in accord with products of ozonolysis. R. S. C.

Synthesis of *pp'*-diphenylene disulphide. V. C.



PAREKH and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 95—100).— p - $C_6H_4(SH)_2$ (improved prep. described) and $EtOH-FeCl_3$ give an amorphous product, $(C_6H_4S_2)_n$, m.p. $>300^\circ$, which with Cu at 300° gives traces of a compound, $C_{12}H_8S_2$, m.p. 148°, which is unaffected by $Zn+HCl$ and is considered to be (I). H. B.

Action of acetic anhydride on α -methylamino-isobutyric acid. R. E. STEIGER (Helv. Chim. Acta, 1934, 17, 555—563).—Acetylation of $\text{NHMe} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ (I) (improved prep.) with Ac_2O in AcOH is complicated by interaction of the products (details tabulated). The *N*-Ac derivative (II), sinters 181° , m.p. 184° (corr., decomp.; initial bath temp. 179°), of (I) [optimum yield 40% of (I) reacting] by cyclisation and loss of H_2O affords $\text{CO} \begin{array}{c} \diagup \text{O} \\ \text{CMe}_2 \text{NMe} \end{array} \text{C} \cdot \text{CH}_2$ which condenses ($-\text{H}_2\text{O}$) with (II) to give α -(3-keto-1:2:2:5-tetramethyl-2:3-dihydropyrrole-4-carboxymethylamido)-isobutyric acid, $\text{NMe} \cdot \text{CMe}_2 \cdot \text{CO} \begin{array}{c} \diagup \text{O} \\ \text{CMe} \cdot \text{CO} \end{array} \text{C} \cdot \text{CO} \cdot \text{NMe}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ (III), m.p. 206° (corr., decomp.; bath at 200°), (optimum yield 8.7%), hydrolysed by H_2O at 100° to (I), 3-keto-1:2:2:5-tetramethyl-2:3-dihydropyrrole, and CO_2 . With Ac_2O (II) does not give (III), (I) being the only cryst. material isolated. Mechanisms are given. J. W. B.

Photopyridine reaction. I. F. FEIGL. II. H. FREYTAG (J. pr. Chem., 1934, [iii], 139, 343, 343—344).—Polemic (cf. this vol., 303). R. S. C.

Isomerisation products of pyridine salts of unsaturated acids. H. LOHAUS (J. pr. Chem., 1934, [ii], 139, 289).—The $\text{C}_5\text{H}_5\text{N}$ salts of piperonylpropargylenemalonic (A., 1928, 1005) and cinnamylidenecyanoacetic acids isomerise (cf. A., 1933, 1169). $\text{C}_5\text{H}_5\text{N}$ salts of similar acids will probably isomerise if the time of reaction is sufficiently long. R. S. C.

β -Hydroxyphenylethylpyridinium chloride and 1- β -hydroxyphenylethyl-2-pyridone. J. A. GAUTIER (Compt. rend., 1934, 198, 1430—1432).—Styrene chlorohydrin combines with $\text{C}_5\text{H}_5\text{N}$ at 120° to form β -hydroxy- β -phenylethylpyridinium chloride, m.p. 210 — 212° (decomp.). This is decomposed at 150° with formation of COPhMe , and is oxidised by $\text{K}_3\text{Fe}(\text{CN})_6$ to 1- β -hydroxy- β -phenylethyl-2-pyridone, m.p. 127° . E. W. W.

Synthesis of pyridiniummethanols by a novel aldehyde condensation. I. F. KROHNKE [with K. FASOLD] (Ber., 1934, 67, [B], 656—667).—The compound obtained by the action of PhCHO and $\text{KOH} \cdot \text{EtOH}$ on phenacylpyridinium bromide (I) is identified as 1- β -hydroxy- β -phenylethylpyridinium bromide (II) (“ α -phenyl- β -pyridiniumbromide-ethanol”), since oxidation of the perchlorate with hot $\text{CrO}_3 \cdot \text{H}_2\text{SO}_4$ gives quantitatively 1-phenacylpyridinium perchlorate. The presence of OH is established by the isolation of an *Ac* derivative [perchlorate, m.p. (vac.) 142 — 145° after softening at 138°]. Catalytic reduction of (I) affords (II) in small amount. (II) is obtained from $\text{OH} \cdot \text{CHPh} \cdot \text{CH}_2\text{Br}$ (improved prep.) and $\text{C}_5\text{H}_5\text{N}$. Hydrogenation of (II) in H_2O leads to 1- β -hydroxy- β -phenylethylpiperidine, m.p. 68.5 — 69.5° (hydrobromide, m.p. 167 — 168° ; perchlorate, m.p. 133 — 134° ; picrate, m.p. 137.5° after softening at 135° ; *Ac* derivative, m.p. 207 — 208° , and its perchlorate). Complete hydrogenation of (II) at 50° (PtO_2 -gum arabic- H_2O) yields 1- β -hydroxy- β -cyclohexylethylpiperidine [hydrobromide, m.p. 230 — 232° after softening at 227° ; hydrochloride, m.p. 240 — 241° (decomp.)

after softening at 238° ; *Ac* derivative, m.p. 218 — 219°]. 1- β -hydroxy- β -phenylethylquinolinium bromide, m.p. 185° (or, $+1\text{H}_2\text{O}$, m.p. 112 — 113.5°) (corresponding perchlorate, m.p. 202° after softening at 198°), and 2- β -hydroxy- β -phenylethylisoquinolinium bromide, m.p. 170 — 172° after softening at 160° (or $+1\text{H}_2\text{O}$, m.p. 110 — 112°) (corresponding perchlorate), are derived from the appropriate base and $\text{OH} \cdot \text{CHPh} \cdot \text{CH}_2\text{Br}$. Condensation of (I) with the appropriate aldehyde in $\text{H}_2\text{O} \cdot \text{EtOH}$ containing NaOH yields the following 1- β -hydroxy- β -phenylethylpyridinium salts with substituents in the Ph nucleus: *o*- NO_2 -, bromide, m.p. 222.5° after softening at 221° ; *p*- NO_2 -, bromide, m.p. 270 — 272° (decomp.); *o*- Cl -, bromide, m.p. 275° (decomp.); *m*- Cl -, bromide, m.p. 213 — 214° , and perchlorate, m.p. 167° ; *p*- Me -, bromide, m.p. 212.5° after softening at 210° ; *p*- Pr^3 -, perchlorate, m.p. 115 — 117° ; *p*- OMe -, bromide, m.p. 180 — 181° , and perchlorate; *m*- OMe -, bromide, m.p. 165 — 166° ; 3:4-(OMe) $_2$ -, bromide, m.p. 180° ; 3:4- O_2CH_2 -, bromide, decomp. 147° . 1- β -Hydroxy- δ -phenyl-*n*-butyl-, m.p. 145° after softening at 142° , γ -phenyl-*n*-propyl-, m.p. 206 — 207° after softening at 205° , γ - γ -trichloro-*n*-propyl-, decomp. 220 — 222° , *n*-octyl-, m.p. 111 — 113° , and *furyl* (III)-, m.p. 215.5° , γ -pyridinium bromide and the perchlorate corresponding with (III) are described. $\text{C}_5\text{H}_5\text{N} \cdot \text{EtBr}$ and PhCHO yield the stereoisomeric β -hydroxy- β -phenyl- α -methyl-ethylpyridinium bromides, m.p. 199 — 200° and m.p. 186° after softening above 180° (corresponding perchlorates, m.p. 181 — 182° after softening and m.p. 180 — 181° after softening at 156° , respectively). 1-Benzylpyridinium bromide, m.p. 89.5 — 91° , and PhCHO give 1- β -hydroxy- α - β -diphenylethylpyridinium bromide, m.p. 234 — 235° after softening at 180° . $\text{CH}_2\text{Ph} \cdot \text{CH}_2\text{Br}$ and $\text{C}_5\text{H}_5\text{N}$ when heated yield 1- β -phenylethylpyridinium bromide, m.p. 126° (corresponding iodide, thiocyanate, and perchlorate, m.p. 140 — 142° after softening at 138°), which with PhCHO affords 1- β -hydroxy- α -benzyl- β -phenylethylpyridinium perchlorate, m.p. 158 — 160° . (I) and $\text{Zn} \cdot \text{AcOH}$ yield COMePh . Triethylphenacylammonium bromide, m.p. 150 — 151° (corresponding perchlorate, m.p. 116 — 117°), appears unaffected by PhCHO . Similarly, PhCHO does not appear to react with 1-methylpiperidine hydrobromide, m.p. 182 — 184° (corresponding picrate, m.p. 145 — 150° to a turbid liquid), or with ethylenedipyridinium bromide, m.p. 295° (decomp.) (corresponding perchlorate)].

H. W.

Preparation of pyridine-2-carboxylamide from 2-bromopyridine. W. R. BRODE and C. BREMER (J. Amer. Chem. Soc., 1934, 56, 993—994).—Pyridine-2-carboxylamide (25%), m.p. 106.3 — 106.8° (corr.) (lit. 103.5°), and a little of the free acid are obtained from 2-bromopyridine (I), aq. KCN , and $\text{Cu}(\text{CN})_2$ at 175° . 2-Cyanopyridine could not be prepared from (I) by essentially Craig's method (this vol., 303).

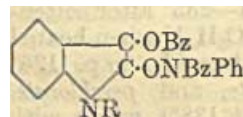
H. B.

Synthesis of medicinal products. VII. Theory of laxatives. II. H. P. KAUFMANN and K. WULZINGER (Arch. Pharm., 1934, 272, 481—502).—By fusion of *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ with the appropriate hydroxydiphenyl and ZnCl_2 are prepared: *oo'*-diphenyl-[bis-(2-hydroxy-4-diphenyl)]-, m.p. 272° (*Ac* $_2$ derivative), and *oo'*-di-*o*-hydroxyphenyl- [bis-(2:2'-dihydr-

oxy-4-diphenyl)-] (Ac_4 derivative), -phenolphthalein [-phthalide]. Similarly from isatin (I) are obtained 3:3-di-(2-hydroxy-4'-diphenyl)-, sinters 110—120° ($OO-Ac_2$, sinters 100°, Ac_3 , and Bz_3 , sinters 100°, derivatives); 3:3-bis-(2:2'-dihydroxy-4-diphenyl)- (Ac_5 derivative, sinters 110—120°); 3:3-di-(4-hydroxy-3-benzylphenyl)isatin ($OO-Ac_2$, sinters 100°, Ac_3 , sinters 70—80°, and Bz_3 , sinters 60—70°, derivatives). Similar condensations with *N*-benzylisatin [from (I), $NaOMe$, and CH_2PhCl] afford 3:3-di-*p*-hydroxyphenyl-, m.p. 227° (Ac_2 and Bz_2 , sinters 100—110°, derivatives), 3:3-di-(2-hydroxy-4-diphenyl)-, sinters 100° (Ac_2 , sinters 100—110°, and Bz_2 , derivatives), 3:3-bis-(2:2'-dihydroxy-4-diphenyl)- (Ac_4 , m.p. 110—115°, and Bz_4 derivatives), and 3:3-di-(4-hydroxy-3-benzylphenyl)-1-benzylisatin (Ac_2 derivative). The laxative properties of these derivatives are discussed in relation to structure and solubility.

J. W. B.

Constitution of the isatides. R. STOLLE and M. MERKLE (J. pr. Chem., 1934, [ii], 139, 329—337).—The following and other reactions favour the pinacone structure for isatides. 1-Phenyldioxindole (I), m.p. 132° [best obtained from 1-phenylisatin (II) and $Zn-EtOH-aq. SO_2$], with 3-acetyl-1-phenyldioxindole (III) and a few drops of piperidine in dry $EtOH$ give 3-acetyl-1:1'-diphenylisatide (IV), m.p. about 180° (variable). (II) and hot, aq. $Na_2S_2O_4$ give 1:1'-diphenylisatide (V), m.p. 195° [Ac_2 derivative, m.p. 221°, also obtained from (IV)], also obtained from (II) and (I). (I) and $BzCl$ in C_5H_5N give a substance (VI) ($R=Ph$), m.p. 184°, hydrolysed by hot 2*N*- HCl to 3-benzoyl-1-phenyldioxindole (VII), m.p. 137°.



(VI.)

(VII) and (II) give 3-benzoyl-1:1'-diphenylisatide, m.p. 172°, giving with $BzCl-C_5H_5N$ the 3:3'- Bz_2 derivative, m.p. 254°, also obtained similarly from (IV). 1-Methyldioxindole (VIII), best obtained by Zn dust- $EtOH-aq. SO_2$, and Ac_2O in CO_2 give the 3- Ac derivative, m.p. 141°. (VIII) and 1-methylisatin (IX) give 1:1'-dimethylisatide (X), m.p. 174°. 3-Acetyl-1-methyldioxindole and (IX) give 3-acetyl-1:1'-dimethylisatide, m.p. about 160° (decomp.), which with Ac_2O gives the 3:3- Ac_2 derivative, m.p. 220°, also obtained from (X). (VIII) and $BzCl-C_5H_5N$ give the substance (VI) ($R=Me$), m.p. 174°, and 3-benzoyl-1-methyldioxindole, m.p. 115° [also obtained from (VI) ($R=Me$) by hot dil. HCl]. (I) and (IX) give 1-phenyl-1'-methylisatide, m.p. 134° (decomp.) [3:3- Ac_2 (XI), m.p. 241°, and 3- Ac (XII) derivative, m.p. about 187° (decomp.) (variable)]. (XII) gives (XI) by further acetylation and is also obtained from (III) and (IX). (XII) and 3'-acetyl-1-phenyl-1'-methylisatide do not give a depression of the m.p.

R. S. C.

Germicidal and antiseptic activities of some derivatives of 8-hydroxyquinoline. E. MONESS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 228—232).—Chlorination of 5:8-dihydroxyquinoline (I) (Et_1 ether (II), m.p. 96—98°; Bu^a_1 ether (III), m.p. 92°) by SO_2Cl_2 in glacial $AcOH$ yields a mixture of Cl_1 - and Cl_2 -derivatives, the germicidal and bacteriostatic actions (IV) of which are only

moderate. (II) and especially (III) exhibit enhanced (IV). A. E. O.

[Comparison of the dimethylquinoline from aniline, isobutaldehyde, and methylal with 2:3-dimethylquinoline and the relationship of 2:3-dimethylquinoline to benzil.] G. ROHDE (Ber., 1934, 67, [B], 715; cf. this vol., 533).—A correction of crystallographic data. H. W.

New synthesis of 3-alkylquinolines. G. DARZENS and M. MEYER (Compt. rend., 1934, 198, 1428—1429).—A modification of the Skraup synthesis, employing substituted glycerols of type $OEt-CH_2-CR(OH)-CH_2-OEt$. When $R=H$, Me , Et , and Bu^i , the products are, respectively, quinoline, and 3-methyl-, 3-ethyl- (picrate, new m.p. 192°), and 3-isobutyl-quinoline, b.p. 114°/2 mm. (picrate, m.p. 160°). E. W. W.

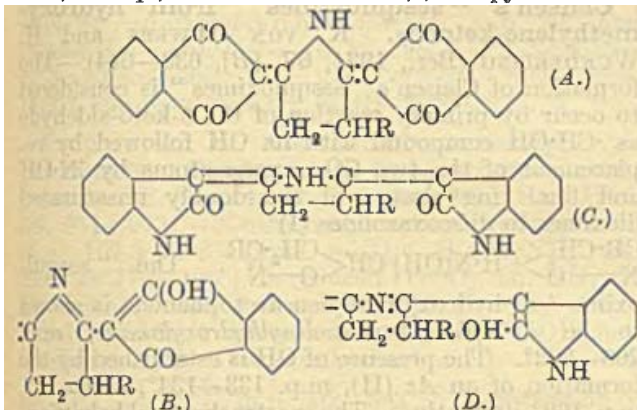
Oxidising action of selenium dioxide. L. MONTI (Atti R. Accad. Lincei, 1933, [vi], 18, 505—507).—In $PhMe$, SeO_2 readily oxidises 2-methylquinoline to quinoline-2-aldehyde. T. H. P.

Antiseptic properties of amino-derivatives of styryl- and anilo-quinoline. C. H. BROWNING, J. B. COHEN, K. E. COOPER, S. ELLINGWORTH, and R. GULBRANSEN (Proc. Roy. Soc., 1934, B, 115, 1—13).—A continuation of previous work (A., 1926, 1153; 1928, 1141). 6-Amino-2-methylquinoline and $CO_2Et-CH_2-CH_2-COCl$ in $CHCl_3$ (cf. A., 1932, 623) give 6-β-carbethoxypropionamido-2-methylquinoline, m.p. 155—156°, the methiodide (I), m.p. 190—192° (decomp.), of which with $p-NMe_2-C_6H_4-CHO$ in $EtOH$ and a little C_5H_5N affords 6-β-carbethoxypropionamido-2-p-dimethylaminostyrylquinoline methiodide. (I) and $p-NO-C_6H_4-NMe_2$ give 6-β-carbethoxypropionamido-2-p-dimethylaminoaniloquinoline methiodide. 6-δ-Carbethoxyvaleramido-2-methylquinoline, m.p. 93—95° (methiodide, m.p. 158—159°), and 6-δ-carbethoxyvaleramido-2-p-dimethylamino-styryl- and -anilo-quinoline methiodides are similarly prepared. 2-Aldehyde-β-naphthquinoline methochloride with m - and p - $C_6H_4(NH_2)_2$ in H_2O give the dianils, $C_{36}H_{30}N_4Cl_2$, p -Nitroso-isopropylaniline, m.p. 86°, -butylaniline (II), m.p. 60°, -phenylethylaniline (III), and -benzylaniline, m.p. 35°, are prepared as previously described (A., 1928, 1141), and condensed (no details) with 2-methylquinoline (A., 1924, i, 990). (II) and (III) are condensed (no details) with β-naphthquinaldine and p -toluquinaldine methochlorides, respectively. The antiseptic action of the above (as methochlorides) and related compounds has been investigated; previous observations (*loc. cit.*) on the effects of substituents are confirmed. H. B.

Action of acid chlorides on azines. E. BENARY (Ber., 1934, 67, [B], 708—710).—Benzaldazine and $CH_3Cl-COCl$ give -chloroacetyl-*N*-benzylidenehydrazine, m.p. 165—166°, transformed by NH_2Ph in boiling $EtOH$ into benzylidenephénylglycinehydrazide. *N*-α,β-Dibromopropionyl-*N*-benzylidenehydrazine, m.p. 135°, is similarly prepared. cycloHexanoneazine and $CH_3Cl-COCl$ in Et_2O afford 9-chloroacetyl-1:2:3:6:7:8:10:13-octahydrocarbazole, m.p. 90—91°, converted by $KOH-EtOH$ into octahydrocarbazole, m.p. 102°. 9-Acetyl-, 9-α-bromoisobutyryl-,

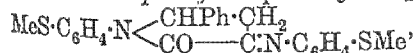
and 9-*p*-nitrobenzoyl-1:2:3:6:7:8:10:13-octa-hydrocarbazole have m.p. 73°, 130—131°, and 163—165°, respectively. H. W.

Reaction of ninhydrin [triketohydrindene] and isatin with proline and hydroxyproline. W. GRASSMANN and K. VON ARNIM (Annalen, 1934, 509, 288—303).—Triketohydrindene hydrate (I) (2.2 mols.) and proline (II) (1 mol.) in H₂O at *p*_H 7 (phosphate) give the dye (III) (A or B, R=H), m.p. 176° (decomp.), also obtained from (I) and pyrrolidine



(IV) in AcOH. (I) (1 mol.) and (II) (1 mol.) in EtOH give a compound, C₁₃H₁₁O₂N, decomp. >190°, which with (I) at *p*_H 7 affords (III). (I) and hydroxyproline (V) give a dye (A or B, R=OH), m.p. >275°. Piperidine (VI) (>2 mols.) and (I) (1 mol.) in EtOH afford a compound, C₁₉H₂₄O₂N₂, m.p. 131° (decomp.), converted by Ac₂O in boiling PhMe into a dye, C₂₃H₁₅O₄N, also obtained from (I) (2 mols.) and (VI) or piperidine-2-carboxylic acid (1 mol.) in AcOH. Isatin (2 mols.) and (II) (1 mol.) in AcOH give a dye (C or D, R=H), also obtained similarly from (IV), which is reduced (Zn, AcOH; TiCl₃) to a leuco-compound (uptake of 2H); (V) similarly affords the dye (C or D, R=OH). Absorption spectra curves of the above dyes are given. Structures are suggested for the intermediate compounds. H. B.

Influence of alkyl- and alkylene-mercaptan groups on the therapeutic activity of organic compounds. I. Methylthiolatophan. K. BRAND and E. VÖLCKER. II. 4-Methylthiol-1-phenyl-2:3-dimethylpyrazol-5-one (4-methylthiolantipyrene). K. BRAND and W. BAUSCH (Arch. Pharm., 1934, 272, 257—268, 269—273).—I. *o*- (I) and *p*- (II) Aminophenyl Me sulphide with AcCO₂H and PhCHO in boiling EtOH give, respectively, 8-, m.p. 257° (13% yield: Me, m.p. 113°, and Et, m.p. 123.5°, esters; Na+6H₂O, m.p. 102°, K+6H₂O, m.p. 125°, and Ba salts), and 6-, m.p. 224° (33% yield: Me, m.p. 125°, and Et, m.p. 94.5°, esters; Na+6H₂O, m.p. 85°, K+6H₂O, m.p. 65°, and Ba salts). -methylthiol-2-phenylquinoline-4-carboxylic acid (methylthiolatophan), the 6-compound being accompanied by a 20% yield of the 4-*p*-methylthiolanil of 4:5-diketo-2-phenyl-1-*p*-methylthiolphenylpyrrolidine,



With NH₂OH, H₂SO₄ and CCl₃·CH(OH)₂ in boiling H₂O (I) gives oximino-*o*-methylthiolacetanilide, m.p. 164°,

which could not be converted into the corresponding isatin, but which with P₂O₅ in boiling PhMe affords (?) 2-hydroxy-8-methylthiolquinoxaline,

MeS·C₆H₃ < $\begin{array}{c} \text{N}\cdot\text{CH} \\ \text{N}\cdot\text{C}\cdot\text{OH} \end{array}$, m.p. 227°; NHPh·CO·CH·N·OH similarly treated gives only a trace of an (unpurified) substance, m.p. 252° (2-hydroxyquinoxaline, m.p. 265°). Neither oximino-*p*-methoxyacetanilide, m.p. 183° (from *p*-anisidine), nor the corresponding *o*-compound gave similar products. With CO(CO₂Et)₂ in AcOH (II) gives an additive compound, m.p. 107°, converted by heating in AcOH into Et 5-methylthiol-dioxindole-3-carboxylate, m.p. 175°, converted, by heating with aq. KOH in a current of air, into 5-methylthiolisatin, m.p. 185°. The introduction of MeS lessens the physiological activity of atophan.

II. Bis-1-phenyl-2:3-dimethyl-5-pyrazolonyl 4-disulphide (Kaufmann *et al.*, A., 1924, i, 209, modified) heated with Na₂S·9H₂O and NaOH in EtOH affords the Na derivative of 4-thiolantipyrene, converted by Me₂SO₄ into 4-methylthiolantipyrene, m.p. 115°, which, although less toxic, has also a much smaller antipyretic action than antipyrene itself. J. W. B.

5-Carboxyhomophthalic acid, 6-nitrophthalide, and 6-nitrophthalimidine.—See this vol., 652.

N-Aminobarbituric acids. M. BUSCH and F. POHLMAN (Arch. Pharm., 1934, 272, 190—197).—Although CH₂(CO₂Et)₂ (I) condenses with NH₂·NH·CO·NH₂ in NaOEt-EtOH to give only [NH₂·CO·NH]₂, with NHPh·NH·CO·NH₂ (II), 3-anilinobarbituric acid, m.p. 206° [Na salt, m.p. 275° (decomp.)], is obtained, its 5-Et derivative, m.p. 94—96°, being similarly obtained from CH₂Et(CO₂Et)₂. CEt₂(CO₂Et)₂ (III) and (II) give 1-phenyl-4:4-diethylpyrazolone and phenylurazole. (I) and CH₂Ph·NPh·NH·CO·NH₂ (IV) give 3-phenylbenzylaminobarbituric acid, m.p. 194°, its 5:5-Et₂ derivative (V), m.p. 131°, being similarly obtained from (III). (I) with as.-dibenzylsemicarbazide, m.p. 157° [from N(CH₂Ph)₂·NH₂ and KCNO], and with NPh₂·NH·CO·NH₂ gives, respectively, 3-dibenzylamino-, m.p. 161°, and 3-diphenylamino-barbituric acid, m.p. 185°, and 3-methylanilino-5:5-diethylbarbituric acid, m.p. 167°, is obtained from (III) and NPhMe·NH·CO·NH₂. Only (V) has marked narcotic, but also irritant, action. J. W. B.

Reduction with lead-sodium alloy. IV. Alkyl-barbituric acids. F. FICHTER and H. STENZL (Helv. Chim. Acta, 1934, 17, 665—669).—Reduction of 5-isopropylbarbituric acid with Pb-Na in aq. AcOH or electrolytically (Pb cathode) gives 5-isopropyluracil, m.p. 288—289°. By similar reduction methods the 5-Et compound gives 5-ethylhydriouracil, m.p. 254° (lit. 274—275°), probably mixed with 5-ethyluracil. J. W. B.

Lævorotatory allantoin.—See this vol., 695.

Organic sulphur compounds. I. Action of hydrogen cyanide, ammonia, and hydrogen sulphide on saturated ketones. K. ABE (Sci. Rep. Tokyo Bunrika Daigaku, 1934, A. 2, 1—7).—COMeEt with KCN-AcOH and subsequent saturation of the solution first with NH₃ and then with H₂S gives an unstable yellow substance, m.p. 58°, which loses H₂S

when warmed with H_2O giving 5-thio-2:4-dimethyl-2:4-diethyl-2-deoxyhydantoin, m.p. 67° (cf. Gatewood *et al.*, A., 1928, 745). Similar treatment of $COPhMe$ affords α -amino- α -phenylpropionthioamide, m.p. 138° (corr.) (compound with $HgCl_2$, darkens about 180°), 5-phenyl-5-methylhydantoin, m.p. 197° (corr.), and α -imino- α -phenylpropionitrile, m.p. 218° (corr.). $COPh$, gives only dibenzhydryl disulphide, m.p. 153° (corr.). J. W. B.

Reactions of purine bases with metallic salts.

A. F. SCHUTZ and B. UMSCHWELF (Biochem. Z., 1934, 268, 326—330).—Adenine, guanine, hypoxanthine, 7-methylhypoxanthine, xanthine, theophylline, and uric acid, but not 7-methyladenine, 7-methylguanine, 7-methylxanthine, 2-chloro-7-methylpurine, 2-chloro-6-hydroxy-7-methylpurine, 1:7-dimethylhypoxanthine, and theobromine, give complex compounds with Cu . This confirms the view that formation of these compounds requires the presence of a free NH -group.

P. W. C.

Chlorophyll. XLIV. Catalytic hydrogenation in chlorophyll series. III. H. FISCHER, E. LAKATOS, and J. SCHNELL (Annalen, 1934, 509, 201—214; cf. A., 1930, 932; 1933, 1308).—Reduction (H_2 , Pd) of 10-ethoxyethylphæophorbide *a* (I) results in the absorption of 3.8 mols. of H_2 ; oxidation (atm. O_2) of the resulting leuco-compound gives phæoporphyrin a_6 Et ester Et ether, m.p. 302° , thus confirming the constitution previously assigned (A., 1933, 1308) to (I). Dihydro-10-ethoxyethylphæophorbide *a*, m.p. 175° , is obtained in 52% yield by partial reduction [H_2 (1 mol.), Pd] of (I). Reduction (PtO_2 , AcOH) of dimethylphæopurpurin 7 (II) with 1 mol. of H_2 affords a green compound (not isolated), which is oxidised (atm. O_2) to (II); 3 mols. of H_2 are absorbed on complete reduction and oxidation affords allphæoporphyrin *a*. Me_3 ester, rhodoporphyrin Me_2 ester, and 17% of dihydro-dimethylphæopurpurin 7, $C_{37}H_{42(41)}O_7N_4$, m.p. 195° . Reduction [H_2 (1 mol.), Pd, HCO_2H] of phæophorbide *b* gives 49% of dihydrophæophorbide *b* (III), $C_{35}H_{36}O_6N_4$, which when heated with C_5H_5N affords pyrodihydrophæophorbide *b*, $C_{33}H_{34(36)}O_4N_4$, m.p. 251° (*Me* ester, m.p. 244°). (III) is hydrolysed ($MeOH$ - KOH in C_5H_5N) to dihydrorhodin *g*, $C_{34}H_{36(38)}O_7N_4$, m.p. 215° (Me_3 ester, m.p. 212°). Phæophorbide *b* heated with C_5H_5N gives pyrophæophorbide *b*, $C_{35}H_{32(34)}O_4N_4 \cdot 0.5H_2O$, m.p. 232° [*Me* ester, m.p. 246° (decomp.) (oxime, m.p. $> 340^\circ$; cyanohydrin, decomp. 280° without melting)], reduced (Wolff-Kishner) to deoxophylloerythrin. The *Fe*, m.p. 197° (not sharp), and *Cu*, m.p. 200° , salts of dihydro-methylphæophorbide *a* (A., 1933, 1308) are described.

H. B.

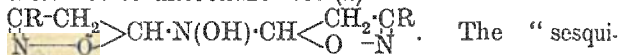
Organic minerals. III. Chlorophyll and hæmin derivatives in bituminous rocks, petrol-eums, etc.—See this vol., 629.

Relation between fluorescence and chemical constitution of benzoxazole derivatives. F. HENRICH and F. BRAUN (J. pr. Chem., 1934, [ii], 139, 338—342).—Anhyd. aminoresorcinol hydrochloride (I) and *o*- $C_6H_4Me \cdot COCl$ at 140° give the *tri-o-toluoyl* derivative, m.p. 125.5° , which at 320 — 360° gives 6-*o-toluoyl*-2-*o-tolyl*benzoxazole, m.p. 102° . Similarly

were obtained the *triphenylacetyl*, m.p. 128 — 129° , and *tri-p-toluoyl*, m.p. 178° , derivatives of (I) and 6-phenylacetyl-2-benzyl- (II), m.p. 154° , and 6-*p-toluoyl*-2-*p-tolyl*-benzoxazole, m.p. 284° after sintering from 240° . The $2-C_6H_4Me$ derivatives fluoresce (blue) as strongly as the 2-Ph compounds. The following order of intensity of fluorescence is recorded: 4:7- $Me_2 > Me$ derivatives (green; 5- $>$ 6- $>$ 7- Me) of 6-hydroxy-2-phenylbenzoxazole. (II) does not fluoresce.

R. S. C.

Claisen's "sesquioximes" from hydroxy-methylene-ketones. K. VON AUWERS and H. WUNDERLING (Ber., 1934, 67, [B], 638—644).—The formation of Claisen's "sesquioximes" is considered to occur by primary reaction of the β -keto-aldehyde as $\cdot CH \cdot OH$ compound with its OH followed by replacement of the two CO oxygen atoms by $\cdot N \cdot OH$ and final ring closure of the doubly unsaturated dioximes to diisooxazolines (I)



oxime" of hydroxymethyleneacetophenone is shown to be *di-3-phenylisooxazolinylhydroxylamine*, m.p. 200 — 202° . The presence of OH is established by the formation of an *Ac* (II), m.p. 133 — 134° , and a *Bz*, m.p. 169° , derivative. The spectrochemical behaviour of (II) accords with the presence of $CPh \cdot N$. (I, $R=Ph$) is transformed by hot conc. HCl into 3-phenylisooxazole (formed by loss of H_2O from 5-hydroxy-3-phenylisooxazoline), accompanied by some 5-phenylisooxazole due to fission and re-closure of the isooxazoline ring under the influence of the acid. Boiling KOH - $MeOH$ converts (I) into 5-amino-3-phenylisooxazole, m.p. 111° , and $BzOH$. With the cold reagent the products are NH_2Bz , a little $PhCN$ and phenylisooxazole, and 5-hydroxylamino-3-phenylisooxazoline, m.p. 108 — 109° .

H. W.

4-p-Halogenophenyl-2-methyl- and -2-ethyl-thiazoles and their derivatives. J. P. WETHERILL and R. M. HANN (J. Amer. Chem. Soc., 1934, 56, 970—971).—The following are prepared from the appropriate *p*- $Hal \cdot C_6H_4 \cdot CO \cdot CH_2Br$ and $SH \cdot CMe \cdot NH$ and $SH \cdot CEt \cdot NH$ in 95% $EtOH$: 4-*p-chlorophenyl*-2-methyl-, m.p. 122 — 123° (all m.p. are corr.) (picrate, m.p. 163° ; mercurichloride, m.p. 202 — 203° ; hydrobromide, m.p. 186 — 187°), and -2-ethyl-, m.p. 72° (picrate, m.p. 143 — 144° ; mercurichloride, m.p. 164°); 4-*p-bromophenyl*-2-methyl-, m.p. 134° (picrate, m.p. 160° ; mercurichloride, m.p. 221°), and -2-ethyl-, m.p. 86° (picrate, m.p. 143° ; mercurichloride, m.p. 177°), and 4-*p-iodophenyl*-2-methyl-, m.p. 138° (picrate, m.p. 152° ; mercurichloride, m.p. 235°), and -2-ethyl-, m.p. 99° (picrate, m.p. 148° ; mercurichloride, m.p. 188°), -thiazoles.

H. B.

Fractionation of two trisubstituted thiodiazolines (dihydrothiodiazoles). (MLLE.) A. LACOURT (Bull. Soc. chim. Belg., 1934, 43, 193—199).—Re-examination (mainly by fractional crystallisation) of the products obtained by condensation of β -(α -thionaphthoyl)- α -phenylhydrazine with β - $C_{10}H_7 \cdot CHO$ (this vol., 537) shows that the dihydrothiodiazole constitutes 56% of the product, two substances, m.p. 101 — 115° and m.p. 92° , which could not be purified also being obtained. No other compound could be

isolated from crude 3-phenyl-5- α -naphthyl-2-methyl-2:3-dihydro-1:3:4-thiadiazole (A., 1933, 839).

J. W. B.

Reactions of aldehydes and ketones : synthesis of thiodiazolines from ketones. (MLEE.) A. LACOURT (Bull. Soc. chim. Belg., 1934, 43, 206—210).—Condensation of the appropriate $\text{NHAr}\cdot\text{NH}\cdot\text{CSAr'}$ and ketone (A., 1933, 839) affords 3-phenyl-5- α -naphthyl-2:2-dimethyl-, m.p. 68°, 2:3-diphenyl-5-benzyl-2-methyl-, m.p. 120°, and - α -naphthyl-2-methyl-, m.p. 110°, 2-spirocyclopentane-3:5-diphenyl-, m.p. 94°, -5-phenyl-3-p-bromophenyl-, m.p. 79°, and -3-phenyl-5- α -naphthyl-, m.p. 98°, -2:3-dihydro-1:3:4-thiadiazole. All give colours with conc. H_2SO_4 and ppts. with aq. $\text{EtOH}\cdot\text{AgNO}_3$. J. W. B.

Preparation of N-o-aminobenzenesulphonylbenzamide. Condensation to heterocyclic compounds. E. WERTHEIM (J. Amer. Chem. Soc., 1934, 56, 971—973).—N-o-Nitrobenzenesulphonylbenzamide, m.p. 197.5—198° (from $\text{o-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}_2$ and BzCl at 170—180°), is reduced (FeSO_4 , aq. NH_3) to N-o-aminobenzenesulphonylbenzamide (I), m.p. 198—198.5°, which is converted by HCl in EtOH into 3-phenyl-1:2:4-isobenzthiadiazine 1:1-dioxide,

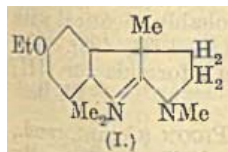
$\text{o-C}_6\text{H}_4\cdot\text{N}=\text{CPh}\cdot\text{SO}_2\cdot\text{NH}$, m.p. 302—303°. Diazotisation of (I) gives a compound, explodes violently when heated, which when heated in kerosene or H_2O , or kept over $\text{H}_2\text{SO}_4(\text{H}_2\text{O})$, affords 3-phenyl-1:4:2-benzthioxazine 1:1-dioxide (II), $\text{o-C}_6\text{H}_4\cdot\text{O}=\text{CPh}\cdot\text{SO}_2\cdot\text{N}$, m.p. 176—177°.

(II) is hydrolysed by cold aq. NaOH to o-benzoyloxybenzenesulphonamide, m.p. 178—180°, and by HCl to BzOH . H. B.

Ergine. S. SMITH and G. M. TIMMIS (Nature, 1934, 133, 579; cf. A., 1932, 759).—Ergine (I) is the amide of $\text{C}_{15}\text{H}_{15}\text{N}_2\cdot\text{CO}_2\text{H}$ (II), now prepared from (I), and its corr. formula is $\text{C}_{16}\text{H}_{17}\text{ON}_3$. Lysergic acid (this vol., 538) appears to be identical with (II).

Alkaloids of Narcissus poeticus. L. F. KOLLE and K. E. GLOPPE (Pharm. Zentr., 1934, 75, 237—239).—Narcipoeine, $\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}$, m.p. 172°, $[\alpha]_D^{25} +84.4^\circ$ [aurichloride, m.p. 131—132° (decomp.)]; picrate, m.p. 261° (decomp.); hydrochloride $+\text{H}_2\text{O}$, m.p. 271° (decomp.), $[\alpha]_D^{25} +111.2^\circ$, contains two OMe or possibly a NMe and may be identical with homolycorine (Morishima, A., 1899, i, 92). S. C.

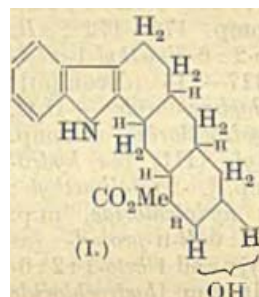
Synthesis of eserine[like substances]. II. T. HOSHINO and T. KOBAYASHI (Proc. Imp. Acad. Tokyo, 1934, 10, 99—102; cf. A., 1932, 952; 1933, 164).—Treatment of dl-dinoreserethole methiodide followed by extraction with Et_2O or of the benzoate with MeI and NaOBz affords a base, $\text{C}_{16}\text{H}_{24}\text{ON}_2$ (I), m.p. 80—81° (picrate, m.p. 140—141°). (I) with $\text{EtOH}\cdot\text{MeI}$ and picric acid gives eserethole dimethopicate, m.p. 150—151°. dl-Noreserethole with $\text{Et}_2\text{O}\cdot\text{MeI}$



(cf. this vol., 89) gives dl-noreserethole hydriodide, m.p. 156—157°, the mother-liquor on addition of alkali, extraction with Et_2O , and treatment with $\text{EtOH}\cdot\text{picric acid}$ affording the picrate, m.p. 192—193°, of

dl-eseretholemethine (II) and dl-eserethole methopicate, m.p. 184—185°. (II) with MeI and picric acid yields 5-ethoxy-3-methyl-3-dimethylaminoethyl-indolenine dimethopicate, m.p. 204—205° (cf. A., 1925, i, 292; 1932, 287). The following have been resolved (m.p. of *H d-tartrates* given): *l*- (164—165°) and *d*-dinoreserethole (166—167°), *l*- (179—180°) and *d*-dinoreseremethole (180—181°), *l*- (181—182°) and *d*-noreserethole (190—191°). F. O. H.

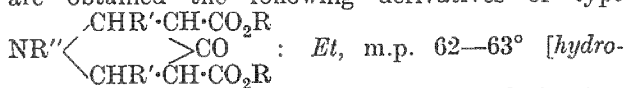
Yohimbe alkaloids. VIII. Dehydrogenation of yohimbine with lead tetra-acetate and the constitutional formula of yohimbine. G. HAHN, E. KAPPEL, and H. LUDWIG (Ber., 1934, 67, [B], 686—696).—Interaction of yohimbine (I) (1 mol.) with $\text{Pb}(\text{OAc})_4$ (II) (1 mol.) in AcOH at room temp. leaves large amounts of unchanged base and gives



dehydrohydroxyacetylyohimboic acid (III), $\text{C}_{20}\text{H}_{24}\text{O}_5\text{N}_2$, m.p. 350—355°, $[\alpha]_D^{25} +391.7^\circ (\pm 12^\circ)$ in 0.32% AcOH , transformed by $\text{MeOH}\cdot\text{HCl}$ into Medehydrohydroxy-yohimboate, m.p. 310—315°, $[\alpha]_D^{25} +348.6^\circ (\pm 12^\circ)$ in 0.13% AcOH [corresponding *Et* ester, m.p. 318—320° (decomp.)], $[\alpha]_D^{25} +368.3^\circ (\pm 12^\circ)$ in 0.22% AcOH . (III) cannot be isolated when (I) and (II) are used in

the mol. ratio 1:2, the main product (obtained in a maximal yield of 50—60% with a 1:3 ratio) being tetrahydroyohimbine, $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_2$, m.p. 248—250° (decomp.) after softening at 240°, $[\alpha]_D^{25} +229.4^\circ (\pm 10^\circ)$ in 0.266% AcOH , hydrolysed to tetrahydroyohimboic acid (IV), $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_2\cdot 2\text{H}_2\text{O}$, m.p. 230—235°, $[\alpha]_D^{25} +247.40^\circ (\pm 10^\circ)$ in 0.157% AcOH [*K* salt; hydrochloride $\text{C}_{20}\text{H}_{20}\text{O}_3\text{N}_2\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$; nitrate; *Et* ester, m.p. 294—297° (decomp.)], $[\alpha]_D^{25} +239.1^\circ (\pm 12^\circ)$ in 0.45% AcOH , and its perchlorate]. Treatment of (IV) with KOH in boiling amyl alcohol gives harman and *m*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ in good yield, thus establishing the structure of (I). Treatment of (I) with 6, 7, 8, or 9 mols. of (II) gives ill-defined results. H. W.

“Open” ecgonine and tropine. C. MANNICH (Arch. Pharm., 1934, 272, 323—359).—A series of “open” analogues of tropine derivatives in which the 2 CH_2 groups of the 5-membered ring are replaced by Me are prepared, the true analogues of the ring derivatives having the *cis*-configuration, which is meso, whereas the *trans*-derivatives are resolvable. By condensation of $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{R})_2$, $\text{R}'\cdot\text{CHO}$, and $\text{NH}_2\text{R}''$, HX , usually in slightly acid solution, are obtained the following derivatives of type



1:2:6-trimethyl-; *Me* 4-keto-1-benzyl-, m.p. 97—98° (nitrate, decomp. 130—133°), -1- β -phenylethyl- (as hydrochloride, decomp. 122—124°), and -1- β -carbo-phenoxyethyl-, m.p. 92° (using β -aminoethyl benzoate hydrochloride, m.p. 144—145°), -2:6-dimethyl-piperidine-3:5-dicarboxylate. Reduction of (I) with Na-Hg gives *Et* 4-hydroxy-1:2:6-trimethylpiperidine-3:5-dicarboxylate as its hydrochloride, m.p. 133—134°, the corresponding *Me* ester, b.p. 170—175°/1 mm., m.p. 69° (perchlorate, m.p. 232°; hydrochloride of the Bz, m.p. 176—177°, *p*-nitrobenzoyl, m.p. 161°, and *p*-aminobenzoyl, m.p. 175°, derivatives), being similarly obtained from (II), and hydrolysed to the acid, m.p. 240—242° (decomp.). Use of $\text{CO}_2\text{Me}\cdot\text{CH}\cdot\text{C}(\text{OK})\cdot\text{CH}_2\cdot\text{CO}_2\text{K}$ in the original synthesis gives the corresponding 3-monocarboxylic acid derivatives and thus are obtained: *Me* 4-keto-2:6-dimethyl- (as hydrochloride, decomp. 172—173°; Bz derivative, m.p. 126°); 4-keto-2:6-dimethyl-1-allyl- [as hydrochloride + H_2O , m.p. 117—118° (decomp.)]; 4-keto-1-carbethoxymethyl- (as hydrochloride + H_2O , m.p. 96—97°), -1-benzyl- (as hydrochloride, decomp. 157—158°), and -1- β -phenylethyl- (III) [as hydrochloride, m.p. 126—127° (decomp.)], -2:6-dimethyl-; 4-keto-1-methyl-2:6-diethyl- [as hydrochloride, m.p. 144—145° (decomp.)], and -2:6-di-*n*-propyl- [as nitrate, m.p. 127—128° (decomp.)]; and 4-keto-1:2:6-trimethyl- (IV), b.p. 127—128°/16 mm. [hydrochloride + H_2O , m.p. 105—106°; *oxime*, m.p. 153—155° (decomp.); *methiodide*, decomp. 116—119°] [resolved by *d*-tartaric acid into the hydrochloride + H_2O , m.p. 106°, $[\alpha]_D^{20}$ -17.0° (*d*-tartrate, m.p. 113—115°), of the *l*-, and the hydrochloride + H_2O , m.p. 106°, $[\alpha]_D^{20}$ +17.0° (*d*-tartrate, m.p. 145—146°), of the *d*-base], -piperidine-3-carboxylate. Reduction of (III) with Pt-black- H_2 in H_2O gives the hydrochloride, m.p. 195—196°, of *Me* 4-hydroxy-1- β -phenylethyl-2:6-dimethylpiperidine-3-carboxylate (*p*-nitrobenzoate, m.p. 133°). Reduction of (IV) with $\text{PtO}_2\text{-H}_2$ gives a mixture of the *cryst.* α -form (V) (ecgonine analogue), m.p. 96°, and a liquid β -form (ψ) (VI), b.p. 135—137°/11 mm. (*picrate*, m.p. 154—155°) (partly resolved by bromocamphorsulphonic acid to give the hydrochloride, decomp. 221—222°, $[\alpha]_D^{20}$ -66.6°, of the *l*-form), of the *Me* ester of, respectively, α -, m.p. 198—200° (decomp.), and β - + H_2O (ψ), m.p. 246—248° (decomp.), -dl-4-hydroxy-1:2:6-trimethylpiperidine-3-carboxylic acid, which result from hydrolysis. The α -form is converted into the β - (ψ) form by heating with 33% aq. KOH. With BzCl (V) gives its Bz derivative (cocaine analogue), m.p. 74—75°, resolved by *d*-tartaric acid to the oily *l*-base (*d*-tartrate + $2\text{H}_2\text{O}$, m.p. 103—104°, $[\alpha]_D^{20}$ -19.94° in MeOH) and the *d*-base (*d*-tartrate, + $3\text{H}_2\text{O}$, m.p. 82—84°, $[\alpha]_D^{20}$ +43.42° in MeOH), whereas (VI) similarly affords its Bz derivative as the hydrochloride, decomp. 204°, the hydrochloride, m.p. 189—190°, $[\alpha]_D^{20}$ +50.8°, of the *d*-base being obtained by benzoylation of the bromocamphorsulphonate, m.p. 155°, of (VI). By HCl hydrolysis of the appropriate 3-carbo-
o esters are obtained: 4-keto-2:6-dimethyl-1-allyl- (*oxime*, m.p. 100°), and 4-keto-2:6-dimethyl-, b.p. 81—82°/12 mm. [hydrochloride, m.p. 204—205° (decomp.)], -piperidine. *cis*-meso-4-Keto-1:2:6-trimethylpiperidine (VII), b.p. 86°/14 mm. [hydrobrom-

ide, m.p. 174—175° (decomp.); *hydriodide*, m.p. 169—170°; *perchlorate*, m.p. 166—168°; *picrate*, m.p. 163—164° (decomp.); *methiodide*, m.p. 180° (decomp.); and *oxime*, m.p. 92°, is obtained by hydrolysis of (II) or (IV), or by condensation of $\text{CO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, NH_2Me , HCl, and MeCHO, in which case some of the *trans*-dl-form (VIII), b.p. 86°/14 mm. [*oxime*, m.p. 93—94°, not free from (VII)], is also obtained. Reduction of (VII) (Na-Hg or electrolytic) gives only *cis*-meso-4-hydroxy-1:2:6-trimethylpiperidine (IX), b.p. 105—107°/11 mm. (stable to NaOC_2H_5 , and therefore the ψ -form) [hydrochloride, m.p. 267—268°; *hydrobromide*, m.p. 265—266°; hydrochloride of Bz derivative, m.p. 238°; *tropate*, m.p. 98° (nitrate, m.p. 163—164°)], but with Zn-HI some *cis*-1:2:6-trimethylpiperidine, b.p. 50—55°/12 mm. (platinichloride, m.p. 174—175°), is also obtained. Reduction of (VIII) gives (IX) and *trans*-dl-4-hydroxy-1:2:6-trimethylpiperidine, m.p. 70° (hydrochloride, m.p. 185°; hydrochloride of Bz derivative, m.p. 165—168°), imperfectly resolved ($[\alpha]_D^{20}$ +15°) by bromocamphorsulphonic acid. The physiological properties of the tropine analogues are recorded.
J. W. B.

Lupin alkaloids. IX. Sparteine. IV. K. WINTERFELD and C. RAUCH (Arch. Pharm., 1934, 272, 273—290).—Dehydrosparteine (I), b.p. 110—112°/1 mm., $[\alpha]_D^{20}$ -124° in EtOH [aurichloride + $2\text{H}_2\text{O}$ and anhyd., m.p. 158° (decomp.); *picrate*, m.p. 147°; *platinichloride* + $1.33\text{H}_2\text{O}$ and anhyd., m.p. 247—248°], as previously prepared is contaminated with didehydrosparteine (II) from which it is separated by Et_2O extraction from H_2O solution and distillation in a high vac., all in H_2 . Catalytic reduction of (I) (+2H) regenerates the original sparteine (III). (II) is also a mixture, separated by fractional crystallisation of the H sulphate into *cryst.* α -didehydrosparteine (IV), m.p. 106—107° (purified by sublimation), $[\alpha]_D^{20}$ -647° in C_6H_6 [H sulphate, m.p. 253°; sulphate; *perchlorate*, m.p. 257° (decomp.); *picrate*, m.p. 164°; *reineckate*, m.p. 174—175°; *aurichloride*, m.p. 156° (decomp.); *platinichloride*, m.p. 242—243°], and from the mother-liquor, oily β -didehydrosparteine (V), $[\alpha]_D^{20}$ -37.4 in C_6H_6 (*reineckate*, m.p. 194°). Reduction of (IV) ($\text{Pd-CaCO}_3\text{-H}_2$) in MeOH gives *cryst.* α -isosparteine, b.p. 99—100°/1 mm., m.p. 118°, $[\alpha]_D^{20}$ -56.2° in MeOH [H sulphate, m.p. 244—245°; sulphate, m.p. 92°; *picrate*, m.p. 214° (decomp.); *mercurichloride*, m.p. 247—248° (decomp.); *aurichloride*, m.p. 191—192°; *platinichloride* + $3\text{H}_2\text{O}$, m.p. 243.5°], reconverted into (IV) by $\text{Hg}(\text{OAc})_2$ in AcOH. Similar reduction of (V) gives β -isosparteine, b.p. 104—105°/1 mm., $[\alpha]_D^{20}$ +19.2° in C_6H_6 (*mercurichloride*, m.p. 208—209°; *picrate*, m.p. 203°), which is probably identical with the *d*-sparteine of Clemons *et al.* (A., 1931, 498). The bearing of these results on Ing's formula for (III) (A., 1933, 727) is discussed.
J. W. B.

Quinine iodobismuthate. PRION (Compt. rend., 1934, 198, 926—928; cf. A., 1923, i, 830).—By determining the heat evolved on adding increasing amounts of COMe_2 to $\text{C}_{20}\text{H}_{21}\text{O}_2\text{N}_2$, 2HI , 2BiI_3 (I) it is shown that a definite compound, (I), 6COMe_2 (II), is formed, containing 20% COMe_2 . With > 60%

COMe₂ (I) forms a clear solution, but with more two layers are formed, the heavier being (II) saturated with COMe₂, the lighter a solution of (II) in COMe₂. (I) is sol. in cyclohexanone forming an increasingly viscous red solution by means of which small quantities of Bi or quinine can be determined colorimetrically.

C. A. S.

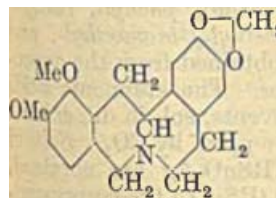
Improved syntheses of physiologically important amines. IX. Synthesis of papaverine and tetrahydropapaverine. K. KINDLER and W. PESCHKE (Arch. Pharm., 1934, 272, 236—241).—Acetoveratrone with anhyd. NHMe₂ and S at 145° (special apparatus described) gives a 65% yield of homoveratrodimehylthioamide, m.p. 121°, hydrolysed by 10% KOH to homoveratric acid (I) in 84% yield. Distilled with homoveratrylamine in tetralin in a current of H₂ (I) gives a 96% yield of its homoveratrylamide, converted (quant. yield) by POCl₃ in boiling C₆H₆ into dihydropapaverine (II). Dehydrogenation of (II) with Pd-black in boiling dihydrophellandrene or tetralin gives an 86% yield of papaverine (III), whereas reduction with Pd-black-H₂ gives a 63% yield of tetrahydropapaverine, similarly dehydrogenated to (III).

J. W. B.

Structural formulæ of the morphine alkaloids and the genetic relationships of the opium alkaloids to one another. W. AWE (Arch. Pharm., 1934, 272, 466—469).—Theoretical.

J. W. B.

Synthesis of 11:12-dimethoxy-2:3-methylenedioxytetrahydropapaverine, an isomeride of tetrahydroberberine, and of 2:3:11:12-tetramethoxytetrahydropapaverine, an isomeride of tetrahydropalmatine. S. N. CHAKRAVARTY and M. SWAMINATHAN (J. Indian Chem. Soc., 1934, 11, 107—113).—2:3-Dimethoxyphenylacetic acid (prepared by way of the azlactone of o-veratrylidenehippuric acid and 2:3-dimethoxyphenylpyruvic acid) and 3:4-CH₂O₂:C₆H₃:CH₂:CH₂:NH₂ at 180° give 2:3-dimethoxyphenylacet-β-3:4-methylenedioxyphenylethylamide, m.p. 108°, converted by POCl₃ at 100° and subsequent reduction (Zn dust, dil. H₂SO₄) into 2':3'-dimethoxy-6:7-methylenedioxy-1-benzyl-1:2:3:4-tetrahydroisoquinoline (hydrochloride, m.p. 160°). Successive treatment of this with HCO₂H at 200°, POCl₃ in PhMe, and Zn dust + dil. HCl gives 11:12-dimethoxy-2:3-methylenedioxytetrahydropapaverine (I), m.p. 127°, converted by I in EtOH+NaOAc into



(I.)

11:12-dimethoxy-2:3-methylenedioxytetrahydropapaverinium iodide (II), m.p. 252° [chloride (III), m.p. 220° [from (II) and AgCl]]. (III) and aq. KOH afford oxy-11:12-dimethoxy-2:3-methylenedioxytetrahydropapaverine, m.p. 230—231°. 2:3-Dimethoxyphenylacet-β-3:4-dimethoxyphenylethylamide, m.p. 131°, is similarly converted into 6:7:2':3'-tetramethoxy-1-benzyl-1:2:3:4-tetrahydroisoquinoline (hydrochloride, m.p. 204°), and thence into 2:3:11:12-tetramethoxytetrahydropapaverine, m.p. 163°.

H. B.

Ergoclavine, a new specific alkaloid of ergot. KUSSNER (Arch. Pharm., 1934, 272, 503—504).—

Extraction with CHCl₃:CCl₄ of the basified mother-liquor after removal of ergotinine and ergotoxin affords ergoclavine, C₃₁H₃₉O₆N₅, m.p. 177—178°, [α]_D²⁰ + 124° in CHCl₃, which constitutes 16—20%, 20%, and 6%, respectively, of the total alkaloids of Spanish, Russian, and Hungarian ergot.

J. W. B.

p_H determinations of solutions of certain alkaloidal salts. A. F. PETERS and A. OSOL (J. Amer. Pharm. Assoc., 1934, 23, 197—201).—The p_H of an alkaloidal hydrochloride or sulphate solution is practically const. over a wide range of concn. Since ppts. are formed with quinchione, colorimetric methods should be used, the vals. obtained being in good agreement with those from titration curves.

A. E. O.

Alkaloids of pereiro bark. II. Constitution of geissospermine. Pereirine. A. BERTHO and F. MOOG (Annalen, 1934, 509, 241—258).—Geissospermine (I), probably C₄₀H₅₀O₃N₄ (cf. A., 1931, 1313), isolated (as sesquihydrate) in 0.2% yield from the dry bark, is hydrolysed (2N-HCl) to a phenol-betaine hydrochloride (II), C₁₃H₁₂O₂NCl, m.p. > 350° (which is OMe- and NMe-free), and MeOH. A pure product could not be isolated from the free betaine and MeOH-MeI at 100°. (I) is converted by EtOH-HCl into an amorphous base, C₂₀H₂₆O₂N₂·0.5H₂O, m.p. 115°, [α]_D²⁰ -57.4° in EtOH (methiodide, m.p. 230—235°), which contains 1 OMe (no NMe) and is hydrolysed (2N-HCl) to (II); the change C₄₀H₅₀O₃N₄+H₂O → 2C₂₀H₂₆O₂N₂ probably involves fission of an ether linking. (I) does not contain NMe (cf. loc. cit.). Distillation of (II) with Zn dust gives 2-methyl-4-ethylpyridine (?) (platini-chloride, m.p. 191—192°) and a substance resembling 3-methylindole. (I), NaOH, and KOH at 250° afford 2:3-dimethylindole (?). (I) could not be reduced (H₂, Pd-BaCO₃, EtOH).

Pereirine, C₂₀H₂₆ON₂·0.5H₂O [methiodide, decomp. 233—235° (darkens from 200°); Me ether (CH₃N₂), m.p. 195—197° (decomp.) (darkens at 175°)], is isolated from the mother-liquors from the crystallisation of (I) as an amorphous powder, m.p. 134—135° (decomp. from 123°), [α]_D²⁰ +137.5° in EtOH; it contains a phenolic OH, is OMe- and NMe-free, and is stable to dil. mineral acid.

H. B.

Arsinic and stibinic acids derived from quinoline and acridine. I. (MISS) M. M. BARNETT, A. H. C. P. GILLIESON, and W. O. KERMAK (J.C.S., 1934, 433—435).—3-Aminoacridone (I) is prepared by heating with 96% H₂SO₄ either 4'-aminodiphenylamine-2-carboxylic acid or its Ac derivative, m.p. 240°, obtained by condensing o-C₆H₄Br·CO₂H and p-NH₂·C₆H₄·NHAc. (I) gives acridone-3-arsinic and -stibinic acids. 6-Amino-2-hydroxyquinoline forms 2-hydroxyquinoline-6-arsinic and -stibinic acids.

F. R. S.

Dissociation constants of chlorophenyl- and phenetyl-boric acids. G. E. K. BRANCH, D. L. YABROFF, and B. BETTMAN (J. Amer. Chem. Soc., 1934, 56, 937—941).—o-C₆H₄Cl·B(OH)₂ (I), m.p. 97—98° (all m.p. are corr.) (lit. 149°) (anhydride, m.p. 171—172°), is prepared (method: Bean and Johnson, A., 1933, 79) from Bu^a borate (II) and

o - C_6H_4Cl -MgBr. *m*-Chlorophenylboric acid (III), m.p. 189—190°, and *p*- C_6H_4Cl -B(OH)₂ (IV), m.p. 306—307° (lit. 275°), are obtained from BF₃ and C_6H_4Cl -MgBr. *m*-Phenetylboric acid (V), m.p. 130° (decomp.) (anhydride, m.p. 152—153°), and *o*- (VI), m.p. 102—103° (lit. 171°), and *p*- (VII), m.p. 150° (decomp.) (lit. 159°) (anhydride, m.p. 171°), -OEt- C_6H_4 -B(OH)₂ are prepared from (II) and OEt- C_6H_4 -MgBr. The following dissociation consts. ($K_a \times 10^{10}$ at 25°) are determined in 25% (vol.) aq. EtOH as previously described (A., 1933, 962): H₃BO₃ 1.34 (6.53 in H₂O), PhB(OH)₂ 1.97 [13.7 in H₂O (cf. *loc. cit.*)], (I) 14.0, (III) 14.5, (IV) 6.23, (V) 3.05, (VI) 0.91, (VII) 0.608, and *o*-, 7.97, *m*-, 3.3, and *p*-, 1.46, - C_6H_4Cl -OH. These vals. are discussed on the basis of the negativities and resonances of the groups involved. RB(OH)₂ of $K < 10^{-10}$ can be titrated (accuracy 2—4%) with aq. NaOH in presence of glycerol. H. B.

Organo-derivatives of bismuth and thallium.

F. CHALLENGER and O. V. RICHARDS (J.C.S., 1934, 405—411).—BiPh₃Cl₂ with Ag₂O under suitable conditions affords triphenylbismuthine dihydroxide, decomp. 100—120° into C₆H₆, BiPh₃, and Bi(OH)₃; with KCN it gives the hydrozycyaniae, m.p. 136°, and with Na azide yields the diazide, which decomposes to BiPh₃, phenylazoimide, and diphenylazidobismuthine, m.p. 168°. TlPhCl₂ and KCN give *K* phenylthallianide, m.p. 265.5° (decomp.), a solution of which on boiling forms thallium diphenyl cyanide, m.p. 318° (decomp.), and TlCl₃. Thallium phenyl dicyanide, m.p. 228°, dithiocyanate, diazide, and dihydroxide, decomp. 280—285°, are similarly obtained. *p*-Tolylboric acid and TlCl₃ give thallium *p*-tolyl dichloride, m.p. 223—224°. Excess of *p*-bromophenylboric acid and TlCl₃ give thallium di-*p*-bromophenyl chloride, decomp. above 300°, whilst excess of TlCl₃ yields thallium *p*-bromophenyl dichloride, m.p. 262—263°. TlPhCl₂ with C₅H₅N gives an additive compound, m.p. 172° (decomp.), and TlPhBr₂ similarly forms a compound, m.p. 85°. MgEtBr and TlPhCl₂ yield Ph₂ and Et₂ halides and no mixed halide, whilst Mg cyclohexyl bromide and TlPhCl₂ form a chloride, converted by KI into thallium dicyclohexyl iodide, m.p. above 300°. Thallium phenyl *p*-tolyl chloride is formed from TlPhCl₂ and *p*-tolylboric acid and from *p*- C_6H_4Me -TlCl₂ and phenylboric acid. The properties of arylboric acids have been examined: *m*-nitrophenylboric acid and HgO give mercury di-*m*-nitrophenyl, m.p. 286—287°. BiPh₃ and AgNO₃ yield a yellow unstable compound, probably PhAg₂AgNO₃, the Ph group being mobile.

F. R. S.

Therapeutic substances derived from unsymmetrical diphenyl compounds. I. S. E. HARRIS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1933, 22, 723—727; see this vol., 663).—The following compounds have been prepared and the Hg derivatives all show marked bactericidal properties: *~*-acetoxymercuri-3-nitro-4-hydroxy- (Na salt), 3-nitro-4-anhydromercuri-5-acinitro-2-hydroxy-, 4-nitro-2-hydroxy-, m.p. 123—124°, and 5-bromo-2-hydroxy-diphenyl, b.p. 158—160°/4 mm.; 4-bromo-2-phenylphenoxyacetic acid, m.p. 138—139° (Et ester), 4-bromo-

2-phenyl-6-acetoxymercuriphenoxyacetic acid; 3:3'-diphenylphenolphthalein [di-(2-hydroxy-4-diphenyl)-phthalide], m.p. 234—235°, brominated to the 5:5'-Br₂-, m.p. 110—111°, and nitrated to the 5:5'-(NO₂)₂-derivatives, m.p. 135°, and 3:3'-dinitrophenolphthalein, m.p. 110—111°; 4-acetoxy- and 4:6-di-acetoxy-mercuri-3:5-dinitro-, and diacetoxymercuri-4-nitro-2-hydroxydiphenyl; 5:5'-dibromo-3:3'-diphenylhydroxymercuri-, 5:5'-dinitro-3:3'-diphenyldiacetoxymercuri-, and 3:3'-dinitro-mono- and -di-acetoxymercuri-phenolphthalein. The Hg compounds decompose above 300°. F. R. S.

Polarity of the co-ordinate linking. E. J. CHAPLIN and F. G. MANN (Nature, 1934, 133, 686—687).—In their reaction with chloramine-*T* the *tert*-phosphines (I) come midway between the org. sulphides and *tert*-arsines, the final product depending primarily on the nature of (I); e.g., tri-*o*-tolylphosphine gives a true phosphinimine (C₆H₄Me)₃PN·SO₂·C₆H₄Me (II) with no other detectable product, tri-*p*-tolylphosphine gives a mixture of the phosphinimine isomeric with (II) and the corresponding hydroxysulphonamide (C₆H₄Me)₃P(OH)·NH·SO₂·C₆H₄Me (III), whilst tri-*m*-tolylphosphine apparently gives no phosphinimine, but only the hydroxysulphonamide isomeric with (III). The results are apparently determined mainly by the position of the Me relative to P. The co-ordinate linking (IV) in (II) tends to give the P and N atoms a weak positive and negative charge, respectively; simultaneously, the polarity induced by the three *o*-Me groups will tend to give the P atom a negative charge. The polarity of (IV) is thus suppressed and a stable phosphinimine results. In the *p*-compound, the effect of the Me groups is similar but weaker, and hence both phosphinimine and hydroxysulphonamide are formed, whilst in the *m*-compound the polarity induced by the Me groups reinforces that of (IV) and the hydroxysulphonamide alone is produced. L. S. T.

Stannonic acids. M. LESBRE and (MLLE.) G. GLOTZ (Compt. rend., 1934, 198, 1426—1427).—Extending the reaction $RX + KHSnO_3 \longrightarrow RSnO_3H + KX$ (J.C.S., 1922, 121, 1859), phenyl-, benzyl-, α -naphthyl-, allyl-, dichloromethyl-, bromoethyl-, and acetonyl-stannonic acids are obtained from the appropriate chlorides or bromides. The stannonic acids are insol. in H₂O or org. solvents, sol. in dil. acid or in alkali, from which they are pptd. by CO₂. Salts of type RSnO₃Na, RSnO₃K, RSnO₃Ag are obtained, as are complexes of type CoO.(RSnO₃)₂Co, corresponding Ni compounds, and more complex Hg, Zn, or Mn salts, from the sulphates etc. From solution in dil. HCl or HBr, acids of type [RSnCl₅]₂H₂ and [RSnBr₅]₂H₂ crystallise, from which salts [RSnX₅]₂K₂ and additive compounds of type [RSnX₅](C₅H₅N)₂ are formed. In conc. solution, the reaction [RSnI₅]₂H₂ \longrightarrow SnI₄ + RH + HI occurs, and when strongly alkaline solutions of alkylstannonic acids are boiled, the insol. stannones R₂SnO are deposited. E. W. W.

Coagulation of albumin by water vapour. E. JUSTIN-MUELLER (J. Pharm. Chim., 1934, [viii], 19, 348—353).—Coagulation of albumin by pigments may be due to the formation of NH₂OH

in presence of an alkaline salt of a weak acid or of an easily reducible substance. H. G. R.

Absorption and phosphorescence spectra of fabrein. M. FONTAINE (Compt. rend., 1934, 198, 1077—1079).—Fabrein, freed from dunalin by Et_2O , in $\text{C}_5\text{H}_5\text{N}$ has absorption bands at λ 612, 566, and (?) 524, and phosphorescence bands at λ 666, 618, and 636 (order: decreasing intensity). R. S. C.

Determination of the homogeneity of proteins by coagulation experiments. B. JIRGENSONS (Biochem. Z., 1934, 268, 406—413).—The coagulation of various proteins by varying concn. of MeOH , EtOH , PrOH is surveyed. Plotting the concn. (x) of the alcohol against the degree of coagulation (y), coagulation curves of two chief types are obtained, one having a single max. and min., the other having several max. and min. Homogeneous proteins, e.g., ovalbumin, give curves of the first, whilst heterogeneous proteins, e.g., caseinogen, oxy- or met-haemoglobin, give curves of the second, type. P. W. C.

Kyrins. W. GRASSMANN and O. LANG (Biochem. Z., 1934, 269, 211—222; cf. Siegfried, Z. physiol. Chem., 1916, 97, 233).—Glutokyrin sulphate (I), prepared by Siegfried's method, consists chiefly of basic di- and tri-peptides composed of NH_2 -acids [arginine (II), proline (III), glycine, lysine (IV), and leucine, 1 mol. of each] and $3\text{H}_2\text{SO}_4$. Elementary analysis suggests the presence of OH-compounds and homologues of these NH_2 -acids. Free (II) and (III) are certainly, other free NH_2 -acids probably, absent. The $\alpha\text{-NH}_2$ of (II) and the NH of (III) are united in peptide linking (V) and the free NH_2 of (I) belong to (IV) and (NH_2)₁-acids. Kidney peptidase readily attacks (I), hydrolysing the (V) of (III) and liberating all the (II). W. McC.

Hydrolysis of iodoproteins. G. BARKAN and G. KINGISEFF (Arch. exp. Path. Pharm., 1934, 174, 444—452).—Iodoprotein ("iodtropon") (I) is hydrolysed by H_2O at 100° , approx. 60% of the total I being liberated in 20 hr., the of the solution falling from 5.9 to 4.9. Approx. 80% of the liberated I can be electrometrically titrated. Hydrolysis of (I) with $\text{Ba}(\text{OH})_2$ liberates more I than that with trypsin (cf. A., 1931, 1090), the I in the ultrafiltrate (35—49% of the total I) being 60—80% precipitable by Ag^+ . The products include 3:5-di-iodotyrosine, the separation of which [0.26 g. from 150 g. of (I)] is described. The partition of I in the hydrolysates is discussed. F. O. H.

Behaviour of aqueous solutions of domestic cocoons. XV. Apparent specific gravities of sericin-A and -B. XVI. Sericin as a protective colloid. XVII. Separation of sericin. H. KANEKO (J. Agric. Chem. Soc. Japan, 1933, 9, 905—907, 1049—1055, 1056—1059).—XV. Vals. of d^{15} (apparent) are 1.356 and 1.309, respectively.

XVI. The Au val. (I) (0.02—0.038) is approx. equal to that of ovoglobulin, ovalbumin, and gelatin. The more reeable the cocoon is, the smaller is (I). (I) is max. at the isoelectric point (p_H 4.2—4.3), and falls with rise in temp. (I) of sericin-A is usually < that of -B. Sericin prevents the oxidation of

pyrogallol by Co complex salts and the decomp. of H_2O_2 by colloidal Pt.

XVII. By electrodialysis sericin-A is rapidly coagulated whilst -B remains dissolved. CH. ABS.

Specific characteristics of proteins. N. N. IVANOV (Izvest. Tzentr. Nauch.-Issledov. Inst. Pisch. Vkus. Prom., 1931, 36 pp.).—A discussion. Analytical data are tabulated. CH. ABS.

Collagens. I. Preparation and properties of collagens. G. FLORENCE and J. LOISELEUR (Bull. Soc. Chim. biol., 1934, 16, 52—63).—The proteins of conjunctive tissue, extracted at room temp. with HCO_2H containing a small amount of EtOH-HCl and pptd. with EtOH , are in their colloidal character and N content similar to those obtained by extraction with H_2O in an autoclave. According to their origin, they show different neutralisation curves, buffering power, and N content. A. L.

Fractions of caseinogen. B. JIRGENSONS (Biochem. Z., 1934, 268, 414—421).—The fraction of caseinogen sol. in 60—70% alcohol and poor in P gives a coagulation curve having a single max. and min. typical of a homogeneous protein, whilst the fraction rich in P gives a flat curve. Fractionation is found to be especially easy by 50—60% PrOH in presence of 0.03 mol. NaCl per litre. P. W. C.

Fractionation of protein catalysts by the aid of organic extraction media. II. V. S. SADIKOV, V. A. VADOVA, and R. G. KRISTALINSKAYA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 500—504).—Products obtained by partial fission of ovalbumin with 2% H_2SO_4 , HCl , H_3PO_4 , and Na_2CO_3 give definite yields of extracts with Et_2O , CHCl_3 , BuOH , and $\text{C}_5\text{H}_{11}\text{OH}$, these extracts containing *cyclo*-peptide and heterocyclic substances without $\text{NH}_2\text{-N}$, but including considerable fractions of the total N. BuOH is a particularly effective solvent. The residue still contains about 60% of *cyclopeptide* substances. J. W. S.

Determination of carbon in the wet way. H. ENGEL (Z. anal. Chem., 1934, 96, 319—321; cf. A., 1931, 1258).—An improved form of reaction flask is described. J. S. A.

Micro-determination of active hydrogen by Zerevitinov's method. W. LUTTGENS and E. NEGELEIN (Biochem. Z., 1934, 269, 177—181; cf. Roth, A., 1932, 709).—1 mg. of substance suffices for a determination if PhMeO replaces Hg in the special manometer, and the concn. of the Grignard solution is increased to 1.4N so that a reaction temp. of about 20° is sufficient. Equilibrium between gas and liquid must be attained by shaking. The method is inapplicable to picric acid. A quartz reaction vessel is used. W. McC.

Argentometric semi-micro-determination of chlorine and bromine in organic substances. F. HÖLSCHER (Z. anal. Chem., 1934, 96, 308—314).—The substance is burned in O_2 over a Pt catalyst, and Cl or Br absorbed in 5% H_2O_2 . Absorbed halogen is titrated with 0.02N- AgNO_3 , using dichloro-fluorescein (Cl) or eosin (Br) as adsorption indicator.

Use of methoxyacetic anhydride for determination of hydroxyl groups. D. W. HILL (J. Amer. Chem. Soc., 1934, 56, 993).—*Di(methoxyacetyl)quinol*, m.p. 89.5–90°, *p-methoxyacetoxybenzoic acid*, m.p. 164–165°, *p-methoxyacetoxyacetophenone*, m.p. 56–57°, *penta(methoxyacetyl)quercetin*, m.p. 97–98°, and *methoxyacetoxychalkone* (?), $C_{18}H_{16}O_4$, m.p. 93°, are prepared using $(OMe \cdot CH_2 \cdot CO)_2O$ (I). It is suggested that the no. of OH groups in a compound can be determined by treatment with (I) and subsequent determination of OMe. H. B.

Reactions with vanadium chloride. K. Woxhoff (Ber., 1934, 67, [B], 554).—A solution of VCl_5 (5 g.) in H_2O (100 c.c.) gives an amethyst-violet colour with $o-OH \cdot C_6H_4 \cdot CO_2H$ (1 in 6000) which becomes orange (1 in 12,000). $o-OH \cdot C_6H_4 \cdot CO_2Na$ gives a reddish-brown colour. $BzOH$ and $PhOH$ do not give colours. Meconic acid gives a dark red colour (pale pink at 1 in 10,000), not impeded by HCl or H_2SO_4 but destroyed by $H_2C_2O_4$ or HPO_3 . Either test is readily applied as a ring reaction. H. W.

Determination of phenol, salicylic acid, and cresols, and the products obtained in the reactions. M. BEUKEMA-GOUDSMIT (Pharm. Weekblad, 1934, 71, 380–397, 438).—Koppeschaar's bromometric method for the determination of $PhOH$ (I) (A., 1877, i, 746) gives satisfactory results even with very low concns. if only a slight excess of KI is used (cf. B., 1930, 648). The bromometric method for determining $o-OH \cdot C_6H_4 \cdot CO_2H$ (II) described in the Dutch Pharmacopœia is liable to give low results due to the formation of dibromosalicylic acid (III), but accurate results are obtained if sufficient H_2O is used to keep (III) in solution. The iodometric method of Messinger and Vortmann (A., 1889, 1150; 1890, 1473) gives satisfactory results with (I) and (II) at 50–75° if ≤ 6 mols. of $NaOH$ are used, the resultant product being tetraiododiphenoquinone; if less alkali is used $C_6H_2Br_3 \cdot OH$ is formed. Mixtures of (I) and (II) can be determined and the components separated by Na_2CO_3 . Of the cresols, only *m*- can be determined by both methods; *o*- and *p*- do not react quantitatively. S. C.

Reactions to differentiate between resorcinol and hexylresorcinol. G. REVILLON (Bull. Soc. Chim. biol., 1934, 16, 305–306).—The colorations produced by hexylresorcinol and Deniges' reagent, sucrose and H_2SO_4 , Fe^{III} alum, $Fe(ClO_4)_3$, Na_2CO_3 , H_2SO_4 and HCO_2H , and $AcCHO$ are different from those given by resorcinol. A. L.

Reactions of adrenaline and ephedrine. L. EKKERT (Pharm. Zentr., 1934, 75, 208–209).—Adrenaline (I) and ephedrine (II) give similar colour reactions with aldehydes and H_2SO_4 (*p*- $OMe \cdot C_6H_4 \cdot CHO$, violet-red; *o*- $OH \cdot C_6H_4 \cdot CHO$, orange; vanillin, lemon-yellow; piperonal or CH_2O bright red). Differences are noted with $SeO_2 \cdot H_2SO_4$ [(I) gives a red colour on warming, (II) brown turning to olive-green], diazobenzene-*p*-sulphonic acid [(I) couples much more rapidly than (II)], KOH in $EtOH$ [(I) gives a transient red coloration, (II) remains colourless]. S. C.

Determination of anabesine. A. WENUSCH and G. BILOWITSKI (Biochem. Z., 1934, 270, 15–16).—Anabesine is pptd. from dil. HCl solution with silicotungstic acid, from dil. $AcOH$ solution with saturated aq. picric acid (I) or with saturated aq. picrolonic acid. With (I) the procedure is as in nicotine determination and the factor 0.29 must be used. W. McC.

Alkaloid determination by displacement titration. F. SCHLEMMER and H. KOCH (Arch. Pharm., 1934, 272, 394–405).—Alkaloid salts may be accurately determined by chemical (phenolphthalein) or, better, electrometric (buffer solution p_H 8.4) titration of the acid with 0.025*N*- KOH in 90% $EtOH$ solution, or by similar titration (thymol-blue: or buffer p_H 1.8) of the base with 0.025*N*- HCl in 90% $COMe_2$ solution. The potentiometric $EtOH$ titrations are not appreciably affected by the presence of inert material such as starch or sugar. Full details are given and the accuracy of the methods is tested with a large no. of alkaloids. J. W. B.

Micro-chemistry of quinine ethyl carbonate (Euchinine). M. WAGENAAR (Pharm. Weekblad, 1934, 71, 435–438).—Quinine Et carbonate (I) when dissolved in dil. mineral acids does not give the usual microchemical reactions of quinine. (I) may be identified by crystallisation and by the formation of herapathite with $I-KI$ solution, CHI_3 with I after hydrolysis with NH_3 , and the green coloration with Cl_2 and NH_3 . S. C.

Detection of strychnine salts. D. VON KLOBU-SITZKY (Biochem. Z., 1934, 270, 120–121).—To 0.05% solutions (2–3 c.c.) of strychnine salts [sulphate, hydrochloride (I), nitrate, phosphate, glycerophosphate] an equal vol. of 4% aq. Na glycerophosphate is added and the mixture is boiled for 0.5 min. The characteristic cryst. ppts. which separate on cooling are at once microscopically examined while moist. 0.01–0.05 mg. is detectable. Except with (I) other alkaloids do not interfere. W. McC.

Determination of strychnine and brucine as hydroferrocyanides and their separation by means of ferrocyanide. I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Pharm. Assoc., 1934, 23, 302–308).—Strychnine can be pptd. and determined as hydroferrocyanide (I), even at great dilutions. (I) contains only 1 H_2O of crystallisation (cf. B., 1925, 226). The determination of brucine is less accurate (hydroferrocyanide more sol.). A. E. O.

Determination of gelatin. G. FARKAS (Magyar Orvosi Arch., 1933, 34, 269–273).—In solutions containing proteins and collagen the former are pptd. by heating to 40° and adding two vols. of saturated picric acid solution (I). To the filtrate 1.5 vols. of (I) are added and the whole is left for 24 hr. at 8°, when the pptd. gelatin is collected and its N content determined (Kjeldahl). NUTR. ABS. (m)

Colorimetric micro-determination of arginine. G. JEAN (Bull. Soc. Chim. biol., 1934, 16, 307–309).—Using Jorpes' modification (A., 1932, 1270) of the method of Weber, 0.015–0.035 mg. of arginine in protein hydrolysates can be determined with an accuracy of 3–4%. A. L.

Biochemistry.

Identification of traces of old blood-stains by means of the hæmatoporphyrin spectrum. M. WAGENAAR (Pharm. Weekblad, 1934, **71**, 478—482).—Details are given for observing the spectrum of hæmatoporphyrin microscopically after treating a blood-stain with H_2SO_4 . S. C.

Oxygenation of concentrated versus normal blood. G. B. RAY, C. I. THOMAS, and J. E. STRONG (J. Clin. Invest., 1933, **12**, 1051—1062).—The tension of O_2 required to produce a given saturation is the same for normal and polycythæmic blood. On perfusion through the surviving lung the former becomes completely oxygenated, whilst the latter is never fully saturated owing to more rapid passage and delayed diffusion. CH. ABS.

Ultra-violet spectrum of oxyhæmoglobin. G. A. ADAMS, R. C. BRADLEY, and A. B. MACALLUM (Biochem. J., 1934, **28**, 482—485).—Laked rabbits' erythrocytes (I) absorb strongly between 4200 and 3900 Å. with a max. at 4100 Å. Unlaked (I) absorb very much less at all λ with no marked band. It is concluded that oxyhæmoglobin is in a different state when outside (I) from that when inside. H. D.

Resistance of hæmoglobin to antiseptics. I—V. A. MAISANI (Boll. Chim.-Farm., 1933, **72**, 761—769, 804—809; 1934, **73**, 246—259).—I. The common antiseptics (I) are reviewed, and those suitable for testing indicated.

II, III. The properties of hæmoglobin (II) are reviewed, and the procedure is described.

IV, V. The resistance of human and other (II) to various (I), as shown by the time of persistence of the (II) absorption band, varied with the species and the (I). The (II) was destroyed in some cases, and denatured and pptd. in others. The effect of the (I) was diminished by dilution, except for $\text{Na}_2\text{B}_4\text{O}_7$, when it was increased. R. N. C.

Osmotic pressures and mol. wts. of hæmocyanins. A. and MME. G. S. ADAIR and M. and MME. J. ROCHE (Compt. rend., 1934, **198**, 1456—1458).—Osmotic pressures of dialysed snail, octopus, and crab hæmocyanins gave approx. mol. wts. comparable with Svedberg's determinations (this vol., 92). B. W. B.

Penetration of glucose into erythrocytes. W. FLEISCHMANN and H. KAUNITZ (Pflüger's Archiv, 1933, **233**, 148—153; Chem. Zentr., 1933, ii, 3003).—The vol. increase of human erythrocytes in isotonic glucose solutions has been measured between 9° and 25°. H. J. E.

Determination of uncombined water of the erythrocytes of human blood. A. SŁAWINSKI (Bull. Soc. Chim. biol., 1934, **16**, 96—104).—By the author's method (A., 1929, 1142), the vol. of free H_2O in the erythrocytes is 59%. A. L.

Permeability of erythrocytes. H. DAVSON (Biochem. J., 1934, **28**, 676—683).—Ox erythrocytes (I) lose K in 0.9% NaCl, glucose solution (II), and diluted serum (III). (I) lose NaCl in 1.5% KCl,

(II), and (III). The corpuscle-Na and -K rise in 1.5% NaCl and KCl, respectively. C. G. A.

Influence of carbonic acid on the permeability of [blood-corpuscles to] ammonium salts. S. L. ØRSKOV (Biochem. Z., 1934, **269**, 349—366).—A method for following the vol. of blood-corpuscles by means of a photo-cell is described, and is used to show that the velocity of swelling is greatly increased by solutions of NH_4 salts, the action being due to the cation. CO_2 does not affect the permeability to anions, but greatly increases that to NH_4 salts and the salts of various amines, e.g., the hydrochlorides of NH_2Et , NH_2Et_2 , and piperidine. P. W. C.

Specific resistance of the interior of the red blood-corpuscle. H. FRICKE and H. J. CURTIS (Nature, 1934, **133**, 651).—The sp. resistance of the interior of the corpuscle of sheep, rabbit, and chicken is $140(\pm 10\%)$ ohms at 20°. L. S. T.

Solubility of ethyl iodide in human blood and its correlation with the erythrocyte count. R. D. COOL, C. J. GAMBLE, and I. STARR, jun. (J. Biol. Chem., 1934, **105**, 97—105).—The average distribution coeff. for EtI between air and human blood was 6.7 ± 0.36 . H. G. R.

Blood of fish and turtles. H. M. VARS (J. Biol. Chem., 1934, **105**, 135—137).—The blood-non-protein-N, -urea- + - NH_3 -N, -uric acid, -Cl', and total plasma- and serum-N were determined in *Esox lucius*, *Cyprinus carpio*, and *Chelydra serpentina*. H. D.

Blood-alkali reserve, -sugar, -urea, and -iron in newborn pigs. A. TRAUTMANN and C. KOCH (Z. Tierzüchtung Zuchtungsbiol., 1933, **28**, 29—39).—In three litters alkali reserve was high at birth, fell at first, and was again high at 5—6 weeks. The level did not vary with body-wt. or sex. Blood-sugar (133 mg. per 100 c.c.) was >, and urea (9—15 mg. N per 100 c.c.) similar to, that in adults. Fe fell during the first 7 days and then rose. In 38-day-old pigs an average of 35.6 mg. of Fe per 100 c.c. was found. NUTR. ABS. (m)

Blood-sugar of healthy Korean adults. Y. C. LEE and C. Y. CHOI (Korean Med. J., 1933, **3**, 65—70).—Vals. are: male 0.09—0.109, female 0.079—0.128%. The average val. in each sex is 0.107%. CH. ABS.

Step-photometric determination of blood-sugar. C. URBACH (Med. Klin., 1933, **29**, 1381—1382; Chem. Zentr., 1933, ii, 2865). L. S. T.

Determination of volatile aldehydes in blood. J. DUPILLE and M. LACHAUX (Bull. Soc. Chim. biol., 1934, **16**, 194—210).—The method of Bougault and Gros (A., 1922, ii, 666) for the determination of volatile aldehydes applied to blood gives a val. of 3—6 mg. CH_2O per litre for the dog. Whilst injection of $(\text{CH}_2)_6\text{N}_4$ into dogs results in the liberation of small amounts of volatile reducing substances, its methiodide is not decomposed. A. L.

Volumetric determination of small amounts of phosphatides, free cholesterol, cholesteryl ester,

neutral fat, and total lipin of blood, plasma, and corpuscles. S. KATSURA, T. HATAKEYAMA, and K. TAJIMA (Biochem. Z., 1934, **269**, 231—240).—The method combines the authors' earlier methods for determination in 0.5 ml. of blood or plasma of total fatty acids and cholesterol (A., 1931, 858) and of phosphatides (A., 1933, 294) and gives reproducible results, the error being $\pm 5\%$. P. W. C.

Amino-acids in maternal blood and that of the umbilical cord. P. DONEDDU (Arch. Farm. speriment., 1934, **57**, 105—127).—Blood- NH_2 -acids (I) remain normal during the first half of the pregnancy period, but rise rapidly during the second; the difference between the (I) in starvation and after protein feeding is unaltered. The (I) remain high during labour, but fall rapidly to normal afterwards. The (I) of the umbilical cord are independent of the maternal (I), but dependent on the wt. and size of the foetus. R. N. C.

Micro-determination of iron in blood. F. RAPPAFORT and E. HOHENBERG (Klin. Woch., 1933, **12**, 1810—1811).—The blood is ashed with H_2SO_4 and H_2O_2 , the solution transferred to a modified Parnas-Wagner apparatus, KI in aq. CdSO_4 is added, and the liberated I is steam-distilled into aq. $\text{NaOH} + \text{Na}_2\text{SO}_3$. I' is oxidised to IO_3^- by Br in AcOH and the I determined titrimetrically with $\text{Na}_2\text{S}_2\text{O}_3$. 0.1—0.2 c.c. of blood suffices. NUTR. ABS. (m)

Iron determination in blood. B. R. BURMESTER (J. Biol. Chem., 1934, **105**, 189—198).—The volumetric Ti^{III} (McFarlane, A., 1932, 1182) (I), the colorimetric CNS' (II), and the colorimetric thioglycollic acid (Hanzal, this vol., 122) (III) methods are compared in the determination of Fe in ashed blood and Wong filtrates (A., 1928, 785). The accuracy of (III) in ashed blood equals that of (II), and is $>$ that of (I), and is maintained in the Wong filtrate. H. D.

Demonstration of copper in snail's blood by electrolytic coloration of a protein membrane. M. CHANOS, P. PONTIUS, and R. NIEL (Compt. rend. Soc. Biol., 1933, **114**, 1109—1112).—After ashing the blood with H_2SO_4 and HNO_3 , removal of excess acid by ignition, and taking up the ash in H_2SO_4 , it is possible, by use of the electrolytic cell previously described (*ibid.*, 1928, **98**, 313), to detect Cu using 0.05 c.c. of blood. NUTR. ABS. (m)

Micro-determination of magnesium in blood-serum. L. VELLUZ (J. Pharm. Chim., 1934, [viii], **19**, 346—348).—Mg is pptd. by 8-hydroxyquinoline in presence of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, without removal of Ca. H. G. R.

Blood-calcium of earthworms. K. AOKI (Proc. Imp. Acad. Tokyo, 1934, **10**, 121—124).—The blood-Ca (I) and -Na of *Pheretima hilgendorfi* average, respectively, 32.9 and 213 mg. per 100 c.c. The level of (I) increases with increasing $[\text{CO}_2]$ of the air. F. O. H.

Alterations in calcium content of blood in relation to the menstrual cycle. R. F. MATTERS and E. U. HUBBE (Austral. J. Exp. Biol., 1934, **12**, 19—23).—Alterations in the Ca content previously reported (A., 1929, 1101) have not been confirmed. A. E. O.

Quick dry ashing of blood-serum for determination of sodium by uranyl zinc acetate method. W. E. WILKINS (J. Biol. Chem., 1934, **105**, 177—179).—Serum is boiled with a $\text{Mg}(\text{NO}_3)_2\text{--MgCO}_3$ solution in a SiO_2 crucible and when dry heated strongly. H. D.

Determination of blood-chlorine and the erythro-plasma coefficient. J. BOTTIN (Bull. Soc. Chim. biol., 1934, **16**, 145—151). A. L.

Determination of iodine in blood with alkaline and acid combustion. H. LUCKER (Deut. Arch. klin. Med., 1933, **175**, 681—690).—Pfeiffer's method gives higher and more accurate results than does von Fellenberg's. 100 c.c. of normal blood contain 0.02—0.04 mg. of I. NUTR. ABS. (m)

Proteins of blood and subcutaneous lymph in dogs. A. A. WEECH, E. GOETTSCH, and E. B. REEVES (J. Clin. Invest., 1933, **12**, 1021—1030).—Vals. of albumin:globulin in serum and lymph are related. The entrance of serum-proteins into the lymphatics is discussed. CH. ABS.

Formula and nomogram for determining the osmotic pressure of colloids from the albumin and total protein concentrations of human blood-sera. H. S. WELLS, J. B. YOUNG, and D. G. MILLER (J. Clin. Invest., 1933, **12**, 1103—1117).— $P = C(21.4 + 5.9A)$, where P is the osmotic pressure (mm. H_2O), C is the total protein, and A is the albumin (g. per 100 c.c.). CH. ABS.

Determination of the p_H of blood-plasma. P. DU NOUY and V. HAMON (Bull. Soc. Chim. biol., 1934, **16**, 177—193).—By means of the inclined rotating electrode (A., 1932, 135) determinations of the p_H of blood-plasma can be made with an error of ± 0.01 . A. L.

Alleged reversal of the denaturation of serum-albumin. L. F. HEWITT (Biochem. J., 1934, **28**, 575—579).—The claim of Anson and Mirsky (A., 1931, 1080) to have reversed the heat-denaturation of serum-albumin (I) has not been confirmed, and there is no evidence that the recovered (I) has been denatured. (I) may be heated in acid solution without being appreciably denatured. H. G. R.

Filtration of serum-proteins through membranes of graduated porosity. P. GRABAR (Compt. rend., 1934, **198**, 1640—1641).—The pore diameters in μ which permit no and total passage of proteins on ultra-filtration are for horse serum 9 and 90 (very little with 40), for solutions of lipin-free serum 15 and > 90 , of serum-albumin 9 (10, if free from lipins) and 30, and of pseudoglobulins 17 and 80, respectively. Correlation of these figures with particle size is dependent on the (unknown) amount of absorption by the membrane. R. S. C.

Ultra-filtration of proteins through graded collodion membranes. I. Serum-proteins. W. J. ELFORD and J. D. FERRY (Biochem. J., 1934, **28**, 650—662).—The filtration curve, end-point curve, and a quant. measure of filterability are defined. The influence of the nature of the solvent medium, p_H , neutral salts (I), concn. of protein (II), and filtration pressure on the ultrafiltration of serum-albumin (III)

and pseudoglobulin (IV) is described. The results indicate two types of filtration, termed normal (a true sieving mechanism occurring at the extreme acid or alkaline portion of the p_H range) and abnormal [when at an early stage the pores are blocked by large deposits of (II) within them]. (I) improve filterability by a peptising action at, and on the alkaline side of, the isoelectric point. Hartley's broth (V) at p_H 7.6—7.8 is the best solvent for the filtration of (II). The ratios, particle size/end-point average pore diameter, are given for (III) and (IV) under optimum filtration conditions. The filtration end-point of (III) and (IV) is the same in pure solution in (V) at p_H 7.8 as in native horse serum. A. E. O.

Serum differences of various animal species. H. IGARASHI (Japan. J. Gastroenterol., 1933, 5, 128—131).—The binding capacity of various sera for dyes falls in the order: man > rabbit > goat, cow, pig, horse > pigeon, chicken. CH. ABS.

Is thrombin a proteolytic enzyme? H. STRUGGOLD and E. WÖHLISCH (Z. physiol. Chem., 1934, 223, 267—280).—In a simplified clotting system, consisting of isolated fibrinogen and thrombin (I) low in protein, trypsin-kinase (II) in small amounts has no action, and in larger amounts delays or prevents clotting. The accelerating effect of (II) on whole-blood clotting is probably indirect, and due to protein breakdown-products. The hypothesis of Waldschmidt-Leitz (cf. A., 1929, 89, 951) that (I) is a proteolytic enzyme is untenable. (I) may be a "fibrinogen denaturase." J. H. B.

Kinetics of hæmolytic systems. V. Lytic effect of mixtures of two lysins. E. PONDER (Biochem. J., 1934, 28, 384—390).—The total hæmolytic effect is rarely the same as the sum of the two individual activities. The lysins probably interact with each other. A. E. O.

Kinetics of hæmolytic systems. VI. Inhibition produced by plasma and serum. E. PONDER and A. S. GORDON (Biochem. J., 1934, 28, 748—753).—The inactivation of saponin by plasma can be accounted for by a reaction between the lysin and plasma-proteins, whereby the former is removed from the system. H. D.

Effect of sodium cyanide on complement hæmolysis. W. H. RANDALL (Proc. Soc. Exp. Biol. Med., 1933, 30, 1412—1413).—Addition of neutralised NaCN solution to red cells (I), sp. hæmolysin (II), and complement (III) inhibits hæmolysis. When (I) are washed after contact with (II) and NaCN, addition of (III) causes hæmolysis. The effect of NaCN is on the (III) and is independent of the p_H of the cyanide. CH. ABS.

Influence of p_H on action of hæmolytic complement. T. W. B. OSBORN (Biochem. J., 1934, 28, 423—425).—A max. rate of hæmolysis of sheep's corpuscles by guinea-pig's serum occurs near p_H 7.5. Inorg. and org. ions retard hæmolysis, whilst BO_2 is hæmolytic to both sensitised and unsensitised corpuscles. H. D.

Volume of precipitate in precipitin reactions. F. S. JONES and R. B. LITTLE (J. Immunol., 1933, 25, 381—396). CH. ABS.

Local organ hypersensitiveness. V. Fate of antigen and the appearance of antibodies during the development of hypersensitiveness in the rabbit eye. B. C. SEEGAL, D. SEEGAL, and D. KHORAZO (J. Immunol., 1933, 25, 207—220).

CH. ABS.

Species specificity of fibrinogens. H. B. KENTON (J. Immunol., 1933, 25, 461—470).—Pigeon, sheep, horse, and rabbit fibrinogens are not of identical protein structure. "Group" antibody reactions were obtained only with sheep and ox fibrinogen.

CH. ABS.

Existence of antigenic determinants of diverse specificity in a single protein. I. Tyrosine- and histidine-diazoarsanilic acids as haptens. S. B. HOOKER and W. C. BOYD (J. Immunol., 1933, 25, 61—69).—Injection of a single "complete" protein coupled with diazotised arsanilic acid probably leads to the production of two different antihaptens, one corresponding more closely with the tyrosine- and the other with the histidine-diazoarsanilic acid group. With gelatin, only one antihapten is produced.

CH. ABS.

Methylated glycine as an antigen. H. LEONTJEV and M. ZNAMENSKAJA (Biochem. Z., 1934, 270, 116—119; cf. A., 1933, 292).—The structure of glycine is not appreciably affected by methylation. The product is an antigen; in dil. solutions it produces anaphylactic shock in guinea-pigs.

W. McC.

Biochemistry of carbohydrates. III. Micro-determination of glucosamine in blood, tissue, and urine. K. KAWABE. IV. **Enzyme hydrolysing conjugated glycuronic acids.** H. MASAMUNE (J. Biochem. Japan, 1934, 19, 319—327, 353—375).—III. Blood and tissue are deproteinised by $CCl_3 \cdot CO_2H$, the filtrate is extracted with Et_2O , and the aq. layer treated successively with $NaOMe$, Ac_2O , $EtOH-KOH$, and $p-NMe_2 \cdot C_6H_4 \cdot CHO$, the resulting colour being compared with that of phenol-red in borate buffer at p_H 8.6. With urine, urea, allantoin, and alloxan interfere and must first be removed.

IV. Pptn. of extracts of autolysates of ox kidney with 95% $EtOH$ (3 vols.) yields preps. which hydrolyse β -menthol- (I) (but not α -menthol-), phenol- (II), β -naphthol-, borneol-, and phloroglucinol-glycuronic acid, the optimum p_H (III) being 5.3—5.6. Emulsin (IV) hydrolyses (I) and (II), (III) being approx. 4. The enzyme (for which the name " β -glycuronosidase" is suggested) does not hydrolyse α - and β -glucosides and is less stable to heat than (IV). F. O. H.

Carbohydrate content of egg-white. M. SORESEN (Biochem. Z., 1934, 269, 271—284).—Egg-white, which contains 0.45% of free glucose, is composed of 7% of globulin containing 4% of mannose (I), 2% of mucin containing 14.9% of a mixture of equal parts of (I) and galactose (II), 70% of albumin containing 1.7% of (I), 9% of conalbumin containing 2.8% of a mixture of 3 parts of (I) and 1 part of (II), and 13% of mucoid containing 9.2% of a mixture of 3 parts of (I) and 1 part of (II). The possibility that this carbohydrate is present in the form of trisaccharides composed of 1 mol. of glucosamine with 2 mols. of (I) or (II) is discussed. P. W. C.

Phosphorus, sulphur, and alkali content of hens' eggs. J. GROSSFELD and G. WALTER (Z. Unters. Lebensm., 1934, **67**, 510—529).—The mean P_2O_5 contents (I) of the yolk (Y) and white (W) are 1.42 and 1.36%, respectively. The lecithin- P_2O_5 (II) of Y=1.01%. Extraction with EtOH, C_6H_6 +EtOH (4:1), Pr^oOH, PrⁿOH, and MeOH gives approx. identical yields of (II). Most previous results are too low. W contains no inorg. P_2O_5 . W contains 0.212%, Y 0.222% of S. Simple ashing, with or without addition of alkali, causes loss of S. Details of ashing with the addition of KOH and KNO_3 are given. Y contains 0.112% of K and 0.045% of Na; W contains 0.153% of K and 0.179% of Na.

E. C. S.

Composition of eel-fat. H. WIEHR (Fettchem. Umschau, 1934, **41**, 71—72). Eel-fry, long-headed and broad-headed eels yielded 27.9, 66.7, and 27.7% of Et_2O -extractable fat (on dry basis), respectively, having I vals. (Margosches) 90.6, 97.4, and 105.8: sap. val. 205, Reichert-Meissl val. 1.9. The fat contained about 2.8% of phosphatides and 0.74% of cholesterol, and yielded 86.5% of fatty acids [66.2% saturated acids, mainly palmitic acid, and 20.3% unsaturated (oleic) acids].

E. L.

Constituents of muke oil. I. Fatty acids. S. UENO and M. IWAI (J. Soc. Chem. Ind. Japan, 1934, **37**, 52—53B).—Palmitic, stearic, and myristic acids are the principal saturated fatty acids. Zoonaric (?), gadolinic (?), cetolinic (?), and mainly oleic acid are the unsaturated acids.

J. L. D.

Fatty substances of shell-fish. I. Asari (*Tapes philippinarum*), shijimi (*Corbicula leana*) karasugai (*Cristaria plicata*), and hamaguri (*Meretrix meretrix*). II. Fatty substances of ear- (*Haliotis gigantea*) and top-shells (*Turbo cornutus*). M. TSUJIMOTO and H. KOYANAGI (J. Soc. Chem. Ind. Japan, 1934, **37**, 81—85B, 85—86B).—I. EtOH and Et_2O extract fatty substances (I) and phosphatides (II) from the shell-fish (freed from shells). (I) (separated by CO_2H) consist of highly unsaturated fatty acids (III) and an unsaponifiable portion (IV) (up to 45%), from which is isolated a sterol, m.p. 135—136° (Ac derivative, m.p. 130—130.7°), different from cholesterol (V), although some (V) is also present.

II. (I) from the two sources contain 20 and 38% of (IV) [which contains (V)], respectively, and are rich in (III).

J. L. D.

Occurrence and secretion mechanism of cetyl alcohol in the animal organism. R. SCHOENHEIMER and G. HILGETAG (J. Biol. Chem., 1934, **105**, 73—77).—Cetyl alcohol was isolated from the faeces of man, dogs, and cats and was demonstrated in human intestinal wall, meconium, and sterile cysts of the large and small intestine. It is secreted through the intestinal mucosa into the lumen and may constitute an endogenous purgative.

H. G. R.

Lipochromes of animals. R. FABRE and E. LEDERER (Bull. Soc. Chim. biol., 1934, **16**, 105—118).—Astacene, isolated from the shell of the Norwegian lobster (A., 1933, 509), is also present as ester in other Crustaceae examined, viz., *Palinurus*

vulgaris, *Leander serratus*, *Portunus puber*, *Cancer pagurus*, *Nephrops*, and *Potamobius astacus*. The foot of the scallop, *Pectunculus glycymeris*, contains a brownish-violet pigment *glycymerin*, m.p. 148—153°, extracted with CO_2H . The absorption spectrum shows a single band with a max. at 495 mμ. The red anemone, *Actinia equina*, contains a violet pigment, *Actinioerythrin* (I), m.p. 85°, present as the ester of an unstable acid. The absorption spectrum of (I) in light petroleum shows three bands having max. at 534, 497, and 470 mμ.

A. L.

Extractives of liver. R. KAPPELLER-ADLER and A. LUISADA (Biochem. Z., 1934, **269**, 397—414).—The total acidity (expressed as CO_2H) in aq. extracts of fresh calves' liver is 0.2%, and increases on autolysis, part of the acid being Et_2O -sol. When such extracts are evaporated at ordinary pressure or in vac., the acidity is increased 2—3 times, the extra acid not being due to the formation of H_3PO_4 , NH_2 -acids, or polypeptides. During evaporation the NH_2-N is decreased to one third the original val. Tables show the albumose, NH_4^+ , purine, creatinine, and base contents of the phosphotungstic acid ppt. and the creatine, urea, NH_2 -acid, and polypeptide contents of the corresponding filtrates of ox liver extracts. The content of volatile base is also determined. The albumose fraction contained tyrosine 3.28%, phenylalanine 1.08%, but no histidine. The results of similar N fractionation of four commercial anti-anæmia liver preps. are tabulated.

P. W. C.

Glycogen in the liver of young larvæ of anurid amphibia. R. FARAGGIANA (Atti R. Accad. Lincei, 1933, [vi], **18**, 580—582).—Both in the rat and in the anurid amphibia, glycogen appears in the liver before the endocrine islets of the pancreas have assumed the typical structure they show in the adult.

T. H. P.

Determination of glycogen in liver tissue. A. CARRUTHERS and S. M. LING (Chinese J. Physiol., 1934, **8**, 77—83).—The aq. extraction procedure (A., 1931, 642) for the total sugar and glycogen (I) fails to extract about 0.20% of (I) from liver, and is therefore inaccurate with material containing < 4.0% of (I).

C. G. A.

Extractives of muscle of *Dromaeus* sp. D. ACKERMANN and F. A. HOPPE-SEYLER (Z. physiol. Chem., 1934, **223**, 257—258).—Polemical against Tolkatschevskaya (this vol., 431).

J. H. B.

Constitution of muscle-proteins. II. Nitrogen distribution in protein starvation. III. Composition of muscle-proteins in protein starvation and muscle-nitrogen stores. A. ROCHE (Bull. Soc. Chim. biol., 1934, **16**, 257—269, 270—284).—II. The N content of the EtOH extract (I) of the muscles of totally starved rats (II) is 39%, that of protein-starved animals (III) 21%, above normal. The N content of the C_6H_6 extract of (I) in (II) is 15%, and in (III) 100%, > normal. The total muscle-N of (II) is 16.27—17.14%, of (III) 15.09—17.38%, and of normal animals 15.38—16.00%, whilst the ratio of the nuclei acid-P to the protein-N diminishes in (II), it increases in (III).

III. The N distribution of the muscle-proteins of

(II) is normal, but that of (III) shows increases in NH_2 -acid content and decreases in $(\text{NH}_2)_2$ -acids, tryptophan, tyrosine, and lysine. The arginine, cystine, and histidine content is normal. A. L.

Difference in creatine concentration of the left and right ventricular cardiac muscles. D. P. SEECOF, C. R. LINEGAR, and V. C. MYERS (Arch. Int. Med., 1934, 53, 574—593).—The left ventricular muscle has a concn. of creatine (I) > the right. When (I) of voluntary muscle exceeds the saturation point a corresponding elevation in (I) of cardiac muscle occurs. H. G. R.

Diadenosinepentaphosphoric acid [from horse heart]. P. OSTERN (Biochem. Z., 1934, 270, 1—5).—1 kg. of fresh horse heart yields 0.2 g. of the Ba salt of a *diadenosinepentaphosphoric acid*. Pig heart, treated in a similar way, yields adenosine-5-phosphoric acid. W. McC.

Filtration of thymonucleic acid under pressure. T. CASPERSSON (Biochem. Z., 1934, 270, 161—163).—Adherent protein is removed and a non-opalescent filtrate obtained when 4% thymonucleic acid is filtered under 75—100 atm. pressure through 25—50 sheets of Swedish filter-paper. Purity much > 90% is attained. W. McC.

Isolation of cytosine from [pig's] spleen. C. MONCORPS and O. GUNTHER (Klin. Woch., 1933, 12, 979—981; Chem. Zentr., 1933, ii, 1199). A. A. E.

Mucoid substance of the cock's comb. A. BERDNIKOW and C. CHAMPY (Comp. rend. Soc. Biol., 1933, 106, 804—805; Chem. Zentr., 1933, ii, 2842).—Extraction of fat-free tissue of the cock's comb with 15% NaCl solution, dialysis of the acidified filtrate, and appropriate solvent treatment of the dialysate yielded a grey, amorphous powder giving no carbohydrate on hydrolysis, positive biuret reaction, P 1.5, N 14.5%. Thin layers give the same histochemical reactions as sections of cock's comb, but are different from ovalbumin solution. The cock's comb contains a substance not possessed by the comb of the capon. L. S. T.

Physiology of the thyroid. Iodine-containing substances of the thyroid. F. BLUM, F. A. LEHMANN, and W. LEISTNER (Endokrinol., 1933, 13, 250—255).—Thyreoglobulin solutions, on treatment with aq. $(\text{NH}_4)_2\text{SO}_4$ in varying concn., yield two fractions, which, after repeated pptn. and dialysis involving elimination of a nucleoprotein, differ in solubility in H_2O , I content, and therapeutic efficiency. NUTR. ABS. (m)

Thyroid iodine. G. ANDREASSI and M. TALENTI (Arch. Farm. speriment., 1934, 57, 169—185).—In thirty cases examined *post mortem* there was a correlation between the wt. of the human thyroid gland (I) and the mean I content (II), wt. decreasing as (II) increased. The mean (II) of (I) in females was > in males. (II) increased with the stature of the subject, but diminished in senility. R. N. C.

Electrical phenomena of the cornea. III. Electrical charge. IV. Isoelectric point. K. HAYASHI (J. Biochem. Japan, 1934, 19, 173 183, 185—199; cf. this vol., 432).—III. The charge (I) of fresh (II) or formolised cornea (III) (ox, rabbit)

in H_2O is indefinite, but appears to be negative. The negative (I) is more marked in Ringer's solution or aq. KCl, LiCl, NaCl, MgCl_2 , BaCl_2 , and CaCl_2 , whilst in aq. $\text{Cu}(\text{NO}_3)_2$, $\text{Th}(\text{NO}_3)_4$, CeCl_3 , AlCl_3 , and HCl, (I) is positive.

IV. Variations in (I) and the diffusion and membrane potentials of (II) and (III) at p_{H} 3.8—8.5 (OAc' buffer) were determined and the effect of variations in electrolyte concn. on the two sides was investigated. The isoelectric point of (II) and (III) measured by the membrane effect is p_{H} 4.7, by electroendosmosis p_{H} 4.3, and by imbibition p_{H} 4.2—4.4. F. O. H.

Solubility of [dental] enamel. J. C. FORBES (J. Dental Res., 1933, 13, 349—358).—Solubility in H_2O is increased by MgSO_4 ; [Mg] in saliva is not an important factor in the etiology of dental caries. In absence of Ca^{++} and PO_4''' , CO_2 has a solvent effect. Decalcification occurs in presence of glucose and acidogenic organisms. CH. ABS.

Behaviour of dyes towards blood and organ pulp. R. OHTA (Japan. J. Gastroenterol., 1933, 5, 113—122).—Organ pulps combine more readily with basic than with acid dyes. CH. ABS.

Acid versus neutral formaldehyde solution as a neurological fixative. H. A. DAVENPORT (Stain Tech., 1934, 9, 49—52).—Better fixation and staining were realised with acid than with neutral CH_2O . AcOH was most effective in concns. of 3—5%; stronger acids (HCO_2H , $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, $\text{CCl}_3\cdot\text{CO}_2\text{H}$, lactic acid) were effective in concns. of 0.5—1%. H. W. D.

Variation of the Pal-Weigert method for staining myelin sheaths. S. L. CLARK and J. W. WARD (Stain Tech., 1934, 9, 53—55).—The variation consists in treating the sections with 4% aq. $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ before and after staining with hæmatoxylin. H. W. D.

Oil of cloves for differentiation in Mallory's phloxine-methylene-blue stain. L. A. MARGOLENA (Stain Tech., 1934, 9, 71).—Clove oil is better than EtOH for differentiation. H. W. D.

Taurocholic acid from fish-bile. H. MAKINO (J. Biochem. Japan, 1934, 19, 249—251).—From 30 c.c. of the fresh bile of *Seriola quinqueradiata* was isolated 0.5 g. of taurocholic acid (Na salt, m.p. 230—231°, $[\alpha]_{\text{D}}^{20} +24.44^\circ$ in H_2O). F. O. H.

Effects of diet on salivary phosphate. W. H. EDDY, H. L. HEFT, S. ROSENSTOCK, and R. RALSTON (J. Dental Res., 1933, 13, 511—519).—Variations in P content of human saliva are > those in p_{H} . In man, salivary P is decreased by ingestion of sugar and other carbohydrates, or protein, unaffected by fat, and increased by Ca phosphate. In fasting rats ingestion of sugar decreased [P], increased p_{H} , and produced little change in [Ca] of the blood. CH. ABS.

Gastric juice of natives of the Japanese South Sea Island. I. K. NAGASAKI (Japan. J. Gastroenterol., 1933, 5, 111—114).—After a rice gruel test meal the HCl and total acidity were 18.5 and 19.4, respectively, and total Cl 0.3—0.44 g. per 100 c.c. CH. ABS.

Comparison of pepsin and rennin activities of gastric secretions. H. HOLTER and B. ANDERSEN (Biochem. Z., 1934, 269, 285—300).—Whilst the pepsin content (I) of gastric juice varied from 12 units in pig to 75 units in a puppy, the rennin activity (II) varied from 1.05 units in an adult dog to 30 units in the pig. The ratio (I) : (II) varied from 0.13 in calf to 12.5 in dog, and for man and dog was almost the same whether young or adult. The presence of relatively large amounts of rennin appears to be typical for calf. P. W. C.

Secretagogues in the gastric juice of dogs. M. MIYAZAKI (J. Biochem. Japan, 1934, 19, 329—344).—The gastric juice (I) secreted by dogs on sham feeding has no action on the isolated frog's heart and rabbit's intestine or uterus. (I) secreted after subcutaneous or intravenous injection of histamine, choline, muscarine, neurine, pilocarpine, eserine, or methylguanidine has an action resembling that of the drug used. Hence the component of (I) functioning as a secretagogue [the "gastrin" of Edkins (A., 1905, ii, 730; 1906, ii, 238; 1909, ii, 414)] probably consists of a mixture of substances varying with the food and condition of the stomach. F. O. H.

Quantitative relationships between oxyntic and other gastric component secretions. A. C. LIU, I. C. YUAN, and R. K. S. LIM (Chinese J. Physiol., 1934, 8, 1—36).—The oxyntic HCl is secreted at a const. concn. of 0.176 millimol., together with an equal concn. of saline secretion. C. G. A.

Mechanism of the inhibition of gastric secretion by fat. Rôle of glucose, insulin, and the parasympathetic system. M. C. LI (Chinese J. Physiol., 1934, 8, 37—51).—Both fat and the intestinal extract "enterogastrone" inhibit gastric secretion induced by feeding, histamine, insulin, or sham-feeding, without causing any change in the blood-sugar; i.e., the central parasympathetic inhibitory mechanism is not involved. C. G. A.

Effect of adenylic acid on gastric secretion. J. VANDOLAH (Proc. Soc. Exp. Biol. Med., 1933, 31, 28—29).—Injection of adenylic acid or of the vaso-depressor substance present in blood after ingestion of meat produced no gastric response. CH. ABS.

Regulation of gastric acidity. I. Influence of acid on the secretion of hydrochloric acid by fundic pouches and by the whole stomach. C. M. WILHELM, I. NEIGUS, and F. C. HILL (Amer. J. Physiol., 1933, 106, 381—397).—In dogs with intact stomach (I) or with fundic pouches (II) receiving intramuscular injections of 1 mg. of histamine, the presence in (I) or (II) of HCl in concns. of 0.024—0.173*N* does not affect, either in concn. or amount, the acid secretion of the gastric glands. HNO₃ and H₂SO₄ are similarly without effect. Increasing [H⁺] of the (I) contents causes a parallel increase in its emptying time. NUTR. ABS. (m)

Effect of alkalosis on acid secretion by the stomach. G. DELRUE and A. LACQUET (Compt. rend. Soc. Biol., 1933, 114, 570—572).—The acid secretion (I) of the stomach, produced by injection of histamine into gastric fistula dogs, has been studied by determining the blood-*p_H* after ingestion of

NaHCO₃. The reduction of (I) observed during the first days at high altitudes is not accompanied by an increase in blood-*p_H*. NUTR. ABS. (m)

Heavy water content of biological fluids. H. ERLÉNMEYER and H. GARTNER (Helv. Chim. Acta, 1934, 17, 549—550).—The H₂O content of H₂O from milk or fresh orange juice does not differ from that of normal H₂O. J. W. B.

Trophic activity of mammary gland during functional repose. M. PIETTRE (Compt. rend., 1934, 198, 1454—1456).—During rest after lactation, the mammary gland of the cow secretes, often very abundantly, a thick liquid, almost entirely free from caseinogen, and very rich in proteins, including globulin, albumin, and a myxoprotein of lower C content. E. W. W.

Physicochemical phenomena accompanying the physiological stimulus of the udder in primiparous females. M. PIETTRE (Compt. rend., 1934, 198, 1551—1553).—A trophic stimulus, independent of functional stimulus of the mammary gland in heifers, is associated with the occurrence in the colostrum of a myxoprotein (I) containing more H and less C and N than the globulin or albumin. With approaching parturition the proportion of (I) declines and none occurs in normal milk. A. G. P.

Yield and composition of the milk of the merino ewe. A. W. PIERCE (Austral. J. Exp. Biol., 1934, 12, 7—12).—Yields (I) of milk from six merino ewes during the ninth week of lactation were only half those obtained during the third week when max. (I) were reached, but total solids increased by 9%, due chiefly to increases in caseinogen and fat. The P content also increased. A. E. O.

Colorimetric determination of milk-proteins. A. D. STEWART and D. D. MITRA (Indian Med. Gaz., 1933, 68, 556—558).—Comparisons are made between the blue colour produced when Folin's PhOH reagent (I) is added to milk and to a standard tyrosine solution. The % of protein (II) is then calc. by the use of a factor, relating the colour given with (I) to the amount of (II) in the milk as determined by Kjeldahl's method. NUTR. ABS. (m)

Correlation between composition of blood and that of milk. M. S. AVDEJEVA, E. J. BORISSENKO, E. I. IVANOVA, N. A. MESSINEVA, E. L. PROVATOROVA, and N. I. SAVITSCH (Z. Tierzücht., 1933, 28, 61—83).—In the blood of cows there is considerable daily variation in hæmoglobin content, serum-K, -Ca, -Cl, dry matter (I), protein (II), creatine and creatinine, NH₂-acids, cholesterol, depression of f.p., conductivity (III) and surface tension (IV), and in the milk of (I), (II), Cl, K, Ca, (III), and (IV), but there is no close correlation between changes of blood and milk. In cows of two different races high blood concn. in general paralleled milk concn. but without close correlation. There were differences, not referable to differences in environmental conditions, between the two races. NUTR. ABS. (m)

Correlation between fat content of milk and absolute fat production in dairy cows. J. KRÍŽ-ENECKÝ (Vest. Česk. Akad. Zemed., 1933, 9, 519—522).—Since the correlation (I) between milk yield (II)

and % fat content (III) is low and negative, whilst that between (II) and fat yield (IV) is positive and high, it follows that with improvement of dairy breeds there will be an increase of milk production and a consequent increase of abs. fat production, whilst the fall of (III) will be considerably smaller. Hence (II) can serve as a basis of selection. Coeffs. of (I) between (IV) and (III) vary from 0.04 (Danish Red, West Finnish) to 0.17 for the Finnish Ayrshire and 0.22 for Bohemian cattle. The average val. for ten breeds is 0.1085. The (I) between (II) and (IV) in the same breeds varies from 0.8824 (East Finnish) to 0.9642 (Swedish Ayrshire), with an average of 0.9379. The ratio of the first coeff. to the second is on the average 1:11.7, i.e., an increase of (IV) will be twelve times as successful through an increase of (II) than of (III). NUTR. ABS. (m)

Distribution of cholesterol and cholesteryl ester between fat and plasma in cow's milk. H. DAM (Biochem. Z., 1934, 270, 112—115).—The fat contains about 0.3% of cholesterol (all free), the plasma about 0.002% (about 90% free).

W. McC.

Human milk. XII. Vitamin- B_1 and - B_2 contents before and during maternal consumption of yeast. E. G. DONELSON and I. G. MACY (J. Nutrition, 1934, 7, 231—249).—The vitamin- B_2 content of milk was increased 0.1 unit by additions of 10 g. of yeast to the maternal diet, but the vitamin-content remained unchanged. Rats receiving vitamin- B_1 and - B_2 from breast milk showed greater N retention during the yeast administration period.

A. G. P.

Comparison of the leucocyte count, the bromothymol-blue reaction, and the catalase content of freshly drawn milk. C. C. PROUTY (J. Dairy Sci., 1934, 17, 75—81).—A general relationship exists between the leucocyte count and the response to the bromothymol-blue (I) and catalase (II) tests. Among many samples examined, fewer reacted normally to the (II) than to the (I) test. The average cell count of milk from normal udders is much lower than is generally supposed. The % of animals giving milk reacting normally to (I) and (II) from all quarters and at all times is very small. A. G. P.

Significance of true *B. coli* (*B. coli communis*) and *B. lactis aerogenes* in samples of milk. C. H. CHALMERS (Zentr. Bakt. Par., 1934, II, 89, 459—474).—Infection of milk with these organisms is discussed. Indole is not produced in milk by *B. coli communis*, which probably utilises lactose in preference to the side-chain of tryptophan. Telluric acid, added to the medium for the presumptive test, inhibits the activity of *B. aerogenes*, whereas brilliant-green inhibits *B. coli*. Distinction between these organisms is thus possible. A. G. P.

Influence of mastitis on the curd tension of milk. H. C. HANSEN, D. R. THEOPHILUS, F. W. ATKESON, and E. M. GILDOW (J. Dairy Sci., 1934, 17, 257—264).—The curd tension of milk was lowered by mastitis when the latter was caused by infection with *Streptococcus*, but was not altered when infection was with *Staphylococcus*. No relationship was apparent

between development of fibrous tissue in the udder and curd tension in the milk. A. G. P.

Absorption of pigment by the intestines. I, II. Behaviour of the lymphatic vessels. S. KAWAWAKI (Japan. J. Gastroenterol., 1933, 5, 101—107, 108—110).—Pigments were introduced into the intestines of dogs and their appearance in the urine, bile, and lymph was recorded. CH. ABS.

Dye excretion through the liver and kidneys. Y. YANO (Japan. J. Gastroenterol., 1933, 5, 123—127).—Acid dyes are excreted through the kidneys if they diffuse readily in sera. Of dyes excreted with difficulty by the liver and kidneys only acid dyes can be detected for a long period in the blood. Lipin solubility of basic dyes interferes with a direct relation between diffusibility and excretion. CH. ABS.

Excretion of dyes through the liver and kidneys. Y. TADA (Japan. J. Gastroenterol., 1933, 5, 143—186).—Most dyes when injected intravenously into dogs appear in the urine or bile. The more diffusible is the dye the greater is the concn. in the urine and the shorter is the time of excretion. The concn. in the blood is related to that in the urine and bile. CH. ABS.

Absorption and excretion of water and salts by the elasmobranch fishes. IV. Secretion of exogenous creatinine by the dog-fish, *Squalus acanthias*. J. A. SHANNON (J. Cell. Comp. Physiol., 1934, 4, 211—220).—The clearance of injected creatinine (I) exceeds that of xylose or sucrose by an amount depending on the concn. of (I) in the plasma, the difference decreasing as the plasma level falls. Phloridzin depresses the secretion of creatinine at both high and low plasma levels.

A. G. P.

Mercury-reducing power of the sulphur-containing pigment of normal urine. B. GWOZDZ (Bull. Soc. Chim. biol., 1934, 16, 211—219).—The ppt. (I) containing the colouring matter obtained by $\text{Cu}(\text{OAc})_2$ from human urine freed from $\text{SO}_4^{''}$ and $\text{PO}_4^{'''}$ has 29—42% of the reducing power (II) of normal urine as determined by the method of Baudouin (A., 1927, 476), and 32—53% of the total neutral S. The (II) due to the neutral S component of (I) is 17—25% of that of (I). A. L.

Osazone reaction in glucosuria and lactosuria. R. FORST (Boll. Chim.-Farm., 1933, 72, 802—804).—In non-defecated urine, glucose can be detected in concn. 0.02%, and lactose in concn. 0.05%, by the osazone reaction (I), using $\text{NHPh}\cdot\text{NH}_2\cdot\text{HCl}$ instead of the free base. The two osazones (II) can be separated in their typical cryst. forms from the pptd. mixture by eliminating the substances promoting polymorphic crystallisation of (II), and adjusting the p_H to the optimum for (I). R. N. C.

Determination of chloride in urine. G. GLOMAUD and G. BON-BERNATETS (J. Pharm. Chim., 1934, [viii], 19, 437—442).—Direct titration with 0.1N- AgNO_3 using $\text{K}_2\text{Cr}_2\text{O}_7$ as indicator gives vals. > those obtained by the normal Volhard method (I), the difference being partly due to uric acid. The method of Votoček (A., 1918, ii, 238) gives vals.

slightly nearer to gravimetric determinations than those by (I). F. O. H.

Influence of bile acids on the $[H^+]$ of urine. T. KURAMOTO (J. Biochem. Japan, 1934, 19, 245—248).—Intravenous injection (I) of Na cholate (10 mg. per kg. body-wt.) into dogs produces parallel increases in the p_H and d of the urine lasting for 8—10 hr., max. vals. occurring 4—5 hr. after (I). F. O. H.

Detection of blood in fæces. M. E. STAS (Pharm. Weekblad, 1934, 71, 489—495).—Fæces are extracted 3 times with CO_2Me_2 to remove H_2O and colouring matter, dried, and re-extracted with $AcOH-EtOAc$ (1:3). The filtrate is evaporated and the residue tested spectroscopically for porphyrins and, after heating to 175° , by the benzidine reaction for hæmatin. S. C.

Determination of phosphorus in fæces. G. ZARDO (Arch. Farm. sperim., 1934, 57, 139—152).—A description of standard methods. R. N. C.

Changes of colorimetric-, volume-, and saturation-index on administration of copper in experimental anæmia [produced by feeding] milk. E. E. FOG (Biochem. Z., 1934, 269, 301—307).—Administration to young rats, rendered anæmic by milk feeding, of $Cu+Fe$ effects a rapid, and of Fe alone a slow, regeneration of red cells. The changes during treatment of the % hæmoglobin, no. and vol. of red cells, etc. are tabulated. P. W. C.

Constancy of iron in the blood-plasma and urine in health and in anæmia. A. MARLOW and F. H. L. TAYLOR (Arch. Int. Med., 1934, 53, 551—560).—Blood-plasma and urine contain 0.4—0.7 and 0.03—0.8 mg. Fe per 100 c.c., respectively. Cases of hypochromic and pernicious anæmia showed no variation, and administration of $Fe^{III} NH_4$ citrate caused no definite increase. H. G. R.

Action of gastric juice on beef muscle-globulin, with reference to anæmia. W. J. GRIFFITHS (Biochem. J., 1934, 28, 671—675).—Normal gastric juice produces larger amounts of sol. N from beef muscle-protein at p_H 6 than does that from cases of pernicious anæmia. The effect is not due to trypsin or pepsin, but possibly to Castle's intrinsic factor (Amer. J. Med. Sci., 1931, 182, 741). C. G. A.

Calcium and phosphorus metabolism in certain diseases of bone. W. DE M. SCRIVER and E. M. VENNING (J. Clin. Invest., 1934, 13, 139—153).—In Paget's disease, bone cyst, and bone sarcoma Ca metabolism was normal. CH. ABS.

Glutathione in circulatory diseases. S. J. MALKIN (Z. ges. exp. Med., 1933, 89, 193—199; Chem. Zentr., 1933, ii, 3586).—Normally, blood-glutathione is 45—55 mg. per 100 c.c. Low vals. in circulatory diseases are increased by administration of glucose. A. A. E.

Creatine content of the heart in experimental cardiac hypertrophy. D. W. COWAN (Proc. Soc. Exp. Biol. Med., 1934, 31, 417—418).—The creatine concn. in hypertrophied ventricles (wt. 36% > normal) in rats in nutritional anæmia was 26.6% < in controls. In normal growth hypertrophy the concn. of creatine in the ventricles was approx. const. CH. ABS.

Electrolytes in human tissue. III. Congestive heart failure. W. E. WILKINS and G. E. CULLEN (J. Clin. Invest., 1933, 12, 1063—1074).—The H_2O content of the right ventricle is normally slightly > that of the left; it is higher in both ventricles in congestive heart failure. Differences in P, Na, and K also exist. CH. ABS.

Nature of the pathological principle contained in malignant tumours. A. BESREDKA and L. GROSS (Compt. rend., 1934, 198, 1460—1462).—The cell-free liquid obtained by grinding and centrifuging an Ehrlich mouse-sarcoma is, even after filtration, capable of causing tumours when subcutaneously injected, and presumably contains a virus. This is easily destroyed, since the ground and suspended tumour loses its activity in $\frac{1}{2}$ hr. at $42-43^\circ$, or in 48 hr. at room temp. The liver and blood of inoculated animals, as well as the tumours, are virulent. E. W. W.

Nitrogen metabolism in white mice in the course of tumour development. I. A. PARFENTYEV (Proc. Soc. Exp. Biol. Med., 1933, 30, 1064—1067).—The urine of the normal mouse contains approx. 1.4 g. per 100 c.c. of a chondromucoid-like protein. The protein, and urea, decrease during growth of sarcoma 180. CH. ABS.

Metabolism of normal and tumour tissue. XII. Action of phenylhydrazine on the Pasteur reaction and on tissue respiration. F. DICKENS (Biochem. J., 1934, 28, 537—549).— $NHPh \cdot NH_2$ (I), in low concn., has no effect on the anaerobic glycolysis of tissues (II) or the anaerobic fermentation of yeast; in presence of O_2 the lactic acid is increased to a val. equal to that of the same cells anaerobically. (II), the respiration (III) of which depends on oxidation of glucose or lactate, give a fall in (III) after heating with (I). The high aerobic glycolysis of tumour (II) is increased to the anaerobic val. by (I). H. G. R.

Calcium and phosphorus [and caries]. VIII. Rat. D. H. SHELLING and D. E. ASHER (J. Dental Res., 1933, 13, 363—378).—Caries-like lesions are frequent in rats receiving a ration containing much coarsely ground maize, and absent when the ration contains caseinogen and starch or grains with particles finer and softer than those of maize. The occurrence is not related to the Ca or P content, or to the blood-serum-Ca and -inorg. P. CH. ABS.

Use of *Solanum fludicum* in diabetes. I. S. KLEINER (Science, 1934, 79, 273).—The fruit has no permanent effect in lowering blood-sugar. L. S. T.

Salt and water in the treatment of diabetic acidosis. D. M. KYDD (J. Clin. Invest., 1933, 12, 1169—1183).—Treatment of diabetics with insulin and carbohydrate alone is unsatisfactory. $NaCl$ gives a rapid recovery with hyperchloræmia, retention of Cl until the base level is normal, followed by excretion of Cl with excess of base. CH. ABS.

Basal metabolism in asthma and epilepsy. A. TOPPER and H. MULIER (Amer. J. Dis. Children, 1933, 46, 963—968).—In children subnormal vals. are observed. CH. ABS.

Hypoglycæmia in the etiology of idiopathic epilepsy. R. L. H. MINCHIN (J. Mental Sci., 1933 (October), 18 pp.).—Epilepsy is associated with low fasting blood-sugar due to hyperinsulinism.

C. G. A.

Chlorine metabolism in Graves' disease. F. HEIMANN (Arch. Verdauungs-Krankh., 1933, 54, 176—182).—Severe cases of Graves' disease exhibit a true achylia after caffeine (I) and after histamine (II). The Cl' of the resting gastric contents is low in very toxic conditions, normal in less severe cases. (I) and (II) have no uniform influence on gastric Cl' secretion; the blood-Cl' remains unaltered or occasionally falls.

NUTR. ABS. (m)

Peculiarity of thyroid extracts in exophthalmic goitre with respect to increased oxygen consumption. III. Rabbits injected with exophthalmic goitre extract. K. SAITO (Tôhoku J. Exp. Med., 1933, 22, 227—251).—Injection of splenic extract (I) or irradiation of the splenic area (II) has only a slight effect on the increased O₂ consumption of rabbits after injection of goitre extracts, but such rabbits react to KI in doses (0.25—0.5 mg. per kg.) which have little effect on normal rabbits. Hyperthyroid rabbits react promptly to (I), (II), or KI.

CH. ABS.

Effect of di-iodotyrosine on basal metabolism in myxœdema. W. O. THOMPSON, J. M. ALPER, P. K. THOMPSON, and L. F. N. DICKIE (J. Clin. Invest., 1934, 13, 29—36).—Intravenous administration of di-iodotyrosine (I) has no effect on basal metabolism in myxœdema. (I) is not the limiting factor in thyroxine (II) formation in individuals with very small amounts of active thyroid tissue, and it cannot be synthesised to (II) outside the thyroid.

CH. ABS.

Maintenance requirements of myxœdema patients. Clinical and chemical assay of commercial thyroid preparations. J. LERMAN and W. T. SALTER (J. Pharm. Exp. Ther., 1934, 50, 298—309).—Determination of the equiv. maintenance doses of various thyroid preps. for twenty patients with myxœdema indicates that the activity per unit wt. varies considerably. The calorogenic action of whole thyroid is dependent on the total I, rather than on the thyroxine-I content.

A. L.

Gastric acidity in thyroid dysfunction. S. A. WILKINSON (J. Amer. Med. Assoc., 1933, 101, 2097—2099).—In hyperthyroidism (I) in man the acidity of the gastric juice (determined every 30 min. after subcutaneous injection of histamine acid phosphate) is below normal, but returns to normal after thyroidectomy. In hypothyroidism there is hyperacidity. The hypoacidity in (I) may be due to over-activity of the sympathetic nervous system.

NUTR. ABS. (m)

Phosphatase activity of bones and kidneys in thyrotoxicosis. M. B. LOW, R. O. WILSON, and J. C. AUB (Proc. Soc. Exp. Biol. Med., 1934, 31, 447—450).—In rats the kidney-phosphatase was slightly diminished; the kidneys were increased in size. Bone-phosphatase was normal.

CH. ABS.

Calcium of milk and serum in thyroparathyroidectomised bitches. C. I. PARHON, R.

CARNATESCO, and I. ORNSTEIN (Compt. rend. Soc. Biol., 1933, 114, 323).—The Ca content of milk and serum is reduced.

NUTR. ABS. (m)

Blood-lactic acid in thyroparathyroidectomised dogs. C. I. PARHON and C. URZICA (Compt. rend. Soc. Biol., 1933, 114, 751—752).—Blood-lactic acid decreases progressively until death ensues. The decrease is due to absence of the parathyroids.

NUTR. ABS. (m)

Adrenaline content of the adrenals in parathyroidectomised animals. L. BINET and G. WELLER (Compt. rend. Soc. Biol., 1933, 114, 985—987).—Progressive reduction, which may be prevented by Ca administration, occurs.

NUTR. ABS. (m)

Magnesium metabolism in hyperparathyroidism. H. A. BULGER and F. GAUSMANN (J. Clin. Invest., 1933, 12, 1135—1142).—There is a negative Mg balance. The effect of the parathyroid hormone on Mg metabolism may be secondary to that on Ca metabolism.

CH. ABS.

[Cause of] hæmorrhagic lipæmia. U. STARUP (Biochem. Z., 1934, 270, 74—92).—Lipæmia (I) of the same kind is produced in rabbits (II) by repeated bleeding, subcutaneous injection of NHPH-NH₂, injection of large amounts of H₂O, or diminution to 340 mm. of the atm. pressure in which (II) live. The decreases in the total protein, neutral fat, cholesterol, lecithin, and hæmoglobin (III) contents of the blood which accompany (I) are similar in all cases, although with NHPH-NH₂ (I) is a secondary phenomenon, a consequence of the anæmia caused by the poisoning involved. In all cases (I) is due to the lack of O₂ caused by the reduced (III) content of the blood.

W.McC.

Lactic acid metabolism in ileus. I. Time course of the lactic acid level. II. Lactic acid metabolism in the liver. J. IZUMI (Tôhoku J. Exp. Med., 1933, 22, 201—216, 217—226).—I. After ligation of the intestine in rabbits at the pyloric level, blood-lactic acid rises, reaching a max. (50—60 mg. per 100 c.c.) immediately before death.

II. After experimental ileus arterial (I), portal (II), and hepatic (III) venous blood-lactic acid rises; the order becomes (III)>(I)>(II) instead of (I)>(II)>(III). The results are ascribed to impaired resynthesis of lactic acid in the liver, its increased formation from hepatic glycogen, and disturbed metabolism in organs drained by the portal vein.

CH. ABS.

Blood-brain barrier in infectious diseases; its permeability to toxins in relation to their electrical charges. U. FRIEDEMANN and A. ELKELES (Lancet, 1934, 226, 775—777; cf. this vol., 548).—Cathaphoresis shows that at the p_H of blood the toxins which do not pass the barrier are negatively charged, whilst those which do are neutral (lamb-dysentery toxin) or positively charged (cobra toxin). The incubation period of toxins appears to be related to electrical charge.

L. S. T.

Action of cinchona and other alkaloids in bird malaria. G. A. H. BUTTLE, T. A. HENRY, and J. W. TREYAN (Biochem. J., 1934, 28, 426—441; cf. A., 1930, 1310).—In tests on canaries infected with

bird malaria, the anti-malarial potency of dihydroquinine is $>$ that of quinine, of dihydroquinidine, quinidine, and cinchonidine $<$ that of quinine, and of dihydro-cinchonine and -cinchonidine $<$ that of all the others. The toxicities of the drugs to mice are approx. the same. H. D.

Titration of sexual hormones in mental diseases. H. SAETHRE (Klin. Woch., 1933, 12, 1409—1410; Chem. Zentr., 1933, ii, 2999).—The female urine had a very high hormone content, usually due to increased excretion of prolan-A.

H. J. E.

Chlorides and inorganic constituents of the serum and cerebrospinal fluid in nephritis. G. C. LINDER (Biochem. J., 1934, 28, 416—417).—A high cerebrospinal fluid- (I) -Cl' titre in uraemia indicates a disturbance of the normal serum (I) relationships, and also a high serum-Cl' with a severe acidosis.

A. E. O.

Amino-nitrogen changes in the blood in nephritis. E. KIRK (J. Clin. Invest., 1933, 12, 1091—1102).—Rise in plasma-NH₂-N, probably due to breakdown in NH₂-acid metabolism elsewhere, is frequent as renal disease becomes more advanced.

CH. ABS.

Trypsin poisoning in acute pancreatic necrosis. Determination of trypsin. J. BAUMANN (Z. ges. exp. Med., 1933, 91, 120—177).—The smallest concn. of trypsin (I) capable of digesting within 30 min. at 38° 0.2 mg. of caseinogen (II) made up to 1 c.c. with phosphate buffer (p_H 8.5) is determined. A solution contains one unit when 1 c.c. digests 0.2 mg. of (II): this is equiv. to 0.125 Willstätter unit. The (I) content of normal human urine is $>$ 1 unit per c.c.; in conditions where the pancreas (III) is affected, as indicated by increased urinary diastase, the urinary (I) is $>$ normal. In dogs with acute fatal necrosis (IV) of (III) produced by injection of oil the (I) concn. of the urine is increased 1000-fold or more. Simple ligation of the pancreatic duct does not cause increase of urinary (I), but non-fatal oil (IV) produces a moderate increase. Probably (I) passes in active form from (III) to kidney, and so is responsible for the pathological manifestations in acute pancreatic (IV).

NUTR. ABS. (m)

Iron metabolism in a normal subject and in a polycythæmic patient. P. REZNIKOFF, V. TOSCANI, and R. FULLARTON (J. Nutrition, 1934, 7, 221—230).—A normal subject stored Fe with a daily intake of 26 mg. and was in balance with 15 mg. Parenteral administration of liver extract (I) caused retention with a 10 mg. intake and increased Fe storage with a 17 mg. intake. With heavy Fe dosages (I) caused a marked increase in Fe excretion. CuSO₄ reduced the Fe elimination. During a remission stage a polycythæmic subject showed an Fe balance with an intake of 14—18 mg. Urinary Fe maintained a const. and low level. Faecal Fe was const., except when heavy dosages of Fe were given.

A. G. P.

Relationship between oxygen consumption and nitrogen metabolism. III. In polycythæmia vera. A. BARER, W. D. PAUL, and C. W.

BALDRIDGE (J. Clin. Invest., 1934, 13, 15—28).—Following administration of NHPh·NH₂ in polycythæmia vera there were observed: temporary negative N balance due to increased excretion of urea, slightly increased proteinuria, retention of Fe liberated by destruction of red cells, formation of urea and bilirubin more rapidly than they were excreted, intermittent urobilinuria, and decrease in blood-viscosity.

CH. ABS.

Blood in normal pregnancy. V. Conductivity, total base, chloride and acid-base equilibrium. VI. Plasma-cholesterol, variations in total amount. W. J. DIECKMANN and C. R. WEGNER (Arch. Int. Med., 1934, 53, 527—539, 540—550).—V. The serum-conductivity, total base, and CO₂ content are decreased, reaching a min. at term. There is no change in p_H or NaCl, and there is no acidosis of pregnancy. There is, however, a mean total increase in NaCl and total base of 22.7% and 20.6%, respectively, with a similar increase in plasma-vol.

VI. Plasma-cholesterol shows an increase of 33.9% at 26 to 35 weeks and of 27.9% at term. There is then a decrease amounting to 21.2% at 8 weeks post partum.

H. G. R.

Factors influencing nitrogen economy during pregnancy. C. M. COONS and G. B. MARSHALL (J. Nutrition, 1934, 7, 67—78).—N retention was somewhat lower than formerly suggested unless the diet was supplemented by additional protein or vitamin-B. Various other factors concerned are discussed.

A. G. P.

Interaction of vitamin-D and dietary factors in the healing of rickets in rats. H. M. BRUCE and R. K. CALLOW (Biochem. J., 1934, 28, 512—516).—The effect of simultaneously administering vitamin-D to rats on a rachitic diet low in P and of increasing the amount of P in the diet is approx. represented by the product of two factors rather than by the sum.

W. O. K.

Cereals and rickets. Rôle of inositolhexaphosphoric acid. H. M. BRUCE and R. K. CALLOW (Biochem. J., 1934, 28, 517—528).—Addition of inositol hexaphosphate (I) to high-Ca low-P rachitogenic diets does not appreciably prevent rickets in rats, although the addition of inorg. P does. The action of diets rich in oatmeal in developing rickets in spite of a non-rachitic Ca : P ratio is attributed to much of the P being in the form of (I), and therefore not available to the animal. The addition of (I) to low-Ca diets appears to have a rachitogenic effect possibly due to non-absorption of Ca in consequence of the low solubility of Ca (I). The effect of acid treatment on the rachitogenic substance present in oatmeal and other cereals (cf. A., 1928, 333) is probably dependent on the acid hydrolysis of (I).

W. O. K.

Surra. I. Blood chemistry in equine trypanosomiasis (*Trypanosoma evansi*). R. RANDALL (Philippine J. Sci., 1934, 53, 97—105).—In horses with *T. evansi* infection (surra), the CO₂ capacity of the blood decreases, whilst the lecithin, non-protein-N, and creatinine increase. The changes in the blood-sugar are irregular. Death is due to asphyxia from an uncompensated acidosis.

F. O. H.

Blood-glutathione in chronic pulmonary tuberculosis. L. BETHOUX and G. CARRAZ (Bull. Acad. Med., 1933, 110, 51—57; Chem. Zentr., 1933, ii, 3586).—Total, particularly S-S-, glutathione diminishes, but not proportionally to the anæmia or to the severity of the disease. A. A. E.

Changes in the lipolytic activity of different organs during tuberculosis. A. I. VIRTANEN and P. SUOMALAINEN (Nature, 1934, 133, 532—533).—Lipolytic activity (I) of liver, pancreas, and blood-serum (II) of guinea-pigs decreases considerably as tuberculosis (III) develops. A decrease in (I) occurs only in (II) when (III) is not general. The destructive action of the tubercle bacilli on the tissues appears also to destroy the lipases. L. S. T.

Immunobiological study of fats. I. Formation of antibodies against lipins in tuberculous rabbits. II. Effect of enteral and parenteral lipins on the serum-lipase of normal and tuberculous rabbits. Y. TOKUNOYAMA (Tôhoku J. Exp. Med., 1933, 22, 252—262, 263—292).—I. Repeated intravenous injection of hydnocarpus oil (I), liver oil (II), tristearin (III), tripalmitin (IV), and triolein (V) into rabbits causes the appearance of complement-fixing antibodies in very low titre, the response decreasing in the above order, and increasing when the lipin was previously mixed with pig serum. Response was more pronounced in animals inoculated with human *B. tuberculosis* (VI).

II. Intravenous or parenteral injection of (I) and (II) increased serum-lipase. Decoic acid and (III) were less effective; (IV) and (V) had no effect. The effect was diminished by previous admixture of the lipin with pig serum and increased by simultaneous inoculation with (VI). Cholesterol causes a decrease, and lecithin a slight decrease, in serum-lipase; lipase (enteral) has no effect. Reticulo-endothelial blockade causes a decrease, and prevents normal reaction to injection of (II). CH. ABS.

Daily secretion of water, hydrochloric acid, and chloride in the normal and ulcerated human stomach. K. P. BECKER and J. FELDHAUS (Deut. Arch. klin. Med., 1933, 176, 138—148).—The total vol. of gastric secretion, the average [HCl], the average [Cl'], the total HCl secreted, and the total Cl' secreted during 12 hr. in the stomachs of sufferers from ulceration are > the corresponding amounts in those of healthy persons. NUTR. ABS. (m)

Sheep ailment in the Westhaven-Cape Farewell district, Collingwood County, Nelson. T. RIGG and H. O. ASKEW (New Zealand J. Sci. Tech., 1934, 15, 258—262).—The ailment, somewhat resembling bush-sickness, is associated with soils deficient in Ca and P; sheep on calcareous pastures are not affected. Applications of Ca and P and the use of bone-meal licks are beneficial. Both soils and pastures in affected areas have a low Fe content. A. G. P.

Sheep sickness in the Pakawau district of the Collingwood County, Nelson. H. O. ASKEW and T. RIGG (New Zealand J. Sci. Tech., 1934, 15, 305—308).—Sickness is related to deficiencies of Ca and P in the soils concerned. Liming, application of P

fertilisers, and the provision of bone-meal licks improved the condition of the sheep. A. G. P.

Physiology of the Blue Whale. A. KROGH (Nature, 1934, 133, 635—637).—A summary dealing with rate of growth, metabolism, circulation, and respiration. L. S. T.

Chemistry of respiration. A. J. KLUYVER (Chem. Weekblad, 1934, 31, 295—308).—Historical development of modern theory. S. C.

Respiratory quotient of the eviscerate cat. J. M. PETERSON (J. Physiol., 1933, 79, 508—518).—In simultaneous determinations of blood-CO₂ (I) and -lactic acid (II) in decerebrate eviscerate cats (III), there is very high correlation and equimol. relationship between (I) fall and (II) increase. The more rapid the rate of fall of (I) the higher is the observed R.Q., and by extrapolation, at the point of zero CO₂ change the R.Q. would be 0.825. The true oxidative quotient is thus of this order, and the higher vals. frequently obtained are due to displacement of CO₂ from the tissues. Calculation from the relative vals. of the R.Q. in decerebrate cats and in (III) shows the R.Q. of the removed viscera to be 0.69, a val. probably associated with liver gluconeogenesis.

NUTR. ABS. (m)

Influence of previous exercise on the metabolism, rectal temperature, and body composition of the rat. K. HORST, L. B. MENDEL, and F. G. BENEDICT (J. Nutrition, 1934, 7, 251—275).—Severely exercised rats had 3.5% less fat and 3% more H₂O (fresh wt.) than unexercised controls. On a dry matter basis, (I) had higher ash and N and low fat contents. Variations in basal metabolism showed no relationship to those in ash, N, or fat contents.

A. G. P.

Effects of some external factors on the metabolism of the rat. K. HORST, L. B. MENDEL, and F. G. BENEDICT (J. Nutrition, 1934, 7, 277—303).—Variations in O₂ consumption and metabolic rates during day and night are examined. Sex differences are recorded. A. G. P.

Effects of fasting on the composition of the blood and respiratory exchange in fowls. K. M. HENRY, H. E. MAGEE, and E. REID (J. Exp. Biol., 1934, 11, 58—72).—No relation exists between the 4-day peak for blood-glucose in fasting chickens and the changes in cholesterol, lipin-P, uric acid, and non-protein-N. Liver-glycogen may fall from 2.6 to 0.13% (const.) after 24 hr., and blood-lipin-P from 18.7 to 13.4 mg. per 100 c.c. on the 3rd day (thereafter, 16.1—17.9). Ingestion of glucose decreases hyperglycæmia (I) during fasting. Adrenaline produces greater (I) in fowls which had fasted for 96 hr. than <96 hr. During 7 days' fasting the R.Q. fell to <0.7; it was unaltered by protein feeding but increased after fat feeding. During fasting uric acid was 50% of urinary N, and after a protein meal 30%. Hence the low R.Q. during fasting is due to uric acid synthesis. CH. ABS.

Fasting metabolism of various breeds of hog. I. Introductory: age, weight, length data, etc. T. DEIGHTON (J. Agric. Sci. 1934, 24, 326—334).—

Changes in length and wt. of fasting hogs of nine breeds are recorded and discussed. A. G. P.

Intracellular oxidation-reduction studies.
VII. Mechanism of reduction potentials in starfish sperm. S. MACHLIS and D. E. GREEN (J. Cell. Comp. Physiol., 1933, 4, 61—78).—Respiratory poisons (KCN, H_2S , CO) shift the aerobic potential (I) of starfish sperm to a more negative range, but do not affect the rate of anaerobic reduction or the intensity factor. Et urethane shifts (I) to a more positive range. The anaerobic potential (II) is not changed, but the rate of reduction is lowered. Neither (I) nor (II) is affected by $CH_3I \cdot CO_2H$. Boiling does not change the val. of (I). (I) of heated sperm is not altered by anaerobiosis, KCN, H_2S , or Et urethane with respect to the corresponding changes in normal sperm. A. G. P.

Influence of thiol groups and respiration on the rate of cell division. E. L. ELLIS (J. Cell. Comp. Physiol., 1933, 4, 127—139).—The rate of division of fertilised eggs of *Urechis caupo* or *Strongylocentrotus purpuratus* is not affected by treatment with $CH_3I \cdot CO_2'$ or F' or by cystine or glutathione. The retardation of fertilised *Urechis* eggs by CN' is partly overcome by oxidation-reduction dyes having potentials of -0.17 to -0.02 volt. A. G. P.

Influence of raw and cooked vegetable foods on oxidation in the body. I. KANAI (Z. ges. exp. Med., 1933, 89, 131—140; Chem. Zentr., 1933, ii, 3304).—With raw vegetables (I) rats attained a positive N balance; urinary C:N and vacat-O:N were <, and increase in body wt. >, with cooked (I). A. A. E.

Physiology of the adrenals. L. BINET and G. WELLER (Paris med., 1933, No. 26, 31—32).—The adrenal is the organ with the highest content (I) of reduced glutathione (II). Perfusion with citrated blood with added cystine and glutamic acid gives an increase in the gland and in the perfusion fluid. Hence (II) is synthesised. Determinations of S indicate that the cortex is the more active part. External factors (pancreatectomy, pregnancy) alter (I). NUTR. ABS. (m)

Dynamic action of amino-acids on the function of individual organs and on the gaseous exchange of the lungs in man. J. SCHUBERT (Biochem. Z., 1934, 269, 241—253).—A table summarises the effect on the tonus and rhythmic movement of the guinea-pig's intestine of varying concn. of glycine, alanine, valine, leucine, aspartic and glutamic acids, asparagine, NMe_3 , histamine, and of a purified (I) and a crude (II) sample of mixed NH_2 -acids obtained by hydrolysing a plant protein. (I) and (II) in concns. of 0.05—0.025 g. N per kg. body-wt. given orally to man always caused a rapid and considerable increase of basal metabolism. P. W. C.

Fission of choline in the organism. K. TODA (J. Biochem. Japan, 1934, 19, 201—216).—The NH_2Me excretion of rabbits (normally approx. 3—5 mg. per day) is increased for approx. 2 days by the intravenous injection of lecithin, whilst the NH_2Me contents of the liver (I) and spleen (II), but not that of the kidney, also markedly increase. The form-

ation (probably enzymic) of NH_2Me from added choline occurs in normal, but not heated, macerates of (I) and (II), a max. occurring at pH 7—8.

F. O. H.

Synthesis of purine in mammals. R. KAPPELLER-ADLER, E. LAUDA, and K. VON MEGAY (Biochem. Z., 1934, 269, 254—262).—The allantoin (I) and purine (II) contents of the urine of dogs receiving diets rich and poor in (II) are large and small, respectively, (I) forming the end-product of dog's (II)-metabolism. The urinary (II) of an animal in equilibrium is always > the (II) intake, indicating (II)-synthesis, and the view that a diet rich in carbohydrate leads to (II) synthesis is confirmed. P. W. C.

Uric acid synthesis in the bird. T. BENZINGER and H. A. KREBS (Klin. Woch., 1933, 12, 1206—1208; Chem. Zentr., 1933, ii, 3006).—Uric acid (I) is formed from NH_3 in the liver and kidneys in pigeons, and in the liver in hens. Urea and tartronic acid cannot form (I). H. J. E.

Inability of the bird to condense urea with pyruvic acid and propionic acid. D. TORRISI and F. TORRISI (Arch. Sci. biol., 16, 589—602; Chem. Zentr., 1933, ii, 3005—3006).—No increased uric acid excretion followed from daily dosage with 0.5 g. of $EtCO_2H$ or $AcCO_2H$. Urea administered with $EtCO_2H$ and $AcCO_2H$ was excreted unchanged. H. J. E.

Protein metabolism in man. H. BORSOOK and G. KEIGHLEY (Proc. Nat. Acad. Sci., 1934, 20, 179—183).—Protein (I) metabolism is largely endogenous in the sense that it is immediately derived not from ingested (I), but from (I) (or its fission product) already in the body. The sp. dynamic action of (I) depends on a factor associated with oxidative deamination and a second factor relating to the metabolism of the deaminised residues. NH_3 is one of the sources of urinary uric acid. W. O. K.

Replacement of part of the protein in the food of cows by ammonium hydrogen carbonate. III. P. EHRENBERG and A. SCHOLZ (Biochem. Z., 1934, 270, 188—202; cf. A., 1933, 309).—Provided that the rest of the diet is suitable and palatable, much of the protein of the food of milch-cows may be replaced by NH_4HCO_3 without lowering appreciably the quantity or quality of the milk. W. McC.

Supplementary relationships between proteins of wheat and rye breads and those of *Pisum sativum*. Z. MARKUZE (Biochem. J., 1934, 28, 463—466).—Using the biological tests previously described (A., 1931, 1451), the biological val. (I) of pea-meal protein is 1.2—1.4, a wheat-pea mixture 1.6—1.9, a rye-pea mixture 1.6—2.1, rye bread 1.1, wheat-gluten protein 1.0, and a gluten-pea mixture 2.2. H. D.

Biological values of proteins. V. Comparative biological values of the proteins of whole wheat, whole maize, and maize gluten, measured by the growth of young rats. M. A. BOAS-FIXSEN, J. C. D. HUTCHINSON, and H. M. JACKSON (Biochem. J., 1934, 28, 592—601).—The nutritive val. (I) and biological val. (II) of the proteins (III) of whole wheat are only slightly > the corresponding vals.

for the (III) of whole maize for support of growth in young rats (IV), the criterion for (II) being the ratio g. wt. increase/(g. protein ingested - 10). The (II) of the (III) of cooked and raw cereals were the same, but the (I) of the former appeared to be slightly the greater. The (I) of "maize-gluten" is inferior to that of the whole grain, doubtless due to the greater proportion of zein in the former. The results are in accord with previous work on the maintenance of the adult rat (cf. A., 1933, 182). A. E. O.

Food value of seeds of *Cicer arietinum*, L. V. ZAGAMI (Atti R. Accad. Lincei, 1933, [vi], 18, 403-406).—These seeds are deficient in salts and probably in vitamin-A and -D. Proteins and vitamin-B and -E are present in sufficient and suitable proportions for the nourishment of adult rats. T. H. P.

Nutritive value of seed of corn-cockle (*Agrostemma githago*). F. ROGOZIŃSKI and Z. GŁÓWCZYŃSKI (Bull. Acad. Polonaise, 1933, B, 189-203).—In small quantities corn-cockle seed has no effect on the growth or the mineral content of the bones of rats. On a diet containing 87% of the seed the rats remain at const. wt. and in good health. C. G. A.

Comparative physiological evaluation of milk powder. E. S. LONDON, A. I. KOLOTILOV, R. M. KUTOK, A. G. GAGINA, and N. I. SHOKHOR (Schr. zentr. biochem. Forschungsinst. Nahr. Genussm., U.S.S.R., 1933, 3, 121-140).—In dogs protein assimilation was 94.6% for dried, and 96% for fresh, milk; digestion of the former was slower. CH. ABS.

Utilisation of dietary protein in the intestine and protein enrichment of the body. A. BICKEL (Z. Volksernahr., 1933, 8, 213-214; Chem. Zentr., 1933, ii, 1209).—A discussion. A. A. E.

Nutritive value of animal tissues in growth, reproduction, and lactation. I. Alcohol-extracted ox liver. II. Presence of a new dietary principle in liver. H. G. SMITH and W. H. SEEGER (J. Nutrition, 1934, 7, 195-207, 209-219).—I. With rations containing EtOH-extracted liver as the protein source normal growth of rats occurred with 20% protein. At a 15% level growth was subnormal. In the second generation growth was subnormal at both protein rates. Lactation was deficient in the first and failed in the second generation. Growth was improved by supplementary feeding of dried whole liver and lactation by raw liver. Extracted liver also induced other serious derangements of the reproductive mechanism.

II. The substance necessary for normal growth and lactation removed from liver by EtOH is not associated with the lipins, but may form a constituent of the vitamin-B complex. A. G. P.

Nutritional requirements of *Zootermopsis* (*Termopsis*) *angusticollis*. S. F. COOK and K. G. SCOTT (J. Cell. Comp. Physiol., 1933, 4, 95-110).—Termites cannot live indefinitely on diets consisting of purified cellulose (cotton), hemicellulose (agar), sugars (I), or protein (II). The presence of (I), (II), mineral salts, and vitamin-A, -B₁, -B₂, and -D is

necessary. (II) in the diet prevents cannibalism and probably increases the N content of the termites. A. G. P.

Metabolism of fowls with artificial anus. W. MAAS (Arch. Geflügelk., 1933, 7, 225-261).—The following digestibility coeffs. (I) were found: rye, crude protein 71.28, crude fat 26.10, crude fibre 2.37, and N-free extractives (II) 92.39%; wheat (III), 71.60, 47.24, 3.60, and 89.99%. (I) for meat meal, soyabean meal, linseed cake meal and maizena, mixed with rye or wheat, were similar to those found by Lehmann with pigs, but those for (II) were lower. When peat litter was used the birds on (III) did better than those on rye. NUTR. ABS. (m)

Changes in muscle volume in tetanic contraction as an expression of the accompanying chemical processes. H. HARTMANN (Biochem. Z., 1934, 270, 164-187; cf. Meyerhof and Mohle, A., 1933, 742).—By making measurements on muscles (I) (frog gastrocnemius) suspended in paraffin oil the differences (due to absorption of H₂O and swelling) in vol. change (II) between muscle extract and living muscle on contraction are avoided. Molar (II) during enzymic and acid hydrolysis of creatinephosphoric acid (III) has been measured. In (I) poisoned with CH₃I·CO₂H (IV) the sum of (II) at various stages until exhaustion serves as a measure of the extent of decomp. of (III) and of adenylyl pyrophosphate. In normal and (IV)-poisoned muscle there is close agreement between (II) found and that expected from consideration of the chemical transformations involved. W. McC.

Phosphagen and pyrophosphate metabolism in muscle poisoned with iodoacetic acid. E. LUNDSGAARD (Biochem. Z., 1934, 269, 308-328).—Muscle poisoned with CH₂I·CO₂H utilises more energy than can be provided by the phosphagen (I) mechanism. The extra energy cannot be derived from pyrophosphate (II), since utilisation of (II) becomes perceptible only after considerable fatigue. Calc. vals. for heat formation, as with normal muscle, are > vals. by direct determination using the frog's gastrocnemius (III). In poisoned muscle, hydrolysis of (I) does not decrease on shortening, and 25% of the hydrolysis occurs subsequently. Hydrolysis of (I) is a recovery process. Anaerobic synthesis of (I) and hydrolysis of (II) were not detected. The mean of fifty-seven resting vals. for the (I) content of (III) corresponded with 1.8 mg. P₂O₅ per g., and for the (II) content 0.68 mg. per g. P. W. C.

Lactic acid formation in striated muscle under the action of direct current. F. LIPPAY and C. RAND (Pflüger's Archiv, 1933, 233, 17-34; Chem. Zentr., 1933, ii, 3007).—The observed increase in lactic acid, which is considerably higher near the anode, is not due to heating. H. J. E.

Lactic acid content of frog muscle washed with solutions of lithium lactate, lactic acid, and hydrochloric acid. P. ROWINSKI (Arch. Sci. biol., 1934, 483-500; Chem. Zentr., 1933, ii, 3007).—On washing frog muscle (I) with Ringer's solution for 1 hr. it contains 40-47 mg. of lactic acid (II) per 100 g. On washing with aq. Li lactate (III), the

amount of (II) in (I) increases with the concn. of (III). HCl has no effect on the amount of (II).

H. J. E.

Relations between glycolysis and respiration in animal tissue. E. BUMM, H. APPEL, and K. FEHRENBACH (Z. physiol. Chem., 1934, 223, 207—214).—Glycolysis (I) in the mucous membrane of the large intestine of the guinea-pig increases with decreasing O_2 pressure, although respiration (II) is const. (I) and (II) are thus independent. The glutathione system may be responsible for the effect of O_2 on (I).

J. H. B.

Role of citric acid in carbohydrate metabolism. O. FURTH, H. MINNIBECK, E. EDEL, E. H. MAJER, and H. REISNER (Biochem. Z., 1934, 269, 379—396).—Urine (mixed human) contains 0.009—0.21% of citric acid (I) (the vals. for one individual varying from 0.07 to 0.11%), rabbit and guinea-pig urines contain only traces, that of the dog on a carbohydrate (II)-rich diet 0.007—0.009 g. daily and on administration of $NaHCO_3$ 0.01—0.014 g. A dog showing adrenaline glucosuria on administration of Na citrate excreted (I), but a phloridzinised dog did not show either a glucosuric or antiketogenic action of (I). With young pigs, the urinary (I) decreased during fasting and on a (II)-free diet, and considerably increased on a (II)-rich diet or on adding $NaHCO_3$ or $NaOAc$ to the diet. Of various supposed precursors of (I) only $NaOAc$ gave any considerable increased excretion of (I). Determination of the C and N distribution in the urine after administration of 2 g. of (I) per kg. showed that it had been destroyed. Experiments with rats show that administration of (I) did not lead to (II) synthesis.

P. W. C.

Ketosis. IV. Comparative ketolytic effect of galactose, glucose, and lactose in rats. J. S. BURTS (J. Biol. Chem., 1934, 105, 87—96).—Administration of galactose causes a lower excretion of ketonic substances than glucose, and there is also a greater decrease in urinary N. Lactose has an intermediate effect.

H. G. R.

Amount of water stored with glycogen in the liver. E. M. MACKAY and H. C. BERGMAN (J. Biol. Chem., 1934, 105, 59—62).—In young albino rats, of 3.8 g. H_2O are stored in the liver with each g. of glycogen after sugar feeding. There is no measurable amount stored with fat, but for each g. of caseinogen fed about 2 g. of H_2O are stored.

H. G. R.

Glycogen formation after oral administration of mannitol to white rats. A. K. SILBERMAN and H. B. LEWIS (Proc. Soc. Exp. Biol. Med., 1933, 31, 253—255).—No increase in liver-glycogen was observed.

CH. ABS.

Liver-glycogenesis and bile acids. T. KURAMOTO (J. Biochem. Japan, 1934, 19, 315—318).—Whilst small amounts of Na cholate subcutaneously injected into rabbits enhance the glycogenesis due to small doses of adrenaline, large amounts have an inhibitory action (cf. A., 1933, 528).

F. O. H.

Passage of substances produced in the liver to the blood-stream. I. Urea content of blood and lymph. II. Sugar content of blood, lymph, and bile. S. TSUNOO, H. MACHIDA, and K. KUSUI (J.

Biochem. Japan, 1934, 19, 231—235, 237—243).—I. In dogs with thoracic fistulae, administration of NH_3 acids (hydrolysed caseinogen) produces a rise in the urea content of the blood (I) and lymph (II). The rate and extent of these changes indicate that urea passes from the liver to (II) partly directly and partly by way of (I).

II. Adrenaline hyperglycaemia in dogs with thoracic and biliary fistulae is accompanied by an increase in the sugar (III) content of (I), (II), and bile. The rate and extent of these changes indicate that the mobilised (III) passes from the liver to (I) both directly and *via* (II).

F. O. H.

Carbohydrate metabolism. M. INUTSUKA (J. Biochem. Japan, 1934, 19, 217—229).—Oral administration of glucose (I) (10 g. per kg. body-wt.) to dogs produces a rapid rise in the blood-sugar (II), the hyperglycaemia (III) (of 4 hr. duration) being followed by a slight hypoglycaemia (of 4—12 hr. duration). The liver-glycogen is max. after 6 hr., returning to normal levels in approx. 24 hr. The muscle-glycogen varies only slightly. The reducing powers of the contents of the stomach (IV) and intestines follow a course parallel to, but respectively > and <, that of (II). The presence of fat does not influence the removal of (I) from (IV) nor the (II) curve. Prolonged starvation produces a marked increase in the degree of (III).

F. O. H.

Carbohydrate metabolism in the lymph and blood vessels of the intestine and in the mesenteric lymph glands. F. P. FISCHER and K. A. WINTER (Biochem. Z., 1934, 270, 157—160).—In fasting cats (I) the sugar content (II) of the peripheral lymph is > those of the intestinal artery (III) and vein (IV), that of (III) being > that of (IV). (II) of the lymph entering is > that of the lymph leaving the lymphatic glands. If sugar is introduced into the stomach of (I), (II) of the lymph is > that of the blood from the same part of the intestine.

W. McC.

Artificial feeding of the beet leaf-hopper; its ability to synthesise glycerides. R. A. FULTON and J. C. CHAMBERLIN (Science, 1934, 79, 346—348).—*Eutettix tenellus* (Baker) can synthesise glycerides for a limited time when fed only on glucose and fructose.

L. S. T.

Metabolism of ducks (*Anas platythymcha*, L.). I. Adiposity through forced and voluntary feeding. T. C. SHEN (Chinese J. Physiol., 1934, 8, 65—76).—The gain in wt. \propto the food intake and is independent of the method of feeding. The fat is deposited in the liver and subcutaneous tissues and around the viscera. The metabolism corresponds with 1400 g.-cal. per sq. m. of body surface, about twice this val. as food being required for max. gain in wt.

C. G. A.

Absorption of *n*-hexadecane from the alimentary tract of the cat. H. J. CHANNON and J. DEVINE (Biochem. J., 1934, 28, 467—471).—The unsaponifiable residues from the tissues of a cat which had taken 33.64 g. of *n*-hexadecane (I) were distilled in vac. after removal of cholesterol, giving 2.7 g. of (I). 3.81 g. were excreted in the faeces. None was found

in the liver. It is concluded that the remainder was metabolised.

H. D.

Role of balanced feeding in the utilisation of castor oil in the organism. R. LECOQ and J. SAVARE (Compt. rend., 1934, 198, 1540—1542).—Administration to pigeons of large proportions (up to 50% of the ration) of castor oil (I) induces digestive disturbances and polyneuritis. The effects are associated with the lipins of the oil. In more balanced amounts (20% of the ration) (I) may be utilised satisfactorily.

A. G. P.

Effect of linoleic acid and yeast on the growth of rats on high fat diet. Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 264—269).—Satisfactory growth of rats was secured only with a diet containing butter. With eleven other animal and vegetable fats and oils, addition of yeast did not improve growth, but supplementary feeding of linoleic acid + yeast resulted in almost normal growth.

A. E. O.

Resorption of fatty acids. F. VERZAR and L. LASZT (Biochem. Z., 1934, 270, 24—34).—In rats the resorption (I) of oleic acid in the small intestine is increased by simultaneous injection of bile acids (II) (glycocholic, taurocholic). In presence of (II), glycerol (III) with phosphate (IV) or glycerophosphoric acid [but neither (III) nor (IV) alone] greatly increases (I) (up to 150%). The increase is inhibited by $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$, which, however, does not affect (I) in presence of (II) alone.

W. McC.

Inhibition of fat resorption by iodoacetic acid and phloridzin. F. VERZAR and L. LASZT (Biochem. Z., 1934, 270, 35—43).—In rats resorption of olive oil, given orally, is inhibited by subcutaneous administration of $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ or phloridzin. Since the inhibition is not due to action on lipase or to insufficiency of fat in the intestine, it is probable that a phosphorylation, which normally occurs, is prevented.

W. McC.

Diffusibility of blood-fat. H. SULLMANN and F. VERZAR (Biochem. Z., 1934, 270, 44—51).—Through membranes which have permeabilities similar to that of blood-capillaries and permit diffusion of water-blue and Congo-red about 25% of the lipins (I) of lipæmic blood-serum (dog) pass. There is no preferential diffusion of unsaturated or other fractions of (I).

W. McC.

Fat metabolism in fishes. III. Selective formation of fat deposits. J. A. LOVERN (Biochem. J., 1934, 28, 394—402).—Porpoise (I) and dolphin (II) fats are similar in type to those from the zoologically related sperm whale. (I) and (II) depôt fats are unique in containing much isovaleric acid (III) (80% of which is combined in glyceride mols. containing at least one unsaturated acid) and are quite different in type from (I) and (II) organ fats. The foetal blubber of (I) contains little (III) and is highly unsaturated. The analyses do not support the theories of fat transfer to and desaturation in the liver before utilisation. The depôt fats show a mol. size gradation which suggests that one cause of specificity may be a mol. filtration. Further evidence is adduced (cf. A., 1933, 183) in support of the theory

of interconvertibility of saturated and unsaturated acids of the same no. of C atoms in the depôt itself. A semi-micro-method of fatty acid analysis, suitable for 10 g. of fat, is described.

A. E. O.

Production of phosphatides in the intestine during resorption of fats. H. SULLMANN and W. WILBRANDT (Biochem. Z., 1934, 270, 52—62).—In rabbits during resorption (I) of fat (olive oil, triolein) the phosphatide (II) and fat contents of the intestinal lymph increase equally, about 20—30% of the total lymph fat being (II). The increase is not due to the passage of leucocytes or to inflammation (experimental), but probably to production of (II) in the wall of the intestine. Transport of lecithin through the portal vein during (I) may occur, but could not be detected.

W. McC.

Blood-lipins in the post-absorptive state and after the ingestion of fat in normal human subjects and in a case of disseminated cutaneous xanthomata. I. L. CHAIKOFF, T. H. MCGAVACK, and A. KAPLAN (J. Clin. Invest., 1934, 13, 1—13).—Ingestion of olive oil (100 g.) is in both cases followed by variations in blood-fatty acids. In 6 of 7 normal cases the blood-cholesterol was unchanged.

CH. ABS.

Effect of specific dietary fats on the blood-lipins of lactating goats. H. H. WILLIAMS and L. A. MAYNARD (J. Dairy Sci., 1934, 17, 223—232).—On fat-free diets (I) the total lipins, phospholipins, free and combined cholesterol (II) in the blood-plasma declined. Inclusion of fats in the ration caused a return towards normal vals. irrespective of the nature of the fat supplied. The I val. of plasma-fat fell during the feeding of (I), but on readministration of fats changed in accordance with the I val. of the fat given. Lipins in the cells tended to remain const. The (II) of the cells was almost entirely in the free, and that of the plasma in the combined, form.

A. G. P.

Effect of adrenal lipins on the chemical composition of blood and organs. C. I. PARHON and G. WERNER (Compt. rend. Soc. Biol., 1933, 114, 749—751).—Changes in blood-sugar, Ca, K, P, lecithin, and cholesterol (I) on subcutaneous injection into dogs of suprarenal lipins are recorded. (I) appears to increase. The H_2O content of the organs decreases, K increases, and P decreases in brain and muscles, but increases in testicle. NUTR. ABS. (m)

Bile acids. II. Effect of ingestion of food on the bile acids in the blood. S. BOKU and K. GON (J. Chosen Med. Assoc., 1933, 23, 111—112).—In healthy persons, but not in those suffering from liver disease, there is a decrease in the bile acids (I) content of the blood during food ingestion. Possibly the liver reabsorbs (I) to aid production of bile.

NUTR. ABS. (m)

Human physiology. V. Urine chemistry; comparison of 24-hour and short-period excretion: correlations between urine constituents and menstrual and seasonal variation. VI. Variations in blood chemistry over long periods of time, including those characteristic of menstruation. G. W. PUCHER, F. R. GRIFFITH, jun., K. A. BROWNELL, J. D. KLEIN, and M. E. CARMER

(J. Nutrition, 1934, 7, 131—167, 169—193).—V. Data showing the N distribution, sugar, acid, PO_4''' , and Cl' contents of 24-hr. and short-period urines are recorded and correlated with other basal metabolic functions. At about the time of menstruation excretion of urea, creatinine, NH_2 -acid, total and undetermined N, sugar, and Cl' reaches a min., and rises to a max. in the latter half of the intermenstrual period. Variations in NH_3 , and possibly total and org. acids and PO_4 , are of a reverse order. Creatine and uric acid are much less affected. Seasonal variations in 24-hr. urines were not observed. In short-period, basal urines the total N and most of its partition products and Cl' show max. vals. in winter and min. vals. in late summer or early autumn. Total and org. acids show min. excretion in spring and max. in late summer.

VI. Statistical examination is recorded of data concerning variations in N distribution, sugar, cholesterol (I), inorg. P (II), Ca, Cl', and corpuscle vol. in blood. No correlation is found between day-to-day, intra-individual variations in any blood constituents and similar variations in basal metabolic rates. Cycles of menstrual variation are found in (I), Ca, Cl', uric acid, and total creatinine, and of seasonal variation in (I), (II), Cl', and most of the N partition products. Uric acid, Ca, and sugars are not definitely influenced by season. A. G. P.

Chemical character of the blood and urine of colts. W. W. DIMOCK and D. J. HEALY (J. Amer. Vet. Med. Assoc., 1933, 83, 806—809).—Serum of normal yearling thoroughbred fillies contains Ca 11.7—12.2, K 14.2—16.3, P 4.7—5.2, non-protein-N 25.8—32.9, SO_4 -S 11.6—15.6, sugar 106 mg. per 100 c.c. Their urine has d 1.033—1.045, p_H 7.0—7.6, NH_3 20—100, Ca 75—180, and SO_4 -S 78—85 mg. per 100 c.c. Animals forced on for early development by heavy feeding of grain and the use of haliver oil and "violet rays" have slightly higher K and sugar and a lower non-protein N and SO_4 -S of serum, with no significant change in serum-Ca or -P, whilst the urine reaction varies greatly (5.0—8.6); the urinary level of NH_3 and Ca rises and that of SO_4 -S decreases. After 11 weeks of rational feeding these animals recover and the blood shows a further rise in K and a slight rise in serum-P. In both urine and serum the SO_4 -S remains low. NUTR. ABS. (m)

Thiocyanic acid metabolism. II. B. STUBER and K. LANG (Deut. Arch. klin. Med., 1933, 176, 213—218).—Most of the HCNS in fasting gastric juice (I) is derived from saliva. Injection of histamine does not increase it. The HCNS excreted in the faeces is much < that in (I). HCNS is not decomposed by intestinal bacteria or by extracts of organs. Hence reabsorption from the intestine appears to occur. The intake of HCNS with food is considerable. Meat contains 0.05—0.07 mg. per 100 g., milk 0.10—0.12 mg. per 100 c.c., and plant-food larger amounts; beet contains 1 mg. per 100 g. 2—3 mg., apparently not derived from protein, are produced daily in the body. Intravenous HCNS is very slowly excreted, and large doses by stomach tube greatly reduce the excretion of Cl.

NUTR. ABS. (m)

Metabolism and the inorganic elements. J. S. HEPBURN (Hahemannian Monthly, 1933, 68, 836—867).—A review. CH. ABS.

Inorganic salts in nutrition. VIII. Variations in proportion of reticulocytes in blood of rats receiving a diet deficient in inorganic salts. J. M. ORTEN and A. H. SMITH (J. Biol. Chem., 1934, 105, 181—187).—Rats fed on a salt-deficient diet exhibit a polycythemia without reticulosis (I) followed by anaemia and (I). An inverse relationship between the pigment concn. and the proportion of reticulocytes was observed. H. D.

Relationship of iron to the ageing of cells. S. G. ZONDEK and J. KARP (Biochem. J., 1934, 28, 587—591).—The Fe content (I) of the epithelial organs (II) of many animals is const. During the middle period of life, and within a short time, the (I) of (II) is increased by >100%, this latter Fe val. being then maintained until death. From the (I) of the kidney and testis, the age-group of the animal may be deduced. A. E. O.

Effect of acid-ash and alkaline-ash foodstuffs on the acid-base equilibrium of man. F. BISCHOFF, W. D. SANBURN, M. L. LONG, and M. M. DEWAR (J. Nutrition, 1934, 7, 51—65).—The min. amount of ingested Na citrate necessary to cause a slight change in the acid-base equilibrium in pre-breakfast blood was 30 g. daily. The effects of milk, oranges, bananas, etc. were small. A. G. P.

Protein, calcium, and phosphorus intakes of college women as indicated by nitrogen, calcium, and phosphorus outputs. M. M. KRAMER, H. F. EVERS, M. G. FLETCHER, and D. I. GALLEMORE (J. Nutrition, 1934, 7, 89—96).—Data for twenty-five subjects are given. Average vals. for protein used were below, and those for Ca and P above, accepted standards. No significant seasonal variations were apparent. A. G. P.

Calcium balance. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1934, 16, 152—155).—A criticism of methods frequently employed. A. L.

Absorption of calcium in normal animals. N. B. TAYLOR, C. B. WELD, and J. F. SYKES (Brit. J. Exp. Path., 1933, 14, 355—366).—The fecal Ca of normal dogs on a diet of meat and biscuit alone, or with addition of CaCl_2 up to nearly 3 g. daily, or during an interpolated week of starvation, is fairly const., so that most of the added Ca is absorbed, even though no irradiated ergosterol (I) is given. Dogs on low-Ca diet excrete more Ca by the bowel than is ingested; (I) in therapeutic doses does not alter this amount, hence (I) in such amounts does not reduce excretion or increase absorption of Ca by the alimentary tract. NUTR. ABS. (m)

Phosphorus requirement of dairy cattle. II. Phosphorus, calcium, and nitrogen metabolism of dairy cattle when lucerne furnishes the principal source of protein. L. W. LAMB, O. B. WINTER, C. W. DUNCAN, C. S. ROBINSON, and C. F. HUFFMAN (J. Dairy Sci., 1934, 17, 233—241).—Comparison is made of the effect on heifers of a basal ration of low P content (I) and the same supplemented with bone

meal (II). Prior to calving, positive P, Ca, and N balances were obtained on both rations, 10.8—12.3 g. of P furnishing the daily requirement from 18 to 30 months of age. During heavy milking the P balance on (I) was negative even when blood meal was added, but became positive when (II) was added to the ration. Utilisation of P from (I) was > when the P content was higher. A. G. P.

Phosphorus requirements of sheep. I. Effect on young merino sheep of diet deficient in phosphorus but containing digestible proteins and vitamins. C. J. MARTIN and A. W. PEIRCE (Coun. Sci. Ind. Res. Australia, 1934, Bull. No. 77, 1—44).—Sheep receiving a low-P diet (I), having Ca:P ratio 4.5, show 60% of the gain in wt. of those receiving adequate P diet with Ca:P ratio 1.7, decreased inorg. blood-P, and rachitic bone lesions. Increasing the Ca:P ratio of (I) to 10.7 by CaCO_3 , with or without cod-liver oil, causes 50% loss in wt. The wool is unaffected in quantity and quality. Pregnancy and lactation are unaffected, although the lambs from ewes on (I) are smaller and gain wt. more slowly. C. G. A.

Influence of phosphorus deficiency in dairy cows on the coefficient of digestibility and the balance of calcium and phosphorus. W. H. RIDDELL, J. S. HUGHES, and J. B. FITCH (J. Agric. Res., 1934, 48, 167—170).—Lactating dairy cows on a diet low in P and suffering from a phosphorus gave coeffs. of digestibility not significantly different from the control. The balances of P and of Ca were negative. W. O. K.

Effects of injection of salts on calcium, magnesium, and inorganic phosphorus of the serum of the rabbit. R. W. BROOKFIELD (Biochem. J., 1934, 28, 725—733).—Successive hæmorrhages produced slight decreases in the serum-Ca (I), -Mg (II), and -inorg. P (III). Changes due to the injection of NaCl solutions were negligible. Injection of Ca salts produced a rise in (I) and a decrease in (II) with an unchanged (III). Mg salts produced a rise in (III) and a lowered (I). Na_2SO_4 lowered (I) and (III). Na_2HPO_4 produced a decreased (I) and (II) and a rise in (III). H. D.

Name for bio-hydraulic activities. D. L. FOX (Science, 1934, 79, 292—293).—"Hydrosyntaxis" (or hydrosyntaxy) is suggested to signify the sum total of functions within an organism which are operative in producing and maintaining the H_2O balance between protoplasm and its external environment. L. S. T.

Skin irritation by hydrocarbons. W. HEUBNER (Arch. Pharm., 1934, 272, 379—383).—A discussion of the classification of the so-called "sp. irritant action" of hydrocarbons on the skin and of the relation of this property to physical properties and structure. J. W. B.

Site of narcosis in a cell; action of a series of paraffin oils on *Amœba dubia*. D. MARSLAND (J. Cell. Comp. Physiol., 1933, 4, 9—33).—Do- and tetra-decane produced narcotic effects when injected into the protoplasm. The narcotic action of paraffins

is localised in the surface (non-aq.) layer of the protoplasm. A. G. P.

Local anæsthetic properties of some aliphatic alcohols. D. I. MACHT and M. E. DAVIS (Proc. Soc. Exp. Biol. Med., 1933, 30, 1294—1295).—Octyl, heptyl, nonyl, decyl, undecyl, dodecyl, and hexyl alcohols (in descending order of potency), but not PrOH , BuOH , $\text{C}_5\text{H}_{11}\text{OH}$, or C_{13-18} alcohols, have local anæsthetic properties. CH. ABS.

Correlation of visceral and somatic activity following administration of hypnotics, (A) barbitol compounds and (B) tribromoethanol (avertin). J. P. QUIGLEY, O. W. BARLOW, and C. K. HIMMELSBACH (J. Pharm. Exp. Ther., 1934, 50, 425—439).—With doses of barbiturates causing equal hypnosis the relative durations of gastro-intestinal depression were barbitol (I), 1.0; amytal (II), 0.6; pentobarbital (III), 0.3. The frequency of restlessness is in the order (II) > (I) > (III). Avertin also depressed the gastro-intestinal tract, the fluid being more powerful than the crystals. C. G. A.

Influence of pyramidone on carbohydrate metabolism. G. KRAUSE and H. MARX (Z. klin. Med., 1933, 125, 341—350; Chem. Zentr., 1933, ii, 3307).—In health, human blood-sugar is scarcely affected by pyramidone; in diabetes it is decreased by small, and increased by large, doses. Insulin hypoglycæmia is accentuated; so also are glucose hyper- and the eventual hypo-glycæmia. A. A. E.

Effect of some barbiturates and urethane [on blood constituents]. N. RAKIETEN, L. H. NAHUM, D. DUBOIS, E. F. GILDEA, and H. E. HIMWICH (J. Pharm. Exp. Ther., 1934, 50, 323—335).—Amytal, nembutal, and luminal administered to dogs in narcotic doses increase the CO_2 content (I), the CO_2 capacity (II), and sugar of blood, and decrease the O_2 content (III), O_2 capacity (IV), and p_{H} (V). "Dialciba" and urethane decrease (I), (II), and (V) and increase (III) and (IV). A. L.

Determination of veronal in urine. J. STRAUB and E. MIHALOVITS (Pharm. Zentr., 1934, 75, 226—228).—The method of van Itallie and Steenhauer (A., 1921, ii, 607) is liable to give high results. In the approved method, urine (100 c.c.), acidified with 5 c.c. of 10% AcOH and 20 c.c. of 10% H_2SO_4 , is oxidised with 5% aq. KMnO_4 at 80—90° and the pptd. MnO_2 dissolved by adding H_2O_2 . The solution is clarified at 70—80° with 0.1 g. of C, filtered, and the veronal extracted with EtOAc and weighed after evaporating the solvent. S. C.

Toxicity and anæsthetic efficiency of thiocaine. L. S. FOSDICK and H. L. HAUSEN (J. Pharm. Exp. Ther., 1934, 50, 323—327).—The anæsthetic efficiency of thiocaine hydrochloride (I) (A., 1933, 948) is 4—6 times that of procaine hydrochloride (II) when used for injection, and approx. twice that of cocaine (III) as a topical anæsthetic. The toxicity is, however, 2.7—3.7 times that of (II), and half that of (III). A. L.

Comparative pharmacology of some thiomorpholine derivatives. D. I. MACHT (Proc. Soc. Exp. Biol. Med., 1933, 31, 234—236).—Thiomorpholine-ethanol (I) and its esters were compared

with the sulphoxy-compound (II) and its esters. The benzoate of (I), but none of the (II) derivatives, had an anæsthetic effect. CH. ABS.

Effects of morphine and its derivatives on intestinal movements. I. Morphine and the codeine isomerides. H. M. KRUGER (J. Pharm. Exp. Ther., 1934, 50, 254—276).—In dogs the effectiveness of morphine, isocodeine, codeine, ψ -, and *allo*- ψ -codeine in decreasing the rhythmic frequency is as 100 : 25 : 8 : 3 : 1, respectively, and in increasing the tone of the ileum 100 : 19 : 58 : 8 : 15 : 4 : 5 : 2, respectively. All these compounds increase the rhythmic amplitude and peristalsis. A. L.

Effect of morphine, caffeine, and strychnine on the serum-calcium of the rabbit. R. HAZARD and C. VAILLE (Bull. Soc. Chim. biol., 1934, 16, 235—247).—Whilst non-lethal doses of morphine (I) lower the serum-Ca (II) of rabbits, during sleep, in chloralised and in partly asphyxiated animals very little change in (II) occurs. Sparteine, caffeine, and strychnine (III), which increase respiration rate, like (I) reduce (II). (I) and (III) in lethal doses increase (II). A. L.

Action of mezcaline and related compounds. G. S. GRACE (J. Pharm. Exp. Ther., 1934, 50, 359—372).—3 : 5-Dimethoxy-4-ethoxy- (I) and 5-methoxy-3 : 4-diethoxy-phenylethylamine (II) are twice as toxic as the 3 : 4 : 5-(OMe)₃-compound (mezcaline), producing fall of blood-pressure (prevented by vagotomy or atropine), motor paralysis, and death from respiratory failure. (I) and (II) paralyse voluntary muscle of the frog at 1 : 4000 dilution; at 1 : 500 all three cause contracture with loss of excitability. They stimulate contraction of the intestine and uterus *in situ*, but not when excised. C. G. A.

Pressor actions of ephedrine and ψ -ephedrine in man. S. B. DIMSON (Quart. J. Pharm., 1934, 7, 23—31).—Subcutaneous injection of 0.067 g. of ψ -ephedrine into hospital patients produced a slight rise in blood-pressure followed by a fall; that of 0.134 g. produced a marked rise approx. equal to that due to 0.067 g. of ephedrine. F. O. H.

Ephedrine and ψ -ephedrine in spinal anæsthesia. J. E. MONRO (Quart. J. Pharm., 1934, 7, 32—35).—In spinally anæsthetised men, ephedrine (50 mg. intramuscularly) produced a rise (10—15 mm.) in the systolic blood-pressure, whilst ψ -ephedrine had a much less marked effect. The action of subsequent injections was variable. F. O. H.

Influence of sinomenine, parasinomenine, and quinine on the action of (a) adrenaline, calcium, nicotine, yohimbine, and ergotoxin, (b) diuretin, pilocarpine, glucose, and insulin, on the blood-picture in rabbits. Y. ARAKAWA (Folia Pharmacol. Japon., 1933, 17, No. 1, 1—12, 13—20).—Insulin hypoglycæmia is increased; in other cases except ergotoxin (increased) the hyperglycæmia is diminished. CH. ABS.

Effect of concentrations of nicotine on growth and development. II. Growth and development of chicks as influenced by the addition of ground tobacco to the ration. J. E. HUNTER,

D. E. HALEY, and H. C. KNANDEL (Poultry Sci., 1934, 13, 91—94).—*Nicotiana rustica*, containing 5% (dry wt.) of nicotine, added to the ration at the rate of 1.2% did not affect the growth of chicks and gave effective control of round worms. Ground cigar leaf (0.86% nicotine) supplied at the rate of 4.65% in the ration retarded growth and increased mortality. Cæcal worms (*Heterakis gallinae*) were not controlled by tobacco treatment. A. G. P.

Tobacco-smoking and blood-sugar. D. L. THOMSON (Science, 1934, 79, 386; cf. this vol., 557). L. S. T.

Effects of cigarette smoking on the blood-sugar. H. W. HAGGARD and L. A. GREENBERG (Science, 1934, 79, 274; cf. this vol., 557).—Acknowledgment of prior observations is made (A., 1932, 1284). L. S. T.

Carbon monoxide content of tobacco smoke. O. EHRLSMANN and G. ABEL (Z. Hyg., 1934, 116, 4—10).—Cigarette tobaccos yielded an average of 17.25 c.c. and other varieties up to 35.0 c.c. of CO per g. A. G. P.

Effect of ethylene glycol on the serum-calcium of the rabbit. J. M. DILLE (J. Amer. Pharm. Assoc., 1934, 23, 202—205).—[CH₂·OH]₂ is oxidised to H₂C₂O₄ so slowly that no change in serum-Ca could be detected. A. E. O.

Influence of various synthetic thymol and carvacrol derivatives on sugar metabolism, and the point of attack of these derivatives; relation between chemical structure and pharmacological action, and comparison with the action of ergotamine. U. SAKURA (Folia Pharmacol. Japon., 1933, 17, 129—170).—In small doses the derivatives produced hypoglycæmia; those in which H in the side-chain NH₂Et is replaced by Me are most active (Me > Et or alkyl), whilst those in which the side-chain contains ethylpiperidine in place of ethyl-alkylamine are weakest. The thymoxyethylamine derivative with an alkyl group introduced is the most active, but somewhat labile. Thymol derivatives are more active than corresponding carvacrol derivatives. Like ergotamine, the derivatives decrease adrenaline hyperglycæmia, but are weaker in action. CH. ABS.

Action of phloridzin on the excretion of glucose, xylose, sucrose, creatinine, and urea by man. H. CHASIS, N. JOLLIFFE, and H. W. SMITH (J. Clin. Invest., 1933, 12, 1083—1090).—The min. requirement of phloridzin by man for raising the glucose to the xylose clearance level is 10—20 mg. per kg. The ratio creatinine : xylose clearance is not depressed. CH. ABS.

Influence of anæsthetics on the biological assay of *Digitalis*. J. C. DAVID and N. RAJAMANICKAM (Quart. J. Pharm., 1934, 7, 36—40).—When comparisons with standard preps. are made under identical conditions, the use of anæsthetics other than Et₂O is applicable to the cat method of Burns (see B., 1926, 719). The highest vals. of the average lethal dose are obtained with chloretone and the lowest with chloralose. F. O. H.

Pharmacology of some members of the tropane group. G. S. R. RAO (Quart. J. Pharm., 1934, 7,

46—56).—The approx. min. lethal dose by intraperitoneal injection into mice of selenotropinone (I), 8:9-benz- $\Delta^8:9$ -homogranaten-3-one (II), and benzoyl- μ -8:9-benz- $\Delta^8:9$ -homogranaten-3-ol (III) (A., 1933, 729) are, respectively, 0.20, 0.50, and 0.42 g. per kg. (II) and (III), but not (I), paralyse the isolated uterus and heart and decrease the blood-pressure and respiration. (III), but not (II) or (I), completely anaesthetises the rabbit's cornea. The influence of structure on pharmacological action is discussed.

F. O. H.

Action of St. John's wort. C. H. HORSLEY (J. Pharm. Exp. Ther., 1934, 50, 310—322).—A method for the isolation of hypericin (I), the fluorescent red pigment of St. John's wort, is described. Injection of (I) into rats causes photosensitisation with development of erythema and, with large doses (40 mg.), prostration and death. The spectrum of the EtOH extract of young plants which contain less (I) is different from that of older plants.

A. L.

Toxicity of derivatives of rotenone to goldfish. W. A. GERSDORFF (J. Amer. Chem. Soc., 1934, 56, 979—980).—Rotenone, acetyldihydrotrotene, dihydro-, acetyldihydro-, and acetyl-rotenolone are decreasingly toxic to goldfish (method: A., 1930, 1316).

H. B.

New Guinea fish poison. A. K. MACBETH (Nature, 1934, 133, 649—650).—The root of a *Derris* (New Guinea) poisonous to fish and to mammals contains 4 to 5% of rotenone.

L. S. T.

Heat regulation and water exchange. XVII. Serum osmotic pressure and the onset of fever. H. G. BARBOUR and A. GILMAN (J. Pharm. Exp. Ther., 1934, 50, 277—285).—Fever in rabbits produced by cocaine (I), tetrahydro- β -naphthylamine (II), and hay infusion is accompanied by corresponding increases in serum osmotic pressure (III), this tending to retard loss of surface H_2O . Serum sp. gr., while usually increasing, sometimes shows no change in mild cases. Whilst the increases in (III) cannot be accounted for by blood-sugar increase, in the case of (I) they are of the same order as the lactic acid increase, with (II), however, much larger. Increased muscular activity may therefore be a factor.

A. L.

Comparison of the antipyretic action and toxicity of *d*-glucono-*p*-phenetidine and aceto-phenetidine. W. E. HAMBOURGER (Proc. Soc. Exp. Biol. Med., 1933, 31, 365—367).—Equimol. proportions have approx. the same action on rabbits. The former has the wider separation of therapeutic and toxic doses.

CH. ABS.

Effect of chaulmoogric acid derivatives on lipolytic activity *in vitro*. G. A. EMERSON, H. H. ANDERSON, and C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1933, 31, 272—273).—If the chaulmoogrates exert an indirect action in leprosy therapy apart from bactericidal action, it is improbable that the fat-splitting enzyme is involved.

CH. ABS.

Comparative biological activity of seven new water-soluble chaulmoogric acid derivatives. G. A. EMERSON, H. H. ANDERSON, and C. D. LEAKE (Proc. Soc. Exp. Biol. Med., 1933, 31, 274—277).

CH. ABS.

Dinitrophenol hyperglycæmia. I. Its independence of asphyxia. V. E. HALL, C. A. BROWN, and M. SAHYUN (Proc. Soc. Exp. Biol. Med., 1933, 31, 380—382).—The hyperglycæmia is not secondary to a general asphyxia.

CH. ABS.

Absorption of salicylic esters by the human skin. E. W. BROWN and W. O. SCOTT (J. Pharm. Exp. Ther., 1934, 50, 373—385).—The degrees of cutaneous absorption of the esters, based on Me salicylate as unity, are monoglycol (spiro-sol) 1.20, Me 1.00, OMe- CH_2 (mesotan) 0.49, Et 0.34, Prⁿ 0.20, Bu 0.26, and isoamyl 0.15. Increasing adsorption corresponds with decreasing partition coeff. between oil and H_2O , rising surface tension, and falling viscosity.

C. G. A.

Toxicology of solvents. F. FLURY and W. WIRTH (Arch. Gewerbehyg. Gewerbepath., 1933, 5, 1—90).—A no. of aliphatic and aromatic acetates, Et₂ phthalate, MeOH, COMe₂, and [CH_3 ·OH], are examined.

A. G. P.

Physiological action of tolylenediamine and its relation to experimental jaundice. H. J. WOLFF (J. Pharm. Exp. Ther., 1934, 50, 407—419).—The absence of icterus in hepatectomised dogs indicates that the liver (I) is the site of the icterogenic activity of tolylenediamine (II); (I) undergoes necrosis. Protection is afforded by excretion of (II) in the urine and secretion into the gastric juice, causing emesis.

C. G. A.

Origin of naphthalene cataract. T. NAKASHIMA (J. Biochem. Japan, 1934, 19, 281—314).—Following administration of $C_{10}H_8$ to rabbits (I) in doses sufficient to cause cataract, the urinary inorg. SO_4 (II) rises and ethereal SO_4 falls, both levels returning to normal vals. within 7—8 days. Both levels rapidly increase after ingestion of $C_{10}H_8$ + cystine or Na_2SO_4 , the return to normal levels (within 3 days), being followed by a secondary rise in (II). Marked changes also occur in the reduced (but not the oxidised) glutathione content of the liver and optic lens, but not in that of the muscle. Both the neutral SO_4 and glycuronic acid of the urine are significantly increased in both non-diabetic and diabetic (I). The bearing of the results on the incidence of cataract and retinal dysfunction is discussed (cf. A., 1932, 641).

F. O. H.

Behaviour of blood-serum in presence of chemotherapeutics. B. BRUNELLI (Arch. Farm. sperim., 1934, 57, 186—200).—Salvarsan and many of its derivatives, Bayer 205, and triparosan enter into stable combination with the euglobulin fraction, and to a smaller degree with the pseudoglobulin fraction of serum-proteins, which are no longer coagulated by heat. Combination does not take place with inactivated plasma. It depends on p_H , being most complete on the alkaline side, whilst at the isoelectric point of globulin (p_H 5.5) it does not occur.

R. N. C.

Toxicity of some azoarsenic compounds. S. BERLINGOZZI and F. P. MAZZA (Arch. Sci. biol., 1933, 16, 404—410; Chem. Zentr., 1933, ii, 2853).—The toxic doses for white rats for each 20 g. are 0.005, 0.0053, 0.0066, 0.007, 0.0085, and 0.0045 g. with

1-amino-3-hydroxybenzene-4- (22.25% As), 1:3-dihydroxybenzene-6- (22.2% As), 1:3-dihydroxybenzene-2:4:6-tris- (28.3% As), 1-phenyl-3-methyl-5-hydroxypyrazole-4- (18.66% As), 2-methyl-3-hydroxyquinoline-4- (19.38% As), and 2-phenyl-3-hydroxyquinoline-4-azo-*p*-phenylarsinic acid (16.7%) (I), respectively. Excretion after 72 hr. amounts to 80—95% except in the case of (I). The connexion between structure and toxicity is discussed.

L. S. T.

Laxative principle in prunes. G. A. EMERSON (Proc. Soc. Exp. Biol. Med., 1933, 31, 278—281).—The substance resembles dihydroxyphenylisatin and caffeic and chlorogenic acids.

CH. ABS.

Synthesis of medicinal products. VII. Theory of laxatives. II.—See this vol., 663.

Anthelmintics.—See this vol., 652.

Sodium chloride metabolism. IV. Diuretics. H. SATO (Japan. J. Gastroenterol., 1933, 5, 85—90).—Salyrgan (I) and pituitrin act as diuretics in rabbits and remove NaCl from the body. Blocking the reticulo-endothelial system inhibits the action of (I).

CH. ABS.

Influence of alkyl- and alkylene-mercaptan groups on the therapeutic activity of organic compounds. I. Methylthioatophan.—See this vol., 665.

Reactions of blood and tissue cells to colloidal thorium dioxide. I. C. WEN and T. S. JUNG (Chinese J. Physiol., 1934, 8, 85—95).—Intravenous injection of ThO₂ is followed by an increase in the no. of monocytes and neutrophile leucocytes (I) which take up the particles as do cells of the liver, suprarenal cortex, and the reticulo-endothelial system (II). Subcutaneous injection is followed by migration of (I) to the connective tissue. (I), clasmatocytes, and fibroblasts show active phagocytosis of the ThO₂ particles. ThO₂-laden cells can still take up trypan-blue or Li-carmin, showing that (II) is not "blocked." From mixed injections the various phagocytic cells take up dye particles more readily than ThO₂, due to greater diffusion of the dye.

C. G. A.

Reticulo-endothelial system and metabolism. T. LEIPERT (Biochem. Z., 1934, 270, 93—111).—In rabbits, blockade (I) of the reticulo-endothelial system (II) with 25% ThO₂ sol has no effect on enzymes which degrade purines, but interferes with excretion of purine, causing it first to increase and then to decrease before gradual restoration to normal. The oxidative degradation of tyrosine, the blood-sugar level, the carbohydrate tolerance, and the oxidation of *d*-lactic acid remain unaffected. In rats (I) does not interfere with the passage of lipins through (II). Hence there is no evidence that (I) inhibits oxidations or that (II) plays any active part in NH₂-acid, carbohydrate, or fat metabolism.

W. McC.

Effect of reticulo-endothelial blockade on blood chemistry. R. I. KLEIN and S. A. LEVINSON (Proc. Soc. Exp. Biol. Med., 1933, 31, 353—355).—In the dog blood-cholesterol decreases and -sugar increases; blood-*p*_H, -CO₂, *n*, and viscosity fall more slowly. With continued injection of India ink

suspension blood-sugar decreases, whilst -non-protein-N increases.

CH. ABS.

Effect of heavy water of low concentration on *Euglena*. T. C. BARNES (Science, 1934, 79, 370).—Cells of *E. gracilis* multiply more rapidly in H₂O containing a low % of H₂O (*d* 1.000061) than in ordinary distilled H₂O. A small proportion of H² may be a necessary constituent of living systems.

L. S. T.

Combination of amyl nitrite with sodium thiosulphate in the treatment of potassium cyanide poisoning. A. BUZZO and R. E. CARRATALA (Semana méd., 1933, ii, 1772—1775).—Inhalation of C₅H₁₁NO₂ causes formation of methæmoglobin, which forms a stable compound with CN⁻ and facilitates the action of the (intravenously injected) Na₂S₂O₃. NaNO₂ is more effective than C₅H₁₁NO₂, but less easily applied.

CH. ABS.

Action of natural arsenical waters on seed germination and larval growth. J. GODONNECHE and G. DASTUGUE (Bull. Soc. Chim. biol., 1934, 16, 248—256).—Growth of seeds in two natural waters containing 0.007 (I) and 0.028% of As was increased (except in the case of wheat) and retarded, respectively. Both, however, accelerated the development of tadpoles, the effects being in the same order as those of aq. solutions of Na₂HAsO₄ of equal concn., (I) being the most favourable for growth.

A. L.

Behaviour of lead in the animal organism. III. Colloidal lead compounds. R. A. KEHOE and F. THAMANN (J. Lab. Clin. Med., 1933, 19, 178—194).—After injection of H₂O-sol. Pb salts into rabbits, Pb was detected in all tissues, especially blood, kidneys, liver, and spleen. Thereafter there is gradual loss from the tissues until equilibrium is established between the amount excreted and that absorbed with food. Colloidal Pb behaves similarly. Pb phosphates are not redistributed or excreted in large amounts. Much of the Pb₃(PO₄)₂ injected into a human subject was found in the liver and little in the skeleton, whilst injected colloidal Pb was found in appreciable quantity in the skeleton.

CH. ABS.

Intake of lead and its distribution in the organism during experimental poisoning. F. WEYRAUCH, A. NECKE, and H. MÜLLER (Z. Hyg., 1934, 116, 28—35).—Characteristic differences in the distribution and accumulation of lead in various organs of different animals are recorded.

A. G. P.

Volatilisation, solubility, and oxidation [and retention by lungs] of metallic mercury.—See this vol., 613.

Detection of dangerous dusts. E. H. KETTLE (Lancet, 1934, 226, 889—890).—Microscopical examination of the lungs of guinea-pigs injected with various dusts shows that finely-ground flint and kaolin, but not wellingtonite or a sample of Fe-coated SiO₂, are harmful.

L. S. T.

Determination of fluorides in waters. [Effect on dental enamel.]—See this vol., 618.

Spectroscopic determination of fluorine in bones, teeth, and other organs, in relation to fluorine in drinking water. C. H. BOISSEVAIN and W. F. DREA (J. Dental Res., 1933, 13, 495—500).—

The method (I), which is described, agrees with the chemical only when the sample dissolves readily in HClO_4 . When fusion is necessary considerable loss of F occurs, and hence the higher vals. of (I) are more accurate. For inhabitants of Colorado Springs (II), where the H_2O contains 2 p.p.m. of F, the average % of F in enamel is 0.065 and in dentine 0.112; for those of New York City, where the H_2O contains no detectable F, the % are nil and 0.068. Human bones from (II) contain 0.7% of F and from the eastern United States, 0.13%. No F can be detected in liver, spleen, kidney, thyroid, heart, or lung of samples from (II). Ingested F is eliminated in urine and faeces; none can be detected in saliva or milk.

NUTR. ABS. (m)

Effects of diets containing fluorine on jaws and teeth of swine and rats. R. M. BETHKE, C. H. KICK, T. J. HILL, and S. W. CHASE (J. Dental Res., 1933, 13, 473—493).—Addition of F compounds to the diet of swine and rats produced hypoplasia of the enamel and dentine proportional to the amount of F and varying according to the compound used. The skull of rats was unaffected. In swine, rock phosphate or NaF increased the thickness of the mandible and the size of the medullary spaces, and increased the width of the dental arch.

CH. ABS.

Influence of fluorine ingestion on nutritional qualities of milk. P. H. PHILLIPS, E. B. HART, and G. BOHSTEDT (J. Biol. Chem., 1934, 105, 123—134).—The average F content of milk from cows on normal diets was 0.138 mg. per litre, and was scarcely influenced by adding F to the diets. Rats fed on milk containing $4.5\text{--}132 \times 10^{-6}$ g. of F per day showed no toxicosis.

H. D.

Fate of enzymes in the digestive tract. W. HEUPKE and H. WIRTZ (Klin. Woch., 1933, 12, 1866—1867).—Myrosin, emulsin, urease, and catalase introduced into the digestive tract remain intact and active as far as the large intestine; zymase and peroxidase are rapidly destroyed. These enzymes do not appear to be absorbed through the intestinal wall.

NUTR. ABS. (b)

Carboxy-catalase and its decomposition by monochromatic light. L. CALIFANO (Naturwiss., 1934, 22, 249—250).—The action of catalase preps. (I) [purified by fractional pptn. with EtOH and CHCl_3 , adsorption on $\text{Ca}_3(\text{PO}_4)_2$, and elution] is inhibited by CO. (I) are markedly inactivated by white and blue (405 and 436 m μ) light, to a smaller extent by blue-green light (492 m μ), and not at all by green or yellow light (546 and 578 m μ). CO-(I), however, are partly re-activated by radiations of λ 405 and, to a smaller extent, of 492 m μ .

F. O. H.

Equilibrium of the fumarase system. K. P. JACOBSON and J. TAPADINHAS (Biochem. Z., 1934, 269, 225—230).—Tables show the final rotation and equilibrium const. for liver-fumarase-fumaric-malic acid systems and the influence thereon of glycerol and $[\text{CH}_2\text{OH}]_2$. In the presence of these substances the formation of fumarate is favoured at the expense of malate.

P. W. C.

Liver-dehydrogenase attacking higher fatty acids. II. F. P. MAZZA and C. ZUMMO (Atti R.

Accad. Lincei, 1933, [vi], 18, 461—463; cf. A., 1933, 747).—Addition of stearic or oleic acid increases the consumption of O_2 by surviving liver by 85 or 82%, respectively, the dehydrogenase of the liver playing a part in the oxidation of these acids.

T. H. P.

Liver enzymes. I. Aldehydease. L. REICHEL [with H. KÖHLE and R. WETZELL]. II. Alcohol-dehydroase [with H. KÖHLE] (Naturwiss., 1934, 22, 219—220).—I. A dry, stable aldehydease has been prepared from liver. It catalyses dehydrogenation (I) of aldehydes as well as their dismutation: (I) occurs with the aid of benzoquinone or methylene-blue anaerobically or aerobically, or with cytochrome aerobically in presence of indophenol-oxidase. In fresh liver only a small part of added aldehyde is transformed in this way. Anaerobically the alcohol and acid formed are equiv.; aerobically more acid is found, owing to the presence of alcoholdehydroase.

II. An alcoholdehydroase has been prepared which converts alcohol into aldehyde under aerobic conditions only. HCN does not inhibit the action. Benzoquinone and methylene-blue accelerate the action; of natural substances, only "omega" and a dry spleen prep. increase the amount of alcohol transformed.

R. K. C.

Effect of temperature on activity of amylase. S. TRAUTMANN and L. AMBARD (Bull. Soc. Chim. biol., 1934, 16, 35—51).—Changes in the Q_{10} of amylase caused by the addition of Cl' , Br' , or I' at const. p_{H} and by change of p_{H} at const. Cl' , Br' , or I' concn. are explained on the basis that the enzyme action takes place in two stages, firstly the combination (I) of the enzyme with the co-enzyme, H' , and the anion, and secondly the actual hydrolysis (II). The Q_{10} is therefore made up of the Q_{10} of (I) with the Q_{10} of (II). The speed of (I) is inversely proportional to that of (II) and independent of the anion concn.

A. L.

Effect of ligature of the pancreatic duct on the amylolytic activity of saliva and blood. T. GAYDA (Arch. Sci. biol., 1933, 19, 62).—Ligature of the pancreatic duct in rabbits causes no change in the amylase (I) content of saliva. Serum-(I) is increased and returns to normal as the gland atrophies. Blood-(I) is therefore not derived from the pancreas.

NUTR. ABS. (b)

Enzymic fission of sucrose and its derivatives. R. WEIDENHAGEN (Chem.-Ztg., 1934, 58, 287—289).—A summary of the specificity etc. of sugar enzymes, especially those of the invertase type (see A., 1928, 1157, 1281; 1929, 352, 722; 1930, 499, 1065; 1931, 653, 873, 1331; 1932, 91, 1063; 1933, 92, 749, 1080).

F. O. H.

Increase in glycogen during autolysis of meat. J. A. SMORODINCEV and L. A. PHILIPPOVA (Bull. Soc. Chim. biol., 1934, 16, 140—144).—The glycogen content of beef undergoing autolysis at 4° or 34° first decreases and then increases, reaching about half the original val. after 18 days. The amount of glucose increases to a max., then after decreasing slightly increases progressively. Lactic acid after increasing steadily reaches a max.

A. L.

Enzymic hydrolysis of phosphatides. III. Hydrolysis of natural and synthetic phosphatides. E. J. KING (Biochem. J., 1934, 28, 476—481; cf. A., 1931, 984).—The rate of hydrolysis (I) of lecithin (II) by lecithinase from intestinal mucosa and kidney is $>$ that of kephalin, phosphatidic acid, synthetic (II), and distearyl phosphate (III). No p_H optimum was found for the hydrolysis of (II) and (III). The (I) of lyso- and bromo-lecithin is $>$ that of (II) and = that of hydrolecithin. H. D.

Physiology of digestion in infants. XVII. Bile activator of prolipase in breast milk. E. FREUDENBERG (Z. Kinderheilk., 1933, 55, 714—719).—Of the bile acids tested, only litho- and dehydrocholic acid showed no activation of the prolipase of human milk. The bile of the pike had less effect than that of other animal species. NUTR. ABS. (b)

Serum-lipases. J. NITZULESCU, I. ORNSTEIN, and D. HERESCU (Compt. rend. Soc. Biol., 1933, 114, 747—749).—With advance of age the serum-lipases decrease in quantity in an irregular manner. Abnormal lipases, hepatic or pancreatic, are not found. NUTR. ABS. (m)

Effect of injected lipase on lipase content of blood in the rabbit. T. OLIARO and J. ADLER (Z. ges. exp. Med., 1933, 91, 362—365).—Repeated subcutaneous or intravenous injections of lipase (I) (from pancreas) produce in rabbits an increase in serum-lipase lasting for several days followed by a fall below the original val. The blood-fat varies inversely with (I). NUTR. ABS. (m)

Asymmetric hydrolysis of esters by enzymes. IX. Optical selection by liver-esterase in the system of "equalising activators." E. BAMANN and P. LAEVERENZ (Z. physiol. Chem., 1934, 223, 185—188; cf. A., 1931, 874).—Ca oleate-albumin scarcely influences the optical selection by liver-esterase (I); Na oleate has a marked effect. This is removed by addition of CaCl_2 , which forms the Ca soap. The (I) of the Arabian baboon is affected by *l*-mandelic acid, which favours the fission of the *d*-ester in the racemate. The *d*-acid shows a slight effect in the opposite sense. EtOH is without effect, but the selective action is influenced by the concn. of the substrate. J. H. B.

Enzymic histochemistry. VIII. Micro-determination of the activity of lipolytic enzymes. D. GLICK (Z. physiol. Chem., 1934, 223, 252—256; cf. this vol., 561).—The lipolysis, conducted in glycine-NaOH buffer at p_H 8.7, is stopped at the desired time by addition of 1.5—2% PhOH. The solution is titrated with 0.05*N*-HCl to p_H 6.5. J. H. B.

Lipolytic enzymes. I. Mechanism of lipolytic enzyme actions. II. Influence of p_H on activity of liver-esterase. H. SOBOTKA and D. GLICK (J. Biol. Chem., 1934, 105, 199—219, 221—230).—I. Enzyme solutions were obtained by digesting $\text{COMe}_2\text{-Et}_2\text{O}$ -dried pig's gland in aq. NH_3 and neutralising with AcOH. Pancreas-globulin (I) and liver-albumin (II) fractions were separated by half and complete saturation, respectively, with $(\text{NH}_4)_2\text{SO}_4$. The hydrolyses by liver-esterase (III) are zero-

order reactions, whilst the curves for pancreas-esterase (IV) flatten after an initial steep rise, further rises being obtained by successive additions of more substrate. The solubilities of butyrins and $\text{C}_8\text{H}_{17}\text{-OH}$ (V) are increased by (I) and (II). The affinities of the butyrins for (II) as expressed by their Michaelis consts. are $>$ those for (I); (V) exerts both competitive and non-competitive inhibition, and the affinity const. for (V) with (III) is calc. from the inhibition observed. Under certain conditions (V) accelerates the hydrolysis of tributyrin with either (III) or (IV) and of monobutyrin with (IV).

II. The p_H -activity curves for human (III) and pig's (III) and (IV) on EtOAc, PrOAc, and the mono- and di-acetates of ethylene and propylene glycols, using $(\text{NH}_4)_2\text{HPO}_4$ buffers, show two max. at p_H 6.7—7.3 and 7.6—8.2. The max. at 6.7 disappears on using borate buffers, and the min. disappears with borate- HPO_4 mixtures. With the (III) from $\text{COMe}_2\text{-Et}_2\text{O}$ -dried human liver the max. at 6.7 vanishes at a definite stage when the stability of (III) has been greatly diminished. H. D.

Effect of halogen salts on steapctic digestion. W. M. CLIFFORD (Biochem. J., 1934, 28, 418—422).—The lipolytic activity of pancreas substance (I) is strongly inhibited by 0.008—0.5*M*-NaF, -KF, or - NH_4F , but not by the corresponding salts of HCl, HBr, or HI. Inhibition varies directly with $[\text{F}^-]$, NH_4F being more inhibitory than NaF or KF at 0.06—0.25*M*. All three fluorides show an equal effect at 0.5*M* and at 0.008—0.03*M*. Halogen salts exert a coagulating effect on milk in presence of the very weak trypsin of (I). A. E. O.

Action of iodoacetic acid on diastase, lipase, and pepsin. F. BARTH (Biochem. Z., 1934, 270, 63—65).—Aq. $\text{CH}_2\text{I-CO}_2\text{H}$ (0.2% upwards) has no inhibiting effect on diastase (I), lipase, or pepsin. (I) is also unaffected by phloridzin. W. McC.

Normal substrates for the determination of soluble enzymes. H. PENAÜ and R. AUDIC (J. Pharm. Chim., 1934, [viii], 19, 329—345).—A special prep. of fibrin is recommended for the assay of pepsin and papain. Details are also given of the determination of diastase, using a special potato-starch, and of pancreatin on the basis of its amylase, lipase, and proteolytic activity. H. G. R.

Plasteins. A. V. BLAGOVESTSCHENSKI and G. V. JEREMEJEV (Biochem. Z., 1934, 270, 66—73; cf. Folley, A., 1932, 651).—The products of the action of pepsin (I) on caseinogen, ovalbumin, and globulin from sunflower seeds on further treatment with (I), at p_H 4.6—4.8, yield plasteins (II), precipitable by $\text{CCl}_3\text{-CO}_2\text{H}$, containing CO_2H and NH_2 decreased by equiv. amounts, and having less N than the original proteins (III). Production of (II) is complete in 4—5 hr. As compared with (III) the distribution of N in (II) is only slightly altered, the free NH_2 being here higher in the mono- and diamino-acid fractions. At p_H 1.5 (I) hydrolyses (II), restoring the original amount of free NH_2 . W. McC.

Parallel adsorption of crystalline pepsin and peptic activity on caseinogen and ovalbumin. J. B. SUMNER (Proc. Soc. Exp. Biol. Med., 1933, 31,

204—206).—Complete adsorption was achieved. Northrop's cryst. pepsin is not simply an enzyme adsorbed on protein. CH. ABS.

Inactivation of crystalline trypsin. M. KUNITZ and J. H. NORTROP (J. Gen. Physiol., 1934, 17, 591—615).—Reversible inactivation (I) of trypsin corresponding with a reversible denaturation of the protein increases with p_H from 2.3 to 13.0 at 0°. (I) is also obtained by heating. On keeping, (I) becomes irreversible. Between p_H 2.0 and 9.0 a bimol. hydrolysis occurs; at $p_H < 2$ or > 13 the trypsin protein is changed into an inactive form irreversibly denatured by heat, and at p_H 9—12 both reactions occur. Min. rates of inactivation occur at p_H 13 and 2.3.

H. D.

Hydrolysis of lecitho-vitellin by pepsin and by trypsin-kinase. J. H. BLACKWOOD and G. M. WISHART (Biochem. J., 1934, 28, 550—558).—With pepsin the liberation of acid-sol. N is $>$ that of acid-sol. P, whereas with trypsin these vals. depend on the enzyme concn. The max. hydrolysis yields 80% of the total N and 70% of the total P. The vitellin mol. must contain two dissimilar P complexes, one of which is resistant to enzymic action. H. G. R.

Activation of pancreatic juice by acid. M. LISBONNE (Ann. Physiol. Physico-chim. biol., 1933, 9, 723—733).—The optimum p_H for activation is 4.1. The mechanism of activation by acids is discussed.

NUTR. ABS. (b)

Proteolytic enzymes of *Rana temporaria* at different stages of metamorphosis. V. DOLJANSKI (Virchow's Archiv, 1933, 291, 418—426).—Tadpoles contain trypsin before and during (but not after) metamorphosis (I) except in the degenerating tail, cathepsin [which is most active during (I)] and dipeptidase (at all stages), but no pepsin.

NUTR. ABS. (m)

Action of the enzymes of *Crotalus adamanteus* on the proteins of blood and milk. E. E. DUNN (J. Pharm. Exp. Ther., 1934, 50, 386—392).—The venom (I) contains enzymes which digest plasma- and serum-proteins and, more slowly, serum-albumin and fibrin. (I) has weak rennin action. Pure caseinogen is digested rapidly and completely, but that of coagulated milk only slightly. (I) converts hæmoglobin in hæmolysed erythrocytes and in solution into methæmoglobin. C. G. A.

Separation of the enzymes and toxic principles of the venom of *Crotalus adamanteus*. E. E. DUNN (J. Pharm. Exp. Ther., 1934, 50, 393—406).—Cephalinase (I) is separated from the proteinases (II) by adsorption on $Al(OH)_3-C$ (aged for 8 months) or by heating to 85° and pptn. with EtOH. (I) retains part of the toxicity of the venom and is hæmolytic. The enzyme oxidising hæmoglobin to methæmoglobin can be separated from (I) and (II) by adsorption on $Al(OH)_3-A$ or $-C$, and is not eluted by phosphate buffer or very dil. alkali. C. G. A.

Intermediary metabolic products and arginase activation. A. PURR and L. WEIL (Biochem. J., 1934, 28, 740—744).—The degrees of activation of arginase (I) by Fe^{II} compounds with cysteine, ascorbic acid, uric acid, and other metabolic products

are determined; Fe^{II} in complex combination does not activate (I). The activation may be dependent on a redox potential. H. D.

Relation between the activity of urease and the oxidation-reduction potential. H. FISCHGOLD (Biochem. J., 1934, 28, 406—410).—The activity of urease is unaffected by H_2 or air, or by the oxidation-reduction potential (I) of the medium within the range covered by the systems $Pd-H_2$ (II), methylene-blue-leucomethylene-blue, and ferricyanide-ferrocyanide. Inhibition by quinol is probably due to a sp. chemical reaction [being absent in presence of (II)] and is not related to (I). A. E. O.

Lævorotatory allantoin. R. FOSSE, P. E. THOMAS, and P. DE GRAEVE (Compt. rend., 1934, 198, 1374—1376).—As well as that of the soya bean (cf. this vol., 534), allantoinase of skate liver will preferentially hydrolyse *d*-allantoin, leaving an excess of the *l*-form; in neutral or alkaline solution the latter quickly racemises. E. W. W.

Phosphatase activity of spleen extracts. D. R. DAVIES (Biochem. J., 1934, 28, 529—536).—The phosphatase (I) action of extracts of spleen (II) with β -glycerophosphate as substrate has two max. at p_H 4.5—5.0 and 9.0, respectively, and is very low at p_H 7.0. The ratio of the two activities of the same extract at the two max. is not const. from animal to animal even of the same species. Mg^{++} activates the (I) of (II) and of red blood-cells at p_H 6.0—9.5. These results as well as the relative rates of hydrolysis of α - and β -glycerophosphate at various p_H vals. suggest that (I) of (II) consists of two enzymes, one of which with its max. activity at p_H 9.0 is identical with blood-(I). W. O. K.

Calcification of hypertrophic cartilage *in vitro*. R. ROBISON and A. H. ROSENHEIM (Biochem. J., 1934, 28, 684—698).— α - and β -Glycerophosphates, hexose monophosphate, fructose diphosphate, and trehalose monophosphate, but neither diphosphoglycerate nor lecithin can act as substrates for bone-phosphatase (I) in calcification *in vitro* (II). Ba, Sr, and Mg salts can be deposited in cartilage *in vitro*. The second mechanism (III) is not completely inhibited by KCN. The activity of (III) falls more rapidly than that of (I) in excised bone stored in salt solutions at 37°; HCO_3^- exerts a protective effect. Vitamin-D and hormone preps. are without effect on (II). Glucose inhibits (II), but fructose, sucrose, dulcitol, erythritol, glycine, and urea do not. NaF (0.0001*M*) and CH_3I-CO_2Na (0.0001*M*) strongly inhibit (III) but not (I). C. G. A.

Effect of serum-proteins on calcification *in vitro*. A. H. ROSENHEIM (Biochem. J., 1934, 28, 699—707).—A Ca : P ratio (I) of 10 : 6 is necessary for calcification (II) in presence of 7% horse serum-protein (III), compared with 10 : 3 alone. The inhibitory effects of glucose and Mg on (II) are still apparent in presence of (III). Glycerophosphoric ester lessens the effect of protein. (II) occurs in serum from rats, rabbits, and man if the Ca \times P product is sufficiently high, added inorg. PO_4^{---} usually being necessary. C. G. A.

Variability in the activity of the calcifying mechanism in the bones of rachitic rats. A. H. ROSENHEIM (Biochem. J., 1934, 28, 708—711).—The calcifying power of the cartilage of the bones of rachitic rats decreases with increasing period on a rachitogenic diet. C. G. A.

Calcification *in vitro* of kidney, lung, and aorta. A. H. ROSENHEIM and R. ROBISON (Biochem. J., 1934, 28, 712—719).—Calcification (I) occurs more slowly than in hypertrophic cartilage, and deposition is irregular. Phosphoric ester seems to be necessary for (I) in kidney and lung, but aorta calcifies in very highly supersaturated inorg. solutions. The deposits resemble those found *in vivo* in hyper-*vitaminosis-D*. C. G. A.

Phosphatase activity of animal tissues. M. G. MACFARLANE, L. M. B. PATTERSON, and R. ROBISON (Biochem. J., 1934, 28, 720—724).—Vals. of the ratio phosphatase activity: dry wt., in presence and absence of Mg, for various tissues of rat, rabbit, guinea-pig, mouse, cat, and dog are given. The bladder of all species is active. In the rat only does the aorta show activity. C. G. A.

Effect of parathormone on bone-phosphatase activity *in vitro*. H. BAKWIN and O. BODANSKY (Proc. Soc. Exp. Biol. Med., 1933, 31, 64—65).—Parathormone, in concns. of 0.1—2.5 units per c.c. of hydrolysing mixture, has no effect *in vitro* on the β -glycerophosphatase activity of aq. extracts of rat- and cattle-bone. NUTR. ABS. (m)

Appearance of triose in desmolytic hexose degradation. M. KOBEL and C. NEUBERG (Biochem. Z., 1934, 269, 441—446).—Tables summarise the yields of triose or triose phosphate (up to 31%) and of AcCO_2H (up to 46%) from hexose diphosphate using an $\text{EtOH-Et}_2\text{O}$ prep. of a top yeast under varying conditions. P. W. C.

Direct fermentation of maltose. H. SOBOTKA and M. HOLZMAN (Biochem. J., 1934, 28, 734—739).—Maltose vals. (I) for various yeasts were determined. A German yeast with a small (I) ferments maltose, after an initial induction period, as fast as glucose. H. D.

Storage of carbohydrate and fat by *Saccharomyces Froberg* when incubated in sugar solutions. R. A. MCANALLY and I. S. MACLEAN (Biochem. J., 1934, 28, 495—498).—Carbohydrate storage of similar extent took place when *S. Froberg* (I) was incubated in solutions of glucose (II), galactose (III), fructose (IV), sucrose (V), and maltose (VI) of equal concns. Increasing concns. of (II) and (III) resulted in increased carbohydrate storage. (I) stored more fat when incubated in solutions of (II) than of (III), (IV), (V), or (VI), the amounts increasing in the cases of (II) and (III) with increased concns. of the sugars. Phosphate added to the medium did not increase fat storage as with brewer's yeast (cf. A., 1924, i, 352; 1925, i, 204). W. O. K.

Glycogen in yeast. A. HEIDUSCHKA and G. SCHÄFER (Arch. Pharm., 1934, 272, 137—142).—Glycogen (I) in yeast is accurately determined by Warkany's method (A., 1925, i, 105). Determination

of (I) and of the yeast-gum (II) (Salkowski) in similar specimens of yeast stored at temp. varying between 2° and 26° shows that the amount of (I) decreases, and of (II) increases, with time, and, above 10°, both vals. become constant after about 10 days. Thus the disappearance of (I) is not due to its change into other carbohydrates, but to the respiration of the yeast, which is very rapid at > 5°. J. W. B.

Simple method for the isolation of glutathione from yeast. A. KOZŁOWSKI (Science, 1934, 79, 388—389).—Glutathione is obtained from yeast by treatment with EtOH , H_2SO_4 , and CuSO_4 . L. S. T.

Investigations in the region of high frequency. II. Biochemical action of ultra-short electromagnetic waves. F. PIRRONE (Atti R. Accad. Lincei, 1934, [vi], 19, 165—168).—Although feebler and variable, the action of Lakhovsky oscillating circuits on brewer's yeast is analogous to that of radio-emitting apparatus capable of transmitting waves of $\lambda=1.7$ m. For continuous exposures of 10—40 min., or discontinuous up to 90 min., the subsequent development of the yeast is accelerated, the effect being \propto the intensity of the radiation. The action falls with longer exposures. T. H. P.

Bios and factor-Z. H. VON EULER and H. LARSSON (Z. physiol. Chem., 1934, 223, 189—206).—In the prep. from different sources and purification (by extraction and pptn. with EtOH , Ba(OH)_2 and EtOH , COMe_2) of the Z-factor (I) stimulating fermentation (II) and of the B(=bios)-factor (III) stimulating cell-increase (IV) of yeast the velocities of (II) and (IV) show a parallel increase and the ratio is unchanged after dialysis. Br at room temp. or aq. Ba(OH)_2 at 100° affects neither activity. Acid KMnO_4 and $\text{CuSO}_4\text{-Ca(OH)}_2$ do not influence (I), but inhibit (III), possibly owing to poisoning by an -SH derivative, which cannot be completely removed. (I) and (III) are not adsorbed by acid-clay. The mean mol. wt. of (I) by diffusion is about 200. There are no characteristic differences between (I) and (III); the stimulation of (II) and (IV) probably represents two different phases of the action of one activator. J. H. B.

Synthesis from inorganic compounds of starch, fats, proteins, and protoplasm in the colourless animal, *Chilomonas paramecium*. S. O. MAST and D. M. PACE (Protoplasma, 1933, 20, 326—358).—*C. paramecium* shows normal growth and synthetic ability when supplied with N, C, O, H, Mg, K, S, and P. Other elements, if necessary for growth, suffice in extremely minute amounts. The organism can utilise N from NH_2 -acids, urea (I), or NH_4 salts, but not NO_3^- , NO_2^- , or atm. N_2 . Glycine, glucose (I), acetates (II), formates (III), or CO_2 (but not $\text{CO}_3^{''}$) are sources of C, (II) being more suitable than (III) or (I). The optimum concn. of CO_2 is 1 vol. to 5 vols. of air. Deviations from this val. cause changes in reaction, higher acidity being associated with increased synthesis of starch (IV) and fat (V), but retarded reproduction and lower acidity with lowered synthesis of (IV) and (V) and slower reproduction only after stored nutrient has been consumed. Si in nutrients appears to function

as a catalyst and very dil. solutions are effective. In this respect Si cannot be replaced by Fe, Al, or B. The oxidation of NH_4Cl in the nutrient to NO_3^- provides much of the energy expended in synthesis.

A. G. P.

Relation between inorganic salt concentration, hydrogen-ion concentration, and physiological processes in *Amoeba proteus*. II. Rate of locomotion, gel/sol ratio, and hydrogen-ion concentration in solutions of single salts. R. F. PITTS and S. O. MAST (J. Cell. Comp. Physiol., 1934, 4, 237—256).—The effects of solutions of K, Na, and Ca salts of varying concn. and p_H on the rate of locomotion (I) and on the gel/sol ratio (II) are recorded. (I) is probably independent of the kind and concn. of the anions present. No sp. correlation exists between (I) and (II) in any of the solutions examined.

A. G. P.

Sugar metabolism and the ability of moulds to accumulate acids. T. CHRZASZCZ and D. TRUKOW (Polish Agric. Forestal Ann., 1931, 26, 71—86).—The amount of acid accumulated is characteristic of the species and independent of sugar consumption. Max. accumulation usually takes place within 10 days.

CH. ABS.

Growth of *Penicillium roqueforti* on synthetic media. N. S. GOLDING (J. Dairy Sci., 1934, 17, 61—74).—Methods are described for obtaining a conc. enzyme extract from *P. roqueforti* and its use in producing a Roquefort flavour in processed cheese after heating. Reaction changes in culture media range from p_H 2.05 to 7.7, depending on the proportion of glucose and caseinogen present. Acid reaction was maintained until all glucose was utilised, and subsequent changes were toward the alkaline side. The p_H of the medium did not materially affect the course of caseinogen breakdown brought about by the mould.

A. G. P.

Composition of fat produced by *Penicillium javanicum*, van Beijma. G. E. WARD and G. S. JAMESON (J. Amer. Chem. Soc., 1934, 56, 973—975).—The oil obtained in 11% yield from the light petroleum extract of the dry mycelium has m.p. about 15°, n_D^{25} 0.9145, n_D^{25} 1.4680, acid val. 10.6, sap. val. 191, I val. (Hanus) 84, Reichert—Meissl val. 0.3, Ac val. 10.7, and contains 2% of unsaponifiable matter. The saturated acids (30.8%) isolated (hydrolysis) are palmitic (69.5%), stearic (28%), and *n*-tetracosic (2.5%); the unsaturated acids (60.8%) are oleic (52.1%) and α - and β -linoleic (47.9%).

H. B.

Nutrient and toxic action on *Aspergillus niger*. G. LOHMANN (Arch. Mikrobiol., 1934, 5, 31—56).—The effects of Zn (considered as an essential nutrient) on the growth of *A. niger* under varying nutritional conditions are recorded, and the nature of Zn-yield curves is compared with those for N and P. The toxic action of Zn and other poisons is influenced not only by the concn. of toxin present, but also by the relative proportions in which other essential nutrients are supplied.

A. G. P.

Mould tissue. IV. Lipins of *Aspergillus nidulans*. F. M. STRONG and W. H. PETERSON (J.

Amer. Chem. Soc., 1934, 56, 952—955).—The oil from the Et_2O — EtOH extract of the dry mycelium has d_4^{25} 0.9198, n_D^{25} 1.4682, I val. (Hanus) 114.4, sap. val. 169.5, acid val. 43.4, ester val. 126.1, and contains P (0.26%) and N (0.39%). A phospholipin is separated as a complex with MgCl_2 . The fatty acids (80.8% of oil) obtained by hydrolysis are palmitic (8.8%), stearic (11%), *n*-tetracosic (0.9%), oleic (29.6%), linoleic (16.3%), and higher unsaturated acids (1.7%). The unsaponifiable matter (8.18%) contains about 66% of sterols; ergosterol is present.

H. B.

Mould tissue. V. Fractionation of the nitrogen in the mycelium of *Aspergillus Fischeri*. H. J. GORCICA, W. H. PETERSON, and H. STEENBOCK (Biochem. J., 1934, 28, 504—511).—Fresh mycelium of *A. Fischeri* contained 30% H_2O -sol. non-protein-N, 55% alkali-sol. protein-N, and 12% of alkali-insol. residue-N. The alkali-sol. protein contained one fraction pptd. by acids (ash 1.2%, N 11.8%, P 0.4%) and a second, acid-sol. and pptd. by CuSO_4 (ash 12.37%, N 12.3% (ash-free basis), P 2.4% (ash-free basis). The residue contained 2.3% N of which 62% was isolated as glucosamine-N.

W. O. K.

Biochemistry of micro-organisms. XXXVII. (a) Production of hydroxyanthraquinones by species of *Helminthosporium*. (b) Isolation of tritisorin, a metabolic product of *H. tritici-vulgaris*, Nisikado. (c) Molecular constitution of catenarin. H. RAISTRICK, R. ROBINSON, and A. R. TODD (Biochem. J., 1934, 28, 559—572).—The mycelium (I) of *H. catenarium*, Drechsler, contains catenarin (II) (formerly hydroxyhelminthosporin), m.p. 246°. Distillation of (II) with Zn dust in H_2 affords 2-methylantracene. Oxidation of (II) with MnO_2 and H_2SO_4 yields hydroxycatenarin, m.p. about 320° (Ac_5 derivative, m.p. 233—234°), which must from its properties be 1:4:5:8-tetrahydroxy-2-hydroxymethylantracene. With HNO_3 , (II) gives a product (tetranitrocatenarin?), chars about 250°. (II) gives no Me or definite Br derivative with MeI or HBr in AcOH, respectively. (II) is probably a 1:5:8-trihydroxy- β -hydroxymethylantracene. *H. velutinum*, Link, produces (II) but the (I) also contains appreciable amounts of ergosterol (III). *H. avenae*, Eidam, produces cynodontin and (III) in small amount. *H. tritici-vulgaris*, Nisikado, yields (II) and tritisorin (IV), $\text{C}_{15}\text{H}_{10}\text{O}_7$, m.p. 260—262° (pyridine salt; Ac_5 derivative, m.p. 215°). On distillation with Zn dust, (IV) affords 2-methylantracene. (IV) is regarded as 1:3:5:8-tetrahydroxy-6-(or 7)-hydroxymethylantracene.

H. G. R.

Anaerobic fermentation of lignin. C. S. BORUFF and A. M. BUSWELL (J. Amer. Chem. Soc., 1934, 56, 886—888; cf. B., 1930, 117, 1043).—Anaerobic fermentation of lignin (I) [isolated from cornstalks (II) by various methods] proceeds very slowly and incompletely; the ratio $\text{CH}_4:\text{CO}_2$ is approx. 1:2, indicating abnormal fermentation (cf. A., 1933, 752). Anaerobic fermentation of (II) removes an appreciable amount of the natural (I).

H. B.

Synthesis of cellulose by *Acetobacter xylinum* from polyhydric alcohols. Y. KHOUVINE (Compt.

rend., 1934, 198, 1544—1546).—C₃—C₇ polyhydric alcohols afford celluloses with *A. xylinum* (cf. A., 1933, 640). Glycerol, erythritol, arabitol, and dulcitol are converted to the extent of 60, 50, 20, and 20%, respectively, and the others completely. J. L. D.

Propionic acid bacteria. Mechanism of glucose dissimilation. H. G. WOOD and C. H. WERKMAN (J. Biol. Chem., 1934, 105, 63—72).—Fermentation of glucose (I) by *Propionibacterium arabinosum* yields a non-reducing substance, which, after removal of all (I), is converted into EtCO₂H, AcOH, CO₂, and possibly C₂H₄(CO₂H)₂. As long as dissimilation of (I) continues a non-volatile, Et₂O-sol. substance containing a CO group is present. H. G. R.

Pyruvic acid in the dissimilation of glucose by propionic bacteria. H. G. WOOD and C. H. WERKMAN (Biochem. J., 1934, 28, 745—747).—NaHSO₃ and CaSO₃ when added to an incubation mixture of *Propionibacterium arabinosum* with glucose fix the AcCO₂H formed. No MeCHO was detected.

H. D.

Acetic bacteria. Action of *B. gluconicum* on galactose. S. HERMANN and P. NEUSCHUL (Biochem. Z., 1934, 270, 6—14; cf. A., 1932, 545).—Species of acetic bacteria (I) differ in the rate at which they oxidise galactose to *d*-galactonic acid (II). *B. gluconicum* differs from other (I) in producing steadily increasing (up to 78%) yields of (II) on continued propagation.

W. McC.

Determination of volatile fatty acids by distillation. J. VAN BEYNUM (Vereen. Exploit. Proef., Hoorn, Ann. Rep., 1932, 1933, 33—51).—In a milk culture of bacteria producing AcOH the determination is made by distilling 50 c.c. of medium + 50 c.c. of H₂O + 10 c.c. of *N*-H₂SO₄, collecting fractions of 50 c.c., restoring with 50 c.c. of hot H₂O after each distillation, and titrating.

NUTR. ABS. (m)

Acidophilus milk. C. N. STARK, R. GORDON, J. C. MAUER, L. R. CURTIS, and J. H. SCHUBERT (Amer. J. Publ. Health, 1934, 24, 470—472).—The consumption of acidophilus (I) milk by normal and constipated subjects caused an increase in the no. of lactobacilli and (I) bacteria in, and in the wt. and H₂O content of, the faeces, and a decrease in other types of bacteria and in the indole content. Certain of these effects were due to the increased ingestion of lactose.

E. C. S.

Effect of temperature of incubation on agar plate count of milk. C. S. PEDERSON and M. W. YALE (Amer. J. Publ. Health, 1934, 24, 477—484).—Incubation at 32° for 48 hr. gives better results than does incubation at 37°.

E. C. S.

Presence of acraldehyde in cider and perry. G. WARCOLLIER, A. LE MOAL, and J. TAVERNIER (Compt. rend., 1934, 198, 1546—1548).—From cider and perry containing acraldehyde (I) a bacterium capable of producing (I) from glycerol was isolated.

A. G. P.

Standard methods and new procedures for the isolation of colon bacilli from water. C. E. A. WINSLOW (Amer. J. Publ. Health, 1934, 24, 456—469).—A review.

E C S

Differential reactions in the colon group of bacteria. M. LEVINE, S. S. EPSTEIN, and R. H. VAUGHN (Amer. J. Publ. Health, 1934, 24, 505—510).—A modification of O'Meara's test (J. Path. Bact., 1931, 34, 401) for CHAcMe·OH, and other improvements of the Voges-Proskauer reaction, are described. *Escherichia*, *Citrobacter*, and *Aerobacter* are differentiated (i) by the use of a medium containing Fe^{III} citrate for detecting H₂S; (ii) by incubation at 45—46°; (iii) by the use of a medium containing H₃BO₃.

E. C. S.

Lysis of fibrin by streptococci. G. HADFIELD, V. MAGEE, and C. B. PERRY (Lancet, 1934, 226, 834—839).—Broth cultures of eleven out of thirty strains of haemolytic streptococci (I) rapidly liquefy human fibrin. The liquefaction of human plasma clot by (I) is not related to its fibrin content. Total immunity to fibrinolysis (II) appears to be a sp. immunity response to infection by (I). The plasma clot of children suffering from rheumatism frequently shows total resistance to (II).

L. S. T.

Decomposition of nitrogenous substances in horse excrement and manure. B. CHROSTOWSKI (Bull. Acad. Polonaise, 1933, B, 83—89).—During the aerobic decomp. of fresh excrement or of farmyard manure in the presence or absence of nitrifying bacteria (I), no marked liberation (II) of N₂ occurs when the N content is low or the C/N ratio is high: with a high N content or a low C/N ratio, (II) occurs independently of the presence of (I).

F. O. H.

Hydrolysis of certain polysaccharides and proteins by the endospores of aerobic bacilli. H. L. A. TARR (Biochem. J., 1934, 28, 391—393).—At *p*_H 7·3, endospores (I) of *B. subtilis* and *B. mesentericus*, previously heated at 80°, hydrolyse starch and glycogen to maltose (II), and various proteins with increase of NH₂-N. (II) is not hydrolysed by (I).

A. E. O.

Nitrogen balance in cultures of aerobic bacteria. M. LEMOIGNE, P. DOPTEY, and R. DESVEAUX (Bull. Soc. Chim. biol., 1934, 16, 18—34).—The N content in cultures of several aerobic bacteria in peptone broth remains const. for about 10 to 15 days, and then decreases, in some cases to about 30% of the original val.

A. L.

Respiration and fermentation of pathogenic bacteria. I. Determination of respiration coefficients for pathogenic bacteria. A. FUJITA and T. KODAMA (Biochem. Z., 1934, 269, 367—374).—Tables summarise the *Q*_o, etc. vals. for a variety of pathogenic organisms. With *B. diphtheriae* and *B. paratyphenteriae*, Ohara-Mita, the quotient varies considerably with the cultural conditions, and no parallelism could be detected between the respiration and catalase content.

P. W. C.

Assimilation of carbon dioxide by red sulphur bacteria. I. H. GAFFRON (Biochem. Z., 1934, 269, 447—453).—For red S bacteria (I) org. substances cannot replace H₂S and other oxidisable S compounds as H donators in the hydrogenation of CO₂, the organisms being therefore very different from the purple S bacteria (II). (I), however, grow well in a medium in which H₂S is replaced by org.

compounds. Whereas (II) cannot use PrCO_2Na in the dark, (I) use it for reduction of $\text{SO}_4^{''}$ to $\text{S}^{''}$, the H_2S then making possible the assimilation of CO_2 on irradiation.
P. W. C.

Dehydrogenases of the filterable organism of *Agalactia*. A. PIRIE (Biochem. J., 1934, 28, 411—415).—Like *B. coli* (I) (A., 1925, i, 1015) *Agalactia* (a very much smaller organism) oxidises many substances if the substrate concn. is high enough. The most active dehydrogenases (II) are those attacking lactate, adenylic acid, adenosine, fructose, and hexose diphosphate in concn. $< 0.1N$. The relative strengths of (II) vary with the culture, and do not depend entirely on the medium or the phase of growth at which (II) are determined. The lactate (II), like that of (I), is strongly inhibited by gluconate and $\text{C}_2\text{O}_4^{''}$.
A. E. O.

Halophilic bacteria. L. M. HOROVITZ-VLASSOVA and M. I. LIVSHITZ (Izvest. Tzentr. Nauch.-Issledov. Inst. Pishch. Vkus. Prom., 1931, 39—46).—Of thirty-five organisms examined four were obligate and thirty facultative; *Micrococcus citreus agilis* will grow without NaCl, but only very slowly.
CH. ABS.

Salt-tolerant bacteria L. S. STUART and T. L. SWENSON (J. Amer. Leather Chem. Assoc., 1934, 29, 142—158; cf. B., 1934, 31).—The appearance of growths on media containing 1% and 25% NaCl differed. The reactions of the parent cultures and the derived cultures were the same on three different sugars. Gelatin (*G*) was hydrolysed at all p_H vals. by the enzymes produced by the bacteria grown on a 1% NaCl medium, but not by those produced by bacteria grown on a 25% NaCl medium at $p_H < 7.2$. The former enzymes liberate additional CO_2H groups from *G* at $p_H < 6.8$, whereas fewer such groups were formed by the latter. Although no chemical action in *G* treated with either type of enzyme at $p_H 6.5$ could be detected by the changes in the Van Slyke $\text{NH}_2\text{-N}$ or CO_2H vals., the rate of subsequent alkaline hydrolysis and trypsin digestion differed from that of untreated *G*, and hence chemical change must have taken place.
D. W.

***Micrococcus eykmanii*, n. sp., a bacterium utilising vitamin-like substances for growth.** L. E. DEN D. DE JONG (Arch. Mikrobiol., 1934, 5, 1—13).—Growth of *M. eykmanii* on peptone-agar is stimulated additions of sterile extracts of plant and animal matter and of cultures of various micro-organisms. No stimulus results in the absence of peptone. The growth-promoting substance is not auxin.
A. G. P.

Presence of a glycol in the wax of the tubercle bacillus. N. STENDAL (Compt. rend., 1934, 198, 1549—1550).—A glycol ("phytoglycol") $\text{C}_{26}\text{H}_{54}\text{O}_2$, m.p. 73° (diacetate, m.p. 34°), was isolated.
A. G. P.

Activation of "methylic" antigen *in vivo* and *in vitro*. NINNI (Ann. Inst. Pasteur, 1934, 52, 502—532).—The *in-vivo* antigenic action of the MeOH-sol. fraction of the lipins (I) of Koch's bacillus is slightly increased by addition (*in vitro*) of PhOH (when the specificity is unaltered) or by preliminary conjugation with horse- or pig-serum. Admixture

with certain bacterial proteins (II) yields a more marked activation, the extent of which is dependent on the time of contact of (I) and (II), on the physical state of (I), and on the adsorbed impurities of (I). Conjugation of a lipin-hapten with a protein reduces the antigenic action (*in vitro* and *in vivo*) of the latter, but does not modify its specificity.
F. O. H.

Pneumococcus antibodies. L. D. FELTON (Science, 1934, 79, 277—278).—The antibodies found in antipneumococcus horse-serum are protein in nature, and one antibody reacting with a single antigen is responsible for the usual immunological reactions.
L. S. T.

Specific carbohydrates of *Vibrio cholerae* and related organisms. R. W. LINTON and D. L. SHRIVASTAVA (Proc. Soc. Exp. Biol. Med., 1933, 31, 406—409).—In most cholera vibrios the characteristic sugar was galactose (I); others contained arabinose (II). Others (non-agglutinable) from H_2O contained (II). Polysaccharides containing both (II) and (I) were isolated from "rice H_2O " and faeces of cholera patients.
CH. ABS.

Autolysis. Specific autolysins. E. WOLLMAN (Compt. rend., 1934, 198, 1642—1643).

Reversible inactivation of bacteriophage by mercuric chloride. A. P. KRUEGER and D. M. BALDWIN (J. Gen. Physiol., 1934, 17, 499—505).—The curve of inactivation of antistaphylococcal phage by 0.01% HgCl_2 is pseudo-unimol. down to 0.5% of the initial phage concn. 100% reactivation can be obtained even after 216 hr. exposure to 2.8% HgCl_2 .
H. D.

Specific inhibition of bacteriophage action by bacterial extracts. P. LEVINE and A. W. FRISCH (J. Exp. Med., 1934, 59, 213—228).—Sp. inhibition of phage by sol. products of bacteria, probably carbohydrates, is more rapid at 37° than at 0° .
CH. ABS.

Detection of arsenicals in spirochaetes and trypanosomes. E. SINGER and V. FISCHL (Z. Hyg., 1934, 116, 36—40).—Org. matter is destroyed by heating with H_2SO_4 and HNO_3 . The resulting solution is treated with Zn in a tube containing paper soaked in HgCl_2 , and the intensity of the stain compared with standards.
A. G. P.

***In-vitro* leprocidal activity of some non-chaulmoogryl compounds.** G. A. EMERSON and A. J. SALLE (Proc. Soc. Exp. Biol. Med., 1934, 31, 428—433).—Merthiolate, metaphen, mercurochrome, solganol, CHPh_3 dyes, methylene-blue, and octyl-resorcinol are highly active; trypan-blue and the aliphatic alcohols are inactive.
CH. ABS.

Germicidal and antiseptic activities of some derivatives of 8-hydroxyquinoline.—See this vol., 664.

Antiseptic properties of amino-derivatives of styryl- and anilo-quinoline.—See this vol., 664.

Relationship between chemical constitution and bactericidal activity. XII. 3-Nitro- and 3-amino-4-hydroxy- and -alkoxy-benzoic esters.—See this vol., 650.

Can the Endo medium be standardised? H. J. CONN and M. A. DARROW (Stain Tech., 1934, 9, 61—69).—If the ratio of Na_2SO_3 to basic fuchsin is 12.5:1 a greater no. of different specimens of fuchsin are satisfactory for the medium than is the case when the ratio is 3:1. H. W. D.

Staining of acid-fast bacilli. Effects of fixatives and p_{H} on acid-fastness. J. W. FIELDING (Austral. J. Exp. Biol., 1934, 12, 1—5).—Ehrlich's original observations on the necessity for alkali treatment are sound. Autolytic action in tissues lowers the p_{H} of the fixative; this should be kept alkaline (for Ziehl-Neelsen stain) or alkaline fuchsin should be used. Treatment with CH_2O or COMe_2 does not destroy acid-fastness. A new method of staining formalised tissues is described. A. E. O.

Destaining agents for iron alum hæmatoxylin. S. H. HUTNER (Stain Tech., 1934, 9, 57—59).—Saturated aq. picric acid is recommended for bringing out the nuclei in protozoa. A mixture of 1 pt. of 30% H_2O_2 and 2 pts. of 95% EtOH differentiates cytoplasmic structures. H. W. D.

Modification of the Dorner spore stain. M. A. SNYDER (Stain Tech., 1934, 9, 71—72).—A thin film of the organisms on a slide is covered with blotting paper, and Ziehl's carbol-fuchsin is applied while the slide is heated for 5—10 min. After decolorisation with 95% EtOH and washing with H_2O , a drop of saturated aq. nigrosin is spread over the film. It is then dried on a hot plate. Spores are stained red, and the vegetative parts of the cells are almost colourless. H. W. D.

Filtration of [solutions of] hormones. E. BELANI (Chem.-Ztg., 1934, 58, 289—290).—The solution (either alone or with clarifying agents of the kieselguhr type), under a pressure of 2 atm., passes through a disc-shaped cloth-covered filtration device, a series of which is connected to a common collecting pipe. The capacity of the apparatus is 4.2 litres and the filtration area 0.5 sq. m. F. O. H.

Chemistry of the active principle of the lymph glands (lymphoganglin). P. MARFORI, G. DE NITTO, and G. AURISICCHIO (Biochem. Z., 1934, 270, 219—226).—8 kg. of fresh lymphatic gland, after drying, powdering, and removing impurities by CHCl_3 , anhyd. Et_2O , and EtOH, yield 6 g. of a hormone (I) (platinichloride; aurichloride) $\text{NMe}_3\text{Cl} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{O} \cdot \text{PO}_3\text{Ca}$. With Ag_2O (I) yields a quaternary base (II) (picrate; tannate; hydrochloride) identical with neosine. (I) is free in the glands; it is produced there by degradation of lecithin and it has a powerful depressant effect on the blood-pressure acting as an antagonist to adrenaline. W. McC.

Callicrein. E. WERLE (Biochem. Z., 1934, 269, 415—434).—Callicrein (I) was detected in the juices from human and dog's pancreatic fistulae, in human duodenal juice, and in human and dog's faeces, and its action on the circulation investigated. Human duodenal juice contains 10 units of (I) per c.c. and the juice of a post-operative pancreatic fistula in man several thousand units per day, which is four times the daily urinary excretion of (I) by a healthy man. (I)

from human sources (urine, faeces, duodenal juice, blood) is different from (I) of dog (cf. A., 1930, 1089, 1624). P. W. C.

Comparative investigation of callicrein and trypsin concentrations in human duodenal juice. E. WERLE and P. ECKEY (Biochem. Z., 1934, 269, 435—440).—Both trypsin and callicrein are present in human duodenal juice, blood, and urine, the concns. and abs. amounts of these substances in duodenal juice varying considerably from time to time and in the same sense. The physiological importance of the hormone during digestion is discussed. P. W. C.

Electrochemical character of insulin.—See this vol., 602.

Lactic acid, sugar, and inorganic phosphorus in the blood of ruminants (a) following adrenalectomy and (b) after intravenous injection of insulin. R. STRAND, W. ANDERSON, and W. M. ALLCROFT (Biochem. J., 1934, 28, 642—649).—In adrenalectomised sheep, the blood-sugar (I) and blood-lactic acid (II) levels were lowered, whilst that of inorg. P (III) was raised, and the sensitivity to insulin (IV) increased in comparison with normals. No change in the (I) and (II) occurred when the sheep were subjected to types of excitement and muscular exercise known to raise (I) and (II) in normal sheep (V). The changes in (III) and the hypoglycaemia produced by injection of (IV) into (V) were similar to those in other animals, except that no sign of convulsions was observed even after large doses of (IV). There was no definite change in (II) after injection of (IV) into (V). A. E. O.

Biological properties of adrenaline. A. C. MARIE (Ann. Inst. Pasteur, 1934, 52, 481—487).—Neutral solutions of adrenaline (I) and its salts inhibit the action of bacterial and vegetable toxins, but do not appreciably influence the toxicity of cobra-venom or the lytic power of a bacteriophage (bacillus of Shiga). With filterable bacteria, (I) inhibits the development to a visible form. Whilst many pathogenic bacteria are unaffected, the virulence of pneumococci, *Trypanosoma lewisi*, and *T. brucei* is diminished. Repeated injection of (I) into rabbits produces marked increases in the blood-urea and cholesterol content of the aorta. F. O. H.

Influence of dopa (dihydroxyphenylalanine) on adrenaline glycogenesis in the surviving toad liver. J. HORIMI (Folia Pharmacol. Japon., 1933, 17, 99—103).—The perfused liver exhibited glycogenesis less pronounced than that caused by adrenaline. CH. ABS.

Blood-cholesterol of rabbits after unilateral and bilateral adrenalectomy. H. TADA (Tôhoku J. Exp. Med., 1933, 22, 385—394).—Increase in blood-cholesterol is more marked after bilateral adrenalectomy, reaching 25—75% in 5—7 days. CH. ABS.

Diuretic-antidiuretic activity of posterior pituitary extracts. E. E. NELSON and G. G. WOODS (J. Pharm. Exp. Ther., 1934, 50, 241—253).—The urine excretion of groups of mice kept under uniform conditions and injected intraperitoneally with H_2O

(5% of body-wt.) varies widely, the curve of distribution of the variation being S-shaped. Injection of such animals with small amounts of pituitary extract (I) causes decreases in diuresis proportional to the amount of (I). Large doses, however, are less effective, but the abs. amount of Cl' excretion increases until a val. of about 1% is reached; the diuresis is still < that caused by H_2O alone. The procedure described may be used for comparing the antidiuretic activity of (I) preps. A. L.

Anterior pituitary growth-hormone and the composition of growth. M. O. LEE and N. K. SCHAFFER (J. Nutrition, 1934, 7, 337—363).—The gain in wt. of rats receiving the hormone extract differed markedly in respect of N, fat, fat-free tissue, H_2O , and ash from that of rats on normal diet. The % composition of the carcasses of treated rats was similar to that at the commencement of treatment, and the N retention was closely paralleled by the live-wt. gains. The energy expenditure per unit gain in both total wt. and protein was higher in the controls. Of the body-constituents, N and the fat- and ash-free dry matter were most specifically affected by the hormone. A. G. P.

Pancreatropic substance from the anterior pituitary lobe. I. Preparation and properties. II. Effects on metabolism. K. J. ANSELMINO and F. HOFFMANN (Klin. Woch., 1933, 12, 1435—1436, 1436—1438; Chem. Zentr., 1933, ii, 3000).—Ox pituitary is dehydrated with COMe_2 , and pulverised, extracted with H_2O , and filtered. To 100 c.c. of the filtrate 20 c.c. of aq. NaOAc of p_H 5.2 are added, and the solution is separated from protein by ultrafiltration. The pancreatropic hormone (I) is insol. in CHCl_3 , COMe_2 , or EtOH , but is sol. in 50% EtOH , and is destroyed by heating or by acids and alkalis. (I) is absorbed by kieselguhr, but not by animal C or kaolin. Subcutaneous injection of (I) lowers the blood-sugar in dogs and rabbits. The effect on alimentary and adrenaline hyperglycaemia is similar. (I) lowers the liver-glycogen of rats. These effects do not occur in depancreatized dogs. H. J. E.

Contra-insulin hormone of the anterior pituitary lobe and pancreas diabetes. Effect of various pituitary preparations on pancreas diabetes in dogs. H. LUCKE, E. R. HEYDEMANN, and O. BERGER (Z. ges. exp. Med., 1933, 90, 120—129, 162—172; Chem. Zentr., 1933, ii, 3000).—The blood-sugar increase in pancreas-diabetic dogs after intramuscular injection of contra-insulin hormone (I) (e.g., Praphyson) is > in normal animals. An animal rendered normal by diet and by insulin is rendered temporarily diabetic by (I). The same effects are observed with oral administration of (I). Prolan and thyrotropic hormone contain no (I). H. J. E.

Parathyrotropic action of anterior pituitary extracts. K. J. ANSELMINO, F. HOFFMANN, and L. HEROLD (Klin. Woch., 1933, 12, 1944).—Injection of anterior pituitary extracts into young male rats causes large increases in the size of the parathyroids, alteration in the histological picture, and increased blood-Ca. NUTR. ABS. (m)

Disturbances of phosphorus metabolism in rickets. IX. Effect on blood-inorganic phosphate and -calcium of thyroid secretion and thyrotropic hormone. W. HEYMANN and E. MAIER (Z. Kinderheilk., 1933, 55, 512—517).—Thyroxine in sufficient doses causes, after a latent period, an increase in blood- PO_4''' in infants, without affecting the Ca. This change occurs independently of those in metabolic rate. NUTR. ABS. (m)

Thyrotropic hormone and fat metabolism. F. SILBERSTEIN, F. GOTTDENKER, and G. GEIGER (Klin. Woch., 1933, 12, 1225; Chem. Zentr., 1933, ii, 3583).—Injection of thyrotropic hormone into the cat frequently leads to a rise in blood-fat. If olive oil is also given orally alimentary hyperglycaemia is diminished and the increase in blood-fat is sometimes absent; frequently it falls. A. A. E.

"Fat-metabolism" hormone and hyperglycaemia. B. HARROW (Nature, 1934, 79, 272—273).—An extract containing "fat-metabolism hormone" prepared by Funk's method (Proc. Amer. Soc. Biol. Chem., 1933, 8, 43) produces a marked hyperglycaemia, comparable with that which results from Doisy's extracts (A., 1933, 98), as well as an increase in COMe_2 in the blood. Both authors appear to be dealing with the same substance. L. S. T.

Preparation and properties of an antithyrotropic substance. E. M. ANDERSON and J. B. COLLIP (Lancet, 1934, 226, 784—786; cf. this vol., 332).—An extract of an antithyrotropic substance (I) has been prepared from the serum of a horse injected with thyrotropic hormone (II). (I) depresses the metabolic rate of normal animals and inhibits the action of (II) in normal and hypophysectomised rats. (I) does not antagonise the action of thyroxine. Hypophysectomised rats treated with (I) in conjunction with (II) have a depressed metabolic rate associated with cellular activity in the thyroid gland. (I) is not produced by the pituitary. L. S. T.

Metabolism of water and endocrine extracts. I. "Plasmohæmiatic" action of thyroid extract. M. PAGET, L. LANGERON, and J. LEDIEU (Bull. Soc. Chim. biol., 1934, 16, 125—139).—The effect of the administration of thyroid extract (I) to man differs according as the ratio (II), vol. of plasma/vol. of erythrocytes, is > or < normal (1.3—1.4). When (II) is > 1.3 (I) increases (II) whilst the total blood- Cl' , the plasma- Cl' /corpuscle- Cl' ratio (III), and blood-serum-protein are unchanged. Diuresis diminishes and does not increase until several days after cessation of (I) administration. When (II) > 1.4 the effect of (I), except on diuresis which is much increased, is not const., and when apparent is much < in the above case. Whilst administration of theobromine (IV) results in a decrease in (II) and (III), with an increase in diuresis, administration of (I) with (IV) causes an increase in (II), with no change in (III). The increased diuresis also is much < that produced by (IV) alone. (I) may therefore, in its action, be regarded as an internal diuretic. A. L.

Effect of thyroid and bone-marrow on plasma-proteins. S. LANG (Z. ges. exp. Med., 1933, 92,

102—107).—Administration of thyroid extract produces no change in the plasma-protein: injection of thyroxine causes a decrease in all the fractions parallel with the increased H_2O content. No change follows thyroidectomy, but injection of $NHPh \cdot NH_2$ causes an increase of total protein and globulin in the thyroidectomised animals, as does injection of red bone-marrow extract in the intact dog.

NUTR. ABS. (m)

Co-operation of cells and colloid in secretory activity of the thyroid. W. GRAB (Klin. Woch., 1933, 12, 1637—1640).—One third of the I in normal colloid (I), which constitutes 65% by wt. of the gland, is in active form. In thyroid activity induced by thyrotropic hormone the cellular elements increase, but (I) remains almost unchanged. (I) has then, however, an increased I content, although two thirds of it is in inactive form, presumably as di-iodo-tyrosine. (I) is only a vehicle carrying the internal secretion.

NUTR. ABS. (m)

Effect of desiccated thyroid, irradiated ergosterol, and ammonium chloride on excretion of calcium in rats. L. I. PUGSLEY and E. ANDERSON (Biochem. J., 1934, 28, 754—758).—Administration of 0.12 g. of thyroid gland (I) daily to rats produced an increased faecal Ca excretion (II); large doses of irradiated ergosterol + (I) increased the urinary (II). 0.25 g. of NH_4Cl administered daily to rats increased the urinary (II).

H. D.

Injury to heart-muscle by thyroxine. C. MATONET (Z. ges. exp. Med., 1933, 90, 237—244; Chem. Zentr., 1933, ii, 3001).—Guinea-pigs, injected daily for 4—11 days with 1 mg. of thyroxine, showed after short treatment a decrease of the total PO_4 , $H_4P_2O_7$, phosphagen, and residual H_3PO_4 in the heart-muscle, and an increase in H_3PO_4 . With prolonged treatment the decrease in the total PO_4 ceases. The decrease in phosphagen corresponds quantitatively with an increase in the H_3PO_4 .

H. J. E.

Efficacy coefficients of the thyroxine effect in biological experiments. H. EUFINGER and J. GOTTLIEB (Klin. Woch., 1933, 12, 1397—1402; Chem. Zentr., 1933, ii, 3001).—The factor in blood interfering with the thyroxine (I) effect in tadpole metamorphosis is associated with the blood-protein. In toxic conditions during pregnancy the antithyroidal protective action (II) of the blood is reduced. Vitamin-A (as Vogan) (III) exerts the same influence on the action of (I) in tadpole experiments as normal blood. Subjects whose blood has a low val. for (II) are rendered normal by (III). The reduction of (II) in toxicosis of pregnancy is attributed to disturbance of the function of the liver in providing (III). Guanidine influences the (I) effect by strengthening the components accelerating development. Choline, carbamyl- and acetyl-choline allow the growth-hindering component of the action of (I) to develop. The reduced antithyroidal action of blood during pregnancy is due to increased amounts of choline derivatives in the blood.

H. J. E.

Form in which iodine is excreted in the urine after oral administration of thyroxine in man. A. W. ELMER and M. SCHEPS (Compt. rend. Soc.

Biol., 1933, 114, 350—351).—Thyroxine cannot be recovered in significant amount from the urine.

NUTR. ABS. (m)

Decomposition by the liver of thyroxine injected intravenously. A. W. ELMER and Z. LUCZYNSKI (Compt. rend. Soc. Biol., 1933, 114, 351—352).—In anaesthetised rabbits about one half of the I of the liver bile is thyroxine-I. NUTR. ABS. (m)

Effect of hormones on creatine-creatinine metabolism; behaviour of total nitrogen, uric acid, and allantoin. S. BUADZE (Z. ges. exp. Med., 1933, 90, 762—804; Chem. Zentr., 1933, ii, 3581).—In dogs, injection of thyroxine increases excretion of creatine-creatinine (I) and allantoin (II), but not total N (III). Adrenaline increases (I), (II), and uric acid, but not (III). Menformone increases (I). Insulin in non-convulsive doses decreases (II), total creatinine (IV), and (III). Guanidine carbonate diminishes (III), (IV), and (II). Parathormone increases (IV) and (III); when it is given with guanidine the effect of the latter is not observed.

A. A. E.

Eight year old testicular transplantation with maintained secretory function. B. ROMEIS (Klin. Woch., 1933, 12, 1640—1642; Chem. Zentr., 1933, ii, 3581).—In the cat the male sexual hormone was still secreted after 8 years.

A. A. E.

Occurrence of the α -follicular hormone (3-hydroxy-17-keto- $\Delta^{1:3:5}$ -oestratriene) in stallion's urine. E. P. HAUSSLER (Helv. Chim. Acta, 1934, 17, 531—535).—Fractional crystallisation of the crude sexual hormone isolated from stallion's urine affords the α -follicular hormone.

J. W. B.

Oestrus-producing hormone. II. Identity of the substance from the urine of pregnant women with that from the urine of pregnant mares. S. E. DE JONGH, S. KOBER, and E. LAQUEUR (Biochem. Z., 1934, 270, 17—23; cf. A., 1931, 1462).—The α -follicular hormone (I) of pregnant mares' urine has $[\alpha] >$ that of women and can be separated by recrystallisation into two fractions. The benzoate of mares' (I) exhibits the double m.p. characteristic of Butenandt's β -hormone (A., 1933, 870). The activity of mares' (I) is identical with that of women's (I). The rat unit for subcutaneous injection of menformone = 10 international units, the equiv. oral administration dose being 40 rat units. W. McC.

Oestrogenic substances of vegetable origin. B. SKARZYŃSKI (Bull. Acad. Polonaise, 1933, B, 347—353).—7.2 mg. of trihydroxycestrin (1000 mouse units per mg.) were extracted from 65 kg. of the female flowers of the willow.

C. G. A.

Action of follicular hormone on tetany and blood-calcium in bitches with chronic parathyroid insufficiency. P. MATHIEU (Compt. rend. Soc. Biol., 1933, 114, 164—166).—Pure follicular hormone causes a fall in blood-Ca and some recurrence of tetany in these animals. It is normally without action in this respect. NUTR. ABS. (m)

Sexual variation in carbohydrate metabolism. IV. Effect of ovariectomy and theelin administration on the glycogen content of rats. M. GULICK, L. T. SAMUELS, and H. J. DEUEL, jun.

Metabolism of acetoacetic acid in normal and castrated male and female rats with and without theelin. C. F. GRUNEWALD, C. H. CUTLER, and H. J. DEUEL, jun. VI. Role of the anterior pituitary in the metabolism of acetoacetic acid. J. S. BUTTS, C. H. CUTLER, and H. J. DEUEL, jun. (J. Biol. Chem., 1934, 105, 29—34, 35—43, 45—58).—IV. After administration to ovariectomised rats of 5 mg. of glucose per sq. cm. body-surface, liver-glycogen (I) rose from 0.25% for the normal animal to 0.55%. No variation in muscle-glycogen was observed. Injection of theelin gives a val. for (I) < that of the controls.

V. The ketonuria (II) following administration of $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$ to ovariectomised female rats, which is one fourth that of normal females and one half that of normal males, is not affected by administration of theelin. (II) is also decreased by castration.

VI. Injection of neutralised alkaline extract of anterior pituitary (III) increases (II) in fasting rats receiving $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{Na}$, which is completely suppressed by small amounts of sugar. Injection of (III) when NaCl is fed gives a marked increase in (II).

H. G. R.

Interrelation of a gonadotropic hormone and vitamin-A. S. B. D. ABERLE (Amer. J. Physiol., 1933, 106, 267—272).—Human placenta yields an EtOH extract (I) which, when injected, produces mucoid cells in the vagina of spayed rats. (I) has no effect on persistent cornification established in rats on a diet deficient in vitamin-A.

NUTR. ABS. (m)

Fate of vitamins in hay on drying. I. O. RYGH (Biochem. Z., 1934, 270, 227—228).—Hay (I) prepared by drying grass for 2 hr. at 68° contains about ten times as much carotene as does field-dried grass (II) and twenty times as much as frame-dried (III). (I) also contains six times as much vitamin-D as do (II) and (III).

W. McC.

Effect of household cooking and canning on the vitamin content of vegetables. J. J. HOFF (Z. Ernährung, 1933, 3, 355—359).—Growth tests on rats showed no significant difference between the vitamin-A content of cooked (I) and canned (II) spinach. As tested on pigeons there was less vitamin- B_1 in (I) than in (II), and in both < in raw. In both processes less vitamin- B_2 was lost, probably owing to its greater heat-stability. There was great loss of vitamin-C in cooking, 90 g. of (I) being needed to protect a guinea-pig from scurvy to the same degree as 10 g. of raw spinach; in (II), 30 g. was the protective dose. Canning is thus less destructive to the vitamin content of vegetables than ordinary household cooking.

NUTR. ABS. (b)

Tuberculosis and vitamin deficiency. N. K. BASU (Z. Vitaminforsch., 1934, 3, 91—93).—Inclusion of vitamin-A, -B, -C, and -D in the diet of guinea-pigs inoculated with tubercle bacilli reduces the mortality from 90 to 33%. All four vitamins appear to participate in the prophylaxis (cf. A., 1933, 973).

F. O. H.

Purification of vitamins. Fractional distribution between immiscible solvents. R. E. CORNISH, R. C. ARCHIBALD, E. A. MURPHY, and

H. M. EVANS (Ind. Eng. Chem., 1934, 26, 397—406).—By means of a special machine, which is described, vitamin-A, -D, and -E are purified by fractional distribution between immiscible non-polar (I) and polar (II) solvents. The mathematical theory of purification by this process is developed. (I) are CS_2 , $n\text{-C}_6\text{H}_{12}$, $n\text{-C}_8\text{H}_{14}$, $n\text{-C}_7\text{H}_{16}$, and $\beta\beta\delta$ -trimethylpentane. (II) are MeOH, MeCN, $\text{C}_2\text{H}_4(\text{NH}_2)_2$, Et_2O , Pr^2O , $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{OMe}$, and $\text{C}_2\text{H}_4\text{Cl}\cdot\text{OH}$. The prep. of the pure anhyd. solvents is described. Many accepted val. of crit. solution temp. are too high, owing to incomplete removal of H_2O ; e.g., $\text{C}_2\text{H}_4(\text{NH}_2)_2$ and Et_2O are completely miscible at all temp. above the f.p. The distribution ratios (III) of ergosterol, cholesterol, sitosterol, and vitamin-A, -D, -E, and -F between (I) and (II) are given. -A exists in < 3 forms, of equal therapeutic val. -D and -E are single substances, or mixtures of substances of equal (III).

E. C. S.

Attempt to isolate vitamin-A. H. N. HOLMES, H. CASSIDY, E. HARTZLER, and R. MANLY (Science, 1934, 79, 255—256).—Vitamin-A concentrates (I) ranging from 10,500 to 14,400 times the potency of standard cod-liver oil have been obtained from the unsaponifiable portion of halibut-liver oil. (I) are pale yellow, viscous oils.

L. S. T.

Biological activity of some carotene preparations. H. N. HOLMES, R. CORBET, H. CASSIDY, C. R. MEYER, and S. I. JACOBS (J. Nutrition, 1934, 7, 321—329).—Carotene (I) adsorbed on $\text{Al}(\text{OH})_3$ improved the growth rate of vitamin-A-deficient rats to almost the normal standard, but did not completely cure xerophthalmia. When adsorbed on SiO_2 gel (II) or norit (III) (I) was inactive in this respect. When desorbed from (II), (I) showed greatly reduced activity, and that from (III) was almost inactive. Rats probably do not utilise the whole of the (I) fed whether the dose is large or small.

A. G. P.

Vitamin of growth. VI. Cryptoxanthin of yellow maize. R. KUHN and C. GRÜNDMANN (Ber., 1934, 67, [B], 593—595).—The isolation is described of zeaxanthin, m.p. 206°, and cryptoxanthin (I), m.p. 168°, from yellow maize which contains only traces of carotenes. Its growth-promoting qualities are attributed to (I), administration of which to rats supplied with a vitamin-A (II) -free diet causes occurrence of (II) in the liver.

H. W.

Properties of carotene. Is local avitaminosis possible? S. BALACHOVSKI and F. RACHEVSKI (Bull. Soc. Chim. biol., 1934, 16, 220—228).—The curative action of carotene in the treatment of forty-four cases of ocular affections is reported.

A. L.

Role of carotene in the organism. S. BALACHOVSKI and V. SOLIANIKOVA (Bull. Soc. Chim. biol., 1934, 16, 119—124).—The presence of carotene accelerates the uptake of O_2 by blood *in vitro*.

A. L.

Influence of carotene (vitamin-A) on the purine content of growing normal and pathological tissue. H. VON EULER and G. SCHMIDT (Z. physiol. Chem., 1934, 223, 215—228).—The val. of the purine-N/total N quotient (I) is high in spleen.

In rats, absence of vitamin-A (II) or carotene from the diet depresses the (I) of the spleen, liver, kidney, and muscle by 15%. (II) favours development and purine content (III) of Jensen sarcoma. Embryonic organs have a higher (III) than normal organs.

J. H. B.

Effect of mineral oil on assimilation of vitamin-A from spinach. H. S. MITCHELL (Proc. Soc. Exp. Biol. Med., 1933, 31, 231—233).—Rats fed on a vitamin-A-deficient diet with a daily supplement of 10 mg. of fresh green spinach (I) with 0.25—1.0 c.c. of mineral oil (II) fail to grow and die in 3—11 weeks, whilst those receiving (I) alone gain about 3 g. weekly. Increasing the amount of (I) to 40 mg., fed with (II) supplement, does not permit growth. When (II) is fed 6 hr. after a dose of 80 mg. of (I), the resulting growth is about equiv. to that on 10 mg. of (I) alone. Hence (II) seems to inhibit assimilation of vitamin-A. Paraffins of higher m.p. appear to have a less detrimental effect than fluid (II).

NUTR. ABS. (m)

Human milk. XIII. Vitamin potency as influenced by supplementing the maternal diet with vitamin-A. S. S. McCOSH, I. G. MACY, H. A. HUNSCHER, B. N. ERIKSON, and E. DONELSON (J. Nutrition, 1934, 7, 331—336).—The vitamin-A content of milks of three women receiving a well-balanced ration was not altered by supplements of 15 g. of cod-liver oil daily.

A. G. P.

Transmission of vitamin-A from parents to young in mammals. III. Effect of the fat content of diet during pregnancy on the transmission of vitamin-A to the foetal rat. W. J. DANN (Biochem. J., 1934, 28, 634—637).—Young rats have only a small store of vitamin-A (I) in their livers at birth, even when the parent doe had received large amounts of (I) before and during gestation. Transmission of (I) to the foetal rat increases with the fat content (II) of the diet, but for ordinary variations of (II) the increase is probably negligible.

A. E. O.

Fat-soluble vitamins. XXXIX. Influence of breed and diet of cows on carotene and vitamin-A content of butter. C. A. BAUMANN, H. STEENBOCK, W. M. BEESON, and I. W. RUPEL (J. Biol. Chem., 1934, 105, 167—176; cf. A., 1933, 986).—The carotene (I) and vitamin-A (II) contents of butter fats determined spectroscopically were 4.3 and 10.1×10^{-6} g. per g., respectively, for Holstein cows, and 7.8 and 5.1 for Guernseys on a winter ration. Higher vals. were obtained on pasture. Individual variations in one breed were $> 100\%$. Assuming that 0.6 g. of (II) is equiv. to 1 g. of (I), it is found that breed differences for total activity (III) are small, and that the (III) of July fat is $>$ that of June fat.

H. D.

(a) **Distribution of vitamin-A in the human organism.** (b) **Vitamin-A content of the human liver in relation to age.** R. DEBRÉ and A. BUSSON (Compt. rend. Soc. Biol., 1933, 114, 1162—1164, 1164—1166).—(a) Vitamin-A (I) was found in the liver (II) and in one case in the kidney of subjects dying by accident. Extracts of suprarenal and of pancreas were inactive. One subject in decline through

anaemia was treated with large quantities of carotene (III): after death (II) contained (I) corresponding with two "rat units" per 0.5 g. The (II) from another subject who had not received (III), after death, was devoid of (I). Thus in man, as in animals, the ingestion of (III) results in the storage of (I) in the (II).

(b) The (II) of only two out of nine infants showed the presence of (I); in sucklings that had been ill for more than 23 days none could be detected, but there was a little in those who had been ill < 15 days. In six children eating for themselves there was slightly more (I), and in the maternal (II) there was a much greater concn. The (I) reserve is evidently low at birth, and increases during the suckling period, but even when the maternal reserve is high the (I) content of the milk does not pass a prescribed limit. The reserve is considerably increased when the child starts to eat for itself.

NUTR. ABS. (b)

Factors affecting the assay of vitamin-A by the spectrographic method. R. J. MACWALTER (Biochem. J., 1934, 28, 472—475).—The curve of absorption at 3280 Å. (I) of a cod-liver oil (II) against time of aeration passes through a min., and then increases linearly with time. The intercept on the ordinate obtained by producing back the straight part of this curve may give a val. for the non-vitamin-A absorption (III). The (I) of the unsaponifiable fraction of (II) decreases with time of aeration, attaining a const. val. at 5 hr. assumed to be that due to (III). By plotting blue val. against (I) a straight line is obtained; no oil studied gives any marked deviation from this relationship.

H. D.

Chemical and physical determination of vitamin-A in liver oil. H. R. V. LINDHOLM (Dansk Tidsskr. Farm., 1934, 8, 73—100).—A comparison of determinations of vitamin-A in a no. of specimens of cod-liver oil biologically, colorimetrically, and spectrographically (using the colour reaction with SbCl_3). The acid val., I val., sap. val., and amount of unsaponifiable material (I) were also determined. The colour reaction was carried out both with the oil itself and with (I). The acid val. does not appear to modify the spectrographic results, but for very dark-coloured oils the colorimetric and spectroscopic determinations must be made on (I).

R. P. B.

Fat-soluble vitamins. XL. Growth method of determining vitamin-A. C. A. BAUMANN, B. M. REISING, and H. STEENBOCK (Z. Vitaminforsch., 1934, 3, 81—89).—With rats on basal diet with the addition (I) of graded doses of carotene (II) (3 — 70×10^{-6} g. weekly), a fourfold increase in (II) within the range 5 — 20×10^{-6} g. of (II) per week produces an increase in the rate of growth. With (I) of 10^{-3} g. per week, the average gain in wt. is 8 g. per week, whilst xerophthalmia (III) is practically absent. With 5×10^{-6} g. the gain in wt. is the same, but (III) frequently occurs. With $> 20 \times 10^{-6}$ g. no further increase in wt. occurs. Growth data are better calc. from the day on which the max. wt. during the depletion period is regained than from that on which (I) of (II) commences.

F. O. H.

Irradiation of a turbot vitamin-A concentrate with homogeneous ultra-violet light. E. BOYLE (Biochem. J., 1934, 28, 573—574).—Initially both *E* and the blue val. (I) of the concentrate decrease, then increase to a max. at 21 min., the absorption band (II) of the blue solutions shifting from 565 to 575 m μ . On further irradiation *E* and (I) decrease and (II) shifts to 570 m μ . H. G. R.

Experiments on rats as evidence of the toxicity of cod-liver oil to man? E. AGDUHR (Z. Vitaminforsch., 1934, 3, 99—102).—Ingestion of cod-liver oil (I) in therapeutic doses by children for periods of 2—24 months produces lesions of cardiac and other tissues. Hence the negative results obtained with rats (A., 1933, 987) do not justify the continuous use of (I) in man. F. O. H.

Third vitamin-D. O. RYGH (Nature, 1934, 133, 533; cf. this vol., 459).—Vitamin-D in extracts of hay, cow's liver, and butter has the same properties. L. S. T.

Irradiated sterols and ultra-violet rays. Physiological and therapeutic differences. P. DUHEM and E. HUAUT (Presse méd., 1933, 76, 1472—1474; Bull. Soc. Pédiat. Paris, 1933, 7, 310—315).—Results obtained on the same subjects by ingestion of irradiated sterols and by direct ultra-violet irradiation showed the neuro-vegetative action of the former to be negligible in comparison with the latter, whilst the antirachitic action of both was the same. The criteria used were observation of the oculo-cardiac reflex, and cardiac reaction to adrenaline and atropine. NUTR. ABS. (b)

Effect of daily massive doses of viosterol on calcium and phosphorus metabolism and blood-calcium and inorganic phosphorus in calves. C. W. DUNCAN and C. F. HUFFMAN (J. Dairy Sci., 1934, 17, 83—91).—Heavy dosage of viosterol (I) lowered the total excretion of Ca and P. Absorption of Ca and P from the intestine increased. Excretion of Ca in urine declined, but that in faeces increased. Feeding of (I) increased the inorg. PO_4''' of the blood-plasma to a greater extent than the Ca content. A. G. P.

Absorption of vitamin-D from the skin. F. J. AMRHEIN (J. Amer. Pharm. Assoc., 1934, 23, 182—190).—Vitamin-D, in vegetable or mineral oil solution, is absorbed through the skin of the rat's tail. A. E. O.

Evaluation of vitamin-D preparations. P. SCHOORL (Z. Vitaminforsch., 1934, 3, 97—99).—With pigs weaned when a wt. of < 25 kg. is attained and fed on a normal balanced diet (e.g., barley and maize grist, wheat bran, flesh-meal, and CaCO_3) until their wt. is approx. 95 kg., the rate of wt.-increase is not enhanced by addition to the diet of cod-liver oil or any other source of vitamin-A and -D. F. O. H.

Occurrence of vitamin-E in soya-bean oil. U. SUZUKI, W. NAKAHARA, and Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 23, 270—273).—Incorporation of a liberal amount of soya-bean oil to a synthetic diet deficient in vitamin-E (I) prevents the development of testicular degeneration characteristic of (I)-deficiency. A. E. O.

Vitamin-E in leguminous seeds. V. ZAGAMI (Atti R. Accad. Lincei, 1934, [vi], 19, 186—190).—Vitamin-E is present in seeds of *Cicer arietinum*, L., *Ervum lens*, L., and *Vicia faba*, L., and, to a smaller extent, of *Lathyrus sativus*, L. T. H. P.

Isolation of oryzanin (antineuritic vitamin) from yeast. S. OHDAKE (Proc. Imp. Acad. Tokyo, 1934, 10, 95—98).—Aeration of a suspension of fresh living yeast (I) in aq. vitamin- B_1 (II) yields (I) with a (II) activity approx. ten times the normal which, by a given method [extraction with dil. H_2SO_4 , adsorption on acid-clay, removal by aq. $\text{Ba}(\text{OH})_2$, successive fractionation with EtOH, AgNO_3 , phosphotungstic acid, etc.], affords cryst. oryzanin hydrochloride [0.7 g. from 142 kg. of wet (I)] identical with that from rice-polishings (A., 1931, 881; 1932, 973). F. O. H.

Formaldehyde-azo test for vitamin- B_1 . H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1934, 28, 667—670).—By suitable choice of alkalinity and use of CH_3O for stabilisation the Pauly reaction is rendered highly sp. for vitamin- B_1 . C. G. A.

Bradycardia in the vitamin- B_1 -deficient rat and its use in vitamin- B_1 determinations. T. W. BIRCH and L. J. HARRIS (Biochem. J., 1934, 28, 602—621).—The technique of determining vitamin- B_1 (I) by the heart-rate method is described. Results from the latter correspond with those given by curative tests on polyneuritic convulsions in rats, and by the growth-rate method. It is suggested that traces of (I) act by keeping the heart rate at a high enough level to enable the animal to survive and so permit the more slowly developing chronic symptoms to develop. The bradycardia is correlated with accumulation of lactic acid in the (I)-deficient animal. A. E. O.

Activation of lactic dehydrogenase and its relation to the role of vitamin- B_1 . T. W. BIRCH and P. J. G. MANN (Biochem. J., 1934, 28, 622—633).—Two factors are necessary for the activation of a cell-free lactic dehydrogenase from heart muscle (improved prep. described). Yeast contains considerable amounts of the complete co-enzyme (I) (fractionation described). The first factor (II) [probably identical with Szent-Györgyi's (I) (cf. A., 1933, 748)] can be obtained relatively free from the second factor (III) which is unstable except in presence of (II). Neither factor appears to be identical with co-enzyme. (III) may be concerned with the removal of AcCO_2H and shows some temporary curative effect on the bradycardia produced in vitamin- B_1 -deficient rats, although (I) contains no B_1 . Addition of methylene-blue is necessary before the system enzyme + lactate + (I) can take up O_2 . A. E. O.

Effect of washing and steaming on the vitamin- B_1 content of rices differently milled. A. G. VAN VEEN (Geneesk. Tijdschr. Ned.-Ind., 1933, 73, 945—957).—A biological test using rice birds (bondols), the Lugol colour reaction, and the chemical method of von Spruyt were used for determination of vitamin- B_1 (I); the results agreed fairly well. With unpolished rice, washing (II) and steaming (III) had no very significant effect, at least half the (I) content remaining intact. Quite short (II) had a great effect

on slightly polished rice (ground by hand), whilst a single (III) did not cause much change. Prolonged (II) removed almost all the (I), although cooking with H_2O caused very little destruction. The samples of highly polished rice used were not as poor in (I) as is generally assumed, but the (I) was easily removed by (II), although (III) was less effective.

NUTR. ABS. (b)

Determination of the beri-beri quotient Q_b : notes on technique. G. AMANTEA (Atti R. Accad. Lincei, 1933, [vi], 18, 399—402; cf. this vol., 460).—Detailed procedure for determining this quotient is given.

T. H. P.

Oat hulls as source of vitamin- B_1 and - B_2 . N. B. GUERRANT and R. A. DUTCHER (Poultry Sci., 1933, 12, 373—377).—Appreciable quantities are present.

CH. ABS.

Vitamin- B_1 and vitamin- B_2 contents of Bosc pears. Use of the Munsell method of assaying foods for vitamin- B_2 . R. DOUGLAS, M. HALLOWAY, J. C. WILLIAMS, and A. GARRISON (J. Nutrition, 1934, 7, 27—40).—Vitamin contents are determined. A technique for the evaluation of vitamin- B_2 is described.

A. G. P.

Flavins and flavoproteins as vitamin- B_2 . P. GYÖRGY, R. KUHN, and T. WAGNER-JAUREGG (Z. physiol. Chem., 1934, 223, 241—244).—Lactoflavin (I) and tetra-acetyl-lactoflavin have a strong vitamin- B_2 (II) action. Ovoflavin, which is less active, is probably a mixture containing some (I). In liver and in yeast a large proportion of the (II) is present as flavoprotein and is not dialysable until the complex has been broken down by boiling or (to some extent) by aq. $COMe_2$.

J. H. B.

Cataract in albino rats resulting from the withdrawal of vitamin- B_2 from the diet. P. L. DAY and W. C. LANGSTON (J. Nutrition, 1934, 7, 97—106).—In nearly all cases examined rats receiving a diet free from vitamin- B_2 (I) developed cataract (II). The appearance of the latter was delayed where small but insufficient amounts of (I) were given. The delayed appearance of (II) is correlated with growth-rate data. The occurrence of (II) is probably a better criterion of deficiency of (I) than is dermatitis.

A. G. P.

Behaviour of rats of different ages on a diet deficient in vitamin- B_2 . E. P. DANIEL and H. F. MUNSELL (J. Nutrition, 1934, 7, 117—130).—The divergence from the normal of the growth rate of rats following the administration of vitamin- B_2 -deficient diets varied with the age of the animals. Up to 6 months the intensity of the effect increased with age. Younger rats survived for rather longer periods. Differences in the response of the sexes to the diets were insignificant.

A. G. P.

Application of the Bourquin-Sherman diet to the determination of vitamin- B_2 and - B_4 . P. GYÖRGY, F. W. VAN KLAVEREN, R. KUHN, and T. WAGNER-JAUREGG (Z. physiol. Chem., 1934, 223, 236—240).—This diet lacks vitamin- B_2 and - B_4 . It may be used for determination of either vitamin if supplemented by a sufficiency of the other.

J. H. B.

Assay for vitamin-B complex in the presence of interfering substances. L. K. RIGGS, B. J. G. CHIEGO, W. L. SAMPSON, and A. BEATY (J. Amer. Pharm. Assoc., 1934, 23, 191—197).—The vitamin-B complex (I) is extracted from yeast extract etc. by glacial $AcOH$ (II). After removal of (II) in vac. below 70° in atm. of N_2 , the residue is mixed with starch for feeding experiments. In the assay of (I) each rat may be used as its own control by feeding an adequate daily dose of dried brewers' yeast (III) at the end of the test period. (III) is a stable and suitable standard of reference for (I).

A. E. O.

Pharmacodynamic action of beer-yeast and its influence on general metabolism in experimental B-avitaminosis. O. KAUFFMANN-COSLA and S. OERIU (Bull. Soc. Chim. biol., 1934, 16, 85—95).—B-Avitaminosis (I) in the pigeon causes increases in total N, total C, urea, uric acid, and NH_4 -acids of the blood which reach a max. coincident with the appearance of the first symptoms of paralysis (II) and polyneuritis (III). Administration of insulin has no effect on these vals., but with additions of yeast to the diet there is a return to normal vals. and (II) and (III) disappear. The symptoms of (I) and periodic (II) are similar, and both may be due to the toxic action of N compounds accumulating in the blood.

A. L.

Occurrence of endogenous vitamins in animal organisms. P. DI MATTEI (Arch. Sci. biol., 1933, 16, 531—562; Chem. Zentr., 1933, ii, 2847).—Extracts of the liver and kidneys, but not of the brain, muscles, or viscera, and the urine of chickens and rabbits fed on a diet free from vitamin-B and -C give reactions for these vitamins. Formation of endogenous vitamin is probable.

L. S. T.

Vitamin-C in the germinating seeds of peas. N. I. GRIAZNOV, E. N. ALIEXEEVA, L. F. GORINA, and Z. V. GORBUNOVA (Nutrition Problems, U.S.S.R., 1933, 2, No. 6, 74—79).—Germinated peas complete with roots protected guinea-pigs from scurvy in doses of fifteen to twenty peas daily raw, or forty peas daily cooked. About 100 peas was calc. as the daily dose for man.

NUTR. ABS. (b)

Vitamin-C in pine needles. N. I. GRIAZNOV and E. N. ALIEXEEVA-RUKINA (Nutrition Problems, U.S.S.R., 1933, 2, No. 5, 30—31).—An extract of pine needles, made by grinding the needles with an equal quantity of H_2O and straining through gauze, protected guinea-pigs from scurvy on Bezssonoff's diet in doses of 2 c.c. (orange juice 1.5 c.c.).

NUTR. ABS. (b)

Antiscorbutic properties of fir needles. N. SHEPILEVSKA (Nutrition Problems, U.S.S.R., 1933, 2, No. 5, 24—30).—A decoction of fir needles (1 part to 9 parts of H_2O) was antiscorbutically active for guinea-pigs in doses of 4—7 c.c. Large doses, up to eight times the min. prophylactic dose, had no harmful effects.

NUTR. ABS. (b)

Vitamin-C content of raw and pickled pumpkin. A. IVANOVA (Nutrition Problems, U.S.S.R., 1933, 2, No. 5, 31—34).—40 g. of raw or 60 g. of pickled pumpkins were required to protect a guinea-pig from scurvy on a diet of oats and autoclaved hay.

NUTR. ABS. (b)

Potatoes as source of antiscorbutic vitamin. B. JANOVSKA (Nutrition Problems, U.S.S.R., 1933, 2, No. 6, 69—72).—Min. protective doses for guinea-pigs were 20 g. of stored or 5 g. of fresh potato, cooked in steam. NUTR. ABS. (b)

Antiscorbutic potency of new and late potatoes grown in Czechoslovakia. H. PELC and M. PODZIMKOVA (Trav. Inst. Hyg. pub. Tchecoslov., 1933, 4, 119—138).—Tested on guinea-pigs, the freshly expressed juice of new potatoes ("Erstling" variety) was fairly rich in vitamin-C, 1 c.c. containing 1 international unit. The juice from a later variety ("Industrie kerkovska"), tested in the spring, contained only about 0.05 unit per c.c. When cooked late potatoes formed 50% of the diet, daily consumption of 30 g. furnished about 0.75 unit. Even the late varieties may thus be regarded as valuable prophylactics against scurvy. NUTR. ABS. (b)

Vitamin-C content of the medlar and winter cherry. E. CASERIO (Z. Vitaminforsch., 1934, 3, 93—97).—The medlar (*Mespilus germanica*) contains little vitamin-C, whilst the juice of ripe winter cherries (*Physalis alkekengi*) contains twice as much as normal lemon juice. F. O. H.

Relation of reducing value and extent of browning to the vitamin-C content of orange juice exposed to air. M. A. JOSYLN, G. L. MARSH, and A. F. MORGAN (J. Biol. Chem., 1934, 105, 17—28).—The loss of vitamin-C and browning of orange juice (I) run parallel to the reducing val. (II). (II) of navel (I) is > that of Valencia (I) and is probably due to a higher concn. of reducing substances other than ascorbic acid. Partly oxidised (I) has inferior keeping properties in cold storage. H. G. R.

Ascorbic acid in the eye-lens and aqueous humour of the ox. T. W. BIRCH and W. J. DANN (Biochem. J., 1934, 28, 638—641).—The presence of ascorbic acid has been confirmed by biological tests (cf. A., 1933, 541). A. E. O.

Structure of vitamin-C (ascorbic acid) and a theory of its formation. P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1933, 2, 167—190).—The formation of L-ascorbic acid in the plant is discussed and methods of synthesis are suggested. F. R. S.

Reversible enzymic oxidation of vitamin-C. S. S. ZILVA (Biochem. J., 1934, 28, 663—666).—Ascorbic acid is reversibly oxidised by a thermolabile enzyme (I), present in apples, without loss of activity. (I) is inactive anaerobically, is inhibited only by very high concn. of KCN, and is not a peroxidase. C. G. A.

Capability of tissue to fix ascorbic acid (in normal condition and in C-avitaminosis). L. DE CARO (Z. physiol. Chem., 1934, 223, 229—235).—After intravenous injection of ascorbic acid (I) into normal guinea-pigs, the (I), as measured by the reducing power, of the adrenals, ovary, liver, kidney, skeletal muscle, and blood increases, returning to the normal val. in 1 hr. In C-avitaminosis (II), the organs etc. show a diminished power of fixation of (I), in proportion to the extent of (II). J. H. B.

Experimental scurvy. XVII. Glycuronic acid formation in guinea-pigs fed on a vitamin-C-free diet. XVIII. Carbohydrate tolerance and blood-sugar changes due to insulin and adrenaline in guinea-pigs fed on a vitamin-C-free diet. J. SHIMADA (J. Biochem. Japan, 1934, 19, 253—256, 257—279).—XVII. The theory of Rygh and Rygh (A., 1932, 1294) that the scorbutic guinea-pig (I) is unable to synthesise glycuronic acid is refuted.

XVIII. The carbohydrate tolerance and the changes in the blood-sugar due to adrenaline or insulin in (I) do not differ from those of normal animals.

F. O. H.

Capillary resistance test as a measure of vitamin-C nutrition. R. E. STOCKING (Arch. Pediatr., 1933, 50, 823—831).—In spring, when the supply of foods rich in vitamin-C is less plentiful, slightly reduced capillary resistance is observed.

CH. ABS.

Amide-nitrogen in germinating seeds. A. G. MCCALLA (Canad. J. Res., 1934, 10, 430—434).—During the germination of wheat, barley, rye, and maize there is a marked elimination of amide-N from the protein. No accumulation of amide-N occurs in the non-protein fraction of seeds or seedlings. These changes do not occur in germinating peas.

A. G. P.

Transport of nitrogenous substances in the cotton plant. VI. Storage in bark. T. G. MASON and E. PHILLIS (Ann. Bot., 1934, 48, 315—333; cf. A., 1930, 1323).—Restriction of supplies of N to the plant limits the growth of young tissue and apical organs and causes a movement of N from mature leaves upwards to young leaves and stems, and also to the bark and wood of older sections of stem which increase in N concn. During flowering and boll formation N is withdrawn from vegetative tissue. Loss of N from bark is more marked in the lower than in upper sections. A reversal of the N gradient results. No withdrawal of Ca from vegetative parts occurs during bolling. Normally Ca does not move in the phloem. Storage of N in bark is probably unaffected by the supply to the roots.

A. G. P.

Growth and differentiation. V. Histological and metabolic changes during wound-healing in *Kleinia articulata*, Haw. N. WOODHEAD (Ann. Bot., 1934, 48, 467—480).—Cells exposed by injury become impregnated with fatty material which completely covers the injured surface. A phellogen occurs close to the fatty deposit and formation of cork initials and phelloderm commences. Partial "collenchymatization" of the phelloderm layer is coincident with the deposition of CaC_2O_4 crystals. In tissue immediately beneath the injured area, initial wounding causes rapid removal of Ca and P and some temporary withdrawal of K. No $\text{PO}_4^{'''}$ or Ca occurs in the phellogen. A. G. P.

Reaction of protoplasm. T. SPEK and R. CHAMBERS (Protoplasma, 1933, 20, 376—406).—Determinations of p_H are made by injection of indicators. The effects of solutions of a no. of acids and salts on reaction changes are recorded and their significance is discussed. A. G. P.

Do relationships exist between carbohydrate formation and nodulation in legumes. A. RIPPEL and W. KRAUSE (Arch. Mikrobiol., 1934, 1, 14—23).—Exposure to light of pea plants previously kept in darkness results in a considerable accumulation of carbohydrates which is more pronounced in plants with roots than in those from which roots were removed. Of the dry matter of the nodules approx. $\frac{1}{3}$ consists of N-free material, hydrolysable with difficulty yielding some reducing sugars.

A. G. P.

Physico-chemical conditions of formation of amylogenic vacuoles in the plastids. A. MAIGE (Compt. rend., 1934, 198, 1537—1539).—The role of sugar concn. in, and H_2O -imbibition by, plastids in starch formation is discussed.

A. G. P.

Modification by temperature of the lipid concretions (Mirande's sterinoplasts) in the bulb of *Lilium candidum*. R. REILHES (Compt. rend., 1934, 198, 1629—1631).—Transformation of these concretions into fatty acids (I) is greatly accelerated by heat. The equilibrium between (I) and carbohydrates (II) thus gives mainly (I) at high and (II) at low temp.

R. S. C.

Methylene-blue and gassed plants. C. G. DEUBER (Science, 1934, 79, 389—390).—Methylene-blue supplied to the roots assists in the recovery of tomato plants which have been exposed to illuminating gas and to C_2H_4 .

L. S. T.

Changes produced in living plant cells by chemical agencies. I. Ultramicroscopic study of cells of *Allium sativum*. M. N. MEISEL (Bull. Acad. Sci. U.R.S.S., 1933, 7, 983—994).—The nuclei (I) of normal cells are faintly opalescent when viewed in dark-field illumination. With increasing concn. of $EtOH$ or $CHCl_3$ the opalescence (II) becomes more intense, and the structure of (I) becomes granular; during the first stages of narcosis ultramicroscopic granules are extruded into the cytoplasm. The (II) of the (I) of dead cells is $>$ that of living ones, and their structure is more granular. The (II) of cells is greatly reduced by KCN or H_3AsO_3 , and is augmented by plasmolytic agents. Within limits, the vital activity of the cells varies parallel with the intensity of (II) of the (I).

R. T.

Effect of light on the respiration of starved leaves. P. PARIJA and A. B. SARAN (Ann. Bot., 1934, 48, 347—354).—Short exposure to light of plants starved in darkness increases respiratory rates. The action of blue and violet is similar to that of white light but red light is ineffective. The effect increases with the prolongation of starvation for a definite period, then becomes approx. const., and finally declines. The increased sugar content of leaves following short exposure (7.5 mins.) is not due to photosynthesis but may result from hydrolysis of reserve carbohydrate, activation of enzymes or altered cell permeability.

A. G. P.

Effect of X-rays on growth substance and plant growth. F. SKOOG (Science, 1934, 79, 256).—The primary action of X-rays on the growth of plants is through inactivation of growth substance probably by oxidation.

L. S. T.

Absorption and accumulation of solutes by living plant cells. VI. Absorption of potassium bromide from dilute solution by tissue from various plant storage organs. W. E. BERRY and F. C. STEWARD (Ann. Bot., 1934, 48, 395—410).—No simple relationship exists between the total respiration and the absorption of KBr from 0.00075M solutions by discs of cut tissue. Only those tissues containing cells capable of renewed growth are able to accumulate KBr .

A. G. P.

Absorption of manganese by plants. C. OLSEN (Biochem. Z., 1934, 269, 329—348).—Plants grown in alkaline soil contain only a few mg. of Mn, but in acid soil > 200 mg. Mn per 100 g. dry leaf substance, the Mn content in the latter case being $>$ that of Fe. Plants grown in H_2O culture at varying pH but the same content of $MnSO_4 \cdot 4H_2O$ (I) absorb most Mn at pH 6—7. With increasing concn. of (I), more (I) is absorbed, but at a concn. of 2.5 mg. (I) per litre, toxic action and inhibition of growth are observed with *Lemna polyrrhiza*. Plants growing in marshes usually contain large amounts of Mn.

P. W. C.

Histochemical detection of iron and zinc in *Citrus* leaves. H. S. REED and J. DUFRENOY (Compt. rend., 1934, 198, 1535—1537).—In leaf sections after micro-incineration (in a manner to retain as far as possible the histological formation) the presence of Fe is established (Prussian-blue) in the plastids of both "mottled" (I) and normal leaves (II). In (II) Zn is detected by the nitroprusside test, at the periphery of palisade cells, especially in those bordering vacuoles containing CaC_2O_4 crystals. Zn was absent from (I) leaves.

A. G. P.

Effect of mineral salts on growth and metabolism of plants. II. Osmotic pressure of the press-juice of tobacco leaves in relationship to the mineral salt nutrition. K. BÖNING and E. BÖNING-SEUBERT (Biochem. Z., 1934, 270, 122—156; cf. A., 1932, 785).—The osmotic pressure (I) of the press-juice of the leaves of tobacco plants varies according to the amount and nature of the mineral salts absorbed; the anions (II) form the series $PO_4''' < SO_4'' < NO_3' < Cl'$ and the cations (III) $Ca^{++} < K^+$. The effect of Na^+ is $<$ that of K^+ , probably only because less is absorbed; Mg^{++} and NH_4^+ also affect (I). The simultaneous action of (II) and (III) causes ionic antagonism: excess of (II) reduces absorption of (III), and conversely. The degree of activity of (II) and (III) varies according to position in the lyotrope series.

W. McC.

Hydration film of cellulose in cell walls. N. H. KOLLSMEIJER and A. N. J. HEYN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 92—93).—X-Ray observations indicate that the hydration film shows the structure of ice.

E. S. H.

Pharmacological diagnosis of *Sarothamnus scoparius*, Koch, and similar drugs. R. JARETZKY and B. AXER (Arch. Pharm., 1934, 272, 152—167).—Sparteine (I) is best detected by extraction with dil. H_2SO_4 , steam-distillation (until distillate gives no KI_3 reaction) after making alkaline, and (a) testing with osmic acid, (b) pptn. with H_2CrO_4 , K Cd bromide, and HI, or, (c) by Jorissen's method

(A., 1911, ii, 1144). Contrary to the lit. (I) is destroyed by KMnO_4 oxidation, and it is best determined by isolation as above, and pptn. with silicotungstic acid as $\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{C}_{15}\text{H}_{23}\text{N}_2 + \text{H}_2\text{O}$. The presence of (I) in 23 species (amounts tabulated) of *Lupinus*, *Genista*, *Cystisus*, and *Sarothamus* is proved. The amount of (I) in the twigs of *S. scoparius* increases from 2.33% in March to 3.0% in May, decreases to 1.25% in June, and then increases gradually to 2.84% in Nov., and then remains const. until Feb. Similar variations occur in the leaves, but not in the buds (0.33–0.35%) or pods (0.37–0.40%). The muscle test (Fühner) for cytisine (II) is valid only in absence of (I). (II) is present in *Genista monosperma*, but not in *S. scoparius*. J. W. B.

[Constituents] of the roots of *Arctopus echinatus*. T. M. MELJER (Rec. trav. chim., 1934, 53, 443–450).—The rhizomes of this plant yield to low-boiling ligroin *arctopusol* (I), $\text{C}_{20}\text{H}_{30}\text{O}_2$, m.p. 171–172.5°, $[\alpha]_D^{20}$ –82.2° in EtOH [*Na* salt; *Me ether* (II), m.p. 98–99°], and then to EtOH sucrose and a hemolytic substance, m.p. 240°, probably a saponin. (I) is a mono-unsaturated (AcO_2H), phenolic diterpene, substituted by I, giving the Salkowsky reaction and a violet colour with $\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$. It is slowly hydrogenated (Pd-black) in AcOH at 61° to a dihydro-derivative, m.p. 204–206°. It gives indefinite products with HBr , Pd-black at a high temp., and oxidising agents. The nature of the second O is unknown. (II) with HI gives a substance, m.p. 216–224.5°. R. S. C.

Detection of hesperidin-like compounds and flavones in plants. R. WASICKY, G. ROTTER, and A. THUMER (Arch. Pharm., 1934, 272, 290–296).—The behaviour of hesperidin-like glucosides (I) and other flavone derivatives in filtered ultra-violet light in the luminescence microscope is discussed as a means of locating (I) in various plant organs. J. W. B.

Orthosiphon stamineus, Benth. O. KELLER [with W. BIEDERMANN] (Arch. Pharm., 1934, 272, 242–256).—The ash (25.49% of H_2O extract) of the drug contains CaO 1.118%, Na_2O 0.1379%, K_2O 3.569%, Fe , Mn , Al , Mg , SO_4 , Cl , PO_4 , NO_3 , and SiO_2 . The following are present: tartaric and citric acids; small amounts of glucosides isolated only as an amorphous hygroscopic powder from the EtOH-extract; saponin, detected but not isolated; hexoses, probably *D*-glucose and *D*-fructose; pentoses (but not methylpentoses); *D*-glycuronic acid; small amounts of essential oils having a $\cdot\text{CHO}$ reaction; fatty oils (1.6%), acid val. 34.51, sap. val. 93.64, I val. 78.48, the unsaponifiable portion (37%) of which yields a phytosterol, m.p. 139° (*Ac* derivative, m.p. 124°; digitonide, m.p. 226°), proved by regeneration from the acetate dibromide to be a single sterol. Alkaloids are absent. The H_2O -extract contains the most active constituents, viz., the alkali salts and the glucosides. J. W. B.

Materials in the bark of *Lophopetalum toxicum*. II. H. DIETERLE, H. LEONHARDT, and K. DORNER (Arch. Pharm., 1934, 272, 172–190).—Physiological activity of the drug (I) is conc. in the crude glucosides (II) (1.5%), isolated from the 90%

EtOH extract after separation of the phytosterol, and from which dulcitol is separated. From the MeOH-sol. portion of (II) are isolated *lophopetalid*, $\text{C}_{59}\text{H}_{78}\text{O}_{25}$ (0.03%), m.p. 195–197° (decomp.) (min. dose 0.03 mg. per g. of frog), which gives only amorphous products by HCl hydrolysis. The H_2O -sol. glucosides, containing hexoses (purified by yeast fermentation), after hydrolysis with 5% HCl give fractions (a) b.p. 58–69°/13 mm., $\text{C}_8\text{H}_{12}\text{O}_2$, and (b) b.p. 60–62°/13 mm., $\text{C}_8\text{H}_{14}\text{O}_2$, probably aglucones, and a residual resin. 0.8% of tannin is also present, and Et₂O extracts from (I) physiologically inactive bases (0.25%) from which a cryst. substance, m.p. 166°, is isolated. J. W. B.

Formation of sucrose [in plants]. J. BURKARD and C. NEUBERG (Biochem. Z., 1934, 270, 229–234).—Although beet with high sugar content contains only traces of org. P the leaves of the sugar beet (and of related species) contain glucose and fructose monophosphate (0.025 g. per kg. of fresh leaves). W. McC.

Glucoside of *Coronilla* seeds. G. TANRET (Compt. rend., 1934, 198, 1637–1639).—*C. scorpioides* (I) and *varia* (II) contain stachyose and sucrose [3 : 7 from (II), < 3 : 7 from (I)], and coronillin (III), $\text{C}_{22}\text{H}_{33}\text{O}_{10}$, amorphous, $[\alpha]_D$ –17.6° [0.7–0.8% from (I), 0.08% from (II)]. (III) with dil. H_2SO_4 gives glucose and an amorphous aglucone, $\text{C}_{17}\text{H}_{23}\text{O}_6$. (III) is unaffected by emulsin or yeast, but is hydrolysed by *A. niger* or snail's digestive juices. With the latter it gives a cryst. compound, $\text{C}_{14}\text{H}_{18}\text{O}_3$, m.p. 243°, $[\alpha]_D$ +38°, and amorphous products. The purity of the amorphous substances is doubtful. (III) is very toxic, and has a moderate cardiac and low diuretic action. R. S. C.

Nucleic acid of rye-ergot. M. GATTY-KOSTYAL and J. TESARZ (Bull. Acad. Polonaise, 1933, B, 1–12).—Various Polish ergots contained H_2O 6.45–7.06, total P_2O_5 1.399–1.597 (of dry material), lecithin- P_2O_5 0.096–0.118, total sol. (in 1% aq. HCl) P_2O_5 1.01–1.14, nuclein- P_2O_5 0.29–0.32%. Nucleic acid (1.5 g.), N 15.21, P 8.73%, was isolated from ergot (1200 g.). F. O. H.

Nitrogenous compounds of the white gourd melon and the musk melon. K. YOSHIMURA and T. IWATA (J. Agric. Chem. Soc. Japan, 1933, 9, 1235–1238).—White gourd melon contains H_2O 97.10, crude protein 0.57, protein 0.193, crude fat 0.086, crude fibre 0.513, crude ash 0.375, total N 0.092, protein-N 0.031, NH_3 -N 0.002, N pptd. by phosphotungstic acid 0.020, N not so pptd. 0.039%. Adenine and trigonelline were isolated. CH. ABS.

Isolation of the active principles of *Urginea burkei*, Bkr. F. STEPHEN (Quart. J. Pharm., 1934, 7, 57–62).—Extraction of the dry bulbs with 70% aq. EtOH yields a H_2O -sol., N-free, resinous substance 0.4 mg. of which is lethal for frogs. A similar substance is yielded by extraction with 90% EtOH, the resin on treatment with MeOH giving a cryst. substance, m.p. 300–317°, lethal to frogs in doses of 0.1 mg. Two toxic glucosides, differing in their solubilities in aq. EtOH and colour reactions with H_2SO_4 - Ac_2O , appear to exist. F. O. H.

Occurrence and distribution of saponin in plant drugs. II. Leaves, fruits, bark, wood, roots, and rhizomes. L. KOFLER and G. STEIDL (Arch. Pharm., 1934, 272, 300—312).—Four species out of 52 leaves, 0 out of 44 fruits, 5 out of 30 barks, 1 out of 10 woods, and 13 out of 71 roots and rhizomes examined contained saponin. J. W. B.

Coffee-bean. II. Composition of glycerides of coffee-bean oil. R. O. BENGIS and R. J. ANDERSON (J. Biol. Chem., 1934, 105, 139—151; cf. A., 1932, 975).—The light petroleum extracts of green, freshly roasted, and aged beans (I) on hydrolysis gave linoleic, oleic, and palmitic acids with small amounts of stearic and tetracosic acids. Glycerol was the chief H_2O -sol. constituent of the $COMe_2$ -sol. fat. The rancid odour of (I) is probably due to volatile fatty acids. H. D.

Chemical composition of some plants used by Australian aborigines as food. I. W. DADSWELL (Austral. J. Exp. Biol., 1934, 12, 13—18).—The org. composition of the vegetable foods eaten by the natives of Central Australia does not greatly differ from that of corresponding cultivated foods. Their P content is inadequate, but other inorg. constituents are plentifully supplied. A. E. O.

Physiology of sandal (*Santalum album*, Linn.). I. Nature and extent of parasitism. II. Influence of host on nitrogen metabolism. Y. V. S. RAO (J. Indian Inst. Sci., 1933, 16A, 167—177, 178—184).—I. Sandal derives its N, P, and K from the host (I) and its Ca, Fe, and Al from the soil. The tissue fluids (II) have higher osmotic pressure and lower p_H than the corresponding (II) of (I). The chemical composition of (II) depends on the nature of (I).

II. Host-fed sandal (III) has higher protein and lower H_2O -sol. and basic N than the hostless plant (IV). (IV) resembles spike-diseased sandal (V) in having high H_2O -sol. N and low protein-N but differs in that the NH_3 content is $>$, and the amide-N content $<$, that of (III), the vals. being approx. the same for (III) and (V). C. G. A.

Iodine content of Black Sea algæ. A. S. KOMAROVSKI, A. F. TJULPINA, and G. B. FISCHER (Ukrain. Chem. J., 1933, 8, 151—154).—The I content per 100 g. of dry substance of Black Sea *Phyllophora* varied from 0.15 to 0.52 g.; other algæ contained only traces of I. R. T.

Pigment of *Cucurbita maxima* Duch. (giant pumpkin). L. ZECHMEISTER and P. TUZSON (Ber., 1934, 67, [B], 824—828).—Chromatographic analysis of the polyene hydrocarbons of *Cucurbita maxima*, Duch, using $Ca(OH)_2$, establishes the presence of much β - and little α -carotene. The polyene alcohols consist of lutein and violaxanthin. The terms "cucurbitene" and "cucurbita-xanthin" introduced by Sugimoto *et al.* (A., 1931, 1200) are unnecessary. H. W.

Formation of aromatic substances and terpenes in plants. T. WEEVERS (Proc. K. Akad. Wetens. Amsterdam, 1934, 37, 183—188).—Theoretical. It is suggested that gum-formation and secretion of terpenes etc. are analogous. The former

results from the side-tracking of pectin and cellulose formation, and the latter is an alternative to the formation of lignin in older cells. R. K. C.

Development of hydrogen cyanide in cholam (*Sorghum vulgare*). C. N. ACHARYA (Indian J. Agric. Sci., 1934, 3, 851—869).—The HCN developing in plant tissue is best determined by permitting the auto-enzymic decomp. of cyanogenetic substances in H_2O extracts of macerated material (48 hr.) with subsequent distillation and determination of HCN by customary methods. Addition of $CHCl_3$ or PhMe to extracts, as a preservative, does not check the action of the enzyme. The HCN content of cholam in the early stages of growth is high and declines steadily to a min. at the flowering stage. High vals. occur in droughted plants and secondary growths. Leaves contain more HCN than stems or roots. The total HCN and the % in dry matter are low in early morning, rising to a max. at approx. 2 p.m. and declining rapidly after 6 p.m. Seedlings grown in darkness have as much HCN as those grown in light. Drying cut plants in the sun reduces their HCN content by 30—40%, and in the shade by 10%. Heating at 100° for several hr. or brief immersion in 10% aq. H_2SO_4 destroys the cyanophoric substance, and only traces of HCN remained in plants after ensilage for 2 months. Poisonous plants are detected by means of the starch accumulation in the stems (I test). The presence in cholam of CN-substances in forms other than glucosides is indicated. A. G. P.

Purification of plant viruses. D. MACCLEMENT (Nature, 1934, 133, 760).—Details of a modification of the Warburg-Christian method (A., 1932, 1285) of purifying a H_2O -sol. enzyme are described for preparing a purified suspension of any of the "x" group of plant viruses from the extracted juice of the diseased plant. L. S. T.

Tobacco plant. IV. Effect of the curing process on the organic acids of tobacco leaves. H. B. VICKERY and G. W. PUTCHER (Connecticut Agric. Exp. Sta. Bull., 1933, No. 352, 649—685).—In the customary methods of extraction of acids from leaves for analysis much $H_2C_2O_4$ may be lost, since the acid is moderately volatile in H_2O or EtOH vapour. A method is described for the determination of $H_2C_2O_4$, which is extracted from acidified leaf tissue with Et_2O and collected as CaC_2O_4 . 85—90% of the titratable acid of H_2O -extracts appears in the Ba salts fraction, which also includes N as dicarboxylic NH_2 -acids and other unknown forms, reducing substances (some fermentable carbohydrate) and a considerable portion of unknown non-N material. During curing of leaves there is a reduction in malic acid and a large increase in citric acid content. The proportion of $H_2C_2O_4$ changes little. The total acidity, monobasic acids and acids precipitable as Ba salts by 60% EtOH remained approx. const. but the proportion of unknown acids decreased considerably; they were replaced by citric acid. Both malic and citric acids remain in the residue from the distillation of esters even at temp. $>$ b.p. of Et_3 citrate and also in the "unesterifiable" fraction. Small amounts of fumaric, succinic, and probably maleic acids occur in the leaves. A. G. P.

BRITISH CHEMICAL ABSTRACTS

A—PURE CHEMISTRY

JULY, 1934.

General, Physical, and Inorganic Chemistry

Width of spectral lines in gases. V. WEISSKOPF (Uspekhi. Fiz. Nauk., 1933, 13, 552—592).—Widths of the Hg line 2537 Å. and the Na D lines in H₂, He, A, Ne, N₂, O₂, CO₂, and CO have been measured. CH. ABS.

Fine structure of the triplets $(2s^2)(2p)3s^3\phi \rightarrow (2s^2)(2p^3)^3\phi$ of the carbon atom. V. M. TSOHULANOVSKI and M. P. MOCHNATKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 18—20).—The structure of the triplets in the neighbourhood of 1656 Å. has been investigated. A. J. M.

Spectral intensities by comparison with total radiation. T. N. PANAY (J. Phys. Radium, 1934, [vii], 5, 171—178).—For the comparative measurement of spectral intensities a black body formed by an electrically heated C tube in A is described. Black bodies of const. temp. have been prepared by the spherical end of a quartz tube in boiling Zn surrounded by N₂, and by C in boiling Pb surrounded by A. N. M. B.

Intensity distributions in molecular spectra: N₂ second positive system. N. R. TAWDE (Proc. Physical Soc., 1934, 46, 324—332).—Intensities of bands in the C³Π → B³Π system of N₂ under four different conditions of excitation were measured by means of calibrated photographs. N. M. B.

Effective rotation temperature of the negative glow in nitrogen. N. THOMPSON (Proc. Physical Soc., 1934, 46, 436—443).—The effective rotation temp. was determined from the intensity distribution in the (0,0) band of the N₂ negative system under varying conditions of excitation, using specially designed discharge tubes. The effective temp. increases slightly with pressure and current strength and to a much greater extent with the temp. of the furnace surrounding the tube; ultimately it becomes < the temp. of the furnace. This anomaly is not explained. N. M. B.

Intensity measurements in the first positive bands of nitrogen. A. ELLIOTT and W. H. B. CAMERON (Nature, 1934, 133, 723). L. S. T.

Hyperfine structure of fluorine. F. W. BROWN BARTLETT, jun. (Physical Rev., 1934, [ii], 5, 527—537).—Mathematical. Application of the theory of Breit (cf. A., 1931, 275) gives multiplet structures in good agreement with experiment. N. M. B.

Presence of forbidden lines of Ne v in nebular spectra. SWINGS and B. EDLÉN (Compt. rend., 1934, 198, 1748—1750).—The nebular lines (I),

λλ 3346 and 3426, are attributed to the forbidden transitions $^3P_2 \rightarrow ^1D_2$ and $^3P_1 \rightarrow ^1D_2$ of Ne v, in agreement with calc. λλ and intensities. (I) are emitted from the central regions of nebulae. B. W. B.

Optical constants of alkali metals. J. HURGIN and N. PISARENKO (Nature, 1934, 133, 690). L. S. T.

Mechanism of glow discharge in the positive column of argon. O. GROOS (Z. Physik, 1934, 88, 741—756).—Measurements are given of the longitudinal field, density of carriers, wall current, and electron temp. to a pressure of 10⁻⁴ tor, and an explanation is given of the dependence of gradients on mean free path. A. B. D. C.

Hyperfine structure of the green krypton line 5570 Å. M. ROMANOVA and A. FERCHMIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 546—548).—At liquid air temp. the hyperfine structure of the 5570 Å. Kr line shows eleven components, the separations of which are in agreement with the term scheme suggested by Kopfermann and Wieth-Knudsen (A., 1933, 1095). J. W. S.

Pressure broadening and displacement of the fourth term of the caesium principal series. F. GÖSSLER and H. E. KUNDT (Z. Physik, 1934, 89, 63—67).—Lack of symmetry, half-width val., and displacement due to presence of He, Ne, A, and N₂ were observed for the 3612 Å. Cs line. A. B. D. C.

Self-energy of the electron. V. WEISSKOPF (Z. Physik, 1934, 89, 27—39).—Theoretical. A. B. D. C.

Action of a stream of slow electrons on the plasma of the mercury arc. S. GVOZDOVER and F. KONOVALOV (Compt. rend., Acad. Sci. U.R.S.S., 1934, 1, 553—557). J. W. S.

Anomalous intensity increase of the 5461 Å. mercury line in the N₂ + O₂ discharge. N. PRILESHAJEWA (Z. Physik, 1934, 89, 24—26).—A phenomenon similar to that observed by Günther-Schulze and Betz (A., 1933, 992) is recorded. A. B. D. C.

Temperature radiation in spark discharges? W. FINKELNBURG (Z. Physik, 1934, 88, 763—767).—The continuous spark spectrum is not temp. radiation (cf. Rathenau, this vol., 129). A. B. D. C.

Continuous electron radiation in spark discharges. W. FINKELNBURG (Z. Physik, 1934, 88, 768—778).—All spark discharges in liquids and gases

show similar continuous spectra due to continuous electron radiation. A. B. D. C.

Spectral intensity distribution of night sky and Northern lights. L. VEGARD and E. TONSBERG (*Z. Physik*, 1934, **88**, 709—726).—A comparison of the intensity of the various lines of the two spectra is given, and night sky light is shown to be due to active N_2 and to O_2 activated by the N_2 . A. B. D. C.

Spectroscopy of ultra-soft X-rays. III. M. SIEGBAHN and T. MAGNUSSON (*Z. Physik*, 1934, **88**, 559—592; cf. this vol., 232).— M and N series are given for wave-lengths between 20 and 500 Å. A. B. D. C.

Transitions to optical levels in the argon L X-ray absorption spectrum. J. A. PRINS (*Nature*, 1934, **133**, 795—796). L. S. T.

Faint lines in the L spectrum of the elements 73 Ta to 83 Bi. II. S. KAUFMAN (*Physical Rev.*, 1934, [ii], **45**, 613—616; cf. this vol., 577).—Data for additional faint diagram and non-diagram lines in the $L\gamma$ region of the X-ray spectra, for three new non-diagram (satellite) lines associated with $L\gamma_1$ and $L\gamma_2$, for the close pair Pb $L\beta_1$ and Pb $L\beta_2$, and for the strong lines of Os in the $L\beta$ and $L\gamma$ regions are given. N. M. B.

Extension of the dynamic theory of X-ray interference. L. POSENER (*Ann. Physik*, 1934, [v], **19**, 849—877).—Mathematical. A. J. M.

Inner potential of crystals. S. KIKUCHI and S. NAKAGAWA (*Z. Physik*, 1934, **88**, 757—762).—Lower-order reflexions of cathode rays give lower vals. of inner potential than the higher orders, possibly due to lack of definition of inner potential at grazing incidence. A. B. D. C.

Discharge rays. A. DAUVILLIER (*J. Phys. Radium*, 1934, [vii], **5**, 184).—Explanations of Reiboul's "discharge rays" (cf. A., 1933, 442) are discussed. N. M. B.

Gamma-ray ionisation in several gases as a function of pressure and collecting field. E. F. COX (*Physical Rev.*, 1934, [ii], **45**, 503—506).—Data for ionisation by low-intensity γ -radiation in N_2 , CO_2 , A, and He over a wide range of pressures and collecting fields discredit Broxon's wall emission theory (cf. A., 1932, 3) and favour a recombination theory. N. M. B.

Photo-electric effect for high energy quanta. H. HALL (*Physical Rev.*, 1934, [ii], **45**, 620—627; cf. A., 1931, 1105).—Mathematical. The cross-section for photo-electric absorption of a Dirac electron in the field of a nucleus is calc. for the case of quantum energies $h\nu >$ the proper energy mc^2 of the electron. N. M. B.

Thoriated tungsten filaments. I. LANGMUIR (*J. Franklin Inst.*, 1934, **217**, 543—569).—From new relations between v_e , the rate of evaporation of electrons from a thoriated W filament, and θ , the fraction of the surface covered by Th atoms, a recalculation of available experimental data gives results for v_a , the atom evaporation rate, as a function of θ and temp. T in good agreement with the vals. of v_a calc. from v_e . The diffusion coeffs. of Th through W crystals, along grain boundaries, and over the free filament surface,

are calc. A theory of the variation of the surface diffusion coeff. with the no. of Th atoms per sq. cm. is given. The probable mechanism of the production of Th within the filament is discussed (cf. Brattain, A., 1933, 441). N. M. B.

Thermionic cathodes. C. G. FOUND (*Physical Rev.*, 1934, [ii], **45**, 519—526).—From the relation between the electron current from a thermionic cathode and the positive ion current two new methods of determining the thermionic emission of a cathode in a gaseous discharge are described. Zero field emission of an oxide-coated cathode is only about 10% of the normal operating current. Emission increases linearly with field up to 150 volts per cm. Total ionising power increases linearly with the accelerating potential of the electron for voltages up to two or three times the resonance potential. N. M. B.

Apparent thermionic constant A of clean metals. A. L. REIMANN (*Nature*, 1934, **133**, 833). L. S. T.

Magnetic refocussing of electron paths. W. E. STEPHENS (*Physical Rev.*, 1934, [ii], **45**, 513—518).—A general method of refocussing slightly divergent electron paths in a uniform magnetic field is described. N. M. B.

Electron spin. J. SOLOMON (*J. Phys. Radium*, 1934, [vii], **5**, 167—170).—The possibility of obtaining experimentally a beam of electrons completely polarised, or with parallel spin, is discussed. N. M. B.

Resonance conditions and acceleration of electrons according to Bloch's theory of electrical conductivity. E. KRETSCHMANN (*Z. Physik*, 1934, **88**, 792—799).—Polemical, against Peierls (cf. this vol., 721). A. B. D. C.

Small-angle scattering of electrons in helium. F. C. POULTNEY and R. WHIDDINGTON (*Nature*, 1934, **133**, 685). L. S. T.

Paramagnetism of electron gas. H. OSTERMANN (*Z. Physik*, 1934, **89**, 68—82).—A paramagnetic electron gas should give a charge current. A. B. D. C.

Polarisation of electrons. G. P. THOMSON (*Phil. Mag.*, 1934, [vii], **17**, 1058—1071; cf. this vol., 126).—Polarisation experiments in which electrons are scattered at right angles and then diffracted by a thin film, and in the second case are scattered twice at right angles, show no asymmetry. Voltages were 153 in the first case, and 30 and 103 kv. in the second case, the last two being contrary to Dirac's theory of the electron. N. M. B.

Statistics of positrons and electrons in equilibrium with radiation at high temperatures. G. WATAGHIN (*Phil. Mag.*, 1934, [vii], **17**, 910—913).—Mathematical. N. M. B.

Radiation originating in collisions of fast electrons. C. F. VON WEIZSACKER (*Z. Physik*, 1934, **88**, 612—625).—Two cases, that of ordinary scattering, and that of transformation of a very high energy photon into a negative and positive electron, are treated theoretically. A. B. D. C.

Multiple acceleration of ions to very high speeds. E. O. LAWRENCE and M. S. LIVINGSTON

(Physical Rev., 1934, [ii], 45, 608—612).—An enlarged form of an apparatus previously described (cf. A., 1932, 554) is capable of generating H ions with energies up to 5×10^6 volt electrons, for use in nuclear research. At 3×10^6 volts ion currents of 0.3 microamp. are obtained.

N. M. B.

Deuteron and disintegration. H. J. WALKE (Phil. Mag., 1934, [vii], 17, 1023—1024; cf. this vol., 471).—An alternative explanation of the new type of positron emission (cf. Curie, this vol., 234) is discussed.

N. M. B.

Fourth Report of the Committee of Atomic Weights of the International Union of Chemistry. G. P. BAXTER, (MME.) P. CURIE, O. HÖNIGSCHMID, P. LEBEAU, and R. J. MEYER (J.C.S., 1934, 499—512, J. Amer. Chem. Soc., 1934, 56, 753—764, and Ber., 1934, 67, [4], 47—67).—The following alterations are recommended: K=39.096; As=74.91; Se=78.96; In=114.76; Te=126.61; Cs=132.91; Yt=173.04; Os=191.5.

H. W.

Revision of the at. wt. of caesium. G. P. BAXTER and J. S. THOMAS (J. Amer. Chem. Soc., 1934, 56, 1108—1110).—From the ratio CsCl : Ag the at. wt. of Cs is 132.91.

E. S. H.

Constitution of hafnium and other elements. F. W. ASTON (Nature, 1934, 133, 684).—The mass spectrum of Hf indicates five isotopes, a weak line at 176 and strong lines at 177, 178, 179, and 180, with the even nos. somewhat more abundant. Th appears to be simple 232. Rh gives the feeblest effect of any element analysed, with only one line at 103 clearly detectable. Intense spectra from Ca showed new isotopes 42 and 43 in addition to 40 and 44 discovered by Dempster. A line at 41 may probably be due in part to another Ca isotope. The main line 48 of Ti is accompanied by faint lines at 46, 47, 49, and 50, the whole forming a symmetrical group. Zr has an additional and fairly abundant isotope 91, and the presence of isotope 96 is now confirmed. Sm has two faint isotopes 144 and 150. Pd, Ir, Pt, and Au still give negative results.

L. S. T.

Research on heavy hydrogen at Princeton. H. S. TAYLOR (Science, 1934, 79, 303—305).—A summary.

L. S. T.

Two kinds of H₃. (SIR) J. J. THOMSON (Phil. Mag., 1934, [vii], 17, 1025—1030).—Bombardment of certain solids by cathode rays gives a permanent gas H₃, and a discharge through normal H₂ gives a H₃ of very short life. Photographs of parabolas and positive-ray analysis show that the permanent H₃ obtained by a discharge in normal H₂ is $< 1/8500$ of the normal H₂, and that permanent H₃ obtained by bombarding KOH was, in two samples, $1/720$ and $1/480$ of the normal H₂. In the photographic method the effects due to the short-lived and permanent forms of H₃ are superposed, but in the electrical method the effect of the fugitive H₃ is eliminated. Parabolas for H₂, H₃, and H₄ for a specimen containing 80% H₃ are of approx. the same intensity and correspond with the electrical effects due to these lines.

N. M. B.

Field combinations in velocity and mass-spectrography. II. W. HENNEBERG (Ann. Physik, 1934, [v], 20, 1—12; cf. this vol., 341).—Mathe-

matical. Use can be made of the large dispersion in the equatorial plane of a magnetic dipole field for spectroscopic purposes. For focussing, an electron lens may be used, or a homogeneous magnetic field and the field of a cylindrical condenser may be superposed.

A. J. M.

Periodic law and its interpretation. (LORD) RUTHERFORD (J.C.S., 1934, 635—642).—Mendeleef Centenary Lecture.

J. W. S.

At. wts. and isotopes. E. C. FRITZMAN (J. Appl. Chem. Russ., 1934, 7, 279—296).—A review.

R. T.

Anomalous thermal activity of radioactive minerals. A. SANIELEVICI (J. Chim. phys., 1934, 31, 192—196).—The abnormal evolution of heat at a const. rate by orange is attributed to adsorption of H₂O and hydration, since the mineral in a sealed vessel gradually loses its anomalous thermal activity.

J. G. A. G.

Mobility of polonium on and in silver. K. SCHWARZ (Z. physikal. Chem., 1934, 168, 241—247).—There is "vaporisation" of Po from a Ag surface even at comparatively low temp. The interpretation of this phenomenon as due to aggregate recoil (cf. A., 1920, ii, 656) agrees with the observation that the rate is independent of the temp. at 100—350°. Thermal evaporation first becomes perceptible at 350—400°. Diffusion over the Ag surface begins to be detectable at 300° and increases with rise in temp. There is no measurable vol. diffusion into the Ag up to 500°.

R. C.

Radioactive elements of F. Joliot and I. Curie. G. C. WICK (Atti R. Accad. Lincei, 1934, [vi], 19, 319—324).—Theoretical.

O. J. W.

Half-life of actinouranium. F. WESTERN and A. E. RUARK (Physical Rev., 1934, [ii], 45, 628—629; cf. A., 1933, 1224; this vol., 234).—Calc. half life vals. for Ac-U from various sources are 3.38×10^8 and 4.45×10^8 years, based on branching ratios 0.03 and 0.04, respectively.

N. M. B.

Properties of samarium radiation. M. MADER (Z. Physik, 1934, 88, 601—611).— α -Rays of 1.16 cm. and H -rays of 1.37 cm. in air were observed.

A. B. D. C.

Magnetic spectrum of β -rays emitted by Th-B+C+C'. R. ARNOULT (Compt. rend., 1934, 198, 1603—1605; cf. this vol., 470).—Similarities between Th and Ra(-B \rightarrow C) spectra suggest that the former is due to electronic reorganisation of atom 83 after ionisation of K levels by a γ -quantum. Nuclear levels are indicated for Th-B at 113.4, 236.7, and 411 ekv.

B. W. B.

β -Radioactivity. D. D. IVANENKO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 537—539).—Theoretical.

J. W. S.

β -Emission of positive electrons. G. BECK and K. SITTE (Nature, 1934, 133, 722).—Theoretical.

L. S. T.

Secondary radiation of hard γ -radiation. W. BOTHE and W. HORN (Z. Physik, 1934, 88, 683—698; cf. this vol., 342).

A. B. D. C.

Artificial production of radioactive elements. Chemical proof of transmutation of elements.

(MME.) I. CURIE and F. JOLIOT (J. Phys. Radium, 1934, [vii], 5, 153—156; cf. A., 1933, 1224; this vol., 234, 343, 470).—B, Mg, and Al after irradiation by Po α -rays show radioactivity. B and Al emit positrons of max. energy 1.5×10^6 and 3×10^6 ev., respectively. Mg emits electrons and positrons forming two continuous spectra corresponding with the transmutation of two Mg isotopes. The decay of the three radio-elements created by transmutation is exponential, the half-decay periods being: B 14 min., Mg 2.5 min., Al 3.25 min., independent of the energy of the exciting α -rays. The new radioactive elements are probably the nuclei ${}^{13}\text{N}$, ${}^{27}\text{Si}$, ${}^{28}\text{Al}$, ${}^{30}\text{P}$, formed from ${}^{10}\text{B}$, ${}^{24}\text{Mg}$, ${}^{25}\text{Mg}$, and ${}^{27}\text{Al}$, respectively. The first chemical proof of artificial transmutation has been effected by the separation of the new elements, which show, from B and Al, the properties of N and P, respectively. N. M. B.

Induced radioactivity of sodium and phosphorus. O. R. FRISCH (Nature, 1934, 133, 721—722).—Na as NaCl, NaF, and $\text{Na}_2\text{C}_2\text{O}_4$ becomes active after α -ray bombardment, emitting chiefly positive electrons, with an initial activity approx. one half that of Al and half-val. period 7 ± 1 sec. Red P behaves similarly, the initial activity being approx. one sixth that of Al; half-val. period 40 ± 5 min. The range of the particles corresponds with an energy of 1.8×10^6 ev. Probable reactions are ${}^{11}\text{Na}^{23} + \alpha = {}^{13}\text{Al}^{26} + \text{neutron}$ and ${}^{15}\text{P}^{31} + \alpha = {}^{17}\text{Cl}^{34} + \text{neutron}$, and in the last case active Cl was separated. ${}^{\text{F}}\text{P}^{19}$ should show induced activity of very short life, but none was detected with CaF_2 . L. S. T.

Radioactivity induced by neutron bombardment. E. FERMI (Nature, 1934, 133, 757).—Bombardment by neutrons from Rn and Be induces strong radioactivity with P, Fe, Si, Al, Ag, I, and Cr; Cl, V, Cu, As, Te, Ba, and F also give definite effects, whilst indications of an effect are obtained with Na, Mg, Ti, Zr, Zn, Sr, Sb, Se, and Br. Some elements may give two or more periods. Active products, probably Si and Mn, respectively, have been separated in the case of P and Fe. The neutron appears to be absorbed and a proton emitted in these two cases. The unstable product, by emission of a β -particle, returns to the original element. L. S. T.

Induced radioactivity. H. J. WATKINS (Nature, 1934, 133, 757—758).—Hypothetical. The radioactivity of the light elements is due to the formation within their nuclei of an unstable proton of excess energy which disintegrates by emitting a positron. L. S. T.

Collisions of neutrons with atomic nuclei. T. W. BONNER (Physical Rev., 1934, [ii], 45, 601—607; cf. A., 1933, 762).—The target area of H, C, and N nuclei for neutrons obtained by the bombardment of Be, B, and F with Po α -particles increased with decrease of neutron velocity. The anomalous increase of absorption by Pb with velocity, as well as cosmic-ray bursts, can be explained by assuming that faster neutrons make relatively more inelastic collisions with the nuclei. The slower neutrons from F were more penetrating in Pb than those from Be or B. N. M. B.

Emission and scattering of neutrons. J. R. DUNNING (Physical Rev., 1934, [ii], 45, 586—600).—Using high-intensity Be-Rn sources, the energy distribution of the neutrons emitted by bombardment of α -particles from Rn, Ra-A, and Ra-C' is analysed in terms of a no. of neutron groups, which are discussed in terms of transitions involving neutrons and γ -rays, with one or two resonance levels. The interaction of high-energy neutrons with matter appears to be mainly one of approx. elastic collisions with at. nuclei, resulting in neutron scattering. Data indicate for the neutron mass 1.0068, and radius 1.2×10^{-13} cm. approx. Nuclear radii $\propto (\text{at. wt.})^{1/3}$, approx., ranging from 2.5×10^{-13} for Li to 7.8×10^{-13} cm. for Pb. N. M. B.

Artificial production of neutrons. H. R. CRANE, C. C. LAURITSEN, and A. SOLTAN (Physical Rev., 1934, [ii], 45, 507—512; cf. *ibid.*, 63; 1933, [ii], 44, 514, 692, 783).—The apparatus employed and results for Be and LiCl bombarded by deuterons, and Be bombarded by He ions, are described (cf. A., 1933, 1225). N. M. B.

Mass of the neutron. I. CURIE and F. JOLIOT (Nature, 1934, 133, 721).—The previous interpretation of the transmutation of B (A., 1933, 883) is confirmed by similar reactions observed with ${}^{13}\text{Al}^{27}$ and ${}^{12}\text{Mg}^{24}$. The reactions are ${}^{10}\text{B} + {}^4\text{He} = {}^{13}\text{N} + \text{neutron}$ and ${}^{13}\text{N} = {}^{13}\text{C} + e^+$; ${}^{24}\text{Mg} + {}^4\text{He} = {}^{27}\text{Si} + \text{neutron}$ and ${}^{27}\text{Si} = {}^{27}\text{Al} + e^+$; and ${}^{27}\text{Al} + {}^4\text{He} = {}^{30}\text{P} + \text{neutron}$ and ${}^{30}\text{P} = {}^{30}\text{Si} + e^+$, where ${}^{13}\text{N}$, ${}^{27}\text{Si}$, and ${}^{30}\text{P}$ are unstable nuclei which disintegrate with the emission of positrons. From these equations and the energies involved calc. vals. for the mass of the neutron are 1.0098, 1.0092, and 1.0089 deduced from B, Al, and Mg, respectively, the first being the most exact. The val. adopted, 1.010 ± 0.0005 , gives 2.1×10^6 ev. for the energy liberated in the transformation neutron \rightarrow proton + e^- and 3.1×10^6 ev. for that absorbed in the change proton \rightarrow neutron + e^+ . L. S. T.

Observations of neutrons from cosmic radiation in a Wilson chamber. L. V. MISOVSKI and M. S. EIGENSON (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 221—224).—Tracks of length 1 mm. to 15 cm., attributed to neutrons produced by cosmic radiation, were observed. H. J. E.

Neutrino. H. BETHE and R. PEIERLS (Nature, 1934, 133, 689—690).—Methods by which the existence of neutrinos could be experimentally tested are discussed. L. S. T.

Atomic disintegration by "non-capture." W. D. HARKINS and D. M. GANS (Nature, 1934, 133, 794).—Theoretical. At present there is no evidence that a nucleus has been disintegrated by a non-capture collision. L. S. T.

Progress of nuclear physics. E. HENRIOT (Bull. Soc. chim. Belg., 1934, 43, 221—238).—A lecture.

Transmutation of elements. T. I. EFREMEENKO (Ukrain. Chem. J., 1933, 8, 182—189).—Speculative. R. T.

Modern ideas on nuclear constitution. G. GAMOW (Nature, 1934, 133, 744—747). L. S. T.

Isomeric nuclei? G. GAMOW (Nature, 1934, 133, 833).—The line 210 in the mass spectrum of Pb indicates that the nucleus with at. no. 82 and at. wt. 210 may exist in two modifications, one of which is stable and the other subject to β -decay. L. S. T.

Constitution of cosmic rays. A. PICCARD (Compt. rend., 1934, 198, 1683—1685).—It is suggested that cosmic rays are primarily electromagnetic rays ($h\nu > 10^6$ ev.) which are almost completely absorbed by at. nuclei in the upper atm. with materialisation of electrons and positrons, the two latter mainly constituting the radiation observed at the earth's surface. B. W. B.

Residual ionisation by measurements with cosmic rays. B. GROSS (Ann. Acad. Brasil. Sci., 1934, 6, 1—10).—The residual ionisation can be obtained indirectly by making observations of the current intensity at two different depths. It can also be derived from an analysis of the absorption curve. A. J. M.

Coincidence counter studies of the corpuscular component of cosmic radiation. T. H. JOHNSON (Physical Rev., 1934, [ii], 45, 569—585). N. M. B.

Waves and photons. III. Dirac's approximation. A. PROCA (J. Phys. Radium, 1934, [vii], 5, 157—166; cf. this vol., 344, 580).—Mathematical. Associated with any light wave is a corpuscle of zero rest mass and for which the wave functions satisfy the Dirac relativistic equations. The corpuscle (neutrino) differs from a photon in its spin val. $h/4\pi$. The influence of the characteristics of the light on the states of the corpuscle is examined. The sign of its energy indicates the sense of rotation of the corresponding light, and gives an interpretation of negative energy states. N. M. B.

Anomalous dispersion in broad absorption bands. D. S. ROSHDESTVENSKI (Bull. Acad. Sci. U.R.S.S., 1934, 2, 35—57).—The anomalous dispersion of broad absorption bands arising from oscillators of fixed characteristic frequency and large damping const. differs from that of bands due to oscillators of variable characteristic frequency and small damping const., when observed by Puccianti's interference method. This method has been applied to the determination of the max. val. of the damping const. J. W. S.

Scattering of light in a medium of non-uniform temperature. L. I. MANDELSHTAM (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 219—221).—Theoretical. H. J. E.

Resolution of crossed linking eigenfunctions in terms of the uncrossed set. H. EYRING and C. E. SUN (J. Chem. Physics, 1934, 2, 299—300).—Simplified rules are given. N. M. B.

Band spectrum of ionised aluminium hydride. W. HOLST (Z. Physik, 1934, 89, 40—49). A. B. D. C.

Isotope effect in the band spectrum of aluminium hydride. W. HOLST and E. HULTHÉN (Nature, 1934, 133, 796—797; cf. this vol., 472). L. S. T.

Significance of molecular absorption spectra. P. K. SEN-GUPTA (Z. Physik, 1934, 88, 647—660).—The discrepancy between the difference of limits of

continuous absorption and of corresponding at. levels is used to deduce the relative steepness of Franck-Condon curves for upper mol. levels, and is checked with the sharpness of absorption edges, and their wavelength variation with temp. Mols. discussed include N_2O , SO_3 , TeO_3 , MoO_3 , TeS_3 , P_2S_5 , HBr , HI , alkali halides, CdS , HgS , PbS , and ZnS . A. B. D. C.

Absorption spectra of ferric compounds. I. Ferric chloride-phenol reaction. E. F. WESP and W. R. BRODE (J. Amer. Chem. Soc., 1934, 56, 1037—1042).—The absorption spectra of aq. mixtures of $PhOH$ with several Fe^{III} salts are identical in shape and position, but not in intensity. The absorption spectra of aq. mixtures of $FeCl_3$ with 44 phenols and 10 naphthols are identical in shape, but differ in intensity and position according to the nature and position of the substituent groups. Salicylic acid produces a colour with $FeCl_3$ only in solvents which are derivatives of H_2O or NH_3 . In 31 such solvents the absorption bands are identical in shape, but vary in position and intensity with the solvent. The Fe^{III} - $PhOH$ colours appear to be due to the formation of complex co-ordinated ions of the type $(OR)_6^{+++}$. E. S. H.

Change in light absorption due to hydrolysis and aggregation processes in alkaline and acid solutions of amphoteric hydroxides exemplified by iso- and hetero-polyvanadate solutions. K. F. JÄHR and H. WITZMANN (Z. physikal. Chem., 1934, 168, 283—290).—The absorption curves of aq. Na vanadate solutions containing varying amounts of $NaOH$ or $HClO_4$ demonstrate the existence of mono-, di-, tetra-, penta-, and octa-vanadic acids. The higher is the mol. wt. of the isopolyacid the flatter is the absorption curve and the further is absorption shifted towards longer waves. R. C.

Optical absorption of substituted benzenes. V. Xylene halides. H. CONRAD-BILLROTH (Z. physikal. Chem., 1934, B, 25, 217—224; cf. this vol., 582).—The ultra-violet absorption spectra of the xylene halides have been determined. Discrepancies between the observed positions of the bands and the positions calc. by the vector addition rule (A., 1933, 445) are perhaps a result of alternating polarity effects. In respect of fine structure and relative intensities of the partial bands there is considerable similarity between Cl - and Br -derivatives of the same geometrical structure. R. C.

Optical absorption curves of adsorbed *p*-nitrophenol molecules and their analysis. J. H. DE BOER and J. F. H. CUSTERS (Z. physikal. Chem., 1934, B, 25, 238—250).—Absorption curves have been determined at various stages of the adsorption by a vac.-sublimed CaF_2 surface. The curves can be resolved into two constituent curves, one corresponding with *p*-nitrophenol mols., the absorption spectrum of which has been shifted towards the red by electrostatic effects (α mols.), and the other with mols. optically unchanged by adsorption (β mols.). When adsorption commences, α mols. are adsorbed, and only when a certain no. of these have been adsorbed does the adsorption of β mols. start. In the final stages of adsorption it is chiefly β mols. which are taken up. The α mols. have their OH dipoles adsorbed on the F'

ions of the surface and the ring lying parallel to the surface, and are bound much more firmly than the β mols., which are held by van der Waals adsorption forces on the initial film of α mols., forming a second film. When the adsorption layer is complete it contains equal nos. of both kinds of mol. The displacement of the absorption spectrum of the α mols. is attributed to the weakening of the effect of the H⁺ of the OH by the F⁻ ion. R. C.

Spectroscopy of terpene alcohols and esters.—See this vol., 658.

Characteristic OH band in the near infra-red (about 0.96 μ). A. NAHERNIAC (Compt. rend., 1934, 198, 1685—1687).—Absorption spectra of vapours (I) of 14 monohydric alcohols were measured with a grating about 1 μ ; practically the only band found was that of OH, about 0.96 μ . The results compared with those of Freymann (A., 1933, 1228) for the liquids (II) show that the simple OH bands of (II) are more intense, slightly displaced towards shorter λ , and, with the exception of *tert.*-alcohols and phenols, are split into two components in (I). The influence of constitution on these phenomena is discussed. B. W. B.

Photography of the infra-red solar spectrum to wave-length 12,900 Å. G. HERZBERG (Nature, 1934, 133, 759).—The H₂O-vapour absorption band at 11,300 Å. has been resolved into its fine structure lines. An atm. O₂ band between 12,500 and 12,750 Å. is also discussed. L. S. T.

Far infra-red solar spectrum. J. DEVAUX (Compt. rend., 1934, 198, 1595—1596).—Absorption spectra were measured at Pic du Midi during Dec., 1933. Absorption in the 6—7 μ H₂O band was high, but not total. The intensity of the 10 μ O₃ band varied with the sun's altitude and was free from interference by H₂O. A new (possibly O₃) band at 7 μ is reported (cf. Gerhard, A., 1933, 208). B. W. B.

Infra-red absorption of water freshly prepared from ice and from steam. J. W. ELLIS and B. W. SORGE (Science, 1934, 79, 370—371).—Infra-red absorption spectra reveal no different concns. of polymers in H₂O freshly prepared from ice or steam. L. S. T.

Infra-red spectrum of methyl deuteride. E. F. BARKER and N. GINSBURG (J. Chem. Physics, 1934, 2, 299).—The replacement of one H in CH₄ by H² introduces a preferred axis, with respect to which the mol. is symmetrical, and increases the no. of active vibrations from two to six. These fundamental bands have been observed; the lowest frequency parallel vibration is at approx. 1090 cm.⁻¹, the interval between rotation lines being 4.5 cm.⁻¹, giving max. $I \sim 12.28 \times 10^{-40}$, and H—H distances 2.51×10^{-8} cm. N. M. B.

Raman effect, molecular refraction, and constitution. Supposed 1-benzylcyclohexene.—See this vol., 649.

Raman effect of seven normal alkyl nitrates. L. MEDARD (J. Chim. phys., 1934, 31, 281—293).—Frequencies in the Raman spectra of RNO₃, where R is Me, Et, Pr, Bu, *n*-amyl, *n*-C₆H₁₃, and *n*-C₇H₁₅, are tabulated. New lines have been found and others are shown to be doublets. The frequency due to the NO₃

ion does not occur in MeOH solutions of MeNO₃ (cf. Ganesan and Thatte, A., 1933, 114). The frequencies 1295 and 1679 cm.⁻¹ in 99.8% HNO₃ correspond with internal vibrations, comparatively little influenced by R, of the ·NO₂ group, whilst the frequency 612, related to the angle subtended by the two O atoms, decreases to 570 when R > Me. 860 (approx.) in RNO₃ increases to 922 in HNO₃ and is assigned to the O₂N·OR linking. The differences between the corresponding frequencies of the C chains decrease as R increases. Although the frequency at 2735 of alcohols is found, that at 2660 (I) does not occur in RNO₃, showing that (I) is not due to the C chain (cf. *ibid.*, 7). J. G. A. G.

Raman and infra-red spectra of the 1:2-dimethylcyclohexane stereoisomerides. J. LECOMTE, L. PIAUX, and O. MILLER (Bull. Soc. chim. Belg., 1934, 43, 239—242; cf. A., 1933, 998).—No absorption is shown in the ultra-violet. Infra-red absorption data are for the range 498—1450 cm.⁻¹. The bands 875—879 and 996—994 are common to the two forms. N. M. B.

Raman spectra of some compounds containing carbon-bromine linkings. Possible changes of the vibration frequencies in ionic solutions. H. E. VOGÉ (J. Chem. Physics, 1934, 2, 264—266).—Raman spectral data for CH₂Br·CO₂Me (liquid) and CHPhBr·CO₂Me in MeOH are tabulated. The C-Br linking of the former is similar to that for EtBr; in the latter it does not appear in its normal position. Revised data for MeOH and EtBr, and shifts of the CH₂Br·CO₂Me and MeOH lines in solutions of bromides, are given. N. M. B.

Raman effect and the benzene problem. J. WEILER (Z. Physik, 1934, 89, 58—62).—Observed infra-red and Raman fundamental frequencies agree not with hexagonal, but with trigonal, symmetry. A. B. D. C.

Action of electric discharge on phosphorescent substances. R. COUSTAL (Compt. rend., 1934, 198, 1596—1598; cf. this vol., 584).—Decay curves of phosphorescent sulphide screens (I) under- or over-excited by a brush discharge were photometrically compared with a normal (I) and shown to preserve const. intensity ratios throughout decay. It is suggested that two states of excitation of phosphorescent centres are involved. B. W. B.

Theory of phosphorescence. D. BLOCHINTZEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 79—81).—Mathematical. H. S. P.

New photo-electric effect in cuprous oxide. I. KIKOIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 73—76).—When a plate of Cu₂O at liquid air temp. is placed in a magnetic field and illuminated perpendicularly to the direction of the field, an e.m.f. perpendicular to both of these directions is produced. The current flowing depends on the intensity of the light and the strength of the field. Since the total conductance is the sum of the thermal and photo-effects, the e.m.f. tends to a limit with increasing intensity of illumination. H. S. P.

Oxide-coated photo-elements. I. G. LIANDRAT (J. Phys. Radium, 1934, [vii], 5, 179—183).—The inexactitude of theories of oxide-coated photo

electric cells is attributed to neglect of the photo-conductivity effect in the oxide layer, which may, as in the "colour effect," be predominant. The impedance of a two-layer system in series is calc. and discussed. N. M. B.

Relation between spectral sensitivity and absorption curves of dye photo-cells. (MLLE.) C. STORA (Compt. rend., 1934, 198, 1763—1765; cf. A., 1932, 898).—The displacements of max. of photo-electric sensitivity (*i.e.*, photo-current/incident energy) of dye/metal cells from the absorption max. of the dyes employed increased with the film-thickness of the dye. The seat of the photo-action was the thin film of dye immediately in contact with metal substrate.

B. W. B.

Determination of dipole moments by the molecular beam method. H. SCHEFFERS (Physikal. Z., 1934, 35, 425—433).—The dipole moments of KI, KCl, and NaI determined by the above method are 6.8×10^{-18} , 6.3×10^{-18} , and 4.9×10^{-18} e.s.u., respectively, thus agreeing with Debye's estimate.

A. J. M.

Dielectric constant of chemically defined substances. F. KELLER and W. R. LEHMANN (Z. Physik, 1934, 88, 677—682).—An attempt to measure dielectric consts. and relate them to the periodic system. Substances investigated include inorg. salts, oxides, and sulphides.

A. B. D. C.

Dipole induction effect in molecular compounds. Dipole moment measurements in molten naphthalene. G. BRIEGLEB and J. KAMBERTZ (Z. physikal. Chem., 1934, B, 25, 251—256).—A detailed account of work the principal results of which have already been published (this vol., 348). R. C.

Temperature dependence of the relaxation time of polarisations in ice. E. J. MURPHY (Trans. Electrochem. Soc., 1934, 65, 309—318).—Determinations of dielectric const. of ice by a static method and by an a.c. method at frequencies from 16 to 10^5 cycles per sec. over a wide range of temp. indicate an exponential increase of the relaxation time of the polarised condition in the dielectric with fall of temp., from about 2×10^{-5} sec. at -0.8° to about 20 sec. at -139° . The nature of the polarisation responsible for the large dielectric const. of ice is discussed.

H. J. T. E.

Dielectric constants and transitions of solid ammonia, hydrogen sulphide, and methyl alcohol. C. P. SMYTH and C. S. HITCHCOCK (J. Amer. Chem. Soc., 1934, 56, 1084—1087).—The dielectric consts. of NH_3 , H_2S , and MeOH have been determined from 83° abs. to the m.p. No mol. rotation or transitions are observed in NH_3 , whilst two transitions are observed in H_2S , and one in MeOH . Mols. of H_2S appear to possess almost the same freedom of rotation as in the liquid state even when some degrees below the m.p.; with MeOH some freedom of mol. rotation exists in the narrow region between the m.p. and the transition point.

E. S. H.

Anomalous dispersion of the dielectric constant of Rochelle salt. G. BUSCH and P. SCHERRER (Helv. phys. Acta, 1933, 6, 234; Chem. Zentr., 1933, u, 2794—2795).—Na K tartrate (I) shows an anomal-

ous dispersion of ϵ , at wave-lengths of a few thousand m., which is attributed to a piezoelectrical resonance of the crystals. ϵ for different sized plates of (I) has been measured for variable frequencies (10^4 — 5×10^5 Hertz) at 6 — 36° . The resonance wave-lengths and ϵ are max. at 22° .

L. S. T.

Dipole moments of liquids. R. F. GOSS (J.C.S., 1934, 696—699).—From the formula of Raman and Krishnan (cf. A., 1928, 348), relating electrical polarisation with anisotropy in the liquid state, a method has been developed for calculating the dipole moment (μ) from measurements on the pure liquid and on its dil. solutions. μ for MeCl and CHCl_3 are calc. from the data of Morgan and Lowry (A., 1931, 148) as 1.85 and 1.20×10^{-18} e.s.u., respectively.

J. W. S.

Dielectric properties of acetylenic compounds.

II. Electric moments of alkyl halogenoacetylenes. D. J. PFLAUM and H. H. WENZKE (J. Amer. Chem. Soc., 1934, 56, 1106—1107; cf. this vol., 585).—Measurements of dipole moments of α -chloro-, α -bromo-, and α -iodo- Δ^2 -hexinene and -heptinene show that the C-halogen linking decreases in polarity as the C becomes less saturated.

E. S. H.

Absorption measurements in liquids in the region of short electric waves. **III.** J. MALSCH (Ann. Physik, 1934, [v], 20, 33—56; cf. A., 1932, 470; this vol., 585).—An abs. method for the determination of refractive and absorption indices of liquids for waves of the order of 1 m. is described. Both consts. are determined simultaneously without alteration of the arrangement of the apparatus. The method was applied to $\text{Bu}^\alpha\text{OH}$ and Bu^βOH using 180-cm. waves. The behaviour of both substances in the range 50—5000 cm. can be explained quantitatively by the dipole theory of Debye.

A. J. M.

Anomalous dispersion in crystalline solids.

C. E. SUN and J. W. WILLIAMS (Trans. Electrochem. Soc., 1934, 65, 219—229).—Dielectric consts. of C_6H_6 , PhNO_2 , COPh , COPhMe , and NH_3 in the cryst. state have been measured over a wide range of temp. and at frequencies from 1 to 600 kilocycles per sec. The significance of the results is discussed with special reference to the application of Debye's dipole theory.

H. J. T. E.

Ionising power of combinations of two partial [dipole] moments. A. E. VAN ARKEL and J. L. SNOEK (Rec. trav. chim., 1934, 53, 675—676; cf. A., 1933, 8).—The ionising power of a solvent is not determined solely by its dielectric const. (Walden's rule), as is shown by measurements of the conductivity of AcOH in C_6H_6 , *p*- and *o*- $\text{C}_6\text{H}_4\text{Cl}_2$, and PhCl . There is much less difference between the first two than between either of them and either of the last two. This indicates that the action of a single Cl-moment may be influenced by the existence in the ring of another such moment, and by its position.

F. L. U.

Explanation of transference of charge and electrophoretic effect on the ionic theory. A. LUSTIG and M. REISS (Physikal. Z., 1934, 35, 340—344).—The theory of Sitte (A., 1933, 761) relative to the occurrence of sub-electrons and electrophoretic effect is shown to be inadequate for the explanation of these phenomena.

A. J. M.

Explanation of transference of charge and electrophoretic phenomena. K. SITTE (Physikal. Z., 1934, 35, 345—346).—A reply to Lustig and Reiss (preceding abstract). A. J. M.

Nature of electroodic capacity with alternating current. N. THON (Compt. rend., 1934, 198, 1681—1683; cf. this vol., 493). B. W. B.

Influence of gases on the unidirectional conductivity of the silicon-carbon couple. (MILLER.) M. QUINTIN (Compt. rend., 1934, 198, 1677—1679; cf. this vol., 240).—The influence of occluded gases on the characteristic of the Si-(SiO₂)-C rectifier was studied. Asymmetry of characteristic was increased by evacuation or heating, was less in He than in A, and varied with gaseous pressure. The results may be attributed to either ionic or electronic effects.

B. W. B.

Electrical conductivity of magnesia at high temperatures. E. ROUSSEAU (Chim. et Ind., 1934, 31, Spec. No., 755—758).—The resistivity, R , of a crystal of MgO follows Joffé's law ($\log r = A + B/T$) between 1400° and 1700°. R for powder MgO does not follow Joffé's law above 1600°. Additions of MgO to Al₂O₃, or vice versa, produce a fall in R and the system has min. at the eutectics. R of spinel is close to that of MgO. Additions of metal oxides, SiO₂, and P₂O₅ improve the conductivity of MgO, the greatest effect being with 10% P₂O₅.

T. W. P.

Refraction and dispersion of crystals. X. Connexions between refraction and absorption of halogen ions in crystalline and dissolved state. P. WULFF (Z. physikal. Chem., 1934, B, 25, 177—207; cf. this vol., 245).—Dispersion formulae for the cryst. alkali halides have been derived by a graphical method (A., 1933, 765). With chlorides of the rock-salt type the first characteristic frequency of the dispersion formula runs parallel with the Madelung potential, P . With NaBr and KBr the frequency of the first absorption max. does not run parallel with P , and probably increases with fall in the frequency of the centre of gravity of the group of absorption bands. With chlorides of the rock-salt type the probability of transition corresponding with the first absorption max. does not change by more than 5% with change in the cation. The val. for CsCl is 8/6 times this val. For Cl⁻, Br⁻, and I⁻ in aq. solution the characteristic frequency and probability of transition are considerably reduced compared with the cryst. state. The variation with concn. of the ionic refraction of dissolved electrolytes is not irreconcilable with the position of the absorption max. not varying with concn. R. C.

Molecular refractivity of sodium chloride. F. H. NEWMAN (Phil. Mag., 1934, [vii], 17, 1072—1075).—Factors affecting mol. refraction for an electrolytic solution are discussed. Data for NaCl indicate that ions in solution are more similar to gaseous ions than ions in crystals. Determinations of n for NaCl in the concn. range 0.002—0.0001 equiv. per 1000 g. of H₂O give the val. $[R_L]_{\infty} = 9.05^\circ$, at infinite dilution, and show definite changes at concns. below 0.002 and 0.0005 equiv. per 1000 g. of H₂O. N. M. B.

Anomalous dispersion by diffraction. A. H. PFUND (J. Opt. Soc. Amer., 1934, 24, 121—124).—

Diffraction bands with black min. are produced with a single slit ruled in an absorbent film. These bands are sharpest in the absorption band of the film, and the anomalous dispersion of org. dyes is thus conveniently studied. Films of Au also appear to exhibit anomalous dispersion. A. G.

Rotatory powers of alkaline-earth tartrates. I. PEYCHES (Compt. rend., 1934, 198, 1600—1602; cf. this vol., 13).— $[\alpha]$ (at λ 5461) was determined for tartrates of Sr and Ba at concns. up to 0.04M and of Ca up to 0.012M, the more conc. solutions being supersaturated. All showed increase of $[\alpha]$ with concn. (cf. Darmon, A., 1928, 1320). Owing to incomplete dissociation the order of $[\alpha]$ for the Ca, Sr, and Ba salts agrees with that of crystal- instead of hydrated-cationic radii. B. W. B.

Magnetic rotatory dispersion of water in the ultra-violet. G. BRUHAT (J. Phys. Radium, 1934, [vii], 5, 152).—Previous results (cf. this vol., 13) are compared with other available data obtained by photographic methods. N. M. B.

Magnetic rotatory dispersion and refraction of aqueous solutions of cerous sulphate. R. W. ROBERTS, L. A. WALLACE, and I. T. PIERCE (Phil. Mag., 1934, [vii], 17, 934—961; cf. this vol., 13).—Using the polarimetric method at 22.2° for three concns., the sp. rotations of Ce₂(SO₄)₃ and La₂(SO₄)₃ are negative, and, for Ce₂(SO₄)₃, independent of concn. Magnetic rotatory dispersion of Ce₂(SO₄)₃ in the range 5780—3341 Å. calc. by taking into account absorption bands at 2960 and 2540 Å. confirms the ground state of the Ce⁺⁺⁺ ion as $4^2F_{5/2}$ and not $5^2D_{3/2}$. The mol. refraction is independent of the concn. N. M. B.

Magnetic double refraction of solutions of paramagnetic salts. C. MUNSTER (Z. Physik, 1934, 88, 593—600).—Magnetic double refraction observed at different temp. and concn. with aq. solutions of Ce nitrate shows that this is due to the undissociated mol. A. B. D. C.

Affinity. III. T. DE DONDER (Bull. Acad. roy. Belg., 1934, [v], 20, 268—281; cf. A., 1933, 211, 450, 1232).—Mathematical. N. M. B.

Existence of bi-radicals. E. MULLER, W. KLEMM, and W. SCHUTH (Naturwiss., 1934, 22, 335).—A mol. of the formula $\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot$ should be paramagnetic at room temp., but is actually diamagnetic. The bi-radical formula is not acceptable. A. J. M.

Structure and properties of homopolar compounds. IV. A. DIBROVA (Ukrain. Chem. J., 1933, 8, 171—178).—Theoretical. R. T.

Configuration of some optically active hexa-co-ordinated complexes. J. P. MATHIEU (Compt. rend., 1934, 198, 1598—1600).—Werner's solubility rules (A., 1918, ii, 822) indicate that $l\text{-}[\text{Rh en}_3]^{3+}$ and $d\text{-}[\text{Co en}_3]^{3+}$ [$\text{en} = \text{C}_2\text{H}_4(\text{NH}_2)_2$] should have similar configurations; also $l\text{-}[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ and $d\text{-}[\text{Rh}(\text{C}_2\text{O}_4)_3]^{3-}$ (α_D in all cases; thus neglecting the possible effects of anomalous dispersion). Jaeger (A., 1919, ii, 310) ascribes dissimilar configurations on other evidence. The mol. dichroisms, coeffs. of absorption, and $M[\alpha]_D$ vals. of $[\text{Co en}_3]\text{Br}_3 \cdot 2\text{H}_2\text{O}$, $[\text{Rh en}_3]\text{I}_3 \cdot \text{H}_2\text{O}$, $[\text{Ir}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 2\text{H}_2\text{O}$, and $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot 2\text{H}_2\text{O}$ were

determined over the absorption region, and indicate that, whatever the sign of $M[\alpha]_D$, complex ions of the same series giving salts of the same relative solubilities show a Cotton effect of the same sign. B. W. B.

Paramagnetism and diamagnetism of substances in magnetic fields of low intensity. A. O. RANKINE (Proc. Physical Soc., 1934, 46, 391—407).—A preliminary form of magnetic gradiometer has been found suitable for demonstrating the para- or dia-magnetism of substances of small susceptibility. Small magnetising fields of the order 50 gauss are used. The principle of the instrument may be adapted to the construction of a highly sensitive galvanometer.

N. M. B.

Paramagnetic rotation and susceptibility in manganous and ferric salts. J. H. VAN VLECK and W. G. PENNEY (Phil. Mag., 1934, [vii], 17, 961—987).—Formulæ are deduced for the temp. variation and anisotropy in the susceptibility of Mn^{II} or Fe^{III} compounds of high magnetic dilution, with a discussion of the Faraday effect. Theoretically, if the cryst. field has perfect cubic symmetry, the susceptibility and paramagnetic part of the Verdet const. are probably proportional, and should show the same temp. dependence. Qual. comparison is illustrated with data for spessartite and dialogite.

N. M. B.

Magnetic properties of cerium, lanthanum, and neodymium at different temperatures. F. TROMBE (Compt. rend., 1934, 198, 1591—1593; cf. A., 1933, 475).—The magnetic susceptibilities, χ , at 16° and 5000 gauss of Ce, La, and Nd containing < 0.05% Si and 0.02% Fe were 17.8, 1.2, and 39.5×10^{-6} , respectively. For the ranges 273—109° and 109—90° abs., Nd gave moments of 17.8 and 11.3 Weiss magnetons; the former val. is comparable with that of Gorter and Haas (A., 1932, 448) for $Nd_2(SO_4)_3 \cdot 8H_2O$ and with the theoretical val. for Nd^{III} .

B. W. B.

Magnetic susceptibility of ammonium hexabromo-hypoantimonate. N. ELLIOTT (J. Chem. Physics, 1934, 2, 298—299).—The val. obtained is -0.036×10^{-6} , the substance thus being diamagnetic, and not containing unpolymerised complexes involving Sb^{IV} . The probable structure is $(NH_4)_4Sb^{III}Sb^{VB}Br_{12}$.

N. M. B.

Magnetic susceptibilities of gases and vapours. S. R. RAO and G. SIVARAMAKRISHNAN (Proc. Physical Soc., 1934, 46, 318—323).—An improved retorsion method with bifilar suspension and provision for the systematic elimination of known sources of error is described. The mol. susceptibility of CO_2 was $-(20.79 \pm 0.08) \times 10^{-6}$.

N. M. B.

Magnetic susceptibilities of gases and vapours. G. SIVARAMAKRISHNAN (J. Annamalai Univ., 1934, 3, 48—58).—Using the method described in the preceding abstract, the molar susceptibility of C_6H_6 vapour at 32° was found to be 79.6×10^{-6} .

R. S. B.

Zero-point energy of molecular crystals. V. DEETZ (J. Chem. Physics, 1934, 2, 296).—Vals. and cal. heats of sublimation at 0° abs. are given for He, Ne, A, N_2 , CO, NO, O_2 , HCl, HBr, and HI.

N. M. B.

Vibrations of tetrahedral pentatomic molecules. I. Potential energy. II. Kinetic energy

and normal frequencies of vibration. (MISS) J. E. ROSENTHAL (Physical Rev., 1934, [ii], 45, 538—544; cf. A., 1933, 204).—Mathematical. N. M. B.

Vibration frequencies of atoms. B. N. SEN (J. Indian Chem. Soc., 1934, 11, 243—248).—A formula for the calculation of at. frequencies from the parachor, at. vol., valency, N , at. wt., and e gives results in good agreement with experimental and other calc. vals.

N. M. B.

sp^3 Configuration of carbon, and [theory of structure of] CH_4 . J. H. VAN VLECK (J. Chem. Physics, 1934, 2, 297—298).—A previous paper (cf. this vol., 241) is extended with the help of data due to Edlén (cf. A., 1933, 991).

N. M. B.

Mutual repulsive potential of closed shells. W. E. BLEICK and J. E. MAYER (J. Chem. Physics, 1934, 2, 252—259).—Mathematical. By means of a generalised Heitler-London method, a representation, in terms of a small no. of integrals, of the mutual potential of two ions or atoms having a rare gas electron configuration is deduced.

N. M. B.

Ground state of C_2 and O_2 and the theory of valency. W. HEITLER and G. POSCHL (Nature, 1934, 133, 833—834).—The apparent contradiction between the experimentally-determined ground states of C_2 and O_2 and the quantum-mechanical theory of the chemical linking is explained.

L. S. T.

Term structure of the non-collinear triatomic molecule of type X_2Y . A. V. BUSHKOVITCH (Physical Rev., 1934, [ii], 45, 545—549).—Mathematical. Group theory methods are employed.

N. M. B.

Lattice energies of RbBr and NaCl. L. HELMHOLTZ and J. E. MAYER (J. Chem. Physics, 1934, 2, 245—251).—The calc. vals., from electrical measurements of the ion emission through an orifice in an equilibrium chamber at high temp. containing salt vapour, are 151.3 and 181.3 ± 3.0 kg.-cal., respectively; the corresponding electron affinities are 84.2 for Br and 88.3 kg.-cal. for Cl.

N. M. B.

Capillary depression of mercury in wide tubes. J. STULLA-GOTZ (Physikal. Z., 1934, 35, 404—407).—By interference experiments it is shown that in tubes of diameter > 45 mm. capillary forces no longer exert an influence on the Hg meniscus.

A. J. M.

Rocking-curves by transmission of the X-ray beam through calcite crystals. T. R. CUYKENDALL and S. W. BARNES (Physical Rev., 1934, [ii], 45, 617—619).—Using a two-crystal spectrometer, rocking-curve widths for calcite crystals in the (1, —1) position are reported at 0.208 Å. ($W K\alpha_1$). The results of etching the faces of two crystals are discussed.

N. M. B.

Nucleus formation in silver halide crystals. M. SAVOSTYANOVA and A. TOPORETZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 225—231).—The colloidal particle size in AgCl and AgBr coloured by ultra-violet light has been measured ultramicroscopically and by finding the position of max. light absorption. Further illumination of the colloidal particles with light absorbed by them, but not by the AgCl or AgBr crystal, leads to their disappearance. In crystals containing

excess of Ag, growth of the particles occurs on further illumination. H. J. E.

Rate of nucleation of copper sulphate in a vacuum. N. F. H. BRIGHT and W. E. GARNER (Nature, 1934, 133, 570).—The rate of growth of the centres of dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ varies with the crystal direction. When a crystal is removed, dried, and placed in a high vac., no nuclei appear until after an induction period (I) (approx. 100 min. at 18°), when the no. of nuclei begins to increase linearly. (I) is probably due to the slow rate of growth of the nuclei when first formed. L. S. T.

Disintegration of sputtered deposits. E. A. JOHNSON and L. HARRIS (Physical Rev., 1934, [ii], 45, 630—634).—The anomalous distribution pattern obtained when an edge or slit is interposed between a cathode and a receiver is due to disintegration of the deposit by neutralised positive ions of the sputtering gas reflected from the cathode, indicating that the sputtered particles either have a low velocity or consist of at. clusters. A similar effect is caused by electrons having an energy > 2000 volts. N. M. B.

X-Ray investigation of rock-salt. "Ideal" reflecting rock-salt. M. RENNINGER (Naturwiss., 1934, 22, 334—335).—X-Ray examination of a crystal of rock-salt showed it to be ideal. The mosaic character of rock-salt is not inherent, but is caused during growth, or by later changes. A. J. M.

X-Ray studies in the system nickel-oxygen-water. III. K-Absorption limits of nickel in various oxide hydrates. R. W. CAIRNS and E. OTT (J. Amer. Chem. Soc., 1934, 56, 1094—1096).—The results obtained support the contention (A., 1933, 352) that $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ contains Ni^{III} . E. S. H.

Multiple Laue spots from aluminium crystals. A. KOMAR and W. OBUKHOFF (Nature, 1934, 133, 687).—The distribution of intensity along the Laue spots from thick (6 mm.) deformed Al crystals (I) depends on the degree of plastic deformation. Multiple Laue spots previously described may be due to reversible or irreversible changes in the perfection of the crystals, and also to focussing in the case of deformed (I). L. S. T.

Crystal structure of the compounds LaMg_3 , CeMg_3 , and PrMg_3 . A. ROSSI and A. IANDELLI (Atti R. Accad. Lincei, 1934, [vi], 19, 415—420).—These compounds are cubic, with a 7.48, 7.37, 7.37 Å., d_{calc} 3.35, 3.43, 3.52 for the La, Ce, and Pr compounds, respectively. At. co-ordinates and a spatial model are given. O. J. W.

Calcium sulphate hemihydrate. W. A. CASPARI (Nature, 1934, 133, 648).—Crystals (I) of the "hemihydrate" grown in dil. HCl , H_2SO_4 , or HNO_3 belong to the trigonal system, and consist of hexagonal prism form; a 6.76, c 6.24 Å., with three mols. per cell and d only slightly $<$ that of anhydrite (II). "Dead-burning" converts (I) into pseudomorphs consisting of ordinary (II), which appears to be dimorphous with the orthorhombic, comparatively inert modification, and the trigonal form, stable up to approx. 200° . This takes up H_2O zeolitically and the behaviour of this form in contact with H_2O causes plaster to set. S. T.

Colusite, $(\text{Cu,Fe,Mo,Sn})_4(\text{S,As,Te})_{3-4}$. W. H. ZACHARIASEN (Amer. Min., 1933, 18, 534—537).—Colusite is cubic; a 5.304 ± 0.001 Å. CH. ABS.

X-Ray study of the n -aliphatic alcohols, $\text{C}_{10}\text{H}_{21}\text{OH}$ to $\text{C}_{18}\text{H}_{37}\text{OH}$. D. A. WILSON and E. OTT (J. Chem. Physics, 1934, 2, 231—238).—Spacings along identity periods perpendicular to the 001 planes (c spacings) were measured at room temp. and -50° , and, when plotted against the no. of C atoms in the chain, show the existence of two cryst. modifications, the second appearing only in members having an even no. of C atoms. The ordinary (α) forms crystallise with the c axis approx. at right angles to the 001 plane, and the others (β) have the c axis at approx. $51^\circ 55'$ to the 001 plane, the packings at the ends of the mols. being different for the two cases. N. M. B.

Intensities of reflexion of a series of n -aliphatic alcohols. D. A. WILSON and E. OTT (J. Chem. Physics, 1934, 2, 239—244; cf. preceding abstract).—Comparison of observed and calc. intensities of c spacings of the α -modification of the series $\text{C}_{13}\text{H}_{27}\text{OH}$ — $\text{C}_{18}\text{H}_{37}\text{OH}$ gives good vals. for the co-ordinates, projected on the c axis, of the constituent atoms. N. M. B.

Alternation in long-chain compounds. II. X-Ray and thermal investigation of the triglycerides. C. E. CLARKSON and T. MALKIN (J.C.S., 1934, 666—671).—The triglycerides from tridecain to tristearin exist in three solid forms: a stable, high-melting β -form, which separates from solvents or slowly from the molten glyceride maintained only slightly below its m.p.; a lower-melting monotropic metastable α -form which separates from the molten glyceride when cooled more rapidly; and a still lower-melting glass form obtained by rapid cooling of the melted glyceride. The m.p. of the glass and α -forms lie on smooth curves, but those of the β -form show alternations. X-Ray examination shows that in the β -form the long C chains are tilted across the planes formed by the terminal Me groups, whilst in the α -forms they are perpendicular to these planes. The results support Malkin's views on alternation (A., 1932, 326). A structure for the glyceride mol. is suggested. J. W. S.

X-Ray photographs of crystalline pepsin. J. D. BERNAL and D. CROWFOOT (Nature, 1934, 133, 794—795).—Crystals (I) of pepsin, c/a 2.3 ± 0.1 , are birefringent and positively uniaxial, with a good interference figure, when examined in their mother-liquor. On exposure to air the birefringence rapidly diminishes, and X-ray photographs give only a blackening, indicating complete alteration of the crystal. Photographs of (I) in their mother-liquor give a 67 and c 154 Å., approx. or multiples of these vals., and using the val. d 1.32 the mol. wt. of the unit cell is 478,000. (I) contain approx. 50% of H_2O removable at room temp. Possible mol. structure is discussed. L. S. T.

X-Ray photographs of crystalline pepsin. W. T. ASTBURY and R. LOMAX (Nature, 1934, 133, 795).—A discussion (cf. preceding abstract). L. S. T.

Structure of rubber studied by means of electron rays. G. BRUNI and G. NATTA (*Atti R. Accad. Lincei*, 1934, [vi], 19, 206—211).—Electron diffraction measurements give the three fundamental distances a 6.53, b 7.68, c 9.60 Å. for thin films of rubber $0.5\text{--}3.0 \times 10^{-5}$ cm. thick. The unit cell, containing 4 isoprene groups, has V 481.0×10^{-24} c.c. and d_{calc} 0.94. Cryst. rubber is rapidly transformed into the amorphous form by the action of the electron beam, probably due to a thermal effect.

O. J. W.

Röntgenography of liquids. II. X-Ray diffraction of allylthiocarbimide and methylaniline mixtures. I. I. TSCHALENKO (*Ukrain. Chem. J.*, 1933, 8, 140—150).—Diffraction data indicate that $\text{C}_3\text{H}_5\text{SCN}$ (I) undergoes association to double mols. on X-ray irradiation, the distance between the optical centres of the constituent mols. being 8.5 Å. Mixtures of (I) and NHPhMe (II) give diffraction corresponding with formation of a 1:1 compound [magnitude of mol. 9.4 Å., corresponding with 4.25 Å. for (I), and 5.1 Å. for (II)].

R. T.

Present position of the study of the nature of liquid structures by diffraction of X-rays. G. W. STEWART (*Kolloid-Z.*, 1934, 67, 130—135).—A review.

E. S. H.

Accurate electron diffraction measurements. G. I. FINCH and A. G. QUARRELL (*Nature*, 1934, 133, 758).

L. S. T.

Electron diffraction by "crossed lattice powder." A. STEINHEIL (*Z. Physik*, 1934, 89, 50—57).—Diffraction of 60- to 75-kv. electrons by mica powder shows effects due to both crossed and space lattices.

A. B. D. C.

Influence of electron streaming on the dielectric strength of crystals. A. VALTER and L. INGE (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 2, 68—71).—Experiments with coloured rock-salt in which the electron concn. can be altered by illumination indicate that conduction in solid insulators is due to the effect of the electric field in drawing out electrons rather than to ionisation by collision.

H. S. P.

Conditions increasing the phenomenon of magnetic viscosity. A. V. MITKEVITSON (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 1, 531—537).—The magnetic viscosity in soft Fe is much greater when the field in the exciting coil is allowed to decrease relatively slowly (through a parallel resistance) than when its circuit is broken suddenly, giving rise to oscillatory conditions. An Fe wire (0.1 mm. diameter) can show magnetic viscosity 30 min. after a change of magnetic force.

J. W. S.

Theory and measurement of the magnetic properties of iron. D. C. GALL and L. G. A. SIMS (*J. Inst. Electr. Eng.*, 1934, 74, 453—468).—The methods of representing ferromagnetic properties by means of vector diagrams and equiv. electric circuits are criticised.

A. J. M.

Magneto-resistance of bismuth, nickel, iron, cobalt, and Heusler alloy by the longitudinal magnetic field at low and high temperatures.

I. MATUYAMA (*Bull. Inst. Phys. Chem. Res. Japan*,

1934, 13, 283—313).—The change of electric resistance by the field up to 1700 gauss, and for the temp. range -196° to 830° , was measured. Magneto-resistances were calc., and their variation with field and temp. is discussed.

N. M. B.

Changes in resistance of metals in magnetic fields. P. KAPITZA (*Magnetismus*, 1933, 1—9; *Chem. Zentr.*, 1933, ii, 2798).—The increase in resistance of metals in a magnetic field varies quadratically with the field strength (I) in weak fields and linearly with (I) in strong fields. With chemically pure or annealed material linearity commences at lower (I). A theory for normal metals can be based on the assumption of a direct action of the magnetic field on the crystal lattice.

L. S. T.

Connexion between magnetisation and electrical resistance of ferromagnetic substances. W. GERLACH (*Magnetismus*, 1933, 10—24; *Chem. Zentr.*, 1933, ii, 2799).

L. S. T.

Resistance and radiation of tungsten as a function of temperature. W. E. FORSYTHE and E. M. WATSON (*J. Opt. Soc. Amer.*, 1934, 24, 114—118).—The log resistance-log temp. curve has a slope of 1.209 between 293° and 1200° abs. and 1.195 between 1200° and 2800° abs.

R. S.

Explanation of superconductivity. J. FRENKEL (*Nature*, 1934, 133, 730—731).—Theoretical.

L. S. T.

Superconductors in a magnetic field. W. J. DE HAAS [with G. J. SIZOO, J. VOOGD, and H. BREMMER] (*Magnetismus*, 1933, 59—73; *Chem. Zentr.*, 1933, ii, 2798).—A discussion.

A. A. E.

Magnetic properties of superconductors. E. F. BURTON (*Nature*, 1934, 133, 684).—Experiments with Sn are described (cf. this vol., 492).

L. S. T.

Theory of metals. R. PEIERLS (*Z. Physik*, 1934, 88, 786—791).—A reply to Kretschmann (this vol., 347).

A. B. D. C.

Molecular theory of external friction. B. DERJAGUIN (*Z. Physik*, 1934, 88, 661—675).—Neglecting intermol. forces of attraction and replacing repulsive forces by quasi-rigid components, empirical formulæ are obtained. Inclusion of cohesive forces gives a generalisation of Amonton's law. The theory can be applied to internal flow of single crystals.

A. B. D. C.

Madelung constants for some cubic lattices. T. S. WHEELER (*Phil. Mag.*, 1934, [vii], 17, 1058).—A correction of the const. for cuprite previously reported (cf. Sherman, A., 1933, 12) is not sustained.

N. M. B.

Strength properties of salt crystals containing water. V. Time variation of solution after-effects with different solvents. K. WENDENBURG (*Z. Physik*, 1934, 88, 727—740).—Dry and wetted NaCl have strength independent of cross-section. Rupture strength measured for crystals dissolving in H_2O , $\text{H}_2\text{SO}_4 + 25\%$ SO_3 , and NH_3 shows time variation up to 2 hr. after immersion, the various solvents acting differently due to dependence on their adsorbability.

A. B. D. C.

Plasticity of bismuth due to occluded gas. W. F. BERG (Nature, 1934, 133, 831; cf. A., 1926, 666). L. S. T.

Slip-bands and twin-like structures in crystals. C. F. ELAM (Nature, 1934, 133, 723).—Slip-bands occurring in crystals of Cu-Zn alloy (48–50% Zn) are described. L. S. T.

Transformation of yellow mercuric iodide into the red form. J. B. M. COPPOCK (Nature, 1934, 133, 570).—In single crystals of the yellow form cryst. from MeOH, nucleation occurs after about 15 min., usually along the whole length of the crystal edge. The interface then moves rapidly across the crystal parallel to the edges. Smaller rhombohedra of the yellow form, obtained by heating the red variety, change into the red form after approx. 5 hr., the reaction spreading slowly inwards from all four edges with the usual parallel advance of the interface. L. S. T.

Is liquid benzene allotropic? E. COHEN and J. S. BUY (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 198–201; cf. A., 1932, 452).—The kink in the v.-p. curve of C_6H_6 suggested by Menzies and Lacoss (cf. A., 1933, 668) does not exist, since the relation between $1/T$ and $\log p$ is not linear between 65° and 100°. Their results afford no evidence for allotropic liquid C_6H_6 . H. S. P.

Is liquid benzene allotropic? E. COHEN and J. S. BUY (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 278–280; cf. preceding abstract).—Vals. obtained by various authors for the sp. heat of C_6H_6 at various temp. show unexplainable divergencies. None of the measurements suggests a break in the sp. heat-temp. curve. J. W. S.

Dispersion of sound. Three energy levels. (a) M. E. ROSE, (b) W. T. RICHARDS (J. Chem. Physics, 1934, 2, 260–262, 263).—(a) Mathematical (cf. Richards, this vol., 135). N. M. B.

"Transition point" of liquid helium. E. A. GUGGENHEIM (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 294–297; cf. this vol., 136).—Theoretical. A transition point of the type postulated by Halpern is thermodynamically impossible. J. W. S.

F.p. of platinum. F. HOFFMANN and C. TINGWALDT (Physikal. Z., 1934, 35, 434–436).—The f.p. of Pt is $1773.8 \pm 1^\circ$. A. J. M.

Heat capacity curves of the simpler gases. V. Heat capacity of hydrogen at high temperatures. Entropy and total energy. Corrected table of free energy above 2000°. C. O. DAVIS and H. L. JOHNSTON (J. Amer. Chem. Soc., 1934, 56, 1045–1047).—Vals. of the above properties have been calc. for the range 250–5000° abs. The influence of anharmonic vibration is about 0.5 g.-cal. per mol. per degree at 5000° abs. The influence of mol. stretching is also relatively large and passes through a max. about 3500° abs. E. S. H.

Specific heats of solid metals at high temperatures. XV. Redetermination of the specific heats of palladium. F. M. JAEGER and W. A. VEENSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1934,

37, 280–283; cf. A., 1932, 220).—The max. previously found in the c_p - t and C_p - t curves for Pd were due to experimental error. The c_p - t curve is almost a straight line, but the slope increases slightly above 1125°. The sp. heat and at. heat are given by $c = 0.058378 + 0.120548 \times 10^{-5}t + 0.258 \times 10^{-9}t^2$, and $C_p = 6.2288 + 0.12862 \times 10^{-2}t + 0.27528 \times 10^{-7}t^2$. The val. of 3R g.-cal. is exceeded for C_p at -150° and for C_v at -120° . J. W. S.

Specific heats of beryllium, germanium, and hafnium at low temperatures. S. CRISTESCU and F. SIMON (Z. physikal. Chem., 1934, B, 25, 273–282).—Measurements extend from 10° abs. to room temp. With Be between 10° and 14° there is an anomaly which at its max. is of the order of the normal val. of the sp. heat at this temp. Ge exhibits an anomaly similar to those observed with grey Sn, Si, and diamond, but whilst the anomaly begins similarly to a Schottky function it goes over into the NH_4 type towards its upper temp. limit. With Hf there is an anomaly with a sharp peak at 75° which resembles the behaviour of ferromagnetic substances at the Curie point. R. C.

Rotational heat of the molecules H^1H^2 and H^2 . K. CLUSIUS and E. BARTHOLOME (Naturwiss., 1934, 22, 297).—The variation of sp. heat between 35° abs. and the temp. of liquid air of mixtures of the H isotopes was determined, and the rotation heat of H^1H^2 and H^2 found. H^1H^2 is a normal diat. rotator. No mol. modifications exist. H^2_2 consists at room temp. of two mol. types, and the mixture contains 2 parts of ortho- H^2_2 and 1 part of para- H^2_2 . The equilibrium $2H^1H^2 \rightleftharpoons H^2_2 + H^2_2$ is fixed by cooling from 1000° to room temp. The equilibrium ortho- H^2_2 para- H^2_2 lies towards the left in the absence of catalysts at 14° abs. It is fixed by cooling to 12° abs. A. J. M.

Spectroscopic calculation of molecular heats of air, oxygen, and nitrogen. M. TRAUTZ and H. ADER (Z. Physik, 1934, 89, 1–11).—Rotation and vibrational contributions to the mol. heat capacities of air, N_2 , and O_2 are determined from spectroscopically observed frequencies and moments of inertia. A. B. D. C.

Rotation heat capacity of water vapour. M. TRAUTZ and H. ADER (Z. Physik, 1934, 89, 12–14).—Mecke's analysis of the H_2O spectrum (A., 1933, 6) is used to determine this heat capacity. A. B. D. C.

Calculation of the molecular heat of molecular and atomic chlorine. M. TRAUTZ and H. ADER (Z. Physik, 1934, 89, 15–23).—The heat capacities of Cl and Cl. are determined, taking into account isotopic effects. A. B. D. C.

The "chemical constant." K. POSTHUMUS (Rec. trav. chim., 1934, 53, 598–606).—The first part of a calculation of errors due to simplifying assumptions in integrating the Clausius-Clapeyron equation. F. L. U.

Fundamental equation of gases. V. K. JABECZYNSKI (Rocz. Chem., 1934, 14, 171–176).—In the form of van der Waals' equation (I) given previously (this vol., 481), $f_1(w)$ may be calc. from $w^2[(dp/dT)_w T - p] = \text{const. } (a_1)$ for a given gas, corre-

sponding with van der Waals' const. a , but independent of temp. and pressure. (I) is given in the form $(p+a/w^2)(w-b)=[R+(w-b)f_2(w)/w^2]T$, in which $f_2(w)T/w^2$ represents the repulsive force between gaseous mols. R. T.

Dependence of "vapour pressure" on temperature above the critical point. M. TRAUTZ and H. ADER (Physikal. Z., 1934, 35, 446—449).—The "v.p." of CO_2 above its crit. temp. has been determined. Using the crit. vol. in the determination of the v.p., the v.-p. curve shows no discontinuities. A. J. M.

Surface vapour pressure and the heat of surface vaporisation. J. SAMESHIMA (Proc. Imp. Acad. Tokyo, 1934, 10, 155—158).—The surface latent heat of vaporisation of myristic acid, calc. from the author's measurements of the temp. dependence of the surface v.p., using the Clausius-Clapeyron equation, is 2457 g.-cal. per mol., from which the range of the attractive force of a mol. is deduced to be 34 Å. R. S. B.

Calculating the vapour pressure of pure liquids. V. A. KIREEV (J. Appl. Chem. Russ., 1934, 7, 1—15).—The v.p., p_a , of a liquid A is given by $\log p_a - L_a \log p_b / L_b + C$, where p_b is the v.p. of a second liquid B , and L_a and L_b are the respective latent heats of vaporisation. The results calc. from this equation are better than those calc. from Henglein's or Düring's equation. A nomogram is given from which the v.p. at various temp. of a no. of liquids can be read. R. T.

Determination of the composition of binary and ternary liquid mixtures by means of V. Meyer vapour density determinations. P. DE PAUW (Chem. Weekblad, 1934, 31, 253—254).—The method of calculating the % of a third substance in a mixture with two others from the vapour density of the binary and ternary mixtures is given, and a convenient form of apparatus for the determination is described. H. F. G.

Viscosity formula for binary mixtures, the degrees of association of the constitutions being considered. IX. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1934, 9, 155—160).—The data of previous workers are recalcd. on the author's theory. D. R. D.

Composition of binary mixtures and their viscosities. B. D. MACLEOD (Trans. Faraday Soc., 1934, 30, 482—493).—The formula $\eta=[\eta_1 m_1 x_1/x_T]$ is proposed for the viscosity η of a mixture of two liquids. x_1 and x_2 represent the free space per c.c. for the pure liquids, x the corresponding quantity for the mixture for which the molar composition is given by m_1 and m_2 . Vals. of M_a/M_c (actual mean mol. wt./calc. mean mol. wt.) given by this equation agree with the law of mass action applied to the formation of an intermol. compound, but the of reaction calc. from the temp. dependence of the dissociation const. shows variations which are attributed to the influence of temp. on the free space. R. S. B.

Porter's rule. A. M. RENTE and F. E. SEUFFERT (Ind. Eng. Chem., 1934, 26, 550—551).—Porter's rule

applies to solutions of electrolytes, and the lines of equal η for different concns. of a given electrolyte are usually concurrent. D. R. D.

Viscosity [and density] of mixed salt solutions.

I. Solutions of potassium and zinc sulphates. A. BANCHETTI (Gazzetta, 1934, 64, 229—234).—Data for 0.1 and 0.5 M aq. solutions at 25° are given. The formation of complexes is suggested. D. R. D.

Refractometric investigation of mixed salt solutions, and ionic deformation. G. SPACU and E. POPPER (Z. physikal. Chem., 1934, B, 25, 460—470).—For solutions of single salts the mol. refraction, R , changes approx. linearly with the concn. Deviations of R from additivity in solutions containing two salts and in which compound formation does not occur are ascribed to ionic deformation, the deviations for $\text{KCl}+\text{NaCl}$ being $>$ for $\text{NaNO}_3+\text{KNO}_3$. The deviation curve consists of two intersecting straight lines. Where compounds are formed the deviation curve is entirely different in form and has one or more max. R. C.

Use of ethyl ether as solvent in electric moment studies. K. HIGASI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 57—78).— Et_2O is claimed to have a low enough mol. field to be a suitable solvent for electric moment studies. Results for electric moments, except where stated at 20°, in 10^{-18} e.s.u.: C_6H_6 (25°) approx. 0, PhMe (25°) 0.3, PhCl (25°) 1.3, COMe_2 2.2, PhNO_2 (25°) 3.2, EtOH 1.8, Bu^nOH 1.8, amyl alcohol 1.8, borneol 1.7, $\alpha\text{-C}_{10}\text{H}_7\text{OH}$ 1.9, H_2O 1.9, I 0.7, $[\text{CH}_2\text{Cl}]_2$ 1.5, cetyl alcohol 1.81. The polarisation curve of EtOH in Et_2O is approx. linear, in contrast to results with non-polar solvents. The temp. dependence of the electric moments of EtOH , $[\text{CH}_3\text{OH}]$, and AcOH is given and discussed. R. S. B.

Faraday effect of strong electrolytes in aqueous solutions. I. A. OKAZAKI (Mem. Ryojun Coll. Eng., 1933, 6, 181—219).—The magneto-optical rotations of twenty strong electrolytes have been measured, using wave-lengths near to 350 $m\mu$, also their magneto-optical dispersions between 590 and 340 $m\mu$. The sp. rotation is generally nearly independent of concn., but decreases with increasing concn. for HCl and LiCl . The latter effect can be explained by the existence in conc. solutions of undissociated mols. F. L. U.

Heats of fusion of titanium tetrachloride, carbon tetrachloride, and antimony pentachloride. N. NASU (Bull. Chem. Soc. Japan, 1934, 9, 198—205).—The heats of fusion of TiCl_4 (12.90 g.-cal. per g.), CCl_4 (4.40 g.-cal. per g.), and SbCl_5 (6.40 g.-cal. per g.) are calc. from the f.-p. data for binary mixtures. D. R. D.

Composition of the vapour phase over binary mixtures. I. KRITSCHESKI and J. KASARNOVSKI (Z. anorg. Chem., 1934, 218, 49—59).—The numerical integration of the Gibbs-Duhem equation has been carried out and applied to the systems $\text{CS}_2\text{-COMe}_2$, PhMe-AcOH , and $\text{AcOH-H}_2\text{O}$. The accuracy of the calc. val. is limited only by that of the observed relation between total v.p. and composition. F. L. U.

Liquid-vapour equilibria of mixtures of aromatic and non-aromatic hydrocarbons. III. Mixtures of benzene and non-aromatic hydrocarbons. M. MIZUTA (J. Soc. Chem. Ind. Japan, 1934, 37, 113B).—The shape of the equilibrium curve for mixtures of C_6H_6 with light petroleum b.p. 50–97° shows that C_6H_6 could be easily conc. in the vapour phase up to 0.7 mol. fraction, but that further concn. would be difficult. A. G.

Vapour-liquid equilibrium of hydrocarbon mixtures. H. A. BEATTY and G. CALINGAERT (Ind. Eng. Chem., 1934, 26, 504–508).—Data are recorded for the following systems at the temp. given: C_6H_6 –*cyclohexane* (78.8°); Δ^7 -heptene– n - C_7H_{16} (I) (97.2°); (I)– β - δ -trimethylpentane (II) (97.2°); (I)–methyl-*cyclohexane* (97.2°); (II)– n - C_8H_{18} (III) (98.1°); (I)–(III) (97.2°); C_6H_6 –PhMe (79.6°); n - C_6H_{14} –(I) (67.5°). The effects of small deviations from the ideal mixture law on the no. of plates required in fractionation are tabulated. D. R. D.

Determination of azeotropic composition. Azeotropes of benzene and cyclohexane. A. BOUZAT and M. SCHMITT (Compt. rend., 1934, 198, 1923–1925).—The compositions of azeotropic mixtures (I) of C_6H_6 and *cyclohexane* have been determined for a range of pressure. The % of C_6H_6 in (I) diminishes with increasing pressure (cf. Merriman J.C.S., 1913, 103, 1807). B. W. B.

B.p. of concentrated solutions of the system $(K, NH_4)(NO_3, Cl)$. S. I. ARONOVA and Z. N. LUNSKAYA (Trans. Sci. Inst. Fertilisers, Moscow, 1932, No. 92, 139–148). CH. ABS.

Concentration by partial condensation in two-component systems. E. KIRSCHBAUM (Chem. Fabr., 1934, 7, 109–111).—The enrichment of the more volatile substance by partial reflux condensation is discussed, and a method is given for deriving the "enrichment curves." A typical example is given for the system C_6H_6 –PhMe. The assumption that the falling liquid is in equilibrium with the adjacent vapour leads to a mean divergence of –60% from experimental results, whilst if it is assumed that the condensed and uncondensed vapours are in equilibrium the mean error is +27%. The author's treatment involves a mean error of only +1.9%. H. F. G.

Diffusion in metals. W. SEITH, E. HOFER, and H. ETZOLD (Z. Elektrochem., 1934, 40, 322–326; cf. A., 1932, 1195).—Velocities of diffusion of Mg, Cd, Ni, and Hg in Pb, and of Pb and Hg in Cd have been measured. Diffusion of Pb in Sn has been observed; diffusibility in Pb decreases in the order Au, Ag, Mg, Cd, Hg, Bi, Tl, Sn. F. L. U.

Superconductivity of alloys. G. TAMMANN (Z. Metallk., 1934, 26, 61).—From a consideration of recent work of Meissner and of Allen rules are derived for the onset of superconductivity in solid solutions, eutectics, and two-phase alloys and the effect thereon of magnetic fields. A. R. P.

Theory of transition of metallic mixed phases. G. BORELIUS (Ann. Physik, 1934, [v], 20, 57–74).—An expression for the free energy of mixed phases as a function of the extent of disorder of atoms is derived

and tested by reference to the X-ray structure of the alloys and resistance data. A. J. M.

Eutectic of the system antimony-lead. O. QUADRAT and J. JIKISTE (Chim. et Ind., 1934, 31, Spec. No., 485–489).—Melts containing 20, 15, and 13% Sb deposit crystals of Sb, leaving a eutectic containing 11.4–11.5% Sb, and not the previously recorded 13% Sb. R. S.

Electrochemical and X-ray examination of solid thallium-lead alloys. A. ÖLANDER (Z. physikal. Chem., 1934, 168, 274–282).—The potential of $Tl_{solid}|(Na, K, Tl)OAc|(Tl, Pb)_{solid}$ and its temp. coeff. have been measured for forty-one alloy electrodes at 245–295°, and X-ray diagrams of various Tl–Pb alloys obtained. The lattice const. show that the boundary between α and β phases is at 54.6 at.-% Tl. Between 54.6 and 92.5 at.-% Tl there is an intermediate phase, Tl₇Pb, which accounts for Kurnakow's conductivity data (A., 1909, ii, 855). R. C.

Electrical conductivity and equilibrium diagram of binary alloys. XII. System lithium-bismuth. G. GRUBE, H. VOSSKUHLE, and H. SCHLECHT (Z. Elektrochem., 1934, 40, 270–274).—The system forms the compounds Li_3Bi (m.p. 1145° without decomp.) and $LiBi$ (formed by a peritectic reaction at 415°). $LiBi$ exists in two polymorphic forms, with a transition temp. at 400°. The formation of solid solutions has not been observed. E. S. H.

Microscopical examination of iron-tin reaction products. W. D. JONES and W. E. HOARE (Iron and Steel Inst., May, 1934, Advance copy, 8 pp.).—Annealing and quenching experiments and diffusion tests at various temp. have afforded evidence of the existence of the compounds $FeSn_2$, $FeSn$, and Fe_2Sn . $FeSn$ decomposes into Fe_2Sn and Sn at 710–850°. No evidence for the existence of a γ -phase at 68.5% Sn and 850° could be obtained (cf. Ehret and Westgren, A., 1933, 562). A. R. P.

Nickel-chromium system. E. R. JETTE, V. H. NORDSTROM, B. QUENEAU, and F. FOOTE (Amer. Inst. Min. Met. Eng., Inst. Met. Div., Tech. Pub., 1934, No. 522, 11 pp.).—X-Ray investigations show that at < 1150° there are two terminal solid solutions with an intervening two-phase area. On the Cr side the solubility of Ni in Cr is low, but increases rapidly at > 900°. The solubility of Cr in Ni increases uniformly and rapidly with rise in temp., that at 1153° being nearly 53 wt.-% Cr, which is beyond the eutectic point as determined by thermal analysis. The only structures observed were body-centred Cr, face-centred α and occasionally rhombohedral Cr_2O_3 . CH. ABS.

Alloys of platinum with chromium. V. A. NEMLOV (Z. anorg. Chem., 1934, 218, 33–44).—1 e Brinell hardness-composition curve of Cr–Pt alloys shows well-marked min. corresponding with compounds Cr_2Pt and $CrPt$. Examination of the microstructure confirms the existence of the latter. A alloy quenched from a high temp. show only mixed crystals from which $CrPt$ separates on annealing. In annealed specimens there is a continuous series of mixed crystals between 0 and 25 at.-%, and another between 100 and 100 at.-% Pt. The electrical resistance rises

steeply with increasing Cr content up to 13 at.-% Cr, beyond which the alloys are no longer ductile. Alloys containing 4–5% Cr have about five times the resistance of Pt, and a higher m.p. H_2SO_4 , HCl , and HNO_3 , dil. or conc., show no action either at room temp. or at their b.p. on polished surfaces of alloys with a Cr content ≥ 14 at.-%. F. L. U.

Transition of β -brass. H. VON STEINWEHR and A. SCHULZE (Physikal. Z., 1934, 35, 385–397).—The thermal change and the variation of the expansion, thermo-electric force, and resistance with temp. show that the transition is not sudden, but takes place over a temp. range (430–480°). The heat change is 3 g.-cal. per g. Equilibrium is rapidly attained at any given temp. A. J. M.

Distribution of thorium-B in some metals. W. SEITH and A. KEIL (Z. Metallk., 1934, 36, 68–69).—The metal obtained by electrolysis of a molten mixture of KCl and PbCl_2 or TlCl containing Th-B (I) gives a radiogram showing regular distribution of (I) throughout. When Cd or Bi is prepared similarly from a bath containing traces of Pb and (I), both these are irregularly distributed along the crystal boundaries, and on annealing tend to migrate towards the outside of the ingot. Th-C distributes itself homogeneously throughout Bi, and by its aid self-diffusion of Bi can be studied. A. R. P.

Equilibrium diagram for ternary alloys. V. FISCHER (Z. Metallk., 1934, 26, 80–82).—The use of an orthogonal plane co-ordinate system for representing the equilibrium of ternary alloys is illustrated by reference to the Ni-Cu-Mn, Cu-Ag-Au, and Ag-Pb-Sn systems. A. R. P.

Constitution and properties of the alloys of magnesium with aluminium and copper. A. PORTEVIN and P. BASTIEN (Chim. et Ind., 1934, 31, Spec. No., 490–518).—Thermal analysis of alloys rich in Mg indicates a liquidus from which the separating solid phases are Mg , Mg_3Al_2 , Mg_2Cu , and $\text{Mg}_2\text{Cu}_3\text{Al}_2$; the eutectics Mg 56.5, Al 26.5, Cu 17%, m.p. 412°, and Mg 67.5, Al 0.5, Cu 32%, m.p. 484°; two saturated solid solutions (a) rich in Mg: Mg 85, Al 8.8, Cu 6.2%, (b) rich in Mg_3Al_2 : Mg 58, Al 41.4, Cu 0.6%. Micrographic data, hardness, coeff. of expansion, density, and electrical conductivity data are also recorded. Alloys containing 12% Cu can be forged, and possess good mechanical properties, hardness, and thermal conductivity, whilst others (Al+Cu $\leq 15\%$) have mechanical properties comparable with those of electron and duralumin. Corrosion of the ternary alloys increases slowly in 1% HCl and more rapidly in 0.5N- MgCl_2 with increasing Cu and const. Al content. Corrosion of Mg-Cu alloys in sea- H_2O is reduced by addition of Al, and becomes const. with Al $> 3\%$. R. S.

Properties of ferromagnetic alloys of the ternary system iron-nickel-vanadium. H. KÜHLEWILN [with R. STÖRMER] (Z. anorg. Chem., 1934, 218, 65–88; cf. A., 1930, 1245).—The structure diagram of alloys with up to 30% V shows (1) a region of mixed crystals of space-centred cubic type (α), (2) mixed crystals of face-centred cubic type (γ), and (3) a heterogeneous field of α + γ mixed crystals. In

the γ -range the Curie point is depressed by addition of V by about 40° per 1%. Diagrams showing the variation of sp. resistance and various magnetic properties with composition are given. F. L. U.

F.p., m.p., and solid solubility limits of alloys of silver and copper with elements of the B sub-groups. W. HUME-ROTHERY, G. W. MABBOTT, and K. M. C. EVANS (Phil. Trans., 1934, 233, A, 1–97).—Solubility limits have been completely determined in the systems Cu-Ga, Cu-Ge, Cu-Sb, Ag-Al, Ag-Ga, Ag-Cd, and Ag-In. Confirmatory investigations have been made on Cu-Zn, Cu-Al, Cu-As, Ag-Sn, Cu-Zn-Ga, Cu-Zn-Ge, and Cu-Ga-Ge. Formation of solid solutions of the substitutional type is determined primarily by the respective at. diameters of solvent and solute. The at. compositions of alloys of a given f.p. vary inversely as the valency (n) of the solute as far as group V, and those of alloys of a given m.p. are $\propto 1/n^2$ as far as group IV, when solvent and solute are in the same period. Methods are given for the accurate calculation of liquidus points in ternary and quaternary alloys where the binary curves are known. In certain ternary alloys solubility limits can be approx. calc. when the at. size factors are favourable, since the max. solubility of the α solid solution and the part of the solubility curve in which solubility diminishes with fall of temp. are determined mainly by the electron concn. F. L. U.

Apparent mixed crystals. I. A. BENRATH and H. SCHACKMANN (Z. anorg. Chem., 1934, 218, 139–145).—The systems BaSO_4 - KMnO_4 - H_2O and CaCO_3 - NaNO_3 - H_2O fulfil the requirements laid down by Grimm for the formation of mixed crystals. No mixed crystals are formed, however, owing to the large differences in solubility between the components. M. S. B.

Ferrites. Formation of solid solution between some ferrites. N. KAWAI (J. Soc. Chem. Ind. Japan, 1934, 34, 174B).—Mixtures containing various proportions of two or three of the ferrites FeO , Fe_2O_3 , NiO , Fe_3O_4 , CuO , Fe_2O_3 , CoO , Fe_2O_3 , ZnO , Fe_2O_3 , CdO , Fe_2O_3 , and MgO , Fe_2O_3 , after heating to sintering, have been examined microscopically and magnetically. It is inferred that solid solutions are formed. R. S. B.

Influence of degree of dispersion on physico-chemical constants. III. E. COHEN and W. A. T. COHEN-DE MEESTER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 270–274; cf. A., 1933, 19).—The solubility of salicylic acid in H_2O is increased by grinding with Au balls either in the dry state or in contact with H_2O . The results cannot be explained as a cold-working effect. J. W. S.

Solubility of silver chloride. P. C. DAVE and K. R. KRISHNASWAMI (J. Indian Inst. Sci., 16, A, 153–165).—The solubility (S) of AgCl in H_2O and aq. solutions of HNO_3 , NaNO_3 , KNO_3 , and NH_4NO_3 has been determined nephelometrically between 0° and 50°. S in H_2O at 25° is 1.388×10^{-5} mol. per litre, as compared with 1.373×10^{-5} from conductivity measurements. S in aq. HNO_3 is slightly greater than in H_2O , and independent of concn. In aq. NaNO_3 S increases rapidly with concn., reaching

18.4×10^{-5} in a saturated solution, this behaviour being attributed to formation of complex ions.

F. L. U.

Solubility of calcium iodate in aqueous solutions of various electrolytes. J. B. CHLOUPEK, V. Z. DANES, and B. A. DANEŠOVA (Chem. Listy, 1934, 28, 93—94).—Data are recorded for solutions containing 0.002, 0.1, and 0.5*M*-KNO₃, -K₂SO₄, -MgCl₂, and -MgSO₄.

R. T.

Solubilities of calcium hydroxide, calcium iodate, and ammonium perchlorate in dilute ammoniacal solutions. I. M. KOLTHOFF and V. A. STENGER (J. Physical Chem., 1934, 38, 639—643; cf. A., 1932, 1084).—Solubilities have been determined at 25° in aq. NH₃ up to 2*N*. The solubility of CaO is (0.1194—0.016*C*_{NH₃}) g. per 100 c.c. solution. Under the above conditions no complex compounds are formed between Ca(OH)₂ or Ca⁺⁺ and NH₃.

F. L. U.

Amphoteric character of silver hydroxide. E. LAUE (J. Amer. Chem. Soc., 1934, 56, 1249—1250).—A criticism (cf. A., 1933, 773).

E. S. H.

Solubility of silver oxide in water and in alkali. H. L. JOHNSTON, F. CUTA, and A. B. GARRETT (J. Amer. Chem. Soc., 1934, 56, 1250).—A reply (cf. preceding abstract)

E. S. H.

"Induced" solubility of ferric hydroxide and other hydroxides in alkali hydroxide in presence of chromic hydroxide. H. KNOCH (Kolloid-Z., 1934, 67, 195—203).—Freshly-pptd. Cr(OH)₃ dissolves in aq. NaOH or KOH when < 1 equiv. of alkali is present, forming sols which may solidify to jellies at certain concns. The effect of KOH is > that of NaOH, but the amount required for dissolution of a given amount of Cr(OH)₃ depends on the concn., the velocity of mixing, and on the age of the Cr(OH)₃. The ageing of Cr(OH)₃ is more rapid as the concn. of alkali increases, and is accelerated by NaCl and KCl. The pptd. Cr(OH)₃ from a green CrCl₃ solution ages more quickly than that from a violet solution. Conductometric titration shows that only a small amount of chromite is formed in the alkaline solution.

E. S. H.

Partition of saturated fatty acids between water and toluene. N. DE KOLOSOVSKI and (MLLE.) E. PONOMAREVA (Bull. Soc. chim., 1934, [v], 1, 66—69; cf. A., 1932, 1198).—Data are recorded for butyric and isovaleric acids. The log. partition coeff.—concn. curves for all fatty acids so far investigated are parallel and tend to ∞ at zero concn. They are of the form to be expected in view of the existence of simple mols. in the PhMe and of dissociated mols. in the H₂O.

J. W. S.

Application of distribution methods to the determination of the activity coefficients of molecules in salt solutions. E. LARSSON (Svensk Kem. Tidskr., 1934, 46, 78—83).—These methods often fail owing to mutual solubility of the phases and hydration or association of the solute. Data are given for activity coeffs. of BzOH, salicylic acid, and CH₂Ph·CO₂H in salt solutions, determined by partition with Et₂O, isoamyl ether, and C₆H₆.

Vals. from solubility determinations are given for comparison.

R. P. B.

Fractional precipitation of radiferous barium sulphate. (MME.) B. E. MARQUES (Compt. rend., 1934, 198, 1765—1767).—The distribution of Ra between BaCl₂ solution and BaSO₄ pptd. by 0.01*N*- or 0.001*N*-H₂SO₄ has been studied. Doerner and Hoskins' law (A., 1925, ii, 381) is verified; the distribution coeffs., however, vary slightly with the rate of pptn.

B. W. B.

Theoretical study of the absorption of a very soluble gas by a liquid drop. S. HATTA and A. BABA (J. Soc. Chem. Ind. Japan, 1934, 37, 162—163B).—An equation is derived for the rate of absorption of a gas by a falling drop of liquid. It is assumed that for a very sol. gas the resistance of the liquid film may be neglected, and that the const. is proportional to the *n*th power of the rate of fall.

Absorption of ammonia by a water drop. S. HATTA, T. UEDA, and A. BABA (J. Soc. Chem. Ind. Japan, 1934, 37, 164—165B).—The absorption of NH₃ mixed with O₂ by falling drops of H₂O is expressed by the equation previously derived (cf. preceding abstract), when the concn. of the NH₃ and the height of fall are varied.

A. G.

Adsorption of hydrogen by palladium-black under high pressure. V. IPATIEFF, jun., and W. G. TRONOV (J. Physical Chem., 1934, 38, 623—633).—Absorption isotherms of H₂ in Pd-black have been determined between 1 and 27 atm. at 15°, 25°, 100°, 150°, 200°, and 300°. The isotherms tend to become straightened out at higher temp. There is no indication of saturation at the highest pressure reached.

F. L. U.

Influence of mercury on the electrolytic adsorption of hydrogen by iron. H. PLOUM (Z. Elektrochem., 1934, 40, 267—270).—Small amounts of HgCl₂ in acid or alkaline solutions catalyse the adsorption of H₂ by Fe cathodes. It is probable that a volatile Hg hydride is formed.

E. S. H.

Diffusion of hydrogen through metals: fractionating the hydrogen isotopes. C. G. FINE, H. C. UREY, and D. B. LAKE (J. Chem. Physics, 1934, 2, 301).—A note on a previous paper (cf. this vol., 360).

N. M. B.

Sorption of water vapour on chabasite at various temperatures. A. TISELIUS and S. BROHULT (Z. physikal. Chem., 1934, 163, 248—256).—Sorption isotherms at 50—150° for H₂O vapour pressures of 0.008—15 mm. have been obtained. At the lower temp. these approximate in form to Langmuir's isotherm. The sorption is reversible. The heat of sorption, calc. from the isotherms, is a max. when the amount of H₂O sorbed is about 20%.

R. C.

Vapour-binding power of active charcoal. II. Dependence of the amount of retained gas on the streaming velocity of the replacing gas. III. Dependence on particle size. F. and H. WEJROCH (Kolloid-Z., 1934, 67, 161—163, 163—167; cf. this vol., 358).—II. The amount of adsorbed C₆H₆ retained by C after a given time in

an air stream is the greater the less is the velocity of the air, but the amount retained after passage of a given quantity of air is independent of its velocity.

III. When the particle size is < 1.5 mm. the rate of removal of adsorbed C_6H_6 by an air stream is independent of particle size, but with larger particles the initial rate is less, becoming $>$ that for small particles at a later stage. E. S. H.

Sorption of water vapour by cellulose acetate. R. SHINODA (J. Cellulose Inst. Tokyo, 1934, 10, 114—126).—Secondary cellulose acetate (I) adsorbs about twice as much H_2O as primary (I), there being a linear relation between Ac content and adsorption. Kinetically adsorption occurs in two stages, a fast stage for which $\log \{S_\infty / (S_\infty - S_t)\} - Kt$ followed by the slower stage $S - K' + a \log t$, where S is H_2O adsorbed and a is a const. Adsorption falls with rising temp. at const. R.H.; it is less for the following substances than for (I) and falls in the order given: mannan acetate, ethylcellulose, benzylcellulose. A. G.

Adsorption properties of various soluble compounds. J. RAE (Pharm. J., 1934, 132, 607).—Samples of Bi, Ca, and Mg carbonates differ considerably in their methylene-blue absorptions, but these are not related to the apparent d . A. G.

Behaviour of the diamino-acids from protein hydrolysis towards permutit. V. S. SADIKOV and E. V. LINDKVIST-RISAKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 575—578).—From the products of hydrolysis of casein, permutit removes up to 93% of the total diamino-acids, and about half the total monoamino-acids. The former cannot be washed out with H_2O , but are almost completely removed with 30% H_2SO_4 . The behaviour of the permutit depends on its origin and composition. J. W. S.

Adsorbing power of some iron hydrates. E. ALLESI (Gazzetta, 1934, 64, 161—168).—The adsorption of Na arsenite from aq. solution by various Fe^{II} and Fe^{II} - Fe^{III} hydroxides is related to the magnetic properties of these hydroxides. The min. adsorbing power corresponds with max. magnetic susceptibility of the hydroxide. The adsorbing power of $Fe(OH)_3$ varies with its method of prep.; e.g., the hydroxide obtained from the cryst. sulphate adsorbs much $<$ that obtained from a solution of a Fe^{II} salt oxidised with hot HNO_3 . O. J. W.

Adsorption of electrolytes at heteropolar crystal surfaces. D. BALAREV and A. KOLUSCHEVA (Kolloid-Z., 1934, 67, 203—207).—Balarev's theory of inner adsorption is discussed. E. S. H.

Determination of surface area by adsorption water molecules. J. H. DE BOER and C. J. DIPPEL (Z. physikal. Chem., 1934, B, 25, 399—410).—^H vapour is very tenaciously adsorbed by powdered or vac.-sublimed films of CaF_2 , and even on exposure to high vac. at room temp. a unimol. adsorbed film still remains. The no. of adsorbed mols. can be ascertained by interaction with Cs and determination of the amount of H_2 or Cs_2O formed. The complete unimol. film each F' ion of the surface adsorbs one H_2O mol. On heating, the H_2O reacts with adsorbing F' ions, forming HF and rendering the

surface alkaline. The sp. surface of vac.-sublimed CaF_2 is about 240 sq. m. per g., and the mean thickness of the lamellae 0.25×10^{-8} to 0.3×10^{-8} cm. In the adsorption of H atoms by a vac.-sublimed film of CaF_2 each F' ion holds one H atom, whereas in the adsorption of I one mol. is adsorbed by every two F' ions. With *o*- and *p*-nitrophenol there are 2 and 4 F' ions, respectively, to each adsorbed mol. in the first layer of adsorbed mols., but a second layer is formed on this by van der Waals forces. R. C.

Nature of adsorption forces. J. H. DE BOER and J. F. H. CUSTERS (Z. physikal. Chem., 1934, B, 25, 225—237).—Polanyi and London's formulæ for van der Waals adsorption give vals. for adsorption energy on C $<$ the observed vals. If the structure and mol. roughness of the surface are taken into account the discrepancy disappears. The rule that energy of adsorption is approx. half the geometric mean of the heats of vaporisation of the two components is accounted for. Mols. with peripherally situated dipoles adsorbed on surfaces constituted of ions will principally be oriented and bound electrostatically. Thus $PhOH$ on $NaCl$ will have the OH group adsorbed electrostatically on the Cl ions, whilst the Ph ring will be held principally by van der Waals adsorption with the flat side parallel to the surface. In van der Waals adsorption the energy is greatest in the fissures or cavities of a surface and the mols. are fixed by preference above the centres of the unit cells. In electrostatic adsorption the energy is greatest on projecting points and edges, and the adsorbed mols. are situated above the ions of the adsorbent. R. C.

Adsorption and amount of adsorbent. III. A. RABINERSON, T. PAPKOVA-KVITZEL, and A. PITTEL (Kolloid-Z., 1934, 67, 154—161; cf. this vol., 359).—In the adsorption of $AcOH$ by C the expression $x = km^{1/n}$ is valid for medium amounts of adsorbent (m). The val. of $1/n$ is not const., but tends towards 1 when m is small and towards 0 when m is great. Anomalies are noted in the adsorption of Me-violet by C. E. S. H.

Mathematical and experimental studies on repeated extraction of adsorption systems in equilibrium. II. J. VOIGT (Kolloid-Z., 1934, 67, 148—154; cf. this vol., 485).—Theoretical.

E. S. H.

Formation and properties of precipitates. Theory of co-precipitation. II. I. M. KOLTHOFF (Chem. Weekblad, 1934, 31, 230—237, 244—251).—Adsorption on ppts. may involve simple ionic exchange, as in the case of a dye on $PbSO_4$, when the difference between the concns. of the lattice cations and anions increases with the quantity and degree of fineness of the ppt.; true adsorption, at active centres only; true adsorption followed by secondary pptn. of the displaced lattice ions; exchange with a third kind of ion already adsorbed on the surface of the ppt., which is of importance in the washing of ppts.; mol. adsorption; and activated adsorption, in which the adsorbed substance is ionised in the surface layer. Wool-violet (I) forms a unimol. layer on $PbSO_4$ (II), there being 1 mol. of (I) per mol. of (II) in the surface, but with an excess of SO_4^{--} in the solution the saturation point is reached at higher (I) concns., since (I) displaces

SO_4^{2-} in the surface layer. Adsorbed dyes retard the rate of crystallisation of (II). Paneth and Vorwerk's view that $\text{Pb}(\text{NO}_3)_2$ (III) at low concns. forms unimol. layers on (II) is incorrect; neither (III) nor Na_2SO_4 is adsorbed by (II), even when freshly pptd.

H. F. G.

Applications of a method of capillary analysis. R. DUBRISAY (Chim. et Ind., 1934, 31, Spec. No., 200—202).—The drop method has been used to study the relative effects of lauric, myristic, palmitic, and stearic acid dissolved in C_6H_6 on the C_6H_6 -aq. NaOH interfacial tension. Applications of the method to the study of neutralisation processes (e.g., of wines, and the attack of glass by H_2O), and the examination of fatty acids are discussed.

H. J. E.

Simple method of testing the orientation of molecules on the surface of water or aqueous solutions. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1934, 9, 161—165).—The end-point in Frumkin's method (A., 1925, ii, 856) is found by the abrupt increase in the time of evaporation of the solvent when the surface is saturated. The no. of mols. per sq. cm. of lauric and palmitic acids, cetyl alcohol, and cetyl and myristyl palmitates is scarcely affected by the presence of small amounts of halides or of sucrose.

D. R. D.

Physical and chemical behaviour of molecules on outside surfaces. R. SUHRMANN (Chem.-Ztg., 1934, 58, 411—413).—Unimol. films on solid or liquid surfaces behave like two-dimensional gases. Electrical polarisation of mols. in films is shown by changes in light absorption, in emission potential, and in contact potential.

A. G.

Physical chemistry of the non-wettability of peat by water. M. V. TSCHAPEK and N. E. SAKUN (J. Appl. Chem. Russ., 1934, 7, 197—204).—Adsorption of H_2O from $\text{EtOH-H}_2\text{O}$ and $\text{C}_6\text{H}_6\text{-H}_2\text{O}$ by peat (I) indicates that (I) is a highly hydrophilic substance, with a well-developed surface. Under ordinary conditions it is not, however, wetted by H_2O ; this is due to a film of air adsorbed on the surface of (I).

R. T.

Dependence of the action of filter and sorption vessels on the direction of streaming. H. REMY [with K. HOLTHUSEN] (Kolloid-Z., 1924, 67, 167—171).—The sorptive effect of a combination of a loosely-packed wad and a CaCl_2 tube on NH_4Cl fumes depends on whether the fumes pass through the wad or CaCl_2 first; with a tightly-packed wad the effect is independent of the direction. The sorption of SO_3 fumes by combinations of a wad with conc. H_2SO_4 or P_2O_5 is independent of the direction of streaming.

E. S. H.

Origin of osmotic pressure and its theoretical calculation. K. WOHL (Z. Physik, 1934, 88, 800—805, 820—822).—A criticism of Fredenhagen (this vol., 252).

A. B. D. C.

Origin of osmotic pressure and its theoretical calculation. K. FREDENHAGEN (Z. Physik, 1934, 88, 806—819).—A reply.

A. B. D. C.

Supposed kinetic explanation of osmotic pressure. W. HÜCKEL (Z. physikal. Chem., 1934, 168, 308—309).—Polemical.

R. C.

Supposed kinetic interpretation of osmotic pressure. A. EUCKEN (Z. physikal. Chem., 1934, 168, 309—312).—A reply to Hückel (preceding abstract) and defence of the theory that the flow of solvent through a semipermeable membrane is due to the transference of momentum from solute mols. rebounding from the membrane to solvent mols.

R. C.

Influence of dipole fields between solute molecules. I. Osmotic properties. II. Molecular polarisation. R. M. FROSS (J. Amer. Chem. Soc., 1934, 56, 1027—1030, 1031—1033).—I. Theoretical. The osmotic properties of a dil. solution of dipole mols. are derived.

II. Theoretical. The dielectric properties of the same system are derived.

E. S. H.

F.p. of some benzene solutions. C. R. BURY and H. O. JENKINS (J.C.S., 1934, 688—696).—The f.p. depression of C_6H_6 for nineteen substances has been measured by an equilibrium method. Errors in previous f.p. data due to adsorption appear to be small. The results do not support Hildebrand's hypothesis (A., 1921, ii, 307) connecting internal pressure with deviation from ideal behaviour, nor is there evidence of a direct relation between degree of association and dipole moment.

R. S.

Theory of cryoscopic determinations made by mixing the solution with the solid solvent. A. BANCHETTI (Gazzetta, 1934, 64, 221—228).—Expressions are derived for the final temp. and quantity of solid melted when excess of the frozen solvent is added to a solution. Application to Hovorka and Rodebush's experimental results (A., 1925, ii, 772) shows that the quantity of solid melted under the conditions specified by these investigators is negligible for solutions $\geq 0.005M$, but if it is ignored when the concn. is $0.01M$, an error of 1—2% in the depression is introduced.

D. R. D.

Theoretical formulæ for the Landsberger method. A. MAZZUCHELLI (Gazzetta, 1934, 64, 213—217).—The fraction of the vapour which would condense in the hot liquid is calc., assuming each bubble to reach equilibrium as it passes through the liquid, and is shown to be very small, indicating that the composition and temp. will not change appreciably during an experiment of normal duration when the solution has reached its b.p. This is confirmed experimentally in the case of resorcinol in Et_2O .

D.

Cryoscopic determination of total hydration of ions of potassium bromide. F. BOURION and (Mlle.) O. HUN (Compt. rend., 1934, 198, 1921—1923; cf. this vol., 596).—Hydration corresponds with $\text{KBr}\cdot 8.1\text{H}_2\text{O}$ and $\text{KBr}\cdot 9.6\text{H}_2\text{O}$ in $1.0M$ and $0.5M$ solutions, respectively.

B. W. B.

Application of the method of eutectic point lowering. H. MÜLLER (Compt. rend., 1934, 198, 1774—1776; cf. A., 1933, 906).—The depressions of the $\text{NH}_4\text{Cl-H}_2\text{O}$ (I) and $\text{KNO}_3\text{-H}_2\text{O}$ (II) eutectics lead to the mol. formulæ $\text{Na}_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (I) and $\text{K}_2\text{P}_2\text{O}_6$ and $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$ (II). Hydrolysis of $\text{K}_2\text{S}_2\text{O}_5$ takes place very rapidly with formation of KHSO_3 . The data also show that $\text{Na}_2\text{S}_2\text{O}_4$ is slowly hydrolysed to $\text{Na}_2\text{S}_2\text{O}_3 + \text{NaHSO}_4$.

B. W. B.

Apparent molal expansibility of electrolytes and coefficient of expansibility (thermal expansion) as a function of concentration. F. T. GUCKER, jun. (J. Amer. Chem. Soc., 1934, 56, 1017—1021).—The apparent mol. expansibility is defined as $\phi(E_2) - \alpha V - \alpha_1 V_1$, where V is the vol. of solvent in which 1 mol. of solute is dissolved, V_1 is the vol. of the resulting solution, and α and α_1 are the expansion coeff. of solution and solvent, respectively. $\phi(E_2)$ is a linear function of the vol. concn. for aq. solutions of HCl, LiCl, LiOH, NaCl, KCl, NaOH, and Na₂SO₄. The limiting val. of $\phi(E_2)$ is more positive and the negative slope greater at low temp. and with electrolytes of higher valency.

E. S. H.

Physico-chemical studies of complex acids. XI. Vapour-pressure measurements. R. A. ROBINSON and D. A. SINCLAIR (J.C.S., 1934, 642—645).—The change in v.p. of aq. Na₂O, V₂O₅, Na₂O, WO₃, and Na₂O, MoO₃ with addition of HCl is recorded, and the lowering due to the acid anions calc. Mol. wt. vals. approaching 1000 are obtained in acid solutions, indicating the occurrence of polymerisation.

R. S.

Application of simple centrifuges to the determination of particle size in colloid solutions. M. SCHLESINGER (Kolloid-Z., 1934, 67, 135—142).—A simple way of applying the sedimentation method is described. The theory is worked out and some results with Au sols are given.

E. S. H.

Tyndall light of milk, ferric chloride, and aluminium chloride solutions. T. KATSURAI (Kolloid-Z., 1934, 67, 143—145).—The change of Tyndall effect with concn. has been determined. With FeCl₃ the effect in the red region is increased by electrolytes in the order NaCl < BaCl₂ < AlCl₃. When NH₃ is added slowly to aq. FeCl₃ the effect is observed to increase only in the red region, whilst with AlCl₃ an increase is observed in the red, green, and violet regions before pptn. occurs.

E. S. H.

Gold sols with mixed complexes. F. EIRICH and W. PAULI (Kolloid-Z., 1934, 67, 186—195).—Hydroxo-Au sols (I), prepared by dispersion in dil. NaOH, are flocculated by boiling or by CO₂, whilst chloro-Au sols (II), prepared by dispersion in dil. HCl, are stable under these conditions. (I) can be converted into (II) by adding excess of the HCl, and addition of excess of NaOH converts (II) into (I). In the transitional stages mixed complexes are obtained, having intermediate properties. Sols prepared by dispersing Au in aq. BaCl₂ or MgCl₂ become red on heating and violet again on cooling.

S. H.

Emulsification of mercury. L. KREMNEV (Kolloid-Z., 1934, 67, 171—178).—Suspensions of many oxides and sparingly sol. salts stabilise Hg emulsions by forming a solid protective sheath around the particles. A similar effect is observed with typical hydrophilic colloids and with hydrated inorg. colloids in sufficient concn. The emulsions are also stabilised by the chlorides of multivalent metals and by oxidising salts, apparently as a result of forming Hg₂Cl₂ or Hg₂O.

E. S. H.

Application of the photographic method for the investigation of the colloidal state of polonium. I. E. STARIK and M. J. DEJZENROT-MISOVSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 540—546).—The method of determining the true or colloidal character of solutions of radioactive materials by bringing a drop of the solution on to a thin mica sheet above a photographic plate (A., 1928, 810; 1929, 620) is untrustworthy, as it is vitiated by adsorption at the mica surface. The method is actually most suited to the study of the latter phenomenon.

J. W. S.

Electric properties of colloid solutions. IV. Difference between the properties of colloidal acid solutions and acids in true solution. J. MUKHERJEE (Kolloid-Z., 1934, 67, 178—186; cf. A., 1933, 1116).—The behaviour of colloidal H₂SiO₃ and H₂SnO₃ differs from that of mol.-dissolved acids on dilution and on neutralisation, different amounts of strong bases [NaOH, KOH, or Ba(OH)₂] being required. The usual conceptions of degree of dissociation and dissociation const. are not applicable without modification; the size of the particles plays a part.

E. S. H.

Structure viscosity. II. Structure viscosity and flow elasticity in gum arabic sols. W. OSTWALD [with R. AUERBACH, I. FELDMANN, V. TRAKAS, and H. MALSS] (Kolloid-Z., 1934, 67, 211—222; cf. A., 1932, 995).—Structure viscosity has been established in gum arabic sols (5—45%) at 21° and 31°. The structural region is limited to low pressures (< 10 cm. H₂O). Flow elasticity is observed in the structural region, particularly at medium and low concns.

E. S. H.

Osmotic properties of colloidal electrolytes and the Hammarsten effect. P. VAN RYSELBERGHE (J. Physical Chem., 1934, 38, 645—653).—The apparent abnormalities in the measured osmotic pressure of colloidal electrolytes are a logical consequence of applying the Debye-Hückel theory to uni-z-valent electrolytes.

F. L. U.

Diffusion of colloids and colloidal electrolytes; ovalbumin; comparison with ultracentrifuge. J. W. MCBAIN, C. R. DAWSON, and H. A. BARKER (J. Amer. Chem. Soc., 1934, 56, 1021—1027).—Rates of diffusion through porous membranes of const. properties lead to correct vals. of mol. wt. if the observations are made at the isoelectric point or, with less certainty, in presence of buffers. Under these conditions the method is rapid and accurate for approx. spherical particles larger than sucrose. Experiments described with ovalbumin indicate mol. wt. 34,000. With insufficient buffering or beyond the isoelectric point widely divergent results may result from the mutual acceleration and retardation of ions and charged particles.

E. S. H.

Conditions for mechanical coagulation. W. HELLER (Compt. rend., 1934, 198, 1776—1778).—Hydrophilic sols coagulate on shaking or stirring, provided that the ζ potential is correctly adjusted. The extent of coagulation varies with the rates of shaking or stirring. It is claimed that all sols can be mechanically coagulated under appropriate conditions (cf. A., 1932, 119).

B. W. B.

Kinetics of coagulation. N. V. KARAKAR and A. M. PATEL (Trans. Faraday Soc., 1934, 30, 493—496).—The coagulation-time curves of $\text{Th}(\text{OH})_4$ sol in presence of KCl , MgCl_2 , and AlCl_3 are S shaped, but with progressive dialysis the auto-catalytic character of the curves disappears. Multivalent cations give a more pronounced S shape to the curves than univalent cations, owing to their greater stabilising influence.

R. S. B.

Soya-bean lecithin. III. Coagulation of lecithin sol by electrolytes. T. IGUCHI and M. SATO (J. Soc. Chem. Ind. Japan, 1934, 37, 198—199B).—The η (Couette) of the sol (2 g. per 100 c.c.) decreases on the addition of electrolytes, giving a min. val. at the end-point of coagulation, which can be more accurately determined by this means than by visual observation. The lecithin particles are negatively charged in colloidal solution, and the coagulation val. decreases with increased valency of the cations of the electrolyte.

E. L.

Influence of dialysis and ebullition on the stability of copper ferrocyanide and arsenic sulphide sols towards some electrolytes. A. BOUCHARIC and F. MORIZOT (Bull. Soc. chim., 1934, [v], 1, 153—156).— $\text{Cu}_2\text{Fe}(\text{CN})_6$ hydrosols become progressively less stable towards the coagulating action of KCl on dialysis, but more stable towards BaCl_2 and AlCl_3 , whereas As_2S_3 sols become more stable towards KCl and less stable towards BaCl_2 and AlCl_3 . Increase of the particle size by boiling $\text{Cu}_2\text{Fe}(\text{CN})_6$ sols make them progressively less stable towards all three precipitants, whilst with As_2S_3 sols the stability towards KCl and BaCl_2 is first increased and then diminished and towards AlCl_3 is practically unaffected.

J. W. S.

Stabilising and protective effect of colloidal hydroxides of polyvalent metals on mineral suspensions. L. V. LJUTIN and G. V. ZACHAROVA (Kolloid-Z., 1934, 67, 222—229).—Sols of $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, and $\text{Cr}(\text{OH})_3$ have a protective effect on suspensions of graphite, BaSO_4 , SiO_2 , and glass.

E. S. H.

Influence of the electric field on silver chromate precipitations in gelatin. M. KÖHN (Kolloid-Z., 1934, 67, 207—210).—When AgNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ interdiffuse in gelatin between two electrodes, the region in which the reagents meet is free from ppt., but the ppt. extends on each side towards the electrodes. A periodic structure is formed on the cathode side. The effects of varying the p.d. are described.

E. S. H.

Silicic acid gels. IV. Effect of hydrogen-ion concentration on time of setting. C. B. HURD, C. L. RAYMOND, and P. S. MILLER (J. Physical Chem., 1934, 38, 663—674; cf. A., 1933, 462).—The time of setting (t) $\propto [\text{H}^+]$ between p_{H} 4.2 and 5.5 for gels made from Na silicate and HCl , and approx. so for those made with AcOH between p_{H} 4.14 and 6.0. Increasing amounts of AcOH and NaOAc at const. p_{H} increase t , whilst NaCl , NaNO_3 , and Na_2SO_4 decrease it without appreciably changing the p_{H} .

F. L. U.

Laws of soil colloidal behaviour. XIV. Ageing of colloids and base exchange. A. J. PUGH (Soil Sci., 1934, 37, 403—427; cf. B., 1934, 32).—Freshly prepared sols of $\text{Al}(\text{OH})_3$ and Al silicate are stable towards $\text{Ba}(\text{OAc})_2$. After 3 weeks there is a decrease in adsorptive capacity and $\text{Ba}(\text{OAc})_2$ causes flocculation. A form of continuous polymerisation of the clay complex is postulated in which the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio is unaffected, but rearrangement of internal bonding of the mols. permits fewer mols. to participate in base-exchange phenomena.

A. G. P.

Ion interchanges in chromium oxychloride hydrosols. F. C. VON WICKLEN (J. Amer. Leather Chem. Assoc., 1934, 29, 194—232).—The p_{H} val. of basic CrCl_3 hydrosols is increased by the addition of K salts but diminished by ageing or heating, and reverts slightly when the heated hydrosols are subsequently allowed to remain at room temp. The p_{H} of heated hydrosols is not affected so much by additions of K salts as is that of the sols before heating. The effect of K salts on p_{H} diminishes in the order: $\text{C}_2\text{O}_4^{2-}$, citrate, tartrate, OAc^- , SO_4^{2-} , CNS^- , Cl^- , NO_3^- . The conductivity of the hydrosols is slightly increased by small additions of AgNO_3 , but diminished very much by Ag_2SO_4 .

D. W.

Swelling capacity of cellulose acetate films. I. D. KRÜGER (Paint and Var. Prod. Man., 1934, 10, No. 6, 22—23).—Published data concerning the influence of the degree of acetylation and of the polarity of the solvent on the swelling of cellulose acetate films are reviewed.

D. R. D.

Rate of flow of cellulose acetate solution. M. NEGISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 133—134B).

A. G.

Intracellular swelling of graphitic acid. I. Isotherms. Influence of lyotropic substances, temperature, and p_{H} on maximum swelling. J. C. DERKSEN and J. R. KATZ (Rec. trav. chim., 1934, 53, 652—669).—During the swelling of graphitic acid in H_2O vapour the distance (D) between adjacent ring-planes increases from 6.02 to 11.31 Å. Absorption of H_2O is therefore intracellular. The max. swelling increases with lowering of temp. and with increase of p_{H} . In 2M solution the effect of Li salts in increasing D is in the order $\text{NO}_3^- > \text{CNS}^- > \text{ClO}_3^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-}$. EtOH and tannic acid inhibit swelling.

F. L. U.

Existence of micelles in aqueous solutions of saponin. W. KLEINBERG (Proc. Soc. Exp. Biol. Med., 1933, 31, 113—114).—In aq. saponin min. surface tension occurs at concns. 1 in 12,500, 24,500, and 37,500, for which calc. vals. of the mol. dimensions are, respectively, 6.3, 3.2, and 2.1×10^{-6} cm., which are about 10 times the expected vals. Hence agglomerates must be capable of orienting themselves in three different ways, corresponding with their three dimensions.

CH. ABS.

Physical chemistry of proteins. XI. Amphoteric properties of zein. E. J. COHN, J. I. EDSALL, and M. H. BLANCHARD (J. Biol. Chem., 1934, 105, 319—326).—Electrometric titration of zein in 80% EtOH solution shows that it takes up approx. 20×10^{-5} mols. of HCl per g. The dissociation curve

corresponds with $pK_1=5.4$ and $pK_2=6.9$, the change taking place at approx. p_H 8. C. G. A.

Properties of proteins as a function of their fine structure. S. J. VON PRZYŁECKI and M. Z. GRYNBERG (Biochem. Z., 1934, 270, 203—218; cf. A., 1933, 125).—Ovalbumin (I) is adsorbed from aq. solutions of varying p_H in large amounts at the surface of org. liquids, whilst gelatin is adsorbed only slightly or not at all, the extent of adsorption depending on the structure of the protein and on the polar nature of the liquid. Addition of salts (Na_2SO_4 , $MgCl_2$) increases adsorption. With alcohols [except amyl (II)] there is no adsorption. Addition of (II), EtOH, or COMe, to (I) solutions greatly decreases adsorption. W. McC.

Cryolysis and bio-technology. F. F. NORD (Chem.-Ztg., 1934, 58, 327—328, 347—349).—A comparison of the physical properties of solutions of ovalbumin, gelatin, gum arabic, saponin, and Na oleate and of emulsions of olive oil in the above solutions before and after cooling to -10° , -18° , -79° , and -180° suggests that cooling diminishes the degree of aggregation in dil. solutions, but that the reverse may occur in more conc. solutions. A. G.

Complex relationships in lyophilic colloidal systems. III. (a) Complex and autocomplex flocculi. (b) "Salt solubility" of globulins at the isoelectric point. H. G. B. DE JONG, W. A. L. DEKKER, and K. C. WINKLER. IV. Influence of neutral salts on the cataphoretic charge of suspended (auto-)complex coacervate drops and of (auto-)complex flocculi. H. G. B. DE JONG and J. L. L. F. HARTKAMP (Rec. trav. chim., 1934, 53, 607—621, 622—642; cf. this vol., 362).—III. Examples of autocomplex flocculation are given. Certain systems can be made to exhibit both flocculation and coacervation by suitably controlling the factors determining the mutual relation of the attraction between oppositely charged groups and the tendency to solvation. The solubility of globulins in salt solutions at the isoelectric point is due to the diminution of the opposite charges by the salt ions, with the consequent dominance of the solvation factor. The peptising capacity of salts increases with the valency of either ion.

IV. The cataphoretic charge of drops and flocculi in a no. of complex and autocomplex systems shows a progressive change by salts in the order 1—3, 1—2, 1—1, 2—1, 3—1, the pairs of figures representing the respective valencies of cation and anion. F. L. U.

Action of alkaline copper solution on silk fibroin. IX. Chemical reactions and dissolution phenomena in the system fibroin-copper-alkali. X. Application of conductometric titration methods to the system fibroin-copper-alkali. Y. TAKAMATSU and S. NOMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 149—150B, 150B). IX. The dissolution of fibroin in $Cu(OH)_2$ -alkali mixtures is accelerated by substances which dissolve $Cu(OH)_2$ without alkali hydroxide (NH_3 , diamines, hydroxy-alkylamines, biguanidine) or in the presence of alkali hydroxide (NH_2 -acids, polyhydroxy-compounds). Their activities are in the same order as their

capacities for dissolving $Cu(OH)_2$, i.e., $C_2H_4(NH_2)_2 >$ tri- and di-(hydroxyethyl)amine $>$ glycine $>$ $NH_3 >$ glycerol. A complex compound [fibroin $Cu_{0.4}$]K has been isolated.

X. Conductometric titration gives quant. separation of free and combined alkali and reveals the existence of the compounds [fibroin $Cu_{0.4}$]M and [fibroin Cu]M, where M is K, Na, or Li. A. G.

Physico-chemical measurements on hydrogen fluoride. II. K. FREDENHAGEN [with W. KLATT, H. KUNZ, and (FRL.) U. BUTZKE] (Z. anorg. Chem., 1934, 218, 161—168).—The isotherms of the vapour at 26° , 32° , and 38° , lead to 86.3, 2.47, and $9.49 (\times 10^{14})$ for the dissociation const. of $(HF)_6$. From the heat of vaporisation at reduced pressure the calc. heat of dissociation of 20 g. of the saturated polymerised vapour is 6020 g.-cal. The saturated vapour of HF at b.p., under atm. pressure, corresponds with $(HF)_3$. M. S. B.

Hydration of unsaturated compounds. II. Equilibrium between isobutene and *tert.*-butyl alcohol and free energy of hydration of isobutene. W. F. EBERZ and H. J. LUCAS (J. Amer. Chem. Soc., 1934, 56, 1230—1234; cf. this vol., 369).—The equilibrium between Bu^iOH (I), H_2O , and $CH_3:CM_2$ (II) has been measured in 0.2N- HNO_3 and 0.1N- HNO_3 +0.1N- KNO_3 , starting with (I). The equilibrium const. (K_e) at $\mu=0.2$ is 7.48×10^3 at 25° and 3.94×10^3 at 35° . The rate of dehydration of (I) at $\mu=0.2$ is calc. from K_e and the rate of hydration of (II) (*loc. cit.*), and is found to be \propto to the concn. of acid. The ratio k_{35}/k_{25} is 6.73 and the heat of activation is 34.82 kg.-cal. per mol. H. B.

Equilibria between the possible tautomeric forms of hydrogen peroxide in aqueous solution. [Blackening of cupric hydroxide.] A. QUARTAROLI (Gazzetta, 1934, 64, 243—247; cf. A., 1925, ii, 806).—The mechanism of the blackening of $Cu(OH)_2$ by H_2O_2 has been studied in greater detail. Pure pptd. $Cu(OH)_2$ does not blacken on keeping under H_2O in complete absence of H_2O_2 . Although low concns. of H_2O_2 produce blackening, higher concns. completely inhibit it. It is suggested that in the first case Cu_2O_3 is formed by the action of $H_2O:O_2$, and reacts with $Cu(OH)_2$ forming the black compound ($\alpha CuO, H_2O$) and H_2O_2 , a chain reaction being thus set up, whereas in the second case CuO_2 is formed by the action of $HO\cdot OH$ and is incapable of further reaction. The negative catalysts Mg^{++} , Co^{++} , and Ni^{++} break the chain by forming compounds of the spinel type, e.g., $Cu_2O_3 \cdot MgO$. D. R. D.

First dissociation constant of phosphoric acid from 0° to 50° . L. F. NIMS (J. Amer. Chem. Soc., 1934, 56, 1110—1112).—The data obtained conform closely with the empirical equation of Harned and Embree (see below) for the dissociation of weak acids and bases. The heat of ionisation is given by $\Delta H = -4.58 \times 10^{-4} T^2 (T - 255.1)$ g.-cal. E. S. H.

Ionisation constant of formic acid from 0° to 60° . H. S. HARNED and N. D. EMBREE (J. Amer. Chem. Soc., 1934, 56, 1042—1044).—The following data have been obtained from e.m.f. measurements of the cells $H_2[HCO_2H(m_1), HCO_2K(m_2), KCl(m_3)]$

AgCl|Ag: ionisation const., $\log K = -(173.624/T) + 17.88348 \log T - 0.0280397T - 39.06123$; heat of ionisation, $\Delta H = 794.972 + 35.5613T - 0.12838T^2$; difference in sp. heats of reactants and resultants, $\Delta C_p = 35.561 - 0.25679T^2$. E. S. H.

Temperature variation of ionisation constants in aqueous solutions. H. S. HARNED and N. D. EMBREE (J. Amer. Chem. Soc., 1934, 56, 1050—1053).—In aq. solution at 1 atm. the ionisation consts. of weak acids, bases, and ampholytes can be represented by $\log K - \log K_m - f(t-0)$, where $f(t-0)$ is a general function, and K_m is the max. val. of K at the temp. 0. The approx. equation $\log K - \log K_m - 5.0 \times 10^{-5}(t-0)^2$ is valid in the region near the max. val. of K . The change in heat content of ionisation is given by $\Delta H = 2.3RT^2[\partial f(t-0)/\partial T]$. E. S. H.

Constitution of homogeneous acids and the influence of solvents on their acidity. A. MÜLLER (Z. anorg. Chem., 1934, 218, 210).—Corrections relative to a previous paper (this vol., 489).

M. S. B.

Apparent dissociation constants of amino-acids and related substances in water-ethanol mixtures. T. H. JUKES and C. L. A. SCHMIDT (J. Biol. Chem., 1934, 105, 359—371).—EtOH depresses the dissociation of CO_2H groups and slightly increases that of $\alpha\text{-NH}_2$ groups, in agreement with the zwitter-ion theory. The effect of glycerol and mannitol on glycine is slight. C. G. A.

Hydrolysis of sodium aluminate. A. MAFFEI (Gazzetta, 1934, 64, 149—160).—From the conductivity of solutions of Na aluminate containing varying quantities of NaOH, the hydrolysis const. is found to be 1.66×10^3 , and the dissociation const. of $\text{Al}(\text{OH})_3$ as a monobasic acid, 6×10^{-12} . O. J. W.

Activity and osmotic coefficients of aqueous solutions of acetic acid at the m.p. P. VAN RYSELBERGHE (Bull. Acad. roy. Belg., 1934, [v], 20, 354—358; cf. this vol., 490).—Methods of calculation and tabulated results are given.

N. M. B.

Activity of zinc chloride solutions. L. BRÜLL (Gazzetta, 1934, 64, 261—270).—The activity coeffs. of ZnCl_2 calc. from e.m.f. measurements with the cell $\text{Zn-Hg|aq. ZnCl}_2|\text{HgCl|Hg}$ at 25° (concn. of ZnCl_2 0.0017—0.84M) agree with Bonino's theory (this vol., 254).

D. R. D.

Activity coefficient of hydrochloric acid in cerous chloride solutions at 25° . C. M. MASON and D. B. KELLAM (J. Physical Chem., 1934, 38, 689—692).—The activity coeff. of HCl in aq. CeCl_3 determined by e.m.f. measurements at 25° is given by $\log \gamma = 0.0740m - 0.1619$, where $m = [\text{HCl}]$ in mol. per kg. H_2O , and when the const. ionic strength $= 1 \mu$.

F. L. U.

Beryllium tartrate. I. PEYCHÈS (Compt. rend., 1934, 198, 1778—1781; cf. this vol., 718).—Rotatory powers (I) of solutions containing different mol. proportions of BeSO_4 and tartaric acid give max. corresponding with $\text{C}_4\text{H}_4\text{O}_6\text{Be}_2$. Measurements of (I), rotatory dispersion (II), Λ , p_H , d , and n have been made for Be_2 tartrate solutions over a wide concn.

range. (I) and (II) are considerably $>$ those for alkali or alkaline-earth tartrates, and vary little with the concn. (I) is attributed chiefly to $\text{C}_4\text{H}_4\text{O}_6\text{Be}^-$.

B. W. B.

Behaviour of the magnesium ion towards ammonia in aqueous solution. II. Determination of the vapour pressure of ammonia over ammoniacal solutions of magnesium salts. H. FREDHOLM (Z. anorg. Chem., 1934, 218, 169—180).—In a dynamical method for the determination of the v.p. of NH_3 over its solution the gas stream is supplied by a H_2O voltameter and the amount of gas passed is measured by a Ag coulometer. Data are given for the following solutions: 1.627N- NH_4Cl , 1.348N- NH_3 , and 0—1.300N- MgCl_2 ; 1.588N- NH_4NO_3 , 1.329N- NH_3 , and 0—1.201N- $\text{Mg}(\text{NO}_3)_2$. By the application of Henry's law the concns. of combined and uncombined NH_3 in solution have been calc. These vals. have been corr. for the salting-out effect of MgCl_2 and $\text{Mg}(\text{NO}_3)_2$ on NH_3 by determining experimentally the salting-out effect of KCl and KNO_3 and assuming that equiv. quantities of salts have the same action. The complex ion $[\text{Mg}(\text{NH}_3)]^+$ is indicated (cf. this vol., 484).

M. S. B.

Determination of calcium-ion concentration and its application to the determination of the dissociation of calcium hydroxide. G. KILDE (Z. anorg. Chem., 1934, 218, 113—128).—The solubility product of $\text{Ca}(\text{IO}_3)_2$ and its variation with temp. and salt concn. have been determined in neutral aq. KIO_3 , CaCl_2 , NaCl , and MgCl_2 , and formulæ are given for the variation of activity coeff. with ionic strength. The solubility of $\text{Ca}(\text{IO}_3)_2 \cdot 6\text{H}_2\text{O}$ in alkaline solution is considerably $>$ in neutral solutions of the same ionic strength. This is attributed to the reaction $\text{Ca}(\text{H}_2\text{O})_6^{++} \rightleftharpoons \text{Ca}(\text{H}_2\text{O})_5\text{OH}^+ + \text{H}^+$, and may be employed for the determination of the second dissociation const. of $\text{Ca}(\text{OH})_2$. From the solubility in HCl the dissociation const. of HIO_3 has been obtained at 18° , 25° , and 30° , and the vals. are in good agreement with those found by conductivity measurements. From the solubility of CaIO_3 in CaO -sucrose solutions $[\text{Ca}^{++}]$ is considerably $<$ the total $[\text{Ca}]$.

M. S. B.

Mathematical treatment of base-carbonic acid-water equilibria in dilute solutions. Y. KAUKO (Suomen Kem., 1934, 7, 86B).—Relations based on the classical dissociation theory are also valid on the modern theory if K is considered as a function of the concn.

S. C.

Acid strength of inorganic cations and basic strength of inorganic acetates in acetic acid. II. I. M. KOLTHOFF and A. WILLMAN (J. Amer. Chem. Soc., 1934, 56, 1014—1016).—The dissociation of inorg. acetates in AcOH decreases with decreasing size and increasing charge of the cation. The acid strength of the cation increases with decreasing size and increasing charge. Salts which do not change the reaction of H_2O undergo solvolysis in AcOH. The acidity of K salts decreases in the order $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NO}_3^-$. Salts of the same anion decrease in acidity in the order $\text{Mg}^{++} > \text{Ca}^{++} > \text{Sr}^{++} > \text{Ba}^{++} > \text{Ag}^+ > \text{Li}^+ > \text{Na}^+ > \text{NH}_4^+ = \text{K}^+ > \text{Rb}^+$. Glycine behaves as a strong base.

E. S. H.

Hydration of solute ions in relation to acidity, alkalinity, and p_H . L. H. FLINT (Plant Physiol., 1934, 9, 107—126). A. G. P.

Theory for concentrated solutions of strong electrolytes. L. BRÜLL (Gazzetta, 1934, 64, 270—278).—The fundamental differences between Bonino's theory (this vol., 254) and the Debye-Hückel theory are examined. A simple interpolation formula for calculating f^* is obtained and shown to give the same vals. (within 1%) as Bonino's more complicated theoretical formula in the case of 0.2—3*M*-KCl, 0.01—5.41*M*-NaCl, and 0.01—1*M*-CaCl₂, -SrCl₂, and -BaCl₂ at 25°.

D. R. D.

Diffusion equilibria of electrolytes. O. HALPERN (J. Chem. Physics, 1934, 2, 300).—Diffusion equilibrium under the influence of external forces, illustrated by the distribution of charged colloidal particles and ions in a gravitational field, shows deviations from the Boltzmann distribution; the diffusion potential of electrolytes does not assume its classical val.

N. M. B.

Activities of life and the second law of thermodynamics. F. G. DONNAN and E. A. GUGGENHEIM (Nature, 1934, 133, 869; cf. this vol., 598).

L. S. T.

Statistical thermodynamics of molecular systems. T. WEREIDE (Z. Physik, 1934, 88, 469—494).—The criterion of thermodynamic equilibrium, $dS=0$, is combined with a statistical calculation of entropy, S , so that quantum conditions appear only in empirically determined coeffs. The method is applied to the principal types of thermodynamical processes, including evaporation, fusion, absorption, osmosis, chemical reactions, and electrode potentials.

A. B. D. C.

Graphical calculations in the study of chemical equilibria. P. MONTAGNE (Chim. et Ind., 1934, 31, Spec. No., 204—209).—Applications of graphical methods are reviewed.

H. J. E.

Thermal dissociation of lead peroxide. J. KRUSTINSONS (Z. Elektrochem., 1934, 40, 246—248).—The dissociation pressure of PbO₂, dried in a current of O₂ at 250°, is 1 atm. at 344±1°. The calc. heat of dissociation is 21,670 g.-cal. The end product is PbO, but solid solutions are formed in the earlier stages.

E. S. H.

V.p.-temperature relations and the heats of hydration, dissolution, and dilution of the binary system magnesium nitrate-water. W. W. EWING, E. KLINGER, and J. D. BRANDNER (J. Amer. Chem. Soc., 1934, 56, 1053—1057).—V.p. measurements are recorded for solutions, and for the hydrates of Mg(NO₃)₂. Heats of dissolution and dilution have also been measured and heats of hydration calc. from the results and from the v.-p. data.

E. S. H.

System sodium nitrite-water. The hydrate NaNO₂·0.5H₂O. J. BUREAU (Compt. rend., 1934, 198, 1918—1920).—Recorded data show the existence of NaNO₂·0.5H₂O with a eutectic at -19.5° and 10% NaNO₂, and transition point hemihydrate → anhyd. salt at -5.1° and 41.65%. Vals. of d for saturated NaNO₂ solutions are tabulated between 15 and 99.9°.

B. W. B.

Binary system lithium nitride-water. A. P. ROLLET and J. WOHLGEMUTH (Compt. rend., 1934, 198, 1772—1774).—An equilibrium diagram is given showing a eutectic (I) (-47.5°, 26.0% LiN₃) and two transition points, (II) (-31.0°, 33.5%) and (III) (68.2°, 48.0%). LiN₃·4H₂O separates between (I) and (II), and LiN₃·H₂O between (II) and (III).

B. W. B.

M.-p. diagram of the system ZrO₂-SiO₂. N. ZIRNOVA (Z. anorg. Chem., 1934, 218, 193—200).—The system gives a max. m.p. at 2430° for the 50% mol. mixture, indicating the presence of the compound ZrSiO₄. There are two eutectics, 2220°, 42 mol.-% SiO₂; 1705°, 97 mol.-% SiO₂. The region of solid solutions lies between 10 and 100 mol.-% SiO₂.

M. S. B.

Dissociation pressures of metal pyridine cyanates. T. L. DAVIS and C. W. OU (J. Amer. Chem. Soc., 1934, 56, 1061—1063).—Data are recorded for Co(NCO)₂, 2, 4, and 6C₅H₅N, Ni(NCO)₂, 4 and 6C₅H₅N, and Zn(NCO)₂, 2C₅H₅N at 20—100°. C₅H₅N is bound by Ni(NCO)₂ and Zn(NCO)₂ less strongly at the lower temp. The dissociation of Co(NCO)₂, 6C₅H₅N in boiling CHCl₃ and of Co(NCO)₂, 6C₅H₅N and Co(NCO)₂, 4C₅H₅N in Ph₃ solution at about 68° has been measured.

E. S. H.

Thermal analysis of binary systems of resorcinol and sulphur with certain organic substances. K. HRYNAKOWSKI and F. ADAMANTS (Rocz. Chem., 1934, 14, 189—196).—The fusion diagrams suggest 1:1 compounds in the systems *m*-C₆H₄(OH)₂ (I)-antipyrine (II), CO(NH₂)₂ (III), but not in the systems (I)-BzOH, NHPh, (IV) *p*-C₆H₄(OH)₂ (V), salol (VI), NHET-CO₂Et (VII), or S-(IV), α -C₁₀H₇-NH₂, quinine. S is immiscible with fused NHAcPh, (II), (III), *p*-OEt-C₆H₄-NHAc, (V), menthol, (VI), and (VII).

R

Molecular compounds of the chalkones and nitro-aromatic compounds. T. ASAHINA (Bull. Chem. Soc. Japan, 1934, 9, 181—186).—M.-p. diagrams are given for the systems *o*-C₆H₄Me·NO₂-3:4-methylenedioxybenzylideneacetophenone (I) [simple eutectic (S.E.)]; *o*-OH-C₆H₄·NO₂ (II)-benzylideneacetophenone (III) (S.E.); (I)-(II) (S.E.); *m*-OH-C₆H₄·NO₂ (IV)-(III), (compound, 1 mol.:1 mol., m.p. 65°); (IV)-(I) (compound, 1:1, m.p. 96.5°), *p*-OH-C₆H₄·NO₂ (V)-(I) (compound, 1:1, m.p. 109.0°); (V)-(III) (compound, 1:1, m.p. 87°).

D. R. D.

Heterogeneous equilibrium in the system CdCl₂-NaCl-H₂O. (MLLE.) M. G. ADOLFF and H. HERING (Compt. rend., 1934, 198, 1770—1772).—Data for the range 19.3—60.0° indicate the existence of CdCl₂·2NaCl·3H₂O (I) (cf. Käthe, A., 1914, ii, 205), 5CdCl₂·4NaCl·17H₂O, and CdCl₂·NaCl·H₂O. (I) exists at all temp.

B. W. B.

Mixed crystals in the vitriol series. III. System NiSO₄-CoSO₄-H₂O. A. BENRATH and W. THIEMANN (Z. anorg. Chem., 1934, 217, 347—352; cf. this vol., 137).—Equilibrium diagrams have been constructed showing the regions of formation of mixed crystals of the respective mono-, hexa-, and heptahydrates of Co and Ni. Hexahydrate crystals contain the Ni salt in the β form.

F. L. U.

Ternary systems. XIX. Calcium sulphate, potassium sulphate, and water. A. E. HILL (J. Amer. Chem. Soc., 1934, 56, 1071—1078).—Equilibrium data for the range 40—100° show that the separation of K_2SO_4 from $CaSO_4$ in natural polyhalite is not appreciably favoured by rise of temp., and that the concn. of K_2SO_4 may increase as a result of the metastable pptn. of anhydrite. E. S. H.

Isotherms of the ternary system P_2O_5 - Li_2O - H_2O at 0° and 20°. A. P. ROLLET and R. LAUFFENBURGER (Bull. Soc. chim., 1934, [v], 1, 146—152).—The only compounds formed are Li_3PO_4 and LiH_2PO_4 , the latter of which has an incongruent solubility at 20°. The solubilities at 0° are 0.022% and 55.8%, respectively, and that of Li_3PO_4 at 20° is 0.030%.

J. W. S.

Acid salts in systems of the type monobasic acid-alkaline-earth salt-water. L. J. DUNN and J. C. PHILIP (J.C.S., 1934, 658—666; cf. A., 1928, 131).—For HCO_2H , $AcOH$, $PhSO_3H$, and their Ba, Sr, Ca, and Mg salts the following solid phases are indicated: (1) $(HCO_2)_2Ba$; $(HCO_2)_2Ba, HCO_2H$; ternary point, 21.8 HCO_2H , 26.7 $(HCO_2)_2Ba$, 51.5% H_2O ; (2) $(HCO_2)_2Sr, 2H_2O$; $(HCO_2)_2Sr$; $2(HCO_2)_2Sr, HCO_2H$; ternary points, 55.9 HCO_2H , 20.0 $(HCO_2)_2Sr$, 24.1% H_2O , and 68.7 HCO_2H , 21.3 $(HCO_2)_2Sr$, 10% H_2O ; (3) $(HCO_2)_2Ca$; (4) $(HCO_2)_2Mg, 2H_2O$; (5) $3Ba(OAc)_2, 3AcOH, 11H_2O$; (6) $2Sr(OAc)_2, H_2O$; $5Sr(OAc)_2, 5AcOH, 9H_2O$; $Sr(OAc)_2, 2AcOH, 2H_2O$; (7) $Ca(OAc)_2, H_2O$; $Ca(OAc)_2, AcOH, H_2O$; ternary point, 7.6 $AcOH$, 25.1 $Ca(OAc)_2$, 67.3% H_2O ; (8) $(PhSO_3)_2Ba, H_2O$; (9) $(PhSO_3)_2Sr, H_2O$; (10) $(PhSO_3)_2Ca, H_2O$; (11) $(PhSO_3)_2Mg, 6H_2O$. The solubilities of $(HCO_2)_2Ba$ and $(HCO_2)_2Sr$ increase with the acid concn. All others decrease. R. S.

Equilibrium between binary compounds and the associated metals. H. GIERSCHE (Metallbörse, 1933, 23, 893—894; Chem. Zentr., 1933, ii, 2935).—The mass-action law of Lorenz and van Laar holds for equilibria of the type $Pb + SnCl_2 \rightleftharpoons PbCl_2 + Sn$.

H. J. E.

Equilibria between metals, sulphides, and silicates in the melt. IV. Heterogeneous equilibrium $FeS + Ni$ silicate — $NiS + Fe$ silicate in the melt. W. JANDER, H. ZWYER, and H. SENF (Z. anorg. Chem., 1934, 217, 417—426; cf. A., 1933, 352).—Data are recorded to show the influence of concn., temp., and additions of foreign substances on the equilibrium. F. L. U.

Phase diagrams of simultaneous crystallisation of sodium chloride and epsomite. V. I. NIKOLAEV and N. P. VINTOVKINA (J. Appl. Chem. Russ., 1934, 7, 29—38).—Data for the system $2NaCl + MgSO_4 \rightleftharpoons Na_2SO_4 + MgCl_2$ at 0—48° are recorded, and the results discussed with reference to conditions prevailing in a no. of U.S.S.R. salt lakes. R. T.

Combination of amino-acids and proteins in the solid state with gaseous acids and bases.—See this vol., 790.

Thermochemistry of aqueous solutions of nickel sulphate. J. PERREU (Compt. rend., 1934, 198, 1767—1769; cf. this vol., 601).—Heats of dissolution of $NiSO_4 \cdot 7H_2O$ together with sp. heats of

solutions and heats of dilution are recorded. The results give calc. vals. in good agreement with Steele and Johnson's data for the eutectic temp. and the transition temp. for the changes hepta- \rightarrow hexahydrate and $\alpha \rightarrow \beta$ hexahydrate (J.C.S., 1904, 85 113).

B. W. B.

Heats of dissolution of calcium oxide and calcium hydroxide in relation to concentration of hydrochloric acid. H. E. SCHWIETE and E. HEY (Z. anorg. Chem., 1934, 217, 396—400).—Heats of dissolution have been measured for 1, 3.5, and 6.4*N*-HCl. The calc. heat of hydration of CaO is 15.55 kg.-cal. per mol.

F. L. U.

Thermochemistry of ferrous halides and their compounds with carbon monoxide. W. HIEBER and A. WOERNER (Z. Elektrochem., 1934, 40, 287—291).—The following thermal data have been determined: $Fe + Br_2$ (liquid) $= FeBr_2 + 59.87$; $Fe + I_2$ (solid) $= FeI_2 + 30.12$ kg.-cal.; $Fe(CO)_5 + X_2$ (gas) $= Fe(CO)_4X_2 + CO + 45.84$ (Cl), 43.38 (Br), 23.14 kg.-cal. (I). Thermal data relating to the system $Fe-CO-X$ are now complete, and independently calc. vals. show a satisfactory agreement. F. L. U.

Heats of formation and constitution of ferrous halide compounds with amines and carbon monoxide. W. HIEBER, H. APPEL, and A. WOERNER (Z. Elektrochem., 1934, 40, 262—267).—Data are recorded for the complexes formed by $FeCl_2$, $FeBr_2$, and FeI_2 with C_5H_5N , $C_2H_4(NH_2)_2$, and CO , respectively, and are discussed in relation to constitution. The prep. of the following compounds is described: $FeCl_2 \cdot 3C_2H_4(NH_2)_2$, $FeBr_2 \cdot 4C_5H_5N$, $FeBr_2 \cdot 6C_5H_5N$, $FeBr_2 \cdot 3C_2H_4(NH_2)_2$, $FeI_2 \cdot 2C_5H_5N$, $FeI_2 \cdot 4C_5H_5N$, $FeI_2 \cdot 6C_5H_5N$, $FeI_2 \cdot 3C_2H_4(NH_2)_2$.

E. S. H.

Heats of formation and constitution of complex cobaltous halide compounds. II. W. HIEBER and A. WOERNER (Z. Elektrochem., 1934, 40, 256—262; cf. A., 1930, 421).—The heats of formation of compounds of $CoCl_2$, $CoBr_2$, and CoI_2 with numerous amines and alcohols have been calc. from the heats of dissolution of the complexes and their components in the same solvent. The results are discussed in relation to constitution. E. S. H.

Heats of combustion of cyclic hydrocarbons. G. BECKER and W. A. ROTH (Ber., 1934, 67, [B], 627—632; cf. Alder and Stein, this vol., 517).—The vals. at const. vol. and const. pressure, respectively, are: α -dicyclopentadiene (1376.6, 1378.4), H_2 - (1411.0, 1413.1) and H_4 - (1451.8, 1454.2) -derivatives; α -tricyclopentadiene (2053.1, 2055.8), H_2 - (2088.6, 2091.6) and H_4 - (2132.4, 2135.6) -compounds; β -di- (2086.4, 2089.4) and β -tetra- (2128.7, 2132.0) -hydrotricyclopentadiene; tetracyclopentadiene (2727.3, 2730.8) and its H_2 -compound (2762.2, 2766.0); norcamphor (944.3, 946.1); dicyclohexadiene (1679.1, 1681.5) and its n_4 -compound (1757.9, 1760.9).

H. W.

Heats of activation of explosive molecules. H. MURAOUR (J. Chim. phys., 1934, 31, 138—140).—The heat of activation calc. by Roginski and Andreev (A., 1933, 1017) does not refer to the explosive decomp. of 2 : 4 : 6-trinitro-1 : 3 : 5-triazobenzene and hence

there is no significance in the comparison with activation energies of other explosives (cf. *ibid.*, 574).

J. G. A. G.

Heats of activation of explosive molecules. C. C. ANDRÉEV (J. Chim. phys., 1934, 31, 141—144).—A reply (cf. preceding abstract).

J. G. A. G.

[**Heats of activation of explosive molecules.**] H. MURAOUR (J. Chim. phys., 1934, 31, 145—146).—A reply (cf. preceding abstract). Activation energies for the slow decomp. of explosives can be calc. from the temp. coeff. only if at the temp. chosen each fraction of the total vol. of gas liberated corresponds with the decomp. of an equal fraction of the explosive.

J. G. A. G.

Visualising and recording the propagation front of ions. R. TOMII (J. Soc. Chem. Ind. Japan, 1934, 37, 166—167B).—By choosing suitable substances, e.g., $K_4Fe(CN)_6$, NaCl, and phenolphthalein, and interrupting the current from time to time the ionic front in a gelatin gel is made visible. With an anode at the centre of a circular cathode the rate of movement of the front is proportional to the c.d.

A. G.

Electrolytic conductivity of alkaline-earth chlorides in water at 25°. T. SHEDLOVSKY and A. S. BROWN (J. Amer. Chem. Soc., 1934, 56, 1066—1074).—Conductivity and λ vals. are recorded for aq. $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ solutions at 25°. The conductivity vals. agree with Onsager's equation.

E. S. H.

Azido-dithiocarbonic acid. VII. Conductivity of the azido-dithiocarbonate ion. G. B. L. SMITH, F. P. GROSS, jun., G. H. BRANDES, and A. W. BROWNE (J. Amer. Chem. Soc., 1934, 56, 1116—1118).—Conductivity measurements show $SH \cdot CS \cdot N_3$ to be a moderately strong acid. Potentiometric titration and cryoscopic determinations confirm this result. The equiv. conductivity of $S \cdot CS \cdot N_3$ at 25° is 41.7.

E. S. H.

Dissociation of inorganic acids, bases, and salts in glacial acetic acid as solvent. I. I. M. KOLTHOFF and A. WILLMAN (J. Amer. Chem. Soc., 1934, 56, 1007—1013).—Conductivity measurements show that the strength of inorg. acids in AcOH decreases in the order $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$. $HClO_4$ behaves as a strong electrolyte, and is present partly as ions and partly in the form of ion pairs, $CMe(OH)_2 \cdot ClO_4$. The remainder behave as weak acids; they are partly dissociated, partly present as ion pairs, and partly non-ionised. Alkali acetates and LiCl behave as strong electrolytes.

E. S. H.

Potential of iron in air-free solution. F. MEUNIER and O. L. BRET (Chim. et Ind., 1934, 31, Spec. No., 444—447).—Measurements made in vac. indicate that OH^- does not produce passivity. In alkaline solution, however, Fe, Ni, Cr-Ni steel, and polished Pt behave like H electrodes. In acid solution the action depends on the nature and concn. of the ion, CrO_4^{2-} producing passivity, whilst SO_4^{2-} has only a feeble effect.

H. S. P.

Potentials of cells in liquid ammonia solutions. Thermodynamic constants of the ammino-zinc chlorides and of zinc chloride. N. ELLIOTT and M. YOST (J. Amer. Chem. Soc., 1934, 56, 105.

1060).—The e.m.f. of the reversible cells Zn (amalgam) $ZnCl_2, 10NH_3(s) | NH_4Cl$ (in liquid NH_3) $| TiCl(s)$, Ti (amalgam) is const. and reproducible. For unit activity of Zn and Ti in the amalgams the standard potential is $E_{298}^\circ = 0.9016$ volt. For the metals in the free state the standard potential is $E_{298}^\circ = 0.8293$ volt. The free energies, heat contents, and virtual entropies of $ZnCl_2$ and its compounds with 10, 6, 4, 2, and 1 mol. of NH_3 have been calc.

E. S. H.

Behaviour of the glass electrode in connexion with its chemical composition. B. LENGVEL and E. BLUM (Trans. Faraday Soc., 1934, 30, 461—471).—Soft soda-glass containing CaO , Na_2O , and SiO_2 acts as an almost perfect H electrode, with no change in electrometric behaviour when the proportions of the constituents are varied, or when Na_2O is replaced by K_2O . For hard Jena glass containing Al_2O_3 or B_2O_3 the concn. of H^+ and of alkali metal ion affects the potential. Glasses containing $> 10\%$ Al_2O_3 or B_2O_3 do not differ electrometrically. There is no relation between the behaviour of glass as an electrode and its solubility in H_2O or electrical resistance. The heats of liberation of the migrating ion (Na^+) have been computed from the temp. dependence of the resistance, but no correlation with electrode phenomena has been found.

R. S. B.

Effect of high concentrations on the deposition potential of polonium. M. GUILLOT and M. HAISINSKY (Compt. rend., 1934, 198, 1758—1760; cf. A., 1933, 355).—The crit. deposition potential (I) of Po has been measured in various acid and salt solutions. (I) is const. at 0.37 volt in HNO_3 (II) up to 4N, but decreases in H_2SO_4 (III) to 0.10 volt at concns. $> 4N$, and is 0.24 volt in 1.12N-AcOH (IV). In N-(II), -(III), -(IV), and $-H_3PO_4$, (I) decreases with addition of corresponding Na salt. Deposition of Po is suppressed by addition of $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$.

B. W. B.

Electrochemical properties of germanium. J. I. HALL and A. E. KOENIG (Trans. Electrochem. Soc., 1934, 65, 79—82).—Coherent, grey deposits of Ge on Cu are obtained by electrolysis of a solution of GeO_2 in 3N-KOH at 78—90° with low c.d. Measurements of the deposition potential of Ge from this solution, of the single potential of $Ge/N-ZnSO_4$, and of the H overvoltage of Ge are recorded. Ge displaces Ag from aq. $AgNO_3$.

H. J. T. E.

Electrochemical behaviour of the tin-iron couple in dilute acid media. T. P. HOAR (Trans. Faraday Soc., 1934, 30, 472—482).—The e.m.f. of the Fe-Sn couple reverses in dil. acids owing to dissolution of oxide films. Sn is cathodic in H_2SO_4 , but anodic in dil. citric and oxalic acid owing to formation of sol. complexes. Sn and Fe corrode in citric acid and citrate buffer of p_H 5, and when coupled the Sn corrodes more and the Fe less rapidly; there is a quant. relation between the amount of corrosion and the couple current. Air increases the corrosion of the couple, but a change in p_H has no effect. The bearing of these results on the corrosion of Sn-plate is discussed.

R. S. B.

Potentiometric studies of passivity. J. STEINER and L. KAHLENBERG (Trans. Electrochem. Soc., 1934,

66, 1—8).—The variation of single potential of metals in HNO_3 with dilution of the acid has been studied. Fe, Co, Ni, and certain Fe alloys are definitely active and definitely passive over certain ranges of concn. In the region of intermediate concns. periodic phenomena are sometimes observed with partly immersed specimens, but never for totally immersed specimens. Cr and an Fe-Cr alloy were found to be passive at all concns. of HNO_3 . Single potentials for Al, W, Pt, and graphite in solutions up to 83% HNO_3 are also shown by means of curves. H. J. T. E.

Passivity of iron and steel in nitric acid solutions. I. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 375—455).—Vals. are given for the crit. concn. above which passivity occurs, and the crit. temp. for each concn. below which passivity occurs, when soft steel is immersed in 50—95 wt.-% HNO_3 solution. In the crit. regions periodic passivity is observed. From 75—95 wt.-% HNO_3 the steel does not become completely active even in the boiling solution. The influence of the temp. of the test-piece is described. R. S. B.

Electrolytic valve action of niobium and tantalum on a.c. circuits. D. F. CALHANE and A. J. LALIBERTE (Trans. Electrochem. Soc., 1934, 65, 287—293).—Oscillograph records show that in 27% H_2SO_4 Ta exhibits very effective rectifying action at 60 volts a.c., whereas Nb shows very little electrolytic valve action even at 2.5 volts. H. J. T. E.

Reaction velocity measurements with heavy hydrogen. K. F. BONHOEFFER, F. BACH, and E. FAJANS (Z. physikal. Chem., 1934, 168, 313—314).—The reaction of H_2 with Br vapour at 578° abs. is "3.3 times as slow" as the reaction with H_2 , and there is a comparable relation between the rates of the reaction $\text{H}_2 + \text{H}_2 = 2\text{H} + \text{H}_2$ and the para-ortho H_2 transformation, both on Ni (cf. this vol., 156). R. C.

Low-pressure explosion limits of deuterium and oxygen. A. A. FROST and H. N. ALYEA (J. Amer. Chem. Soc., 1934, 56, 1251—1252).—Explosion limits are compared for $\text{H}_2 + \text{O}_2$ and $\text{D}_2 + \text{O}_2$ mixtures at 500° and 520° in KCl-coated Pyrex vessels. E. S. H.

Reaction between oxygen and the heavier isotope of hydrogen. C. N. HINSHELWOOD, A. T. WILLIAMSON, and J. H. WOLFENDEN (Nature, 1934, 133, 836—837).—With H_2 the chain reaction which occurs in the gas phase at 560° and pressures > the upper explosion limit (I) has a speed 64% of that shown by H_2 . The ratio of the rates for H_2 and for H_2 is approx. 0.65—0.70 for the surface reaction in a packed vessel at 525°. (I) is higher with H_2 than with H_2 , and the shift of the limit is practically that predicted from the theory of deactivation by ternary collisions. H_2 by reason of its smaller speed is a less efficient deactivating agent. The energy of activation of the branching process is 26,500 g.-cal., which is approx. the same as the vals. 25,500 and 26,500 for H_2 . There appears to be little difference in the actual probability of chain branching with the two isotopes. The mechanism of the reaction is discussed in the light of these results. L. S. T.

Thermal decomposition of fluorine monoxide. A unimolecular decomposition represented by a second-order reaction. W. KOBLITZ and H. J. SCHUMACHER (Z. physikal. Chem., 1934, B, 25, 283—300).—The thermal decomp. in glass, quartz, or Mg vessels at 250—270° is homogeneous and unimol. and follows the equation $-d(\text{F}_2\text{O})/dt = k_1[\text{F}_2\text{O}]^2 + k_2[\text{F}_2\text{O}][\text{O}_2] + k_3[\text{F}_2\text{O}][\text{SiF}_4] + \dots + k_x[\text{F}_2\text{O}][\text{X}]$, where $[\text{O}_2]$ and $[\text{SiF}_4]$ are the concns. of O_2 and SiF_4 formed by reaction with the wall of the F_2 formed by decomp., and X is a foreign gas. The temp. coeff. is 2.0+0.1 and is the same for $k_1, k_2, k_3, \dots, k_x$. Although the decomp. of the F_2O is unimol., the life of the activated F_2O mols. is so short that under the experimental conditions the rate of decomp. is determined by the rate of activation of activated mols. necessary for decomp. Assuming three activated degrees of freedom, there must be complete equalisation of energy at practically every collision, and every mol. with the requisite energy must decompose. The relative probabilities of activation on collision of F_2O and various foreign gases have been calc. The life of the activated F_2O is estimated at $< 10^{-12}$ sec.; the products of dissociation are uncertain. R. C.

Kinetics of ethylene polymerisation. M. V. KRAUZE, M. S. NEMTZOV, and E. A. SOSKINA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 301—306; cf. A., 1930, 709; 1931, 436).—With high C_2H_4 concns. at temp. > 300° no catalytic action could be detected at the surfaces of Fe, Ni, Cu, Cr, ZnO, or activated C, the homogeneous reaction only occurring. The latter is bimol., but a slight fall of the velocity coeff. occurs with increasing initial concn. of C_2H_4 . The effect of temp. is expressed by $\log K - 10.85 - 8400/T$, and the energy of activation is $37,700 \pm 200$ g.-cal. Comparison of the experimental data with theory shows that only one out of every 400 active contacts leads to reaction. J. W. S.

Chains in the acetaldehyde decomposition.—See this vol., 758.

Double hydrolysis of monochloroacetates and their mutual action. A. TIAN (Bull. Soc. chim., 1934, [v], 1, 115—119; cf. A., 1933, 678).—The abnormal temp. coeff. of the elimination of the Cl, and the fact that this action is much more rapid for the salts than for the free acid, in spite of the fact that addition of HCl has little effect on the reaction, are explained by the normal saline hydrolysis of the salts, yielding OH^- ions which activate the Cl hydrolysis. This view also explains previous conflicting data on the temp. coeff. of the reaction. J. W. S.

Calculations of the activation energies of reactions between the halogens and the ethylene double bond. A. SHERMAN and C. E. SUN (J. Amer. Chem. Soc., 1934, 56, 1096—1101).—Theoretical. The mechanism of decomp. of $\text{C}_2\text{H}_3\text{I}$, $\text{C}_2\text{H}_3\text{Br}$, and $\text{C}_2\text{H}_3\text{Cl}$ is discussed. E. S. H.

Velocity and equilibrium point of the reaction of formation of benzanilide from benzoic acid and aniline. E. S. CHOTINSKI, B. Z. AMITIN, and I. Z. CHASKES (Ukrain. Chem. J., 1933, 8, 196—201).—The equilibrium point of the reaction $\text{NH}_2\text{Ph} + \text{BzOH} \rightleftharpoons \text{NHBzPh}$ (I) + H_2O is attained in 15 hr. at

155° [52.5% yields of (I)], and in 5 hr. at 212° (64% yields); the velocity of reaction is in both cases greatest during the first hr. R. T.

Hydrolysis of aqueous alkali cyanides during evaporation. I. M. NOSALEVITSCH (Ukrain. Chem. J., 1933, 8, 226—236).—At atm. pressure boiling $N\text{-KCN}$ undergoes hydrolysis at the rate of 10% per hr., whilst under reduced pressure % hydrolysis (I) diminishes by 0.32 per 10 mm. pressure. (I) diminishes rapidly with increasing concn. of KCN to 5*N*, above which it falls very gradually. R. T.

Alcoholysis of glyceryl triacetate in feebly alkaline media. E. M. BELLET (Compt. rend., 1934, 198, 1785—1786; cf. A., 1933, 696).—Triacetin (I) (0.1 mol.), ROH (50 c.c.), and $N\text{-ROH-KOH}$ (6 c.c.) heated at 100° (bath) for 8 hr. give ROAc = decomp. of 48.3, 43.2, and 37.6% of (I) when R = Me, Et, and Pr³, respectively. Similarly (I) (0.2 mol.) with 0.5*N*-EtOH-KOH (10 c.c.) gives EtOAc and diacetin = 42.6% decomp. of (I), the ester of the sec.-OH underdoing preferential hydrolysis in slightly alkaline medium. J. W. B.

Velocity of bromination of ethyl acetoacetate. II. General basic catalysis. K. J. PEDERSEN (J. Physical Chem., 1934, 38, 601—621; cf. A., 1933, 910).—The velocity of bromination is determined by the consecutive enolisations of Et acetoacetate and the $\alpha\text{-Br-ester}$, which reactions are catalysed by bases. Catalytic consts. of the "bases" AcO^+ , $\text{CH}_2\text{Cl}\cdot\text{CO}_2^+$, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2^+$, H_2PO_4^+ , SO_4^{++} , and H_2O have been determined. Velocities of enolisation are considered to be determined by those of dissociation of the keto-forms. F. L. U.

Velocity of hydration of acetic anhydride. O. FELSENFELD (Chem. Listy, 1934, 28, 89—93).—The velocity coeff. k of the reaction $\text{Ac}_2\text{O} + \text{H}_2\text{O}$ 2AcOH does not vary with the initial concn. at 10—35° between 0.01 and 0.115*N*; at higher concns. k diminishes to a greater extent at higher than at lower temp. At a given concn. $k_{10} : k_{20} : k_{25} : k_{30}$ are as 2² : 3² : 4² : 5². Various acids in concns. >0.1*N* accelerate the reaction, in the order $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HBr} > \text{HCl}$, whilst NaOH and KOH retard reaction. The val. of k varies in presence of the nitrates, sulphates, chlorides, and bromides of K, Na, Li, and Mg (with the exception of MgSO_4 and LiBr) in accordance with the Grube-Schmid rule (A., 1926, 474). R. T.

Decomposition of $\alpha\text{-nitrocarboxylic acids}$. K. J. PEDERSEN (J. Physical Chem., 1934, 38, 559—571).—From a study of the velocity of decomp. of $\text{NO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and $\text{NO}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$ in acetate buffers and aq. HCl of different concns. it is inferred that the ion $[\text{C}(\text{NO}_2)\cdot\text{CO}_2]^+$ decomposes to give $\text{C}\cdot\text{NO}_2^+$ and CO_2 . The calc. dissociation consts. of the two acids are 0.0208 and 0.0118, respectively, at 17–84°. A mechanism for the decomp. of $\alpha\text{-nitro-}$ and $\beta\text{-keto-}$ carboxylic acids is suggested. F.

Velocity of reaction at sulphide surfaces. S. A. KAMENETZKI (J. Appl. Chem. Russ., 1934, 7, 12).—The velocity of reaction, v , of aq. AgNO_3 with a no. of natural cryst. sulphides \propto the surface contact; the amount of Ag_2S deposited per sq. cm.

of surface is const. and characteristic of the given sulphide. The val. of v increases in the order chalcopryrite > coveline > pyrites > Zn blende > orpiment > galena > chalcocine; this order is identical with that of solubility. R. T.

Influence of oxygen, sulphur dioxide, and moisture on the homogeneous combination of hydrogen with sulphur. E. E. AYNSLEY and P. L. ROBINSON (Nature, 1934, 133, 723—724; A., 1933, 911).—In the reaction between S and H_2 containing 0.06 to 7 vol.-% O_2 , between 290° and 343° all the O_2 goes to SO_2 in the first few min., after which H_2 reacts with the remaining S at the velocity expected for H_2 alone. Contrary to Norrish and Rideal (J.C.S., 1923, 123, 1689), neither free O_2 nor SO_2 affects the velocity of the $\text{H}_2\text{-S}$ reaction. In packed bulbs some SO_2 and H_2S react according to the scheme $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + 3\text{S}$, but only at the glass surface; in unpacked bulbs the reaction is undetectable. H_2O has no effect on the $\text{H}_2\text{-S}$ reaction. L. S. T.

Velocity of reaction between iron and cupric sulphate. S. A. VOZNESENSKI and I. T. NAGATKIN (J. Appl. Chem. Russ., 1934, 7, 51—60).—The process of extraction of Cu from H_2O by Fe ceases when the Fe becomes covered with a uniform layer of Cu; the layer is less adherent with low than with high [Cu]. The velocity of reaction with steel is > with Fe, and is at a max. at 50°; Cl^- greatly accelerates reaction. Traces of Cu cannot be removed by passing the H_2O through a column filled with Fe wire; the best procedure is to leave the H_2O in a tank with Fe. R. T.

Passivity of magnesium in chromic acid.—See B., 1934, 542.

Inert gas effect in the radiochemical polymerisation of acetylene. W. MUND (J. Physical Chem., 1934, 38, 635—637).—The catalytic efficiency of CO_2 calc. according to a theory previously developed (A., 1931, 1139) agrees with recently published experimental data (A., 1933, 238). F. L. U.

Efficiency of argon as a radiochemical catalyst. C. ROSENBLUM (J. Physical Chem., 1934, 38, 683—688; cf. A., 1933, 238).—By correcting for the proper efficiency of an ionic catalyst the "depletion" effect is eliminated. About 40% of the ionisation produced in A is utilised in promoting oxidation of H_2 and of CO, and about 60% in the polymerisation of C_2H_2 . Corrections of this kind lead to satisfactory velocity coeffs. and vals. of the ratio (no. of mols. per ion-pair) in regions where most of the total ionisation is carried by the A. F. L. U.

Effect of nitrogen peroxide on the kinetics of ethane oxidation. A. I. SERBINOV and M. B. NEIMAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 297—300).—The velocity of oxidation of C_2H_6 at about 100 mm. and at temp. < 500° is increased by addition of traces of NO_2 , the auto-catalytic character of the oxidation ceasing. The following reaction mechanism is suggested: $\text{NO}_2^* + \text{O}_2 = \text{NO}_2 + \text{O}_2^*$; $\text{O}_2^* + \text{O}_2 = 2\text{O}_2^+$; $\text{O}_2^* + \text{C}_2\text{H}_6 = \text{C}_2\text{H}_5\text{O}_2$. J. W. S.

Thermal decomposition of acetaldehyde under the influence of various catalysts. H. FROMHERZ (Z. physikal. Chem., 1934, B, 25, 301—318).—The

homogeneous decomp. is catalysed by Br, HCl, and H_2S , the velocity being proportional to the catalyst concn. Temp. coeffs. have been determined. NH_3 , $\text{C}_2\text{H}_5\text{N}$, C_2N_2 , HCN, and SO_2 have no catalytic action. Substances which react at low temp. with MeCHO are catalytically inactive; the substances which are catalysts have a high polarisability. The MeCHO, but not the catalyst, has more or less of a deactivating effect on the intermediate compound which determines the reaction, an active complex of MeCHO and catalyst.

R. C.

Protolytic reactions and prototropic isomerisation. K. J. PEDERSEN (J. Physical Chem., 1934, 38, 581—600).—A theory of prototropic reactions similar to that proposed by Ingold, Shoppee, and Thorpe (A., 1926, 939) is discussed. Experiments on the decomp. of $\text{NH}_2\cdot\text{NO}_2$ afford strong support for Bronsted's theory of acid and basic catalysis.

F. L. U.

Enzyme catalysis of the ionisation of hydrogen. B. CAVANAGH, J. HORIUTI, and M. POLANYI (Nature, 1934, 133, 797; cf. this vol., 37).—*B. coli* and *B. acidilactici* (I) catalyse the reaction $\text{HH}^2 + \text{H}_2\text{O} \rightarrow \text{H}_\bullet + \text{HH}^2\text{O}$. For (I) k is 0.0065 at 37°.

L. S. T.

Active spots of catalysts. A. FROST and M. SCHAPIRO (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 243—248).—A discussion. Active spots are identified with defects in the crystal lattice (cf. Smekal, A., 1929, 1370).

H. J. E.

Yield of the reaction of synthesis of ammonia at high pressures. L. KOWALCZYK (Przemysł Chem., 1934, 18, 69—84).—A thermodynamical consideration of the reaction leads to the conclusions that the yield of NH_3 in the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ should increase with pressure, and that an excess of one of the substrates should adversely affect the yield.

R. T.

Catalytic decomposition of lead tetraphenyl. M. KOTON (J. Amer. Chem. Soc., 1934, 56, 1118—1119).—The decomp. of PbPh_4 is catalysed by Pb.

E. S. H.

Activity and crystal structure of mixed metal catalysts. J. H. LONG, J. C. W. FRAZER, and E. OTT (J. Amer. Chem. Soc., 1934, 56, 1101—1106).—Four series of mixed catalysts (Ni-Fe, Ni-Co, Ni-Cu, and Fe-Co) were prepared by reduction of the hydroxides; their crystal structure was determined by the X-ray method and their catalytic activity by the hydrogenation of C_6H_6 to cyclohexane. A substitutional type of solid solution is formed. The activity is related to the arrangement of the atoms in the mixed catalyst.

E. H. S.

Physico-chemical study of the iron catalyst used in the synthesis of liquid hydrocarbons. J. ANTHEAUME, E. DECARRIÈRE, and R. RÉANT (Chim. et Ind., 1934, 31, Spec. No., 421—423).—The catalyst used for the oxidation of CO to liquid hydrocarbons consists of a mixture of oxides of Fe and Cu with K_2CO_3 ; to be effective it must contain both Fe_2O_3 and Fe_3O_4 . The activity is the greater the finer is the crystal. structure.

H. S. P.

Catalytic preparation of aniline and its homologues from tar phenols and ammonia.—See B., 1934, 491.

Neutral salt action in the hydrolysis of wool by acids and bases. E. KIMMEL (Bul. Soc. Chim. Romania, 1934, 15, 121—127).—NaCl favours hydrolysis of wool by 1% HCl, but Na_2SO_4 hinders hydrolysis by 1% H_2SO_4 . Na_2SO_4 and Na_2CO_3 hinder to equal extents the action of 0.4*N*- and 0.1*N*-NaOH, the temp. effect being negligible, but in 0.00125*N*-NaOH addition of Na_2SO_4 produces a max. rate of hydrolysis when the salt concn. is about 10%.

H. F. G.

Production of large quantities of heavy water. L. TRONSTAD (Nature, 1934, 133, 872).—The efficiency of separation is only slightly affected by conditions of electrolysis.

L. S. T.

Electrolytic separation of isotopes. R. P. BELL (J. Chem. Physics, 1934, 2, 164—166).—Gurney's treatment of overvoltage (cf. A., 1932, 25), applied to the relative rates of discharge of two isotopes, gives a separation efficiency independent of, or varying only slightly with, the electrode material and c.d. A rough estimate of the possibility of separating Li^6 and Li^7 by electrolysis is given.

N. M. B.

Mechanism of electrodeposition. L. B. HUNT (Trans. Electrochem. Soc., 1934, 65, 95—105; cf. B., 1932, 644).—As an alternative to Volmer's "migration" theory of lattice development (cf. A., 1932, 688), which is criticised, it is suggested that metal ions accumulate by adsorption in the double layer until a continuous lattice can be formed therefrom over the face of any particular crystal. The movement of electrons through the cathode surface is dependent on the presence of adsorbed ions in a condition permitting their acceptance of electrons. The lateral spreading observed by Volmer is interpreted as a wave-like succession of electron transitions passing through the adsorbed layer and incorporating it into the lattice.

H. J. T. E.

Electrodeposition of indium from cyanide solutions. D. GRAY (Trans. Electrochem. Soc., 1934, 65, 283—286).—The tendency for $\text{In}(\text{OH})_3$ to ppt. from its solution in excess of aq. NaCN is counteracted by addition of 0.5 g. of glucose per g. of In. The resulting solution keeps indefinitely and can be boiled without decomp.; electrolysis of such a solution containing 30—60 g. of In per litre at 15—40° using insol. anodes yields white, coherent deposits of In at 1—16 amp. per sq. dm.

H. J. T. E.

Electric phenomenon at the surface of the photographic dry plate. T. KINBARA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 275—282).—When a pole of Pt, Pd, Au, Ag, Al, Ni, Cu, Zn, Mg, Cd, Bi, Sb, Pb, or C was kept in contact with the centre of a dry plate laid on sheet metal, and a const. field of 500 volts was applied between the pole and the sheet for about a day, the plate, on developing, showed a characteristic figure consisting of a nucleus and halo, and, in the case of an Fe or Sn pole, a corona. An alternating field gave no figure.

N. M. B.

Preparation of calcium silicide by electrolysis of molten [silicate] bath. M. DODERO (Compt. rend., 1934, 198, 1593—1594; cf. this vol., 372).—Electrolysis of a molten CaSiO_3 bath ($\text{SiO}_2 + \text{CaCO}_3 + 2\text{CaF}_2 + 1/3\text{CaCl}_2$) at 25 amp. per sq. cm. gave cathodic mixtures of CaSi_2 (I) and Si in proportions depending on the temp. (I) was practically the sole product at the m.p. of the bath, 1000°. Yield about 2.5 g. per hr. B. W. B.

Nickel-plating of aluminium.—See B., 1934, 504.

Oxidation-reduction processes at the surface of an interposed membrane during electrolysis of a cupric solution. (MME.) L. GUASTALLA (Compt. rend., 1934, 198, 1679—1680).—A pig's bladder membrane (I), 0.15 mm. thick, was interposed in a cell containing 0.002M- CuCl_2 , passing 5 milliamp. per sq. cm. $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 3\text{H}_2\text{O}$, and later CuO , Cu_2O , and Cu, were formed on the anode-chamber (II) surface of (I), and Cu_2O , Cu, and O_2 on the cathode chamber (III) surface, whilst p_{H} increased in (II) and decreased in (III). A section through (I) showed that pptn. was confined to within < 0.03 mm. of either surface. B. W. B.

Electro-crystallisation of metals. IV. Structure of aluminium deposited in the electrolysis of the fused salts AlCl_3 and NaCl. K. M. GORBUNOVA and Z. A. ADSHEMJAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 564—570; cf. A., 1933, 767).—The optimum concn. of electrolyte for the electrolytic deposition of Al is an equimol. mixture of AlCl_3 and NaCl. The lower is the c.d. the finer are the crystals and the less is the tendency to form dendrites. Pre-treatment of the cathode by anodic dissolution facilitates the formation of a solid deposit, but the latter is generally readily detachable from the cathode as a fine powder. The lower is the temp. the more compact is the deposit. X-Ray measurements show the absence of characteristic orientation in the growth of the crystals, the magnitude of which is always 10^{-2} — 11^{-3} mm. J. W. S.

Electrolytic oxidation of β -hydroxypropionic acid. E. TOMMILA (Suomen Kem., 1934, 7, 87—90b).—Electrolytic oxidation of $M\text{-OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}_2\text{H}$ (I) in 5N-NaOH affords at the anode O_2 , CO_2 , CO, H_2 , $\text{H}_2\text{C}_2\text{O}_4$ (II), HCO_2H , and $\text{CH}_2(\text{CO}_2\text{H})_2$, a (?) hydroxyketo-acid giving a green colour with naphthoresorcinol being obtained when a Pt anode is used. Contrary to Miller *et al.* (A., 1894, i, 228), very little resinification occurs when a neutral solution of the pure Na or K salt of (I) is electrolysed, the anodic products being as above [except H_2 and (II)] and, in addition, C_2H_2 , C_6H_4 , C_2H_6 , AcOH, and MeCHO. The amounts of these products obtained with different electrodes (Pt, Ni, Fe), c.d., time, and temp. (0° and 25°) are tabulated and the mechanism of their formation is fully discussed. Anode potential (ϵ_a)-c.d., and ϵ_a -time curves are plotted. J. W. B.

Oxidation of selenium in the glow discharge. N. KRAMER and V. W. MELOCHE (J. Amer. Chem. Soc., 1934, 56, 1081—1083).—By the action of O_2 on Se in the region of the negative glow of the discharge

tube, a white deposit, consisting of SeO_2 with $\approx 57\%$ of SeO_3 , is formed. The product is stable at room temp. and dissolves in H_2O , giving a solution of H_2SeO_3 and H_2SeO_4 . E. S. H.

Heterogeneous chemical reactions in the silent electric discharge. VIII, IX. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1934, 9, 165—174, 175—181).— Cu^{II} , Zr, Ti^{II} , UO_2 , Fe^{III} , and Cr^{III} nitrates in H_2 yielded NH_4 salts, the hydroxide of the metal, N oxides, and, in some cases, metal and nitrite. Ca and Na sulphites gave hydroxide and H_2S . CdBr_2 , $\text{Hg}(\text{CN})_2$, and AgCN were reduced to metal and the corresponding acid. KCN was unattacked, whilst KClO_4 gave KCl and H_2O . $\text{Hg}(\text{CNS})_2$, NaCNS, and $\text{Pb}(\text{CNS})_2$ gave sulphide, H_2S , and HCN. With $\text{Hg}(\text{CNS})_2$, Hg and HCNS were also produced.

D. R. D.

Absorption of light by hydrogen peroxide in alkaline solution. G. BREDIG, H. L. LEHMANN, and W. KUHN (Z. anorg. Chem., 1934, 218, 16—20).—By the progressive addition of NaOH to aq. H_2O_2 the absorption curves are strongly displaced towards longer wave-lengths. The curve for NaOH : $\text{H}_2\text{O}_2 = 2 : 1$ relates to HO_2' , and the marked difference between the absorption of H_2O_2 and that of HO_2' indicates that the ionisation is accompanied by a change in the mode of interat. linking.

F. L. U.

Kinetics of photochemical decomposition of ammonia. Occurrence of an intermediate product NH_4 . L. FARKAS and P. HARTECK (Z. physikal. Chem., 1934, B, 25, 257—272; cf. this vol., 374).—The stationary [H] established on irradiation of NH_3 under various conditions has been determined by means of the reaction $\text{H} + \text{H}_3^{\text{am}} \rightleftharpoons \text{H} + \text{H}^{\text{ortho}}$. The effect of temp. on [H] indicates that the H atoms formed by light absorption are used up in reactions with insignificant heat of activation. [H] is largely independent of the total pressure at 250—760 mm., but falls below 250 mm., is proportional to $I_{\text{be}}^{0.60}$, where I is the light intensity, and passes through a max. with increasing NH_3 pressure. In explanation it is suggested that the H atoms formed by $\text{NH}_3 + h\nu = \text{NH}_2 + \text{H}$ form NH_4 by addition and an equilibrium $\text{NH}_3 + \text{H} \rightleftharpoons \text{NH}_4$ set up, which at room temp. is almost entirely over to the right, but at 300° has moved to the left. At small NH_3 pressures the establishment of equilibrium is prevented by diffusion of H atoms to the wall. The quantum yield of $\frac{1}{4}$ is explained by the alternative reactions $\text{NH}_4 + \text{NH}_2 = 2\text{NH}_3$ or $= \text{NH}_3 + \text{NH} + \text{H}_2$, the first of which is three times as probable as the second. The rise of the quantum yield above 400° may be due to the above equilibrium moving so far to the left that not sufficient NH_4 remains to react with the NH_2 in this way. R. C.

Photochemical action of complex light. II. C. WINTHER (Z. wiss. Phot., 1934, 33, 52—56).—The val. 9.0% for the transparency of a saturated NiSO_4 solution, as found by Padoa and Vita (this vol., 155), is incorrect, since the spherical aberration of the flask used as a lens was not considered. New, corr. measurements, using a flask of diameter 8.5 cm.,

give an average transparency of 74%. The author's previous criticisms are sustained. J. L.

Sensitivity of photographic films to X-rays at low temperatures. G. E. M. JAUNCEY and H. W. RICHARDSON (*J. Opt. Soc. Amer.*, 1934, 24, 125—126).—Measurements at 103°, 203°, and 295° abs. show that at const. temp. the density of a film \propto the time of exposure to X-rays provided the density is not too high, and that the slope of the density-time curves is a linear function of the temp. if this is not too low. The slopes at 295°, 203° and 103° abs. \propto 1, 0.452, and 0.388. A. G.

Formation of chlorine heptoxide on illumination of mixtures of chlorine and ozone. A. C. BYRNS and G. K. ROLLEFSON (*J. Amer. Chem. Soc.*, 1934, 56, 1250—1251).—The amount of Cl_2O_7 produced \propto the initial O_3 pressure and increases with increasing Cl_2 pressure, but is only slightly dependent on temp. between 20° and 30°. E. S. H.

Photochemical decomposition of phosgene. C. W. MONTGOMERY and G. K. ROLLEFSON (*J. Amer. Chem. Soc.*, 1934, 56, 1089—1092).—On the basis of kinetic measurements a mechanism is put forward from which is derived the rate law $-d[\text{COCl}_2]/dt = kI_{\text{abs.}} - k'I_{\text{abs.}}^{1/2}[\text{CO}]^{1/2}[\text{Cl}_2]$, which is in accordance with the experimental facts. E. S. H.

Photochemical decomposition of keten. W. F. ROSS and G. B. KISTIAKOWSKY (*J. Amer. Chem. Soc.*, 1934, 56, 1112—1115).— CH_2CO is decomposed by wave-lengths $< 3700 \text{ \AA}$., yielding CO and C_2H_4 . The quantum yield = 1 approx. at 3130 \AA ., which with the diffuse structure of the spectrum suggests that CH_3 is formed first. In presence of C_2H_4 , CH_2 forms a solid polymeride. E. S. H.

Formation of carbon tetrachloride from chloroform and chlorine in light. H. J. SCHUMACHER and K. WOLFF (*Z. physikal. Chem.*, 1934, B, 25, 161—176).—The rate of reaction in the vapour state at 50—70° is given by $d[\text{CCl}_4]/dt = k[\text{Cl}_2]^{1/2}(I_{\text{abs.}})^{1/2}$. The temp. coeff. at 50—60° is 1.45 ± 0.1 . O_2 practically suppresses CCl_4 formation and COCl_2 is formed. The reaction has a chain mechanism: $\text{Cl}_2 + h\nu = 2\text{Cl}$ (1), $\text{Cl} + \text{CHCl}_3 = \text{CCl}_3 + \text{HCl}$ (2), $\text{CCl}_3 + \text{Cl}_2 = \text{CCl}_4 + \text{Cl}$ (3), $\text{CCl}_3 + \text{CCl}_3 + \text{Cl}_2 = 2\text{CCl}_4$ (4). The energies of activation of (2), (3), and (4) are < 4.3 , ~ 8 , and $\sim 0 \text{ kg.-cal.}$, respectively. R. C.

Primary process of photochemical decomposition of formaldehyde. I. F. PATAT (*Z. physikal. Chem.*, 1934, B, 25, 208—216).—Investigation of the decomp. of CH_2O vapour under low pressure in presence of O_2 has shown that in decomp. in the continuous region of the absorption spectrum, but not in that in the fine-structure region, H atoms are formed. R. C.

Formation of coloured compounds from primary aromatic amines exposed to the ultra-violet spectrum. H. FREYTAG (*Z. wiss. Phot.*, 1934, 33, 33—38).—Strips of hardened filter-paper, impregnated with aq. or EtOH solutions of the amines, were exposed in a quartz spectrograph. The intensities of colouring at the different wave-lengths were measured, and the results for 18 compounds are

detailed. The amines examined are sensitive only to ultra-violet light, and, for the majority, from 313 $\text{m}\mu$ to the shorter wave-lengths, the intensity of the reaction varying greatly with λ . J. L.

Photochemistry and absorption spectrum of acetone. R. G. W. NORRISH (*Nature*, 1934, 133, 837).—A criticism (cf. this vol., 582). L. S. T.

Photovoltaic cells containing dye solutions. B. S. V. R. RAO (*J. Physical Chem.*, 1934, 38, 693—701).—Using aq. erythrosin and chrysoidine with Pt electrodes, the max. in the potential-concn. curve is shown to be due to absorption of active radiation by the dye solution. Erythrosin gives rise to negative, chrysoidine to positive, potentials. The e.m.f. \propto (intensity) $^{1/2}$. The greatest effect is produced by light of λ slightly $>$ that of the principal absorption band of the dye. F. L. U.

Photolysis of diazo-compounds. M. HORIO (*Mem. Coll. Eng. Kyoto*, 1934, 8, 1—7).—Many diazo-compounds are sensitive to light of $\lambda < 4000$ —4500 \AA ., and the upper limit agrees with that of mol. absorption. For copying papers of 1-diazo- β -naphthol-4-sulphonic acid and of *p*-diazodiphenylamine sulphate the curve of λ -spectral sensitivity is similar to that of λ -extinction coeff. A. G.

Mutual effect of dyes and fatty acids when exposed to light. M. HORIO (*Mem. Coll. Eng. Kyoto*, 1934, 8, 26—28).—The addition of linoleic acid (I) accelerates the bleaching of eosin (II) and of Victoria-violet (III) by light, and the addition of (II) or of erythrosin accelerates peroxide formation when (I) is exposed to light. A rapid stream of O_2 hinders bleaching of (II) or (III) in the presence of (I). A. G.

Photochemical investigation of plant oils and fatty acids. M. HORIO (*Mem. Coll. Eng. Kyoto*, 1934, 8, 8—25).—When olive oil (I), linseed oil (II), or linoleic acid (III) is exposed to light in presence of O_2 peroxides are formed; in absence of O_2 illumination has no effect. The spectral sensitivity and the extinction curves are parallel. For (II) and (III) λ of the active rays is $< 4000 \text{ \AA}$. The rate of the photochemical reaction is independent of the time of exposure (1—8 hr.), the supply of O_2 (0.7—7.5 litres per hr.) and the temp. (0.5—25°); it is \propto the concn. of fatty acid (2.5—20%) and to $I^{1/2}$ (1.1—14); a chain mechanism is proposed. For (I) the velocity is a max. at a definite light intensity (I), which is explained by a modification of the chain mechanism. The reaction persists after the exposure is interrupted.

Dynamics of photosynthesis. W. O. JAMES (*New Phytol.*, 1934, 33, 8—40).—A mathematical interpretation of photosynthesis as a heterogeneous photochemical reaction. A. G. P.

Origin of the β - and γ -ray coloration of alkali, baryta, and alkali borate glasses. J. HOFFMANN (*Z. anorg. Chem.*, 1934, 218, 129—138).—Alkali silicate and borate glasses show, under the action of β - and γ -rays, parallel colour changes apparently connected with the constitution of the glasses. A violet colour, probably due to Na_2SiO_3 or $\text{Na}_2\text{B}_2\text{O}_4$, is obtained with high alkali conten.

This changes as acidity increases through grey, due to a labile form of SiO_2 or B_2O_3 adsorbed by the silicate or borate, to yellow or brown due to reduction to Si and B, respectively. It is possible that the similar changes observed in Ba glasses may have a similar origin. M. S. B.

Mechanism of oxidation promoted by ultrasonic radiation. S. LIU and H. WU (J. Amer. Chem. Soc., 1934, 56, 1005—1007).— O_2 mols. at the surface of bubbles are activated by ultrasonic radiation, and have the property of liberating I from KI and reacting with H_2O to give H_2O_2 . CCl_4 and CHCl_3 are oxidised, yielding Cl_2 . E. S. H.

Purity of distilled water. W. L. A. WARNIER (Chem. Weekblad, 1934, 31, 254—255).—The Dutch Pharmacopœia specification for distilled H_2O requires revision, since it permits the presence of sufficient dissolved CO_2 to yield a turbidity with 5% AgNO_3 solution. H. F. G.

Preparation of distilled water. A. A. GUNTZ (Chim. et Ind., 1934, 31, Spec. No., 238—243).—The effect of additions of acid, alkali, and salts, and of conditions of distillation has been studied by measuring the conductivity of fractions of the distillate. H. J. E.

Per-compounds. II. Distinction between different types of per-compounds. F. KRAUSS and C. OERTNER (Z. anorg. Chem., 1934, 218, 21—32; cf. A., 1932, 350).—A discussion of methods of distinguishing "true" per-salts from H_2O_2 -additive products. F. L. U.

Reaction of sodium with dry oxygen. B. L. HERRINGTON (J. Physical Chem., 1934, 38, 675—682).—Na amalgams are instantly attacked by O_2 that has been dried with P_2O_5 for more than a year. A surface film of oxide, which protects the metal from further attack, is formed. In presence of H_2O vapour the film is unstable and the Na is slowly but completely oxidised. Oxidation is accompanied by the emission of light. F. L. U.

Preparation of carbonate-free sodium hydroxide. W. STAHL (Z. anal. Chem., 1934, 97, 86—89).—Na reacts with H_2O vapour in a vessel sealed against CO_2 by KOH, warmed to 40° . Explosion may occur if the temp. rises to 50° . J. S. A.

Preparation of pure anhydrous sodium carbonate. W. H. WITHEY (J. Soc. Glass Tech., 1934, 18, 69—70T).—A product free from Fe_2O_3 is obtained by pptn. with EtOH from aq. solution at 50° . The $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ so formed is easily dehydrated without fusion at $> 250^\circ$. J. S. A.

Complexes of mannitol and sorbitol with sodium arsenite and borax. M. SRINIVASAN and SREENIVASAYA (J. Physical Chem., 1934, 38, 703—711).—Mixing of mannitol (I) with borax or Na arsenite in aq. solution is accompanied by a considerable increase of vol. Sorbitol behaves similarly. The expansion, as well as the change in optical rotation observed in the case of (I), is regarded as an indication of the formation of compounds. F. L. U.

Phosphorescent beryllium nitride. S. SATOH (Nature, 1934, 133, 837).—The product obtained by

passing NH_3 over a mixture of Be+10% Al_2O_3 at 1000° shows a blue luminescence after exposure to a Hg-arc lamp. L. S. T.

Complex calcium aluminates. J. FORET (Chim. et Ind., 1934, 31, Spec. No., 722—726).— $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and Ca salts form two series of double salts having the general formulæ $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(A)_2 \cdot 10\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(A)_2 \cdot 30\text{H}_2\text{O}$ (where A is the acid radical). The conditions of pptn. and solubility curves, in the first series for $A=\text{Cl}', \text{Br}', \text{I}', \text{NO}_3'$, and NO_2' and in the second series for $A=\text{SO}_4'', \text{CrO}_4'', \text{SeO}_4'', \text{MnO}_4'', (\text{HCO}_2)'$, have been determined. T. W. P.

Hydrated calcium aluminates. M. EROULISSE (Chim. et Ind., 1934, 31, Spec. No., 727—731).—A discussion of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ based on results from the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$. T. W. P.

Reactions in the solid state at high temperatures. XI. Reaction between calcium oxide and silica. W. JANDER and E. HOFFMANN (Z. anorg. Chem., 1934, 218, 211—223).—By heating, at $1000-1200^\circ$, mixtures of CaO and SiO_2 in different proportions, powdered together for a longer or shorter time, $2\text{CaO} \cdot \text{SiO}_2$ is first formed. For high proportions of CaO (4CaO to SiO_2) and a sufficiently high temp., $3\text{CaO} \cdot \text{SiO}_2$ may next be obtained. In other circumstances the next product is $3\text{CaO} \cdot 2\text{SiO}_2$. As heating continues more SiO_2 , if sufficient is present, enters into combination, and the final product is $\text{CaO} \cdot \text{SiO}_2$. M. S. B.

Action of nitrogen on calcium. H. HARTMANN and H. J. FROHLICH (Z. anorg. Chem., 1934, 218, 190—192).—The combination of N_2 with pure Ca, free from alkali and N, ceases as soon as a thin layer of Ca_3N_2 has been formed on the surface. With Ca activated by $< 1\%$ Na, the velocity of N absorption depends on temp. Two modifications of Ca_3N_2 have been obtained, a pseudo-hexagonal form (I) at 300° , a 3.553, c 4.11 Å., $d_{\text{calc.}}$ 2.72, and a cubic form (II) at 800° , a 11.38 Å., $d_{\text{calc.}}$ 2.66. (II) is obtained when (I) is heated at 500° (cf. Franck *et al.*, A., 1933, 666). M. S. B.

Calcium oxychloride $3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 11\text{H}_2\text{O}$. V. I. NIKOLAEV and S. A. GLINSKICH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 1, 572—574).—The compound to which the formula $3\text{CaO} \cdot \text{CaCl}_2 \cdot 16\text{H}_2\text{O}$ was attributed by Ditte (Z. anorg. Chem., 1893, 3, 34), Schreinemakers and Figeé (A., 1911, ii, 983) and Milikan (A., 1917, ii, 257) is actually $3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 11\text{H}_2\text{O}$, the previous errors being due to the fact that the crystals contain up to 16% of mother-liquor. J. W. S.

New pernitride of strontium and calcium and the imides of the alkaline-earth metals. H. HARTMANN, H. J. FROHLICH, and F. EBERT (Z. anorg. Chem., 1934, 218, 181—189).—By heating the alkaline-earth amides $\text{M}(\text{NH}_2)_2$ at approx. 400° , without removing the gases formed, the imides MNH are obtained as yellow, cubic, face-centred crystals. X-Ray data are given. By heating the amides in a high vac. the pernitrides Sr_3N_4 and Ca_3N_4 have been obtained as reddish-brown powders, probably mixed with the corresponding imide.

They dissolve slowly in dil. HCl or H₂O with evolution of NH₃ and N₂. The X-ray spectra contain, besides the imide lines, new lines which cannot be measured owing to a cloudiness which is apparently always found when the pernitride is present. Ba₃N₄ is probably formed similarly. M. S. B.

Precipitation of mercurous hydroxide. W. H. BENNETT (J. Physical Chem., 1934, 38, 573—579).—It is inferred from results of the potentiometric (glass electrode) titration of a dil. HNO₃ solution of Hg₂(NO₃)₂ with NaOH that the ppt. has the approx. composition 3Hg₂O.Hg₂(NO₃)₂.xH₂O. The solubility product of Hg₂(OH)₂ is calc. to be 7.8×10^{-24} . Hg₂(NO₃)₂ is considerably hydrolysed in HNO₃ at *p*_H between 2 and 3. F. L. U.

Double thiocyanates of mercury and cobalt. II. S. AUGUSTI (Gazzetta, 1934, 64, 169—175).—By the action of an aq. solution of KCNS and a Co^{II} salt on a solution of a Hg^I salt (or on solid HgCl) a bluish-green ppt. of Hg₄[Co(SCN)₆]₃ is obtained. This reaction can be used as a qual. test for Hg^I. O. J. W.

Fractionation of actinium in the presence of rare earths. M. CURIE and S. TAKVORIAN (Compt. rend., 1934, 198, 1687—1689).—Fractionation of originally inactive mixtures of La, Nd, and Sm with added Ac, (i) as double NH₄ nitrates and (ii) as double Mg nitrates, gave max. of Ac in different fractions, (ii) being the more effective in concentrating Ac. The activity of fractionated monazite concentrates previously attributed to element 61 is due to Ac (A., 1933, 442). B. W. B.

Combustion of graphite. II. V. SIHVONEN (Suomen Kem., 1934, 7, 83—85B; cf. A., 1933, 1254).—Theoretical. F. L. U.

Preparation of hydrogen compounds of silicon. W. C. JOHNSON and T. R. HOGNESS (J. Amer. Chem. Soc., 1934, 56, 1252).—A mixture of Si hydrides in good yield is obtained by dropping Mg₂Si into a solution of NH₄Br in liquid NH₃. E. S. H.

Nitrosonium chloride. R. SCHWARZ and F. HEINRICH (Ber., 1934, 67, [B], 776—778; cf. Tiede, this vol., 499).—The red compound from NO and HCl is not formed in complete absence of higher oxides of N, although neither N₂O₃ nor NO₂ gives a red compound with HCl. Determination of the m.p. of mixtures of NO and HCl does not disclose a max. at NO.HCl, but the m.p. of HCl is steadily depressed. The other H halides do not appear to react with NO. H. W.

Transformation of phosphorus pentanitride into mononitride. H. MOUREU and P. ROCQUET (Compt. rend., 1934, 198, 1691—1693).—The action of liquid NH₃ on (PNCl₂)₃ gives PN₃H₄ [possibly PN(NH₂)₂; cf. A., 1908, ii, 583] which yields PN₂H at 380°. PN₂H heated in vac. at >400° gives P₃N₅+NH₃; P₃N₅ decomposes at 700° to PN+N₂, and not to P+N₂ (cf. this vol., 158). PN is volatile at high temp., is decomposed by conc. H₂SO₄, and appears to be dimeric. B. W. B.

Transposition of insoluble phosphates by means of sodium carbonate solution. D. HART, J. COHEN, and J. SIMON (Rec. trav. chim., 1934, 53,

579—583).—The degree of transformation of 24 insol. phosphates by boiling with 1.5*M*-Na₂CO₃ has been determined. The results do not generally agree with calculations from available solubility data. 3*M*-K₂CO₃ is more effective than 1.5*M*-Na₂CO₃. F. L. U.

Preparation of pure arsenic. A. DE PASSILLE (Compt. rend., 1934, 198, 1781—1783; cf. this vol., 377).—Sb was completely eliminated by successive recrystallisation of (NH₄)H₂AsO₄, which was then reduced at 1000° in a current of NH₃, and the As finally redistilled in vac. Analysis of As prepared in this way revealed no impurities. B. W. B.

Action of sodium carbonate on niobium pentoxide. P. SUE (Compt. rend., 1934, 198, 1696—1698).—Study of the rates of evolution of CO₂ from various heated mixtures of Nb₂O₅+Na₂CO₃ indicated the formation of NaNbO₃ at 625° (cf. A., 1932, 1192) and of Na₂NbO₄ (I) at 775°. (I), *d* 3.725, was slightly sol. in H₂O and was decomposed by H₂SO₄ and HCl. B. W. B.

New compounds of bismuth and antimony with iodine and tri(hydroxyethyl)amine. E. JAFFE (L'Ind. Chimica, 1934, 9, 618—622; cf. this vol., 396).—The *cryst. compounds*, N(CH₂.CH₂.OH)₃.HI.BiI₃, m.p. 193°, and NH₄.C₆H₄.OH.SbI₃, m.p. 174°, are described. T. H. P.

Binary system sulphur dioxide-water. Two modifications of solid SO₂. E. TERRES and G. RUHL (Angew. Chem., 1934, 47, 331—332).—A metastable *modification* (β-SO₂, m.p. 62.5°) is first to crystallise from the liquid in presence of traces of H₂O. D. R. D.

Existence of lead and zinc complexes with sulphurous acids. E. TERRES and G. RUHL (Angew. Chem., 1934, 47, 332—334).—The mutual solubilities of SO₂ and H₂O are not greatly altered in presence of FeO, PbO, ZnO, or CuO even in the crit. regions. Complex Pb-Zn minerals may be extracted with conc. aq. SO₂ under increased pressure and temp. to recover the metals as simple salts. D. R. D.

Decomposition of dithionic acid. H. STAMM and R. ADOLF (Ber., 1934, 67, [B], 726—730).—The hypothesis that the decomp. of H₂S₂O₆ is connected with its transformation into the *ψ* form is supported by the observation that decomp. occurs at much greater dilution in MeOH or EtOH than in H₂O. Attempts to prepare Me₂S₂O₆ from Ag₂S₂O₆ and MeI led to evolution of SO₂ and production of MeHSO₄ or Me₂SO₄. N₂H₄.H₂S₂O₆ is unexpectedly stable and its behaviour throws little light on the effect of the addition of H⁺ to S₂O₆²⁻. Solutions of KHS₂O₆, NaHS₂O₆, and LiHS₂O₆ can be conc. without decomp. until crystallisation commences but the normal salts separate. A hyd. K₂S₂O₆ and Na₂S₂O₆ lose SO₂ at about 260° and (NH₄)₂S₂O₆ at 242°; the *ψ*-salt, Ag₂S₂O₆, decomposes at 80—100°, but is stablised by NH₃. H. W.

Action of sulphur dioxide on solutions of molybdc anions. R. LAUTIE (Bull. Soc. chim., 1934, [v], 1, 105—109).—Saturation of aq. solutions of K₂MoO₄, Na₂MoO₄, and (NH₄)₂MoO₄ with

gives molybdosulphites, $2\text{SO}_2, 5\text{MoO}_3, 2\text{M}_2\text{O}, n\text{H}_2\text{O}$, where $n=5, 6$, and 4 , respectively (cf. Rosenheim, A., 1897, ii, 497), which form small transparent crystals, slowly turning blue in the air with evolution of SO_2 . Solutions of molybdosulphites slowly lose SO_2 , especially on heating, this being more pronounced in presence of H_2SO_4 or HCl . SO_2 reduces alkali molybdates in presence of a little H_2SO_4 or HCl , giving a blue solution, which on extraction with BuOH and evaporation of the latter at $80-85^\circ$ yields $\text{Mo}_5\text{O}_{15}, 6\text{H}_2\text{O}$. J. W. S.

Ammonium selenites. J. JANICKIS (Z. anorg. Chem., 1934, 217, 89—103; cf. A., 1932, 584).—The following cryst. salts have been prepared and analysed: $(\text{NH}_4)_2\text{SeO}_3$; $(\text{NH}_4)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$; $(\text{NH}_4)_2\text{Se}_2\text{O}_5$; $(\text{NH}_4)_2\text{Se}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$; $\text{NH}_4\text{H}_3(\text{SeO}_3)_2$. Neither NH_4HSeO_3 nor a sesquiselenite, the existence of which has been reported, could be obtained. Solubility curves for the normal selenite and pyroselenite have been determined. F. L. U.

Formation of perchromates in solution. (MME.) P. RUMPF (Compt. rend., 1934, 198, 1694—1696).— H_2O_2 was added to acid aq. $\text{K}_2\text{Cr}_2\text{O}_7$ or $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, the linear decay of the blue perchromate (I) followed photometrically, and extrapolated to zero time. Max. concn. of (I) always occurred at $\text{CrO}_3/\text{H}_2\text{O}_2=0.5$, supporting the peranhydride CrO_5 suggested by Schwartz and Giese (A., 1932, 708). In solutions of $p_H > 4$ a brown colour formed slowly and was also due to CrO_5 . Equilibrium consts. were determined for acid and alkaline solutions, respectively. B. W. B.

Compounds of uranyl oxalate with alkaline-earth oxalates.—See this vol., 756.

Halogen bleaching liquor reactions. A. SKRABAL (Z. Elektrochem., 1934, 40, 232—246).—Theoretical. On the basis of the known reactions of HOX ($X=\text{halogen}$) under different conditions, a complete scheme of the steps involved is worked out. E. S. H.

Mixed perchloric and sulphuric acids. I. Simultaneous oxidising and reducing properties of hot concentrated perchloric acid. G. F. SMITH (Ind. Eng. Chem. [Anal.], 1934, 6, 229—230).—The oxidising properties are believed to be due to the decomp. $4\text{HClO}_4 \rightarrow 2\text{Cl}_2 + 7\text{O}_2 + 2\text{H}_2\text{O}$, whilst the reducing properties are assumed to be due to H_2O_2 formed by the reaction $2\text{HClO}_4 \rightarrow \text{Cl}_2 + 3\text{O}_2 + \text{H}_2\text{O}_2$. E. S. H.

Iron complexes. I. Electrical conductivity of system $n\text{FeCl}_3-m\text{H}_3\text{PO}_4[-x\text{H}_2\text{O}]$. B. RICCA and P. MEDURI (Gazzetta, 1934, 64, 235—242).—The data indicate the presence of the acid $\text{H}_3[\text{FeCl}_3(\text{PO}_4)]$ (insol. Ag salt). D. R. D.

Introduction of the azide group into complex salts of cobalt. W. STRECKER and H. OXENIUS (Z. anorg. Chem., 1934, 218, 151—160).—The following complex azides and azido-compounds of Co^{III} have been prepared: $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]\text{N}_3$, sol. in cold H_2O and solution decomposed on heating, decomposed $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{N}_3)_2$, rather less stable; $[\text{Co}(\text{NH}_3)_4(\text{N}_3)_2]\text{N}_3$, formed first as a reddish-brown violeo- or *cis*-salt, slightly sol. only in cold H_2O , 3 D

but dissolving in hot H_2O with decomp., a green *praseo*- or *trans*-salt formed on keeping; *cis*- $[\text{Co}(\text{NH}_3)_4(\text{N}_3)_2]\text{SO}_4$, red, slightly sol. in cold H_2O ; *trans*- $[\text{Co en}_2(\text{N}_3)_2]\text{N}_3$, dark green, red *cis*-salt formed in solution on heating with H_2O ; $[\text{Co en}_2\text{Cl}_2]\text{N}_3$, light green, slightly sol. in H_2O ; *cis*- $[\text{Co en}_2(\text{N}_3)_2]\text{N}_3$, red, easily sol. in H_2O ; $[\text{Co}(\text{C}_6\text{H}_5\text{N})_4\text{ClN}_3]\text{N}_3$, dark green, insol. in H_2O ; *azido-amminocobaltic chlorate*, $\text{Co}_2(\text{NH}_3)_6(\text{N}_3)_4\text{ClO}_3$, for which a suitable co-ordination formula has not been found, green, slightly sol. in cold H_2O and decomposed on boiling. All the compounds are more or less explosive. M. S. B.

Physico-chemical methods for the detection of chemical intermediate products. H. SCHMID (Z. Elektrochem., 1934, 40, 274—278).—A review. E. S. H.

"Fundamental error" in mechanical analysis according to Oden's principle. M. VENDL and E. SZADECKY-KARDOS (Kolloid-Z., 1934, 67, 229—233).—A discussion of the errors in sedimentation analysis. E. S. H.

Analysis of gases. P. WALTER (Chim. et Ind., 1934, 31, Spec. No., 210—212).—The gas is passed through a vertical column in which the absorbent is atomised. The used absorbent is collected and the change in its concn. measured conductometrically. The apparatus is suitable for continuous determination of several gases, a no. of absorbing units being arranged in series. Absorbents for H_2S , SO_2 , NH_3 , CO_2 , O_2 , C_2H_2 , CO , NO , Cl_2 , Br_2 , and S_2Cl_2 are described. H. J. E.

Microanalysis of gaseous mixtures by pressure-temperature curves. J. J. S. SEBASTIAN and H. C. HOWARD (Ind. Eng. Chem. [Anal.], 1934, 6, 172—177).—Apparatus and procedure are based on Campbell's method (Proc. Physical Soc., 1921, 33, 287), in which <1 ml. of the sample is required. The method is suitable for the analysis of synthetic mixtures of pure hydrocarbons, commercial gas, and gaseous products obtained by the thermal decomp. of coal. The procedure is especially simple when two components form a heterogeneous condensed phase. E. S. H.

New method of gravimetric analysis. (MLLE.) S. CHATELET (Chim. et Ind., 1934, 31, Spec. No., 199).—Pptn. is carried out in a 100-c.c. pyknometer, the vol. is made up to 100 c.c. with H_2O , and the wt. of the ppt. is calc. from its d and that of the supernatant liquid. The method has been tested for the pptn. of AgCl , BaSO_4 , PbSO_4 , and PbCrO_4 . H. J. E.

Capillary analysis. R. DUBRISAY (Compt. rend., 1934, 198, 1605—1607; cf. A., 1918, ii, 368).—The rate of drop formation of 0.5% sapamine (cf. B., 1928, 199) solution in C_6H_6 gave sharp end-points in the titration of 0.01N-HCl with aq. NH_3 and piperazine. B. W. B.

Analytical method for converting the p_H into the hydrogen-ion concentration of a solution. M. DÉRIBÉRE (Ann. Chim. Analyt., 1934, [ii], 16, 193—197).—Corresponding vals. of p_H and c_H are tabulated. J. G. A. G.

Indicators for oxidimetry; phenanthroline and diphenylamine derivatives. L. P. HAMMETT, G. H. WALDEN, jun., and S. M. EDMONDS (J. Amer. Chem. Soc., 1934, 56, 1092—1094).—The prep. of *nitrophenanthroline* (I), m.p. 202°, is described; the relative oxidation potentials and indicator properties of the (I)-ferrous ion, *p*-nitro-, *p*-amino-, and 2:4-diamino-diphenylamine have been investigated. New potential ranges are covered by some of these indicators. E. S. H.

Photo-electric colorimetry in water analysis. E. NAUMANN and K. NAUMANN (Z. anal. Chem., 1934, 97, 81—86).—Photo-electric colorimetry by Lange's direct deflexion method (A., 1933, 44) is employed for the determination of Fe, Mn, and PhOH. Nephelometric determination of H_2SO_4 as BaSO_4 , and of Pb as PbS in NH_3 solution, is possible, using gum arabic as stabiliser. J. S. A.

Determination of bromide in presence of large excess of chloride. R. F. NEWTON and E. R. NEWTON (Ind. Eng. Chem. [Anal.], 1934, 6, 213—215).—Br is liberated by adding a moderate excess of aq. Cl_2 , collected in aq. Na_2SO_3 , and titrated potentiometrically after oxidation of excess Na_2SO_3 in the air. The max. error is about 0.2% on a sample containing > 4 mg. Br' and about 0.5% for 0.5—1 mg. Br'. Moderate quantities of I do not interfere. E. S. H.

Mercurimetric determination of iodine using diphenylcarbazone as indicator. J. V. DUBSKÝ and J. TRTILEK (Mikrochem., 1934, 115, 95—98; cf. A., 1933, 364).—I' is titrated with 0.1N- $\text{Hg}(\text{NO}_3)_2$, using diphenylcarbazone to indicate excess of Hg^{2+} . A sharper end-point is obtained by filtering from pptd. HgI_2 when titration is nearly complete, and completing the titration on an aliquot portion of filtrate. J. S. A.

Sensitivity of the iodine-starch reaction. I. M. KORENMAN (Mikrochem., 1934, 15, 25—31).—The sensitivity in neutral solution rises with increase in [KI] to a max., $[\text{I}]=5 \times 10^{-6}\text{N}$, when [KI] < 0.1%. [KI] necessary to attain max. sensitivity decreases with increasing $[\text{H}^+]$. J. S. A.

Determination of iodine. A. ITANO (Ber. Ohara Inst. landw. Forsch., 1933, 6, 53—58).—McClendon's closed combustion method gave better results than those of Fellenberg or of Andrew (B., 1930, 579), although in all cases the presence of org. matter markedly lowered the vals. recorded. A modified method is described in which the I is determined colorimetrically (treatment with H_2SO_4 -nitrite and extraction with CS_2) or volumetrically (liberation of I by Br and titration with $\text{Na}_2\text{S}_2\text{O}_3$). An accuracy of 94—99% is claimed. The min. amount of I determinable by this method is $1 \times 10^{-8}\text{g}$. A. G. P.

Drop methods of detection and determination of fluorine. I. V. TANANAIEV and G. S. SAVTSCHENKO (J. Appl. Chem. Russ., 1934, 7, 229—232).—5 ml. of solution are made alkaline to phenolphthalein with aq. NaOH, excess of aq. AgNO_3 (I) is added, the solution is warmed, and aq. $\text{Ca}(\text{NO}_3)_2$ is added to the filtrate, which becomes turbid if < 0.4 mg.

F is present: $\text{CrO}_4^{''}$, $\text{Cr}_2\text{O}_7^{''}$, $\text{PO}_4^{'''}$, $\text{AsO}_3^{'''}$, $\text{AsO}^{''}$, $\text{BO}_2^{''}$, $\text{SiO}_3^{''}$, $\text{CO}_3^{''}$, Cl^+ , Br^+ , I^+ , CN^+ , CNS^+ , $\text{Fe}(\text{CN})_6^{'''}$, $\text{Fe}(\text{CN})_6^{''''}$, ClO_3^+ , IO_3^+ , NO_2^+ , NO_3^+ , S^{++} , $\text{SO}_3^{''}$, $\text{SO}_4^{''}$, $\text{S}_2\text{O}_3^{''}$, $\text{C}_2\text{O}_4^{''}$, and OAc^+ do not interfere. F' is determined by adding excess of (I) to 5—10 ml. of warm solution, diluting to 100 ml., adding excess of NaCl to an aliquot portion, and titrating the solution at 70—80° with standard AlCl_3 (Me-red indicator). R. T.

Determination of minute quantities of sulphide-sulphur. C. E. LACHELE (Ind. Eng. Chem. [Anal.], 1934, 6, 200—201).—The H_2S , obtained by treatment with acid, is collected as a stain on a paper diaphragm impregnated with $\text{Pb}(\text{OAc})_2$. A uniform coating is ensured by using a stream of N_2 to dilute the gas. An accuracy of $\pm 0.002\text{ mg.}$ is possible for 0.008—0.080 mg. volatile sulphide-S. E. S. H.

Determination of sulphur in sulphides. J. HOMME (Przemysł Chem., 1934, 18, 84—86).—Brunck's method (A., 1905, ii, 762) is modified as follows: 1 g. of substance is mixed intimately with 2 g. of CoO and 3 g. of Na_2CO_3 , the mixture is covered with Na_2CO_3 , and heated at 1000° in O_2 during 25 min. for pyrites, and 40 min. for Zn blende. The melt is extracted repeatedly with 2% Na_2CO_3 , the extract is filtered, and $\text{SO}_4^{''}$ is determined as usual in aliquot parts of the filtrate. R. T.

Bromo-iodometric researches. IX. [Selenites, selenates, and selenium.] J. H. VAN DER MEULEN (Chem. Weekblad, 1934, 31, 333—335).— $\text{SeO}_3^{''}$ (I) is converted into $\text{SeO}_4^{''}$ (II) with KI-HCl in presence of a large excess of starch paste to keep the pptd. Se (III) in solution during titration with $\text{Na}_2\text{S}_2\text{O}_3$. (I) is converted into (II) by NaOBr in presence of KHCO_3 and excess of OBr' determined iodometrically. (II) is reduced to (I) with HBr and (III) is converted into (II) by boiling with KBrO_3 solution prior to determination. S. C.

Detection of selenium and tellurium in presence of one another. N. S. POLUEKTOV (Mikrochem. 1934, 15, 32—34).—Addition of conc. HI (or KI+HCl) to solutions containing Se ppts. $\text{Se}+\text{I}$ (dissolved by $\text{Na}_2\text{S}_2\text{O}_3$), forming a red spot. Te forms $\text{TeI}_6^{''}$, and does not interfere. $\text{TeO}_3^{''}$, but not $\text{SeO}_3^{''}$, is reduced by Sn^{++} in alkaline solution to a greyish-black stain of Te. Bi, Ag, and metals with coloured hydroxides interfere. J. S. A.

Macro- and micro-detection of nitrous acid, especially with chrysean. J. V. DUBSKÝ, J. TRTILEK, and A. OKAČ (Mikrochem., 1934, 15, 99—106).—Chrysean (2-aminothiazole-4-thioamide) gives with NO_2^+ in acid solutions a red coloration or dark red-brown ppt., which can afford a quant. separation from NO_3^+ . Metals of the H_2S group interfere. Limit of detection $0.25 \times 10^{-6}\text{ g.}$ 2-Thiol-4-*p*-amino-phenylthiolthiodiazole in presence of HNO_2 gives with $\alpha\text{-C}_{10}\text{H}_7\text{-OH}$ a deep red colour (limit $0.1 \times 10^{-6}\text{ g. NO}_2^+$). J. S. A.

Analysis of phosphosilicates. A. LASSIEUR (Ann. Chim. Analyt., 1934, [ii], 16, 197—202).—after separating $\text{PO}_4^{'''}$ from the metals by H_2MoO_4 , the Mo is removed from the filtrate () by evaporating with HCl and passing H_2S , a Mo- u

is formed if Fe is present. This is avoided if excess of aq. NH_3 and $(\text{NH}_4)_2\text{CO}_3$ is added to (I) and the ppt. dissolved in HCl before passing H_2S . The traces of Ca and Mg in the filtrate are pptd. by NH_4 oxalate and phosphate, respectively. If the P_2O_5 is $< 10\%$ of the wt. of $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, the first is almost completely pptd. together with $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$, leaving Ca in solution. J. G. A. G.

Determination of traces of arsenic by Cribier's method. II. Application to complex mixtures, in particular to the normal arsenic in urine. H. GRIFFON and M. BUISSON (*J. Pharm. Chim.*, 1934, [viii], 19, 477—497).—Cribier's method (I) is trustworthy only when the As is in relatively pure solution. For urine or other biological fluids, As can be determined by (I) after liberation as AsH_3 and absorption in KMnO_4 . H. G. R.

Selenium as oxidation-reduction indicator in the volumetric determination of arsenite with potassium bromate. L. SZEBELLEDY and K. SCHICK (*Z. anal. Chem.*, 1934, 97, 186—191).—Colloidal Se functions as a rapid oxidation-reduction indicator for free halogens. To 35 c.c. of As_2O_3 solution containing 5 g. of NaBr , 25 c.c. of conc. HCl are added and after heating at $55\text{--}60^\circ$ 1 c.c. of $\text{M-H}_2\text{SeO}_3$ is added, and the solution titrated at 55° with 0.1N- KBrO_3 . J. S. A.

Micro-determination of boric acid. C. ŞUMULEANU and G. GHIMICESCU (*Bul. Soc. Chim. Romania*, 1934, 15, 79—89).—The dry sample (0.03—10 mg. of H_3BO_3) and 10 c.c. of MeOH are placed in a distilling flask and 5 c.c. of conc. H_2SO_4 are added slowly. The distillate is passed into 15 c.c. of saturated $\text{Ba}(\text{OH})_2$ solution. When H_2SO_4 fumes appear the flask is cooled, 5 c.c. of MeOH are added, and the distillation is repeated (3 times). The H_3BO_3 in the neutralised $\text{Ba}(\text{OH})_2$ solution (phenolphthalein) is titrated with 0.04N- $\text{Ba}(\text{OH})_2$. The error is $\pm 1.7\%$. If wine is to be examined it is neutralised with Na_2CO_3 and the determination is carried out on the ignited residue on evaporation. Jorgensen's titration method, Hebebrand's colorimetric method, and the Rumanian official method give errors of the order of 40—50% when only 1—2 mg. of H_3BO_3 is present, although they are satisfactory with 50—100 mg. H. F. G.

Sensitive reaction for boric acid. A. S. KOMAROVSKI and N. S. POLUEKTOV (*Mikrochem.*, 1934, 14, 317—320).—A 0.005% solution of *p*-nitrobenzene-azochromotropic acid (Chromotrope 2B) (I) forms a very sensitive reagent for H_3BO_3 . A drop of slightly alkaline solution under test is evaporated to dryness on a porcelain dish, and 2 or 3 drops of (I) added. In presence of B the colour changes from bluish-violet to greenish-blue. This method detects 2 p.p.m. of H_3BO_3 . Presence of oxidising anions causes a rose or yellow ppt., so in such cases a drop of the solution should be heated with solid $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ until H_2SO_4 fumes are evolved before addition of (I). In presence of F the acidified test solution should be warmed with SiO_2 to remove the F as SiF_4 before adding the reagent. The method is particularly suited to the detection of B in minerals. J. W. S.

Determination of carbonic acid by loss in weight. C. MAHR (*Z. anal. Chem.*, 1934, 97, 93—95).—The substance is decomposed with 1 vol. of 70% $\text{HClO}_4 + 2$ vols. of saturated aq. NaClO_4 in an apparatus described, warming to 35° if necessary. In presence of Cl' or CN' , $\text{Hg}(\text{ClO}_4)_2$ is added to avoid loss of HCl or HCN . $\text{K}_2\text{Cr}_2\text{O}_7$ may be added to oxidise SO_3 if present. J. S. A.

Determination of carbon monoxide in air.—See B., 1934, 557.

Determination of potassium in mineral waters and other solutions. V. CRASU and V. MANOLE (*Bul. Soc. Chim. Romania*, 1934, 15, 129—136).—The K is separated by the use of $\text{Na}_3[\text{Co}(\text{NO}_2)_2]_6$ solution and determined by a modified platinichloride method. The KCl solution (1—2 c.c.) is treated with H_2PtCl_6 and 96% EtOH is added until the EtOH concn. is 80%; pptn. is complete within a few min. The ppt. is dissolved in H_2O and reduced at the b.p. with HCO_2Na , the pptd. Pt being removed and weighed. The error is usually $< 2\%$. A stable solution of $\text{Na}_3[\text{Co}(\text{NO}_2)_2]_6$ which may be kept indefinitely may be prepared by dissolving 100 g. of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 650 g. of NaNO_2 in 800 c.c. of H_2O at room temp., adding 4 c.c. of glacial AcOH , and keeping for 24 hr. The filtered solution is diluted to 1 litre.

H. F. G.

[Determination of potassium.] F. ALTEN and H. WEILAND (*Z. Pflanz. Düng.*, 1934, A, 34, 108—110).—A reply to Tischer (this vol., 620).

A. G. P.

Rapid centrifugal determination of small amounts of sodium. E. R. CALEY, C. T. BROWN, and H. P. PRICE (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 202—205).—Na is pptd. by a solution of $\text{Mg}(\text{OAc})_2$, $\text{UO}_2(\text{OAc})_2$, and AcOH in EtOH . The voluminous ppt. is collected by centrifuging in a capillary tube, and its vol. is determined. K and Li interfere seriously when present in sufficiently high concns.

E. S. H.

Determination of sodium in potassium salts.—See B., 1934, 539.

Determination of small quantities of sodium carbonate. Warder's method with improved technique. J. E. S. HAN (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 209).—The solution is filtered after reaching the first end-point and before commencing the second titration. E. S. H.

Determination of sodium thiosulphate by means of potassium dichromate. H. C. S. SNETHLAGE (*Rec. trav. chim.*, 1934, 53, 567—578).—In presence of HCl the accuracy of the determination is influenced by illumination, concn. of acid, and rate of addition of KI. Reproducible results are not obtainable except in very dil. solutions. The above factors are far less important when H_2SO_4 is used, and a mode of procedure has been worked out whereby results accurate to 0.01% may be obtained.

F. L. U.

Application of spectrum analysis to determination of alkalis and alkaline earths. II. Micro-determination of sodium and lithium. W. H. JANSEN and J. HEYES. III. Micro-determin-

ation of sodium in native blood serum. W. H. JANSEN, J. HEYES, and C. RICHTER (Z. physikal. Chem., 1934, 168, 257—266, 267—273; cf. A., 1932, 1103).—II. The spectroscopic determination by spraying the solution containing the Na or Li into a flame has been studied. The first step is to ascertain the concn. range over which there is an approx. linear relation between the concn. and the blackening of the photographic plate caused by the light emitted, the unknown concn. then being determined by interpolation. To eliminate errors due to local variations in the emulsion the test solution is photographed between solutions of known concns. Determinations of satisfactory precision can be made with Na and Li concns. down to 0.05 and 0.001 mg. per litre, respectively.

III. In applying the above method to the determination of Na in blood serum the latter is diluted at least 1000 times and sprayed directly into the flame; the high α and η of undiluted serum interfere with the spraying and render the method inapplicable. The results agree with those obtained from a solution of the serum ash. The Na content of the blood serum of a healthy person varies from 300 to 350 mg. per 100 c.c. R. C.

Direct potentiometric determination of heavy-metal ions with potassium cyanide and sodium sulphide. W. HILTNER and W. GRUNDMANN (Z. anorg. Chem., 1934, 218, 1—15; cf. this vol., 48).—Accurate results in the potentiometric titration of Ag and a no. of bivalent metals can be obtained by using a Ag_2S electrode. Ag, Ni, Co, and Cu, Ag in presence of Ni, Cd, Zn, Cu, or Co, Ni in presence of Cd or Zn, and Co in presence of Cd or Zn are determined by titration with KCN. Ag, Cu, Cd, and Zn, Ag in presence of Cu, Cd, Zn, Cu+Cd, or Cu+Zn, and Zn in presence of Mn can be determined with Na_2S . The following pairs are determined by combined titration with KCN and Na_2S : Ni+Cd, Ni+Zn, Co+Cd, Co+Zn. F. L. U.

Identification of silver cyanide and thiocyanate. L. M. KULBERG and J. A. SEMENTZOV (Ukrain. Chem. J., 1933, 8, 168—170).—The Bunsen flame is coloured violet-red by AgCN , and blue by AgCNS ; these colorations afford a means of detection of CN' and CNS' . R. T.

Potentiometric determination of heavy-metal ions with sodium sulphide. W. HILTNER and W. GRUNDMANN (Z. physikal. Chem., 1934, 168, 291—307).—Ag, Cu, Cd, and Zn can be determined potentiometrically by titration with 0.1N- Na_2S using a Ag_2S electrode with a valve potentiometer and titrating rapidly to minimise the adsorption error. The determination of Ag, Cu, and Cd, of Ag, Cu, and Pb, and of Ag, Cu, and Zn in presence of each other is also possible. The heavy-metal sulphides are pptd. one after another and do not form solid solutions. The solubility products increase in the order $\text{CuS} < \text{PbS} < \text{CdS} < \text{ZnS}$. Although Ag_2S is more sol. than CuS it is pptd. first. Bi, Pb, Ni, Co, Mn, Sb, and As cannot be determined as above owing either to sulphide formation being too slow or adsorption of S'' ions too great. R. C.

Drop reaction of beryllium. A. S. KOMAROVSKY and N. S. POLUEKTOV (Mikrochem., 1934, 14, 315—317).—When a HCl solution of 1.38 g. of $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-NO}_2$, cooled to 0° , is diazotised by addition of an aq. solution of 0.85 g. of KNO_2 , and the product mixed with a NaOH solution of orcinol (1.42 g.) at 0° , a bright red solution is obtained, which on acidifying gives bright red flakes of *p-nitrobenzeneazo-orcinol*, which dissolve in alkali hydroxide with a yellow colour. When a drop of a 0.025% solution of the compound in NaOH is placed on a filter paper, a drop of the solution to be tested for Be added in the centre of this with a capillary tube, and then another drop of reagent applied, Be gives an orange-red and Mg a brownish-yellow colour. Zn gives a similar colour to Be, but the colour disappears on addition of a drop of 25% KCN solution. The latter also removes oxide colours due to Ni, Co, Cu, Cd, and Ag. Ca, Sr, Ba, Al, La, Pr, Nd, Ce, Zr, and Th do not affect the test. The sensitivity is 1 part in 200,000 for Be alone, or 1 part in 66,000 in presence of 750 times the same amount of Zn. J. W. S.

Determination of magnesium with titan-yellow by Kolthoff's method. C. URBACH and R. BABIL (Mikrochem., 1934, 14, 343—361).—Kolthoff's method (A., 1927, 847) is rendered more rapid and accurate by employing comparison with Mg solutions of known concn. J. W. S.

Detection of zinc by an induced precipitation. P. KRUMHOLZ and J. V. SANCHEZ (Mikrochem., 1934, 15, 114—118).—Co-pptn. of $\text{Co}[\text{Hg}(\text{CNS})_2]$ from solutions containing 0.01% Co with $\text{Zn}[\text{Hg}(\text{CNS})_2]$ (cf. this vol., 49) occurs immediately with traces of Zn down to a limiting concn. 1 : 500,000. A blue ppt. collects at the interface on shaking with Et_2O . In the absence of Zn, pptn. is delayed. J. S. A.

Determination of small amounts of zinc in steel and iron.—See B., 1934, 542.

Oxidation of thallous to thallic salts, and reduction of the latter by sodium arsenite in analytical chemistry. F. ČUTA (Chem. Listy, 1934, 28, 37—41, 58—59).— Tl^{II} is oxidised to Tl^{III} by Br in acid solution containing NaCl, in absence of which reduction of Tl^{III} takes place readily on warming. The solution is added to standard alkaline aq. Na_3AsO_3 , excess of which not oxidised by Tl^{III} is determined by titration with 0.1N-I, and the Tl content is hence calc. The mean error is $\pm 0.2\%$. R. T.

Indirect potentiometric determination of copper. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 97, 99—102).—Cu is pptd. as $[\text{Cu}(\text{CNS})_2(\text{C}_5\text{H}_5\text{N})_2]$ by addition of excess of 0.1N-KCNS + $\text{C}_5\text{H}_5\text{N}$, and the vol. made up to 100 c.c. Excess KCNS in 50 c.c. of the liquid is titrated back potentiometrically with 0.1N- AgNO_3 . J. S. A.

Potentiometric determination of copper with thiocyanate. W. HILTNER and W. GRUNDMANN (Z. anal. Chem., 1934, 97, 172—179).—Titration is performed at $65\text{--}70^\circ$ in presence of NaHSO_3 as reducing agent, using a AgBr or AgI indicator electrode (cf. this vol., 48). Indirect titration is preferable, using glucose or $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$ as reducing agent, in

presence of NaOAc. The solution is then acidified with AcOH and excess CNS' titrated back directly with AgNO₃, using a AgI electrode. The pptn. is sp. except in presence of Ag or Hg. J. S. A.

Volumetric determination of copper with iodide+thiocyanate. D. KRÜGER and E. TSCHIRCH (Z. anal. Chem. 1934, 97, 161—171).—The side reactions leading to a progressive decrease in the titre are discussed. For stability, the proportion of KI should be $\leq 8-10\%$ of the KCNS. Standardisation of the Na₂S₂O₃ against Cu solutions under identical conditions is desirable (cf. A., 1930, 444).

J. S. A.

Rapid determination of copper. A. TETTA-MANZI (L'Ind. Chimica, 1934, 9, 609—610).—When halides are absent, the method previously described (Atti Sci. Torino, 1933—1934, 69, 197) may be modified to determine larger amounts of Cu as follows. The neutral or slightly acid solution is treated, in a 250-c.c. flask, with 15% aq. C₅H₅N and a known vol. of 0.1N-KCNS. After 30 min. the liquid is made up to 250 c.c. with H₂O, mixed, and filtered through a dry filter. 200 c.c. of the filtrate are treated with excess of 0.1N-AgNO₃ and a few c.c. of aq. ferric alum, and the liquid is titrated with KCNS. The method is disturbed by salts of Ni, Co, Mn, Zn, or Cd. T. H. P.

Determination of aluminium in nickel alloys.—See B., 1934, 504.

Direct analysis of mixtures of aluminium hydroxides and calcium aluminates. H. LAFUMA (Chim. et Ind., 1934, 31, Spec. No., 234—235).—The sample is treated with 0.1N-HCl, the residual insol. Al₂O₃ and the sol. Al₂O₃ and CaO being determined. These operations are repeated on a further sample ignited for 1 hr. at 600°. Ignition renders free hydrated Al₂O₃ insol., the Ca aluminates remaining sol. The existence of hydrated Al₂O₃.2CaO has been confirmed. At 80° in presence of mother-liquor it forms cubic Al₂O₃.3CaO.6H₂O. H. J. E.

Crum-Volhard reaction as a drop reaction for manganese. M. P. BABKIN (Ukrain. Chem. J., 1933, 8, 179—181).—1 ml. of solution is boiled for 1 min. with excess of NaOH and 2—3 drops of 3% H₂O₂, and the washed ppt. is boiled with PbO₂ and 2—3 ml. of 10% HNO₃ or 2N-H₂SO₄, when a violet coloration is indicative of Mn. Other cations do not interfere. R. T.

Spectral analysis by sensitive lines within the range of the glass spectrograph. Spark spectrum of a selenium-chromium-nickel steel. W. KRAEMER (Z. anal. Chem., 1934, 97, 89—93; cf. this vol., 621).—Results are given for a Cr-Ni steel containing Se, using the apparatus described previously (A., 1932, 355). J. S. A.

Drop reaction for (a) cobalt, (b) zinc. L. M. KULBERG (Ukrain. Chem. J., 1933, 8, 133—139, 190—192).—(a) A drop of solution, containing 1.85×10^{-3} mg. Co, gives a blue spot when placed on filter paper moistened with saturated aq. (NH₄)₂Hg(CNS)₄ (I). The reaction is untrustworthy when the proportion of other metals to Co is : Cu:Co >

50:1; Fe > 1500:1; Zn > 2000:1; Cd or Ag > 1000:1.

(b) 3—4 drops of dil. aq. CoSO₄ and 0.5 c.c. of (I) are added to 1 c.c. of the slightly acid solution under examination, when a dark blue ppt. indicates the presence of $\leq 1.5 \times 10^{-5}$ mg. Zn; NH₄, Mg, Ca, Ba, Sr, Al, Mn, Pb, Ag, Hg^{II}, Sn^{IV}, As, Sb, and small quantities of Co, Ni, and Cr do not interfere. In presence of Fe excess of NaF should first be added, in presence of Hg^I excess of NH₄Cl, and in presence of Sn^{II} excess of HgCl₂. R. T.

Indirect potentiometric determination of cobalt. P. SPACU (Z. anal. Chem., 1934, 97, 192—195).—Co(SCN)₂(C₅H₅N)₄ is pptd. by addition of excess of 0.1N-KCNS and 1 c.c. of C₅H₅N, and excess of KCNS in an aliquot portion of the liquid titrated back potentiometrically with AgNO₃. J. S. A.

Separation of nickel and cobalt by means of alkali phosphates. M. H. WUNSCHENDORFF and (MME.) P. VALIER (Bull. Soc. chim., 1934, [v], 1, 85—90).—The NiS and CoS are treated with the min. quantity of aqua regia, and, after complete dissolution, evaporated to dryness. The NiCl₂ and CoCl₂ are taken up in very little H₂O and filtered. To 2 c.c. of this solution are added 1.5 c.c. of 2N-(NH₄)₂CO₃ and then 1.5 c.c. of 2N-(NH₄)₂HPO₄, after which it is brought to the b.p. 20 drops of conc. aq. NH₃ are added, boiling is continued for 4 min., and the liquid is filtered immediately. The presence of Ni is shown by a turquoise-blue filtrate and the presence of Co by a violet-blue ppt. on the filter. Ni and Co can also be separated in a buffer solution of p_H 6.2 (8.06 c.c. M/15 KH₂PO₄ + 1.94 c.c. M/15 Na₂HPO₄) in the cold or of p_H 5.5 (9.55 c.c. M/15 KH₂PO₄ + 0.45 c.c. M/15 Na₂HPO₄) at the b.p. If 2 drops of N-CoCl₂-NiCl₂ solution are added to 10 c.c. of the buffer solution, Co gives a ppt., whilst Ni can be detected by the blue colour produced on adding NH₃ to the filtrate. The separation is not quant. J. W. S.

Microanalysis of uraninite. F. HECHT and H. KRAFFT-EBING (Mikrochem., 1934, 15, 39—54; cf. A., 1933, 366).—A detailed account of procedure, using 30 mg. of material. J. S. A.

Quantitative spectral determination of tin in copper. J. E. R. WINKLER (Z. anorg. Chem., 1934, 218, 45—48).—Homologous pairs of lines are given for 17 bronzes containing 0.02—14% Sn. F. L. U.

Colorimetric determination of titanium in silicates. N. I. BUDAKOV (J. Appl. Chem. Russ., 1934, 7, 233—234).—0.5 g. of substance is fused with 3.5 g. of Na₂CO₃, the melt is treated with 25 ml. of H₂O and 6 ml. of conc. H₂SO₄, 100 ml. of H₂O are added on complete pptn. of SiO₂, the solution is filtered, 3—5 ml. of 3% H₂O₂ are added to the filtrate + washings, and TiO₂ is determined as usual. R. T.

Quantitative separation of antimony and tin. RAYMOND (Compt. rend., 1934, 198, 1609—1611).—A solution of Sn and Sb in HCl is oxidised with Br and excess of NH₄HCO₃ is added. SnO₂ is pptd. by N(C₂H₄.OH)₃ (cf. Jaffe, A., 1933, 246) and washed with 2—3N-HCl, further separation of Sn from the washings being necessary. Sb is determined in the final combined filtrates. B. W. B.

Colorimetric determination of bismuth. II. Absolute colorimetric determination of bismuth using "grey solution." C. MAHR (Z. anal. Chem., 1934, 97, 96—99).—Bi is determined colorimetrically by comparison with the standard "grey solution" in light of 462 m μ as its complex with CS(NH₂)₂ (I), in 5–8% HNO₃ solution saturated with (I) at 18° (cf. A., 1933, 1134). CNS' if present produces a yellow colour with an absorption max. and extinction coeff. close to those produced by (I), and does not interfere. Cl' interferes, as do Cu and Pb in large amount.

J. S. A.

Quantitative spectroscopic analysis of solutions. W. R. BRODE and J. G. STEED (Ind. Eng. Chem. [Anal.], 1934, 6, 157—159).—Calibration curves have been determined for the spectrographic determination of Nb, Be, Ti, V, W, Fe, Mo, Cr, Pb, and Co in solutions of their compounds. The average error in samples of known composition is < 5%.

E. S. H.

Detection and determination of small contents of platinum metals. H. WOLBLING (Ber., 1934, 67, [B], 773—776).—The solution of the chlorides of the Pt metals from which Os, Ru, and Au have been removed is rendered ammoniacal, treated with so much HCl that the solution is approx. N, and then gradually with SnCl₂ until the intensity of the colour does not increase. The solution is shaken with 2 vols. of EtOAc, the aq. and ester layers are washed with EtOAc and SnCl₂—HCl, respectively, and Pt is determined colorimetrically in the EtOAc. After 1–2 hr. the Rh colour is removed by EtOAc in which Rh is determined colorimetrically. The aq. phase is treated with NH₃ to develop the green reaction of Pd and, after its determination, is treated with excess of Cl₂—H₂O, allowing Ir to be determined from the intensity of the brown colour. Occasionally the Pd reaction is ill-defined; in such cases Pd is pptd. by contact with KI over-night and determined after dissolution in Cl₂—H₂O. By means of active C minute amounts of Pt, Pd, Os, and Ru can be adsorbed from 0.1N-HCl to a residual concn. of 10⁻⁸ g. per litre, or 10⁻⁷ g. per litre in the case of Rh. Little adsorption occurs with Ir. The metals can be removed from the adsorbates by hot conc. solutions of NaCl or HCl. Higher concns. of acids or small amounts of C render adsorption less complete. The adsorptive power of SiO₂ gel for Pt metals is slight in acid, immediate and marked in ammoniacal, solution. Pt, Ir, Rh, and Ru are completely, Os and Pd incompletely, co-pptd. when Fe⁺⁺⁺ or Al is pptd. by NH₃.

H. W.

Liquefaction of helium by an adiabatic method without pre-cooling with liquid hydrogen. P. KAPITZA (Nature, 1934, 133, 708—709).—The apparatus described liquefies He at the rate of 1 litre per hr., 45 min. after the preliminary cooling to the temp. of liquid N.

L. S. T.

Isothermic diphenylmethane calorimeter, and its applications. A. N. SCHTSCHUKAREV, I. P. KRIVOBABKO, and L. A. SCHTSCHUKAREVA (J. Appl. Chem. Russ., 1934, 7, 259—261).—A Bunsen calorimeter containing CH₂Ph₂ in place of H₂O is more convenient for measuring heat evolved in slow reactions.

R. T.

Comparison of gas analysis by fractional combustion with calorimetric measurements. S. MISCHONSKIY (Chim. et Ind., 1934, 31, Spec. No., 258—263).—An apparatus is described. C. W. G.

Improvements in the adiabatic microcalorimeter. W. SWIENTOSŁAWSKI (Rocz. Chem., 1934, 14, 185—188).—A description of apparatus. R. T.

Measurement of dew point of natural gases. A. MICHELS and G. W. NEDERBRACHT (Ind. Eng. Chem. [Anal.], 1934, 6, 165—166).—Apparatus and technique are described. E. S. H.

Apparatus for the determination of the dew point. E. B. MOSS (Proc. Physical Soc., 1934, 46, 450—458).—An optical system, using diffraction by the dew droplets in a mirror, is applied to an automatic photo-electric apparatus for maintaining a mirror at the dew point.

N. M. B.

Thermocouples for the measurement of small intensities of radiations. L. HARRIS (Physical Rev., 1934, [ii], 45, 635—640).—The use of a.c. amplification of voltages produced in very thin thermocouples is developed, and gives a sensitivity 100 times that with thermocouple galvanometer arrangements.

N. M. B.

Measurement of temperature of sound fields. E. A. JOHNSON (Physical Rev., 1934, [ii], 45, 641—645).—A thermocouple for measuring alternating temp. in air due to sound waves up to 5000 cycles per sec. is described.

N. M. B.

Comparator for p_H determinations. H. C. P. GEERLIGS (Tijds. Alg. Tech. Ver. Beet. Fabr. Raff., 1934, 29, 89—90).—A roulette form of comparator, in which there is a field of vision divided into two parts brought to equal intensity by manipulating a screw, is described. There are 17 cavities to take the standard tubes, each of which in succession can be brought into line with the comparator containing the assay tube to effect comparison.

J. P. O.

Photronic colorimeter and its application to the determination of fluoride. L. V. WILCOX (Ind. Eng. Chem. [Anal.], 1934, 6, 167—169).—The instrument uses two photo-electric cells of the type that transforms light energy into electrical energy directly without the use of an external e.m.f. The cells are electrically opposed and the current developed is balanced by a variable resistance. The method may be applied to the determination of small amounts of F' by Armstrong's method (A., 1933, 1132) with an accuracy of ± 0.1 p.p.m.

E. S. H.

Colorimetry with a spectrometer. R. A. HOUSTOUN (Phil. Mag., 1934, [vii], 17, 1047—1057).—An improved instrument by means of which the colour is interpreted graphically in terms of λ on a colour diagram is described.

N. M. B.

Colorimetry with the photo-electric tube. I. K. YAMAMOTO and M. ABE (Bull. Waseda Appl. Chem. Soc., 1933, 21, 1—16).—Results of studies with methylene-blue, quinoline-yellow, and eosin-red are described.

CH. ABS.

Apparatus for colorimetric examination of traces. A. A. GUNTZ (Chim. et Ind., 1934, 31, Spec. No., 236—237).—A simply constructed color-

meter, with comparison tubes of 2—6 mm. diam., is described. H. J. E.

Autocollimation mirror monochromator and spectroscope of focal aperture 1:4. C. FORCH (*Z. Physik*, 1934, 89, 87—89). A. B. D. C.

Immersion liquids of intermediate refraction (1.450—1.630). R. D. BUTLER (*Amer. Min.*, 1933, 18, 386—401).—A kerosene fraction of high b.p. and $1\text{-C}_{10}\text{H}_7\text{Cl}$ are used. CH. ABS.

Optical properties of ideal solution immersion liquids. M. J. BUEGER (*Amer. Min.*, 1933, 18, 325—334).—Mixtures of two chemically similar liquids have optical properties which are linear functions of composition. The properties and the prep. of a correction chart are discussed. CH. ABS.

Measurement of concentration during photographic recording of chemical reactions. G. FOURETIER (*Compt. rend.*, 1934, 198, 1689—1691).—The apparatus previously described (*A.*, 1932, 486, 491) has been improved and adapted to record reactions occupying up to 18 hr. B. W. B.

Highly reflecting films of zinc sulphide. A. H. PFUND (*J. Opt. Soc. Amer.*, 1934, 24, 99—102; cf. *A.*, 1933, 1226).—Thin films of ZnS showing first-order interference and high reflecting power can be produced by distillation of sphalerite. The use of such films in physical instruments is discussed. R. S.

Zone plate determination of dominant wavelengths of filtered lamp light. J. W. ELLIS and B. W. SORGE (*J. Opt. Soc. Amer.*, 1934, 24, 103—106).—Dominant λ have been determined for a no. of Wratten gelatin filters and compared with the centres of gravity of the appropriate luminosity curves. R. S.

Physical methods in the chemical laboratory. XXI. New applications of dielectric measurements to technical and analytical purposes. L. EBERT (*Angew. Chem.*, 1934, 47, 305—315).—The theory and practice of measuring dielectric const. ϵ are described. ϵ may be used for testing the purity of liquids. A cell for continuous measurement of ϵ of a distillate as it flows from a condenser is illustrated. ϵ may be used as an indicator in sedimentation analysis of powders. Total H_2O , or its partial pressure over hydrates, may be determined by its effect on the ϵ of dioxan. Mechanical measurements, such as variations in thickness of wires, are also detailed. D. R. D.

Determination of dielectric constants by means of radio. M. M. OTTO and H. H. WENZKE (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 187—188).—Results obtained with the apparatus and procedure described are in good agreement with the recognised vals. E. S. H.

Laboratory apparatus for the measurement of dielectric constants. L. EBERT and E. WALDSCHMIDT (*Chem. Fabr.*, 1934, 7, 180—183).—The apparatus measures the square of the electric refractive index (I) for electromagnetic waves of 150 m. length. It is based on the principle that the frequency of a vibrating electromagnetic circuit depends on the sum of all capacities in the circuit. Capacity

is the quantity actually measured, an empty condenser being filled with the liquid to be tested. (I) can be determined if the apparatus can be calibrated with sufficiently pure liquids. C. I.

Electrical indicator for viscosity measurements.—See B., 1934, 507.

Simple arrangement for the measurement of small conductivities ($\kappa \sim 10^{-8}$) of non-aqueous solutions. W. PHILIPPOFF (*Ber.*, 1934, 67, [B], 811—818).—An apparatus for measurement of the conductivity of very dil., non-aq. solutions (mainly glacial AcOH) is described. H. W.

Apparatus for exact determination of conductivity. E. MICHALSKI (*Rocz. Chem.*, 1934, 14, 177—184).— SiO_2 conductivity apparatus which obviates the possibility of contamination by atm. CO_2 , NH_3 , or H_2O , by sol. constituents of the vessels, or by tap-grease, is described. R. T.

Choice of catalysts for the hydrogen electrode. A. E. LORCH (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 164—165).—A discussion of the relative merits of Pt, Pd, and Ir. E. S. H.

Metallised-glass quinhydrone electrodes. E. NEWBERY (*Trans. Electrochem. Soc.*, 1934, 65, 107—113).—Of various metallised glass surfaces (cf. B., 1933, 925) used as quinhydrone electrodes in solutions of various types, bright platinised or Au-coated glass proved as accurate as Pt wire or sheet; it has the advantages of very low cost, less liability to damage during "flaming," lower sensitivity to impurities, and easy renewal of surface. The rate of attainment of equilibrium is about the same for both types of metallised glass electrode. H. J. T. E.

Glass electrode. E. P. LAUG (*J. Amer. Chem. Soc.*, 1934, 56, 1034—1036).—The trustworthiness of the membranes in the MacInnes glass electrode can be checked by means of their H_2 electrode function, asymmetry potential, and d.c. resistance. E. S. H.

Cells with air electrodes. E. BAUR (*Z. Elektrochem.*, 1934, 40, 249—252).—The cells described contain an air electrode consisting of a "cushion" of Ni wire net, filled with C granules, which is immersed partly in the electrolyte (aq. NaOH), the remainder being exposed to the air. An Fe electrode, consisting of Fe shavings in a Ni wire net container, is described. The electromotive behaviour of these electrodes has been examined. E. S. H.

Adsorption electrodes. I. Glass electrode. H. J. C. TENDELOO (*Proc. K. Akad. Wetensch. Amsterdam*, 1934, 37, 212—215).—Certain glass membranes after treatment with CaCl_2 solution, in order to replace the cations in the capillary layers of the glass by Ca, appear to be able to function as Ca electrodes. H. S. P.

Use of the quinhydrone electrode in the determination of the activity of the hydrogen ion in a solution of sucrose that is undergoing catalytic inversion by hydrochloric acid at 25°. W. W. FLOYD (*Trans. Kansas Acad. Sci.*, 1933, 36, 118).—The cell $\text{Ag (s), AgCl (s), Cl}^- (0.1M\text{-HCl} + 0.1M\text{-sucrose}) || \text{H}^+ (0.1M\text{-HCl} + 0.1M\text{-sucrose}) + \text{benzoquin-}$

one (s), quinol (s), Au (s) does not give reproducible potentials. CH. ABS.

Static charge on a galvo-millivoltmeter. H. A. BRONLEY (*Nature*, 1934, 133, 760).—Attention is directed to a possible source of error in p_n determinations owing to a static charge on the glass being responsible for an erratic behaviour in a Unipivot galvo-millivoltmeter. L. S. T.

Geiger-Muller counters. M. COSYNS and J. DE BRUYN (*Bull. Acad. roy. Belg.*, 1934, [v], 20, 371—394).—A general survey of the construction and factors affecting the working of the instrument. N. M. B.

Magnetic objective for the electron microscope. E. RUSKA (*Z. Physik*, 1934, 89, 90—128). A. B. D. C.

Camera for electron diffraction. W. G. BURGERS and J. C. M. BASART (*Physica*, 1934, 1, 543—548).—The apparatus described is adaptable for the transition or reflection method. The specimen may be heated at 500°. H. J. E.

Tapless micro-burette with liquid cut-off for serial determinations. R. LINKS (*Mikrochem.*, 1934, 15, 87—94).—A precision form, operated by a Hg-immersed screw plunger, is described. J. S. A.

Calibration [of pipettes]. J. E. HEARN (*Science*, 1934, 79, 458—459). L. S. T.

Stirrer for solvent extraction. J. A. PATTERSON, jun. (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 171). E. S. H.

Drier for sensitive materials. E. JANTZEN and H. SCHMALFUSS (*Chem. Fabr.*, 1934, 7, 112).—The vapour of a liquid of suitable b.p. passes through a series of hollow shelves on which the material to be dried is placed. The shelves are covered with a bell-jar connected to a condenser and vac. pump. H. F. G.

High-temperature vacuum desiccator of Jena glass. E. RUPP (*Chem.-Ztg.*, 1934, 58, 403).—A desiccator composed of Jena Durax vessels (a baking dish and a bell-jar) may be heated with a H_2O -bath, an electric hot plate, or a free flame covered with gauze or asbestos. A. G.

Growth of large specimens of single-crystal zinc. C. A. CINNAMON (*Rev. Sci. Instr.*, 1934, [ii], 5, 187—190).—Apparatus and technique for growing a strain-free crystal about 1.2 sq. cm. in cross-section and 35 cm. long of any desired orientation are described. An initial gross mosaic structure may be eliminated by a steep temp. gradient. The ratio of the temp. gradient to the rate of growth must be near a certain favourable val. peculiar to each orientation. N. M. B.

Improved model of the Salvioni spring balance. A. FRIEDRICH (*Mikrochem.*, 1934, 15, 35—38).—A robust micro-balance, based on the deflexion of a steel watch-spring beam, is described. J. S. A.

Ozoniser for liquid air temperature. A. C. BYRNS (*J. Amer. Chem. Soc.*, 1934, 56, 1088—1089).—

In the apparatus described pure liquid O_3 can be prepared. E. S. H.

Automatic mercury air pump with electromagnetic pressure gas distributor. P. SAFFERT and W. WUSTROW (*Z. Elektrochem.*, 1934, 40, 231—232). E. S. H.

Rapid determination of specific gravity. V. F. SHURAVLEV (*J. Appl. Chem. Russ.*, 1934, 7, 263—269).—Apparatus for determining the d of solids is described. R. T.

Volumetric determination of the density of air adsorbed by powders. M. V. TSCHAPPEK (*Kolloid-Z.*, 1934, 67, 145—148).—Apparatus and technique for determining the adsorbed air by displacement with H_2O are described. Results are given for SiO_2 , Al_2O_3 , Fe_2O_3 , C, starch, and clay. E. S. H.

Laboratory apparatus. P. FUCHS (*Chem. Fabr.*, 1934, 7, 97—99).—Methods are described of (a) folding filter-paper for direct filtration into test tubes etc., without the use of a funnel; (b) obtaining samples of the filtrate during vac. filtration; (c) economising filter-paper; (d) effecting rapid vac. filtration with an ordinary conical funnel; (e) using the filter pump for filling pipettes; (f) erecting a simple reflux condenser (a vertical tube rests in a conical funnel placed in the neck of the distilling flask; losses are very low); (g) constructing an extremely simple self-priming glass siphon; and (h) priming siphons. H. F. G.

Falling-sphere viscosimeter. E. SCHROER (*Chem. Fabr.*, 1934, 7, 113—115).—Very closely reproducible results may be obtained with a simple form of apparatus consisting of an accurately cylindrical glass tube (I) and a steel ball (II) if diameters are chosen for (I) and (II) appropriate to the material under examination. For a fall of 20 cm. the vals. may be 4.01 and 3.99 mm., respectively, for air, and 4.01 and 3.90 mm., respectively, for C_6H_6 , the max. deviation (20 results) being $\pm 1.8\%$ and the mean $\pm 1.0\%$. The method may be employed at high and low pressures and for the analysis of gas mixtures. †

Capillary gas flow-meters. A. PINKUS (*J. Chim. phys.*, 1934, 31, 241—257).—Several instruments and auxiliary apparatus are discussed. Rates of flow between 0.2 and 10 litres per hr. are determined to within 0.2%, in general, and corrections for variations of temp. and pressure are applied by means of an empirical relation. The results generally accord with the indirect method of standardisation (cf. A., 1933, 481) but direct calibration is preferred. J. G. A. G.

Magnetic effect on Pirani gauges using nickel wires. E. McMILLAN (*Nature*, 1934, 133, 831—832). L. S. T.

Apparatus for determination of helium in gases. F. E. E. GERMANN, K. A. GAGOS, and C. A. NEILSON (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 210—217).—The apparatus described is a modification of that of Guye and Germann (A., 1914, ii, 740). E. S. H.

Geochemistry.

Distribution of ozone in the atmosphere and the "Umkehrreffekt." J. GAUZIT (Compt. rend., 1934, 198, 1800—1802).—Polemical against Pekeris (Pub. Univ. Observ., Oslo, 1934, No. 9, 1). Gotz' views are supported. B. W. B.

Electrical resistance of rain-water at Mulhouse. E. BANDERET and P. BOEHLER (Bull. Soc. Ind. Mulhouse, 1934, 50, 101—108).—An effort has been made to correlate the electrical resistance (E) of rain- H_2O with the time of the rainfall during the day, the intensity of the rainfall, the height of the cloud, and the season of the year, but much more numerous measurements are required to confirm the tentative conclusions. E varies widely with heat-treatments (e.g., boiling and freezing) of rain- H_2O . A. J. H.

Existence of water of abnormal density in natural conditions. G. J. VERESCHTSCHAGIN, A. I. GORBOV, and I. D. MENDELEEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 134—137).—Preliminary measurements indicate that H_2O taken from a depth of 1200 m. in Lake Baikal has d of the order of 0.00024 > that of the surface H_2O . The difference between the two diminishes on long keeping and after distillation. H. S. P.

Composition of thermal waters of Aix-les-Bains and its geological significance. A. LEPAPE, L. MORET, and G. SCHNEIDER (Compt. rend., 1934, 198, 1706—1707).—A discussion. Data on dissolved solids and dissolved He/A ratios (I) of natural waters are quoted in support of the view that the source of Aix-les-Bains water is not Triassic. (I) is a valuable indication of the source of H_2O . B. W. B.

Nitrates in aquarium water. C. HONIG (J. Marine Biol. Assoc., 1934, [ii], 19, 723—725).—Expressed as $NaNO_3$, > 1 g. per litre was found. Addition of lactate or tartrate to the H_2O stimulated denitrifying bacteria, leading to almost complete removal of NO_3' and NO_2' in the H_2O . L. D. G.

Physico-chemical characteristics of the waters of the Bay of Villefranche. P. CHAUCHARD (Compt. rend., 1934, 198, 1710—1712; cf. A., 1932, 594).—Dissolved O_2 (I) and org. matter (II) were determined in surface and deep H_2O at different points of the Bay of Villefranche. (I) showed daily evening max. due to photo-synthesis. (I) decreased and (II) increased following a storm. B. W. B.

Oxygen absorption of the lake deposit. D. MIYADI (Proc. Imp. Acad. Yokyo, 1934, 10, 236—239).— p_H falls as O_2 content falls, and is a min. when $[O_2]=0$ if the rate of absorption by mud is very great. C. W. G.

Viscosity of molten rocks. M. P. VOLAROVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1933, 1, 561—).—the concentric cylinder method the viscosities of Trans-Caucasian basalt (I), techenite (II) from Coursebi, andesite (III) from Casbec, diabase (IV) from Olonetz, and a mixture of (III) with 16% $(OH)_2$ have been measured over the temp. range . . . They follow the order (III) > (II) > (IV) > (I). The viscosities of (IV) and (I) become

identical above 1200°, where they both show an inflexion point, associated with crystallisation. Addition of 16% $Ca(OH)_2$ decreases the viscosity of (III) 15—20 times. J. W. S.

Composition of palygorskites. (MLLE.) S. CAILLÈRE (Compt. rend., 1934, 198, 1795—1798).—Chemical and thermal analyses, d , and n are given of specimens from a group of reputed palygorskites (I) (cf. Fersmann, A., 1913, ii, 784) which comprised: (i) serpentines from St. Gothard and Johangeorgensstadt (Saxony); (ii) sepiolites from Mont Bidy (Madagascar), Portsoy, Vallecas and Dehiro (Chili); (iii) clays from Rochette près Allevard (Isère); (iv) true (I) from Kadinsk (Siberia), Nijni Novgorod, Vigan (Gord), Mevatanana (Madagascar), M'Fouati (Middle Congo), Odivellas (Portugal), and Gorbator. B. W. B.

Sodalite from Bolivia. W. BRENDLER (Amer. Min., 1934, 19, 28—31).—The dark ultramarine-blue mineral has $d^{25} 2.295$, $n 1.4837$. Weathered sodalite is low in alkalis and Cl and high in H_2O .

CH. ABS.

Geomorphology and petrology of the Isle of Capraja. G. ROVERTO and M. AIROLDI (Mem. R. Accad. Lincei, 1934, 5, 319—410).—A very detailed account is given of a geological survey of the island, and of the results of examination of specimens of the rocks from ten different points. The rocks are notably uniform both chemically and mineralogically. The Loewinson-Lessing coeff. of acidity, α , is high, frequently 2.4—2.8. The $M_2O_3:MO$ ratio varies between 1:1.85 and 1:5.27, and the $K_2O:Na_2O$ ratio between 1:1.3 and 1:4.67. H. F. G.

Radium content of some South African granites. M. N. S. INMELMAN (Phil. Mag., 1934, [vii], 17, 1038—1047).—An improved form of electric furnace is described, and results are tabulated for 18 specimens of granite. N. M. B.

Alteration forms of detrital staurolite etc. C. H. EDELMAN and D. J. DOUGLAS (Tsch. Min. Petr. Mitt., 1934, 45, 225—234).—The forms resulting from the corrosion of staurolite, kyanite, garnet, epidote, and sphene in detrital deposits are described. L. J. S.

Pyroxenites from the Bohemian Midland Mountains. E. TROGER (Tsch. Min. Petr. Mitt., 1934, 45, 209—224).—A gauteite dyke near Aussig contains enclosures of the deep-seated rocks felspar-yamaskite and felspar-jacupiringite. L. J. S.

Geochemical concealment ("Tarnung") in anomalous mixed crystals. H. SEIFERT (Tsch. Min. Petr. Mitt., 1934, 45, 191—208; cf. A., 1933, 369).—The states in which I and ClO_4 may be present in Chile saltpetre and SO_4 in limestone are discussed. L. J. S.

Activity of Komagataké in 1929. S. KÔZU (Tsch. Min. Petr. Mitt., 1934, 45, 133—174).—A large amount of newly formed dacite pumice fell as a "pumice-flow" on the sides of the mountain and as a "pumice-fall" of finer material over a wide area. It consists of 44.88% of a glassy base ($n 1.494$ —1.497;

SiO₂ 74.07%) with embedded crystals of plagioclase, hypersthene, augite, and magnetite. Analyses are given of each of these. When heated at 450° the "flow" yields much more HCl than the "fall." At 850° the compact glassy rock expands explosively and is changed into pumice. The "flow" retained heat for a long period, and small fumaroles on its surface deposited NH₄Cl. The NH₃ for this was probably formed from atm. N₂ during the lightning discharges produced by the eruption. L. J. S.

Role of water in basaltic magma. II. T. C. PHEMISTER (Tsch. Min. Petr. Mitt., 1934, 45, 99—132).—Continuation (cf. this vol., 387). L. J. S.

Carboniferous dolomites of the north of France. A. BOREL (Chim. et Ind., 1934, 31, Spec. No., 272—276).—Analyses are given and modes of formation are discussed. C. W. G.

Chemical and micrographical study of a Devonian limestone. A. BOREL (Chim. et Ind., 1934, 31, Spec. No., 271).—Analyses are given. C. W. G.

Hydrothermal synthesis of kaolin. W. NOLL (Tsch. Min. Petr. Mitt., 1934, 45, 175—190).—Full details are now given (A., 1932, 716). L. J. S.

Adsorptive properties of clays in connexion with their structure. S. S. URAZOVSKI and M. M. SCHTSCHERBAK (Ukrain. Chem. J., 1933, 8, 155—167).—The adsorptive capacity (I) for C₆H₆ vapour of Tschasov Jar and Vladimirov kaolins increases on

preheating to a max. at 500°, and falls almost to 0 at 1000°. A quant. connexion exists between diameter of pores and (I) of a given clay. R. T.

Conclusions derived from the gravitation measurements carried out in the Emba district. V. P. SKVORTZOV (Nef. Choz., 1933, 25, No. 10, 14—17).—The relation between geological formation and oil deposits is discussed. CH. ABS.

Genesis of the Central Asiatic petroleum deposits. V. B. PORFIRIEV and V. A. VASILIEV (Nef. Choz., 1933, 25, No. 10, 18—22).—A discussion. CH. ABS.

Rare gases of the sub-soil of Lille. L. DOLLE (Chim. et Ind., 1934, 31, Spec. No., 277—278).—He, A, Kr, and Xe are comparatively abundant. C. W. G.

Classification of forest humus types by means of their catalytic power. W. GÜNTHER (Z. Pflanz. Düng., 1934, A, 34, 30—89).—The catalytic power (I) of soils is not necessarily shown by the total O₂ liberated during a definite period. The rate of evolution of O₂ varies considerably with time and the whole course of the reaction should be examined. Vals. obtained are influenced by the H₂O content of the sample, the ratio of soil to H₂O₂ used, and temp. (approx. const. over the range 15—20°). Appropriate technique for determining (I) is established. A system of classification of forest humus accumulations, based on the form of the catalytic curves, is described. A. G. P.

Organic Chemistry.

Controlled oxidation of methane under pressure. A. PARIS (Chim. et Ind., 1934, 31, Spec. No., 411—420).—The influence of temp., pressure, and amount of O₂ on the process has been studied. The main products of the oxidation are MeOH, CO₂, and H₂O. The isolation of MeOH in appreciable quantities is rendered possible owing to the preferential increase with pressure of the speed of the reaction CH₄ + 0.5O₂ = MeOH, compared with other possible reactions. The best yields of MeOH are obtained when the % of O₂ in the mixture is low and the temp. > 450°. The process does not appear to be practicable industrially owing to the large quantities of gas which must be circulated relative to the yield of MeOH obtained. H. S. P.

Preparation of ethane. S. GLASSTONE and A. HICKLING (Chem. and Ind., 1934, 23, 512).—The statement that C₂H₆ can be prepared (along with 2 vols. of CO₂) by warming Ac₂O with BaO₃ seems to be misleading. The reaction is often violent whether Ac₂O or AcOH is used and little C₂H₆ is produced. C. I.

Preparation of normal heptane. C. H. KAO and W. S. CHANG (J. Chinese Chem. Soc., 1934, 11, 18—20).—Heptyl bromide with a Zn couple in boiling 85% EtOH during 18 hr. affords *n*-heptane (76%), which cannot be prepared from heptaldehyde. Zn-Hg, and HCl (cf. A., 1913, i, 733). J. L. D.

Hexamethylethane. D. T. FLOOD and G. CALINGAERT (J. Amer. Chem. Soc., 1934, 56, 1211—1212).—CMe₃·CMe₃, m.p. 100.7—101.4°, is obtained in 10% yield when Mg is added to Bu^νCl in boiling Et₂O containing a little I. The main products of the reaction are *isobutene* and *isobutane*; a little *ββ*-trimethylpentane is also formed. H. B.

Preparation of ethylene and its homologues by cracking heptane in presence of water vapour. C. MATIGNON and M. SÉON (Compt. rend., 1934, 198, 1649—1652).—C₇H₁₆ (I) at 700° in a quartz tube affords very little C₂H₄ (II), but mainly its homologues (III) (39%). At 900°, when H₂O:(I) is 2.7:1 about 42% of (II) is formed, and at 935°, when H₂O:(I) is 5.2:1, 62% of (II) results. (III) is much reduced in presence of H₂O vapour. J. L. D.

Peroxide effect in addition of reagents to unsaturated compounds. V. Addition of hydrogen bromide to Δ^α-butene. VI. Addition of hydrogen bromide to *isobutene*. M. S. KHARASCH and J. A. HINCKLEY, jun. (J. Amer. Chem. Soc., 1934, 56, 1212—1214, 1243—1245).—V. Addition of HBr to Δ^α-butene (I) in presence or absence of air, in AcOH, or in presence of anti-oxidants gives 70–90% yields of *sec*-BuBr, which is considered to be the normal product. In presence of 0.06–0.1 mol. of ascaridole, a 76–95% yield of Bu^αBr (the abnormal product) is obtained. If air or O₂ is passed through

(I) at -80° for 2 hr. no peroxide is formed. External effects (solvent, temp., light) affect the peroxide-catalysed reaction only.

VI. Addition of HBr to *isobutene* in absence or presence of air, in AcOH or xylene, or in presence of anti-oxidants gives 85–95% yields of $\text{Bu}^{\text{v}}\text{Br}$ (the normal product). In presence of ascaridole (0.03–0.04 mol.) a mixture of $\text{Bu}^{\text{v}}\text{Br}$ (80–90%) and $\text{Bu}^{\text{v}}\text{Br}$ (10–20%) results. Temp. and light have no effect on the normal reaction. H. B.

Reaction of bromine with ethylene derivatives in methyl alcohol. I. K. MENDEL (Annalen, 1934, 510, 129–155).—The ratio Br : OMe in the products formed from the following compounds and a 5% solution of Br in MeOH containing 5% of CaBr_2 is: *cyclohexene* (I), 3.48 : 1 (2.66 : 1 in absence of CaBr_2); *allylbenzene*, 4.62 : 1; *anethole* (II) 1.1 : 1 (the *p*-OMe group being disregarded); *isosafole*, 1.16 : 1; $\text{CH}_2\text{:CPh}_2$, 1.34 : 1. More OMe is added when the C:C linking is conjugated with the C_6H_5 ring. (I) affords a mixture of 1 : 2-dibromo- (III) and 1-bromo-2-methoxy- (IV) *-cyclohexane*; subsequent reduction (H_2 , Pd– BaSO_4 , MeOH–NaOH) removes (III). The resultant (IV), b.p. $76^{\circ}/10$ mm., and AgOAc –AcOH give [after hydrolysis (MeOH–conc. HCl)] 2-methoxy-*cyclohexanol*, b.p. $49^{\circ}/0.3$ mm. (II) does not yield any dibromide but gives a mixture (A) of about 95% of *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHMeBr}$ and 5% of *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHMe}\cdot\text{OMe}$. Treatment of (A) with NaOEt and subsequent hydrolysis (HCl) gives *p*-OMe- $\text{C}_6\text{H}_4\cdot\text{COEt}$ (*oxime*, m.p. 72 – 73°), whilst reduction (Zn dust, MeOH) affords impure (II) [Br-derivative dibromide, m.p. 111° (lit. 108°)]. β -Hydroxy- α -methoxy- α -anisylpropane, b.p. $112^{\circ}/0.35$ mm., is obtained from (A) and KOAc–AcOH followed by hydrolysis (MeOH–conc. HCl); a small amount of a ketone (semicarbazone, m.p. 188°) is also formed.

The “Br-binding nos.” (A., 1932, 717) of 28 unsaturated substances are determined using 5% MeOH–Br containing 5% CaBr_2 ; with the exception of safole, C_8H_8 has the highest val. Compounds containing C:C conjugated with the C_6H_5 ring give vals. < 67 , whilst the non-conjugated substances show vals. > 67 . The val. for (I) decreases if a more dil. solution of Br is used (concn. of MeOBr being thereby increased) or if the CaBr_2 is omitted (decrease in the concn. of Br'). H. B.

Acetylene polymerides and their derivatives.

XIX. Structure of divinylacetylene polymerides. M. E. CUPERY and W. H. CAROTHERS (J. Amer. Chem. Soc., 1934, 56, 1167–1169).—Divinylacetylene (I) (A., 1932, 40) heated at 80° in N_2 gives an oily polymeride (II) (*M* about 230), separable from unchanged (I) by evaporation of (I) in a vac. (II) and Br in cold CCl_4 afford a compound, $\text{C}_{12}\text{H}_{12}\text{Br}_6$, (II) [from (I) in presence of a little pyrogallol at 82°] carefully distilled at 0.1 mm. in gives a compound (III), $\text{C}_{12}\text{H}_{12}$, b.p. 53 – 55° /about 1 mm. (*octa* m.p. 137° , and *deca*-, m.p. 211° , -bromides), which is oxidised by alkaline KMnO_4 at 50 – 60° to *trans-cyclobutane*-1 : 2-dicarboxylic acid (IV), $\text{H}_2\text{C}_2\text{O}_4$, succinic acid, and an oily acid: oxidation in the cold affords (IV) and (probably) a hydroxycyclobutane-carboxylic acid (*p*-bromophenacyl ester, m.p. 145°).

(II) is a mixture of EtOH-sol. and -insol. products; reduction (H_2 , PtO_2 , EtOH) of the former gives products, b.p. 36 – 38° /about 0.1 mm., and 38 – 40° /about 0.1 mm., with the composition $\text{C}_{12}\text{H}_{24}$, and a fraction, b.p. 111 – $113^{\circ}/1$ – 1.5 mm., composition $\text{C}_{18}\text{H}_{24}$. (III) is represented as 1 : 2-di(vinylacetylenyl) cyclobutane. H. B.

Preparation of alkyl bromides. I. C. L. TSENG and C. S. HOU (J. Chinese Chem. Soc., 1934, 11, 57–72).—Interaction of alcohols with PBr_3 affords a better yield of Br-compound than when a mixture of P and Br is used, although yields are best when HBr is used. J. L. D.

Addition of hydrogen bromide to Δ^{β} -pentene. W. M. LAUER and F. H. STODOLA (J. Amer. Chem. Soc., 1934, 56, 1215–1218).— Δ^{β} -Pentene (I) [prepared by the method of Sherrill *et al.* (A., 1929, 1419) or from $\text{CHBrMe}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$ (synthesis described) and aq. Na_2CO_3 (cf. Fittig and Howe, A., 1880, 375)] and HBr in absence or presence of AcOH give a mixture of approx. equal amounts of β - and γ -bromopentanes. Analysis is effected by converting the mixtures into Grignard reagents, treatment with PhNCO , and subsequent thermal analysis of the mixture of anilides so produced. The results do not conform with the rule of Wagner and Saytzeff (A., 1876, i, 547). It is considered that current views regarding electromeric displacements in (I) must be modified. H. B.

Preparation of octyl alcohol and methyl hexyl ketone from Chinese castor oil. C. H. KAO and J. Y. YEN (J. Chinese Chem. Soc., 1934, 11, 21–31).—When castor oil soap (prep. described) is heated a mixture of octyl alcohol (I) and Me hexyl ketone (II) is obtained, separated by interaction with *o*- $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ at 110° into a *sec*-octyl phthalate [decomposed by NaOH into pure (I)] and pure (II) (also obtained from (I) with boiling $\text{Na}_2\text{Cr}_2\text{O}_7$ – H_2SO_4 during 4 hr.) which when reduced with Na in H_2O affords (I) admixed with traces of neutral hydrocarbons. Sebacic acid is always formed in this reaction. J. L. D.

Preparation of methylethylamylcarbinol, methylethylamylcarbonyl iodide, δ -methyloctanol- γ -ol, and γ -bromo- δ -methyloctane. J. H. GREEN (J. Amer. Chem. Soc., 1934, 56, 1167).—Me *n*-amyl ketone and MgEtBr give methylethyl-*n*-amylcarbinol, b.p. 36 – $37^{\circ}/3$ mm. (iodide, b.p. $58^{\circ}/5$ mm.). β -Bromohexane, b.p. 142 – 144° (from $\text{CHMcBu}^{\text{v}}\text{OH}$), Mg, and EtCHO in cold Et_2O afford δ -methyloctan- γ -ol, b.p. 132 – $133^{\circ}/20$ mm. (bromide, b.p. 180°). H. B.

Abnormal reaction of hypochlorous acid with dimethylpentenol. (MLLE.) M. VEILER (Compt. rend., 1934, 198, 1704–1705).—Interaction of $\beta\delta$ -dimethyl- Δ^{γ} -penten- β -ol with HOCl affords the chlorohydrin and γ -chloro- $\beta\delta$ -dimethylpentane- $\alpha\beta\delta\epsilon$ -tetraol (?), m.p. 132° (hydrolysed by K_2CO_3 to a Cl-free substance), together with γ -chloro- $\beta\delta$ -dimethyl- Δ^{β} -penten- β -ol, b.p. $47^{\circ}/10$ mm. J. L. D.

Dehydration of *tert*-butyl-*tert*-heptylcarbinols. I. N. NAZAROV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 85–88).—Ditert-butylcarbinol undergoes dehydration and fission in presence of anhyd. $\text{H}_2\text{C}_2\text{O}_4$ (I) at 120 – 130° (cf. A., 1933, 1271).

Pinacolin, NH_2Na , and EtI give readily di- and, with difficulty in boiling C_6H_6 , tri-ethylpinacolin (40–50% yield), reduced by Na-EtOH to $\beta\beta$ -dimethyl- $\delta\delta$ -diethylhexan- γ -ol, b.p. 225–228°, dehydrated by (I) at 140–160° to a little CMe_2CHMe , more $\text{CHMe}\cdot\text{CEt}$, and much of a mixture (II) of dodecenes.

$\text{OH}\cdot\text{CHBu}^\gamma\cdot\text{CMc}_2\text{Bu}^\gamma$ gives, however, only (II).

R. S. C.

Complexes of mannitol and sorbitol with sodium arsenite and borax.—See this vol., 741.

Ethoxy-derivatives of α -glycols of high mol. wt. D. BARDAN (Bull. Soc. chim., 1934, [v], 1, 141–146).—Hexoyl chloride with excess of Br affords α -bromohexoyl chloride, b.p. 110–112°/33 mm., converted by EtOH and NaOEt into *Et* α -ethoxyhexoate (I), b.p. 98–101°/22 mm. Similarly prepared, α -bromo-octoyl chloride has b.p. 129–133°/25–26 mm. and *Et* α -ethoxyoctoate (II), b.p. 134–137°/31 mm. Interaction of (I) and (II) with excess of the necessary Mg alkyl compound (cf. A., 1932, 41) affords γ -ethoxy- β -methylheptan- β -ol, b.p. 100–102°/28 mm.; γ -hydroxy- δ -ethoxy- γ -ethyl-octane, b.p. 128–129°/45 mm., and -decane, b.p. 143–148°/33–34 mm.; δ -hydroxy- ϵ -ethoxy- δ -n-propyl-nonane, b.p. 141–145°/27–28 mm., and -undecane, b.p. 171–175°/35–37 mm.; ϵ -hydroxy- ζ -ethoxy- ϵ -n-butyl-decane, b.p. 164–167°/27 mm., and -dodecane, b.p. 189–193°/34 mm.; α -hydroxy- β -ethoxy- α -diphenyl-hexane, m.p. 57.5°, and -octane, m.p. 38.5–39°, respectively.

J. L. D.

Alcoholysis of glyceryl triacetate in feebly alkaline media.—See this vol., 737.

Unexpected formation of glycerol- β -phosphoric acid. O. BAILLY and J. GAUME (Compt. rend., 1934, 198, 1932–1934).— Na_2MePO_4 and epichlorohydrin give the mixed Na ester, which with hot aq. KOH yields glycerol- β -phosphoric acid.

R. S. C.

Synthesis of dihydroxyacetonephosphoric acid. W. KIESSLING (Ber., 1934, 67, [B], 868–874).—Treatment of $\text{CO}(\text{CH}_2\text{OH})_2$ in quinoline with POCl_3 leads mainly to dihydroxyacetonediphosphoric acid (I) at 0–10°, whereas at –15° to –20° the monophosphoric acid (II) is almost exclusively formed. (I) is unstable in acid and, probably, in alkaline solution, and does not yield PO_4''' under the influence of N-NaOH . (II) is isolated as the Ca salt (III) $\text{C}_5\text{H}_5\text{O}_6\text{PCa}_2\cdot 0.5\text{H}_2\text{O}$ (also compound $\text{C}_3\text{H}_5\text{O}_6\text{PCa}_2\cdot \text{HSO}_3\text{Ca}_{0.5}$) and Ba salt (IV). (III) and (IV) decompose slowly when preserved or in neutral solution into PO_4''' and polymerisation and condensation products. Like other triosephosphoric acids (V), (II) is converted by N-HCl at 100° into AcCHO and PO_4''' , and by N-NaOH at 15–20° into PO_4''' and $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$. The acid hydrolysis curve of (II) is closely similar to that of glyceraldehydephosphoric acid (VI). Unlike (VI), but similarly to (V), (II) is unchanged by I , and only slightly changed by Br . With dinitrophenylhydrazine (II) gives products containing P and consisting mainly of methylglyoxal-oxazone. (II) is largely fermented and exhibits the enzymic equilibrium (II) hexosediphosphoric acid. It is considered that (VI) consists mainly, (V) entirely, of (II).

H. W.

Partly acylated sugar alcohols. IV. Structure of the *p*-toluenesulphonyl derivatives of mannitol $\alpha\zeta$ -dibenzoate. A. MULLER (Ber., 1934, 67, [B], 830–835; cf. A., 1933, 931).—Anhydromannitol $\alpha\zeta$ -dibenzoate di-*p*-toluenesulphonate in CHCl_3 is hydrolysed by NaOMe-MeOH to anhydromannitol di-*p*-toluenesulphonate, m.p. 129–130°, $[\alpha]_D^{25} +38.2^\circ$ in CHCl_3 , which, with NaOAc and Ac_2O , gives the corresponding $\alpha\zeta$ -diacetate, m.p. 86°, $[\alpha]_D^{25} +52.9^\circ$ in CHCl_3 , and, with *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$ at 15–20°, gives the $\alpha\zeta$ -tetra-*p*-toluenesulphonate, m.p. 170° after softening at 168°, $[\alpha]_D^{25} +48.0^\circ$ in CHCl_3 , which rapidly yields $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Na}$ with anhyd. NaI in COMe_2 at 130°. Dianhydromannitol *p*-toluenesulphonate, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, and $\text{C}_5\text{H}_5\text{N}$ at 15–20° afford dianhydromannitol $\alpha\chi$ -di-*p*-toluenesulphonate, m.p. 100°, $[\alpha]_D^{25} -28.6^\circ$ in CHCl_3 , transformed by anhyd. NaI in COMe_2 at 130° into dianhydromannitol *p*-toluenesulphonate ζ -iodohydrin, m.p. 121–122°, $[\alpha]_D^{25} -68.3^\circ$ in CHCl_3 , which, with AgF in $\text{C}_5\text{H}_5\text{N}$, gives dianhydro- Δ^4 -mannitene *p*-toluenesulphonate, m.p. 80° after softening at 65°, $[\alpha]_D^{25} -66.5^\circ$ in CHCl_3 . Mannitol $\gamma\epsilon$ -diacetate $\alpha\zeta$ -dibenzoate $\beta\delta$ -di-*p*-toluenesulphonate is hydrolysed by NaOMe-MeOH to mannitol $\beta\delta$ -di-*p*-toluenesulphonate, m.p. 157° (decomp.), $[\alpha]_D^{25} +20.0^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (whence mannitol tetra-benzoate $\beta\delta$ -di-*p*-toluenesulphonate, m.p. 153° after softening at 150°, $[\alpha]_D^{25} +41.6^\circ$ in CHCl_3), oxidised by $\text{Pb}(\text{OAc})_4$ to CH_2O and *d*-arabinose $\beta\delta$ -di-*p*-toluenesulphonate, m.p. 168°, $[\alpha]_D^{25} -14.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$. *d*-Sorbitol $\alpha\zeta$ -dibenzoate, *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$, and $\text{C}_5\text{H}_5\text{N}$ at 40° give anhydro-*d*-sorbitol $\alpha\zeta$ -dibenzoate di-*p*-toluenesulphonate, m.p. 123.5°, $[\alpha]_D^{25} +66.35^\circ$ in CHCl_3 .

H. W.

Meltzer's reaction and detection of ether peroxide. A. CASTIGLIONI (Annali Chim. Appl., 1934, 24, 209–212).—With the Et_2O extract of a soap, Meltzer's reaction (A., 1898, ii, 650) as modified by Kreis (A., 1899, ii, 827) gave an eosin-red colour, traceable to the presence of "peroxide" in the Et_2O used. To detect the "peroxide," 1–2 c.c. of the Et_2O is evaporated in a porcelain dish and to the residue are added a drop each of 95% EtOH , PhCHO , and conc. H_2SO_4 ; an eosin-red colour shows "peroxide" with certainty.

T. H. P.

Acetylene polymerides and their derivatives. XX. Addition of alcohols to vinylacetylene. R. A. JACOBSON, H. B. DYKSTRA, and W. H. CAROTHERS (J. Amer. Chem. Soc., 1934, 56, 1169–1170).— $\text{CH}_2\text{:CH}\cdot\text{C}\cdot\text{CH}$ and ROH in presence of NaOR at about 100° give $\text{CMe}\cdot\text{C}\cdot\text{CH}_2\cdot\text{OR}$ (I); $\text{CH}_2\text{:C}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OR}$ is probably an intermediate and is converted by NaOR into (I). The following are described: Me (II), b.p. 99.5–100°, *Et* (III), b.p. 119–120°, *Pr* ^{β} , b.p. 132–134°, *Bu* ^{α} , b.p. 161–162°, *Bu* ^{γ} , b.p. 125–135°, cyclohexyl, b.p. 64°/2 mm., benzyl, b.p. 94–96°/3 mm., β -hydroxyethyl, b.p. 71–73°/4 mm., and β -methoxyethyl, b.p. 84–87°/30 mm., Δ^2 -butinenyl ethers. (II) and (III) are reduced (H_2 , PtO_2 , AcOH) to MeOBu^α and EtOBu^α , respectively; (II) is oxidised (alkaline KMnO_4 at 35–40°) to AcOH and $\text{OMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

H. B.

Preparation of primary *n*-alkyl sulphates. C. BARKENBUS and J. J. OWEN (J. Amer. Chem. Soc.,

1934, 56, 1204—1206).— $\text{ClSO}_3\cdot\text{OR}$ (from SO_2Cl_2 and ROH) and $\text{SO}(\text{OR})_2$ (from SOCl_2 and ROH) at 115—140° in absence or presence of ZnCl_2 give R_2SO_4 (cf. Levailant, A., 1933, 1274). The following are described: *Bu*^a, b.p. 97.4°/3 mm., *n*-*amyl*, b.p. 117°/2.5 mm., *n*-*hexyl*, b.p. 125.3°/2 mm., *n*-*heptyl*, b.p. 146.6°/1.5 mm., m.p. 11.4°, *n*-*octyl*, b.p. 166.1°/2 mm., m.p. 20.3°, *n*-*nonyl*, m.p. 41.9—42.1°, *n*-*decyl*, m.p. 37.6—37.8°, *n*-*dodecyl*, m.p. 48.4—48.5°, *n*-*tetradecyl*, m.p. 57.8—58°, *n*-*hexadecyl*, m.p. 66.2—66.3°, and *n*-*octadecyl*, m.p. 70.2—70.7°, *sulphates*. All b.p. and m.p. are corr. The method does not appear to be applicable to branched-chain primary, *sec.*-, or *tert.*-alcohols.

H. B.

Enzymic equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid. See this vol., 807.

Synthetic glycerides. V. Mixed triglycerides of the dilaurin series. O. E. McELROY and C. G. KING (J. Amer. Chem. Soc., 1934, 56, 1191—1192).—The following *sym.*-glycerides (I) are prepared from α -dilaurin and the requisite acyl chloride in quinoline, whilst the *as.*-isomerides (II) are obtained similarly from glyceryl α -acylate and lauryl chloride: α -, m.p. 44.8°, and β -, m.p. 47.8°, -*palmityl*-; α -, m.p. 42.8°, and β -, m.p. 50.2°, -*myristyl*-; α -, m.p. 32.6°, and β -, m.p. 38.8°, -*deco*-; α -, m.p. 28.4°, and β -, m.p. 30.2°, -*octo*-dilaurins. α -, m.p. 55.2°, and β -, m.p. 62°, -*Acetyldistearins* and β -*butyryldistearin*, m.p. 51°, are described. (I) generally have higher m.p., higher *n*, and lower solubilities than (II) (cf. A., 1932, 364).

H. B.

Relation of m.p. to the number of carbon atoms in normal mercaptans. D. E. TEETS (J. Amer. Chem. Soc., 1934, 56, 1143—1144).—The m.p. of the following RSH are determined essentially by the method of Andrews *et al.* (A., 1925, ii, 852): R=Me, —123.1° (lit. —121°); Et, —147.3°; Pr, —113.3° (lit. —115.5°); Bu, —115.9°; *amyl*, —75.7°; *hexyl*, —81.03°; *heptyl*, —43.4°; *octyl*, —49.2°; *nonyl*, —20.1°; alternation is exhibited. When the log. of the mol. wt. is ≤ 2 , the m.p. lie on a straight line (cf. Austin, A., 1930, 675). Austin's relationship (*loc. cit.*) between m.p. and mol. wt. does not hold if the mol. wt. is < 100 .

H. B.

Influence of dipole moment on the number of molecules of a base fixed by a salt. A. ABLOV (Compt. rend., 1934, 198, 1789—1791).—By evaporation of EtOH solutions of the components at room temp. $(\text{CCl}_3\cdot\text{CO}_2)_2\text{Ni}$ forms additive compounds of the type $+4\text{NH}_2\text{Ar}$ with NH_2Ph (I), *o*- (II) $+ \text{H}_2\text{O}$, *m*- (III), and *p*- (IV) $-\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, *o*- (V) and *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, *o*- $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (VI), and *m*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$; of the type $+3\text{NH}_2\text{Ar}$ with *o*- and *m*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$; of type $+5\text{NH}_2\text{Ar}$ with *p*- $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$; and of type $+6\text{NH}_2\text{Ar}$ with *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ (VII) and *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$ (VIII). $(\text{CHCl}_3\cdot\text{CO}_2)_2\text{Ni}$ gives additive compounds of type $+4\text{NH}_2\text{Ar}$ with (I), (III), (IV), [no compound with (II) and (VI)]; of type $+2\text{NH}_2\text{Ar}$ with (V) $+0.5\text{H}_2\text{O}$; of type $+5\text{NH}_2\text{Ar}$ with (VII) and of type $+6\text{NH}_2\text{Ar}$ with (VIII).

J. W. B.

Effect of the α -nitro-group in three-carbon tautomerism.—See this vol., 772.

Structure of acids obtained by oxidation of triisobutene. I. β -Acid of Conant and Wheland. F. C. WHITMORE and K. C. LAUGHLIN (J. Amer. Chem. Soc., 1934, 56, 1128—1130).—The acid $\text{C}_{12}\text{H}_{24}\text{O}_2$, m.p. 129° (prep. described), of Conant and Wheland (A., 1933, 804) is *methyltert.-butylneopentylacetic* (α -*trimethyl- α -tert.-butylvaleric*) acid (I), and is probably formed from $\beta\beta\delta\zeta\zeta$ -pentamethyl- Δ^7 -heptene (cf. McCubbin, A., 1931, 333) by addition of neutral O (electron sextet) to the pair of electrons in the activated double linking. The acid chloride [hydrolysed to (I) with m.p. 130—130.5°] and NaN_3 in PhMe give [after hydrolysis (HCl)] an amine (hydrochloride, m.p. 215—217°), which with HNO_3 affords *methyltert.-butylneopentylcarbinol*, b.p. 61°/6 mm., m.p. 10—11° (chloride, b.p. 72.5—74°/8 mm.), also prepared from *Bu*^v neopentyl ketone and MgMeI . The α -acid of Conant and Wheland does not possess either of the structures suggested (*loc. cit.*).

H. B.

***p*-Phenylphenacyl esters of the hexoic acids.** F. WREDE and A. ROTHHAAS (Ber., 1934, 67, [B], 739—740).—The acid is neutralised with 1% NaOH and the solution rendered just acid, mixed with a suspension of *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ in EtOH, and boiled for 1 hr. The esters, which separate from the cooled solution, are well adapted for the identification of the acids. *p*-Phenylphenacyl *n*-hexoate (I), m.p. 69—70°, *γ*-methylvalerate (II), m.p. 69—70°, *r*- β -methylvalerate, m.p. 47°, *r*- α -methylvalerate, m.p. 46°, *r*- α - β -dimethylbutyrate, m.p. 73.5°, α -dimethylbutyrate, m.p. 86.5°, β -dimethylbutyrate, m.p. 92°, and α -ethylbutyrate, m.p. 77.5°, are described. *n*-Hexoic and *γ*-methylvaleric acid are best distinguished as their amides, m.p. 100° and 119°, respectively, obtained by heating the NH_4 salts in sealed tubes at 250° for 5 hr. (I) and (II) do not give a depression of m.p. when mixed. $\text{CH}_2\text{Bu}^v\cdot\text{CO}_2\text{H}$ is obtained by allowing Bu^vI to react with $\text{CHNa}(\text{CO}_2\text{Et})_2$ during several days at room temp., then heating to boiling, and proceeding as usual.

H. W.

***p*-Substituted phenacyl esters of *trans*-olefinic acids.** W. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 154—156B; cf. A., 1932, 946).—Interaction of the *trans*-olefinic acid with *p*-substituted phenacyl bromides affords the following *trans*-compounds: *p*-chloro-, m.p. 56°, *p*-bromo-, m.p. 65°, *p*-iodo-, m.p. 74°, and *p*-phenyl-phenacyl elaidate, m.p. 73.5°; *p*-chloro-, m.p. 69.5°, *p*-bromo-, m.p. 74.2°, *p*-iodo-, m.p. 84°, and *p*-phenyl-phenacyl brassidate, m.p. 85.6°; *p*-chloro-, m.p. 69.5°, *p*-bromo-, m.p. 74°, *p*-iodo-, m.p. 82°, and *p*-phenyl-phenacyl cetelaidate, m.p. 84.5°. J. L. D.

Olefinic acids. XII. β -Phenylhexenoic and β -methylpentenoic acids.—See this vol., 770.

Polymerisation of methyl esters of higher unsaturated fatty acids. XIII. Action of halogens on the polymerised ester. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 25—32).—The I vals. of polymerides (I) prepared from linoleic acid (II) and higher unsaturated fatty acids in H_2 during several hr. at 280—290° increase with the time of contact with the halogen. (I) absorb Br, which is easily removed with Zn-HCl-MeOH , but very little depolymerisation occurs with (I) from (II);

the (I) of clupanodonic acid is depolymerised about 40%. The four-membered rings formed in (I) are unattacked by Br; besides substitution, addition occurs at the double linkings which results in high I and Br vals. in protracted reactions. J. L. D.

Hofmann degradation of α -methoxy-acids. F. MICHEEL and K. KRAFT (Ber., 1934, 67, [B], 841—844).—The degradation of lact-, α -methoxypropion-, mandel-, α -methoxyphenylacet-, glucon-, and the corresponding $\alpha\beta\delta\epsilon$ -Me₄-amide by NaOCl under Weerman's conditions occurs with formation of aldehyde and CNO'. Detection of CNO' is not a certain criterion of the presence of α -OH. The more rapid reaction of the OH-amide and the greater quantity of CNO' produced permits discrimination between α -OH- and α -OMe-acids. Degradation of (I) in presence of much MeOH gives a compound (?) OMe·CHPh·NH·CO₂Me, m.p. 67°, immediately decomposed by acid with production of PhCHO. H. W.

Electrolytic oxidation of β -hydroxypropionic acid.—See this vol., 739.

Acetoacetic ester condensation. VI. Mechanism of the reaction. R. F. B. COX, E. H. KROEKER, and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 1173—1178).—Et α -isobutyl- β -phenylpropane- $\alpha\gamma\gamma$ -tricarboxylate does not lose EtOH when heated to 250° (much decomp. occurs); in presence of NaOEt (1 mol.) at 120°, Et 5-phenyl-2:2-dimethylcyclohexane-1:3-dione-4:6-dicarboxylate, m.p. 144—145°, is obtained in 42% yield, as the result of an internal acetoacetic ester condensation (cf. Dieckmann and Kron, A., 1908, i, 388). Et α -methylglutarate (I) (1 mol.), Et₂C₂O₄ (2 mols.), and NaOEt (1 mol.) at 125—130° give 37% of Et butane- $\alpha\alpha\gamma$ -tricarboxylate [formed by loss of CO from the intermediate CO₂Et·CO·CH(CO₂Et)·CH₂·CHMe·CO₂Et]; Et 3-methylcyclopentane-1:2-dione-3:5-dicarboxylate is not produced [in agreement with Dieckmann (A., 1899, i, 676)]. Et α -methylacrylate and Et isobutyl- α' -methylglutarate, b.p. 144—147°/10 mm., which with NaOEt (1 mol.) at 115—125° affords EtOH (0.85 mol.), (II) (0.63 mol.), and a little (I); a cyclic condensation product is not formed. A mechanism for the acetoacetic ester condensation must explain (i) condensation between the CO₂Et of a simple ester and a C atom attached to 2H and a negative group (CO₂Et, CN, acyl), (ii) condensation between CO₂Et which is part of a C(CO₂Et)₂ group and a C atom to which is attached a negative group and only 1 H. An extension of Michael's mechanism (A., 1888, 1054) is favoured: 2EtOAc \rightarrow OEt·CMe(OH)·CH₂·CO₂Et \rightleftharpoons OH·CMe·CH·CO₂Et + EtOH. H. B.

Compounds of uranyl oxalate with alkaline-earth oxalates. A. COLANI (Compt. rend., 1934 198, 1510—1512; cf. A., 1917, i, 513, 535).—UO₂C₂O₄ (I) and CaC₂O₄ do not react in H₂O at 15° 50°. (I) with SrC₂O₄ at 15° and 50° affords UO₂Sr(C₂O₄)₂·4H₂O, and with BaC₂O₄ it affords UO₂Ba(C₂O₄)₂·5H₂O and UO₂Ba₂(C₂O₄)₃·7H₂O. J. L. D.

Ethyl Δ^1 -cyclopentenylmalonate. G. A. R. KON and Z. T. LING (J.C.S., 1934, 596—599).—Work previously described (A., 1930, 773) is repeated and amplified. cyclopentylidenemalononic acid (A., 1926, 1246) [Et ester (I), b.p. 138—141°/10 mm., prepared by the Ag salt method (A., 1932, 252)] with (i) 2N- and (ii) 0.7N-EtOH-HCl at room temp. for 1 week gives (mainly) Et Δ^1 -cyclopentenylmalonate (II), with (i) b.p. 150°/17 mm., I addition (method; A., 1931, 608) 41.5%, and (ii) b.p. 136°/10 mm., I addition 44.9%. Decomp. of the solid K derivative obtained from (II) and dry KOEt in light petroleum with Et₂O-BzOH gives the ester (A) with b.p. 140°/15 mm., I addition 57.3% [indicating that the min. $\beta\gamma$ -content of (A) is 57.3%; the actual val. is undoubtedly much higher, since esters of this type react slowly and incompletely with ICl]. (I) has no measurable I addition. Attempted reduction (Al-Hg, moist Et₂O) of (A), in the hope of converting the $\alpha\beta$ -ester present into a bimol. product, results in an increase in the amount of $\alpha\beta$ -form present. Refractometric data for (I), (A), and Et α -methyl- Δ^1 -cyclopentenylmalonate, b.p. 146°/11 mm., I addition 43.3%, indicate that the max. amount of $\alpha\beta$ -ester in (A) is 18%. Similar data also indicate that the Et Δ^1 -cyclohexenylmalonate, b.p. 150°/14 mm., I addition 23.5%, prepared by the Ag salt method, is not a pure $\beta\gamma$ -ester; the $\beta\gamma$ -content of the ester, b.p. 154°/16 mm., I addition 32%, obtained by esterification with cold 2.2N-EtOH-HCl, is of the same order as that of (A) and is not increased by regenerating the ester from its K derivative. Et α -methyl- Δ^1 -cyclohexenylmalonate has b.p. 155.5°/16 mm., I addition 42.7%. All attempts to convert Et α -cyanocyclohexylideneacetate into the $\beta\gamma$ -form have been unsuccessful. K derivatives (as above) have the anionic charge localised on O. Treatment with a non-ionised polar mol. (e.g., alkyl iodide) causes redistribution of the charge to C α and an α -alkyl derivative is formed. Acidification with aq. acid causes redistribution of the charge within the anion and both $\alpha\beta$ - and $\beta\gamma$ -forms are produced (according to their respective stabilities). Acidification with a weak org. acid in a neutral solvent may not bring about redistribution of the charge beyond C α . Tautomerism in compounds such as the above is best considered as three-carbon and not pentad keto-enol (Shoppee, A., 1928, 1240). Enolisation frequently facilitates, but is not essential to, tautomerism. H. B.

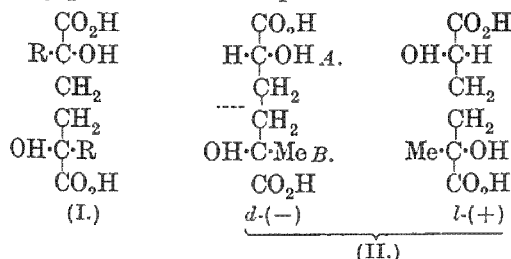
Walden inversion. II. Mutual transformation of the tartaric acids by means of Walden's inversion; attempt to transform mesotartaric acid into active tartaric acids. V. A. RAO and P. C. GUHA (Ber., 1934, 67, [B], 741—749).—Et mesotartarate (I) is converted by PCl₅ in CHCl₃ at 65—70° into Et chlorohydroxysuccinate, b.p. 147—150°/13 mm., transformed by Ag₂O-H₂O into mesotartaric acid (II), but not affected by Pb(OH)₂. For the determination of (II) in presence of *r*- (III) or *d*- (I) -tartaric acid, the suitably conc. solution is divided into two equal portions, one of which is exactly neutralised with KOH, mixed with EtOH-AcOH (3:1 vol.), and added to the other portion. After 1 day the pptd. *r*- or *d*-C₄H₅O₆K is collected, dried,

and weighed, and (II) is determined in the filtrate as the Ba or Pb salt. Treatment of *l*-chlorohydroxy-succinic acid with $\text{Pb}(\text{OH})_2$ yields exclusively (II), whereas with KOH a feebly laevorotatory product containing much (II) and little (III) is obtained. Treatment of (I) with SOCl_2 at room temp. leads to the ester $\text{SO} \begin{smallmatrix} \text{O-CH-CO}_2\text{Et} \\ \text{O-CH-CO}_2\text{Et} \end{smallmatrix}$, b.p. $166^\circ/9$ mm., hydrolysed by acidified H_2O exclusively to (II) and by KOH mainly to (II) accompanied by (III). Hydrolysis of the corresponding ester of (IV) yields almost exclusively (IV). Et mesodichlorosuccinate is converted by Ag_2O entirely into (II), by KOH into (II) accompanied by a little (III). Et *l*-isodichlorosuccinate and KOH yield (IV) with a small proportion of (III). *l*-isoDichlorosuccinic acid and Ag_2O give small amounts of *l*-tartaric acid.

H. W.

Beryllium tartrate.—See this vol., 732.

Steric series. XIX. Configuration of the tertiary carbon atom. II. α -Hydroxy- α -methylfatty acids. K. FREUDENBERG, W. F. BRUCE, and E. GAUF (Annalen, 1934, 510, 206—222; cf. A., 1933, 502).—(—)- $\alpha\alpha'$ -Dihydroxyadipic acid has the optical properties of a *d*-hydroxy-acid and is assigned the constitution (I, R=H), whilst *d*-(—)- $\alpha\alpha'$ -dihydroxy- $\alpha\alpha'$ -dimethyladipic acid is (I, R=Me). The racemoid form of $\alpha\alpha'$ -dihydroxy- α -methyladipic acid must be (II), since it gives a dilactone; the configurations of the *d*-(—) and *l*-(+)-forms are deduced from the rotatory powers of the components *A* and *B*.



When freshly distilled laevulaldehyde (III) (prep. by ozonolysis of caoutchouc and subsequent reductive fission described) is kept at 0° , it polymerises to the trimeride, $\text{O} \begin{smallmatrix} \text{CHR}\cdot\text{O} \\ \text{CHR}\cdot\text{O} \end{smallmatrix} \text{CHR}$ (R= $\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$),

m.p. $78\text{--}79^\circ$ (trioxime, m.p. $139\text{--}149^\circ$); polymerisation is retarded by dilution with H_2O or abs. Et_2O . The nitrile from (III), aq. KCN, and conc. HCl in the cold is hydrolysed (cold conc. HCl- Et_2O) to mesoid *d*-dihydroxy- α -methyladipic acid, m.p. $177\text{--}178^\circ$, and racemoid $\alpha\alpha'$ -dihydroxy- α -methyladipic acid (II), m.p. $164\text{--}165^\circ$ [dilactone, b.p. $154\text{--}155^\circ/11\text{--}12$ mm., m.p. $75\text{--}76^\circ$; Ac_2 derivative, m.p. $157.5\text{--}158^\circ$; di(phenylhydrazide), m.p. 216° ; diamide, m.p. 141°]. (II) is resolved by brucine into the (+)-form, m.p. $173\text{--}174^\circ$ (decomp.), $[\alpha] +13.8 \pm 0.1^\circ$ in H_2O , -7.8° as K_2 salt [dilactone, m.p. $110\text{--}111^\circ$, $[\alpha]_{578} +27.5 \pm 0.3^\circ$ in salt [dilactone, m.p. $110\text{--}111^\circ$, $[\alpha]_{578} +27.5 \pm 0.3^\circ$ in dioxan; Me_2 ester, $[\alpha]_{578} +9.7^\circ$ in MeOH; di(phenylhydrazide), m.p. $227\text{--}228^\circ$, $[\alpha]_{578} -19.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$; diamide, m.p. $155\text{--}155.5^\circ$, $[\alpha]_{578} -36.5^\circ$; Ac_2 derivative, m.p. $142\text{--}143^\circ$, $[\alpha]_{578} -13.1^\circ$ in MeOH]. Δ -ethylacetone and HCN similarly give (cf. Fittig, A., 1906, i, 471) meso-, m.p. 210° , and *r*- (IV), m.p. 210° , $\alpha\alpha'$ -dihydroxy- $\alpha\alpha'$ -dimethyladipic acids; (IV) is isol-

ated and purified through its dilactone. Resolution of (IV) with cinchonidine affords the (—)-form, $[\alpha]_{578} -17^\circ$ in H_2O , $-0.5 \pm 0.2^\circ$ as K_2 salt [dilactone, m.p. $110\text{--}111^\circ$, $[\alpha]_{578} -38.2^\circ$ in dioxan; Me_2 ester, m.p. $49\text{--}50^\circ$, $[\alpha]_{578} -18.4^\circ$ in MeOH; Ac_2 derivative, m.p. 101° , $[\alpha]_{578} +17.8^\circ$ in MeOH; di(phenylhydrazide), m.p. 234° (decomp.), $[\alpha]_{578} +26^\circ$ in $\text{C}_5\text{H}_5\text{N}$; diamide, m.p. $219\text{--}220^\circ$, $[\alpha]_{578} +19.8^\circ$ in H_2O]. *l*-(+)- $\alpha\alpha'$ -Dihydroxyadipic acid, $[\alpha]_{578} +4.2^\circ$ in H_2O , -30.3° as Na_2 salt [dilactone, m.p. $120\text{--}121^\circ$, $[\alpha]_{578} +11.2^\circ$ in dioxan; Me_2 ester, $[\alpha] < -0.5^\circ$; Ac_2 derivative, m.p. 159° (decomp.), $[\alpha]_{578} -28.5^\circ$ in MeOH; diamide, m.p. 164° , $[\alpha]_{578} -64.6^\circ$ in H_2O ; di(phenylhydrazide), m.p. 191° , $[\alpha]_{578} -15.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$], is prepared by a modification of Le Sueur's method (J.C.S., 1908, 93, 718).

H. B.

Unsaturated polycarboxylic acids. Derivatives of ethylenetricarboxylic acid. (MLLE.) T. GRADOWSKA, A. KRYNICKI, and R. MATACHOWSKI (Bull. Acad. Polonaise, 1933, A, 552—559).—With Br in CCl_4 Me ethane- $\alpha\alpha\beta$ -tricarboxylate affords its α -Br-derivative, b.p. $148.5\text{--}149.5^\circ/9$ mm., converted by NaOMe-MeOH into the α -OMe-ester, b.p. $142\text{--}143^\circ/7$ mm. (Et α -ethoxy-ester, b.p. $158\text{--}160^\circ/11$ mm.), and by $\text{C}_5\text{H}_5\text{N}$ into Me ethylenetricarboxylate (I), b.p. $128\text{--}134^\circ/8$ mm., m.p. $40\text{--}41^\circ$ (Et ester, b.p. $155\text{--}156^\circ/11$ mm.). (I) readily forms additive compounds and hydrolysis with cold 4% aq. $\text{Ba}(\text{OH})_2$ gives the Ba salt of an acid + H_2O , m.p. $145\text{--}146^\circ$, which does not regenerate (I) with CH_3N_2 . Addition of H_2O , NH_2Ph , or NH_3 to (I) affords, respectively, Me β -hydroxy- (Et ester, b.p. $158\text{--}160^\circ/11$ mm. with slight decomp.) and β -anilino-, m.p. 82° , ethane- $\alpha\alpha\beta$ -tricarboxylate, and di-($\alpha\beta\beta$ -tricarboxymethoxyethyl)amine, m.p. 122° .

J. W. B.

Properties of citric acid. S. BERLINGOZZI (Annali Chim. Appl., 1934, 24, 217—224).—The heating curve of citric acid (+ H_2O) shows a point of inflexion at about 56° , at which temp. the anhyd. acid (free from aconitic acid) is formed. Fusion occurs at about $70\text{--}100^\circ$ and decomp. at 140° . To detect aconitic in citric acid (1 : 10,000 or more), 10 g. of the powdered acid are well shaken with about 20 c.c. of H_2O -free Et_2O , this being filtered and the residue washed with a little Et_2O . The filtrate is evaporated, the residue dissolved in H_2O , and the solution made faintly alkaline with dil. NaOH, cooled, and treated with 2—3 drops of 2% KMnO_4 ; a green colour shows aconitic (or itaconic, mesaconic, or citraconic) acid.

T. H. P.

Resolution of *dl*-erythronic acid. J. W. E. GLATTFELD and L. R. FORBRICH (J. Amer. Chem. Soc., 1934, 56, 1209—1210).—*dl*-Erythronolactone, m.p. $91\text{--}92^\circ$, prepared by oxidation (AgClO_3 ; Braun, A., 1929, 293) of γ -hydroxyisocrotonolactone (A., 1931, 1148), is resolved by brucine and quinine into *d*-(—), m.p. 105° (corr.), $[\alpha]_{546} -87.62^\circ$, and *l*-(+), m.p. 105° (corr.), $[\alpha]_{546} +87.32^\circ$, -forms.

H. B.

Convenient modification of the Kiliani synthesis of higher carbon acids (or their lactones) from reducing sugars. C. S. HUDSON, O. HARTLEY, and C. B. PURVES (J. Amer. Chem. Soc., 1934, 56, 1248—1249).—Glucose (3 mols.) is treated with NaCN (3.3 mols.) and CaCl_2 (3.6 equivs.) in H_2O at

room temp. for 22 hr.; $\text{Ca}(\text{OH})_2$ (3 mols.) is then dissolved in the solution. The basic Ca salts which subsequently separate are washed with cold aq. $\text{Ca}(\text{OH})_2$ and then decomposed with $\text{H}_2\text{C}_2\text{O}_4$ or H_2SO_4 . α -Glucoheptonolactone is thus obtained in 58% yield; the β -lactone (21%) is obtained through the brucine salt. The method has been applied to xylose and lactose; the gluco-octonolactones have been prepared.

H. B.

Thio- and thionyl-difatty acids. E. LARSSON and K. JONSSON (Ber., 1934, 67, [B], 757—760).—Conc. solutions of $\text{SK} \cdot \text{CMc}_2 \cdot \text{CO}_2\text{K}$ and $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{Na}$ in H_2O at 100° yield $\alpha\alpha$ -dimethylthiodiacetic acid, m.p. 111° , oxidised by 30% H_2O_2 in COMe , at room temp. to $\alpha\alpha$ -dimethylthionylthiodiacetic acid, $\text{CO}_2\text{H} \cdot \text{CMc}_2 \cdot \text{SO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, m.p. 114° . Trimethylthiodiacetic acid, m.p. 111° , from $\text{SH} \cdot \text{CMc}_2 \cdot \text{CO}_2\text{H}$ and $\text{CHBrMe} \cdot \text{CO}_2\text{H}$ or from $\text{SH} \cdot \text{CHMe} \cdot \text{CO}_2\text{H}$ and $\text{CBrMe}_2 \cdot \text{CO}_2\text{Et}$, followed by hydrolysis, is converted by H_2O_2 in AcOH at 0° into trimethylthionylthiodiacetic acid, m.p. 87° . Thioacetic- β -propionic acid, m.p. 94° , from $\text{SH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and $\text{CH}_2\text{Cl} \cdot \text{CO}_2\text{H}$ or from $\text{SH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, with H_2O_2 in COMe_2 gives thionylacetic- β -propionic acid, m.p. 90° (decomp.). Thio- β -propionic- α -isobutyric acid, m.p. 106° (from $\text{SH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ and $\text{CBrMe}_2 \cdot \text{CO}_2\text{Et}$), or m.p. 109° (from $\text{SH} \cdot \text{CMc}_2 \cdot \text{CO}_2\text{H}$ and $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$), is oxidised by H_2O_2 to the non-cryst. (?) thionyl acid and by $\text{Br} \cdot \text{H}_2\text{O}$ to sulphonyl- β -propionic- α -isobutyric acid, m.p. 156° .

H. W.

Sulphoglutaric acid. J. M. VAN DER ZANDEN (Rec. trav. chim., 1934, [iv], 53, 591—597).—Glutaconic acid (modified prep.) and $(\text{NH}_4)_2\text{SO}_3$ at 100° give β -sulphoglutaric acid, $+\text{H}_2\text{O}$, m.p. 109 — 111° (Ba , $\text{Pb}_{1.5}$, K_2 , K , and Ti_3 salts) (could not be obtained pure from β -bromoglutaric acid), which with H_2SO_4 gives probably impure trisulphoglutaric acid (Ba_2 salt), whilst the Et H ester gives mixtures.

R. S. C.

Formation of formaldehyde in the oxidation of ethyl alcohol. M. FLANZY (Compt. rend., 1934, 198, 1793—1795).— CH_3O (I) is formed in the oxidation of EtOH with $\text{MnO}_2 + \text{H}_3\text{PO}_4$ or H_2SO_4 at 100° , H_2O_2 in conc. aq. NH_3 [increased by Cu ; larger amounts of (I) from NH_4Et and EtI ; HCO_2H in alkaline media free from NH_3], $\text{K}_2\text{Cr}_2\text{O}_7 - \text{H}_2\text{SO}_4$ at 100° (greater if the concn. of active O is $>$ that of EtOH), but not if oxidation is begun in the cold and the temp. then raised to 100° . The formation of (I) may be due to intermediate production of $\text{CH}_2 \cdot \text{CH}_2\text{OH}$.

J. W. B.

Chains in the acetaldehyde decomposition. D. V. SICKMAN and A. O. ALLEN (J. Amer. Chem. Soc., 1934, 56, 1251).— MeCHO (I) decomposes completely at 300° in presence of a few % of azomethane (II), indicating the existence of a chain decomp. which is initiated by free Me radicals. Chain lengths (calc. from rate measurements) are about 30. The rate \propto to the pressure (p) of (I) and \sqrt{p} of (II), as predicted by the chain theory.

H. B.

Extension of the Cannizzaro reaction to aliphatic and arylaliphatic aldehydes. S. SABETAY and L. PALFRAY (Compt. rend., 1934, 198, 1513—1515; cf. A., 1932, 867).—0.5—1.5 g. of an aliphatic

or arylaliphatic aldehyde with 25 c.c. of boiling 0.5N. $\text{CH}_2\text{Ph} \cdot \text{OK}$ during 2—5 hr. often affords the corresponding acid and alcohol quantitatively. J. L. D.

Detection of the simplest hydroxy-aldehydes and ketones by means of colour reactions. E. TOMMILA (Suomen. Kem., 1934, 7, 85—86b).—Characteristic coloured ppts. and solutions in Et_2O (I) are obtained by treating OH-aldehydes with naphthoresorcinol in conc. HCl . The following are described, the sensitivity being given in parentheses: $\text{OH} \cdot \text{CH}_2 \cdot \text{CHO}$ (II), greyish-green ppt., insol. in CHCl_3 (III), bluish-green, fluorescent solutions (10^{-5} g.); AcCHO , red ppt. and red solutions in (I), (III), and NaOH with powerful blue fluorescence (5×10^{-6} g.); glyceraldehyde, greyish-blue ppt., insol. in (III), yellow, non-fluorescent solution (10^{-5} g.); dihydroxyacetone, greyish-violet ppt., yellow—pale violet, non-fluorescent solution [colourless in (III)], transient violet with NH_3 ; tetrose from (II), bright red insol. ppt. Similar, less characteristic reactions are described with resorcinol, orcinol, and phloroglucinol.

S. C.

Catalytic reduction reactions. K. PACKEN-DORFF (Ber., 1934, 67, [B], 905—908).—An active catalyst is obtained by reducing H_2PtCl_6 by H , in presence of $\text{Pt} \cdot \text{C}$. It is particularly suitable for operation in HCl , whereas HNO_3 is reduced to NH_3 and the reduction products of H_2SO_4 restrict its activity. The optimal concn. of HCl varies from case to case, but if > 10 — 12% the activity is restricted. In alkaline solution absorption of H is slower than in acid medium. Ketones not belonging to the type COPhMe are reduced to the carbinols generally accompanied by the hydrocarbons. The following examples are cited: COEt_2 to $\text{CHEt}_2 \cdot \text{OH}$; $\text{COMe} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ph}$ to $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Ph}$; acetyl-cyclohexane to methylcyclohexylcarbinol; laevulic acid to valerolactone and valeric acid; phthalimide to phthalimidine; cyclohexanone to cyclohexanol and cyclohexane, and cyclopentanone to cyclopentanol and cyclopentane, whereby reaction ceases before production of hydrocarbon is complete even when the amount of catalyst is greatly increased; citral ($+2\text{H}$) to unchanged material, geraniol+citronellol, and hydrocarbon.

H. W.

Action of sodium on aliphatic ketones. (Existence of metal ketyls in the acyclic series.) A. E. FAVORSKI and I. N. NAZAROV (Bull. Soc. chim., 1934, [v], 1, 46—65).—The dimeride of the Na derivative of $\beta\beta\delta\delta$ -tetramethylpentan- γ -one [which with CO_2 in Et_2O in absence of O_2 gives $\alpha\alpha$ -ditert.-butylglycollic acid, an oil (Ag salt)] is converted by acid into $\beta\beta\delta\delta$ -tetramethylpentan- γ -ol and tetratert.-butylethylene glycol (I), m.p. 85 — 86° , which with conc. H_2SO_4 at — affords $\beta\beta$ -dimethyl- $\delta\delta$ -tritert.-butylbutan- γ -one, b.p. 135 — $136^\circ/20$ mm. [Br_2 -derivative, m.p. 74 — 75° (decomp.)]. The dimeride of the Na derivative of $\beta\delta\delta$ -trimethylpentan- γ -one (II) is decomposed by H_2O into (II) and the corresponding tert.-alcohol, together with $\beta\epsilon$ -dimethyl- $\gamma\delta$ -ditert.-butylhexane- γ -diol, b.p. 133° . The Na derivative of pinacolin (I) when heated in a sealed tube at 110° for 15 min. gives an alcohol, $\beta\beta\delta\delta\epsilon\epsilon$ -hexamethylhexan- γ -one (I) b.p. 90 — $91^\circ/15$ mm. [reduced ($\text{Na} \cdot \text{EtOH}$) to a

alcohol, b.p. 99°/15 mm. (Bz derivative, m.p. 48—49°), which is oxidised (KMnO₄) to (III), Bu^νCO₂H (V), and COBu^ν·CO₂H (VI)], and βγ-ditert.-butyl-Δ^α-butan-γ-ol (VII), b.p. 105—107°/15 mm. (Br-compound, an oil), oxidised (KMnO₄) to (III), (V), and (VI), and converted by distillation with anhyd. H₂C₂O₄ into βγ-ditert.-butylbutadiene (VIII), b.p. 62—64°/15 mm. (Br₂-compound, an oil), and (III). Interaction of (VIII) with maleic anhydride in C₆H₆ in a sealed tube at 100° during 3 hr. affords βγ-ditert.-butyltetrahydrophthalic anhydride, m.p. 128—129°, hydrolysed to the acid, m.p. 183—184° (decomp.) (Ag salt). J. L. D.

Condensation of alkylacetylenes with hydroxy-compounds. G. F. HENNION and D. B. KILLIAN [with T. H. VAUGHN and J. A. NIEUWLAND] (J. Amer. Chem. Soc., 1934, 56, 1130—1132).—CH₃·CBu and MeOH in presence of BF₃ (prep.: A., 1933, 932) and HgO give the Me₂ acetal, b.p. 58—60°/30 mm., of COMeBu. Δ^α-Heptinene and (·CH₂·OH)₂ similarly afford the acetal, $\frac{\text{CH}_2\text{O}}{\text{CH}} > \text{CMe} \cdot \text{C}_5\text{H}_{11}$, b.p. 180—181°/745 mm.; with AcOH, α-amylvinyl acetate (I), b.p. 92—94°/40 mm., and a little Me amyl ketone (II) result. (I) is hydrolysed (20% EtOH-KOH) to (II); ammonolysis of (I) gives (II) and NH₄Ac. (I) is stable to dil. acid or alkali. H. B.

Action of magnesium ethyl bromide on sebactetramethyldiamide. (Mlle.) V. PARASKOVA (Compt. rend., 1934, 198, 1701—1703; cf. A., 1928, 50).—Interaction of sebactetramethyldiamide (I) with excess of MgEtI in boiling Et₂O during many hr. affords tetradecane-γu-dione, m.p. 78° (disemicarbazone, m.p. 186—187°; dioxime, m.p. 105—106°). u-tetradecodideethylamide, b.p. 216—218°/15 mm., hydrolysed to the acid, m.p. 72° (semicarbazone, m.p. 169°; Et ester, b.p. 175—176°/13 mm., and its semicarbazone, m.p. 81—82°); μ-diethylamino-μ-ethyltetradecan-γ-one, b.p. 209—212°/12 mm. (semicarbazone, m.p. 98—99°) (converted by boiling Ac₂O into a product, free from N, b.p. 173—174°/16 mm.), γu-di-(diethylamino)-γu-diethyltetradecane and u-diethyl-amino-u-ethyltetradeceethylamide, oils, which lose N with boiling Ac₂O. (I) probably reacts through its enolic form (cf. A., 1931, 831). J. L. D.

Polarity and alcoholysis of αγ-diketones and β-keto-esters. L. J. BECKHAM and H. ADKINS (J. Amer. Chem. Soc., 1934, 56, 1119—1123).—Mechanisms for the alcoholysis of αγ-diketones and β-CO-esters in acid and alkaline solutions are formulated and the influence of the polarity (+I; ±T) of substituent groups considered. Predictions are in accordance with the results previously obtained (A., 1930, 1273, 1559; 1931, 69; 1932, 1020, 1112). H. B.

Preparation of l-ribose. W. C. AUSTIN and L. HUMOLLER (J. Amer. Chem. Soc., 1934, 56, 1152—1153).—Acetobromo-l-arabinose is reduced (Zn +5% Zn-Cu, AcOH) to l-arabinal diacetate. Oxidation of l-arabinal in H₂O with BzO₂H in EtOAc at <8° gives (cf. A., 1933, 147) 40% of l-ribose, m.p. 85—87°, [α]_D²⁰⁻²⁵ +22.6° in H₂O (p-bromophenylhydrazone, m.p. 170—172°), and 8% of l-arabinose (p-bromophenylhydrazone, m.p. 161—162°). H. B.

Preparation of β-d-allose. F. P. PHELPS and F. BATES (J. Amer. Chem. Soc., 1934, 56, 1250; cf. Levene and Jacobs, A., 1911, i, 14).—d-Ribose (from yeast-nucleic acid) is converted (cf. loc. cit.) into d-altronic acid (as Ca salt) and d-allonolactone (I). Reduction (Na-Hg) of (I) gives β-d-allose, m.p. 128—128.5°, [α]_D²¹ (in H₂O?) +0.58° (after 2 min.) → +14.41° (const.). H. B.

Preparation of two new crystalline aldohexoses, l-allose and l-altrose, from l-ribose by the cyanohydrin reaction. W. C. AUSTIN and F. L. HUMOLLER (J. Amer. Chem. Soc., 1934, 56, 1153—1155).—l-Ribose is treated with aq. Ca(CN)₂ at 10° until the solution shows no reducing power; successive treatment with Ba(OH)₂, H₂C₂O₄, and Ca(OH)₂ and concn. of the resulting solution gives Ca l-altronate (+3.5H₂O). Removal of Ca from the residual solution with H₂C₂O₄ and evaporation give l-allonolactone (I), m.p. 130°, [α]_D +6.32° → +4.34°. Reduction (Na-Hg, dil. H₂SO₄) of (I) affords l-allose, m.p. 128—129°, [α]_D -1.9° → -13.88° (cf. A., 1933, 699) (phenylosazone, m.p. 165°; p-bromophenylhydrazone, m.p. 141—145°). l-Altronolactone, [α]_D -37.2°, is similarly reduced to l-altrose, m.p. 107—109.5°, [α]_D -28.75° → -32.3° (phenylosazone, m.p. 165°; phenylbenzylhydrazone, m.p. 147—148°). Brucine l-allonate, m.p. 168—169°, [α]_D -24.75°, and l-altronate, m.p. 171—175°, [α]_D -21.44°, and l-allonphenylhydrazide, m.p. 151—155°, are described. All rotations are in H₂O at 20—25°. H. B.

Structure and properties of acetone-methyl-rhamnopyranoside. P. A. LEVENE and I. E. MUSKAT (J. Biol. Chem., 1934, 105, 431—442).—2:3-isoPropylidinemethylrhamnopyranoside (α+β), b.p. 110—112°/1 mm., [α]_D²¹ -14.1° in H₂O, is converted by MeI and Ag₂O or MeI and K in liquid NH₃ into a 4-Me derivative, b.p. 67—68°/0.3 mm., [α]_D²¹ -24° in H₂O (p-toluenesulphonate, m.p. 58°, [α]_D²¹ +14° in MeOH; unaffected by NaI in COMe₂ at 100°), which is hydrolysed by dil. H₂SO₄ at 100° to 4-methylrhamnopyranose, m.p. 122°, [α]_D²¹ +12.9° in MeOH [purified through its Ac₃ derivative (I), b.p. 114—116°/0.17 mm., [α]_D²¹ -12.2° in MeOH; phenylhydrazone, decomp. 176°], the structure of which is determined by oxidation with aq. Ag₂O to β-hydroxy-α-methoxy-n-butyric acid (Ag salt). With HBr in AcOH (I) gives bromomethylrhamnopyranose diacetate, m.p. 140.5°, [α]_D²¹ -178.6° in CHCl₃, which with Ag₂O and MeOH gives methylmethylrhamnopyranoside diacetate, b.p. 125—130°/0.7 mm., [α]_D²¹ +17.2° in MeOH, and with Ag theophylline in xylene at 100° gives methyltheophyllinerhamnopyranoside diacetate, [α]_D²¹ -36.7° in MeOH, and finally with MeOH and a little quinoline affords evidence of the formation of an orthoacetate not isolated pure. H. A. P.

New acetone [isopropylidene] sugar. R. WEIDENHAGEN (Z. Ver. deut. Zuckerind., 1934, 84, 335—340).—Gradual addition of dry Ag₂CO₃ to acetobromoglucose in anhyd. COMe₂ containing ignited K₂CO₃ at about 5° causes vigorous evolution of CO₂. After removal of solvent, the residue is dissolved in C₆H₆ and the solution is washed with H₂O at 25—28° until reducing substances of the trehalose type are removed. When preserved the

C_6H_8 solution deposits *isopropylidenedi-1:1-glucose octa-acetate* (I), m.p. 154.5—156° (corr.), $[\alpha]_D^{20} -31.1^\circ$ in C_6H_6 , hydrolysed by NaOMe in MeOH to non-cryst. *isopropylidenedi-1:1-glucose*, from which (I) is regenerated by Ac_2O in C_5H_5N . H. W.

Ring opening of galactose acetates. J. COMPTON and M. L. WOLFROM (J. Amer. Chem. Soc., 1934, 56, 1157—1162).— β -Galactopyranose tetra-acetate (I), m.p. 112° [127—128° in alkali-free glass (cf. Georg, A., 1932, 835)], from acetobromogalactose (Unna, Diss., Berlin, 1911), and $NPhMe \cdot NH_2$ (II) in dil. AcOH give aldehydogalactosephenylmethylhydrazone 2:3:4:6-tetra-acetate, m.p. 122—123°, $[\alpha]_D^{20}$ (in C_5H_5N) $-12^\circ \rightarrow +37.5^\circ$, acetylated (Ac_2O , C_5H_5N) to the penta-acetate (III) (A., 1931, 1276), and converted by $p-C_6H_4Me \cdot SO_2Cl$ in C_5H_5N into aldehydogalactosephenylmethylhydrazone 2:3:4:6-tetra-acetate *o-p-toluenesulphonate*, m.p. 143—144°, $[\alpha]_D^{20} +21.4^\circ$ in C_5H_5N . (I) and $NHPh \cdot NH_2$ (IV) in dil. AcOH give aldehydogalactosephenylhydrazone 2:3:4:6-tetra-acetate, $[\alpha]_D^{20} +5^\circ$ in C_5H_5N , acetylated to the corresponding penta-acetate (V) (*loc. cit.*). β -Galactofuranose tetra-acetate (VI) (improved prep. given; cf. Hudson and Johnson, A., 1916, i, 546) and (II) similarly afford aldehydogalactosephenylmethylhydrazone 2:3:5:6-tetra-acetate, m.p. 126°, $[\alpha]_D^{20} +59.1^\circ$ in C_5H_5N (4-*p-toluenesulphonate*, m.p. 102—103°, $[\alpha]_D^{20} +60.7^\circ$ in C_5H_5N), also acetylated to (III). (VI) and (IV) give aldehydogalactosephenylhydrazone 2:3:5:6-tetra-acetate, m.p. 139—140°, $[\alpha]_D^{20} +80.1^\circ$ in C_5H_5N , acetylated further to (V). The reactions of aldehydogalactose penta-acetate, (I), and (VI) with (II) and (IV) at 0° are all unimol.; reaction is about 45 times as rapid with (VI) as with (I). H. B.

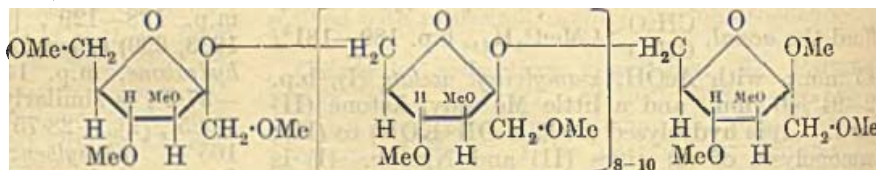
Carbohydrates. XIX. Synthetic derivatives of fructofuranose. P. BRIGL and R. SCHINLE (Ber., 1934, 67, [B], 754—757; cf. this vol., 173).—Fructofuranose tetrabenzoate is converted by Ag_2O and MeI into methylfructofuranoside tetrabenzoate, $[\alpha]_D^{20} +5.0^\circ$ in $CHCl_3$, hydrolysed by $Ba(OH)_2 \cdot 8H_2O$ in MeOH at 15—20° to α -methylfructofuranoside (I), $[\alpha]_D^{20} +48.8^\circ$ in H_2O , $+42.4^\circ$ in EtOH, isolated by filtration of $Ba(OBz)_2$, evaporation of the filtrate in vac., and extraction of the residue with $COMe_2$. (I) is transformed by Me_2SO_4 and NaOH into tetramethylmethylfructofuranoside, b.p. 100—102°/0.6 mm., $[\alpha]_D^{20} +77.6^\circ$ in H_2O , the furanose structure of which is confirmed by the val. $[\alpha]_D^{20} +22.6^\circ$ of the product of its hydrolysis by 1% HCl. H. W.

Acetylation of sorbose in presence of pyridine. G. ARRAGON (Compt. rend., 1934, 198, 1508—1510; c., A., 1933, 811).—Sorbose in Ac_2O containing C_5H_5N at 0° affords the tetra-acetate (50%), m.p. 101.5°, $[\alpha]_D^{20} -22^\circ 35'$, whereas that formed in presence of $ZnCl_2$ has m.p. 96.5°, $[\alpha]_D^{20} -21^\circ 30'$ in $CHCl_3$. At room temp. some penta-acetate is formed.

J. L. D.

Polysaccharides. XVII. Constitution and chain-length of levan. S. W. CHALLINOR, W. N.

HAWORTH, and E. L. HIRST (J.C.S., 1934, 676—679).—Levan, $[\alpha]_D^{20} -47^\circ$ in H_2O , prepared (cf. Harrison *et al.*, A., 1931, 267) from sucrose by the action of *B. mesentericus*, is hydrolysed (0.5% aq. $H_2C_2O_4$) to fructose and methylated (method: Hilbert *et al.*, *ibid.*, 827) to trimethyl-levan (I), $[\alpha]_D^{20} -60^\circ$ in $CHCl_3$. The fractions obtained by successive additions of light petroleum to a solution of (I) in $CHCl_3 \cdot COMe$, (1:1) are (apart from the first which contains all the mineral impurities) similar ($[\alpha]$; η_{sp} ; OMe; the m.p. varies somewhat), indicating that (I) is homogeneous. Hydrolysis (aq. $MeOH \cdot H_2C_2O_4$ at 80°) of the various fractions and subsequent treatment with $MeOH \cdot HCl$ gives 1:3:4:6-tetra-methyl- (10—11%) (II) and 1:3:4-trimethyl-methylfructofuranoside (III). (II) is converted (A., 1927, 1057) into 2:3:4:6-tetramethylfructuronamide, whilst (III) is hydrolysed to 1:3:4-trimethylfructose, m.p. 75°. These results indicate that (I) has the following structure.



The I no. of levan indicates an apparent mol. wt. of 3800. Viscosity measurements with (I) indicate a chain-length which is about twice that determined chemically. H. B.

Glucoside of *Coronilla* seeds.—See this vol., 709.

Highly polymerised compounds. LXXXXII. Constitution of cellulose. H. STAUDINGER (Cellulosechem., 1934, 15, 53—59, 65—67).—The author's views are stated at length. Measurements of the viscosity of cellulose (I) in Schweitzer's reagent (II) can be applied to the determination of (I) if a large excess of Cu salts and NH_3 is used and observations are made in absence of light and air. (I) has a degree of polymerisation of about 750. Technical (I) is less highly polymerised, since marked degradation occurs during the removal of lignin. The very high viscosity of cellulose nitrate is explained by the hypothesis that native (I) consists of very complex esters which are hydrolysed by (II) or by mercerisation. After the alkaline treatment (I) and the nitrate (III) derived from it have the same mol. structure and the viscosity of (I) in (II) is the same as that of (III) in $BuOAc$. Nitration of native (I) is not accompanied by rupture of ether or ester linkings, and hence a very viscous nitrate results. V

Precautions necessary in measuring the mol. wt. of cellulose derivatives. M. MATHIEU (Comm. et Ind., 1934, 31, Spec. No., 792—796).—For correct determinations of mol. wt. by measurements of η or osmotic pressure it is essential that the mols. be completely dispersed. Evidence on this point for cellulose nitrate may be obtained by the X-ray examination films dried on H_2SO_4 at room temp. I.

Mol. wts. of celluloses. E. O. KRAEMER and W. D. LANSING (Nature, 1934, 133, 870—871). Mol. wts. of cellulose determined by sedimentation

equilibrium range from 60,000 to 180,000, and the estimated mol. wt. of native cellulose is near 300,000.

L. S. T.

Asymmetric nitrogen atom. LIX. Decomposition of quaternary ammonium nitrates under the influence of amines; rate of decomposition as function of the basicity of amines. E. WEDEKIND and F. FEISTEL (Ber., 1934, 67, [B], 845—853; cf. A., 1931, 75).—The rate of reaction of quaternary ammonium nitrates with amines, $\text{NR}'\text{R}''\text{R}'''\text{R}''''\text{NO}_3 + \text{HNXY} \rightleftharpoons \text{NR}'\text{R}''\text{R}'''\text{R}'''' + \text{NR}''''\text{XY} + \text{HNO}_3$ has been determined generally by measurements of electrical conductivity, less frequently polarimetrically. *tert.*-Bases ($\text{C}_5\text{H}_5\text{N}$, quinoline, NPhMe_2 , NEt_3 , NPhMeEt , dimethylaminoantipyrine) are inactive. The relationship between the strength of the base and its effect is very pronounced. β - is more powerful than α - $\text{C}_{10}\text{H}_7\text{NH}_2$. For $\text{C}_6\text{H}_4\text{MeNH}_2$ and $\text{C}_6\text{H}_4\text{ClNH}_2$ basicity and effect diminish in the sequence *p*-, *m*-, *o*-, which holds also for $\text{C}_6\text{H}_4(\text{NH}_2)_2$. NH_2Ph is somewhat weaker than *o*- $\text{C}_6\text{H}_4\text{MeNH}_2$. The half-val. periods for NHEt_3 , NHEtCH_2Ph , and $\text{NH}(\text{CH}_2\text{Ph})_2$ are in the ratio, 26:40:80. A similar increase in effect is observed in the sequence NH_2Ph , NHPhEt , NHPhMe . The action of tetrahydro-isoquinoline is about three times as great as that of quinoline. The inactivity of $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and NHPh_2 is in harmony with the slight basicity. *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ is more active than $[\text{C}_6\text{H}_4\cdot\text{NH}_2]_2$ which greatly excels NH_2Ph , whereas $[\text{NHPh}]_2$ is inactive. Modifications of the apparatus necessitated by the high resistances are described. H. W.

Preparation of hexamethylenetetramine. C. L. TSENG and M. HU (Sci. Quart. Nat. Univ. Peking, 1934, 4, 243—249).— $(\text{CH}_2)_6\text{N}_4$ has m.p. 293—295° (lit. 263°, 280—4°). W. R. B.

Proteolytic enzymes. III, IV. Synthesis of peptides etc. See this vol., 809.

Synthetic sugar-amino-acid compounds. M. BERGMANN, L. ZERVAS, and J. OVERHOFF (Z. physiol. Chem., 1934, 224, 52—55).—The Na compound of benzylideneglucose (I) with carbobenzyloxyglycyl chloride (II) affords 1-(carbobenzyloxyglycyl)-4:6-benzylideneglucose, m.p. 180° (corr.), which on hydrogenation gives 1-glycyl-d-glucose [sulphate, sinters >110° (decomp.), $[\alpha]_D^{20} +12.8^\circ$ in H_2O . In presence of $\text{C}_5\text{H}_5\text{N}$, (I) and (II) yield 1:2:3-tri(carbobenzyloxyglycyl)-4:6-benzylideneglucose, m.p. 96°, which on hydrogenation gives 1:2:3-triglycyl-d-glucose (sulphate). J. H. B.

Stability of cystine in acid solution. K. SHINOHARA and M. KILPATRICK (J. Biol. Chem., 1934, 105, 41—251).—Cystine (I) is produced when cystine (II) in HCl is kept even in an atm. of N_2 in the dark at room temp., the change becoming detectable (by I titration) after an induction period of 7 days. Formation of (I) is much more rapid at 80°, or in alkaline solution, and is not affected by Cu or Fe. modified nitroprusside test for the determination of SH compounds, and a colorimetric method for the determination of (I) in presence of (II) based on the reaction between (I) and CoCl_2 and alkaline H_2O_2 ,

are described. (I) can be qualitatively differentiated from other similar compounds by means of the complex Co test. A. E. O.

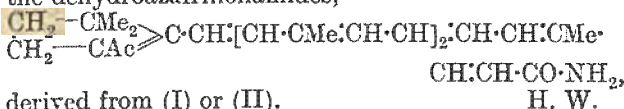
Biuret reaction. IV. (a) Biuret salt of triglycylglycine. (b) Biuret salt of glycine anhydride. (c) Barium biuret salt of succinimide. M. M. RISING, F. M. PARKER, and D. R. GASTON (J. Amer. Chem. Soc., 1934, 56, 1178—1180; cf. A., 1933, 382).—Triglycylglycine and $\text{Cu}(\text{OH})_2$ in aq. NaOH give *Na Cu triglycylglycine*, $\text{Na}_2\text{CuC}_8\text{H}_{16}\text{O}_5\text{N}_4\cdot 2\text{H}_2\text{O}$, m.p. 280° (decomp.; corr.) (chars at 278°). The unstable *Na Cu glycine anhydride*, $\text{Na}_2\text{CuC}_8\text{H}_8\text{O}_4\text{N}_4\cdot 4\text{H}_2\text{O}$, decomp. >120°, is similarly prepared. *Ba Cu succinimide*, $\text{BaCuC}_{16}\text{H}_{16}\text{O}_8\text{N}_4$, m.p. 257° (decomp.; corr.), is obtained from succinimide, $\text{Cu}(\text{OAc})_2$, and $\text{Ba}(\text{OH})_2$ in aq. EtOH . Structures are suggested. The view (A., 1931, 77) that four basic N atoms are involved in the biuret reaction is supported. H. B.

Catalytic preparation of nitriles from esters in presence of Japanese acid clay. J. ABE (Bull. Waseda Appl. Chem. Soc., 1933, 21, 27—31).—Japanese acid clay is an effective dehydration catalyst for the prep. at 350—400° of MeCN and PhCN ; yield 85%. CH. ABS.

Decomposition of lead tetraethyl in ethylene and hydrogen in benzene. P. L. CRAMER (J. Amer. Chem. Soc., 1934, 56, 1234—1238).—Thermal decomp. of PbEt_4 in C_6H_6 in absence and presence of varying amounts of H_2 and C_2H_4 at 180—275° is studied. Reaction occurs in the liquid phase, the C_6H_6 acts as solvent only, H_2 takes little or no part, and C_2H_6 and a little C_4H_{10} are the paraffin hydrocarbons produced; CH_4 is not formed. Evidence is given favouring the assumption that the main reaction of Et radicals in solution is $2\text{Et} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$; the C_2H_4 is then converted into higher hydrocarbons (reaction being induced by Et). Large amounts of C_6H_4 are converted into light-coloured oils by the simultaneous decomp. of PbEt_4 ; these reactions are probably induced by Et. H. B.

Indium trimethyl. L. M. DENNIS, R. W. WORK, and E. G. ROCHOW [with E. M. CHAMOT] (J. Amer. Chem. Soc., 1934, 56, 1047—1049).—The prep. and properties of InMe_3 , m.p. 89—89.5°, are described. The mol. wt. in freezing C_6H_6 indicates $(\text{InMe}_3)_4$. E. S. H.

Constitution of β -carotene. R. KUHN and H. BROCKMANN (Ber., 1934, 67, [B], 885—888).—A complete scheme is given of the course of the fractional oxidation of β -carotene (I) and azafrin (II) with CrO_3 . (I) is thereby proved to be α -di-2:2:6-trimethyl- Δ^6 -cyclohexenyl- γ - η -tetramethyloctadecanonaene, the crucial point being the identity of the dehydroazafrinonamides,



derived from (I) or (II).

H. W.

Further instances of formation of chlorobenzene from magnesium phenyl bromide and chlorinated substances. R. J. W. LE FEVRE and P. J. MARKHAM (J.C.S., 1934, 703—705; cf. A.,

1932, 862).—PhCl is formed in 60% yield from MgPhBr (I) and EtOCl in Et₂O: MgPhBr + EtOCl → PhCl + OEt·MgBr. (I) and PhSO₂Cl give Ph₂SO₂ (in agreement with Hepworth and Clapham, J.C.S., 1921, 119, 1188; cf. Wedekind and Schenk, A., 1921, i, 664), a little PhSO₂H, and about 25% of PhCl (MgPhBr + PhSO₂Cl → PhCl + PhSO₂·MgBr). *p*-C₆H₄Me·SO₂Cl (II) and (I) afford slightly <25% of PhCl. (II) and MgEtBr give EtCl. PhCl is not produced from (I) and PhICl₂; some chlorination of the Et₂O occurs. H. B.

Halogenation. VIII. Bromination and iodination of monochlorotoluenes. P. S. VARMA and V. SAHAY (J. Indian Chem. Soc., 1934, 11, 293—294; cf. A., 1916, i, 469).—*o*- or *m*-C₆H₄MeCl with Br in AcOH containing HNO₃ or H₂SO₄ at 100° during 2—4 hr. affords 2-chloro-5-bromo- and a mixture (3:1) of 3-chloro-4-bromo- and 3-chloro-6-bromo-toluene. *p*-C₆H₄MeCl affords similarly *p*-C₆H₄Cl·CH₂Br. *o*-C₆H₄MeCl and I in AcOH containing NaNO₂ and oleum at 100° during 4 hr. afford 2-chloro-5-iodotoluene. *m*-C₆H₄MeCl affords similarly 3-chloro-6-iodotoluene. J. L. D.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. III. Benzyl Δ^α- and Δ^β-propenyl sulphones. E. ROTHSTEIN (J.C.S., 1934, 684—687).—CH₂Ph·SO₂Na (prep. of acid described) and allyl bromide in EtOH give benzyl Δ^β-propenyl sulphone (I), m.p. 64—65°, oxidised (O₃) to benzylsulphonylacetaldehyde (*p*-nitrophenylhydrazone, m.p. 195—196°); prolonged treatment with O₃ affords benzylsulphonylformaldehyde (*p*-nitrophenylhydrazone, m.p. 178—180°). Benzyl β-hydroxypropyl sulphone (II), m.p. 98—99°, prepared by oxidation (H₂O₂, AcOH) of the sulphide, b.p. 55—56°/11 mm. (from CH₂Ph·SNa and CH₂Cl·CHMe·OH), and PCl₅ in CHCl₃ give benzyl β-chloropropyl sulphone (III), m.p. 88°, converted by boiling C₆H₅N into benzyl Δ^α-propenyl sulphone (IV), m.p. 83·6° (ozonolysis product, BzOH). α,β-Dibenzylthiolpropane, b.p. 218—222°/14 mm. (from CH₂Ph·SNa and CH₂Br·CHMeBr in 80% EtOH), is oxidised (H₂O₂, AcOH) to the disulphone, m.p. 201°. Direct interconversion of (I) and (IV) could not be effected; treatment with NaOR (R—H or Alk) gives CH₂Ph·SO₂·CH₂·CHMe·OR in each case. (I) and (IV) with HI (*d* 1·9) afford benzyl β-iodopropyl sulphone, m.p. 105—107°, hydrolysed (aq. EtOH—NaOH) to (II). Benzyl β-methoxypropyl sulphone (V), b.p. 214°/14 mm. [from (III) and MeOH—KOH], is demethylated (HI—AcOH) to (II). (I), (II), (IV), and (V) are decomposed by boiling 3*N*-KOH to CH₂Ph·SO₂Me and MeCHO. Benzyl γ-hydroxypropyl sulphone (VI), m.p. 127°, prepared by oxidation (H₂O₂, AcOH) of the sulphide, b.p. 185°/19 mm. (from CH₂Ph·SNa and CH₂Cl·CH₂·CH₂·OH in EtOH), is stable to 3*N*-KOH; with KHSO₄ at 220°, di-(γ-benzylsulphonylpropyl) ether, m.p. 111—112°, is formed. Benzyl γ-chloropropyl sulphone, m.p. 96° [from (VI) and PCl₅ in CHCl₃], is converted by C₆H₅N or EtOH—KOH into (VI). Me Δ^β-propenyl sulphone, b.p. 130°/15 mm., from (MeSO₂)₂Mg and allyl bromide in Et₂O, is decomposed by 3*N*-KOH to MeCHO. H. B.

Reduction of phenylated olefines with alkali metals in liquid ammonia. C. B. WOOSTER and J. F. RYAN (J. Amer. Chem. Soc., 1934, 56, 1133—1136).—CHPh:CH₂ (I) and excess of Na in liquid NH₃ give PhEt and polymerised (I); CHPh:CHPh affords CH₂Ph·CH₂Ph (formed by ammonolysis of the intermediate CHNaPh·CHNaPh); CPh₂:CH₂ yields (mainly) CNaPh₂Me and CNaPh₂·CH₂·CH₂·CNaPh₂ [ammonolysis of the ·CNaPh₂ group does not occur (cf. A., 1932, 838)], which are converted by NH₄Cl into CHPh₂Me and CHPh₂·CH₂·CH₂·CHPh₂, respectively; CPh₂:CHPh furnishes CNaPh₂·CH₂Ph (cf. *loc. cit.*); CPh₂:CPh₂ (II) gives CNaPh₂·CNaPh₂ (III) and some CHNaPh₂ (or CNaPh₂?), since treatment with EtBr affords CHPh₂·CHPh₂ (IV) and CHPh₂Et whilst decomp. with NH₄Cl yields (IV) and CH₂Ph₂; CPh₂:CHMe furnishes CNaPh₂Et (cf. *loc. cit.*); CPh₂:CH·CHPh₂ gives CNaPh₂·CH₂·CHPh₂, hydrolysed (NH₄Cl) to CHPh₂·CH₂·CHPh₂ (V) and converted by Me₂SO₄, EtBr, and CH₂PhCl into αγγγ-tetraphenylbutane (VI), m.p. 118° [also prepared by reduction (Na, EtOH) of αγγγ-tetraphenyl-Δ^α-butene], αγγγ-tetraphenylpentane (VII), m.p. 128°, and (probably) αγγγδ-pentaphenylbutane (VIII), m.p. 122—123°, respectively; CPh₂:C:CPh₂ (IX) affords CNaPh₂·CH₂·CNaPh₂, hydrolysed (NH₄Cl) to (V). (III), obtained from (II) and 2 equivs. of Na in liquid NH₃, when treated with dry air, Me₂SO₄, or CH₂PhCl regenerates (II). Hydrolysis (H₂O) of the product from (IX) and 2 equivs. of Na gives CPh₂:CH·CHPh₂, indicating that addition of Na to (IX) occurs in stages. Treatment of the product from (IX) and excess of K with Me₂SO₄, EtBr, and CH₂PhCl affords (VI), (VII), and (VIII), respectively; a small amount of a second product (not identified) was formed in each case. H. B.

Conjugated systems. XV. Addition of hydrogen chloride to the geometrical isomerides of phenylbutadiene. I. E. MUSKAT and K. A. HUGGINS (J. Amer. Chem. Soc., 1934, 56, 1239—1241).—*trans*-α-Phenylbutadiene and HCl in cold Et₂O give *trans*-γ-chloro-α-phenyl-Δ^α-butene, b.p. 103°/5 mm. (A., 1931, 349) (ozonolysis product, PhCHO). *cis*-α-Phenylbutadiene (I) similarly affords the unstable *cis*-γ-chloro-α-phenyl-Δ^α-butene, b.p. 106°/5 mm. (ozonolysis products, PhCHO and CHClMe·CHO), converted by 10% NaOH at room temp. into (I), and by Ag₂O in H₂O into *cis*-styrylmethylcarbinol (*loc. cit.*). The above results are in accordance with the theory previously developed (A., 1930, 451). H. B.

Iodination in liquid ammonia. T. H. VAUGHN and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 1207—1209).—α-Iodo-β-2:4:6-trimethylphenyl-, m.p. 91·8—92·2°, -β-xylyl-, b.p. 121—122° (slight decomp.)/4 mm., -β-o-, m.p. 37·7—38°, -*m*-, m.p. 11·1°, and -*p*-, m.p. 84·7—85°, -chlorophenyl-, -β-*p*-bromophenyl-, m.p. 93·8—94°, and -β-α'-methylvinyl- (I), b.p. 80·8—81°/72 mm., -acetylenes are prepared from the appropriate CH:CR and I in liquid NH₃; they are unstable to light and heat. (I) polymerises in presence of O₂ to a black solid. α-Chloro-2:4:6-trimethylstyrene, b.p. 122—124°/25 mm. (from 2:4:6-C₆H₂Me·COMe and PCl₅), and NaNH₂ in mineral

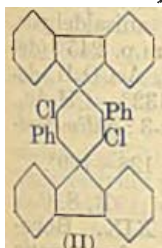
oil at 150° give 2:4:6-trimethylphenylacetylene, b.p. 100.6—101.5°/20 mm. (lit. 168—175°/20 mm.), m.p. 2.7—3.5° (*Hg* derivative, m.p. 238.5—239°). *α*-*Dichlorostyrene*, b.p. 115—116°/20 mm. (from *p*-C₆H₄Cl·COMe and PCl₅), and 25% EtOH-KOH afford *p*-chlorophenylacetylene, m.p. 45.5—46.1° (*Hg* derivative, m.p. 221.5—222°). Of the CH·CR so far examined, those where R is unsaturated and conjugated with C:C are readily and completely iodinated.

H. B.

Condensation reactions under pressure. II. Formation of diphenyl from benzene by heat under pressure in the presence of catalysts. J. P. WIBAUT, H. M. ROMIJN, and H. D. T. WILLINK (Rec. trav. chim., 1934, 53, 584—590; cf. A., 1931, 632).—The yield of Ph₂ from C₆H₆ is increased by pressure, being about 4—5% at 440—450°/170 atm. This is increased to 7.4% by a Ni catalyst, to 14—17% by 6% of I at 420—440°/125 atm., and to 9% by 10% of HI at 420°/120 atm.

R. S. C.

Attempted preparation of rubene derivatives from fluorene with production of a red compound not derived from rubene. Ring tension and probability of rubene formation. C. DUFRAISSE and A. P. DE CARVALHO (Compt. rend., 1934, 198, 1615—1617).—*Phenylethinylfluorene*, m.p. 83—83° (from CH·CPh and fluorenone), is readily isomerised to fluorenylideneacetophenone, but attempts to remove HCl from the corresponding chloride (I) give a red non-fluorescent substance, C₁₂H₁₀Cl₂, possibly (II), m.p. 290° (block), which has not the absorption spectrum of a rubene derivative



and with O₂ in light gives only very slowly a non-dissociable product. An intermediate product from (I) is a colourless substance, m.p. 120—121° (block) (containing 10.63% of Cl), which, when heated, gives (II), and a yellow Cl-free substance, m.p. 250° (block). Attachment of rings to the C₆ rings forming part of the rubene skeleton introduces such strain that the compound cannot be prepared.

R. S. C.

Synthesis of thiocarbamide derivatives. I. K. MURATA (J. pr. Chem., 1934, [ii], 140, 8).—CH₂Cl·CO₂Et reacts with cold CS(NHPh)₂ and MgMeI in Et₂O to give the *Et* ester, m.p. 176°, of *thiocarbamildiacetic acid*, CS(NPh·CH₂·CO₂H)₂, m.p. 144° (*Me* ester, m.p. 148°).

J. W. B.

Third hydrate of phenylmethylethylbetaine, and its conditions of formation. (MME.) GUAINET-PILAUD (Compt. rend., 1934, 198, 1520—1522).—MeI and NPhEt·CH₂·CO₂Et (I) (prepared from CH₂Cl·CO₂Et and NPhEt at 150°) afford a product which with Ag₂O gives a mixture of phenylmethylethylbetaine dihydrate, m.p. 79.5°, and a *monohydrate* (II), m.p. 103° (*picrate*, m.p. 186°; *chloroplatinate*, m.p. 168°), isomeric with the monohydrate of m.p. 175° (cf. A., 1933, 948). If (I) is prepared from CH₂I·CO₂Et and NPhMeEt followed by decomp. with Ag₂O, (II) only is obtained.

J. L. D.

Reactions of aromatic amine-oxides and of phenylhydroxylamine. E. HOPE (Chem. and Ind.,

1934, 425).—Formation of *o*- and *p*-NMe₂·C₆H₄·SO₃H and -NMe₂·C₆H₄·NO₂ from NPhMe₂ oxide and SO₃ and NO₂ and of *p*-OH·C₆H₄·NH₂, *p*-OEt·C₆H₄·NH₂, and *p*-C₆H₄Cl·NH₂ from NPh·OH is explained by anionoid addition to the cations ⁺NPhMe₂·OH and ⁺NH₂Ph·OH, respectively.

S. C.

Derivatives of salicylic acid. V. Synthesis and constitution of 2-nitrotoluene-6-sulphonic acid. A step towards the synthesis of 6-sulphosalicylic acid. N. W. HIRWE and M. R. JAMBHEKAR (J. Indian Chem. Soc., 1934, 11, 239—242; cf. A., 1933, 607).—4-Nitrotoluene-2-sulphonic acid in H₂SO₄ and HNO₃ (*d* 1.51) at 100° during 3 hr. affords 2:4-dinitrotoluene-6-sulphonic acid (I), m.p. 120° [Pb, K(+2H₂O), Na, Ca (+4H₂O), and Ba (+4H₂O) salts], which with PCl₅ affords the *sulphonyl chloride*, m.p. 107°, which does not give the *sulphonamide* with NH₃. (I) with boiling EtOH-(NH₄)₂S during 2 hr. affords 2-nitro-*p*-toluidine-6-sulphonic acid (II), m.p. 270° (decomp.) [K salt, which with PCl₅ gives the *sulphonyl chloride*, m.p. > 260° (decomp.), converted by NH₃ into the *sulphonamide*, m.p. 230°], also obtained from 2-nitro-*p*-toluidine with oleum at 100° during 6 hr. The diazonium derivative of (II) with boiling EtOH during 3 hr. affords 2-nitrotoluene-6-sulphonic acid [+2H₂O, m.p. 127°; Ba salt (+8H₂O); *sulphonamide*, m.p. 165°]. 2:4-Dinitrotoluene cannot be sulphonated.

J. L. D.

New case of molecular asymmetry. A. SEMENTZOV (Ukrain. Chem. J., 1933, 8, 193—195).—*o*-Toluidine-3:5-disulphonic acid (I) yields insol. salts with strychnine and brucine; the acid regenerated from the former, but not the latter, salt has α +0.35°, pointing to the partial resolution of (I). This result supports the octahedral or prismatic structure of the C₆H₄ mol.

R. T.

Hexahydrodiphenylamine and its derivatives. H. T. BUCHERER and H. FISCHBECK (J. pr. Chem., 1934, [ii], 140, 69—89).—Condensation of cyclohexyl bromide (I) with the appropriate NH₂Ar and subsequent treatment with NaCl or alkali followed by HCl affords the *hydrochlorides* of cyclohexyl-aniline, -*p*-, m.p. 205°, and -*o*-toluidine, m.p. 126°, -α-, m.p. 187°, and -β-naphthylamine, m.p. 261°, and -*p*-phenylenediamine, m.p. 267° [4-*Ac* derivative, m.p. 311°, of the free base from (I) and NH₂·C₆H₄·NHAc]. Condensation is not effected in the presence of NaOH alone, but with NaOH-Cu powder the hydrobromide is obtained. Primary bases (NH₂Ph) may be separated from *sec.* (NHPHMe; 99% recovery) by their interaction with OH·CH₂·SO₃Na at 80—100°. In C₆H₆ solution cyclohexanone (II), KCN, and NH₂Ph·HCl (or NH₂Ph with passage of dry HCl) afford the nitrile (III), m.p. 73°, of 1-anilinocyclohexane-1-carboxylic acid, m.p. 158° (*amide*, m.p. 148°), *o*-NH₂·C₆H₄·CO₂H similarly giving *o*-1-cyanocyclohexylaminobenzoic acid (IV), m.p. 168° (1-carboxylamido-compound, m.p. 218°). Alternatively the cyanohydrin (V) of (II) (from the NaHSO₃ compound and KCN) is condensed with NH₂Ph (but not with NHPHMe; hence separation of primary and *sec.* bases) to give (III), and with the appropriate arylamine to give the *nitrile* of 1-*o*-, m.p. 76° (*amide*, m.p.

224°), and 1-*p*-toluidino-, m.p. 79°, 1-*p*-aminoanilino-, m.p. 200° (p-*N*-Ac derivative, m.p. 143°; *amide*, m.p. 263°), 1-*m*-aminotoluidino-, m.p. 130°, 1- α -, m.p. 135° (*amide*, m.p. 143°), and 1- β -naphthylamino-, m.p. 122°, -*cyclohexane*-1-carboxylic acid, and (IV). With 2 mols. of the appropriate diamine at 34–40° are obtained NN'-*dicyclohexyl-p*-phenylenediamine-1:1'-*dicarboxylamide*, m.p. 280°, through the *nitrile*, m.p. 169°, and corresponding derivatives from *m*-phenylenediamine, m.p. 207° and 116°. With (NH₄)₂CO₃ (V) gives a *substance*, m.p. 215°, hydrolysed by 50% H₂SO₄ to give the sulphate of the NH₂-acid.

J. W. B.

Nuclear alkylation of aromatic bases. II. Action of methyl alcohol on the hydrochlorides of 2- and 4-aminodiphenyl. D. H. HEY and E. R. B. JACKSON (J.C.S., 1934, 645–649; cf. A., 1931, 950).—4-Aminodiphenyl hydrochloride (1 mol.) and MeOH (1.5 mols.) at 250–300° for 12 hr. (all experiments are carried out in an electrically-heated Monel metal autoclave) give unchanged material and some didiphenylamine, m.p. 205°; carbonisation also occurs. With 3 mols. of MeOH, 4-amino-3:5-dimethyl- and 4-amino-3:5:4'-trimethyl- (I) -diphenyls are formed; 4-amino-3-methyldiphenyl (which must be an intermediate) could not be detected. A small amount of (I) is obtained using 6 mols. of MeOH; the major portion of the product consists of *sec.*- and *tert.*-bases. 2-Aminodiphenyl hydrochloride and 3 mols. of MeOH similarly give mainly *tert.* (A), some *sec.*-, and practically no primary base. (A) and MeI afford the *methiodide*, m.p. 293–295° (decomp.), of a dimethylphenanthridine [*picrate*, m.p. 241° (decomp.)]. In all the above experiments some separation of N from the nucleus occurs, since volatile bases are liberated when the reaction product is treated with alkali; evidence of phenol formation (cf. *loc. cit.*) was not obtained.

cyclohexanone and Mg *m*-5-xylyl bromide (II) give 1-*m*-5-xylylcyclohexanol, b.p. 150–160°/20 mm., dehydrated (HCO₂H; Sherwood *al.*, A., 1932, 843) to 1-*m*-5-xylyl- Δ^1 -cyclohexene, b.p. 157–158°/20 mm., which is dehydrogenated (S in quinoline at 250°) to 3:5-dimethyldiphenyl, b.p. 273–276°. Successive treatment of this with HNO₃ (*d* 1.42) in AcOH, SnCl₂-conc. HCl, and Ac₂O gives 4-acetamido-3:5-dimethyldiphenyl, m.p. 200–201°, oxidised (CrO₃, AcOH) to BzOH. 4-Methylcyclohexanone (III) and (II) afford 1-*m*-5-xylyl-4-methylcyclohexanol, b.p. 154–164°/20 mm.; the *cyclohexene* is dehydrogenated (S) to 3:5:4'-trimethyldiphenyl, m.p. 44–45° (4-NO₂-derivative, m.p. 94–95°); 4-Acetamido-3:5:4'-trimethyldiphenyl, m.p. 241–242°, is oxidised by CrO₃-AcOH to *p*-C₆H₄(CO₂H)₂ and by neutral KMnO₄ to 4-acetamidodiphenyl-3:5:4'-tricarboxylic acid (*Et* ester, m.p. 129–130°). 3:4'-Dimethyldiphenyl is similarly prepared from 1-*m*-tolyl-4-methylcyclohexanol, b.p. 155–165°/20 mm. [from (III) and *m*-C₆H₄Me-MgBr]. 2-Aminodiphenyl is methylated (Me₂SO₄ at 150°) to 2-dimethylaminodiphenyl (IV) [*methiodide*, m.p. 228° (decomp.)]; with MeI and aq. Na₂CO₃, (IV) and some 2-methylaminodiphenyl are produced. The *methiodide*, m.p. 260° (decomp.) (lit. 247°), of 9-methylphenanthridine (Morgan and Walls, A., 1931, 1308) [*picrate*, m.p. 248° (decomp.)

(lit. 233°)] is prepared for comparison with that from (A).

H. B.

Relative reaction velocities of amines with phenylcarbimide.—See this vol., 604.

Dimethyldihydroresorcinol. III. Azo-dyes and diazo-oxy-compounds. B. H. IYER and G. C. CHAKRAVARTI (J. Indian Inst. Sci., 1934, 17, A, 41–47).—Dimethyldihydroresorcinol with PhN₂Cl in the presence of acid gives *benzeneazodimethyldihydroresorcinol*, m.p. 142° (*diphenylhydrazone*, m.p. 191–192°). The following are similarly obtained: *o*-, m.p. 125°, *m*-, m.p. 122–123°, and *p*-toluene-, m.p. 156–157° (*diphenylhydrazone*, m.p. 185°), α -, m.p. 141°, and β -*naphthalene*-, m.p. 200°, and *p*-sulpho-benzene-azodimethyldihydroresorcinol, decomp. 360° (shrinks 300°). In an alkaline medium alkali-insol. substances are obtained, which are considered to be diazo-oxy-derivatives. Those from diazotised NH₂Ph and *o*-, *m*-, and *p*-C₆H₄Me·NH₂ have the same m.p. as the true azo-compounds, into which they are converted by heat and by alkali. Those from α - and β -C₁₀H₇·NH₂ are less readily converted, and have m.p. 200° (decomp.) and 255° (decomp.), respectively.

A. A. L.

Derivatives of *p*-dihydrazinobenzene. H. A. J. SCHOUTISSEN (Rec. trav. chim., 1934, [iv], 53, 561–566).—*p*-C₆H₄(NH·NH₂)₂·2HCl and NaNO₂ in conc. HCl at 0° give *p*-bistriazobenzene (*p*-phenylenediazide), m.p. 83°, and with NaOAc in aq. EtOH it forms *dihydrazones* with the following CO-compounds: PhCHO, m.p. 251° (decomp. from 225°), *o*-OH·C₆H₄·CHO, m.p. about 255° (decomp. from 200°), vanillin, m.p. 230° (decomp.), anisaldehyde, m.p. 225–230° (decomp.), piperonal, m.p. 245° (decomp.), C₆H₅CO·CH₃, m.p. 214° (decomp.), AcCO₂H, decomp. 174°, and CH₃Ac·CO₂Et, m.p. 132°. CH₃Ac, however, gives *p*-phenylene-1:1'-bis-3:5-dimethylpyrazole, *p*-C₆H₄(N< $\begin{smallmatrix} \text{NMe} & \text{CMe} \\ \text{CO} & \text{CH} \end{smallmatrix}$)₂, m.p. 128–129°.

R. S. C.

Aromatic fluorine compounds. XIX. Borofluoride process for the preparation of aromatic fluorine compounds. G. SCHIEMANN and (in part) R. PILLARSKY, W. WINKELMULLER, T. B. MAU, and H. G. BAUMGARTEN (J. pr. Chem., 1934, [ii], 140, 97–116).—A full bibliography and discussion of the technique of the prep. of aromatic F-derivatives by the decomp. of the diazonium borofluoride. The (improved) prep. of the following is described (yields in parentheses): *o*- (44) and *m*-C₆H₄F₂ (68), 1:2:4-C₆H₃F₃ from 2:4- (17) or 2:5- (55) (*Bz* derivative, m.p. 115°) -C₆H₃F₂·NH₂, PhCl (65) from the *stannichloride*, decomp. 110°, of PhN₂C₆H₄·OH (82) from its Me ether, and *o*-C₆H₄F·CO₂H (45) from *o*-carbethoxybenzenediazonium borofluoride, decomp. 105–106°. Free OH and CO groups are unfavourable to the reaction and should be protected.

J. ...

Coupling of α -amino-acids with diazonium salts. M. BUSCH, N. PATRASCANU, and W. WEB (J. pr. Chem., 1934, [ii], 140, 117—NH₂·CH₂·CO₂H (I) couples with PhN₂Cl (II) in *N*-NaOH at 0° to give (45–48% yield) *di*(benzene-diazo)aminoacetic acid (III), decomp. 124°, decomp.

posing in HCl-EtOH to give PhN_2NHPh (IV), MeCl , CO_2 , and N_2 . With NH_2Me (II) gives $(\text{PhN}_2)_2\text{NMe}$, similarly decomposed to (IV). The product from (I) and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ (V) decomposes more readily, to a mixture of *di*-(*p*-nitrobenzene-diazo)aminoacetic acid, decomp. $166\text{--}167^\circ$ (26%), and $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (VI) (20%). In absence of the NaOH the clear solution obtained slowly decomposes with increasing formation of (VI). The Et ester of (I) with (II) affords (III) (due to hydrolysis) and a substance, $\text{C}_8\text{H}_7\text{ON}_3$, m.p. 134° (decomp.), probably $\text{CO} \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} \text{N}\cdot\text{N}_2\text{Ph}$ or $\text{CO} \begin{smallmatrix} \text{NPh}\cdot\text{N} \\ \text{CH}_2 \end{smallmatrix}$, but with (V) in presence of NaOAc is obtained *Et p*-nitrobenzene-diazoaminoacetate, m.p. 99° (63% yield), hydrolysed by aq. NH_3 to the corresponding acid, m.p. 163° . With (V) alanine gives (VI) and an unidentified substance, m.p. 117° ; sarcosine affords its *p*-nitrobenzenediazo-derivative, m.p. $107\text{--}108^\circ$ (45% yield), and tyrosine gives 3:5-*di*-*p*-nitrobenzeneazotyrosine (ring coupling), m.p. 175° . J. W. B.

Reactivity of resorcinol monoalkyl ethers towards diazonium compounds. H. H. HODGSON, R. J. H. DYSON, and (in part) H. CLAY (J.C.S., 1934, 629—631).—4-Benzeneazoresorcinol 3-Me (I), m.p. $137\text{--}138^\circ$, 3-Et (II), m.p. 145° , 3-Pr^a (III), m.p. 117° , and 3-Pr^b (IV), m.p. 92° , ethers are prepared by slow addition of a cold solution of PhN_2Cl (1 mol.) [freed from HNO_3 by $\text{CO}(\text{NH}_2)_2$ and HCl by NaOAc] to a well-stirred solution of $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OR}$ (1 mol.) in EtOH+aq. NaOAc. With 2 mols. of PhN_2Cl , 4:6-bisbenzeneazoresorcinol 3-Me ether (V), m.p. 190° [not the 2:4-derivative as stated by Orndorff and Thebaud (A., 1901, i, 774)] [also prepared from (I)], and 3-Et ether (VI), m.p. 147° , are obtained; disubstituted derivatives do not accompany (III) and (IV), and coupling does not occur with $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{OBu}^a$. Repression of ionisation by Oalk progressively deactivates C_4 as the series is ascended. (V) and (VI) with HNO_3 (*d* 1.42) at $30\text{--}40^\circ$ give the 2- NO_2 -derivatives, m.p. 228° and 225° , respectively. 6-Nitro-2:4-bisbenzeneazoresorcinol 3-Me, m.p. 142° , and 3-Et, m.p. 126° , ethers are prepared from 6-nitroresorcinol 3-alkyl ether (1 mol.) and PhN_2Cl (2 mols.). (I)–(IV) are de-alkylated to 4-benzeneazoresorcinol. (I) and (II) are reduced to 4-aminoresorcinol 3-Me and 3-Et ether, respectively, whilst (III) and (IV) are readily methylated (CH_3N_2 ; Me_2SO_4 -alkali) thus indicating coupling in the *p*-position to the OH (cf. Orndorff and Thebaud, *loc. cit.*). A mixture of (I) and (V) is always produced if alkali hydroxide is present in the coupling medium. 4-*N*-Nitrobenzeneazoresorcinol 3-Me, m.p. 189° , 3-Et, m.p. 167° , 3-Pr^a, m.p. 133° , 3-Pr^b, m.p. 115° , and 3-Bu^a, m.p. 88° ; 4-*m*-nitrobenzeneazoresorcinol 3-Me, m.p. 153° , 3-Et, m.p. 125° , 3-Pr^a, m.p. 114° , 3-Pr^b, m.p. 95° , and 3-Bu^a, m.p. 125° , and 4-*p*-nitrobenzeneazoresorcinol 3-Me, m.p. $198\text{--}199^\circ$, 3-Et, m.p. $185\text{--}187^\circ$, 3-Pr^a, m.p. $156\text{--}157^\circ$, m.p. $145\text{--}146^\circ$, and 3-Bu^a, m.p. $149\text{--}150^\circ$, ethers are described; the decrease in m.p. as the series is ascended is attributed to a form of coordination which increases in intensity with the size of the alkyl group. 4-*p*-Chlorobenzeneazoresorcinol 3-Me, m.p. 142° , and 3-Et, m.p. 133° , and 4-*p*-sulpho-

benzeneazoresorcinol 3-Pr^a, decomp. when heated, and 3-Pr^b ethers are also described. H. B.

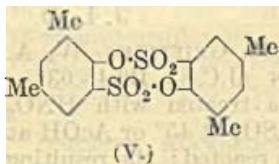
Additive compound of phenol and hexamethylenetetramine. L. H. SMITH and K. N. WELCH (J.C.S., 1934, 729—730).—Interaction of CH_3O , NH_3 , and PhOH affords $\text{C}_6\text{H}_{12}\text{N}_4\cdot 3\text{C}_6\text{H}_5\text{O}$ (I) (cf. A., 1893, i, 298) together with a compound, $\text{C}_6\text{H}_{12}\text{N}_4\cdot\text{C}_6\text{H}_5\text{O}$, m.p. $176\text{--}176.5^\circ$ (decomp.), which with excess of PhOH gives (I). J. L. D.

Nitration of anisole. P. H. GRIFFITHS, W. A. WALKEY, and H. B. WATSON (J.C.S., 1934, 631—633).— PhOMe (I) (1 mol.) is treated with HNO_3 (*d* 1.42) (1 mol.) alone or in H_2SO_4 at 45° or AcOH at 65° until about 70% of (I) has reacted; the resulting mixture (yield 30%) of $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ contains *o*- (30.8—45%), *m*- (1.3—1.7%), and *p*- (53.5—67.5%). With HNO_3 (*d* 1.42 and 1.5) in Ac_2O at 10° , the mixture (99% yield) contains *o*- (69.4—71.5%), *m*- (2.2—2.3%), and *p*- (26.3—28.4%); benzoyl nitrate (from BzCl and AgNO_3) in CCl_4 at 0° gives *o*- (63.5%), *m*- (1.9%), and *p*- (34.6%). Contrary to Francis (A., 1907, i, 53), the use of acyl nitrate does not lead to exclusive *o*-nitration. The results provide some confirmation of Arnall's work (A., 1924, i, 636) on the nitration of PhOH . The composition of the above mixtures [shown to be free from (I) or $(\text{NO}_2)_2$ -derivative] is determined by thermal analysis. H. B.

Condensation of *o*-anisidine with formaldehyde and benzaldehyde. E. BUREŠ and Z. SCHLESINGER (Časopis ceskoslov. Lek., 1933, 13, 165—175; Chem. Zontr., 1933, ii, 2663).—Condensation of *o*-anisidine (I) with CH_2O yields *N*-methylene-*o*-anisidine (II), m.p. 85° , and *NN'*-methylenedi-*o*-anisidine, m.p. 155° . (II) with NaHSO_3 gives *Na o*-anisylaminomethanesulphonate, decomp. 200° ; with HgCl_2 , the compound $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2\cdot\text{HgCl}_2$, decomp. $150\text{--}160^\circ$; and a picrate, decomp. 160° . The NO-compound of (II) with $\beta\text{-C}_{10}\text{H}_7\cdot\text{ONa}$ forms *o*-di(hydroxynaphthyl)amino-*N*-methylene-*o*-anisidine. The corresponding *N*-benzylidene derivative forms red crystals. (I) with PhCHO yields benzylidene-*o*-anisidine, m.p. $56\text{--}57^\circ$ (NaHSO_3 compound, decomp. 200° ; HgCl_2 compound, decomp. 120° ; picrate, decomp. $140\text{--}150^\circ$). These condensation products are very labile. H. J. E.

***m*-Xylenols.** G. LER (Anilinokras. Prom., 1934, 4, 77—84).—*m*-5-Xylenol (I) and SO_2Cl_2 afford 5-hydroxy-*m*-xylene-2:4-disulphonyl chloride (II), m.p. $117\text{--}119^\circ$, and an isomeride (III), m.p. $89\text{--}91^\circ$; these yield the corresponding sulphonamides, m.p. $205\text{--}207^\circ$ and $160\text{--}161^\circ$, respectively. With NH_3 in Et_2O (II) affords the disulphonamide, m.p. $206\text{--}208^\circ$, whilst (III) yields unstable products. (II) when heated with NaOAc in COMe_2 affords 1:3-dimethyl-2:5-sulphobenzoquinone-4-sulphonyl chloride, m.p. $>300^\circ$; under similar conditions (III) yields only oily products. The conc. HCl solution of the product of reaction of (I) and ClSO_3H acid yields with H_2O_2 at 0° the 2:4:6- Cl_3 -derivative of (I), m.p. $175\text{--}177^\circ$, which is also obtained, together with *K* 2:6-dichloro-*o*-hydroxy-*m*-xylene-4-sulphonate, m.p. $>300^\circ$, by adding H_2O_2 to the acidified products of alkaline hydrolysis of (II). Reduction of (II) with Zn and AcOH yields 5-hydroxy-2:4-dithiol-*m*-xylene,

m.p. 75° (*Bz*₃, m.p. 160—161°, and *Ac*₃ derivative, m.p. 124—125°; *dipicrate*, m.p. 237—238°), which when heated at 100° during 3—4 hr. with aq. CH2Cl.CO2Na and KOH affords the corresponding 2:4-dithioglycollic acid derivative, m.p. 151°. 4-Hydroxy-*m*-xylene-5-sulphonyl chloride (IV) [5-sulphonanilide, m.p. 142—143° (*N-Me*, m.p. 111—112°, and 4-*Ac* derivative, m.p. 105°); 4-*Ac* derivative, m.p. 62°] affords the sulphonyl chloride (V), m.p. > 300°, when heated with 2*N*-KOH, with NaOAc in COMe2, or on passing NH3 into its Et2O solution. With Zn and AcOH (IV) affords 4-hydroxy-5-thiol-*m*-xylene (VI), m.p. 91—93° (*Bz*₃ derivative, m.p. 72°; *monopicrate*, m.p. 164°), which when heated with KOH and CH2Cl.CO2H yields *m*-xylene-4-glycollic-5-thioglycollic acid, m.p. 155°. *m*-4-Xylenol and diazotised *m*-NH2.C6H4.NO2 (VII) afford 5-*m*-nitrobenzeneazo-4-hydroxy-*m*-xylene, m.p. 194—195°; (IV) and (VI) do not react with (VII).



R. T.

Oxidation of *p*-*n*-propylphenol to 2-*n*-propylquinol. G. BADDELEY and J. KENNER (J.C.S., 1934, 633—634).—*m*-C6H4.Pr.OH and dil. HNO3 in C6H6 give (after removal of *o*-nitrophenols in steam) 4-nitro-3-*n*-propylphenol (I), b.p. 157°/0.6 mm., m.p. 58°; using Schultz's conditions (A., 1907, i, 1030), a dinitro-*m*-propylphenol, b.p. 145°/0.5 mm., m.p. 125°, results. (I) is reduced (Sn, HCl) to the NH2-compound (*Ac* derivative, m.p. 140°), oxidised (aq. FeCl3) to *n*-propyl-*p*-benzoquinone, which is reduced (H2SO3) to *n*-propylquinol (II), m.p. 90°. (II) is also formed when *p*-C6H4.Pr.OH is oxidised with Caro's acid at 70—80°; this reaction is an expanded form of the conversion of glycolaldehydes into α-hydroxyketones (Danilov and Danilova, A., 1928, 64; 1929, 1448; 1931, 90; 1933, 1277): $\text{OH}\cdot\text{CR}_2\cdot\text{CHO} + \text{H}^+ \rightarrow \text{OH}\cdot\text{CR}_2\cdot\text{CH}^+\cdot\text{OH} \rightarrow \text{COR}\cdot\text{CHR}\cdot\text{OH} + \text{H}^+$. The analogous isomerisation of CR3.CHO is: $\text{CR}_3\cdot\text{CHO} + \text{H}^+ \rightarrow \text{CR}_3\cdot\text{CH}^+\cdot\text{OH} \rightarrow \text{CR}_2\cdot\text{CHR}\cdot\text{OH} \rightarrow \text{CHR}_2\cdot\text{COR} + \text{H}^+$. H. B.

Synthesis of halogenated thiophenols. R. C. DOSSER and G. H. RICHTER (J. Amer. Chem. Soc., 1934, 56, 1132—1133).—2-Chlorotoluene-5-sulphonyl chloride, m.p. 64°, is reduced (Zn and HCl in C6H6) to 6-chloro-*m*-thiocresol, b.p. 122—123°/26 mm. (*Hg* salt, m.p. 193—194°; corresponding disulphide, m.p. 65°). 2-Chloro-*m*-xylene-5-sulphonyl chloride, m.p. 121° (sulphonamide, m.p. 205°), similarly gives 4-chloro-3:5-dimethylthiophenol, b.p. 141—142°/29 mm. [*Hg* salt, m.p. 240—245° (decomp.); disulphide, m.p. 124—125°], whilst 2-chloro-*p*-xylene-5-sulphonyl chloride, m.p. 49—49.5° (sulphonamide, m.p. 189—190°), affords 4-chloro-2:5-dimethylthiophenol, m.p. 92.5° (disulphide, m.p. 103°). 2-Chloro-1-thiol-, m.p. 66.5° (disulphide, m.p. 134°), and 4-chloro-1-thiol-naphthalene, m.p. 51° (disulphide, m.p. 124—125°), are similarly prepared. H. B.

Organic sulphides. C. LEFEVRE and C. DESGREZ (Compt. rend., 1934, 198, 1432—1434).—The action of S at 140—200° on aliphatic acids is variable, but

aromatic amines and phenols are readily attacked, especially in presence of glycerol and a metallic carbonate, forming compounds of type [C6H4(NH2).S]2 and [C6H4(ONa).S]2. Di- and poly-phenols are still more readily attacked. At higher temp. monosulphides are formed. E. W. W.

Synthesis of compounds related to the sterols, bile acids, and œstrus-producing hormones. III. 7-Methoxy-1:2-cyclopentenophenanthrene, a dehydrogenation product of œstrin and equilenin. A. COHEN, J. W. COOK, C. L. HEWETT, and A. GIRARD (J.C.S., 1934, 653—658).—Interaction of equilenin (I) with *p*-C6H4.Me.SO3Me (II) in 10% KOH during 2.5 hr. at 100° affords the *Me* ether, m.p. 195.5—197.5°, the semicarbazone of which with NaOEt—EtOH at 180° during 20 hr. affords a demethylated product (a gum) which gives a *Me* ether (III), m.p. 121—122° (*picrate*, m.p. 128—129°). (III) is dehydrogenated by Se at 300—320° during 8 hr. to 7-methoxy-1:2-cyclopentenophenanthrene (IV), identical with the product prepared from œstrone (cf. this vol., 404), which suggests that dehydrogenation is accompanied by the loss of a quaternary Me. The diazonium derivative of α-naphthylamine-6-sulphonate with CuBr2 in HBr (*d* 1.4) at 75—80° during 0.5 hr. affords Na 1-bromo-naphthalene-6-sulphonate, in which attempts to replace SO3H also attacked Br. 5-Nitro-β-naphthylamine (A., 1892, 1232) is converted into 5-nitro-β-naphthol (A., 1923, i, 550), which with (II) in 10% KOH at 100° during 3 hr. affords 1-nitro-6-methoxynaphthalene, m.p. 74.5—75.5°, reduced (cf. A., 1925, i, 535) to 6-methoxy-α-naphthylamine (V), b.p. 190°/13—14 mm. (*Bz* derivative, m.p. 184—185°). (V) by the Sandmeyer or Gattermann reactions gives only very small (4%) yields of 1-bromo-6-methoxynaphthalene (*picrate*, m.p. 105—106°), but the 1-*I*-compound (VI), m.p. 33—33.5° (*picrate*, m.p. 98—99°), is formed in 45% yield. The Grignard derivative of (VI) with (CH2)2O affords β-6-methoxy-1-naphthylethyl alcohol, b.p. 120—130°/0.2 mm. (3:5-dinitrobenzoate, m.p. 177.5—178°), converted by SOCl2 into the chloride (VII), b.p. 160—165°/0.2 mm. (*picrate*, m.p. 74—76°). The Mg derivative of (VII) with 2-methylcyclopentanone in dry Et2O at room temp. during 1 hr. affords αδ-di-(6-methoxy-1-naphthyl)butane, m.p. 150—150.5°, and a carbinol, b.p. 185—190°/0.15 mm., converted by KHSO4 at 160—165° during 1 hr. into 1-(β-6'-methoxy-1'-naphthylethyl)-2-methyl-Δ¹-cyclopentene, b.p. about 157°/0.15 mm. (*picrate*, m.p. 90—91°), which with AlCl3 in CS2 at 0° during 7 hr. affords 7-methoxy-1-methyl-1:2:3:4-tetrahydro-1-cyclopentenophenanthrene (VIII), a gum (*picrate*, m.p. 89.5—90°; *s*-C6H3(NO2)3 compound, m.p. 110—110.5°), free from unwanted spirans (cf. A., 1042; this vol., 519). (VIII) with Se at 300—320° during 21.5 hr. affords 7-methoxy-1:2-cyclopentenophenanthrene, m.p. 136—137° (*picrate*, m.p. 137.5°; *s*-C6H3(NO2)3 compound, m.p. 161—161.5°), identical with specimens obtained from œstrone and (I), but different from 1:2-cyclopentenophenanthrene. The ring system of œstrin and (I) is therefore same as that of the sterols and bile acids, and OH is attached to the same position as the OH of cholesterol.

Ring I of œstrone and œstriol must be aromatic (cf. A., 1933, 605).

J. L. D.

Structure of œstrin. R. D. HAWORTH and G. SHELDRIK (Chem. and Ind., 1934, 431).—Synthetic 7-hydroxy-1:2-dimethylphenanthrene, m.p. 191—192° (OMe, m.p. 154°, OBz, m.p. 211°, derivatives), is identical with the dimethylphenanthrol obtained by the degradation of œstriol.

S. C.

Derivatives of *p*-xylorcinol (β -orcinol). F. HENRICH, M. DANNEHL, H. HAERTLEIN, and W. HOFFMANN (J. pr. Chem., 1934, [ii], 140, 1—7).—With NaOH-EtOH and $C_6H_{11}ONO$, 2:6-dihydroxy-*p*-xylene (β -orcinol) gives the *K* salt of its 3-*NO*-derivative (red and yellow forms), darkens 151°, m.p. 158°, which is obtained by acidification and is reduced by $SnCl_2-HCl$ to the 3- NH_2 -compound, decomp. 198° (oxidised in air, but no definite products isolated), the hydrochloride of which with Ac_2O affords the *O*-*Ac* derivative, b.p. 275—280°, m.p. 101°, of 6-hydroxy-2:4:7-trimethylbenzoxazole, m.p. 175—176°, obtained by KOH-MeOH hydrolysis. With $BzCl$ is similarly obtained 6-hydroxy-2-phenyl-4:7-dimethylbenzoxazole, sinters 185°, m.p. 187—188° (6-*Bz* derivative, b.p. 260°/15 mm., m.p. 142—143°).

J. W. B.

isoChavibetol. III. Oxidation of isochavibetol ethyl ether with potassium dichromate and hydrogen peroxide. M. IMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 117—118b).—*isoChavibetol* Et ether (I) with $K_2Cr_2O_7$ in dil. H_2SO_4 during 45 min. at 51—53° affords *isovanillin* Et ether, also formed from (I) with 3% H_2O_2 in $H_2O-FeSO_4$ during 15 min. at 51—53°.

J. L. D.

Substitution in 2-methoxy-nitrodiphenyl ethers. S. BUCHAN and H. A. SCARBOROUGH (J.C.S., 1934, 705—708).—4'-Nitro-2-methoxydiphenyl ether (I) with HBr (*d* 1.4) in boiling AcOH during 6 hr. affords the 2-*OH*-compound, m.p. 109°, and with $SnCl_2-HCl$ it gives 4'-amino-2-methoxydiphenyl ether, m.p. 97° [*Ac* derivative (II), m.p. 118°, nitrated at 15° to 3'-nitro-4'-acetamido-2-methoxydiphenyl ether (III), m.p. 124°, converted into the NH_2 -compound (IV), m.p. 98°]. Deamination of (IV), or interaction of $m-C_6H_4I-NO_2$ with guaiacol (*K* salt) and Cu powder at 250° during 12 hr. gives 3'-nitro-2-methoxydiphenyl ether (V), m.p. 86°. (II) or (III) in HNO_3 (*d* 1.5) at 80° during 0.5 hr. affords 3':5-dinitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 181° [NH_2 -compound (VI), m.p. 163°]. Interaction of $m-C_6H_4I-NO_2$ with 5-nitroguaiacol (*K* salt) at 220°, the deamination of (VI), or (V) with HNO_3 during 2 hr., affords 3':5-dinitro-2-methoxydiphenyl ether, m.p. 123°; similarly prepared, 4':5-dinitro-2-methoxydiphenyl ether has m.p. 121° (*OH*-compound, m.p. 157°) and does not give a 4-substituted Br-compound. Interaction of $p-C_6H_4Cl-NO_2$ with 4-chloroguaiacol (*K* salt) at 220°, during 5 hr. affords 4-chloro-4'-nitro-2-methoxydiphenyl ether (VII), m.p. 104°, demethylated to the *OH*-compound, m.p. 121°. Similarly prepared, 4-bromo-4'-nitro-2-methoxydiphenyl ether (VIII) has m.p. 107°. Chlorination of (I) in AcOH, or interaction of (I) with SO_2Cl_2 at room temp., affords 5-chloro-4'-nitro-2-methoxydiphenyl ether (IX), m.p. 94° (which affords a

and hence has no 4-substituent), demethylated to the *OH*-compound, m.p. 94°, and reduced to 5-chloro-4'-amino-2-methoxydiphenyl ether, m.p. 90° [*Ac* derivative (X), m.p. 192°]. Similarly prepared Br-derivatives are: 5-bromo-4'-nitro-2-methoxydiphenyl ether (XI), m.p. 96°; *OH*-compound, m.p. 89°; 4'- NH_2 - and $NHAc$ -compounds (XII), m.p. 105° and 195°, respectively. Nitration of (X) in AcOH at 90° during 0.5 hr. affords 5-chloro-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 163° [base, m.p. 105°, deaminated to 5-chloro-3'-nitro-2-methoxydiphenyl ether (XIII), m.p. 85°, also formed from (V) with SO_2Cl_2 in Et_2O at 0°]. (I), (VII), or (IX) with Cl_2 in AcOH at room temp., or with excess of SO_2Cl_2 , or by interaction of $p-C_6H_4Cl-NO_2$ with 4:5-dichloroguaiacol (*K* salt) affords 4:5-dichloro-4'-nitro-2-methoxydiphenyl ether, m.p. 147° (further chlorinated to a Cl_3 -compound), demethylated to the *OH*-compound, m.p. 132° [also prepared by chlorinating the *OH*-derivatives of (I) and (IX)], and reduced to an amine, m.p. 122° [*Ac* derivative, m.p. 189°, which with HNO_3 (*d* 1.5) in AcOH at 80° affords 4:5-dichloro-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 164°, converted into the base, m.p. 174°, which is deaminated to 4:5-dichloro-3'-nitro-2-methoxydiphenyl ether, m.p. 123°, also obtained from (V) or (XIII) with Cl_2 in AcOH. (XII) with HNO_3 in AcOH at 90° affords 5-bromo-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 142° [base, m.p. 112°, deaminated to 5-bromo-3'-nitro-2-methoxydiphenyl ether (XIV), m.p. 93°, also obtained from (V) with Br in AcOH]. Interaction of $p-C_6H_4Cl-NO_2$ with 4:5-dibromoguaiacol (*K* salt), or bromination of (I), (VIII), or (XI) affords 4:5-dibromo-4'-nitro-2-methoxydiphenyl ether, m.p. 156° (not further brominated), demethylated to the *OH*-compound, m.p. 153° [also obtained from the *OH*-analogues of (I) and (XI) with Br in AcOH], and reduced to the amine, m.p. 106° [*Ac* derivative, m.p. 190°, nitrated in AcOH at 90° to 4:5-dibromo-3'-nitro-4'-acetamido-2-methoxydiphenyl ether, m.p. 165°, converted into the base, m.p. 179°, which is deaminated to 4:5-dibromo-3'-nitro-2-methoxydiphenyl ether, m.p. 131°, also obtained from (V) or (XIV) with Br in AcOH at 90° during 5 hr.].

J. L. D.

Analogues of tetryl. Hexanitrodiphenyl-aminoethyl nitrate. LE R. V. CLARK (Ind. Eng. Chem., 1934, 26, 554—556).—The explosive properties of β -di-2:4:6-trinitrophenylaminoethyl nitrate, m.p. 184° (corr.) (prepared in 80% yield from β -di-2:4-dinitrophenylaminoethyl alcohol and $H_2SO_4-HNO_3$), are recorded in detail. They compare favourably with those of other substances used as base charges in detonators.

R. S. C.

Preparation of *p*-dimethylaminobenzyl alcohol. L. H. SMITH and K. N. WELCH (J.C.S., 1934, 730).—Interaction of $NPhMe_2$, conc. HCl , and CH_2O at 37° during 48 hr. affords *p*-dimethylaminobenzyl alcohol, b.p. 125°/1 mm., identical with the product of Clemo and Smith (A., 1928, 1239), and 4:4'-tetramethyldiaminodiphenylmethane.

J. L. D.

Steric series. XXI. Validity of the rules of optical activity. K. FREUDENBERG and H. BILLER (Annalen, 1934, 510, 230—240).—(+)-Methyl-*n*-hexyl-, (+)-cyclohexylmethyl-, (I), $[M]_{589}^{25} + 7.5^\circ$ {acet-

ate, $[M]_{589}^{18} -5.4^\circ$; carbomethoxy-derivative, b.p. $58^\circ/0.1$ mm., $[M]_{589}^{18} -6.1^\circ$ [from (I) and ClCO_2Me in $\text{C}_6\text{H}_5\text{N}$ at $> 5^\circ$]; nitrite, b.p. $56^\circ/9$ mm., $[M]_{589}^{18} -9.8^\circ$ [from (I) and NOCl in $\text{C}_6\text{H}_5\text{N}$ at -15°], and (—)-phenylmethyl-carbinol, $[M]_{589}^{18} -51.6^\circ$ [prepared by Houssa and Kenyon's method (A., 1930, 1576) (acetate, $[M]_{589}^{18} -192.8^\circ$; carbomethoxy-derivative, b.p. $77^\circ/0.1$ mm., $[M]_{589}^{18} -169.7^\circ$; nitrite, b.p. $33^\circ/0.1$ mm., $[M]_{589}^{18} -74.8^\circ$), *d*-mandelonitrile, $[M]_{589}^{18} +62.1^\circ$ in hexane- Et_2O (4:1) [prepared by a slight modification of Smith's method (A., 1931, 483)], *Me d*-mandelate, *d*-mandeldimethylamide, *Me d*-atrolactate, and *d*-atrolactdimethylamide are all configurationally related. The effect of various groups on rotation is discussed briefly. The results of Levene and Meyer (this vol., 241) are attributed to a wrong application of the displacement rule, which demands large differences in the optical activity of similar compounds in order to settle questions of configuration. The validity of the vicinal rule cannot be taken for granted with compounds containing Ph groups (the contribution of which is liable to be affected by adjacent substituents). (I) is prepared by a modification of Domleo and Kenyon's method (A., 1926, 948) from *dl*-cyclohexylmethylcarbinol (benzoate, b.p. $132^\circ/2$ mm.) (improved prep. given; cf. Sabatier and Mailhe, A., 1904, i, 809). The benzoate of *dl*-CHPhMe·OH has b.p. $131^\circ/0.5$ mm.

H. B.

Formation of carbinols in condensation of aldehydes with hydrocarbons. F. D. CHATTAWAY and R. J. K. MUIR (J.C.S., 1934, 701—703).—Slow addition of C_6H_6 (1 mol.) to a vigorously shaken mixture of $\text{CCl}_3\text{CH}(\text{OH})_2$ (3 mols.) and conc. H_2SO_4 gives $\beta\beta\beta$ -trichloro- α -phenylethyl alcohol (I), b.p. $145^\circ/15$ mm., m.p. 37° (acetate, m.p. 87.5° ; benzoate, m.p. 97.5°) (cf. Dinesmann, A., 1905, i, 645), and CCl_3CHPh , m.p. 64° ; PhMe similarly affords $\beta\beta\beta$ -trichloro- α -*p*-tolylethyl alcohol (II), b.p. $155^\circ/13.5$ mm., m.p. 63° (acetate, m.p. 107.5° ; benzoate, m.p. 100.5°) (cf. *loc. cit.*), and $\beta\beta\beta$ -trichloro- α -*di-p*-tolylethane, m.p. 89° ; PhEt yields $\beta\beta\beta$ -trichloro- α -*p*-ethylphenylethyl alcohol, b.p. $175^\circ/25$ mm.; PhI furnishes $\beta\beta\beta$ -trichloro- α -*di-p*-iodophenylethane, m.p. 172° (a carbinol could not be isolated). (I), PhMe (> 1 mol.), and conc. H_2SO_4 give $\beta\beta\beta$ -trichloro- α -phenyl- α -*p*-tolylethane (III), m.p. 72.5° , also prepared similarly from (II) and C_6H_6 . The following are similarly prepared: $\beta\beta\beta$ -trichloro- α -phenyl- α -*p*-chloro-, m.p. 74° , -*p*-bromo-, m.p. 96° , and -*p*-iodo-phenylethane, m.p. 119.5° ; $\beta\beta\beta$ -trichloro- α -*p*-chloro-, m.p. 81° , -*p*-bromo-, m.p. 102° , and -*p*-iodo-, m.p. 117° , -phenyl- α -*p*-tolylethane. (III) and conc. EtOH -KOH give $\beta\beta$ -dichloro- α -phenyl- α -*p*-tolylethylene, m.p. 87.5° . $\beta\beta$ -Dichloro- α -phenyl- α -*p*-chloro-, m.p. 93° , -*p*-bromo-, m.p. 113° , and -*p*-iodo-phenylethylene, m.p. 108° , and $\beta\beta$ -dichloro- α -*p*-iodo-phenyl- α -*p*-tolylethylene, m.p. 90° , are similarly prepared.

H. B.

Steric series. XX. Configuration of ephedrine. K. FREUDENBERG and F. NIKOLAI (Annalen, 1934, 510, 223—230; cf. A., 1932, 267).—*d*-(+)- α -*Di*-methylaminopropiondimethylamide (I), b.p. 83 — $84^\circ/12$ mm., $[\alpha]_{578}^{18} +17.9^\circ$ [the *dl*-form (*picrate*, m.p. 127 — 128°) has the same b.p.], prepared from *l*-(+)- α -

chloropropiondimethylamide (A., 1930, 1556) and Et_2O - NHMe_2 at 20° , gives a (+)-methiodide, m.p. 190 — 191° (the *dl*-form has m.p. 172 — 173°), $[\alpha]_{578}^{18} +35.4^\circ$ in H_2O . Reduction (H_2 , Pt-black, H_2O) of the (+)-dimethylamide of *l*-(—)- α -azidopropionic acid gives the (+)-dimethylamide, b.p. 64 — $66^\circ/0.5$ mm., $[\alpha]_{578}^{18} +14.6^\circ$, of *l*-(+)-alanine, which with EtOH -MeI and subsequent treatment with TIOEt affords the (—)-methiodide, $[\alpha]_{578}^{18} -15.4^\circ$ in H_2O , of *l*-(—)- α -dimethylaminopropiondimethylamide. (I) and MgPhBr give (+)- α -dimethylamino- α -benzoylthane, b.p. 115 — $117^\circ/11$ mm., $[\alpha]_{578}^{18} +24.9^\circ$ [the *dl*-form (II) (*picrate*, m.p. 134 — 135°) has the same b.p.], which is reduced (H_2 , Pt-black, $2N\text{-HCl}$) to a mixture (A), b.p. 122 — $124^\circ/10$ mm., $[\alpha]_{578}^{18} +14.21^\circ$, of *d*-methylephedrine and *l*-methyl- ψ -ephedrine; (II) similarly affords a mixture (Bz derivative, b.p. 138 — $140^\circ/0.1$ mm.) which with picric acid gives *dl*-methyl- ψ -ephedrine *picrate*, m.p. 148 — 149° . Natural (—)-ephedrine (III) is converted by Schmidt's method (A., 1914, i, 989) into (+)- β -methylamino- α -phenylpropane hydrochloride, m.p. 172° , $[\alpha]_{578}^{18} +21.6^\circ$ in H_2O (free base, b.p. 88 — $89^\circ/12$ mm.), which with MeI and TIOEt gives the (—)-methiodide, m.p. 204 — 205° , $[\alpha]_{578}^{18} -32.89^\circ$ in H_2O , of β -dimethylamino- α -phenylpropane; (A) similarly affords the (+)-methiodide, m.p. 198 — 199° , $[\alpha]_{578}^{18} +39.65^\circ$ in H_2O . The results show that (III) is configurationally related to natural *l*-(+)-alanine (cf. Leite, A., 1932, 627). *dl*- α -Aminopropiondimethylamide *picrate* has m.p. 203 — 204° .

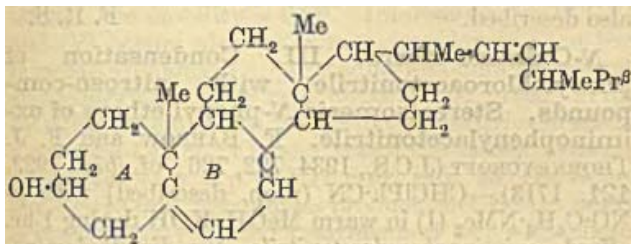
H. B.

Condensation of oleyl acetate with aromatic hydrocarbons. J. P. SISLEY (Chim. et Ind., 1934, 31, Spec. No., 763—764).—Oleyl acetate, b.p. 152 — $153^\circ/33$ mm., from oleyl alcohol, Ac_2O , and conc. H_2SO_4 , with AlCl_3 and C_6H_6 at 35 — 65° affords phenylstearyl acetate, b.p. 188 — $190^\circ/33$ mm., hydrolysed by KOH - EtOH to phenylstearyl alcohol (I), b.p. 175 — $180^\circ/28$ mm.; indications of the presence of a solid isomeride of (I) are obtained.

H. W.

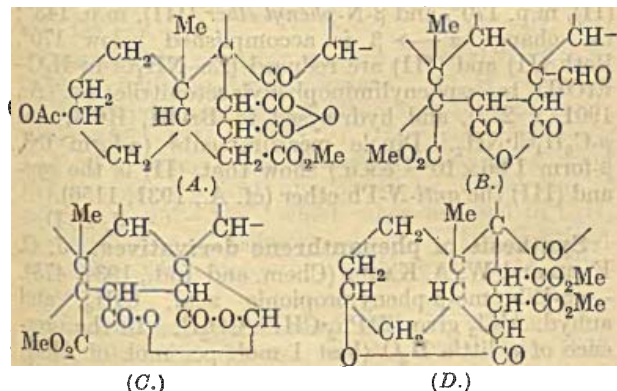
Constitution of ergosterol. A. WINDAUS, H. H. INHOFFEN, and S. VON REICHEL (Annalen, 1934, 510, 248—259).—Ergostanetriol (I), m.p. 247 — 248° [the diacetate, m.p. 190° , $[\alpha]_{578}^{18} +6.5^\circ$ (all rotations are in CHCl_3), is prepared by reduction of ergostenetriol diacetate B, m.p. 210 — 211° , $[\alpha]_{578}^{18} +25.9^\circ$ (Heilbron *et al.*, A., 1933, 500)], consumes 10 when oxidised with $\text{Pb}(\text{OAc})_4$ in AcOH , thus showing that the two new OH groups in ergostadienetriol (A., 1930, 1178) are adjacent. Since one of these OH groups is *sec.* and the other *tert.*, the structure previously proposed (this vol., 186) for ergosterol (II) is excluded. (I) oxidised (CrO_3 , AcOH) to ergostanoldione, m.p. 26 —(decomp.), $[\alpha]_{578}^{18} -26.6^\circ$, dehydrated by HCl in CHCl_3 to ergostenedione (III), m.p. 156° , $[\alpha]_{578}^{18} -51.4^\circ$ [eno *Et ether* (IV), m.p. 161°], which is reduced (Zn dust , AcOH) to ergostanedione, m.p. 199° , $[\alpha]_{578}^{18} -$ [pyridazine derivative, m.p. 210° (decomp.) (sinters at 190°), formed with EtOH - N_2H_4 , H_2O]. (III) the same absorption spectrum as cholestenedione () (cf. A., 1906, i, 580; 1907, i, 212) and stigmastadienedione (Fernholz, this vol., 292), whilst (IV) shows the same spectrum as the enol *Et ether* of (V). The group $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{C}\cdot\text{CO}\cdot$ is, therefore, common to

both (III) and (V) and indicates that the OH group of (II) is on C₃. The chloroallocholanolic acid of Heilbron *et al.* (A., 1933, 1290) is considered to be a stereoisomeride of 3-chloroallocholanolic acid. The following constitution is now assigned to (II).



It is reported that neoergosterol must contain three double linkings in ring *B*, since it is dehydrogenated (Pt-black) to a phenol, $C_{27}H_{36}O$, in which ring *A* is aromatic also.

Ozonisation of 22 : 23-dihydroergosteryl acetate-maleic anhydride. A. WINDAUS and H. H. INHOFFEN (Annalen, 1934, 510, 260—268).—Fission of the ozonide (I) of 22 : 23-dihydroergosteryl acetate-maleic anhydride with boiling AcOH or CrO₃-AcOH at 100° (bath) and subsequent esterification (Et₂O-CH₂N₂) give a *Me* ester (II), m.p. 307—308° [as *A* or



B (or *C*); remainder of mol. as in dihydroergosterol], which when hydrolysed (MeOH-KOH) and then treated with Me₂SO₄ affords the Me₂ ester lactone, m.p. 237—238° (as *D* or *E*). Hydrolysis (MeOH-conc. HCl) of (II) gives an amorphous ester [acetylated to (II)], oxidised (CrO₃, AcOH) to the keto-derivative, m.p. 244—245° (as *A*, *B*, or *C* with CH·OAc=CO). Reduc-

tive fission (Zn dust, AcOH, Et₂O or H₂, Pt, AcOH-EtOAc) of (I) and subsequent esterification (CH₂N₂) gives a *Me* ester, m.p. 253—254° (? as *B*, with CHO=CH₂·OH) (*Ac* derivative, m.p. 238—239°), which is oxidised (CrO₃, AcOH) to (II). The above alternative structures are based on the old (this vol., 186) and new (preceding abstract) structures for ergosterol. It is possible that the formation of the maleic anhydride adduct involves an isomerisation, but the ready thermal decomp. of the adducts (regenerating the original products) suggests that this is improbable.

H. B.

Constitution of ergosterol. J. W. Cook and G. A. D. HASLEWOOD (Chem. and Ind., 1934, 507—508).—Neoergosterol (I) and KHSO_4 at $145\text{--}150^\circ$ in CO_2 give *neoeergostapentaene* (II), $\text{C}_{27}\text{H}_{38}$, m.p. $93\text{--}94^\circ$, $[\alpha]_D^{25} +51^\circ$ in EtOH , also obtained (contaminated with a trace of a Cl-compound) from (I) and SOCl_2 in NPhMe_2 . (II) could not be reduced by Na and EtOH or amyl alcohol, indicating that if ring II is aromatic then the double linking in ring I is not $\text{C}_3\text{:C}_4$. (II) is also unaffected by boiling 20% NaOEt , indicating that the double linking of ring I is not $\text{C}_2\text{:C}_3$. These results are difficult to reconcile with the structure proposed by Windaus *et al.* (see above) for ergosterol.

H. B.

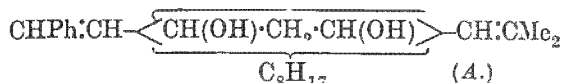
Colloidal condition of cholesterol, cholesteryl ester, and lecithin. IX. Nature of catalysis by cholesterol.—See this vol., 606.

So-called "law of periodicity." A. HANTZSCH and A. BURAWOY (Ber., 1934, 67, [B], 788—792).—Mainly in reply to the criticisms by Petrenko-Kritschenko (this vol., 186) of the authors' conception of triarylmethyl compounds (A., 1933, 1158), it is pointed out that periodicity is observed only in the behaviour of the Cl-compounds of CH_4 towards the strongest bases. A general law of periodicity does not exist. The absorption of the triarylmethyl ion does not change periodically with the no. of positive groups.

Valency isomerism of derivatives of triarylmethanes. A. HANTZSCH and A. BURAWOY (Ber., 1934, 67, [B], 793—798).—A reply to Lifschitz (A., 1933, 1104). H. W.

Relative reaction velocities of alcohols with phenylcarbimide.—See this vol., 604.

Onocerin, the phytosterol of *Ononis spinosa*, L. H. DIETERLE and A. SALOMON (Arch. Pharm., 1934, 272, 142—151).—Degradation products of onocerin (I), $C_{26}H_{44}O_2$, m.p. 232°, $[\alpha]_D^{20} +12.05^\circ$ in $CHCl_3$ (cf. Thoms, A., 1897, i, 201; Hemmelmayr, A., 1906, i, 356; 1907, i, 184), have now been obtained cryst. With CrO_3 -AcOH (I) gives onoceric acid (II) and *onodiketone*, $C_{26}H_{40}O_2$, m.p. 189° (*bisdinitrophenylhydrazone*, m.p. 206—207°), and with fuming HNO_3 it affords *dinitro-onoceric acid*, sinters 146°, decomp. 184°, also obtained from HNO_3 and (II). Oxidation of (I) with O_3 in AcOH gives *dioxyonodiketone*, $C_{26}H_{44}O_4$, m.p. 211° (*bisdinitrophenylhydrazone*, m.p. 227°), which with CrO_3 gives $COMe_2$ and a *ketone*, $C_{12}H_{24}O$, m.p. 90—91° (*dinitrophenylhydrazone*, m.p. 175—176°), further oxidised by alkaline $KMnO_4$ to an acid (III), $C_7H_{12}O_4$ (*Ag salt*), and $COMe_2$. Ozonolysis of (I) affords $COMe_2$, $PhCHO$, and a *keto-acid*, $C_{10}H_{18}O_3$, m.p. 150—151° (*dinitrophenylhydrazone*, m.p. 165—166°), further oxidised to (III). The presence of two double linkings in (I) is shown by the formation of a Br_4 -derivative, m.p. 76—77°, titration with BzO_2H , and reduction (PtO_2-H_2 -AcOH) to a



tetrahydro-derivative. The partial formula (A) is assigned to (I).
J. W. B.

Relations between acidity and tautomerism.

II. Amide group, hydroxamic, sulphinic, and sulphydroxamic acids. F. ARNDT and H. SCHOLZ (Annalen, 1934, 510, 62—71; cf. A., 1933, 146).—Saccharin (I) in Et₂O and Et₂O-CH₂N₂ (II) give [in agreement with Heller (A., 1925, i, 1323)] *O*- (III) and *N*- (IV) -Me derivatives in the ratio 1 : 4. Addition of solid (I) to (II) affords [in agreement with Schönberg *et al.* (A., 1933, 291)] essentially (IV). In the former case, the amount of (III) depends on the conversion (in solution) of the NH- into the OH-form. Phthalimide does not react with (II) except in presence of H₂O or MeOH; the *N*-Me derivative is the main product with MeOH-(II), but a small amount of a OMe-containing compound is also produced. Benzhydroxamic acid reacts as OH·CPh·N·OH with (II) to give (mainly) OMe·CPh·N·OMe, b.p. 105—106°/13 mm.; the compound, CPh<math display="block">\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NPh} \cdot \text{CO} \end{array} m.p. 170° (lit. 167°), is formed as a by-product (probably by elimination of MeOH from the intermediate OMe·CPh·N·OH, subsequent isomerisation of the PhCNO to PhNCO, and the interaction of these compounds). *p*-C₆H₄Me·SO₂H (V) and (II) afford (mainly) the Me ester of (V) and no *p*-tolyl Me sulphone, indicating that the H of (V) is not attached to S. *p*-Toluenesulphydroxamic acid and an excess of (II) give some *p*-C₆H₄Me·SO₂Me and (mainly) the ester, *p*-C₆H₄Me·SO₂·NMe·OMe, m.p. 57°, which is stable to conc. HCl and Zn-AcOH or Zn-EtOH-HCl, thus emphasising the difference (cf. *loc. cit.*) between CO and SO₂ groups. H. B.

Di-β-bromoallylaminoethyl *p*-aminobenzoate. W. BRAKER and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 322—324).—*Di*-β-bromoallylaminoethyl alcohol, b.p. 141—145°/9—10 mm. (prepared in 66% yield by condensing βγ-dibromo-Δ^α-propylene with aminoethyl alcohol in presence of Ag₂O), in C₆H₆ solution was refluxed with *p*-aminobenzoyl chloride to yield the dihydrochloride of *di*-β-bromoallylaminoethyl *p*-aminobenzoate (I), a yellow oil. (I), in aq. solution, is too acid for anaesthetic tests. Buffering ppts. the base from solution. A. E. O.

Constitution of the reduction products of chloral and bromal amides. B. H. YELBURG and T. S. WHEELER (J. Indian Chem. Soc., 1934, 11, 217—223).—ββ-Dichlorovinylbenzamide, obtained by reducing chloralbenzamide with Zn-AcOH, with Br in CHCl₃ and subsequent hydrolysis with H₂O gives ββ-dichloro-α-bromo-α-hydroxy-, m.p. 128—130°, and with HCl or HBr followed by Na₂CO₃ forms ββ-dichloro-α-hydroxy- (I), m.p. 118—119°, which with PCl₅ yields αββ-trichloro- (II), m.p. 102—103°, and with PBr₅, ββ-dichloro-α-bromo-ethylbenzamide, b.p. 158°/8 mm. (II) and NH₂Ph in NMe₂Ph give ββ-dichloro-α-anilinoethylbenzamide, m.p. 190—192°. (I) and Ac₂O at the b.p. form ββ-dichlorovinylbenzamide, and at 0° afford ββ-dichloro-α-acetoxyethylbenzamide, m.p. 146—148°; (I) with NaOH and Ac₂O at 0° yields the anhydro-compound (COPh·NH·CH·CHCl₂)₂O, m.p. 189—190°. (I) and BzCl at room temp. give the anhydro-derivative, at 0° with C₅H₅N forms ββ-dichloro-α-benzoyloxy-, m.p. 131°, and with NaOH-Me₂SO₄, ββ-dichloro-α-methoxy-ethylbenzamide, m.p.

99—100°. ββ-Dichloro-α-hydroxyethyl-acetamide, m.p. 118—119°, and -propionamide, m.p. 116°; ββ-dibromovinylbenzamide, m.p. 75° ββ-dibromo-α-hydroxyethylbenzamide, m.p. 130°, its anhydro-, m.p. 162° OAc-, m.p. 138°, and *O*-Me derivative, m.p. 124—126°, are also described. F. R. S.

***N*-Oximino-ethers. III. Condensation of phenylchloroacetonitrile with nitroso-compounds. Stereoisomeric *N*-phenyl ethers of oximinophenylacetonitrile.** F. BARROW and F. J. THORNEYCROFT (J.C.S., 1934, 722, 726; cf. *ibid.*, 1922, 121, 1713).—CHClPh·CN (prep. described) with *p*-NO·C₆H₄·NMe₂ (I) in warm MeOH-KOH during 1 hr. afford oximinophenylacetonitrile *N*-*p*-dimethylamino-phenyl ether, m.p. 185°, hydrolysed (25% HCl at 100°) to BzCN, (I), and *p*-NH₂·C₆H₄·NMe₂ (*p*-nitrobenzoate, m.p. 258°). The following are also described: oximinophenylacetonitrile *N*-*p*-methylaminophenyl ether, m.p. 193°; *N*-*p*-diethylamino-, m.p. 153°; *N*-*p*-ethylamino-, m.p. 185°; *N*-*p*-benzylethylamino-, m.p. 142°; *N*-*p*-phenylamino-, m.p. 154°, and *N*-*p*-amino-phenyl ether, m.p. 195°. None of these compounds can be obtained in stereoisomeric forms. CHClPh·CN with PhNO in KOH during 45 min. at 30° affords a mixture of α- and β-ethers, separated by C₆H₆ into the α- (II), m.p. 170°, and β-*N*-phenyl ether (III), m.p. 143°; the change α→β is accomplished below 170°. Both (II) and (III) are reduced (Zn-NH₄Cl in H₂O-EtOH) to α-phenyliminophenylacetonitrile (cf. A., 1901, i, 272), and hydrolysed to BzOH, HCN, and *p*-C₆H₄Cl·NH₂. Dipole measurements (α-form 6.3, β-form 1.06×10⁻¹⁸ e.s.u.) show that (II) is the *syn*- and (III) the *anti*-*N*-Ph ether (cf. A., 1931, 1156). J. L. D.

Synthesis of phenanthrene derivatives. J. C. EARL and W. A. KABLE (Chem. and Ind., 1934, 475).—αβ-Dibromo-β-phenylpropionic acid, C₆H₅, and anhyd. AlCl₃ give CHPh₂·CHPh·CO₂H. In the presence of a little H₂O (best 1 mol. per mol. of AlCl₃) 9-phenyl-9 : 10-dihydrophenanthrene-10-carboxylic acid is formed (cf. A., 1932, 382). R. S. C.

Olefinic acids. XII. β-Phenylhexenoic and β-methylpentenoic acids. G. A. R. KON, R. P. LINSTAD, and J. M. WRIGHT (J.C.S., 1934, 599—604).—β-Phenyl-Δ⁸-hexenoic acid (I), b.p. 154—156°/3 mm. (Et ester, b.p. 153—155°/22 mm.), is obtained by hydrolysis (cold aq. EtOH-KOH) of the crude Et ester (A., 1926, 1245) and partial esterification (method : A., 1930, 1582) of the resulting acid. Equilibrium between *cis*- (II) or *trans*- (III) -β-phenyl-Δ⁸-hexenoic acid (Stoermer *et al.*, A., 1917, i, 647; *loc. cit.*) and (I) is established slowly with boiling alkali, the equilibrium mixture contains 32% of αβ-form and the mobility [(*k*₁+*k*₂)×10] is 0.05—0.1. Each acid appears to give a mixture of all three; interconversion of (II) and (III) is incomplete and very slow, and the nature of the equilibrium (if any) between (II) and (III) could not, therefore, be determined. The amount of (I) in mixtures of (I), (II), and (III) can be determined by a bromometric method, an approx. separation of (II) and (III) is effected through their basic Cu salts. β-Methyl-Δ⁸-pentenoic acid (A., 1925, i, 506) is separated into a *trans*- (IV), m.p. 49° (chloride, b.p. 85—86°/20 mm.; amide, m.p.

94.5°) (cf. *loc. cit.*), and a *cis-form* (V), b.p. 96°/5 mm., m.p. 12° [which gives the same derivatives as (IV)]. Equilibration of (IV) or (V) gives mixtures containing 62.5% of *cis*- β -methyl- Δ^2 -pentenoic acid (VI), b.p. 90–94°/7 mm., m.p. 1° (separated by partial esterification); the mobility is 0.69. Interconversion of (IV) and (V) occurs also (at a more rapid rate than the tautomeric change); approx. equal amounts are present at equilibrium. The acid obtained (A., 1932, 1110) by dehydration of Et β -hydroxy- β -methylvalerate is a mixture (A) of (VI) and trans(?) β -methyl- Δ^2 -pentenoic acid (VII), b.p. 95°/11 mm., m.p. 35° [Et ester, b.p. 63°/13 mm. (ozonolysis product, MeCHO)]; (VII) is isolated by repeated treatment of (A) with alkali followed by partial esterification. (VII) does not appear to participate in the tautomeric interchange in presence of alkali. (IV), (V), and (VI) are converted by cold conc. H₂SO₄ into β -methyl- γ -valerolactone (VIII) at approx. the same rate; the change $\alpha\beta \rightleftharpoons \beta\gamma$ -acid must, therefore, be more rapid than lactonisation. In agreement with this view, the $\alpha\beta$ -acid can be isolated from the product of incomplete lactonisation of (VI). β -Hydroxy- β -methylvaleric acid also accompanies (VIII); this is not an intermediate since it is converted by cold conc. H₂SO₄ into (VIII) (and the unsaturated acids) at a much slower rate than (IV)–(VI). H. B.

Dissociable organic oxides. Ethyl 1:1':3'-triphenylrubene-3-carboxylate, C₃₅H₂₃·CO₂Et; its dissociable oxide. M. BADOCHÉ (Compt. rend., 1934, 198, 1515–1518; cf. this vol., 523).—Ag 1:1':3'-triphenylrubene-3-carboxylate and excess of EtI in cold dry Et₂O during 48 hr. afford the Et ester, m.p. 237–238°, which when exposed in C₆H₆ to sunlight and O₂ yields a peroxide, C₃₆H₂₃·CO₂Et[O₂], m.p. 239–240° (decomp.), which evolves O₂ when heated. J. L. D.

Asymmetric syntheses. III. R. WEGLER (Annalen, 1934, 510, 72–87; cf. A., 1932, 1094; 1933, 1139).—*dl*-OAc·CHPh·COCl and MeOH in presence of CCl₄ (or CHCl₃) and a small amount of brucine (I) at 40° give (usually) a (+)-ester (not homogeneous); increase in the quantity of (I) affords an ester which is (–) [or slightly (+)]. CHPhCl·COCl and OMe·CHPh·COCl similarly give (–)-esters, irrespective of the amount of (I) used. CHRPh·COCl (R = Et, Pr, Bu) give (–)- and (+)-esters with small and large amounts, respectively, of (I). With CHEtPh·COCl + BzCl and (I), a (–)-ester is obtained. The probable course of the reaction is discussed. (–)-CHPhEt·OH and HCl at –8° give an almost inactive chloride; in presence of brucine hydrochloride (II), the racemisation is largely suppressed. *dl*-CHPhEt·OH and HCl in CCl₄ + (II) give CHPhEtCl of varying rotation, according to the conditions [temp.; amount of (II)] used. Selective adsorption of the alcohol by (II) probably occurs. The original must be consulted for details. H. B.

Synthesis of Δ^1 - and Δ^2 -cyclopentene-1:2-dicarboxylic acids. B. L. NANDI (J. Indian Chem. Soc., 1934, 11, 213–216).—Et cyclopentan-1-one-2-

11 mm., which is hydrolysed to a mixture of Δ^1 -, m.p. 178°, and Δ^2 -cyclopentene-1:2-dicarboxylic acid, m.p. 146°, identified by ozonolysis. Attempts to follow the equilibration of the two acids were not successful. F. R. S.

Synthesis of Δ^2 -cyclopentene-1:3-dicarboxylic acid. Relation to glutaric acid derivatives. B. L. NANDI (J. Indian Chem. Soc., 1934, 11, 277–281).—Et butane- $\alpha\alpha\delta\delta$ -tetracarboxylate (J.C.S., 1894, 65, 578) is cyclised by NaOEt in boiling EtOH during 3 hr. to Et cyclopentanone-2:5-dicarboxylate, b.p. 169–175°/5 mm., reduced (H₂-Pt) to Et cyclopentanol-2:5-dicarboxylate, b.p. 173–175°/27 mm., dehydrated by SOCl₂ in cold C₅H₅N during 12 hr. to Et Δ^2 -cyclopentene-1:3-dicarboxylate (I), b.p. 168°/21 mm., which is hydrolysed (NaOH–EtOH) at room temp. to the acid, m.p. 150.5°. Et Δ^1 -cyclopentenecarboxylate (A., 1932, 1127) does not react with Et₃C₂O₄ in PhMe or C₆H₆ containing Na or K (cf. J.C.S., 1901, 79, 1265). The sodio derivative of (I) with MeI in boiling C₆H₆ during 1 hr. affords a methylated ester, hydrolysed to an acid, m.p. 225° (decomp.), which is stable to 20% KOH and affords neither a neutral nor an enolic anhydride. This confirms previous observations (A., 1932, 1127) that tautomerism and stereoisomerism are independent of one another in the glutaric acids. J. L. D.

Preparation of ammonium phthalate. C. L. TSENG and M. HU (Sci. Quart. Nat. Univ. Peking, 1934, 4, 237–242).—The action of dry NH₃ on phthalic acid in EtOH yields *o*-C₆H₄(CO₂NH₂)₂, m.p. 199°. W. R. B.

Condensation of *o*-2-fluorenylbenzoic acid. A. DANSI and A. SEMPRONJ (Gazzetta, 1934, 64, 218–221; cf. this vol., 78).—*o*-2-Fluorenylbenzoic acid (I) has m.p. 259–260° (not 248–250°, cf. A., 1904, i, 168) and is identical with the acid described as phenylanthraquinonecarboxylic acid (this vol., 78). At above 370°, it undergoes carboxyl-scission, yielding 2-benzoylfluorenone, m.p. 175–177° (cf. Fortner, A., 1903, i, 177). When, however, the acid is heated at 360–365°, ring-closure occurs, with formation of 2:3-benzoyleneanthraquinone, m.p. 351° (cf. Ullmann and Gupta, A., 1914, i, 413). The course followed by the condensation of (I) cannot be determined, but it seems probable that the CH₂ of the fluorene also takes part and that the product is not a phthaloyl-fluorene, but a compound of high mol. wt. T. H. P.

Preparation of homopiperonylic acid. T. S. STEVENS (J. pr. Chem., 1934, [ii], 140, 46).—The modification of Slotta *et al.* (this vol., 407) is best for the prep. of the methylenedioxy mandelate, but the author's earlier procedure (A., 1927, 265) for its reduction is recommended. J. W. B.

Synthesis of dicyclic compounds. P. C. GUHA, K. N. GAIND, and D. R. MEHTA (Current Sci., 1933, 2, 53).—The Na₂ derivative of Et₂ 4:6-diketo-2:2-dimethylcyclohexane-1:3-dicarboxylate in C₆H₆ reacts at a high temp. in a closed vessel with CH₂I₂, with subsequent hydrolysis, to give ketonopinone. Succinosuccinic ester similarly affords the 1:4-bridged compound. CH. ABS.

Attempts to synthesise cantharidin. V. N. PAI and P. C. GUHA (J. Indian Chem. Soc., 1934, **11**, 231—237).—Me cyclohexane-3:6-dione-1:2-carboxylate (improved prep.) with NaOMe in MeOH-MeI gives the 2-*C*-Me derivative (I), m.p. 91—93° (cf. Helferich, A., 1921, i, 185), whilst with NaOH-Me₂SO₄ it forms Me 3:6-dimethoxy-4:5-dihydrophthalate, b.p. 140—143°/1 mm., hydrolysed with KOH-EtOH to succinic acid and with H₂SO₄ to 1:4-diketocyclohexane. The K derivative of (I) and MeI forms a mixture of the C-Me, and C-methyl-O-methoxy-derivatives.

F. R. S.

Preparation of ethyl α -isobutyryl- β -phenylpropane- $\alpha\gamma\gamma$ -tricarboxylate. Retrogression of the Michael reaction. E. H. KROEGER and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, **56**, 1171—1173).—isoButyrylacetonitrile, b.p. 102—104°/12—13 mm. (from Pr^oCO₂Et, MeCN, and NaOEt at 115—120°), is hydrolysed (EtOH-HCl and H₂O) to Et isobutyrylacetate (I), b.p. 90—92°/15—16 mm., which with PhCHO and piperidine at -5° to room temp. gives Et α -isobutyrylcinnamate (II), b.p. 148—153°/3 mm. The amounts of Et α -isobutyryl- β -phenylpropane- $\alpha\gamma\gamma$ -tricarboxylate, b.p. 188—190°/3 mm., (I), CH₃(CO₂Et)₂ (III), and (II)+CHPh:C(CO₂Et)₂ (IV) obtained under varying conditions from equimol. amounts of (I) and (IV) and of (II) and (III) in Et₂O containing a little NaOEt are determined; some Et β -phenylpropane- $\alpha\gamma\gamma$ -tetracarboxylate [from (III) and (IV)] is probably formed also. (II) and (III) are best used in the above synthesis.

H. B.

Structures of olivil and its derivatives. B. L. VANZETTI (Atti R. Accad. Lincei, 1934, [vi], **19**, 421—424; cf. A., 1912, i, 352; 1931, 226).—The "difficultly sol. acid" obtained by oxidation of methylisoolivil is shown to be 2-(3':4'-dimethoxybenzoyl)-4:5-dimethoxybenzoic acid, and the "neutral substance," obtained at the same time, the corresponding phthalide. A mechanism is suggested for the conversion of olivil into isoolivil. Experimental data are to be published later. T. H. P.

Reduction products of Δ^1 -cyclopentene-1-aldehyde. E. URION (Compt. rend., 1934, **198**, 1518—1520; cf. A., 1930, 1039).—Reduction (H₂-Pd) of Δ^1 -cyclopentene-1-aldehyde (I) affords cyclopentane-aldehyde (this vol., 389), whereas with Zn-Cu in AcOH it affords Δ^1 -cyclopentenylcarbinol, b.p. 66°/11 mm. [*phenylurethane*, m.p. 64—65°; *H* phthalate, m.p. 234° (decomp.)], and $\alpha\beta$ -di- Δ^1 -cyclopentenylethylene glycol, m.p. 123° (Bz₂ derivative, m.p. 127°), reduced (H₂-Pd) to $\alpha\beta$ -dicyclopentenylethylene glycol, m.p. 133°.

J. L. D.

Nitration of chloro-*p*-xylene. H. WAHL (Compt. rend., 1934, **198**, 1612—1615).—Nitration of chloro-*p*-xylene by H₂SO₄-HNO₃ is accompanied by oxidation to 3-chloro-*p*-toluic acid (I), 3-chloro-*p*-tolualdehyde (II), b.p. 115—118°/15 mm., m.p. 30° [oxime, m.p. 95°; phenylhydrazone, m.p. 118°; semicarbazone, m.p. 230° (decomp.)]; NaHSO₃ compound. M.p. are corr., and another aldehyde, b.p. about 160°/15 mm. (II) with 50% KOH gives (I) and 3-chloro-4-methylbenzyl alcohol, b.p. 135—136°/15 mm., m.p. 29°.

R. S. C.

Cannizzaro reaction.—See this vol., 604.

Effect of the nitro-group in three-carbon tautomerism. H. B. FRASER and G. A. R. KÖN (J.C.S., 1934, 604—610).—cycloHexanone (I) and MeNO₂ in EtOH-NaOEt give 1-nitromethylcyclohexanol (II), b.p. 125—130°/17 mm., dehydrated (best with SOCl₂ in cold C₅H₅N) to 1-nitromethyl- Δ^1 -cyclohexene (III), b.p. 106—108°/17 mm.; condensation with piperidine (usual method) leads to a mixture of (II) and (III). (III) and O₃ in EtOAc give a stable ozonide, m.p. 105°, decomposed by aq. 10% NaHCO₃ to adipic acid (IV), which is also formed by oxidation (aq. KMnO₄) of (III). (III) can be titrated fairly rapidly with alkali in EtOH (end-point not sharp) and its dil. aq. solution is acidic (litmus); freshly prepared solutions do not give a colour with FeCl₃. (III) and NaOEt in Et₂O give a Na derivative (V), which dissolves in H₂O to an alkaline solution (this develops a purple colour with FeCl₃); cautious acidification affords the *aci*-form, m.p. 63—65°, which is sol. in aq. NaHCO₃, gives a colour with FeCl₃, and rearranges fairly rapidly to (III). (V) is unaffected by MeI or EtI in C₆H₆ or Et₂O, but in EtOH Δ^1 -tetrahydrobenzaloxime, m.p. 98°, results (cf. Kohler and Stone, A., 1930, 464); these results show that the anionic charge in the nitroate ion remains throughout on O and that there is no tendency for its redistribution even to C₃ of the three-carbon system. Rearrangement of the *aci*- to the NO₂-form does not involve the three-carbon system. (III) and NH₃ in Et₂O give an NH₄ salt, which decomposes in a vac. desiccator regenerating (III), and develops a brilliant green colour when treated with dil. HCl in Et₂O. (I) and EtNO₂ afford 1- α -nitroethylcyclohexanol, b.p. 122—125°/14 mm., dehydrated (as above) to 1- α -nitroethyl- Δ^1 -cyclohexene, b.p. 120—123°/24 mm. [oxidised (KMnO₄ or O₃) to (IV) and AcOH], whilst (I) and Pr^oNO₂ give 1- α -nitropropylcyclohexanol, b.p. 140—145°/12 mm., dehydrated to 1- α -nitropropyl- Δ^1 -cyclohexene, b.p. 117—118°/11 mm. [oxidised (KMnO₄ or O₃) to (IV) and EtCO₂H; in the former case a little EtCHO is also produced]; the *aci*-forms of these nitro-olefines resemble that of (III). cyclopentanone and MeNO₂ give a poor yield of chiefly 1-nitromethyl- Δ^1 -cyclopentene, b.p. 89—91°/14 mm., oxidised (KMnO₄) to glutaric acid. The above nitro-olefines exist solely in their $\beta\gamma$ -forms; this is attributed to the inductive effect of the NO₂-group, which increases the toleration of C₃ for covalent union with H. The mobility of such systems is not apparent. CORR and MeNO₂ in presence of NaOEt, piperidine, C₅H₅N, NH₃Me, or "mol." Na give 15—25% of CRR'(CH₂NO₂)₂; $\alpha\gamma$ -dinitro- $\beta\beta$ -dimethyl-, b.p. about 135—138°/9 mm., m.p. 89—90°, - β -methyl- β -ethyl-, b.p. 135—138°/9 mm., - $\beta\beta$ -diethyl-, b.p. 135—138°/10 mm., and β -methyl- β -propyl-, b.p. 144°/11 mm., -propanes are described.

The structures of Et α -nitro- β -methyl- Δ^1 - (VI) and Δ^2 -butenoate (VII) (Bouveault and Wahl, A., i, 5) are confirmed. (VI) is oxidised (KMnO₄) to COMe₂ and H₂C₂O₄ (also formed with a little CH₃ on ozonolysis), whilst (VII) is oxidised (O₃) to CH₃, AcOH, and H₂C₂O₄. The NH₄ derivative of NO₂-CH₂-CO₂Et (VIII) has m.p. 131° (cf. *loc. cit.*). (VI) and (VII) do not give colours with FeCl₃, aq. solutions do so after keeping and become faintly *aci*.

(VII) can be titrated rapidly with alkali in EtOH. Acidification of the K derivative from (VI) with dil. HCl gives (VII) containing no measurable amount of the *aci*-form; equilibrium between NO₂- and *aci*-form is established very rapidly probably owing to the additional activation due to the CO₂Et group. Acidification with Et₂O-BzOH affords a mixture of (VI) and (VII) showing that there is a definite tendency in these compounds for a redistribution of the anionic charge in the three-carbon system, also owing to the presence of the CO₂Et group. *Et* α-nitrocyclohexylideneacetate (IX), b.p. 130–134°/4 mm. [oxidised (KMnO₄ or O₃) to (I)], is prepared by nitration of *Et* cyclohexylideneacetate; it could not be obtained from (I) and (VIII). Successive treatment of (IX) with Et₂O-NH₃ and dil. acid gives (I) and (VIII), whilst cautious acidification of the K derivative (X) of (IX) affords *Et* α-nitro-Δ¹-cyclohexenylacetate, b.p. 124–126°/3 mm. [oxidised (KMnO₄) to H₂C₂O₄ and (IV)], which could not be obtained by nitration of *Et* Δ¹-cyclohexenylacetate. (X) does not react with EtI in C₆H₆ or Et₂O; in EtOH, the *oxime*, m.p. 98°, of *Et* Δ¹-cyclohexenylpyruvate is probably formed. *Et* α-nitro-β-ethyl-Δ^α-pentenoate, b.p. 119–122°/13 mm. [oxidised (KMnO₄) to COEt₂ and H₂C₂O₄], is prepared by nitration of CEt₂:CH·CO₂Et and is converted through its K derivative into *Et* α-nitro-β-ethyl-Δ^β-pentenoate, b.p. 117–120°/14 mm. (ozonolysis products, MeCHO, AcOH, and EtCO₂H). *Et* α-nitro-β-methyl-Δ^α-hexenoate, b.p. 119–122°/13 mm. [oxidised (KMnO₄) to COMePr and H₂C₂O₄], is prepared from CMePr:CH·CO₂Et and is similarly converted into *Et* α-nitro-β-methyl-Δ^β-hexenoate (?), b.p. 118–120°/14 mm. [oxidised (O₃) to MeCHO, H₂C₂O₄, and PrCO₂H]. H. B.

Reactions catalysed by aluminium chloride.
IX. Mechanism of ketone formation from cycloparaffins and acetyl chloride in presence of aluminium chloride. C. D. NENITZESCU and J. P. CANTUNARI (Annalen, 1934, 510, 269–279).—The formation of 2-acetyl-1-methyl-cyclopentane (I) and Δ¹-cyclopentene (II) from cyclohexane (III), AcCl, and AlCl₃ involves the following reactions: (III) → methylcyclopentane → 1-methyl-Δ¹-cyclopentene → 1-chloro-2-acetyl-1-methylcyclopentane → (I) (by loss of HCl and addition of 2H) or (II) (by loss of HCl) (this reaction occurs when the AlCl₃ is "poisoned" cf. A., 1932, 1132). The results of Zelinski and Tarassova (*ibid.*, 1120; this vol., 295) are criticised; six-membered ring compounds are not formed in detectable amounts in the above reaction. Unger's work (A., 1932, 514) on the labile and stable forms of (I) is confirmed.

[With J. CHICOS and G. VÂNTU.] 1-Chloro-2-acetyl-cyclohexane, prepared by Wieland and Bettags method (A., 1922, i, 1033) from cyclohexene, AcCl, and AlCl₃, with an excess of AlCl₃ in (III) at room temp. gives cyclohexyl Me ketone, b.p. 180–181° [also prepared by reduction (H₂, Pd-C, MeOH) of 1-acetyl-Δ¹-cyclohexene]; C₆H₁₀Cl·COMe + 2H → C₆H₁₁·COMe + HCl (the 2H are formed thus: 2C₆H₁₂ → C₁₂H₂₂ + 2H). cycloHexylmethylcarbinol [acetate, b.p. 208° (corr.)] has b.p. 190° (corr.), whilst α-methylcyclopentylmethylcarbinol (acetate, b.p. 192°),

obtained by reduction (Na, aq. MeOH, Et₂O) of (I) or (II), has b.p. 177°.

H. B.

Masking of certain chemical functions. R. POGGI and P. SALTINI (Gazzetta, 1934, 64, 189–191; cf. A., 1931, 1057; 1932, 1032).—With 2:6-dibenzylidenecyclohexan-1-one, excess of NH₂OH yields the

compound,
$$\text{CH}_2 \begin{array}{c} \diagup \text{CH}_2\text{CH} \text{---} \text{CHPh}\cdot\text{NH} \\ \diagdown \text{CH}_2\text{CH} \text{---} \text{CHPh}\cdot\text{NH} \end{array} \text{CO} \text{---} \text{O}, \quad \text{m.p.}$$

199–200° (gas). As in the interaction of NH₂OH and pinacolin, the CO group appears to take no part in the reaction.

T. H. P.

Action of sulphur on ketones. T. W. JEZERSKI (Rocz. Chem., 1934, 14, 216–221).—COPhMe (I) yields diphenacyl (II) on heating with S at 155–175° for 7.5 hr. in an atm. of N₂; at 180–210° thioindigo (III) is also obtained. (III) is not obtained from (II) and S at 180–210°, and must originate directly from (I). The sole products yielded by α- or β-naphthyl Me ketone are 1:2- and 2:1-naphthathioindigo. R. T.

Second-order Beckmann rearrangement. A. H. BLATT and R. P. BARNES (J. Amer. Chem. Soc., 1934, 56, 1148–1151).—*p*-Bromophenyl styryl ketoxime and PhSO₂Cl in C₅H₅N at room temp. give the normal rearrangement product cinnam-*p*-bromoanilide. The oxime of benzoyldiphenylcarbinol (phenylbenzoin) (I) when similarly treated affords COPh₂ and PhCN, and the *oxime*, m.p. 125°, of α-benzoyl-α-phenylethyl alcohol (methylbenzoin) (II) gives COPhMe and PhCN; these second-order rearrangements are considered to be essentially cleavage reactions. (I) is cleaved by aq. EtOH-KCN to COPh₂ and PhCHO [which is then converted into benzoin (III)]; (II) similarly gives COPhMe and (III), which condense further to COPh·CH₂·CHPh·COPh; α-benzilmonoxime affords BzOH and PhCN; β-benzilmonoxime yields PhCN; α-benzoinoxime (?) furnishes PhCHO and PhCN, whilst β-benzoinoxime (IV) is completely destroyed. Mandelanilide [the normal rearrangement product of (IV)] and PCl₅ in Et₂O give CHClPh·CO·NHPh and not PhNC (cf. Buck and Ide, A., 1931, 844), indicating that the second-order rearrangement (formation of PhNC) of (IV) is not normal rearrangement followed by cleavage. α-Benzoinoxime acetate (V) and cold aq. 5% NaOH give PhCHO, PhCN, and AcOH; fission does not occur with β-benzoinoxime acetate (VI), since (IV) is produced. Thermal decomp. of (V) and (VI) gives PhCHO and PhCN; α-benzilmonoxime acetate affords BzOH and PhCN, whilst the β-isomeride is unaffected at 190°.

H. B.

Indones. Synthesis of 1-phenyl-α-naphthind-en-3-one. F. PIRRONE (Atti R. Accad. Lincei, 1934, [vi], 19, 102–103).—The action of CH₂Br·CO₂Et on α-C₁₀H₇·COPh under de Fazi's conditions (A., 1919, i, 529) but for 8 hr. yields *Et* β-phenyl-β-1-naphthyl-lactate, m.p. 113–114°, which, on hydrolysis with conc. H₂SO₄, gives first the corresponding two substituted cinnamic acids and then (1) 1-phenyl-α-naphthinden-3-one, m.p. 133–134°, and (2) 1-phenyl-perinaphthinden-3-one, m.p. 142–143°. T. H. P.

Preparation of aromatic nitro-ketones. S. BERLINGOZZI (Atti R. Accad. Lincei, 1934, [vi], 19,

332—336).—Treatment of an aromatic nitro-aldehyde with an aromatic magnesyl compound (MgRCl) gives the nitro-carbinol ($\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHR}\cdot\text{OH}$), which is oxidised to the nitro-ketone by CrO_3 . The following were thus prepared: *o*-, m.p. 122°, *m*-, m.p. 117°, and *p*-nitrophenyl α -naphthyl ketone, m.p. 95°; *Ph* 2-nitro-4:5-methylenedioxyphenyl ketone, m.p. 146°; 2-nitro-4:5-methylenedioxyphenyl α -naphthyl ketone, m.p. 175°; *Ph* 3-nitro-*p*-anisyl ketone, m.p. 97°; 3-nitro-*p*-anisyl α -naphthyl ketone, m.p. 102°.

T. H. P.

Reversibility of the Friedel-Crafts reaction. Interconversion of $\beta\beta$ -diphenylethyl *tert*-butyl ketones. H. H. WEINSTOCK, jun., and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1241—1242).—*p*-Chlorostyryl *Bu*^{*v*} ketone, m.p. 85—85.5° (from COMeBu^v and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ in aq. $\text{EtOH}\cdot\text{NaOH}$), C_6H_6 , AlCl_3 , and HCl (cf. A., 1933, 1170) give $\beta\beta$ -diphenylethyl *Bu*^{*v*} ketone (I), m.p. 83.5—84.5°, also obtained similarly from $\text{CHPh}^i\cdot\text{CH}\cdot\text{COBu}^v$ and *o*-chlorostyryl *Bu*^{*v*} ketone, m.p. 53.5—54.5°. With PhCl instead of C_6H_6 , $\beta\beta$ -di-*p*-chlorophenylethyl *Bu*^{*v*} ketone (II), m.p. 153—153.5° [oxidised (alkaline KMnO_4) to 4:4'-dichlorobenzophenone], results. (II) is similarly obtained from (I) and PhCl , whilst (II) and C_6H_6 give (I). Addition of aromatic compounds to the $\text{C}^i\text{C}\cdot\text{CO}$ group is thus reversible.

H. B.

Phototropism of semicarbazones of ethylenic ketones. III. Thiosemicarbazones and δ -phenylsemicarbazones. C. V. GHEORGHIU (Bull. Soc. chim., 1934, [v], 1, 97—105; cf. this vol., 656).—Styryl Me ketone (I), α -piperonylidene- (II), α -piperonylidene- γ -methyl-, α -*p*-isopropylbenzylidene- (III), α -*o*-methoxybenzylidene- γ -methyl-, γ -*p*-hydroxybenzylidene-, γ -*o*-methoxybenzylidene-butan- β -one, α -*p*-isopropylbenzylidene- (IV), and γ -anisylidenepentan- β -one (V) afford thiosemicarbazones (VI), m.p. 146—147°, 170—172°, 157°, 138°, 118—120°, 134—135°, 212—214°, 130—132°, and 168—169°, respectively, all of which are phototropic. (I), *o*-hydroxybenzylidenebutan- β -one (VII), (III), (IV), α -piperonylidene-pentan- β -one, (II), and (V) afford δ -phenylsemicarbazones (VIII), m.p. 186—189° (decomp.), 168°, 173—174°, 183—184°, 175°, 180—190°, and 158—161°, respectively, all of which [except (V)] are phototropic. (V) shows "inverse phototropism" in both compounds, and the (VIII) of (VII) is reversibly phototropic. Many ketones of the type $\text{CHAr}^i\cdot\text{CH}(\text{or R})\cdot\text{CO}\cdot\text{R}$ ($\text{R}=\text{alkyl}$) fail to give (VI) or (VIII), probably due to the mutual influence of R and CO. The (VI) are also thermochromic, the (VIII) much less so.

J. L. D.

Structure of oximes and semicarbazones from their colour. (MME.) RAMART-LUCAS and (MME.) BRUZAU (Bull. Soc. chim., 1934, [v], 1, 119—141; cf. A., 1933, 1278).—The oximes of many deoxybenzoin (I), *meso*-methyl- (II) and *meso*-dimethyldeoxybenzoin (III) have similar absorption spectra, by measuring which it is deduced that the oximes of (I) contain the grouping $>\text{C}^i\text{N}\cdot$ (A) or $>\text{C}^i\text{C}\cdot\text{NH}\cdot$ (B), whereas those of (III) have the *iso*-structure $>\text{C}^i\text{C}^i\text{O}$ (C).

Oximes of (II) consist of mixtures of (A) or (B), and (C). The following oximes are described: *p*-methyl-,

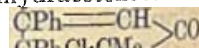
m.p. 130—131°; *p*-methoxy-, m.p. 118—119°; *meso*-dimethyl-, m.p. 192—193°; *meso*-dimethyl-*p*-methyl-, m.p. 205—206°, and *meso*-dimethyl-*p*-methoxy-deoxybenzoin, m.p. 193—194°. The semicarbazones show parallel absorption properties. *meso*-Methyldeoxybenzoin affords two semicarbazones, m.p. 159° (mainly transparent form) and 212° (mainly absorbing form). The following semicarbazones are described: *p*-methoxy-, m.p. 148—149°; *meso*-methyl-*p*-methyl-, m.p. 150—151°; *meso*-methyl-*p*-methoxy-, m.p. 125—126°; *meso*-dimethyl-, m.p. 179°; *meso*-dimethyl-*p*-methyl-, m.p. 223—224°; *meso*-dimethyl-*p*-methoxy-deoxybenzoin, m.p. 210—211°; *p*-methoxybenzophenone, m.p. 179—180° and 151—152° (*syn*- and *anti*-forms); α -phenylethyl Me ketone, m.p. 172—173°, and α -methyl- α -phenylethyl Me ketone, m.p. 185—186° and 163—164° (*syn*- and *anti*-forms).

J. L. D.

Grignard reaction in synthesis of ketones. V. Preparation of isomeric *p*-chlorobenzanilins. S. S. JENKINS (J. Amer. Chem. Soc., 1934, 56, 1137—1138).—*p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{MgBr}$ (3 mols.) give *p*-chlorophenyl *p*-methoxybenzyl ketone, m.p. 111° (all m.p. are corr.) [oxime, m.p. 87.5—88°, converted by PCl_5 in Et_2O into *p*-methoxyphenylacet-*p*-chloroanilide, m.p. 138°, also prepared from *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ at 180—190°], brominated (method: this vol., 526) to *p*-chlorophenyl α -bromo-*p*-methoxybenzyl ketone (I), m.p. 85.5—86°. Anisyl α -bromo-*p*-chlorobenzyl ketone, m.p. 106.5°, and (I) are converted as described previously (*loc. cit.*) into anisoyl-*p*-chlorophenylcarbinol, m.p. 84.5—85.5°, and *p*-chlorobenzoyl-anisylcarbinol, m.p. 70.5—71.5°, respectively; these are both oxidised (Fehling's solution) to 4-chloro-4'-methoxybenzil, m.p. 129.5°.

H. B.

Chlorides of dimethylanhydracetonebenzil. C. F. H. ALLEN and E. W. SPANAGEL (Canad. J. Res., 1934, 10, 315—317).—Dimethylanhydracetonebenzil and AcCl give chiefly the chloride



(I) which is easily isomerised to $\begin{array}{c} \text{CPh}\cdot\text{CHCl} \\ | \\ \text{CPh}\cdot\text{CMe}_2 \end{array} > \text{CO}$, m.p. 120° (cf. Burton *et al.*, A., 1933, 826). Hydrolysis of (I) may yield the OH-compound $\begin{array}{c} \text{CPh}\cdot\text{C}(\text{OH}) \\ | \\ \text{CHPh}\cdot\text{CMe}_2 \end{array} > \text{CO}$ or sometimes the bimol. compound $\begin{array}{c} \text{CPh}=\text{O} \\ | \\ \text{CPh}\cdot\text{CMe}_2 \end{array} > \text{CO}$, m.p. 181°.

F. K.

Anthrone series. V. Structure of so-called aglycone of aloin. T. F. McDONNELL [with J. H. GARDNER] (J. Amer. Chem. Soc., 1934, 56, 1246—1247).—Aloin (from Curacao aloes) and aq. borax give aloe-emodin-9-anthrone (I), m.p. 201—202° (all m.p. are corr.) (cf. Hauser, A., 1932, 370; Ca n and Simonsen, *ibid.*, 1252) (anthranyl acetate, p. 197.2—197.8°), reduced (SnCl_2 , AcOH -conc. HCl) to 1:8-dihydroxy-3-methyl-9-anthrone (*ibid.*, 197.1), which is oxidised (CrO_3 , AcOH) to chrysophanic acid. (I) is, therefore, 1:8-dihydroxy-3-hydroxymethyl-9-anthrone.

Derivatives of hydroxyphloroglucinol. G. BARGELLINI and S. M. ZORAS (Gazzetta, 1934, 64, 1202).—The action of AcCl and AlCl_3 on 1:2-

$C_6H_2(OMe)_4$ in CS_2 yields: (1) 2:3:4:6-tetrahydroxyacetophenone Me_4 ether, m.p. 53—54° (not 43—45°; cf. A., 1911, i, 211; also Chapman *et al.*, A., 1928, 183); (2) the Me_3 ether, m.p. 112—113° (not 105—107°, *loc. cit.*); (3) the Me_2 ether (*loc. cit.*); (4) products, m.p. 160—180°, probably containing the compounds, m.p. 177—178° and 162—163°, of Chapman *et al.* (*loc. cit.*) and Hattori (A., 1931, 493; 1932, 64). When heated with Ac_2O and $NaOAc$, (2) gives 5:7:8-trimethoxy-4-methylcoumarin; Hattori's conclusion that (2) is 2-hydroxy-3:4:6-trimethoxyacetophenone is thus confirmed. Condensation of (2) with anisaldehyde gives 2'-hydroxy-3':4':6':4-tetramethoxychalkone, m.p. 138—140°.

T. H. P.

Substantive dyes of the β -diketone type. W. LAMPE, J. MAJEWSKA-MŁOSZEWSKA, T. CZYSTO-HORSKI, and T. SKULIMOWSKI (Rocz. Chem., 1934, 14, 222—232).— $CHNaAc \cdot CO_2Et$ (I) and piperonyl chloride at 100° yield *Et* α -piperonylacetate, m.p. 92—94°, which is converted into *Et* piperonylacetate (II), m.p. 73—75°, when kept at room temp. for 24 hr. with 10% aq. NH_3 . The *K* salt of (II) condenses with cinnamoyl chloride at room temp. to *Et* cinnamoylpiperonylacetate (III), m.p. 135—137°, and with *p*-carbomethoxycinnamoyl chloride to *Et* *p*-carbomethoxycinnamoylpiperonylacetate m.p. 176—177°. (III) is converted into cinnamoylpiperonylmethane (IV), m.p. 133—135°, by heating. β -Styrylacrylyl chloride (V) and (I) condense to yield *Et* α -(β -styrylacrylyl)acetate (VI) (*Cu* salt, m.p. 193—196°), from which β -styrylacrylylacetone, m.p. 140—142°, is obtained by autoclaving with H_2O . Cinnamoyl- β -styrylacrylylmethane (VII), m.p. 153—155°, is prepared from (IV) and the *Na* salt of cinnamoylacetone. (VI) decomposes on keeping during 3 days with aq. NH_3 to yield *Et* β -styrylacrylylacetate (VIII), m.p. 81—83°, the *Na* salt of which condenses with (IV) to afford *Et* *di*- β -styrylacrylylacetate, m.p. 166—168°, and this, on autoclaving, yields *di*- β -styrylacrylylmethane (IX), m.p. 189—191°. (V) and $CHNaAc \cdot CO_2Me$ condense to the *Me* analogue (X), m.p. 58—60°, of (VI), and this gives similarly the *Me* analogue, m.p. 90—92°, of (VIII), into which it is converted by heating with $KOEt$ in $EtOH$. (X) yields *Me*, α β -*di*-(β -styrylacryloyl)-succinate, m.p. 182—184°, on adding I to its *Na* salt in Et_2O , and *Me* *p*-carbomethoxy-*m*-methoxycinnamoyl- β -styrylacrylylacetate (XI), m.p. 144—147°, on adding *p*-carbomethoxy-*m*-methoxycinnamoyl chloride to its *Na* salt. On autoclaving, (XI) affords *p*-carbomethoxy-*m*-methoxycinnamoyl- β -styrylacrylylmethane, m.p. 139—141°, and this, on keeping with 5% $NaOH$, yields *p*-hydroxy-*m*-methoxycinnamoyl- β -styrylacrylylmethane (XII), m.p. 156—159°. (IV), (VII), (IX), and (XII) are substantive yellow dyes for cotton.

R. T.

Constitution of carthamin. G. BARGELLINI and M. ZORAS (Gazzetta, 1934, 64, 202—212). The different m.p. for 4:2':3':4':6'-pentamethoxychalkone given by Bargellini and Bini (A., 1911, i, 212) (88—90°) and Kuroda (J.C.S., 1930, 752, 705) (112°) are due to the existence of a metastable form, m.p. 95—96° (triclinal; $a:b:c=0.5708:1:0.7506$; α 73° 46', β 102° 9', γ 72° 12'),

3 F

which passes into the stable form, m.p. 111—112° (monoclinic; $a:b:c=1.1267:1:0.83412$; β 58° 10' 5''), when heated. Similarly 3:4:2':3':4':6'-hexamethoxychalkone (cf. Bargellini, A., 1919, i, 545) exists in metastable (m.p. 114—116°) and stable (m.p. 127—128°) forms. Condensation of 2-hydroxy-3:4:6-trimethoxyacetophenone with anisaldehyde gives 2'-hydroxy-3':4':6':4-tetramethoxychalkone, m.p. 138—140° (*Ac* derivative, m.p. 146—147°), and this, when heated with HCl or H_2SO_4 in $EtOH$, yields 5:7:8:4'-tetramethoxyflavanone, m.p. 138—140°, which, on the basis of Kuroda's constitution of carthamin, is carthamin Me_4 ether. T. H. P.

Flavanone series. P. C. MITTER and S. K. SAHA (J. Indian Chem. Soc., 1934, 11, 257—264).—Interaction of 2:4-dimethoxybenzaldehyde with $CH_2(CO_2H)_2$ in boiling C_5H_5N containing piperidine during 1 hr. affords 2:4-dimethoxycinnamic acid (I), m.p. 187°, which cannot be demethylated. β -Resorcyraldehyde with $ClCO_2Me$ in $COMe_2$ - $NaOH$ affords dicarbomethoxybenzaldehyde (II), m.p. 72° (phenylhydrazone, m.p. 138°; semicarbazone, m.p. 185°), oxidised ($KMnO_4$ at 40—45°) to dicarbomethoxybenzoic acid, m.p. 159°. (II) with $CH_2(CO_2H)_2$ in $AcOH$ at 100° during 16 hr. affords some dicarbomethoxycinnamic acid, m.p. 190°, and carbomethoxyumbelliferonecarboxylic acid, m.p. 201—202°, which when boiled with 10% Na_2CO_3 during 15 min. affords umbelliferonecarboxylic acid, m.p. 262°, decarboxylated just above its m.p. Phloracetophenone Me_3 ether (A., 1899, i, 891) and dimethyl- β -resorcyraldehyde (III) in warm $EtOH$ containing 5% $NaOH$ afford 2:4:6:2':4'-pentamethoxychalkone (IV), m.p. 124°, which is different from the methylated product of fission of cyanomaclurin (J.C.S., 1905, 87, 715) with alkali. (IV) is reduced (H_2 -Pt) in $EtOAc$ during 3 hr. to 2:4:6:2':4'-pentamethoxydihydrochalkone (V), m.p. 80° (oxime, m.p. 142°; semicarbazone, m.p. 134°), which condenses with piperonal in $EtOH$ containing $NaOH$ to 2:4:6-trimethoxybenzoyl-2':4'-dimethoxybenzyl-3'':4'':-methyleneedioxybenzylidenemethane, m.p. 215°. Phloracetophenone Me_2 ether with (III) in $EtOH$ - $NaOH$ affords 2-hydroxy-4:6:2':4'-tetramethoxychalkone, m.p. 125° (lit. 152°), converted with difficulty into an impure flavanone, and reduced (H_2 -Pt) in $EtOAc$ to 2-hydroxy-4:6:2':4'-tetramethoxydihydrochalkone, m.p. 100°, methylated to (V).

J. L. D.

Bisdi-indonylenes. *cis*-Bisdi-indonylene. G. WANAG (Annalen, 1934, 510, 280—287; cf. A., 1932, 746).—Successive treatment of *trans*- α ω -diphthaloyl- β ϵ -*di*-*o*-carboxyphenyl- $\Delta^{\alpha\omega}$ -hexatriene (I) (*loc. cit.*) with $Br \cdot H_2O$ and aq. $NaHSO_3$ gives a mixture of *cis*-bisdi-indonylene (II), green, m.p. 344° (decomp.) (*Cu* block), and *trans*-dioxidobisdi-indonylene (III); (II) probably arises by loss of Br from bisdi-indonylene dibromide, which is formed by loss of $2H_2O$ from the dibromide of (I). Solutions of (II) in $CHCl_3$ are stable, but in many solvents (*e.g.*, hot $CH_2Ph \cdot OAc$) rapid isomerisation to the *trans*-form (IV) (*loc. cit.*) occurs. Hydrolysis (dil. $NaOH$) of (II) gives (I), whilst autoxidation (Br in $CHCl_3$ followed by evaporation in air) affords (III). (II) and Br in $AcOH$ at 100° (bath) give dibromodi-indone (V),

$C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown CBr \end{smallmatrix} CO$, m.p. 251°, fission of a C:C linking taking place. Oxidation (PbO_2 , $CHCl_3$) of bromodi-indone affords (II) and (V) [probably formed owing to the liberation of Br from the first formed dibromide of (II)]. Di-indone (VI) and (V) with K_2CO_3 in C_6H_6 give (II) and a little (IV), whilst (V) and (VI) in C_5H_5N afford a little (IV) and a compound, probably $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C:C \begin{smallmatrix} \diagup C_6H_4 \\ \diagdown CH \end{smallmatrix} C-C_5H_4N$, m.p. 290°. H. B.

Instance of the reversed field effect of the methyl group. J. KENNER and F. MORTON (J.C.S., 1934, 679—680).—The failure (A., 1931, 1061) to obtain a quinone by thermal decomp. of 4-nitro-2:6-di-*o*-tolylphenol is ascribed to the reversed field effect of the Me groups (Bennett and Mosses, A., 1930, 1555; cf. A., 1933, 499). In agreement with this view, 4-nitro-2:6-di-*o*-chlorophenylphenol (I), m.p. 140° (Me ether, m.p. 107°), furnishes a coloured Na salt and decomposes in boiling AcOH to 2:6-di-*o*-chlorophenyl-*p*-benzoquinone (II), m.p. 103°, best prepared by oxidation [$Pb(OAc)_4$, AcOH] of (I). 4-Amino-2:6-di-*o*-chlorophenylphenol hydrochloride, m.p. 231°, is oxidised (aq. CrO_3) to (II). *m*-Chlorophenylacetonitrile, b.p. 261°/757 mm., m.p. 11.5° (from the chloride), is hydrolysed (H_2SO_4 , AcOH, H_2O) to *m*-chlorophenylacetic acid, m.p. 76° (cf. Muenzen *et al.*, A., 1926, 972). Distillation of the Pb salts of $C_6H_4Cl \cdot CH_2 \cdot CO_2H$ gives 2:2', m.p. 102° (oxime, m.p. 112°; semicarbazone, m.p. 149°), 3:3', m.p. 89° (oxime, m.p. 73°; semicarbazone, m.p. 121°), and 4:4'-dichlorodibenzyl ketone, m.p. 93° (oxime, m.p. 135—136°; semicarbazone, m.p. 118°); with nitromalonaldehyde, these afford (I), 4-nitro-2:6-di-*m*-, m.p. 177—178° (Me ether, m.p. 131°), and -*p*-chlorophenylphenol, m.p. 202° (Me ether, m.p. 190°), respectively. 2:6-Di-*m*-, m.p. 183°, and -*p*-chlorophenyl-*p*-benzoquinone, m.p. 263°, are prepared [as (II)]. 4-Amino-2:6-di-*m*- and -*p*-chlorophenylphenol hydrochlorides have m.p. 254° and 247°, respectively.

H. B.

Chemistry of lipins of tubercle bacilli. XXXVIII. New synthesis of phthiocol, the pigment of the human tubercle bacillus. M. S. NEWMAN, J. A. CROWDER, and R. J. ANDERSON (J. Biol. Chem., 1934, 105, 279—281; cf. this vol., 192).—Phthiocol (3-hydroxy-2-methyl-1:4-naphthaquinone) is formed in 41% yield when 3-hydroxy-1:4-naphthaquinone-2-acetic acid is decarboxylated by heating with Cu Ba chromite catalyst (A., 1932, 477). A. E. O.

Molecular compounds of halogenated anthraquinones with metallic salts. K. BRASS and H. EICHLER (Ber., 1934, 67, [B], 779—787; cf. A., 1931, 1061).—The mol. compounds of halogenoanthraquinones and $SbCl_5$ prepared in $CHCl_3$ are washed with $CHCl_3$ and preserved in a vac. (method A) or washed with light petroleum and not placed in a vac. (method B). The mol. ratio of the adducts varies greatly, and is not conditioned by the nature and position of the halogen. The commonest ratio is 1:2. The introduction of halogen at 1 or 2 in anthraquinone does not appear to alter the available

valency, although occasionally an increase is observed. The following compounds of anthraquinone derivatives with $SbCl_5$ are described, the method of prep. and the mol. ratio being placed in parentheses; the addition of a third no. indicates mols. of $CHCl_3$: 2-chloro- (A, 1:2; B, 1:2:1; A, 1:2:2; A, 1:3; A, 1:4); 1-bromo- (A, 1:1:2; A, 1:2; A, 1:2:1; B, 1:3:8); 2-bromo- (A or B, 1:2; A or B, 1:2:1; B, 1:3:8; B, 2:1:16); 1-iodo- (A, 1:2); 2-iodo- (B, 1:2; B, 2:4:1; B, 1:2:1; A, 1:3:6; A, 1:4:4; B, 2:5:1); 1:5-dibromo- (B, 1:1). 1:8-Dibromo- and 1:3-dichloro-anthraquinone do not combine with $SbCl_5$. Quinizarin gives mol. compounds, 2:1:1 and 1:1:1. 6:7-Dichloroquinizarin yields the substances $4C_{14}H_6O_4Cl_2 \cdot SnCl_3$, $2C_{14}H_6O_4Cl_2 \cdot SbCl_4 \cdot CHCl_3$, and $4C_{14}H_6O_4Cl_2 \cdot 7SbCl_4$. H. W.

Quinones. I. Preparation of anthraquinone and phenanthraquinone by hydrolysis of their monoximes. C. L. TSENG, M. HU, and E. J. H. CHU (J. Chinese Chem. Soc., 1934, 11, 47—56).—Anthraquinonemonoxime (cf. A., 1902, i, 795) with boiling dil. HCl during 0.5 hr. readily affords anthraquinone (95%). Phenanthraquinonemonoxime with boiling HCl and CH_2O during 3—5 hr. affords the quinone (92%). J. L. D.

Biochemistry of micro-organisms. XXXVII. Production of hydroxyanthraquinones by species of *Helminthosporium*. Isolation of tritisporin. Constitution of catenarin.—See this vol., 697.

Resinols. II. Oxidation of α - and β -amyryns with chromic anhydride. F. S. SPRING and T. VICKERSTAFF (J.C.S., 1934, 650—651).—Oxidation (CrO_3) of β -amyrin gives β -amyrone oxide, m.p. 237°, $[\alpha]_D^{25} +143^\circ$ in $CHCl_3$ (semicarbazone, m.p. 232°), and two oxide-dicarboxylic acids $C_{30}H_{48}O_5$, m.p. 252° and m.p. 286° (Me_2 ester, m.p. 268°, $[\alpha]_D +137^\circ$ in $CHCl_3$). α -Amyrin and α -amyrone similarly afford α -amyrone oxide, m.p. 193°, $[\alpha]_D^{25} +141^\circ$ in $CHCl_3$ (semicarbazone, m.p. 223°), and an acid, $C_{30}H_{48}O_5$ (Me_2 ester, m.p. 251°, $[\alpha]_D +170^\circ$ in $CHCl_3$). The cyclic group $\cdot CH_2 \cdot CH(OH)CH_2 \cdot$ is indicated in β -amyrin.

F. R. S.

Resins. III. Action of ozone on α - and β -amyrin. P. HORMANN and J. MARTINIUS (Arch. Pharm., 1934, 272, 607—642; cf. A., 1930, 215).—Unless otherwise stated the following results refer to both α - (I) and β -amyrin (II). The O taken up by amyryns with 8% O_3 in EtOAc increases with time of ozonolysis to a max. of 32% (110) and in CCl_4 to 20%. The amount of acid products formed on decomp. increases with the degree of ozonolysis. The ozonide obtained in CCl_4 retains much CCl_4 , accounts for the high O contents previously recorded. The product (22.5% O) obtained in EtOAc, when decomposed with $N \cdot KOH$ or H_2O , gives $COMe_2$, a ketone (IV), $C_{21}H_{34}O$, m.p. 155—156°, $[\alpha]_D^{25} +141.2^\circ$ in $CHCl_3$ [from (I); ketone from (II) has $\alpha 0^\circ$] [semicarbazone, m.p. 290—291° (decomp.); oxime, m.p. 217—218° (decomp.)], an acid, $OH \cdot C_{18}H_{28} \cdot CO_2H$, amorphous, m.p. about 140—152° (decomp.) (Ag salt), and indefinite substances. The ozonide obtained in CCl_4 from (I) with H_2O gives $COMe_2$, (IV), an unsaturated substance, $C_{21}H_{33}O_2 \cdot OH$, m.p. 95°, $[\alpha]_D^{25}$

+89.7° in CHCl_3 , and an acid, $\text{C}_{21}\text{H}_{33}(\text{OH})_2\cdot\text{CO}_2\text{H}$, amorphous, m.p. 112—160° (decomp.) (Ag salt).

R. S. C.

Lonchocarpic acid, a new compound from a species of *Lonchocarpus*. H. A. JONES (J. Amer. Chem. Soc., 1934, 56, 1247—1248).—Addition of CCl_4 to the conc. COMe_2 extract of the bark and inner portion of the root of an unknown species of *Lonchocarpus* gives 3.7 and 1.5%, respectively, of *lonchocarpic acid*, $\text{C}_{26}\text{H}_{46}\text{O}_6$, m.p. 201.5° (occasionally 220—221°), which contains 1 OMe.

H. B.

Toad poisons. V. Bufagin and bufalin. M. KOTAKE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 39—48; cf. A., 1928, 1138).—Bufagin (prep. described) with Ac_2O containing NaOAc at 100° during 5 hr. affords diacetylbufagin (I) and anhydroacetylbufagin (II), $\text{C}_{26}\text{H}_{36}\text{O}_5$, which with conc. HCl at room temp. during several hr. gives a product, m.p. 267—268° (Ac derivative, m.p. 234°). (II) affords with MeOH —50% KOH at room temp. during several hr. *anhydrobufalinic acid*, $\text{C}_{24}\text{H}_{36}\text{O}_5$, m.p. 211—212°. (I) in boiling MeOH — NH_3 during 3.5 hr. affords a product, $\text{C}_{20}\text{H}_{28}\text{O}_8$, m.p. 224—228°, different from (II).

J. L. D.

Guaiazulene. K. S. BIRRELL (J. Amer. Chem. Soc., 1934, 56, 1248).—The S- and Se-guaiazulenes of Ruzicka and Haagen-Smit (A., 1931, 1301) are probably identical; they are obtained solid (both m.p. 31.5°) by cooling in liquid air.

H. B.

Effect of selenious acid on terpenes. Synthesis of carvotanacetone and Δ^3 -menthen-5-one. E. BORGWARDT and E. SCHWENK (J. Amer. Chem. Soc., 1934, 56, 1185—1187; cf. A., 1932, 1253).— Δ^1 -Menthene and SeO_2 in EtOH give carvotanacetone (Δ^1 -menthen-6-one), b.p. 95°/7—8 mm. (semicarbazone, m.p. 177—178°), and some 1:2-oxidomenthene, b.p. 63—65°/0.25 mm., which is rearranged by boiling dil. H_2SO_4 to a ketone (semicarbazone, m.p. 140—142°). Δ^3 -Menthene similarly affords Δ^3 -menthen-5-one, b.p. 107—108°/12.5 mm. (semicarbazone, m.p. 176—177°), which when reduced (Na, EtOH) and then oxidised (CrO_3) gives 3-menthone. α -Phellandrene and piperitone are similarly oxidised and dehydrogenated to cumaldehyde and thymol, respectively.

H. B.

Resolution of *dl*-menthyl (–)-mandelate. A. McKENZIE and E. M. LUIS (J.C.S., 1934, 715—716).—Esterification (HCl) of (–)-mandelic acid with *dl*-menthol and fractional crystallisation from EtOH and dil. AcOH gives (+)-menthyl (–)-mandelate (I), m.p. 98—99°, $[\alpha]_D^{20} +9.1^\circ$ in EtOH , also obtained by esterification with (+)-menthol (II), and giving (II) on hydrolysis. Evaporation of a COMe_2 solution (I) and (–)-menthyl (–)-mandelate gives *dl*-menthyl (–)-mandelate, m.p. 76—77°, $[\alpha]_D^{20} -64.4^\circ$ in EtOH , which undergoes partial resolution on crystallisation from ligroin, (I) predominating in the crystals. Evaporation of an EtOH solution of (I) and (–)-menthyl (+)-mandelate affords *r*-menthyl *r*-mandelate, m.p. 80—81°.

J. W. B.

Acid products of oxidation of pinene. K. ŚLAWINSKI and W. ZACHAREWICZ (Rocz. Chem., 1934, 14, 213—215).—67% of the acids produced by

KMnO_4 oxidation of *l*-pinene consist of pinonic acid, and the remainder of α -pinonic acid.

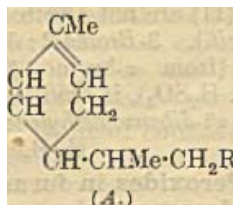
R. T.

Optically inactive bornyl fumarates. A. McKENZIE and E. B. ABBOT (J.C.S., 1934, 711—715).—Admixture of (–) and (+)-bornyl fumarate in CHCl_3 affords *r*-bornyl fumarate (I) ($:\text{CH}:\text{CO}_2\text{C}_{10}\text{H}_{17-r}$), m.p. 116—117°. (–)Bornyl (+)bornyl fumarate (II) $[(+)\text{C}_{10}\text{H}_{17}\text{O}_2\text{C}:\text{CH}:\text{CO}_2\text{C}_{10}\text{H}_{17}(-)]$, m.p. 131°, is obtained (a) by heating (+)bornyl H fumarate (III) with (–)-borneol at 130—140° (50% yield), (b) by heating (–)bornyl H fumarate (IV) with (+)-borneol (V) (prep. of optically pure specimen described) (32% yield), some (I) and (+)bornyl fumarate also being formed, and (c) from (–)bornyl fumaryl chloride, b.p. 136—137°/4 mm., $[\alpha]_D^{20} -40.8^\circ$ in CHCl_3 [from (IV) and SOCl_2] and (V) in C_6H_6 . *r*-Bornyl H fumarate (VI), m.p. 118—119°, and dimorphous form, m.p. 125—126° (stable), is obtained by admixture of (III) and (IV) in CHCl_3 . Esterification of *dl*-borneol with fumaric acid gives (VI) and a mixture of (I) and (II), and half hydrolysis of (II) gives (VI).

J. W. B.

Volatile plant materials. II. Turmerone, the perfume of curcuma oil. H. RUPE, G. CLAR, A. S. PFAU, and P. PLATTNER (Helv. Chim. Acta, 1934, 17, 372—389).—The neutral portion (I), b.p. 155—156°/10 mm., of curcuma (turmeric) oil contains no OH (AcCl , Zerevitinov, CH_2N_2 , and PhNCO), but is mainly a mixture of ketones, and reacts with MgEtBr to give a hydrocarbon $\text{C}_{17}\text{H}_{26}$, b.p. 142°/10 mm., gives an amorphous semicarbazone, and only an (?) additive compound $\text{C}_{15}\text{H}_{23}\text{O}_2\text{N}$, m.p. 111° [from (II)] with NH_2OH . Fractional distillation of (I) affords pure *ar*-turmerone (II), b.p. 164°/10 mm., $[\alpha]_D +80.52^\circ$, which is *p*- $\text{C}_6\text{H}_4\text{Me}:\text{CHMe}:\text{CH}_2:\text{CO}:\text{CH}:\text{CMe}_2$, since O_3 gives COMe_2 and curcumatic acid (A., 1924, i, 1066), and with KOH — MeOH , COMe , and curcumone (III) are obtained. With H_2 —Ni (II) affords a H_2 -derivative (IV), isolated as its oxime, b.p. 146.5—147°/1 mm. The following results show the presence of a sesquiterpene ketone turmerone $\text{C}_{15}\text{H}_{22}\text{O}$ (V), not isolated pure. Reduction of (I) with Ni — H_2 in 70% EtOH at room temp. gives a mixture, b.p. 142.5°/10 mm., of (IV) and hexahydroturmerone, and Na — EtOH affords a mixture, b.p. 106—108°/1 mm., of dihydroturmerol and dihydro-*ar*-turmerol (VI), which with Ni — H_2 in EtOH at 70°, gives a mixture, b.p. 108—110°/1 mm., of hexahydroturmerol and (VI). Hydrolysis of (I) with KOH —aq. EtOH gives COMe_2 , 4-methyl- Δ^3 -cyclohexenyl Me ketone (identical with a specimen obtained from atlantone, which is

thus present in traces), (III), and an unsaturated ketone which must be (A) ($\text{R}=\text{Ac}$), or its $\Delta^{1:3}$ - or $\Delta^{1:4}$ -isomeride (from (V)), dehydrogenated by FeCl_3 — AcOH in CO_2 to (III), and removed from the mixture by KMnO_4 oxidation or by addition of $(:\text{CH}:\text{CO})_2\text{O}$. De-



terminations of the no. of double linkings in all these mixtures give expected vals. intermediate between those of (II) and (V); (V) is therefore (A) ($\text{R}=\text{CO}:\text{CH}:\text{CMe}_2$), or its $\Delta^{1:3}$ - or $\Delta^{1:4}$ -isomeride. From

these results (I) contains 50% of (V), 40% of (II) [increasing on keeping, possibly due to auto-oxidation of (V)], and 10% of a sesquiterpene alcohol.

J. W. B.

Stability of the tetrahydrofuran ring. II. Dehydration of tetrahydrofurfuryl alcohol. R. PAUL (Bull. Soc. chim., 1933, [iv], 53, 1489—1495; cf. A., 1933, 954).—Tetrahydrofurfuryl alcohol and Al_2O_3 at 370—380° give Δ^2 -dihydropyran, b.p. 86—87° (44% yield), the dibromide, b.p. 106°/17 mm., 223—224° (corr.)/758 mm., of which with NH_2Ph gives *N*-phenylpiperidine [*picrate*, m.p. 144—146° (block); *platinichloride*, +2 H_2O , decomp. 186—190°].

R. S. C.

Relative aromaticities. IV. Alkali furyls. H. GILMAN and F. BRÜER (J. Amer. Chem. Soc., 1934, 56, 1123—1127).— NaR ($\text{R}=\text{Et}$, Ph , CH_2Ph) (usually prepared *in situ* from HgR_2 and Na) and an excess of furan (I) give Na 2-furyl (II); removal of excess of (I) by distillation, addition of *n*-hexane, destruction of excess of Na by Hg , and treatment with CO_2 affords 2-furoic acid (5—58%) (III). 2-Methylfuran (IV) similarly gives a little 5-methyl-2-furoic acid (V), which may be formed as the result of an allylic rearrangement. 2-Methylthiophene and Na 2-thienyl in *n*-heptane similarly afford 21% of 5-methyl-2-thienoic acid. Na 2-thienyl (VI) (from Hg di-2-thienyl and Na) and (I) give (II); thiophene and (II) similarly afford (VI). K 2-furyl is obtained from (I) and liquid Na-K alloy; subsequent carbonation gives a little (III) and (mainly) an unidentified oil. (IV) similarly affords a little (V). (I) and NaCPh_3 give (II) (which reacts to a certain extent with CHPh_3), indicating that (I) is more acidic than CHPh_3 . (I) is a weaker acid than CH_2CPh_3 . (II), prepared from Hg di-2-furyl and Na , is insol. and relatively stable in Et_2O . The above results also show that (I) is much more aromatic than C_6H_6 (cf. this vol., 415).

H. B.

Evidence for the $\alpha\delta$ -addition of hydrogen halides to $\alpha\beta$ -unsaturated ketones. Monohalogenodibenzoyl ethylenes. R. E. LUTZ and F. N. WILDER (J. Amer. Chem. Soc., 1934, 56, 1193—1195).—*cis*- α -chloro- $\alpha\beta$ -dibenzoyl ethylene (I), m.p. 70.5—71° (all m.p. are corr.) [obtained from 3-chloro-2 : 5-diphenylfuran and HNO_3 - AcOH or by the action of sunlight on the *trans*-isomeride (II) (designated the β -form in A., 1925, i, 681) in EtOH], and (II) with EtOH-HCl give the same mixture of (mainly) *meso*- $\alpha\beta$ -dichloro- $\alpha\beta$ -dibenzoyl ethane and 3 : 4-dichloro-2 : 5-diphenylfuran; the formation of the latter and the const. ratio of the products are explained only by the $\alpha\delta$ -addition of HCl . (I) and (II) are not affected by sunlight in CHCl_3 -I (cf. *loc. cit.*). 3-Bromo-2 : 5-diphenylfuran, m.p. 82—82.5° (from α -bromo- $\alpha\beta$ -dibenzoyl ethane, Ac_2O , and conc. H_2SO_4), is oxidised (HNO_3 - AcOH) to *cis*- α -bromo- $\alpha\beta$ -dibenzoyl ethylene, m.p. 66.5°.

H. B.

Organic peroxides. III. Peroxides in furan series. IV. Spontaneous decomposition of furoyl hydrogen peroxide. N. A. MILAS and A. McALEVY (J. Amer. Chem. Soc., 1934, 56, 1219—1221, 1221—1225).—III. Furoyl chloride and Na_2O_2 in H_2O at $\pm 3^\circ$ give difuroyl peroxide (I),

m.p. 86—87° (decomp.), which explodes violently when heated or rubbed. β -Furylacrylyl chloride similarly affords (at $\pm 0^\circ$) di- β -furylacrylyl peroxide, m.p. 104° (decomp.), which also explodes violently when heated. (I) and MeOH-NaOMe in cold Et_2O give furoyl hydrogen peroxide (II), m.p. 59.5° (decomp.), which hydrolyses in aq. solution to furoic acid (III) and H_2O_2 , but is stable in CHCl_3 at 0°. These peroxides are more unstable and more reactive than the corresponding compounds of the C_6H_6 and camphoric acid series (A., 1933, 279). The no. of mols. of (II) consumed when the following are treated in CHCl_3 at room temp. for 1 hr. are: *isoeugenol* 1.037, *isosafole* 1.081, *safrole* 1.015, *cholesterol* 1.02, *ergosterol* 3.127, *citronellol* 1.043, *pinene* 1.083, *limonene* 1.685, *geraniol* 1.38, $\text{CMe}_2\text{:CMe}_2$ 0.29, *allyl alcohol* 0.15, (III) 0. Irradiation of furaldehyde (IV) containing a little (II) in N_2 at 25° for 1 hr. does not cause complete disappearance of (II). (IV) absorbs O_2 when irradiated in air, but peroxide could not be detected; in light petroleum at 0°, (II) may be produced.

IV. Spontaneous decomp. of (II) (solid) at 0° occurs slowly after an induction period of 72 hr.; decomp. begins at "active spots" or "nuclei" (probably formed on the corners or edges of crystals). The induction period is shortened by raising the temp.; at 40°, detonation occurs. The effects of addition of various solids (org. and inorg.) are studied. Decomp. of (II), alone or in AcOH , is accelerated by light of 4500—3600 Å. Decomp. of (II) at 35° in a vac. gives (III) (50.7%), CO_2 (10.1%), an alkali-sol. polymeride (37%), and (probably) 4 : 5-epoxyfuroic acid (1.5%) (*Ba* salt). Decomp. of (II) in CHCl_3 at 35° and 40° is unimol. and (III) and O_2 are produced; the temp. coeff. is 2.3 and the heat of activation is 15,800 g.-cal. per mol.

H. B.

Geometrical isomerism of $\alpha\alpha'$ -disubstituted tetrahydro- γ -pyrones. R. CORNUBERT and P. ROBINET (Bull. Soc. chim., 1934, [v], 1, 90—97).—Interaction of acetonedicarboxylic acid with PhCHO (3 parts) and dry HCl at about 0° affords two stereoisomeric forms of $\alpha\alpha'$ -diphenyltetrahydropyrone, m.p. 131° [oxime (I), m.p. 154—155°] and 76° [oxime, m.p. 144—145°, different from (I)].

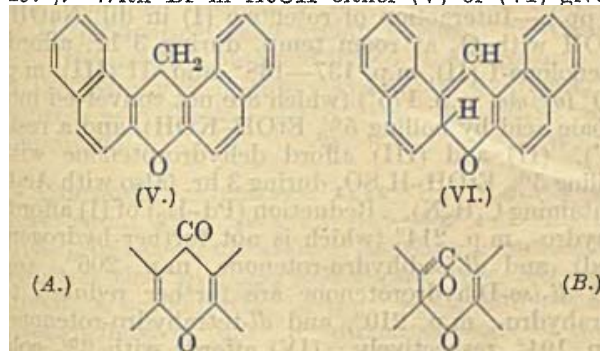
J. L. D.

Catalytic reduction of dehydracetic acid. R. MAŁACHOWSKI and T. WANCZURA (Bull. Acad. Polonaise, 1933, A, 547—557).—Reduction of dehydracetic acid with H_2 - PtO_2 in MeOH affords 2-keto-6-methyl-3-ethyl-2 : 3-dihydro- γ -pyrone (I), m.p. 185° (oxime, m.p. 226°), hydrolysed by H_2O at 130 to *n*-heptane- $\beta\delta$ -dione. The *K* derivative of $\text{CO} \begin{array}{c} \text{CH}_3\text{OMe} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CO} \end{array} \text{O}$ with Et_2SO_4 at 105° gives, not (I), but the isomeric 4-ethoxy-6-methyl- α -pyrone, b.p. 142—148°/10 mm., m.p. 62°.

J. W. B.

s- $\alpha\beta$ -Dinaphtho- γ -pyrone. K. DZIEWOŃSKI, S. PIZON, and (MLLE.) M. MAZURKIEWICZOWNA. Two isomeric $\alpha\beta$ -dinaphthopyrans. K. DZIEWOŃSKI and S. PIZON (Bull. Acad. Polonaise, 1933, A, 565, 566—572).—Oxidation of dinaphtho- γ -methylpyrone (I) (9-methyl-1 : 2 : 7 : 8-dibenzoxanthene) (from β - $\text{C}_{10}\text{H}_7\text{-OH}$ and MeCHO ; Claisen, A., 1884, 270, 494) with CrO_3 in AcOH affords 1 : 2 : 7 : 8-

dibenzoxanthone (II), the supposed 2:3:7:8-dibenzoxanthone, m.p. 149°, similarly obtained by Claus *et al.* (A., 1890, 510), being a mixture of (II) and unchanged (I). The anil (III) (A., 1932, 859) of (II) with H_2S in AcOH gives 1:2:7:8-dibenzothioxanthone, m.p. 210°. Condensation of β - $C_{10}H_7$ -OH with the appropriate $CS(NHAr)_2$ affords the o-, m.p. 195—196.5° [4':6'-(NO_2)₂-derivative, m.p. 256—257°], and p-, m.p. 206—207°, -methyl- and p-chloro-, m.p. 193—195°, -anil of (II). With HI (*d* 1.96) and red P at 180° (II) or (III) affords 1- $C_{10}H_7$ Me. Distillation of di-(2-hydroxy-1-naphthyl) ketone with Zn dust, or treatment of 1:1':2:2'-dinaphthopyrylium bromide $\left| C_{10}H_6 \begin{smallmatrix} CH \\ \parallel \\ O \end{smallmatrix} C_{10}H_6 \right| Br'$ (IV) (Fosse, A., 1901, i, 604) with hot EtOH affords 1:2:7:8-dibenzoxanthone (V), m.p. 202° (Wolf, A., 1893, i, 222). Reduction of (II) or (III) with red P and HI at 150—160° gives the iso-form (VI), m.p. 185° (picrate, m.p. 197°). With Br in AcOH either (V) or (VI) gives



(IV). (V) and (VI) are regarded as derived, respectively, from the tautomeric forms (A) and (B) of (II).

J. W. B.

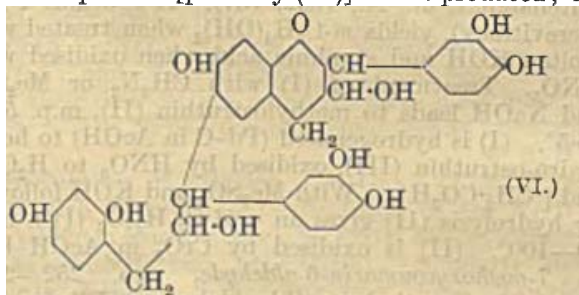
Diphenylene oxide series. IV. N. M. CULLINANE, H. G. DAVEY, and H. J. H. PADFIELD (J.C.S., 1934, 716—719).—Diphenylene oxide (best prepared in 20% yield by destructive distillation of PhOH with PbO) is also obtained (a) by heating pyrocatechol (I) and PhOH at 240°, some diphenylene dioxide (II) [prep. by condensation of (I) with o - $C_6H_4Cl_2$] also being formed if P_2O_5 is used, (b) by boiling 2:2'-dihydroxydiphenyl [by diazotisation of the 2:2'-(NH_2)₂-compound] with H_2O , or (c) by heating 4:4'-dihydroxydiphenyl with P_2O_5 . By heating guaiacol, KOH, and o - $C_6H_4Cl \cdot NO_2$ at 190—195° is obtained 2-nitro-2'-methoxydiphenyl ether, m.p. 71°, converted by boiling HI (*d* 1.7) into the 2-amino-2'-hydroxy-compound, m.p. 116°, which by diazotisation and successive treatment with $CuSO_4$ and 50% H_2SO_4 gives (II), and at 270—280° affords phenoxazine. 2:2'-Dinitrodiphenyl ether (in 6% yield by heating o - $NO_2 \cdot C_6H_4 \cdot ONa$ with o - $C_6H_4Cl \cdot NO_2$ at 220°) is reduced by aq. EtOH- NH_3 - H_2S to the 2-nitro-2'-amino-derivative, m.p. 56°. With Br-AcOH 2-nitrodiphenylene oxide gives its 6-Br-derivative, m.p. 248°, also obtained from 3-bromo-diphenylene oxide (III) and HNO_3 (*d* 1.5)-AcOH. With Br-AcOH (III) affords the 3:6-Br₂-derivative.

J. W. B.

Composition of *Daphne genkwa*.—See this vol., 820.

Preparation of diphenylphenolphthalein [2-hydroxydiphenylphthalein] and substitution products.—See B., 1934, 556.

Tannins and similar substances. XXVII. Quebracho-tannin. K. FREUDENBERG and P. MAITLAND (Annalen, 1934, 510, 193—205).—Reduction (H_2 , PtO₂, EtOH) of crude fisetinidin chloride (improved prep.; cf. Leon and Robinson, A., 1931, 1423) and subsequent acetylation (Ac_2O , C_5H_5N) gives the tetra-acetate, m.p. 184—186°, of dl-epiquebrachocatechin (7:3':4'-trihydroxyflavanol) (I), m.p. (hydrated) 93—96°. (I) is rearranged by aq. $KHCO_3$ at 115° into dl-quebrachocatechin (II) (tetra-acetate, m.p. 144—146°). The Ac_2 derivative of 3:4-dihydroxyacetophenone, m.p. 119—121° (lit. 114—116°) (improved prep.; cf. Stephen and Weizmann, J.C.S., 1914, 105, 1051), with β -resorcyaldehyde and HCl in cold EtOAc, followed by treatment with conc. HCl in MeOH, gives butinidin chloride; reduction and subsequent acetylation (as above) of this affords a little of the triacetate (III), m.p. 137—139°, of 7:3':4'-trihydroxyflavan (IV), m.p. 175—178° (to a red liquid). (IV) is obtained from (III) and EtOH-KOAc in H_2 ; hydrolysis with aq. $Ba(OH)_2$ gives a product contaminated with red amorphous material. (IV) is unstable in air or hot H_2O ; warm 2% HCl converts it into a red "phlobaphen," which when methylated and then oxidised gives veratric acid (V). When (II) is heated with dil. acid, an insol. condensation product [probably (VI)] is first produced; more

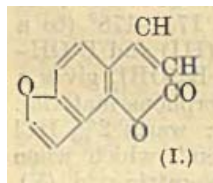


prolonged heating causes a secondary elimination of H_2O . The material extracted (Et_2O then $COMe_2$) from quebracho wood is separated into a small H_2O -sol. fraction, a main portion (A) sol. in hot but insol. in cold H_2O , and a small H_2O -insol. fraction. (A), which contains 1.2% OMe, gives m - $C_6H_4(OH)_2$ when heated with KOH; successive methylation (Me_2SO_4 , 55% KOH) and oxidation (aq. $KMnO_4$) affords (V). When (A) is heated with dil. acid, the C content increases (elimination of H_2O); acetylation of (VI) and (A) (and the other fractions) indicates that these are inter-related [and probably arise from (II) by a condensation which does not involve elimination of H_2O]. The OMe content of (A) is probably due to an admixed impurity.

H. B.

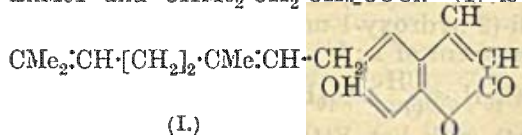
Natural coumarins. XI. Constitution of angelicin (from *Angelica archangelica*, L.). E. SPÄTH and O. PESTA. **XII.** Constitution of ostruthin (from *Imperatoria ostruthium*, E. SPÄTH and K. KLÄGER (Ber., 1934, 67, [B], 853—858, 859—868).—XI. Extraction of angelica root with Et_2O , treatment of the extract with 3% KOH-EtOH, removal of Et_2O , and treatment of the residue

with 10% KOH-MeOH at 15–20° leads to the isolation of sterols and indifferent substances from which sitosterol, m.p. 135°, $[\alpha]_D^{25}$ –37.3° in CHCl_3 , is isolated [this has been previously described as "angelicin," but it is proposed (see below) to use this designation for another compound]. The lactone fraction contains a compound, m.p. 83° (cf. Bocker *et al.*, A., 1911, i, 313), identified as osthol and *angelicin* (I), $\text{C}_{11}\text{H}_6\text{O}_3$, m.p. 138–139.5°, which does not contain OMe and does not afford $[\text{CH}_2\cdot\text{CO}_2\text{H}]_2$ (II) when oxidised. After hydrogenation (I) is oxidised by HNO_3 to $\text{H}_2\text{C}_2\text{O}_4$ and (II). Treatment of (I) with $\text{KOH}\cdot\text{H}_2\text{O}_2$ yields $\text{H}_2\text{C}_2\text{O}_4$ and furan-2 : 3-dicarboxylic acid (Me_2 ester, m.p. 36.5°), whereas (I) is converted by $\text{KMnO}_4\text{-C}_5\text{H}_5\text{N}$ and subsequent decarboxylation into umbelliferone. Treatment of osthol with $\text{NaOMe}\cdot\text{Me}_2\text{SO}_4$ and subsequently with H_2O yields 2 : 4-dimethoxy-3- γ -methyl- Δ^8 -butenylcinnamic acid, m.p. 82–84°, and an ester hydrolysed to an isomeric acid (III), m.p. 151–152°. Oxidation of (III) by KMnO_4 in dil. KOH followed by esterification of the product, hydrolysis, and successive treatment of the acid with SOCl_2 and NH_2Ph , leads to 2 : 4-dimethoxybenzene-1 : 3-dicarboxydianilide (IV), m.p. 206–207° (vac.). Since similar treatment of (I) leads to (IV), the annexed constitution is ascribed to it.



XII. Ostruthin (I), m.p. 119°, is $\text{C}_{19}\text{H}_{22}\text{O}_3$ (cf. Butenandt *et al.*, A., 1932, 751). It contains 1 OH (Zerevitinov), yields $m\text{-C}_6\text{H}_4(\text{OH})_2$ when treated with molten KOH and styphnic acid when oxidised with HNO_3 . Treatment of (I) with CH_2N_2 or Me_2SO_4 and NaOH leads to methylostruthin (II), m.p. 55–55.5°. (I) is hydrogenated (Pd-C in AcOH) to hexahydro-ostruthin (III), oxidised by HNO_3 to $\text{H}_2\text{C}_2\text{O}_4$ and $[\text{CH}_2\cdot\text{CO}_2\text{H}]_2$. With Me_2SO_4 and KOH followed by hydrolysis (II) gives an acid $\text{C}_{21}\text{H}_{23}\text{O}_4$ (IV), m.p. 99–100°. (II) is oxidised by CrO_3 in $\text{AcOH}\cdot\text{H}_2\text{O}$ to 7-methoxycoumarin-6-aldehyde, m.p. 252–254° (vac.) (the "methylostruthinaldehyde" of Butenandt *et al.*), the oxime of which is dehydrated by Ac_2O at 140–145° to 6-cyano-7-methoxycoumarin (V), m.p. 282° (vac.). Oxidation of (V) by KMnO_4 (=50) in $\text{C}_5\text{H}_5\text{N}$ leads to 5-cyano-2-hydroxy-6-methoxybenzoic acid (VI), m.p. 236° (decomp.) (Me ester, m.p. 117–118°). When heated with Cu powder in quinoline at 235–240°, (VI) yields 4-hydroxy-2-methoxybenzonitrile, m.p. 156–157°, identical with the product obtained by the action of Ac_2O on 4-hydroxy-2-methoxybenzaloxime, m.p. 178°. 2-Hydroxy-4-methoxybenzaloxime, m.p. 136–138°, and 2-hydroxy-4-methoxybenzonitrile, m.p. 177–178°, are described. Oxidation of (IV) by KMnO_4 (=300) yields 4 : 6-dimethoxybenzene-1 : 3-dicarboxylic acid, m.p. 264° (vac., decomp.) (Me_2 ester, m.p. 152–152.5°). Oxidation of (I) by KMnO_4 in very dil. KOH affords $\text{H}_2\text{C}_2\text{O}_4$ and $\text{OH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$. (III) is transformed by $\text{H}_2\text{O}_2\text{-NaOH}\cdot\text{H}_2\text{O}$ into γ -dimethylnonoic acid (VII), b.p. 150–151°/10 mm., converted by SOCl_2 into the corresponding chloride, b.p. 115–120° (bath)/10 mm., and thence into the amide, m.p. 79–81° (vac.), identical with a specimen prepared from the acid obtained from tetrahydrogeraniol through

the corresponding bromide and nitrile. The *phenyl*- and *p-tolyl-hydrazide* of (VII) have m.p. 113–114° and m.p. 119.5–120°, respectively. Oxidation of (II) with $\text{CrO}_3\text{-AcOH}$ gives COMe_2 . β -Methyl- Δ^8 -hepten- ζ -one, b.p. 170–173°/746 mm., obtained as by-product in the oxidation of (II) (see above) (semicarbazone, m.p. 137°, identical with that derived from citral) is hydrogenated (Pd-C in AcOH) to β -methylheptan- ζ -one; the semicarbazone, m.p. 156–157°, is identical with that of the ketone from ZnMeI and $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COCl}$. (I) is therefore



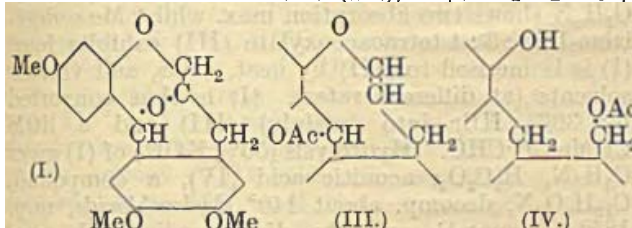
H. W.

Rotenone, the active constituent of *Derris* root. XIV–XVI. S. TAKEI, S. MIYAJIMA, and M. ONO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 1–24, and Mem. Coll. Agri. Kyoto, 1934, No. 31, 24 pp.).—Interaction of rotenone (I) in dil. NaOH-EtOH with O_2 at room temp. during 3 hr. affords rotenolone-I (II), m.p. 137–138°, and -II (III), m.p. 210° (oxime, m.p. 175°) (which are not converted into tubaic acid by boiling 5% EtOH-KOH), and a resin (IV). (II) and (III) afford dehydrorotenone with boiling 5% EtOH- H_2SO_4 during 3 hr. (also with Ac_2O containing $\text{C}_5\text{H}_5\text{N}$). Reduction (Pd- H_2) of (I) affords dihydro-, m.p. 214° (which is not further hydrogenated), and *dl*-isodihydro-rotenone, m.p. 206°. *iso*- and *dl*-*iso*-Dihydrorotenone are further reduced to tetrahydro-, m.p. 210°, and *dl*-tetrahydro-rotenone, m.p. 194°, respectively. (IV) affords with 2% cold NaOH in Et_2O *l*-deguelin, m.p. 166° converted by Pd- H_2 into the *dl*-form, which in EtOAc with Pd-H₂ gives dihydrodeguelin, m.p. 170°. Interaction of deguelin (VI) with alkali and O_2 affords deguelinol-I and -II [identical with tephrosin (A., 1931, 491) and *isotephrosin* (A., 1933, 69), respectively], which with EtOH- H_2SO_4 afford dehydrodeguelin, hydrolysed to deguelinic acid. Hydrolysis of (VI) affords β -tubaic acid, reduced (Pd- $\text{BaSO}_4\text{-H}_2$) in EtOAc to β -dihydrotubaic acid, m.p. 170°, identical with the acid prepared by hydrolysis of β -dihydrorotenone. *iso*Dihydrotubaic acid with conc. H_2SO_4 affords *iso*- β -dihydrotubaic acid, m.p. 193°. 4-Methoxytetrahydrotubaic acid (A., 1932, 400) at 200–230° during 0.5 hr. affords tetrahydrotubanol Me_1 ether, b.p. 1.0/7 mm., which gives with malic acid in hot conc. H_2SO_4 during a few min. 8-*iso*amyl-7-methoxycoumarin, m.p. 85–85.5° (cf. A., 1932, 751; 1933, 614). The physiological properties of some of these substances are investigated.

J. L. D.

Brazilin and hæmatoxylin. XIV. Trimethylallobrazilin. P. PFEIFFER and P. SCHNEIDER (J. pr. Chem., 1934, [ii], 140, 9–28).—Reduction of trimethylbrazilone with Na-Hg in EtOH-AcOH affords α -trimethylallobrazilone, trimethylbrazinol, β -trimethylbrazilpinacone, α - (I) and the stereoisomeric β - (II), m.p. 143.5°, -trimethylallobrazilin, $\text{C}_{19}\text{H}_{20}\text{O}_5$ (no OH or CO), and the compounds $\text{C}_{19}\text{H}_{20}\text{O}_6 + \text{H}_2\text{O}$ and anhyd., m.p. 110°, $\text{C}_{19}\text{H}_{18}\text{O}_6$, m.p. 165°, and $\text{C}_{19}\text{H}_{20}\text{O}_5$, m.p. 220°. Warm EtOH (+1 drop NaOH) effects quant. conversion of (I)

into (I). With Ac_2O - NaOAc (I) or (II) yields an unsaturated *Ac* derivative (III), m.p. 121—122.5°.



(saturated oily H_2 -derivative), and readily hydrolysed by dil. AcOH back to (I). Reduction (Pd - BaSO_4 - H_2 in AcOH) of (I) gives (with pinacolinic rearrangement)

2-hydroxy-2'-acetonyl-4:4':5'-trimethyldiphenylmethane (IV) [*Ac* derivative, m.p. 102°; *oxime*, m.p. 193°; *Me* ether (V), m.p. 91° (*oxime*, m.p. 118°)], oxidised by 30% H_2O_2 - KOH - MeOH to 2-hydroxy-4:4':5'-trimethyldiphenylmethane-2'-carboxylic acid, m.p. 222—224° [*Ac* derivative, m.p. 99°, *Me* ester, m.p. 159° [*Me* ether, m.p. 118°, by similar oxidation of (V)] identical (and giving identical derivatives) with the product obtained by Zn - AcOH reduction of 6-(2-hydroxy-4-methoxybenzoyl)-3:4-dimethoxybenzoic acid (Perkin, J.C.S., 1907, 91, 1079; prep. improved). J. W. B.

Thiophen derivatives. IV. I. J. RINKES (Rec. trav. chim., 1934, [iv], 53, 643—651; cf. this vol., 81).—The ease of nitration of thiophen is intermediate between that of C_6H_6 and furan. The NO_2 -group directs a second NO_2 to the "m"-position, unless overwhelmed by the "o"-directing power of the S. 3-Nitro-2-methylthiophen, KMnO_4 , and MgSO_4 in hot COMe_2 give a poor yield of 3-nitrothiophen-2-carboxylic acid, m.p. 137° (*Me* ester, m.p. 56°). *Me* thiophen-3-carboxylate and HNO_3 (*d* 1.51) in Ac_2O at -10° give *Me* 5-nitrothiophen-3-carboxylate, m.p. 81° (corresponding acid, m.p. 147°). Oxidation of 2-nitro-3-methylthiophen affords 2-nitrothiophen-3-carboxylic acid, m.p. 155—156°. Tetraiodothiophen, m.p. 199°, with Al-Hg in Et_2O - EtOH (3:1) yields 3-iodothiophen, b.p. 77°/11 mm., affording the 2- NO_2 -derivative, m.p. 140—141°, with HNO_3 - Ac_2O . 2-Iodothiophen with HNO_3 - AcOH in Ac_2O gives much 5-, m.p. 75°, and a little 3- NO_2 -derivative (I), m.p. 131°, both giving with HNO_3 - H_2SO_4 the 3:5-(NO_2)₂-derivative, m.p. 145°. 2-Iodo-5-acetothienone, when oxidised first with alkaline KMnO_4 and then with H_2O_2 , gives 3-iodothiophen-5-carboxylic acid, m.p. 133—134° (lit. 131°), affording with HNO_3 - Ac_2O (I) and 2-iodo-3-nitrothiophen-5-carboxylic acid, m.p. 201° (*Me* ester, m.p. 118°). *Me*₂ thiophen-3:5-dicarboxylate (modified prep.) with HNO_3 (*d* 1.51)- H_2SO_4 at -10° gives a NO_2 -derivative, m.p. 94°. R. S. C.

Stereoisomerism of disulphoxides and related substances. IX. Disulphoxides in the thianthren series. H. BAW, G. M. BENNETT, and (Miss) P. DEARNS (J.C.S., 1934, 680—684).—Oxidation of 2:6-dimethoxythianthren with HNO_3 (*d* 1.2) affords α - (Fries *et al.*, A., 1915, i, 155) (main product α H_2O_2 - AcOH is used) and the stereoisomeric β -disulphoxide, m.p. 198—200°. Similarly 2:6-dimethylthianthren (H_2O_2 - AcOH at 80°) gives α -, m.p. 202.5°

(corr.), and β -(?*cis*-), m.p. 174° (corr.), -disulphoxides, and (with 3 atoms of O) a trioxide (sulphone sulphoxide), m.p. 223°, reduced by Zn - AcOH to the monosulphone, m.p. 170—171°. 2:6-Dichlorothianthren (I), m.p. 186° (corr.), prepared by the action of oleum on *p*- $\text{C}_6\text{H}_4\text{Cl-SH}$, is also the only pure product isolated from the condensation of PhCl , S_2Cl_2 , and AlCl_3 (Fries *et al.*, A., 1909, i, 406), isolation of the 2:7-isomeride being doubtful. Oxidation of (I) affords α -, m.p. 313° (corr.), and β -, m.p. 267.5° (corr.), -disulphoxides, a monosulphoxide, m.p. 235—237° (decomp.), and a trioxide, reduced to a monosulphone, m.p. 215°; with excess of CrO_3 - AcOH a disulphone, m.p. 305° (corr.), is obtained. J. W. B.

Salts of pyridine-like amines. P. PFEIFFER and F. TAPPERMANN (J. pr. Chem., 1934, [ii], 140, 29—38).—By determining the solubility of various amines (B) in H_2O and in dil. acids (A) the mol. proportions of A and B in the salt formed in solution is ascertained. α - and β -Naphthoquinoline, β - $\text{C}_{10}\text{H}_7\text{-NH}_2$, and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ in dil. HCl or HNO_3 all give A:B=approx. 1:1 (ions BH^+ and X^-), but *o*- (improved prep.) and *m*-phenanthroline with aq. HNO_3 and *d*-camphor- β -sulphonic acid give A:B=approx. 1:2 (ions $[\text{B}\cdot\text{H}\cdot\text{B}]^+$ and X^-), of which type *di-o*-phenanthroline mononitrate, $+\text{H}_2\text{O}$ and anhyd., is isolated. J. W. B.

Metal pyridine methylnitroamine complexes. T. L. DAVIS and C. W. OU (J. Amer. Chem. Soc., 1934, 56, 1064—1065).—The prep. and properties of $\text{Co}(\text{NMe}\cdot\text{NO}_2)_2\cdot 2\text{C}_5\text{H}_5\text{N}$, $\text{Cu}(\text{NMe}\cdot\text{NO}_2)_2\cdot 1, 2$, and 3 $\text{C}_5\text{H}_5\text{N}$, and $\text{Ni}(\text{NMe}\cdot\text{NO}_2)_2\cdot 2\text{C}_5\text{H}_5\text{N}$ are described and their dissociation pressures have been measured at 20°. The Ni compound decomposes at low temp. E. S. H.

Reduction of nitriles. R. GRAF (J. pr. Chem., 1934, [ii], 140, 39—45).—Addition of aq. KOH in H_2 to PhCN and $\text{Cr}(\text{OAc})_3$ in EtOH effects reduction to $\text{CH}_2\text{Ph}\cdot\text{NH}_2$ and $\text{NH}(\text{CH}_2\text{Ph})_2$. Similarly MeCN affords NH_2Et , 2-cyanopyridine gives 2-pyridylmethylamine, b.p. 78—80°/12 mm. [*dihydrochloride*, m.p. 209—212° (decomp.)], and 2:6-dichloro-4-cyanopyridine gives 2:6-dichloro-4-pyridylmethylamine (Wibaut *et al.*, A., 1933, 282) (*hydrochloride*, decomp., 275—277°; *Bz* derivative, m.p. 61—63°). J. W. B.

Oximes of 3-benzoyl-6-phenylpyridine. H. NIENBURG (Ber., 1934, 67, [B], 874—878).—Treatment of 3-benzoyl-6-phenylpyridine with $\text{NH}_2\text{OH}\cdot\text{HCl}$ (I) and NaOH in EtOH - H_2O yields in addition to the β -ketoxime (II), m.p. 183—184° (cf. Benary *et al.*, A., 1924, i, 872), the α -ketoxime (III), m.p. 160° after softening at 157° when slowly heated. The proportion of (II) to (III) appears to depend on the purity of (I). Partial isomerisation of (III) to (II) occurs under the action of PCl_5 in Et_2O . The Beckmann transformation of (III) therefore yields *BzOH*, NH_2Ph , 6-phenylpyridine-3-carboxylic acid, m.p. 229° (*loc. cit.*), and 3-amino-6-phenylpyridine, m.p. 105—106° [*aurichloride*, m.p. 169° (decomp.)]; *Ac*, m.p. 148—149°, and *Bz*, m.p. 201°, derivatives). (II) or (III) does not appear to yield internal complex salts with Co, Ni, or Fe salts. H. W.

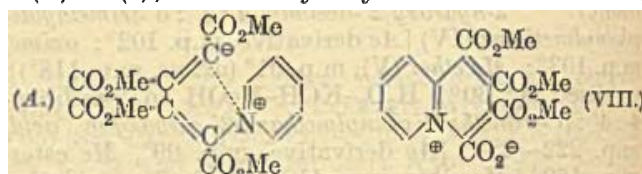
Manganohalides of pyridine and quinoline. F. S. TAYLOR (J.C.S., 1934, 699—701).—The light green compound, m.p. 152—155° (decomp.), given the formula $\text{MnCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ by Reitzenstein (A., 1899, i, 160) is actually $(\text{C}_5\text{H}_5\text{NH})_2\text{MnCl}_4$ (I) and is also obtained from $\text{MnCl}_2 \cdot \text{HCl} \cdot \text{C}_5\text{H}_5\text{N}$, by Pincussohn's method [A., 1897, i, 540, this author's compound being a mixture of (I) and a pink compound $\text{MnCl}_2 \cdot \text{C}_5\text{H}_5\text{NHCl} + \text{H}_2\text{O}$], or from hot solutions of anhyd. MnCl_2 and dry $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ in abs. EtOH. The corresponding $(\text{C}_5\text{H}_5\text{NH})_2\text{MnBr}_4$, m.p. 173° (Meyer *et al.*, A., 1900, ii, 77), is also light green, the colour of these salts being due to MnCl_4'' . By similar methods from quinolinium halides (QH_X) are obtained the compounds $(\text{QH})\text{MnCl}_3 + 2\text{H}_2\text{O}$ and $+\text{H}_2\text{O}$, $(\text{QH})_2\text{MnCl}_4$, and $(\text{QH})_2\text{MnBr}_4 + 2\text{H}_2\text{O}$ and anhyd. J. W. B.

Oxidation of homologous pyridines and quinolines by selenium dioxide. M. HENZE (Ber., 1934, 67, [B], 750—753).—The base is heated with SeO_2 in presence of xylene or amyl alcohol (to moderate the sudden violence of the action) for several hr. at about 125°. Pure $\text{C}_5\text{H}_5\text{N}$ is unaffected, whereas 2-methylpyridine affords pyridine-2-carboxylic acid with small amounts of pyridine-2-aldehyde. 3-Methyl- and 2:6-dimethyl-pyridine give the corresponding acids. Quinoline is unaffected, whereas 2-methylquinoline affords quinoline-2-carboxylic acid and -2-aldehyde (I), m.p. 71° (hydrate, m.p. 51°; *hydrazone*, m.p. 195—198° after subliming at 180°; *p-nitrophenylhydrazone*, m.p. 250°; condensation product, m.p. 261°, formed by action of KCN). Use of a smaller proportion of SeO_2 and lower temp. does not improve the yield of (I). Oxidation of 3-methyl-2-ethylquinoline affords mainly 3-methylquinoline-2-carboxylic acid, m.p. 142° (Cu salt). Application of the process to technical pyridines discloses the presence of higher homologues. H. W.

High-boiling bases from anthracene oil. S. K. GANGULI and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 197—206).—The fraction, b.p. 180—200°/30 mm., of the bases on oxidation to the carboxylic acids and esterification with $\text{C}_6\text{H}_4\text{Ph} \cdot \text{CO} \cdot \text{CH}_2\text{Br}$ gives the phenylphenacyl esters, m.p. 208°, 201°, 101°, the first being derived from quinoline- or isoquinoline-dicarboxylic acid (?). The fraction, b.p. 100—105°/2 mm., affords *picrates*, m.p. 230° (salt from PtCl_4 , m.p. 220°; base, unknown dimethylquinoline), m.p. 181° (salt from PtCl_4 , m.p. 202—203°; base, unknown monomethylisoquinoline), and m.p. 212° [salt from PtCl_4 , m.p. 256—257° (decomp.); base, dimethylquinoline or -isoquinoline]; the fraction, b.p. 105—110°/2 mm., yields *picrates*, m.p. 201° (salt from PtCl_4 , m.p. 207°; base, monomethylisoquinoline), m.p. 203° [salt from PtCl_4 , m.p. 218° (decomp.); base, dimethylquinoline or -isoquinoline] and m.p. 198° [salt from PtCl_4 , m.p. 234° (decomp.); base, 5:8-dimethylquinoline]. F. R. S.

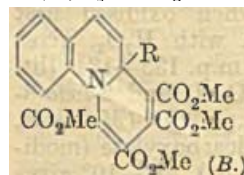
Syntheses in the hydroaromatic series. XIX. Diene syntheses with heterocyclic nitrogen compounds. VII. Primary products in diene syntheses with pyridine, quinoline, and 2-methylquinoline. O. DIELS and K. ALDER [with W. FRIEDRICHSEN, PETERSEN, BRODERSEN, and KECHE] (Annalen, 1934, 510, 87—128).—The labile red com-

pound (I), m.p. 124° (A., 1932, 1144) (improved prep. described), from Me acetylenedicarboxylate (II) and $\text{C}_5\text{H}_5\text{N}$ shows two absorption max. whilst Me quinolizine-1:2:3:4-tetracarboxylate (III) exhibits four. (I) is isomerised to (III) by heat, acids, and various solvents (at different rates). (I) is thus converted by 30% HBr into (mainly) (III) and a little $\text{CHMe}:\text{CH}:\text{CHO}$. Hydrolysis (50% KOH) of (I) gives $\text{C}_5\text{H}_5\text{N}$, $\text{H}_2\text{C}_2\text{O}_4$, aconitic acid (IV), a compound, $\text{C}_{12}\text{H}_9\text{O}_6\text{N}$, decomp. about 140° [*hydrochloride*, m.p. 185° (decomp.)], and the dicarboxylic acid, m.p. 229°, previously described (*loc. cit.*; A., 1933, 1058). These results are explained by assigning structure (A) to (I); alkaline hydrolysis involves addition of



H_2O and the resulting pyridinium hydroxide decomposes to $\text{C}_5\text{H}_5\text{N}$ and $\text{CO}_2\text{Me} \cdot \text{CH}:\text{C}(\text{CO}_2\text{Me}) \cdot \text{C}(\text{CO}_2\text{Me}) \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{Me}$ [which gives $\text{H}_2\text{C}_2\text{O}_4$ and (IV)]. (I) and CH_2N_2 in $\text{Et}_2\text{O} \cdot \text{C}_6\text{H}_6$ afford two isomeric adducts, $\text{C}_{18}\text{H}_{19}\text{O}_8\text{N}_3$, m.p. 159° (decomp.) (V) and 169° (decomp.) (VI), both hydrolysed (conc. HCl) to $\text{C}_5\text{H}_5\text{N}$ and pyrazole-4:5-dicarboxylic acid (VII). (V) is reduced (H_2 , Pd, MeOH) to a tetrahydro-derivative, m.p. 189° [also hydrolysed (conc. HCl) to (VII)], whilst (VI) similarly gives a dihydro-derivative, m.p. 155°. (III) does not react with CH_2N_2 in C_6H_6 . (I) is oxidised by $\text{Hg}(\text{OAc})_2$ in AcOH to the ester (VIII) (cf. A., 1933, 1058). (I) and Et azodicarboxylate in C_6H_6 give an adduct, $\text{C}_{23}\text{H}_{27}\text{O}_{12}\text{N}_3$, m.p. 170°, which absorbs 8H on reduction (H_2 , PtO₂, AcOH); in MeOH, the Me methoxyquinolizine-1:2:3:4-tetracarboxylate, m.p. 160°, previously described (*loc. cit.*) results.

A labile adduct (IX), $\text{C}_{21}\text{H}_{19}\text{O}_8\text{N}$, m.p. 177°, yellow, is also obtained from quinoline and (II) in C_6H_6 . (IX) passes when heated to 195° or treated with conc. H_2SO_4 into the stable isomeride (X) (B, R=H), m.p. 234°, red. (IX) and (X) are oxidised [HNO_3 (d 1.17) or CrO_3] to a compound, $\text{C}_{18}\text{H}_{15}\text{O}_6\text{N}$, m.p. 1.9°, which is hydrolysed (50% KOH) to a substance $\text{C}_{14}\text{H}_9\text{O}_4\text{N}$, m.p. 259° (decomp.). (IX) is hydrolysed



(16.6% KOH) to quinoline and $\text{H}_2\text{C}_2\text{O}_4$. Hydrolysis (24% KOH) of (X) gives 2-methylquinoline; with 5% KOH, a dicarboxylic acid, $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}$, m.p. 247°, results. (IX) and CH N_2 in C_6H_6 afford an adduct, $\text{C}_{22}\text{H}_{21}\text{O}_8\text{N}_3$, m.p. 153°, hydrolysed (conc. HCl) to quinoline and (VII); (X) does not react with CH_2N_2 . (IX) is reduced (H_2 , Pd, MeOH) to a dihydro-derivative, m.p. 151°, but (X) is similarly unaffected. (X) could not be reduced using H_2 , PtO₂, and AcOH, (IX) gives a tetrahydro-derivative, m.p. 177°. The ester (B, R=OMe), m.p. 150°, is obtained from (IX) and Et azodicarboxylate in MeOH. Oxidation (H_2O_2 , AcOH) of (IX) or (X) gives quinoline-2-carboxylic acid 1-oxide, m.p. 171° (decomp.).

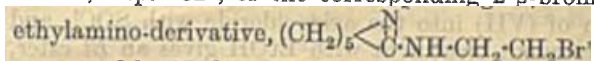
The stable red adduct (XI) (B, R=Me), m.p. 204°

(A., 1932, 1145) [from 2-methylquinoline and (II)], and Br in AcOH give a *tetrabromide*, m.p. 145—147° (decomp.), which is reduced (Zn dust, H₂O) to (XI), and converted by aq. HClO₄ into a *bromide perchlorate*, C₂₂H₂₁O₈NBrClO₄, m.p. 217° (previous decomp.), and by HCO₂H into a *dibromide*, C₂₂H₂₁O₈NBr₂, m.p. 145°. (XI) is reduced (H₂, PtO₂, AcOH) to a *dihydro-derivative* (XII), m.p. 164°, whilst the labile yellow adduct (XIII) (*loc. cit.*) similarly gives a *dihydro-*, m.p. 125°, and then a *tetrahydro-*, m.p. 170°, -derivative. (XI) is oxidised [HNO₃ (d 1.4) or CrO₃-AcOH] to a *base*, C₂₂H₂₁O₉N, m.p. 138° [nitrate, m.p. 215° (decomp.)], reduced (H₂, PtO₂, AcOH) to a *decahydro-derivative*, m.p. 181°. Hydrolysis (dil. MeOH-KOH) of (XII) gives an *acid*, C₂₁H₂₁O₈N, m.p. 247—248°, whilst (XI) is hydrolysed (conc. HCl) to a *tricarboxylic acid*, C₁₇H₁₃O₆N.H₂O, decomp. 245°, decarboxylated (CaO) to 2-methylquinoline. (XIII) and CH₂N₂ in C₆H₆ give an *adduct*, C₂₃H₂₃O₈N₃, m.p. 138°, hydrolysed (conc. HCl) to (VII). Structures are suggested for many of the above compounds. H. B.

Hypnotics containing the α -ethylpropyl group; syntheses with higher esters of *p*-toluenesulphonic acid. D. L. TABERN and E. H. VOLWILER (J. Amer. Chem. Soc., 1934, 56, 1139—1142).—CHET₂Br (I), b.p. 118.5—119.5°, prepared from CHET₂OH (II) and HBr in H₂ at -25° to -20°, does not react with CHNa(CO₂Et)₂ in C₆H₆. *p*-C₆H₄Me·SO₂Cl and (II) in C₆H₆-C₅H₅N give α -ethylpropyl *p*-toluenesulphonate (III), m.p. 32—35°, which decomposes on attempted distillation. CNaEt(CO₂Et)₂ and (III) in C₆H₆ afford Et ethyl- (α -ethylpropyl)malonate, b.p. 155—160°/45 mm., which condenses with CO(NH₂)₂ to give 5-ethyl-5- α -ethylpropylbarbituric acid (IV), m.p. 158.5—159.5°. CN·CHNa·CO₂Et and (I) in EtOH at 50—60° afford CN·CH(CHET₂)·CO₂Et, ethylated (NaOEt, EtBr at 60°) to Et ethyl- (α -ethylpropyl)cyanoacetate, b.p. 150—155°/40 mm. This with CO(NH₂)₂ and NaOEt at 100—110° gives [after hydrolysis (dil. H₂SO₄)] (IV). 5-Methyl-, m.p. 204—206°, 5-n-propyl-, m.p. 130—133°, and 5-n-butyl-, m.p. 126—127°, -5- α -ethylpropylbarbituric acids are similarly prepared. 5-Allyl-5- α -ethylpropylbarbituric acid, m.p. 129—130°, is obtained from 5- α -ethylpropylbarbituric acid and allyl bromide in aq. KOH containing a little CuSO₄. 5-Methyl-, m.p. 180—182°, 5-ethyl-, m.p. 128—129°, 5-n-propyl-, m.p. 85—88°, 5-n-butyl-, m.p. 110—111°, and 5-allyl-, m.p. 98—100°, -5- α -methylbutylbarbituric acids are prepared by the malonate method; they are more efficient hypnotics than the corresponding α -ethylpropyl derivatives. H. B.

Preparation of dihydroimidazoles [glyoxalidines]. R. STOLLE, M. MERKLE, and F. HANUSCH (J. pr. Chem., 1934, [ii], 140, 59—64).—NH·CPh·OEt (I) and CH₂Br·CH₂·NH₂·HBr (II) in EtOH-NaOEt give 2-phenyl-4 : 5-dihydroglyoxaline; NMe·CPh·OMe (in NaOMe-NaOH) affords the corresponding 1-Me derivative only as its *picrate*, sinters 116°, m.p. 130°, but with the *N*-Ac derivative of (I) only a *picrate*, m.p. 146° (not pure), is obtained. 2-Ethoxy- Δ^1 -homopiperidine and (II) in boiling EtOH give the *hydro-*

bromide, m.p. 182°, of the corresponding 2- β -bromo-



converted by NaOEt-EtOH into 1 : 2-pentamethylene-4 : 5-dihydroglyoxaline, b.p. 105—107°/15 mm. [*hydrobromide*, m.p. 172°; *picrate*, m.p. 166°; *urate* (base : acid = 2 : 1) and (1 : 1), m.p. 250°], hydrolysed by conc. HCl at 120° to the *dihydrochloride* of ϵ -(2-aminoethylamino)-*n*-hexoic acid [*picrate*, m.p. 147°; *dipicrate*, m.p. 144°, *di*(phenylurethane), m.p. 143°, and *dihydrochloride*, m.p. 196°, of its Me ester]. J. W. B.

Structure of monotrityluridine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1934, 105, 419—430).—5-Monotrityluridine (I) with MeI and Ag₂O in COMe₂ gives a *Me*₃ derivative, m.p. 177—178°, [α]_D²⁵ +96.1°, which on hydrolysis (HCl in abs. MeOH) gives 2 : 3-dimethyluridine (II), m.p. 168—169°, and therefore has one Me in the uracil nucleus. In C₅H₅N (II) gives a (5)-*p*-toluenesulphonyl derivative which with NaI in COMe₂ gives the corresponding *I*-derivative, m.p. 94°, indicating the presence of the *p*-C₆H₄Me·SO₂ group, and hence of the original trityl group, in the 5-position (cf. A., 1932, 254). (I) on the other hand gives a *di-p*-toluenesulphonate, [α]_D²⁵ +27.7°, hydrolysed by HCl-MeOH to 2 : 3-di-*p*-toluenesulphonyluridine, m.p. 199°, [α]_D²⁵ -26.6°, which is unaffected by NaI. Action of *p*-C₆H₄Me·SO₂Cl in C₅H₅N on uridine gives 5-*chloro*-2 : 3-di-*p*-toluenesulphonyluridine, m.p. 170—171°, [α]_D²⁵ -9.3°, which with NaI gives the corresponding 5-*I*-compound, m.p. 160° (darkens 130°), [α]_D²⁵ -25°. Ditrityluridine has m.p. 223—224°, [α]_D²⁵ +91.4°. All vals. of [α]_D are in COMe₂. H. A. P.

Hydrogenation of cyclic ureides under elevated temperatures and pressures. I. 2-Keto-1 : 2 : 3 : 4-tetrahydropyrimidines. K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 1180—1185).—Et 2-keto-4-phenyl-6-methylhexahydropyrimidine-5-carboxylate (I), m.p. 231.5—233.5° (all m.p. are corr.), and a small amount of an *isomeride*, m.p. 175—177.5°, are obtained by reduction [H₂ and Cu-Ba-Cr oxide at 200° (method *a*)] of the 1 : 2 : 3 : 4-tetrahydro-derivative (II). (I) is further reduced [H₂ and Ni at 145° (method *b*)] to Et 2-keto-4-cyclohexyl-6-methylhexahydropyrimidine-5-carboxylate (III), m.p. 181—184.5°, also obtained by reduction [H₂ and Ni at 175° (method *c*)] of (II). Reduction (method *b* or *Pt*) of (II) gives Et 2-keto-4-cyclohexyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate (A., 1933, 515), reduced (method *a*) further to (III). Et 2-keto-4-styryl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate (IV) is reduced (H₂ and Cu-Ba-Cr oxide at 150°) to the 4- β -phenylethyl derivative, which is then reduced (method *a*) to Et 2-keto-4- β -phenylethyl-6-methylhexahydropyrimidine-5-carboxylate (V), m.p. 160.5—162.5°. Reduction (method *c*) of (IV) affords Et 2-keto-4- β -cyclohexyl-6-methylhexahydropyrimidine-5-carboxylate (VI), m.p. 147—152°. Hydrolysis (EtOH-NaOH) of (I), (III), (V), and (VI) gives 2-keto-4-phenyl- (VII), m.p. 256.5—258°, -4-cyclohexyl- (VIII), m.p. 290—291° (*loc. cit.*), -4- β -phenylethyl- (IX), m.p. 275—276°, and -4- β -cyclohexylethyl-, m.p. 296—297°, -6-methylhexahydro-

pyrimidine-5-carboxylic acid, respectively. Conversion of (VII) into the acid chloride with SOCl_2 and subsequent treatment with EtOH gives an *Et* ester, m.p. 178—179.5°, which differs from (I) and is hydrolysed to (VII); (VIII) similarly affords *Et* esters, m.p. 161—162° and 169—170.5°, whilst (IX) gives an *Et* ester, m.p. 145.5—147°. H. B.

Nucleic acids. IV. Constitution of the pyrimidine-nucleotides. H. BREDERECK (Z. physiol. Chem., 1934, 224, 79—85; cf. this vol., 394).—Deamination of cytidylic acid (I) with HNO_2 gives uridylic acid (II), isolated as the *dibrucine* salt, which with $\text{C}_5\text{H}_5\text{N}$ and CPh_3Cl affords triphenylmethyluridylic acid (III) as the *monobrucine* salt, m.p. from 184°, $[\alpha]_D^{20} -26.2^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Elimination of brucine with aq. NH_3 gives the NH_4 salt, m.p. 165—170° (corr.), $[\alpha]_D^{20} +32.6^\circ$ in $\text{C}_5\text{H}_5\text{N}$. (III) yields *Na*, m.p. 170—175°, *Na*₂, m.p. 215—220°, and hence *Pb*, m.p. 211—213°, salts. Therefore in (I) and (II), H_3PO_4 is attached to a *sec. C*, probably atom 3. In confirmation, (I) and (II) do not yield complexes of greater dissociation const. with H_3BO_3 . J. H. B.

ψ -Bases. V. Reactions of *N*-methyldihydropyrazinium salts and their derivatives. J. G. ASTON, D. E. AILMAN, C. H. SCHEUERMANN, and J. M. KOCH (J. Amer. Chem. Soc., 1934, 56, 1163—1166).—When 6-hydroxy-1:2:2:5:5-pentamethyltetrahydropyrazine (I) is heated with MeOH and EtOH, 6-methoxy- (II), b.p. 111.5—113°/27 mm., and 6-ethoxy-, b.p. 118—122°/30 mm., -1:2:2:5:5-pentamethyltetrahydropyrazine, respectively, are formed. (II) is also obtained from 1:2:2:5:5-pentamethyldihydropyrazinium iodide (III) and MeOH-NaOMe. 1:2:2:3:5:5:6-Heptamethyldihydropyrazinium iodide (IV) and MeOH-NaOMe similarly give 1:2:2:3:5:5-hexamethyl-6-methylenetetrahydropyrazine (V) (A., 1931, 367). (I) or (III) and $\text{CH}_3\text{Ph}\cdot\text{MgCl}$ afford 6-benzyl-1:2:2:5:5-pentamethyltetrahydropyrazine, b.p. 192—194°/30 mm., m.p. 63—64°. 6-Phenyl-1:2:2:5:5-pentamethyl-, b.p. 146.5—154°/10 mm., and 1:2:2:5:5:6-hexamethyl-, b.p. 72—74°/13 mm., -tetrahydropyrazines are obtained from (I) and MgPhBr and MgMeI , respectively. (IV) and $\text{CH}_2\text{Ph}\cdot\text{MgCl}$ give 6-benzyl-1:2:2:3:5:5:6-heptamethyltetrahydropyrazine, b.p. 210—213°/28 mm. (V) does not form additive compounds with Grignard reagents. (I) is converted by boiling *N*-NaOH into 2:2:5:5-tetramethyldihydropyrazine. H. B.

Reduction of isatin. A. WAHL (Chim. et Ind., 1934, 31, Spec. No., 761—762).—In cold MeOH isatin (I) is almost quantitatively reduced by H_2S to dithioisatin, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2\text{S}_2$, which, slowly in cold but more rapidly in warm $\text{C}_5\text{H}_5\text{N}$, passes into *isoindigotin* and *oxindole*. Interaction of (I) and H_2S in $\text{C}_5\text{H}_5\text{N}$ affords isatan, $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{C}(\text{OH})\text{CH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{NH}$, m.p. about 260° (slight decomp.). H. W.

1-Arylindazoles. W. BORSCHKE and K. DIACONT (Annalen, 1934, 510, 287—297).— PhN_2Cl and 2:4-(NO_2)₂ $\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ in MeOH + NaOAc at 0° give

the phenylhydrazone, m.p. 182—183°, of Me 2:4-dinitrophenylglyoxylate (I), which with *N*-NaOH in boiling MeOH loses HNO_2 and affords 6-nitro-1-phenylindazole-3-carboxylic acid, m.p. 272° (decomp.). This at 280° gives 6-nitro-1-phenylindazole, m.p. 120°, reduced (H_2 , Pd-C, MeOH) to 6-amino-1-phenylindazole (II), m.p. 150°. Reduction (H_2 , Pd-C, MeOH) of 6-iodo-1-phenylindazole, m.p. 156°, affords 1-phenylindazole, m.p. 78° (platinichloride, m.p. 170°), also prepared by diazotisation of (II) and subsequent treatment with EtOH or H_3PO_2 . The *o*-tolylhydrazone, m.p. 185°, *anisylhydrazone*, m.p. 170°, *o*- (III), m.p. 185°, *m*-, m.p. 198—199°, and *p*-, m.p. 228—230°, -nitrophenylhydrazones, *o*-carboxyphenylhydrazone (IV), m.p. 262°, β -naphthylhydrazone, m.p. 170°, and 1-phenyl-6-indazolylhydrazone, m.p. 232°, of (I) are similarly prepared. (III) and (IV) are hydrolysed (as above) to the *o*-nitrophenylhydrazone, m.p. 205°, and *o*-carboxyphenylhydrazone, m.p. 225° (decomp.), respectively, of 2:4-dinitrophenylglyoxylic acid; the remainder give 6-nitro-1-*o*-tolyl-, m.p. 245° (decomp.), -1-*anisyl*-, m.p. 265° (decomp.), -1-*m*-, m.p. 248° (decomp.), and -1-*p*-, m.p. 275° (decomp.), -nitrophenyl-, -1- β -naphthyl-, m.p. 268° (decomp.), and -1-1'-phenyl-6'-indazolyl-, m.p. 295°, -indazole-3-carboxylic acids. 6-Nitro-1-*anisyl*-, m.p. 128—130°, -1-*m*-nitrophenyl-, m.p. 163°, -1- β -naphthyl-, m.p. 135°, and -1-1'-phenyl-6'-indazolyl-, m.p. 185°, -indazoles are prepared by thermal decomp. of the appropriate acids. Me 2-nitro-4-carbomethoxyphenylacetate (V) (improved prep.; cf. A., 1917, i, 15) and PhN_2Cl similarly give the phenylhydrazone, m.p. 177°, of Me 2-nitro-4-carbomethoxyphenylglyoxylate; hydrolysis affords the phenylhydrazone, m.p. 208° (decomp.), of 2-nitro-4-carboxyphenylglyoxylic acid. (V) and *isoamyl* nitrite in MeOH-NaOMe give the *oxime*, m.p. 208° (decomp.), of Me 2-nitro-4-carboxyphenylglyoxylate, hydrolysed (*N*-NaOH) to 3-hydroxy-4-cyanobenzoic acid, m.p. > 300° (formed by way of benzisooxazole-3:6-dicarboxylic acid). Me 4-nitro-2-carbomethoxyphenylacetate and PhN_2Cl in MeOH + NaOAc give Me 7-nitro-1-keto-2-phenyl-1:2-dihydroquinoxaline-4-carboxylate, m.p. 218° [free acid, m.p. 238° (decomp.)]; with *isoamyl* nitrite, the *Me*₁ ester, m.p. 145—150° (decomp.), of 4-nitro-2-carboxyphenylglyoximic acid results. H. B.

Photochemical behaviour of lactoflavin; model experiments in the quinoxaline series. R. KUHN and F. BAR (Ber., 1934, 67, [B], 898—904).—Irradiation of 2-tetrahydroxybutylquinoxaline (I) [obtained by condensation of *d*-glucose with *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$] in alkaline solution with ultra-violet light results in the production of quinoxaline, with consequent disappearance of optical activity. (I) gives an *o*- C_6H_4 derivative, m.p. 120°, $[\alpha]_D^{20} -29.3^\circ$ in $\text{C}_5\text{H}_5\text{N}$. There is therefore a very close resemblance between (I) and lactoflavin (II) which does not extend to their behaviour towards acids and oxidising agents. Possibly 3 C of the tetrahydroxybutyl group are photochemically removed, leaving an aldehyde which Cannizzaro change passes into the acid which suffers decarboxylation. (II) resembles alloxazine (I), $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{NH} \cdot \text{CO} \\ \text{N} \cdot \text{C} \cdot \text{CO} \cdot \text{N} \end{smallmatrix}$, and dimethylalloxazine (IV) in

forming a bright red, radical-like intermediate when reduced by Zn, Sn, or Na-Hg in strongly acid solution. This change is not shown by quinoxaline (V) or 2-hydroxyquinoxaline (VI), and appears to be due to the presence of the intact, alkali-labile pyrimidine ring. The absorption spectra of (II) and (III) are very closely similar. Alkaline hydrolysis of (III) leads to 2-hydroxyquinoxaline-3-carboxylic acid, m.p. 265° (decomp.) when rapidly heated, which passes by loss of CO₂ into (VI). (IV) can be obtained by the action of MeI on the Ag salt of (III), thus establishing the presence of two active H in (III). (IV) in EtOH has marked blue fluorescence reversibly discharged by mineral acid and slowly destroyed by alkali by hydrolytic fission of the pyrimidine ring. (V) and benziminazole (VII) in H₂O do not fluoresce, whereas 2:3-dihydroxyquinoxaline in dil. Na₂CO₃ has strong blue fluorescence destroyed by Na₂S₂O₄, but recurring in presence of air. Pentahydroxy-*n*-amylbenziminazole, m.p. 246° (decomp.), $[\alpha]_D^{20} +50^\circ$ in C₅H₅N, +52.5° in AcOH, yields very little (VII) when irradiated; its Ac₆ derivative has m.p. 179°, $[\alpha]_D^{20} +75^\circ$ in C₆H₅N.

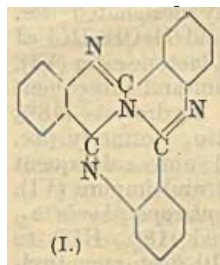
Action of acid chlorides on aryl- β -naphthylamineazo-compounds. F. KROLLPFEIFFER [with G. WOLF and H. WALBRECHT] (Ber., 1934, 67, [B], 908—916).—The action of boiling BzCl on benzeneazophenyl- β -naphthylamine (I) in presence or absence of air gives 2 : 3-diphenyl- α - β -naphtha-1 : 2 : 3-triazolium chloride, $\left[\text{C}_{10}\text{H}_6 \begin{array}{c} \text{NPh} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \text{NPh} \right] \text{Cl}$ (II) or

$\left[\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NPh} \end{array} \text{NPh} \right] \text{Cl}$ (II'), *chloro-1:2-diphenyl- α -naphthiminazole*, m.p. 207.5—208.5°, *ang.-naphtha-phenazine* (III), NHPhBz (IV), NPhBz , $\alpha\text{-C}_{10}\text{H}_7\text{-NPhBz}$, C_6H_6 , HCl , and N_2 . At room temp. little (I) is produced, the main products being (III) and (IV). BzCl and (I) in presence of $\text{C}_5\text{H}_5\text{N}$ yield the *Bz* derivative, m.p. 186—187°, (II), and Cl -compounds. Formation of (II) is not induced by AcCl , CH_2PhCOCl , or POCl_3 , and only to a slight extent by SOCl_2 or crotonyl chloride. With $p\text{-C}_6\text{H}_4\text{MeSO}_2\text{Cl}$ in boiling xylene the *p-toluenesulphonate*, m.p. 225—226°, of (II) is formed in 70% yield. SO_2Cl_2 reacts violently with (I) with elimination of PhN_2Cl and formation of substitution or additive products of Cl and $\text{C}_{10}\text{H}_7\text{-NHPH}$, but not of (II). Cautious chlorination of (I) in AcOH leads to elimination of PhN_2Cl . SO_2Cl_2 and NHPH_2 smoothly afford 2:4:2':4'-*tetrachlorodiphenylamine*, m.p. 141—142°. HNO_3 converts (I) into *tetranitrodiphenylamine*, m.p. 254—255° (decomp.), also obtained from *p*-chlorobenzeneazo-phenyl- β -naphthylamine, whereas benzeneazo-*p*-chlorophenyl- β -naphthylamine gives a mixture of di- and tri-nitrated *p*-chlorophenyl- β -naphthylamines. Non-cryst. *benzeneazodi-p-tolylamine* is converted by amyl nitrite in boiling AcOH into 2-phenyl-3-*p*-tolyl-*o*-methylbenzo-1:2:3-triazolium picrate, m.p. 156.5—157.5° [corresponding chloride, m.p. 196—197° (decomp.) after softening]. W.

Tricycloquinazoline. I. J. KOZAK and A. KALMUS (Bull. Acad. Polonaise, 1933, A, 532—539). By heating $o\text{-NH}_2\cdot\text{C}_6\text{H}\cdot\text{CHO}$ with NH_4Cl at 230° a 22%

yield of *tricycloquinazoline* (I), m.p. 308—310°, is obtained. With AcOH-HNO_3 (*d* 1.32) (I) gives a $(\text{NO}_2)_3$ -decomp. $> 360^\circ$, and with AcOH-HNO_3 (*d* 1.52) a $(\text{NO}_2)_6$ -, not melting at 400° , -derivative. With Cl_2 in AcOH solution (I) gives a Cl_3 -derivative, m.p. $344\text{--}346^\circ$ [$(\text{NO}_2)_3$ -derivative, decomp. 400°], and with hot 60% oleum, a hexasulphonic acid as its *Ba* salt.

Oxidation of (I) with $\text{Na}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$ gives 4-hydroxyquinazoline (*picrate*, m.p. 204°). J. W. B.

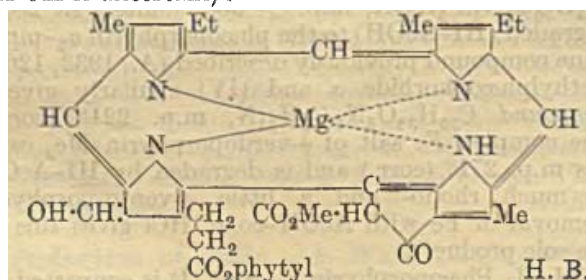


Chlorophyll. XLV. Partial synthesis of chlorophyllide *a*. H. FISCHER and G. SPIELBERGER. XLVI. Oxidation products of phæophorbide *a* and phæoporphyrin *a*₅. H. FISCHER, J. HECKMAIER, and T. SCHERER. XLVII. Chlorophyll *b*. IV. Conversion of rhodinoporphyrin *g*₇ into rhodinoporphyrin *g*₈. H. FISCHER and S. BREITNER (Annalen, 1934, 510, 156—169, 169—182, 183—192). —XLV. A mixture of Et₂O-MgEtBr and Mg is evaporated to dryness in absence of O₂ and the residue treated successively with EtOH, C₅H₅N, and methylphæophorbide *a* (in C₅H₅N); a chlorophyllide (I), C₃₇H₃₈O₅N₄Mg (which appears to consist largely of ethylchlorophyllide), is thus obtained. (I) gives a good phase test and is degraded (HI) to phæoporphyrin *a*₅ ester. (I) (in EtOH) absorbs approx. 1 mol. of O₂; subsequent degradation (HI) gives 10-ethoxyphæoporphyrin *a*₅ (II), phæoporphyrin *a*₇ Et ester, and some rhodoporphyrin. Allomerisation of (I) with benzoquinone-EtOH in N₂ and subsequent reduction (HI) gives (II). Ethylchlorophyllide *a*, C₃₇H₃₈O₅N₄Mg, prepared [as (I)] from ethylphæophorbide *a*, is converted by MeOH-CH₂N₂ into chlorin *e* ester. Contrary to Stoll and Wiedemann (this vol., 308) phæophorbide *a* (III) is readily oxidized in C₅H₅N; the resulting oxime is identical with that obtained (*loc. cit.*) by hydrolysis of methylphæophorbide *a*-oxime. (III) and piperidine (IV) in MeOH give a compound C₃₅H₃₆O₄N₄C₅H₁₁N, m.p. > 300° (sinters at 280°), degraded (HI-AcOH) to the phæoporphyrin *a*₅-piperidine compound previously described (A., 1932, 1264). Methylphæophorbide *a* and (IV) similarly give a compound C₃₆H₃₈O₅N₄C₅H₁₁N, m.p. 221° (corr.). The complex Fe salt of *ψ*-verdoporphyrin Me₂ ester has m.p. 271° (corr.) and is degraded by HI-AcOH to much rhodo- and a little *ψ*-verdo-porphyrin (removal of Fe with AcOH-conc. HCl gives this as the sole product).

XLVI. Phæoporphyrin a_5 ester (I) is converted by EtOH-I into 10-ethoxyphæoporphyrin a_5 [previously described (A., 1932, 757) as a phæoporphyrin a_6 ester], hydrolysed (18% HCl) to phæoporphyrin a_7 Et ether (II), m.p. 287° [formerly designated (*loc. cit.*) isophæoporphyrin a_7] (Cu salt), which is degraded (HI-AcOH) to rhodoporphyrin ester (III). Hydrolysis (hot 30% MeOH-KOH) of (II) gives (III); in the cold, rhodoporphyrin- γ -carboxylic acid and its anhydride result. (II) is converted by conc. H_2SO_4 into (after esterification with CH_3N_2) phæoporphyrin a_7 Me₃ ester (IV) [formerly described (this vol., 421)

as *allophæoporphyrin a₇* ester]. 10-Hydroxyphæoporphyrin *a₅* ester (V) [previously designated (*loc. cit.*) neophæoporphyrin *a₆* ester] and MeOH-HCl at room temp. give chloroporphyrin *e₇* lactone ester (VI), m.p. 284°, converted by 30% oleum and subsequent esterification (CH₂N₂) into (IV). Hydrolysis (18% HCl) of 10-acetoxyp hæoporphyrin *a₅* [formerly (*loc. cit.*) acetylneophæoporphyrin *a₆*] and subsequent esterification (CH₂N₂) affords (IV) and impure (VI). (I) and MeOH-I give 10-methoxyphæoporphyrin *a₅*, C₃₇H₄₀O₈N₄, m.p. 254°, hydrolysed (18% HCl) to phæoporphyrin *a*-Me ether. 10-Acetoxymethylphæoporphorbid (VII) is hydrolysed (cold 80% H₂SO₄ or MeOH-HCl) to 10-hydroxymethylphæoporphorbid (VIII), m.p. 280°, degraded (HI-AcOH) to (V). (VII) and a little HI in AcOH give oxoacetoxyp hæoporphyrin *a₅*, C₃₈H₃₈O₈N₄, m.p. 307°. (VII) is converted by Et₂O-CH₂N₂ in MeOH-C₅H₅N into a chlorin, m.p. 261°. (VIII) and 10% NaOH in Et₂O afford an unstable chlorin, converted by CH₂N₂ into phæopurpurin 7; (V) similarly gives (IV), whilst (VI) furnishes chloroporphyrin *e₅*. Prolonged treatment of phæoporphyrin *a*-Me₁ ester with Et₂O-CH₂N₂ in MeOH-C₅H₅N gives [by way of (IV)] phæoporphyrin *a*-Me₂ ester Me ether. Structures are suggested for several of the above compounds.

XLVII. The complex *Fe* salt of rhodinoporphyrin *g*-Me₃ ester (I) (A., 1933, 1173) and HI (*d* 1.96) in AcOH and air give rhodinoporphyrin *g₈* (II), C₃₇H₄₀O₈N₄, m.p. 285° (decomp.), which contains 3 CO₂Me and 1 CO₂H [which probably arises from the CO group of (I)] and is esterified (CH₂N₂) to the Me₄ ester, m.p. 268°. (II) does not give an oxime. Rhodin *g* Me₃ ester is similarly converted into rhodinoporphyrin *g*-. (II) and 48% HBr at 220° afford a porphyrin, which with Br in AcOH gives a compound, C₃₀H₃₀O₂N₄Br₂, resembling pyrroporphyrin. Prolonged treatment of phæoporphorbid *b* with Et₂O-25% HCl gives rhodin *g* (III) and pyrophæoporphorbid *b*. (III) is converted by MeOH-NaOMe in C₅H₅N-N₂H₄ at 137–142° into phylloporphyrin. Chlorophyll *b* is formulated as follows (the position of the CH-OH is uncertain):



Synthesis of indolenines. II. 3-Methyl-3-β-oxyethylindolenine. T. HOSHINO (Proc. Imp. Acad. Tokyo, 1934, 10, 159–160).—Et β-indolylacetate has m.p. 42–43° (cf. A., 1931, 97). The Grignard compound from tryptophol, m.p. 58–59° (*loc. cit.*), with MeI gives 4-methyl-1:2-dihydrofuroindolenine (I), m.p. 42–43°, b.p. 110–112°/2 mm. The *Ac*, m.p. 74–75°, and *Bz*, m.p. 151–152°, derivatives are insol. in dil. acids, and regenerate (I)

with MeOH-KOH. Hence it is concluded that (I) has the annexed structure. A. A. L.

Condensation of 1:8-naphthalyl chloride with *m*-ethylcarbonatodimethylaniline. W. R. BROWN and F. A. MASON (J.C.S., 1934, 651–653; cf. A., 1933, 1173).—*m*-OH·C₆H₄·NMe₂ and ClCO₂Et in 10% NaOH at 0° afford *m*-ethylcarbonatodimethylaniline, b.p. 160–164°/13 mm., which with 1:8-naphthalyl chloride at 0° in C₂H₂Cl₄ containing AlCl₃ during 24 hr. gives 4':4''-bisdimethylamino-2':2''-diethylcarbonatodiphenyl-1:8-naphthalide (I), m.p. 253–254° (decomp.), converted by 10% NaOH into the rhodamine dye which dyes silk bluish-red. (I) when boiled with MeOH-Ba(OH)₂ and treated with H₂SO₄ affords 4':4''-bisdimethylamino-2'-hydroxy-2''-ethylcarbonatodiphenyl-1:8-naphthalide sulphate (?), m.p. 176–180° (decomp.), converted into (I) with NaOH.

J. L. D.

Formation and stability of polybromide derivatives of heterocyclic compounds. III. Bromination of *μ*-substituted benzthiazoles. M. A. S. CHAUDHRI, R. D. DESAI, and R. F. HUNTER (J. Indian Chem. Soc., 1934, 11, 249–256; cf. A., 1933, 284).—1-Chlorobenzthiazole (I) and Br in CHCl₃ give a dibromide (A., 1925, i, 987) with partly labile Br; H₂SO₃ gives (I). 1-Phenylbenzthiazole (II) similarly gives a dibromide, m.p. 119° [converted into (II) with H₂SO₃], and a tetrabromide (III) (cf. A., 1930, 483) which cannot have a thiazonium structure (cf. A., 1922, i, 576). 1-Thiolbenzthiazole (prep. described) and Br in CHCl₃ at 0° give benzthiazolyl 1:1-disulphide dihydrotetrabromide, m.p. 127° (decomp.), reduced (H₂SO₃) to benzthiazolyl 1:1-disulphide. Similarly, 1-methylbenzthiazole affords a hydrotribromide (IV), m.p. 70°, of 5(?)-bromo-1-methylbenzthiazole, m.p. 120°, into which it is converted by H₂SO₃. (IV) is probably formed by way of a true Br additive compound. 5-Bromo-1-aminobenzthiazole affords the hydrotribromide (golden-yellow) of 3:5-dibromo-1-aminobenzthiazole (which, when heated, gives Br and a product, m.p. > 285°), reduced (H₂SO₃) to 3:5-dibromo-1-aminobenzthiazole (V), m.p. 261°. 2:4-Dibromoaniline (prep. described) with CSCI₂ in CHCl₃-H₂O affords 2:4-dibromophenylthiocarbimide, m.p. 63°, converted by boiling EtOH-NH₃ into 2:4-dibromophenylthiocarbimide, m.p. 171°, which with Br in boiling CHCl₃ followed by reduction with H₂SO₃ gives (V). (V) in CHCl₃ with Br affords a tetrabromide [converted into (V) by H₂SO₃], which when heated gives Br and a product, m.p. > 285°. Thiobenzanilide with Br in boiling CHCl₃ followed by reduction with H₂SO₃ affords a compound, m.p. 206°, and not 1-phenyl- or 5-bromo-1-phenyl-benzthiazole. J. L. D.

Aminobenzthiazoles. XIII. Nature of the bromo-additive compounds of 5-bromo-1-alkylaminobenzthiazoles obtained from *s-p*-bromophenylalkylthiocarbamides and bromine. M. ALIAZAM, R. F. HUNTER, and N. A. KEAN (J.C.S., 1934, 708–710).—The alleged dibromides of 5-bromo-1-alkyl(R)aminobenzthiazole (A., 1927, 263) are actually hydrodibromides. The following are described: R=Et (I), hydrodibromide, sinters 200–200°, m.p. 240–245° (decomp.), hydrotribromide, labile, m.p. 105°, and stable form, m.p. 140° (decomp.), and hydro-

pentabromide, m.p. 65°. Bromination of (I) with Br-CHCl_3 at 0° affords not the dibromide (*loc. cit.*), but the hydrotribromide of 3(?) : 5-dibromo-1-ethylamino-benzothiazole, m.p. 156—157° [contaminated with the Br-additive compound of (I)], which is obtained by reduction ($\text{SO}_2\text{-H}_2\text{SO}_3$); $\text{R}=\text{Pr}^a$, hydrobromide, m.p. 224°, and hydrodibromide, m.p. 146—147°; $\text{R}=\text{Bu}^a$, hydrobromide, m.p. 194°, and hydrodibromide, m.p. 150°; $\text{R}=\text{Bu}^b$, m.p. 147° (lit. 137°), hydrodibromide, m.p. 126—127°, and hydrotribromide, m.p. 80°; and $\text{R}=\text{isoamyl}$, m.p. 131—132°, hydrodibromide, m.p. 111—112°.

J. W. B.

Synthesis of α -nicotine and α -nornicotine. L. C. CRAIG (J. Amer. Chem. Soc., 1934, 56, 1144—1147).—2-Cyanopyridine and $\text{OEt-CH}_2\text{-CH}_2\text{-CH}_2\text{-MgBr}$ give 2-pyridyl γ -ethoxypropyl ketone, b.p. 125°/5 mm., the oily oxime of which is reduced (Zn dust, EtOH-AcOH) to α -amino- δ -ethoxy- α -2-pyridylbutane, b.p. 132—135°/5 mm. De-ethylation (45% HBr at 140—150°) of this and dehydration of the resulting product with K_2CO_3 in Et_2O gives α -nornicotine (2-2'-pyridylpyrrolidine), b.p. 120°/12 mm. (picrate, m.p. 166°). Methylation (Me_2SO_4 , aq. NaOH) of α -p-toluene-sulphonamido- δ -ethoxy- α -2-pyridylbutane, m.p. 96°, and subsequent treatment with 46% HBr and K_2CO_3 (as above) gives α -nicotine (2-2'-pyridyl-1-methylpyrrolidine), b.p. 122°/25 mm. (picrate, m.p. 169°). Mg 2-pyrryl bromide and $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{-CN}$ give 2-2'-pyrryl-4 : 5-dihydropyrrole, b.p. 144—145°/5 mm., reduced (Zn dust, EtOH-HCl) to (probably) 2-(2 : 5-dihydro-2-pyrryl)pyrrolidine, b.p. 135—140°/12 mm. (phenylthiocarbamate, m.p. 151°; picrate, m.p. 141°). Reduction (H_2 , PtO_2 , EtOH or AcOH) gives (probably) 2-pyrrylpyrrolidine, which decomposes in air to a tar.

H. B.

Alkaloids of ergot. V. Nature of ergine. S. SMITH and G. M. TIMMIS (J.C.S., 1934, 674—675).—Ergine (I) $\text{C}_{16}\text{H}_{17}\text{ON}_3$ (not $\text{C}_{17}\text{H}_{21}\text{ON}_3$ as in A., 1932, 526) is decomposed by alkalis (N-NaOH-MeOH); 30% aq. NaOH to 1 mol. of NH_3 and lysergic acid (II) (Jacobs *et al.*, this vol., 538) (sulphate, decomp. 245°). (I) is therefore the amide of (II).

J. W. B.

Alkaloids of *Holarrhena antidysenterica*. II. Two new alkaloids from the bark and seeds of Indian *Holarrhena*, and their relationship to conessine. S. SIDDIQUI (J. Indian Chem. Soc., 1934, 11, 283—291; cf. A., 1933, 289).—Conessimine (I), isoconessimine (II), and conimine (III) are isolated (isolation described) from the seeds. (I) (1 mol.) [Bz derivative, m.p. 121° after softening at 115° (hydrochloride, m.p. 348° (decomp.) after softening at 233°); Ac derivative, an oil (hydrochloride, m.p. 278—280°; platinichloride, m.p. 254—256° (decomp.))] with CH_2O and HCO_2H (each 1.2 mols.) in boiling EtOH affords Me conessimine (conessine) (IV), m.p. 123—124°, identical with an authentic specimen. (II), m.p. 92°, $\alpha_D^{20} +30.0^\circ$ in 1% EtOH [$+2\text{H}_2\text{O}$, m.p. 88 92°; hydrochloride, m.p. 335°; platinichloride, m.p. 285° (decomp.); hydriodide, m.p. 316°; picrate, m.p. 198—200° (decomp.) after sintering at 160°; hydrobromide, m.p. 344° (decomp.)], contains two NMe groups and one active H , and is methylated [as is (I)] to (IV). (III), m.p. 130°, $\alpha_D^{20} -30^\circ$ in 1% EtOH [$+ \frac{1}{2}\text{H}_2\text{O}$, m.p. 130°; hydrochloride, m.p. 318 3.0

(decomp.); platinichloride, m.p. 296—298° (decomp.); picrate, m.p. 140—141° after sintering at 134°; hydriodide, m.p. 293°], contains one NMe and two active H atoms, and is methylated to (IV). (II) and (III) are different from conessidine and conkurchine (cf. A., 1933, 728).

J. L. D.

Alkaloids of *Salsola Richteri*. II. Constitution of salsoline. A. OREKHOV and N. PROSKURNINA (Ber., 1934, 67, [B], 878—884; cf. A., 1933, 727).—The yield of alkaloid is doubled when EtOH is replaced by $\text{C}_2\text{H}_4\text{Cl}_2$ in the percolation process. The close relationship of salsoline (I) to the *Anhalonium* alkaloids, and particularly to carnegine, is stressed. (I) is transformed by excess of CH_3N_3 in MeOH into *O-methylsalsoline* (II), m.p. 117—119° [hydrochloride ($+2\text{H}_2\text{O}$ and anhyd.), m.p. 193—195°; N-Bz compound, m.p. 125—126°]. Treatment of (II) with MeI-MeOH or with $\text{Me}_2\text{SO}_4\text{-NaOH}$ followed by KI leads to *ON-dimethylsalsoline methiodide*, m.p. 206—208°, readily converted by boiling KOH-MeOH into the non-cryst. base, $\text{C}_{10}\text{H}_9(\text{OMe})_2\text{NMe}_2$, b.p. 153—155°/15 mm., which appears to yield a mixture of isomeric methiodides transformed by KOH-MeOH or $\text{Ag}_2\text{O-H}_2\text{O}$ into NMe_3 and 3 : 4-dimethoxy-1 : 2-divinylbenzene (III), m.p. 37—39°. Oxidation of (III) affords methahemipinic acid, m.p. 177—183° (ethylimide, m.p. 231—232°). Treatment of (II) with CH_3O and HCO_2H leads to *ON-dimethylsalsoline*, identical with carnegine (Spath, A., 1929, 707). (I) is therefore A ($\text{R}=\text{Me}$ or H ; $\text{R}'=\text{H}$ or Me).

H. W.

Cupreidine, a phenolic base derived from quinidine. R. LUDWICZAKÓWNA, J. SUSZKO, and R. ZWIERZCHOWSKI (Rocz. Chem., 1934, 14, 197—202).—Quinidine (I) when boiled with 60% H_2SO_4 loses Me to give cupreidine (II), m.p. 186—190° [methiodide, m.p. 277° (decomp.); dimethiodide, m.p. 248° (decomp.); Bz , m.p. 100—105°, 5-benzeneazo-, m.p. 145—146°, and 5-benzeneazosulphonic acid derivatives]. (II) regenerates (I) on methylation with CH_3N_2 .

R. T.

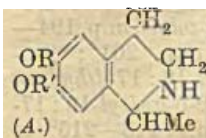
[Action of hydrogen iodide on lupanine.] K. WINTERFELD and F. W. HOLSCHNEIDER (Ber., 1934, 67, [B], 778—779).—Examination of the action of red P and fuming HI on γ -lupanine confirms the production of β -lupinane. The small yield obtained by Clemo *et al.* (this vol., 538) is attributed to the difficulty of its isolation from the small amount of material used.

H. W.

Identity of peganine with vasicine. E. SPATH and F. KUFFNER (Ber., 1934, 67, [B], 868—869; cf. this vol., 310).—Direct comparison of the bases, the hydrochlorides, chlorodeoxy-compounds, aurichlorides, platinichlorides, and picrates establishes the identity of peganine (I) with vasicine (II) (Ghose *et al.*, A., 1933, 77). Since the constitution of (I) is confirmed by the isolation of glycine by hydrolysis of Me 4-keto-3 : 4-dihydroquinazoly-3-acetate, that of (II) must be amended.

H. W.

Crystal forms and m.p. of opium alkaloids. L. KOFLER and A. KOFLER (Arch. Pharm., 1934, 272, 537—545).—Optical data are recorded for micro-



sublimates (photomicrographs) obtained from codeine, papaverine, thebaine, and narcotine. The m.p. of the sublimates are 155° (anhyd.), 147°, 194°, and 174°, respectively. R. S. C.

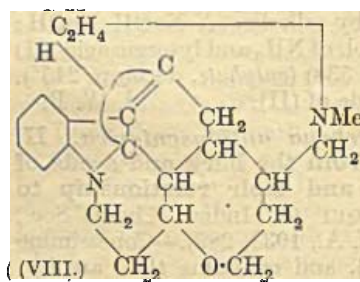
Berbine derivatives. III. Application of amalgamated zinc to the reduction of dehydroberberinium salts to berbine derivatives and new derivatives of berbine. W. AWE [with H. ETZRODT] (Ber., 1934, 67, [B], 836—840; cf. A., 1933, 289).—For reduction of 1 g. of the base, 10 g. of Zn-Hg and 30 c.c. of 30% AcOH are used. The product is separated by addition of NH_3 to the resulting solution, followed by a single extraction with CHCl_3 . The following examples are cited: berberinium sulphate to dihydrodeoxyberberine, m.p. 169—170°; palmatinium H sulphate to 16:17-dihydrodeoxypalmatine, m.p. 149—150°; jatrorrhizinium chloride to 16:17-dihydrodeoxyjatrorrhizine, m.p. 217—218°; 9-phenyldeoxyberberine and 9-phenylberberinium chloride to 9-phenyl-16:17-dihydrodeoxyberberine, m.p. 222°; 9-benzyl- to 9-benzyl-16:17-dihydrodeoxyberberine, m.p. 164°. The following -deoxyberberines, obtained from berberinium iodide and the requisite Grignard reagent, are reduced by Zn-Hg in presence of AcOH and $2\text{N-H}_2\text{SO}_4$: 9-*o*-tolyl-, m.p. 188—189°, to 9-*o*-tolyl-16:17-dihydro-, m.p. 204°; 9-*m*-tolyl-, m.p. 194—195°, to 9-*m*-tolyl-16:17-dihydro-, m.p. 201°; 9-*p*-tolyl-, m.p. 168—169°, to 9-*p*-tolyl-16:17-dihydro-, m.p. 206°; 9-*o*-anisyl-, m.p. 181°, to 9-*o*-anisyl-16:17-dihydro-, m.p. 202°; 9- α -naphthyl-, m.p. 213—215°, to 9- α -naphthyl-16:17-dihydro-, m.p. 230°; 9-*veratryl*-, m.p. 191°, to 9-*veratryl*-16:17-dihydro-, m.p. 195°.

H. W.

Strychnine and brucine. XXV. Reduction of methylstrychnidinium salts by means of sodium amalgam in the presence of carbon dioxide. W. H. PERKIN, jun., R. ROBINSON, and J. C. SMITH. XXVI. Hofmann degradation of methylidihydrostrychnidinium-*A* carbonate. Isolation of a fourth isomeride of dihydrostrychnidine. O. ACHMATOWICZ and R. ROBINSON. XXVII. Methoxymethylchanodihydrostrychnone and the constitution of strychnidone. L. H. BRIGGS and R. ROBINSON. XXVIII. (a) Methoxymethylchanodihydrostrychnane. (b) Constitution of anhydrotetrahydromethylstrychnine- K^5 . (MISS) T. M. REYNOLDS and R. ROBINSON. XXIX. *N(b)*-Methylidihydrochanopseudostrychnine. B. K. BLOUNT and R. ROBINSON (J.C.S., 1934, 574—581, 581—590, 590—592, 592—595, 595—596).—XXV. The base K'' (A., 1932, 628) is contaminated by a compound of high C content which has not been entirely removed. Anhydrotetrahydromethylstrychnine- K^5 on electrolytic reduction gives dihydroanhydrotetrahydro-*N(b)*-methylstrychnidine- K^5 , m.p. 112°. Strychnidine methosulphate is reduced (Na-Hg) in CO_2 to $\text{C}_{22}\text{H}_{30}\text{O}_2\text{N}_2$ (I), m.p. 235—236°, $\text{C}_{22}\text{H}_{28}\text{ON}_2$ (II), m.p. 142—143°, and $\text{C}_{22}\text{H}_{30}\text{ON}_2$ (III), m.p. 192—193°, methylstrychnidinium and methylneostrychnidinium salts remaining behind. (I) is hydroxydihydro-*N(b)*-methylchanodihydroestrychnidine- θ , (II) *N(b)*-methylchanodihydroestrychnidine- θ , and (III) *N(b)*-methylidihydrochanodihydroestrychnidine- θ . (I) and POCl_3 give (II), showing that (I) is the hydrate of (II). (II)

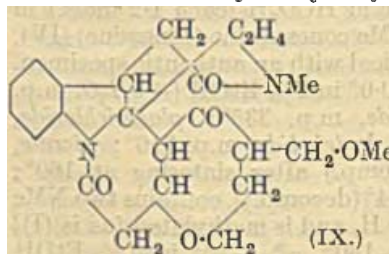
is reduced (Pd-H_2) to *N(b)*-methylidihydrochanodihydrostrychnidine-*A* (A., 1933, 406). (III) forms a methiodide, m.p. 270°. After separation of (I), (II), and (III) the residual bases have been reduced electrolytically to give (I) and *N(b)*-methylhexahydrostrychnidine- θ , b.p. 230—232°/42 mm. (methiodide, m.p. 278—280°). Reduction of *N(b)*-methylneostrychnidinium chloride affords (II) in small yield. The crude mixed bases on oxidation (KMnO_4) give an acid, $\text{C}_{22}\text{H}_{22}\text{O}_5\text{N}_2$ or $\text{C}_{22}\text{H}_{24}\text{O}_5\text{N}_2$, decomp. 210—220°; (II) similarly forms oxy-*N(b)*-methylchanodihydroestrychnidine- θ , m.p. 235—240°, a substance, m.p. 180°, and an acid, $\text{C}_{22}\text{H}_{21}\text{O}_6\text{N}_2$. The view is maintained that the ring fission occurs at different points in the formation of (II) and (III), and the significance of these results is discussed.

XXVI. By thermal decomp. methylidihydrostrychnidinium-*A* hydrogen carbonate and hydroxide each gives a mixture of five substances: dihydrostrychnidine-*A* (IV), a *des*-base, $\text{C}_{22}\text{H}_{28}\text{ON}_2$ (V), m.p. 143—144°, a substance $\text{C}_{23}\text{H}_{32}\text{O}_2\text{N}_2$ (VI), m.p. 220°, a substance $\text{C}_{22}\text{H}_{30}\text{O}_2\text{N}_2$ (VII), m.p. 158—159°, and a *des*-base $\text{C}_{22}\text{H}_{28}\text{ON}_2$ (VIII), m.p. 196—197°. (V) is identical with (II) as above; (VI) is methoxymethyltetrahydrostrychnidine; (VII) is hydroxymethyltetrahydrostrychnidine hydrate; (VIII) is anhydromethylstrychnidinium-*D* hydroxide (methiodide, m.p. 289—290°; methochloride, m.p. 308—310°). Oxidation of (V) and its dihydro-derivative gives AcOH, but the series *D* does not. Oxidation of (VIII) with KMnO_4 yields two oxyanhydromethylstrychnidinium-*D* hydroxides, m.p. 234—236°, and m.p. 162°. Catalytic hydrogenation of (VIII) affords methylidihydrostrychnidinium-*D* acetate, m.p. 307—308° [iodide ($+\text{H}_2\text{O}$), m.p. 317—318°; chloride ($+\text{H}_2\text{O}$), m.p. 318—319°]. The chloride decomposes to form dihydrostrychnidine-*D*, m.p. 197—199°. (VII) gives an *O*-Ac derivative, m.p. 254—255°, is methylated to the corresponding *OMe*-derivative,



and on reduction (P-HI) yields an isomeride of methylidihydrostrychnidinium-*A* iodide, m.p. 225—228°. *N(b)*-Ethylidihydrostrychnidinium-*A* iodide, m.p. 345—350°, and *H* carbonate are described, the carbonate decomposing to give (IV). Dihydrostrychnidine-*E*, m.p. 254—255°, has been isolated in small yield during the prep. of -*A* salts. The constitution of the compounds is discussed and the structure (VIII) is suggested.

XXVII. Methoxymethylidihydroestrychnine is oxidised by $\text{Pb}(\text{OAc})_4$ to oxy-methoxymethylidihydroestrychnine, m.p. 210—243° (decomp.), and by perbenzoic acid to methoxymethylchanodihydrostrychnone (IX), m.p. 198—199° [oxime, m.p. 260—261° (decomp.); P-



nitrophenylhydrazones, m.p. 263°; *benzylidene derivative*, m.p. 235°]. (IX) and KOH give *anhydrobismethoxymethylchanodihydrostrychnone*, decomp. 268—273° (*benzylidene derivative*, m.p. 251—253°). "Strychnidonedisemicarbazone" (A., 1927, 888) consists of impure hydrazodicarbonamide. (IX) has the structure indicated.

XXVIII. Clemmensen reduction of (IX) leads to *methoxymethylchanodihydrostrychnane*, m.p. 160—161°; it is not a derivative of $\text{HCO}\cdot\text{NH}_2$. Oxidation of anhydrotetrahydromethylstrychnine- K^5 by KMnO_4 gives MeCHO and hence contains the group $\cdot\text{CH}\cdot\text{CMe}:\text{CHMe}$. A series of strychnine derivatives has been examined for the occurrence of $\cdot\text{CMe}$ groups by the Kuhn-Roth method: from these results strychnine does not contain $\cdot\text{CHMe}$ and the C_2H_4 has the ethylene arrangement.

XXIX. Reduction of *N(b)-methylchanopseudostrychnine* (X) (Pt-H_2) yields *N-methyldihydrochanopseudostrychnine*, m.p. 296—297°, which forms a *benzylidene derivative*, m.p. 264—266°, but no derivative. The result favours the view that the second reactive CH_2 in (X) is in the system $\text{CO}\cdot\text{C}:\text{C}\cdot\text{CH}_2$.

F. R. S.

Preparation and investigation of cyclic polymethylenearsenic compounds. I. GORSKI, V. SCHPANSKI, and L. MULJAR (Ber., 1934, 67, [B], 730—735).—Methylcyclopentamethylenearsine (improved prep.) is transformed by Cl_2 in CCl_4 into the corresponding *dichloride*, m.p. 153°, which at 95—101°/25 mm. affords *chlorocyclopentamethylenearsine* (I), b.p. 89°/19 mm., m.p. 26—27°. (I) and $\text{NaOMe}\cdot\text{MeOH}$ afford *cyclopentamethylenearsine oxide*, b.p. 118°/2 mm., oxidised by 25% H_2O_2 to *cyclopentamethylenearsinic acid*, $[\text{CH}_2]_5>\text{As}(\text{O})\cdot\text{OH}$, m.p. 200.5—202°. Addition of dichloro- β -chlorovinylarsine to the Grignard compound from Mg and α , α -dibromopentane in Et_2O leads to *cyclopentamethylene- β -chlorovinylarsine*, b.p. 89—91°/5 mm., the *dichloride*, m.p. 121°, of which is decomposed by heat mainly into *chloro- β -chlorovinyl-3-chloropentamethylenearsine* (II), b.p. 151—152°/5 mm., with smaller amounts of α , α -dichloropentane (III), β -chlorovinylarsine, and (?) As β -chlorovinyl *dichloride* (IV). Non-cryst. As β -chlorovinyl- α -chloropentamethylene trichloride, from (II) and Cl_2 in CCl_4 , is decomposed by heat into (III) and (IV). H. W.

Reactions of phenylarsine with organic compounds of mercury, lead, and tin. A. N. NESMEJANOV and R. C. FRIEDLINA (Ber., 1934, 67, [B], 735—738).—The reaction between AsH_2Ph and HgPhCl , HgPh_2 , PbPh_2Cl_2 , PbPh_2I_2 , PbPh_4 , PbEt_4 , SnPh_4 , SnPh_2Et_2 , SnEt_4 , and SnEt_2Cl_2 has been examined. Hg compounds react at room temp., whereas Sn compounds require a temp. of 200—250°. In all cases of observed action Ph is eliminated as C_6H_6 , and AsPh_2 after loss of H is converted into $[\text{AsPh}]_2$. Symmetrical aliphatic compounds react similarly, but with greater difficulty. $[\text{AsPh}]_2$ is obtained as such or in cases which require a very high temp. is decomposed into $[\text{AsPh}_2]_2$ and As. With mixed organometallic compounds, aryl is more readily eliminated than halogen. AsH_2Ph and SnEt_2Cl_2 do not react at 240—250°.

H. W.

Arsonium compounds. J. PRAT (Bull. Soc. chim., 1933, [iv], 53, 1475—1488).—The solubility of four aromatic arsenic acids in HCl increases with increasing concn. of HCl, but suddenly falls at a definite concn., indicating compound formation. Using a special technique (detailed) to exclude atm. H_2O , there are obtained *chlorides*, $[\text{AsR}(\text{OH})_3]\text{Cl}$, in which $\text{R}=\text{Ph}$, o - and α - C_{10}H_7 , p - $\text{C}_6\text{H}_4\cdot\text{NH}_2$ (with the *dichloride*, $+\text{H}_2\text{O}$), $\text{C}_6\text{H}_4\cdot\text{NHAc}$, the *trichloride*, $[(\text{C}_6\text{H}_4\cdot\text{NH}_3\text{Cl})_2\text{As}(\text{OH})_2]\text{Cl}+\text{H}_2\text{O}$, and *perchlorates* of two types, $[\text{AsR}(\text{OH})_3]\text{ClO}_4$ and $[\text{AsR}(\text{OH})_3]\text{ClO}_4\cdot\text{AsRO}_3\text{H}_2$, in which $\text{R}=\alpha$ - C_{10}H_7 (first type only), $\text{C}_6\text{H}_4\cdot\text{NH}_2$, $\text{C}_6\text{H}_4\cdot\text{NHAc}$, and 3-*acetamido-4-hydroxyphenyl*.

R. S. C.

Use of camphor in cryoscopic determinations of mol. wt. of [organic] acids of arsenic. G. SCHUSTER (J. Pharm. Chim., 1934, [viii], 19, 497—498).—The mol. wt. of an insol. acid of As is determined in camphor after conversion into sol. thioglycollanilide.

H. G. R.

Allylic rearrangement of lithium benzyl. H. GILMAN and F. BREUER (J. Amer. Chem. Soc., 1934, 56, 1127—1128).—*o*-Tolylcarbinol is obtained from LiCH_2Ph and CH_2O (gas) + N, in cold Et_2O .

H. B.

Organo-metallic compounds. IV. Aromatic stannonic acids and their reactions. K. A. KOZESCHKOV and M. M. NADJ (Ber., 1934, 67, [B], 717—721; cf. A., 1929, 712; this vol., 423).— $\text{Sn}(\text{p}-\text{C}_6\text{H}_4\text{Me})_4$ (I) and SnCl_4 (mol. ratio 0.083 : 0.25) at 210—215° yield *Sn p-tolyl trichloride* (II), b.p. 156—157°/23 mm. (I) and SnCl_4 (1 : 1) at 200—205° give *Sn di-p-tolyl dichloride*, m.p. 49—50°, converted into (II) by SnCl_4 at 210—215°. $\text{Sn}(\text{o}-\text{C}_6\text{H}_4\text{Me})_4$ is transformed by SnCl_4 (1 : 3) into *Sn o-tolyl trichloride* (III), b.p. 154—158°/20 mm., or (mol. ratio 1 : 1) into *Sn di-o-tolyl dichloride*, m.p. 49—50°. (II) or (III) is transformed by HgCl_2 in boiling EtOH into *o*- (or *p*-)tolylmercurichloride. Cautious addition of 20% KOH to (III) in cold H_2O affords *o-tolylstannonic acid* (V), decomp. about 295°, readily displaced by CO_2 from its solutions in KOH. *p-Tolylstannonic acid* has similar properties. (III) and H_2S in H_2O give *o-tolylthiostannonic thioanhydride*, sol. in $(\text{NH}_4)_2\text{S}$. (IV) and HgO in boiling H_2O - EtOH afford $\text{Hg}(\text{o}-\text{C}_6\text{H}_4\text{Me})_2$, m.p. 108°, and H_2SnO_3 quantitatively. Oxidation of (IV) by $\text{K}_3\text{Fe}(\text{CN})_6$ in alkaline solution at room temp. gives PhMe and a small amount of $\text{o}-\text{C}_6\text{H}_4\text{Me}\cdot\text{CN}$; exclusively inorg. compounds of Sn are produced. (II) and $\text{C}_5\text{H}_5\text{N}$ in Et_2O give the substance, $\text{C}_7\text{H}_7\text{SnCl}_3\cdot 2\text{C}_5\text{H}_5\text{N}$.

H. W.

Micro-hot-plate for protein hydrolysis. A. R. PATTON (Ind. Eng. Chem. [Anal.], 1934, 6, 201).

E. S. H.

Preparation of gluco-protein. H. BIERRY (Compt. rend., 1934, 198, 1542—1543).—The complex which constitutes the glucoside linking (prep. described) decomposes about 195°, and has $[\alpha]_D^{25} -4.5^\circ$ in H_2O .

J. L. D.

Structure and solubility of proteins. A. BONOT (J. Chim. phys., 1934, 31, 258—280).—Chiefly a review. The separation of serum-proteins by fractional pptn. with $(\text{NH}_4)_2\text{SO}_4$ is described. The solubility

data for serum-albumin in aq. $(\text{NH}_4)_2\text{SO}_4$ are consistent with a theory developed from the view that a protein is a mixture of different species with almost identical properties. J. G. A. G.

Combination of amino-acids and proteins in the solid state with gaseous acids and bases. E. J. CZARNETZKY and C. L. A. SCHMIDT (J. Biol. Chem., 1934, 105, 301—317).—From the phase-rule diagrams obtained by gasometric titrations the combining power of certain proteins for NH_3 is correlated with the CO_2H content; it is chemical in nature and takes place in stoichiometric proportions. The uptake of HCl is correlated with the content of $\epsilon\text{-NH}_2\text{-N}$ of lysine, NH-N of tryptophan, the guanidine group of arginine, the *tert.*- and NH-N of histidine, and the -CO-N- of proline and hydroxyproline. The changes in heat, free energy, and entropy with dissociation of the salts were determined. Similar data are given for the compounds of hexone bases with H_2S . C. G. A.

Copper ignition tubes. C. L. TSENG (Sci. Quart. Nat. Univ. Peking, 1934, 4, 250).—An improved construction (cf. A., 1933, 1022) is described.

W. R. B.

Determination of iodine in organic compounds. E. RUPP and O. LEMKE (Z. anal. Chem., 1934, 97, 180—181).—The substance is heated in a Kjeldahl flask with $\text{H}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_8 + \text{AgNO}_3$ (25 c.c. of 0.1*N* solution, evaporated down). Escaping HI or I vapours are trapped by moist Na_2SO_3 . Excess Ag is titrated back with KCNS . J. S. A.

Micro-determination of fluorine in organic substances. D. M. HUBBARD and A. L. HENNE (J. Amer. Chem. Soc., 1934, 56, 1078—1080).—The org. substance is decomposed over SiO_2 at 900° , and the SiF_4 produced is collected in H_2O or dil. aq. NaOH and titrated with $\text{Ce}(\text{NO}_3)_3$. The combustion tube is swept with H_2 to remove adsorbed SiF_4 . Cl may be determined simultaneously. E. S. H.

Gauge receiver for micro-methoxyl determination by Viebock and Brecher's method. L. KAHOVEC (Mikrochem., 1934, 14, 341—342; cf. A., 1931, 246).—An inexpensive attachment is described for addition to the condenser tube, in which the absorbing solution can be held and from which it can be transferred rapidly to the titration flask. J. W. S.

Analysis of mixtures of oxalic and citric acids by titration with ceric sulphate. J. A. WILKINSOW, I. R. SIPHERD, E. I. FULMER, and L. M. CHRISTENSEN (Ind. Eng. Chem. [Anal.], 1934, 6, 161—163).—Citric (I) and oxalic acids in mixtures obtained by fermentation are separated as Pb salts. After recovery by H_2S , they are determined by (a) titration with NaOH and (b) oxidation in 0.01—0.02*N* solution by an excess of $\text{Ce}(\text{SO}_4)_2$ (modified prep.) in presence of a little H_2SO_4 at $90\text{--}95^\circ$ and back-titration of the excess. Oxidation of (I) to CO_2 and H_2O under these conditions is only 87.7% complete. R. S. C.

Application of drop reactions to the identification of organic compounds. I. Identification of the atomic groupings $>\text{C:S}$ and C:SH . F. FEIGL. II. Detection of carboxylic acids and their derivatives. F. FEIGL, V. ANGER, and O. FREHDEN. III. Detection of sulphonic acids.

F. FEIGL and V. ANGER (Mikrochem., 1934, 15, 1—8, 9—22, 23—24).—I. Reaction, with visible evolution of N_2 , between NaN_3 and I is catalysed by the CS and C:SH groups, but not by other types of org. S compounds. 1 drop of 3% NaN_3 in 0.1*N*-I suffices for the test. S dyes on cotton may be so detected, and vegetable fibres distinguished from (cysteine-containing) animal fibres.

II. Acid anhydrides dissolved in Et_2O are evaporated with a drop of 0.5% FeCl_3 in EtOH , saturated with $\text{NH}_4\text{OH.HCl}$. Addition of H_2O gives a red to violet colour, due to the formation of a Fe hydroxamate (I). Esters are warmed with saturated $\text{NH}_4\text{OH.HCl}$ + saturated KOH (both in EtOH), acidified with HCl , and dil. aq. FeCl_3 is added, giving (I). Thio-esters give yellow to red colorations. Acid chlorides (II) are treated with $\text{NH}_4\text{OH.HCl} + \text{Na}_2\text{CO}_3$, then with HCl and FeCl_3 . Acids (1 drop) are converted into (II) by evaporating with 10 drops of SOCl_2 , then treated with KOH and NH_4OH as above.

III. $\text{R}\cdot\text{SO}_3\text{H}$ is converted into $\text{R}\cdot\text{SO}_2\text{Cl}$ by evaporation with SOCl_2 . 2 drops of saturated NH_4OH in EtOH + 1 drop of MeCHO are added, and the liquid is made alkaline with 5% aq. Na_2CO_3 . $\text{R}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH}$ is formed, which with MeCHO gives $\text{NHAc}\cdot\text{OH}$, detected by FeCl_3 as above. J. S. A.

2 : 4-Dinitrophenylhydrazine : reagent for carbonyl compounds. C. TORRES and S. BROSA (Anal. Fis. Quim., 1933, 31, 649—662).—2 : 4-Dinitrophenylhydrazine in dil. H_2SO_4 is not in general a useful reagent for α -hydroxycarbonyl compounds. Benzoin yields a 2 : 4-dinitrophenylhydrazone, m.p. $234\text{--}235^\circ$, but no osazone. Furoin and benzofuroin yield 2 : 4-dinitrophenylhydrazones, m.p. 223° (decomp.) and m.p. 170° , respectively, under certain conditions, but osazones cannot be isolated. 2 : 4-Dinitrophenylhydrazones are obtained from glucose and fructose [m.p. 238° (decomp.)] and from galactose [m.p. 216° (decomp.)]. Methods are described for the determination of COMe , or CH_2O in dil. aq. solution, of $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (after oxidation to MeCHO by KMnO_4), and of $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$ in pharmaceutical preps. of cinnamon. R. K. C.

Detection of aldehydes and ketones by means of micro-m.p. determination. R. FISCHER and A. MOOR (Mikrochem., 1934, 15, 74—86; cf. A., 1933, 843).—M.p. data for the semicarbazones, *o*-, *m*-, and *p*-nitrophenylhydrazones and -nitrobenzhydrazones, semioxamazones, and thiosemicarbazones of a no. of aldehydes and ketones are given. J. S. A.

3 : 5-Dinitrobenzoylhydrazine as a reagent for the identification of aldehydes and ketones. P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1934, 11, 40—46).—Interaction of 3 : 5-dinitrobenzoylhydrazine (A., 1907, i, 970) with aldehydes and ketones in cold 30% EtOH affords 3 : 5-dinitrobenzoylhydrazones. The following are described : *acet*-, m.p. $215\text{--}216^\circ$; *prop*-, m.p. $194\text{--}195^\circ$; *but*-, m.p. $171\text{--}172^\circ$; *isobut*-, m.p. $195\text{--}196^\circ$; *valer*-, m.p. $154\text{--}155^\circ$; *hex*-, m.p. $145\text{--}146^\circ$; *hept*-, m.p. $149\text{--}150^\circ$; *isohex*-, m.p. $127\text{--}129^\circ$; *oct*-, m.p. $106\text{--}107^\circ$; *non*-, m.p. $125\text{--}126^\circ$; *dec*-, m.p. $121\text{--}122^\circ$; *m-nitrobenz*-, m.p. $260\text{--}261^\circ$ (decomp.); *cinnam*-, m.p. $226\text{--}227^\circ$.

and *furfur-aldehyde-3:5-dinitrobenzoylhydrazone*, m.p. 234—235°. *Me hexyl ketone*-, m.p. 103—104°; *acetophenone*-, m.p. 228—229°; *benzophenone*-, m.p. 184—185°; *benzylideneacetone*-, m.p. 213—214°; *benzylideneacetophenone*-, m.p. 121—122°; *Et acetoacetate*-, m.p. 121—122°; *pyruvic acid*-, m.p. 166—167°; *lævulic acid-3:5-dinitrobenzoylhydrazone*, m.p. 161—162° (*Et*, m.p. 136—137°, and CH_2Ph , m.p. 117—118°, ester). J. L. D.

Semicarbazides. I. Phenylsemicarbazide as a reagent for the identification of aldehydes and ketones. P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1934, 11, 32—39).—Interaction of $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ (A., 1899, i, 137) with ketones and aldehydes in hot EtOH affords phenylsemicarbazones. The following are described: *acet*-, m.p. 151—152°; *prop*-, m.p. 130—131°; *n-but*-, m.p. 134—136°; *iso-but*-, m.p. 133—134°; *n-valer*-, m.p. 126—127°; *n-hex*-, m.p. 135—136°; *n-hept*-, m.p. 134—135°; *isohept*-, m.p. 93—95°; *n-oct*-, m.p. 128—129°; *n-non*-, m.p. 131—132°; *n-dec*-, m.p. 108—110°; *m-nitrobenz*-, m.p. 194—195°, and *furfur-aldehyde-phenylsemicarbazone*, m.p. 180—181°; *Me hexyl ketone*-, m.p. 94—95°; *m-nitroacetophenone*-, m.p. 245—246°; *Et acetoacetate*-, m.p. 154°; *lævulic acid-phenylsemicarbazone*, m.p. 186—187° (*Et*, m.p. 118°, and CH_2Ph , m.p. 112—114°, ester). J. L. D.

Volumetric determination of amino-nitrogen in acetone solution. R. WOLFF and R. LAFRANCAISE (Bull. Soc. Chim. biol., 1934, 16, 419—423).—The influence of H_2O and EtOH on the volumetric determination of $\text{NH}_2\cdot\text{N}$ in protein matter in COMe_2 is studied. A mixture of aq. $\text{Co}(\text{NO}_3)_2$, $\text{K}_2\text{Cr}_2\text{O}_7$, and a little BaSO_4 serves as a control for the end-point colour. A. L.

Determination of secondary in presence of primary and tertiary amines. A. NELIUBINA (Anilinokras. Prom., 1934, 4, 120—121).—0.3—3.5 g. of NH_2Ph and alkyraniline mixture are dissolved in an excess (10%) of conc. HCl , 500 c.c. of H_2O are added, and the solution is titrated with 0.1*N*- NaNO_2 (at room temp. for NHPhEt and at $> 5^\circ$ for NHPhMe). NHPh_2 is determined separately as picrate and NPhEt_2 is calc. by difference. R. T.

Determination of cholesterol.—See this vol., 822.

Microchemical detection of coumarin. A. KOFER and J. GEYR (Mikrochem., 1934, 15, 67—73).—Coumarin is best identified by microsublimation, followed by a micro-m.p. determination. Two crystalline modifications exist, a stable rhombic hemihedral form, m.p. 67°, and a metastable monoclinic form, m.p. 64°. J. S. A.

Reaction of cantharidin applicable to its colorimetric determination. G. DENIGES (Compt. rend., 1934, 198, 1783—1785).—A colorimetric method (sensitive to 0.01 mg.) for determining cantharidin, based on the intense brown colour produced when it is heated with 1 drop of 10% aq. CH_2O and a const. (4—5 c.c.) quantity of H_2SO_4 , is described. J. W. B.

Detection of nitrobenzene and phenol by formation of resorufin. P. W. DANCKWORTT (Z. anal. Chem., 1934, 27, 185—186; cf. this vol., 289).—The resorufin reaction is given also by other NO_2 -compounds, and is not sp. for PhNO_2 . The sensitivity is increased by examination for fluorescence in ultra-violet light, and by extracting the dye with amyl alcohol. J. S. A.

Volumetric determination of 8-hydroxyquinoline. H. R. FLECK, F. J. GREENANE, and A. M. WARD (Analyst, 1934, 59, 325—328).—The end-point in the titration of 8-hydroxyquinoline may be obscured by the formation of a brown cloudiness. This may be avoided by adding CS_2 to the solution before adding KI . E. C. S.

Potentiometric determination of *o*-[8-]hydroxyquinoline by bromination. J. A. ATANASIU and A. J. VELCULESCU (Z. anal. Chem., 1934, 97, 102—106).—8-Hydroxyquinoline (or its salts) is brominated quantitatively to 5:7-dibromo-8-hydroxyquinoline in 10% HCl solution with 0.1*N*- KBrO_3 containing 5.246% KBr . Titration is best carried out at 50—55°; above 70°, reaction is not stoichiometric. Pt wire is used as indicator electrode. J. S. A.

Detection of nicotine. A. WENUSCH (Mitt. Österr. Tabakreg., 1932, 2, 2; Bied. Zentr., 1934, A, 4, 365—366).—The reaction between nicotine (I) and $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ is due to the presence of oxidation products of (I). The Schundelmeier reaction with CH_2O and HNO_3 is unsatisfactory. The epichlorohydrin test is a suitable general reaction for $\text{C}_5\text{H}_5\text{N}$ ring compounds and serves to distinguish (I) from coniine. A. G. P.

Microchemical contributions. L. ROSENTHALER (Mikrochem., 1934, 14, 363—368).—Quinine, diocaine, codeine, pantocaine, psicaine, stovaine, and strychnine salt solutions yield characteristic ppts. with solid $(\text{NH}_4)_2\text{SiF}_6$. Veramon (a 1:1 mol. mixture of pyramidone and pyramidone-veronal compound) gives barbituric acid-type ppts. with $\text{Cu}\text{-C}_5\text{H}_5\text{N}$ solution and with $(\text{NH}_4)_2\text{HPO}_4$, but not with $\text{Pb}(\text{OAc})_2$, TlOAc , or I . With Br it gives the same long fine needle ppt. as pyramidone. Traces of $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ give characteristic ppts. with AgNO_3 , $\text{Hg}(\text{OAc})_2$, $\text{UO}_2(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$, and larger amounts also with $\text{Ce}(\text{NO}_3)_4$ and $\text{La}(\text{NO}_3)_3$. *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ also gives ppts. with $\text{Hg}(\text{OAc})_2$, AgNO_3 , and $\text{Al}(\text{NO}_3)_3$, but only when present in larger concn. PhOH , $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{OH}$, $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, quinol, and salicylic acid give brown ppts., with I in KI . Phenolic acids give ppts. with $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}$, but they are not characteristic without crystallographic examination. *iso*Propylantipyrene gives characteristic ppts. with $\text{K}_2\text{Cr}_2\text{O}_7$, NaClO_4 , Reinecke's salt, $\text{K}[(\text{NO}_2)_4\text{Co}(\text{NH}_3)_2]$, and $\text{KI}+\text{SnCl}_2$. Ba can be distinguished from Ca and Sr by the needle ppt. it gives with 5% Na 5-chloro-5-nitrotoluenesulphonate. In presence of traces of Al , Mn , or Sn , CoCl_2 gives brown needles with a crystal of K_2CrO_4 . Alkaline-earth hydroxides give a characteristic blue to green ppt. with tannin. J. W. S.

Biochemistry.

Nature of the osmotic effect of solutions of non-electrolytes on the erythrocyte. M. H. JACOBS (Amer. J. Med. Sci., 1934, 187, 147).—The first change which takes place when ox erythrocytes are placed in sucrose solution is a reversible exchange of anions from the cell for OH⁻ from the solution: later there is an irreversible escape of salts into the solution.

CH. ABS.

Photo-electric determination of oxygen content and hæmoglobin concentration in hæmoglobin solutions and hæmolyzed blood. K. KRAMER (Z. Biol., 1934, 95, 126—134).—The plot of the light absorption of a hæmoglobin (I) solution, measured by a photo-electric cell, against the % of O₂ in the (I) solution is a straight line for any given (I) concn. The validity of Beer's law for a wide range of (I) concn. is demonstrated and equations are derived whereby the O₂ content of a given (I) solution can be determined with an error of ± 0.1 vol.-%. H. D.

Determination of hæmoglobin in chicken blood. M. O. SCHULTZE and C. A. ELVEHJEM (J. Biol. Chem., 1934, 105, 253—257).—In a modified Newcomer method the blood is diluted with 0.4% aq. NH₃ and then acidified to yield a clear solution of acid hæmatin. The Fe content of chicken blood (I) gives only an approx. val. for its hæmoglobin content. Standard methods for determining O₂ capacity of blood cannot be used for (I) owing to gel formation.

A. E. O.

Blood-fats and hæmoglobin. Effect on chloroform fixation. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1933, 106, 1049—1053; Chem. Zentr., 1933, ii, 2844).—There is no relation between CHCl₃-solubility and the fat content of different kinds of animal blood, but there is a definite relation with the hæmoglobin content.

L. S. T.

Effect of hæmoglobin derivatives and hæmatin solution on the value of the chloroform solubility coefficient. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1933, 106, 1053—1055; Chem. Zentr., 1933, ii, 2844; cf. preceding abstract).—Cryst. hæmoglobin (I), methæmoglobin, and reduced (I) affect the CHCl₃ solubility ratios (II), in the same way as laked blood. The loss of respiratory function of the blood in no case reduces the CHCl₃ solubility, but it can result in a small increase. The (II) in a hæmatin solution is considerably > in slightly alkaline H₂O, but < in blood; hence it can be assumed that it is the prosthetic group in (I) which increases (II).

L. S. T.

Chloroform fixation in serum: sensitisation and the presence of small quantities of hæmoglobin. L. SCOTTI-FOGLIENI (Compt. rend. Soc. Biol., 1933, 106, 1055—1059; Chem. Zentr., 1933, ii, 2844).—The CHCl₃-solubility coeff. (I) of specially-prepared serum is practically the same as that of distilled H₂O, but sera containing small quantities (> 0.7—1.0%) of hæmoglobin (II) have vals. of (I) which equal those of blood. The (I) of diluted sera shows that the CHCl₃ solubility depends not only on dilution, but also on the physico-chemical condition of the (II) mol.

L. S. T.

Influence of physical factors on the lacto-gelatinisation of serum. W. KOPACZEWSKI (Compt. rend., 1934, 198, 1947—1950).—The rate of gelatinisation of serum (I) by lactic acid (II) is unaffected by coating the tube with paraffin, is greater if (I) is added to (II) than *vice versa*, decreases with age of (I) up to 144 hr., rises with temp., is accelerated by ultra-violet light, possibly by X-rays, by lowering the surface tension or increasing the viscosity of the solution, and by addition of neutral, insol. substances. The gel liquefies partly if heated to 45—50°, but resolidifies on cooling. It partly liquefies if dialysed or violently agitated.

R. S. C.

Alcoholic fission of serum-albumin. V. S. SADIKOV and V. A. VADOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 185—187).—Serum-albumin with EtOH at 180° for 6 hr. yields 14.8% of the total N as NH₂-acids. Extraction with Et₂O and CHCl₃ followed by hydrolysis of the extract of the H₂O-sol. fraction (I) (82.5%) of the alcoholysate affords NH₂-N equiv. to 50—60% of the total N, but no (NH₂)₂-N. The H₂O-insol. fraction (II) on similar treatment yields no NH₂-N. Thus (I) and (II) contain, respectively, 40—50 and 100% of the total N as heterocyclic N. Hydrolysis of the corresponding residues does not increase the NH₂-N of (I), whilst that of (II) rises from 11.4 to 78.4% of the total N.

F. O. H.

Blood-sugar: physiological variation in non-diabetic patients. M. R. CASTEX and M. SCHEINGART (Compt. rend. Soc. Biol., 1933, 114, 78).—The fasting blood-sugar levels of 1000 patients, as determined by the Folin-Wu method, were 0.14—0.09% (in 450 cases > 0.10%). Of any 100 patients with levels below 0.10% 55 were female and 45 male; the levels of adolescents and of old people were slightly > the average, but the diurnal and seasonal variations in fasting patients were very small.

NUTR. ABS. (b)

Fermentation of blood-sugars. H. GIOVAMBATTISTA (Rev. fac. cienc. quim., La Plata, 1933, 8, ii, 47—63).—Identical results were obtained by the use of *Saccharomyces cerevisiae*, *S. ellipsoideus*, and *Zigosaccharomyces mali*. Whole blood deproteinised with H₂WO₄ gave higher vals. for non-fermentable reducing substances than that treated with Zn(OH)₂. For plasma or serum little difference was observed. Treatment with Hg(OAc)₂ or NaHCO₃ gave still lower vals.

CH. ABS.

Glycolysis of blood and its clinical interpretation. W. LOEWENSTEIN and B. BOTSTIEBER (Klin. Woch., 1933, 12, 1402—1404).—Determinations of blood-sugar by the Hagedorn-Jensen method are subject to error if the blood is not heated in presence of the protein precipitants immediately on withdrawal. A diminution in reducing power, affecting the non-sugar reducing substances as well as the sugar, attains a max. in about 3 hr. When glycolysis is prevented, an increase in reduction may occur.

NUTR. ABS. (b)

Paradoxical hypoglycæmic reaction following glucose in hyperglycæmia due to hydrochloric

acid. G. LINO (Arch. Sci. biol., 1933, **19**, 194—203).—Simultaneous injection of HCl and glucose (I) lowers blood-sugar (II). The increase in (II) induced by injection of HCl is not only arrested by subsequent injection of (I), but (II) falls below normal.

NUTR. ABS. (b)

Determination of sugar in 0.02 c.c. of blood (plasma etc.). F. RAPPAPORT and R. PISTINER (Mikrochem., 1934, **15**, 111—113).—A modification of the Hagedorn-Jensen method is described.

J. S. A.

Blood-sugar. I. Determination. M. LORA Y TAMAYO (Anal. Fis. Quím., 1933, **31**, 559—576).—1—2 c.c. of blood or plasma is deproteinised with Na_2WO_4 , filtered, and warmed with Fehling's solution (Folin formula); unreduced Cu is determined in the filtrate with KCN and AgNO_3 (A., 1930, 444). The method is accurate for >1 mg. of glucose (I). No (I) is found in blood or plasma treated with yeast, and after addition of (I) to such material the recovery is satisfactory.

R. K. C.

Sugar of cerebrospinal fluid. Determination by the cyanometric method. M. LORA Y TAMAYO (Anal. Fis. Quím., 1933, **31**, 577—581).—The method described above (preceding abstract) is applied.

R. K. C.

Zinc hydroxide powder as a precipitant in a simplified procedure for the preparation of protein-free filtrate of blood. T. V. LETONOFF (Amer. J. Med. Sci., 1934, **187**, 146).—Powdered $\text{Zn}(\text{OH})_2$ offers all the advantages of Somogyi's procedure, but eliminates the need for standardised solutions of NaOH and ZnSO_4 . Only traces of Zn appear in the filtrate. The true fermentable sugar level can be determined directly by alkaline Cu reagents. The neutral filtrates can be used for the determination of N fractions.

CH. ABS.

Relations between glucose, nitrogen, and cholesterol of blood. M. R. CASTEX and M. SCHTEINGART (Compt. rend. Soc. Biol., 1933, **114**, 745—746).—The blood-sugar level is not related to the level of cholesterol or N in the blood, although hyperglycemia is often accompanied by a rise of these.

NUTR. ABS. (b)

Cholesterol of horse serum. D. BROCC-ROUSSEU, G. ROUSSEL, and G. GALLOT (Compt. rend. Soc. Biol., 1933, **114**, 1075—1076).—The mean in 10 horses was 1.112 and in 13 mares 0.982%. It was increased in one horse after frequent bleeding from 1.047 to 1.103% and was also increased during gestation, the mean val. for 55 mares after 4 months being 1.201 and after 5—10 months 1.308%.

NUTR. ABS. (m)

Variations during the day and from day to day in total blood-fatty acids. J. M. MUNOZ (Compt. rend. Soc. Biol., 1933, **114**, 803—806).—In dogs on a standard diet there are rapid and irregular variations during the day and from day to day, and in summer the vals. are $>$ in autumn or winter.

NUTR. ABS. (m)

Origin of the lipæmia due to bleeding. F. ROSENTHAL, E. FRIEDLANDER, and R. KOHN (Arch. exp. Path. Pharm., 1934, **175**, 343—352).—Repeated bleeding of rabbits produces a lipæmia (I) which is

not inhibited by rapid injection of plasma, erythrocytes, or whole blood, and appears to be due to cell destruction, and not to the removal of some blood constituent. (I), which does not increase the deposition of fat in the liver, occurs when the liver-glycogen is increased by insulin-glucose administration.

F. O. H.

Lipæmia after bleeding. U. STARUP (Z. physiol. Chem., 1934, **224**, 116—120).—After cutting the medulla spinalis of rabbits above the seventh vertebra dorsalis (I) before successive bleedings, the lipæmia (II) is not so marked, and the lecithin/cholesterol quotient is not depressed so much as in ordinary (II) due to blood-letting, although (II) is not entirely prevented. Cutting below (I) has little or no effect.

J. H. B.

Determination of urea by urease methods in fluoride blood. C. F. M. ROSE (Brit. J. Exp. Path., 1933, **14**, 339—342).—Caffeine Mg salicylate counteracts the inhibitory effect of F'. The principal mechanism involved is one of adsorption.

CH. ABS.

Detection and occurrence of preformed acetylcholine in blood and tissue. G. KAHLSON (Arch. exp. Path. Pharm., 1934, **175**, 198—222).—In guinea-pigs, rabbits, cats, pigs, and man, the serum has the same content of free choline (I) as the erythrocytes; with oxen, the contents are 1:40. Of the intestine preps. of various animals, that of the mouse has the greatest sensitivity (0.05×10^{-6} g.) to acetylcholine (II). The frog's rectus abdominis muscle when sensitised with eserine is, however, suitable for the determination of (II) in tissue extracts. The blood (normal or hæmolysed with $\text{CCl}_3\text{-CO}_2\text{H}$ or Et_2O) of guinea-pigs, rabbits, cats, man, oxen, and horses does not contain (II) in detectable amounts (< 0.05 mg. per litre). With oxen, the (I) of the spleen is present totally as (II). The skeletal muscle of various animals is free from (II), whilst the large intestine contains considerable amounts. The formation and action of (II) in the body are discussed.

F. O. H.

Does normal blood contain chemically detectable amounts of acetylcholine? G. KAHLSON and R. ROMER (Arch. exp. Path. Pharm., 1934, **175**, 223—232).—Ox-blood was treated with EtOH and $\text{CCl}_3\text{-CO}_2\text{H}$, the filtrate conc. in vac., the residue reprecipitated with $\text{CCl}_3\text{-CO}_2\text{H}$, extracted with Et_2O , and finally pptd. with Reinecke acid. The ppt. contained the reineckates of choline and creatinine, but not that of acetylcholine (cf. A., 1932, 765; Dudley, J. Physiol., 1933, **79**, 248).

F. O. H.

Blood-glutathione in old age. J. NITZULESOV and I. ORNSTEIN (Compt. rend. Soc. Biol., 1933, **114**, 1134—1136).—The glutathione content of the blood varied from subject to subject, and with the limited nos. available could not be correlated either with age or sex.

NUTR. ABS. (b)

Blood-glutathione in Sebright cocks and hens. L. R. CHANTON and F. CARIDROIT (Compt. rend. Soc. Biol., 1933, **114**, 893—894).—Whereas normally the blood-glutathione (I) of the cock is much $>$ that of the hen, in the Sebright cock, where plumage is the same as that of the hen, the (I) has the same val.

NUTR. ABS. (b)

Determination of reduced glutathione in blood. F. MURATA (*Sei-i-kwai Med. J.*, 1932, **51**, No. 10, 92—95).—In a modification of the Perlzweig-Dettrue method, 3 c.c. of blood are added slowly and with shaking to 10 c.c. of H_2O , followed immediately by 10 c.c. of 1% $CCl_3 \cdot CO_2H$. The protein is then pptd. with 10 c.c. of 30% $CCl_3 \cdot CO_2H$. Rabbit's blood contains 0.0201—0.0264% (average 0.023%) of reduced glutathione. CH. ABS.

Non-protein-sulphur of blood and its relation to the adrenals. R. H. DE MEIO (*Compt. rend. Soc. Biol.*, 1933, **114**, 807—809).—There was no increase in blood-total S in dogs after removal of one adrenal, but after removal of the second the total S rose to 3—5 times normal. Neutral S was generally increased after removal of one or both glands. Non-protein-N was increased to a similar degree, suggesting that renal insufficiency was the cause.

NUTR. ABS. (b)
Mineral balance of normal blood-serum in man. A. URBEANO (*Compt. rend. Soc. Biol.*, 1933, **114**, 467—469).—The excess of bases (Na, K, Ca, Mg) over acids (Cl, P) has been calc. Normal serum contains 59.3% of bases. Disease (pellagra, cancer) alters the val. NUTR. ABS. (m)

Mineral composition of the blood-serum of the horse and the pig. W. G. ROBINSON (*Univ. Cambridge, Inst. Animal Pathol., Rep. Director*, 1932—1933, 156—158).—Figures are given for the Ca, inorg. P, Na, and K contents. NUTR. ABS. (m)

Determination of non-protein-bound calcium in serum. G. TAUBMANN (*Arch. exp. Path. Pharm.*, 1934, **175**, 182—188).—Determinations of Ca in the filtrates from the pptn. of serum by phosphomolybdic acid and, to a smaller extent, by $CCl_3 \cdot CO_2H$ give erroneous results for the non-protein-bound Ca owing to adsorption of Ca by the ppt. Ultra-filtration is more difficult, but gives the most accurate results. F. O. H.

Determination of calcium in 0.2 c.c. of serum. F. RAPPAPORT and D. RAPPAPORT (*Mikrochem.*, 1934, **15**, 107—110).— CaC_2O_4 is pptd. by saturated aq. $(NH_4)_2C_2O_4$, and collected by centrifuging. The ppt. is dissolved in 4N- H_2SO_4 , excess of 0.001N-Ce(SO_4)₂ added, and titrated back with 0.001N- $Na_2S_2O_3$ after addition of KI. J. S. A.

Calcium and phosphorus contents of the blood-serum of healthy cattle. W. HIPPMAN (*Diss.*, Hanover, 1930; *Bied. Zentr.*, 1934, **A**, 4, 353—354).—Serum-Ca (I) and -P in males was somewhat > in females and in young > in older animals. Ca vals. for calves were especially high. After administration of Ca (I) increased over 90 hr., and subsequently declined (30 hr.) to normal. Following intravenous injection (I) attained max. val. in a few min. and reverted to normal in 15 min. A. G. P.

Concentration of calcium and phosphorus in the serum of children. L. SCHOENTHAL and D. K. LURIE (*Amer. J. Dis. Children*, 1933, **46**, 1038—1044).—No change in the level of serum-Ca occurs in children from 5 to 16 years of age. The serum-P declines significantly beginning with the fifteenth year, especially in girls. Administration of viosterol (10—40

drops daily) or 1 quart. of milk does not regularly increase the levels. NUTR. ABS. (m)

Micro-determination of serum-calcium and -potassium. K. IN (*J. Chosen Med. Assoc.*, 1933, **23**, 1844—1852).—In a modification of the Kramer-Tisdall method excess of $KMnO_4$, then KI, are added, the liberated I being titrated with $Na_2S_2O_3$. CH. ABS.

Calcium content of cow's blood. II. (a) Calcium in the blood of parturient heifers; (b) effect of injections of parathyroid and irradiation; (c) some case reports of milk fever. W. L. LITTLE and E. C. V. MATTICK (*Vet. Rec.*, 1933, **13**, 1091—1097).—Heifers about parturition time show no change in total serum-Ca (I), but a lowering of diffusible serum-Ca (II) is noted at calving and is more pronounced 2—4 days *post partum*. Irradiation *ante partum* has no effect on (I). In milk fever (I) seldom exceeds 6 mg. and (II) is never above 3 mg. per 100 c.c. NUTR. ABS. (m)

Changes in blood-calcium and -potassium following intravenous injection of hypertonic salt solutions. G. DUCLOS and P. C. FABRE (*Compt. rend. Soc. Biol.*, 1933, **114**, 491—492).—A rise in alkali reserve and a fall (I) in plasma-Ca occur after intravenous injection of 30% NaCl into a dog, the vals. returning to normal within 1 hr. Since a diminution in Ca decreases the tonus of the splanchnic nerves, (I) accounts for the mechanism of the action of hypertonic NaCl in intestinal obstruction. NUTR. ABS. (m)

Calcium, potassium, phosphorus, and K : Ca ratio in the blood after partial removal of the liver. C. I. PARHON, H. DEREVICI, and M. DEREVICI (*Compt. rend. Soc. Biol.*, 1933, **114**, 67—68).—5—6 hr. after removal of about $\frac{2}{3}$ of the liver from guinea-pigs the serum-Ca tends to fall and the -P to rise. The K is diminished (average from 22.4 to 14.2 mg. per 100 c.c.). The average K : Ca ratio falls from 1.92 to 1.41. NUTR. ABS. (m)

Effect of injection of potassium and calcium on the K : Ca ratio in dogs. L. BALLIF and I. GHERSCOVICI (*Compt. rend. Soc. Biol.*, 1933, **114**, 324—325).—A progressive increase of blood-Ca and -P follows injection of KCl, the K : Ca ratio being increased up to three times the normal val. Injection of $CaCl_2$ generally leads to increased vals. for blood-K and -Ca, the K : Ca ratio being raised about 50%. NUTR. ABS. (m)

Alkali reserve and chloride ratio. M. CHATRON (*Bull. Soc. Chim. biol.*, 1934, **16**, 400—404).—The ratio corpuscle-Cl/plasma-Cl is important as a measure of the acid-base equilibrium in the blood, but it is elevated by increase of total Cl as well as by decrease of alkali reserve. W. O. K.

Blood-chlorine in afferent and efferent vessels of the chief viscera. L. BOTTIN (*Compt. rend. Soc. Biol.*, 1933, **114**, 1386—1389).—The blood-Cl of the dog, after fasting and immediately, or up to 1 hr., after a meal of 250 c.c. of milk, is unchanged in the afferent (I) and efferent vessels (II) of the liver, spleen, lungs, and brain. The (II) of the stomach, superior mesentery, and kidney, however, contain marked

less CI after a meal than the (I), the differences in vals. decreasing with fasting. NUTR. ABS. (b)

Physiological values of blood-iodine. T. LEIPERT (Biochem. Z., 1934, 270, 448—454).—The normal blood-I content (I) in man is $13 \pm 4 \times 10^{-6}$ g. per 100 c.c., no difference being detectable with age or sex. In woman (I) increases by $> 100\%$ at menstruation, and then quickly returns to normal, and in pregnancy gradually increases, the mean max. val. at the end being 31.5×10^{-6} g. per 100 c.c. The vals. fall rapidly during lactation. P. W. C.

Action of acid on the protein precursor of thrombin. A. FISCHER (Biochem. Z., 1934, 270, 235—249).—Traces of acid acting for a short time cause irreversible changes in the muscle-globulin [prothrombin (I)], the protein being no longer sol. in neutral salt solutions and the coagulation max. (II) being displaced from 5.3 to 9. Similar but not such large differences are obtained with serum- and plasma-globulins when (II) is displaced to the alkaline side, but only by 0.6—1.0 Mellanby's fibrinogen (III) is stable to acid so long as the amount added is not sufficient to cause any visible coagulation. Mixtures of (III) and (I) behave like pure (I). Heparin, but not nucleic acid, protects (I) against denaturation by acid, but cannot reverse the effect of acid. P. W. C.

Activation of prothrombin. A. FISCHER (Biochem. Z., 1934, 270, 250—260).—In the activation of prothrombin (I) by thrombokinase (II) a denaturation occurs which is non-sp. and can also be obtained by physical, chemical, and actinic reactions. This action results in the depression of the solubility of (I) at the neutral point. Heparin effects an inhibition of clotting by inhibition of the denaturation of (I) by (II). (II) exerts also a sp. action on the conversion of fibrinogen into fibrin. P. W. C.

Latent stage in blood-clotting. A. FISCHER (Biochem. Z., 1934, 270, 261—274).—The latent portion of the clotting process is investigated from the moment of addition of thrombokinase (I) to a plasma free from thrombin (II) to the end of the clotting process. Coagulation of plasma-protein in buffer solution poor in electrolytes at p_H 5 decreases as the latent period progresses, the increasing stability being due to the behaviour of fibrinogen (III). If (I) is added to pure solutions of (III) and prothrombin (IV), coagulation of (III) decreases and of (IV) increases, a mixture of (III) and (IV) behaving like whole plasma. Pre-heated (48—50°) plasma on treatment with (I) coagulates more quickly the larger is the pretreatment. In this process, denaturation occurs, (IV) and (II) proteins being so changed that after coupling with (I), () is immediately formed.

Identity of muscle- and blood-thrombin. A. FISCHER (Biochem. Z., 1934, 270, 275—280).—Muscle extract contains prothrombin (I) which can be converted into thrombin (II). Muscle- and plasma-globulin have the same physico-chemical properties as (I) and (II). Muscle-(II) and plasma-(II) can coagulate oxalate- and heparin-plasma. Muscle-(II) can also coagulate fibrinogen solution. Plasma-(I) can be replaced by muscle-(I). P. W. C.

Specific carbohydrates of blood-groups. K. FREUDENBERG and H. EICHEL (Annalen, 1934, 510, 240—248).—The substance (I) previously isolated (A., 1932, 1153) from the urine of individuals of blood-group A has C 43, H 6—6.5, and N 5.0—5.5% (of which about 10% is NH_2-N), $[\alpha] -5^\circ$ to $+5^\circ$, and contains about 9—10% of *N*-Ac group. The activity (retardation of hæmolysis) of (I) is destroyed by *N*-alkali at 60° (not at room temp. during 48 hr.), but is unaffected by pancreatic amylase, emulsin, diastase, takadiastase, papain, I in various solvents, H_2O_2 , aq. CH_2O , or conc. HCO_2H ; acetylation (Ac_2O , C_5H_5N) gives an inactive product, partial hydrolysis of which regenerates (I). Hydrolysis ($0.2N-H_2SO_4$) of (I) gives galactose (II) and an amino-hexose. Similar substances (possessing much smaller activities) are isolable from the urine of blood-groups O and B; both give (II) on hydrolysis. H. B.

Method of applying the precipitin test. C. C. HADDON (Analyst, 1934, 59, 342).—Drop preps. of antiserum and the experimental fluid are made on slides and examined microscopically. E. C. S.

Device for uniform lighting in precipitin tests. H. P. BEALE (Contr. Boyce Thompson Inst., 1904, 6, 165—166).

Action of light on visual purple. M. L. VERRIER (Compt. rend., 1934, 198, 1806—1808).—Although visual purple (I) (in retina films or in 4% solution in ox bile) of *Scyllium canicula*, L., and *Scorpaena scrofa*, L. [poor in (I)], is decolorised by exposure to feeble illumination (65 c.p.), that of *Eledone moschata*, Leach, and *Julis giofredi*, Risso [rich in (I) and in melanin], is stable to intense illumination for prolonged periods [same absorption spectrum as with (I) from animals kept in dark]. Hence the alternate destruction and regeneration of (I) cannot be responsible for light-sensibility. J. W. B.

Extraction and determination of free choline [in tissues]. G. KAHLSON (Arch. exp. Path. Pharm., 1934, 175, 189—197).—The tissue is extracted with EtOH or $COMe_2$, the extract evaporated in vac., and the residue freed from lecithin etc. by extraction with light petroleum. The residue of free choline (I) is then acetylated and the acetylcholine assayed by its action on the mouse's small intestine. Blood, serum, muscle, and intestine (guinea-pig, rabbit, man) have (I) contents of 0.28—1.17, 0.37—1.37, 0.30—1.13, and 4.27—7.28 mg. per 100 g., respectively. F. O. H.

Distribution of nitrogen in the muscular tissue of *Mullus barbatus*. L. G. BINI (Atti R. Accad. Lincei, 1934, [vi], 19, 111—115).—The % of the total N present in different forms are: amide 12.0, humin 2.5, arginine 9.4, histidine 15.9, lysine 7.45, non- NH_2 9.8, and NH_2 42.7. T. H. P.

Lipin content of the parathyroids in different animal species. C. I. PARHON and I. ORNSTEIN (Compt. rend. Soc. Biol., 1933, 114, 753—754).—The mean contents for 10 dogs, cats, and rabbits were 32.39, 57.91, and 60.63%, respectively.

NUTR. ABS. (m)

Fat content of the foetal lung. H. R. KANITZ (Virchow's Archiv, 1933, 291, 410—417).—The fat

content of the lungs during foetal life remains at first fairly const. (6th to 8th month, 15.7%), and then rises considerably until after birth (10th month 23.35%) and finally decreases (11th month 10.95%).

NUTR. ABS. (b)

Colloidal properties of pupa oil. H. KANEKO and K. YAMAMOTO (Bull. Sericult. Japan, 1934, 6, 4—5).—The relative viscosity (η) of pupa oil is given by $\log \eta = 1.85 - 0.009t$ ($t > 20^\circ$), $\log \eta = 5.30 - 0.166t$ ($t > 6^\circ < 20^\circ$). When mixed with oils of higher η the η -concn. curves are S-shaped, with oils of lower η they are concave. In dispersions in org. solvents $\log \eta \propto$ concn.

A. G.

Saturated fatty acids of Japanese chrysalis oil. S. UENO and H. IKUTA (J. Soc. Chem. Ind. Japan, 1934, 37, 124—126b).—The Me esters of the solid fatty acids when fractionally distilled afford Me palmitate and stearate, and the ester of a C_{20} or C_{22} acid, but no Me isopalmitate (cf. A., 1921, i, 699).

J. L. D.

Insect waxes. VII. Fractionation of schizoneuric acid. F. N. SCHULZ and M. BECKER (Biochem. Z., 1934, 270, 386—388).—The Me esters of the acids from schizoneura wax on fractionation at 0.12 mm. indicated the presence of $\frac{2}{3}$ myristic and $\frac{1}{3}$ palmitic acid (cf. A., 1933, 1066).

P. W. C.

Formation of a fat-soluble red pigment in cured meats. O. NOETZEL and A. PAVLETTA (Pharm. Zentr., 1934, 75, 361—365).—A red pigment (I) appears in the fat (II) of meat after 5 days' curing at room temp. with KNO_3 . (I) is destroyed when (II) is saponified or becomes rancid. The absorption spectrum (III) of (I) in melted (II) is identical with that of oxyhaemoglobin, except that the band in the yellow-green is absent. (I) turns first brown, then yellow, when exposed to air, and then gives the (III) of methaemoglobin. (I) is also formed, although to a smaller extent and more slowly, when meat is cured without KNO_3 .

E. C. S.

Determination of pyruvic acid in muscle. A. HAHN and H. NIEMER (Z. Biol., 1934, 95, 169—172).—The minced muscle is treated with semicarbazide hydrochloride (I); proteins are removed with boiling aq. $(NH_4)_2SO_4$. Excess of (I) is removed with $PhCHO$, and the $AcCO_2H$ converted into phenylhydrazone, and weighed as such.

H. D.

Use of aqueous extracts for determining glycogen and total carbohydrate in the liver. C. TSAI (Chinese J. Physiol., 1933, 7, 343—352).—After one aq. extraction of rabbit-liver, the glycogen (I) content of the residue is 30—60% > that of the extract, and after several aq. extractions, the residue still contains 0.356 g. of (I) per 100 g. A single boiling- H_2O extraction may not therefore be used for the determination of total carbohydrate or (I).

A. L.

Carbohydrate content of liver and muscle in the wild and domestic duck. S. SUZUKI (Japan. J. Med. Sci. Biochem., 1933, 2, 277—283).—The glycogen and glucose vals. for the wild are similar to those for the domestic duck. In both species breast muscle contains more carbohydrate than leg muscle.

NUTR. ABS. (m)

Localisation of mineral salts in cells of mammalian tissues by micro-incineration. G. H. SCOTT (Amer. J. Anat., 1933, 53, 243—288).—Only Fe and Si can be recognised with certainty. Ca in large, or aggregates of small, cells can be recognised. In dividing cells the mineral matter is conc. in the chromatin. Exposed surfaces such as cell surfaces along vascular channels show concn. of inorg. salts.

CH. ABS.

Relation of specific potential of gastric mucous membrane of warm-blooded animals to hydrochloric acid secretion. H. SARRE (Z. Biol., 1934, 95, 135—145).—A portion of the mucous membrane of a cat's stomach was ligatured to a ring; the membrane potential (I) was determined by a KCl-agar electrode dipping into the trough so formed; $[H^+]$ and $[Cl^-]$ were determined by Sb and AgCl electrodes, respectively. Secretion is accompanied by an increased negativity of (I), independent of its initial val., corresponding with the increased $[H^+]$. The $[Cl^-]$ remains const. during secretion.

H. D.

Composition of pure intestinal juice from the lowest segment of the ileum in man. A. BICKEL and H. R. KANITZ (Biochem. Z., 1934, 270, 378—381).—General chemical analysis of the juice is carried out, and the presence of amylase and erepsin but absence of lipase is detected. The type of nutrition does not affect the enzymic content of the secretion.

P. W. C.

Taurocholic acid. II. T. KAZUNO and K. YAMAZAKI (Z. physiol. Chem., 1934, 224, 160—162).—From the Na salt isolated from dog's bile by Tanaka (A., 1933, 1162) amorphous taurocholic acid (I), m.p. about 125° (decomp.), $[\alpha]_D^{25} + 38.8^\circ$ in EtOH [Na salt, m.p. 180° , $[\alpha]_D^{25} + 23.9^\circ$; cryst. Ba salt (+5 H_2O), decomp. 225 — 227° , $[\alpha]_D^{25} + 25.6^\circ$ in H_2O], was obtained. (I) was isolated as Na salt from the bile of *Scomberomorus Nipponius*.

J. H. B.

Variations in the solids-not-fat content of milk. I, II. S. BARTLETT (J. Dairy Res., 1934, 5, 113—123).—Little change occurs in the solids-not-fat during an individual milking. Variations over a complete lactation period are recorded, and indicate the influence of age and pregnancy.

A. G. P.

Phosphorus compounds of milk. V. Phosphorus partition in milk with preliminary observations on milk-phosphatase. W. R. GRAHAM, jun., and H. D. KAY. VI. Effect of heat on milk-phosphatase. Simple method for distinguishing raw from pasteurised milk, raw from pasteurised cream, and butter made from raw from that made from pasteurised cream. H. D. KAY and W. R. GRAHAM, jun. (J. Dairy Res., 1933, 5, 54—62, 63—74).—V. Methods for determining the distribution in milk are examined. The acid-sol. ester-P (I) in milk is approx. $\frac{1}{4}$ — $\frac{1}{2}$ of the inorg. P. Phosphatase in milk (optimum pH 9.0) causes far γ rapid changes in the amount of (I) in milk on keeping, and possibly within the mammary gland. Differences in the level of (I) are associated with different breeds of cows.

VI. The phosphatase of milk is sufficiently heat labile to be destroyed by effective pasteurisation (10 min. at 72°).

and its presence or absence serves to indicate (II). A simple technique for performing the test is described.

A. G. P.

Cholesterol content of milk in relation to that of food. H. DAM (Z. physiol. Chem., 1934, 224, 127—128).—Administration of cholesterol (I) to goats for 3 days caused no increase of (I) in the milk.

J. H. B.

Cholesterol content and antirachitic activation of milk constituents. S. ANSBACHER and G. C. SUPPLEE (J. Biol. Chem., 1934, 105, 391—404).—A colorimetric method for determination of cholesterol (I) after pptn. with digitonin is described. (I) in butter-fat (II) varies between 0.24 and 0.34%. In milk 18% of (I) is associated with the proteins (III), of which most is with the lactalbumin in a relatively const. amount. The fat associated with (III) holds more (I) than does (II). (I) associated with (III) contains a substance which can be activated antirachitically.

H. G. R.

Presence of cholesterol in faeces. R. SCHOENHEIMER (J. Biol. Chem., 1934, 105, 355—357).—By bromination in EtOH unsaturated sterols are rendered unprecipitable by digitonin, and can thus be separated from saturated sterols. In this way cholesterol was isolated from human and canine faeces.

C. G. A.

Urine of normal dairy cows. G. F. BODDIE (Vet. Rec., 1933, 13, 1128—1133).—Samples of urine taken during autumn, winter, and spring from apparently healthy cows on good mixed diets contained no albumin, bile-pigment or -salts, blood-pigment, (except in three cases), or blood. Sugar (58% of cases), indican, creatinine (small amounts), glycuronic acid, mucus (25% of cases), urea, and COMe₂ (44% of cases) were present.

NUTR. ABS. (b)

Comparison of urinary total nitrogen for one-day and four-day periods. B. L. KUNERTH (Trans. Kansas Acad. Sci., 1933, 36, 157—158).—A composite sample may be used to calculate daily N excretion.

CH. ABS.

Determination of thiocyanate in urine. E. J. BAUMANN, D. B. SPRINSON, and N. METZGER (J. Biol. Chem., 1934, 105, 269—277).—HCN, formed by the action of CrO₃ on SCN', is removed by aeration, trapped in NaOH, and titrated with AgNO₃ (cf. A., 1919, ii, 530). If < 5 mg. SCN' per 100 c.c. of urine are present, a preliminary purification is necessary to remove traces of NH₂-acids and other N compounds (cf. A., 1933, 1188).

A. E. O.

Detection and determination of glycogen in urine. H. CAPPENBERG (Arch. Pharm., 1934, 272, 559—561; cf. A., 1931, 758).—Glycogen (I) occurs most frequently in urine of patients suffering from liver- or bile-infection, gout, or arteriosclerosis, being accompanied in the last two cases by much PO₄' and

Pure (I) gives the same reactions as when obtained from urine, whether or not sugar or ovalbumin is also present. (I) gives the Mayrhofer (Polenske) reaction for intact starch. It can be determined by its slow reduction of Fehling's solution (II); if sugar is also present, the Cu₂O formed thereby is removed, and (I) determined by further oxidation of the filtrate. (I)

can be pptd. by Esbach's reagent and then determined by (II).

R. S. C.

Incidence of sugars in the urine of infants and children. M. FIKRI and M. A. EL-SAYED (Arch. Dis. Children, 1933, 8, 409—412).—In 63 healthy children only 1 case, a breast-fed infant, showed a reducing agent, lactose (I), in the urine, and it was present only once. Out of 87 sick children, 11 showed a reducing substance in the urine, which was found to be (I) in 8 cases, and (I) plus glucose in 3 cases. In the (I) cases, the excretion of the sugar was transient in 5, and persistent in 3, these 3 being cases of Pott's disease, multiple boils, and pulmonary tuberculosis.

NUTR. ABS. (b)

Fasting blood-sugar and blood-sugar curves after oral administration of glucose in allergic subjects. J. VAN NIEKERK (Z. ges. exp. Med., 1933, 90, 617—624).—In allergic patients, during a period without an attack, the fasting blood-sugar was normal. After 50 g. of glucose, the fall in blood-sugar to fasting level was usually delayed: occasionally the peak was higher or lower, and the rise slower than normal. The type of curve cannot be used as diagnostic of allergy.

NUTR. ABS. (b)

Nutritional anaemia of the rat. X. Haemoglobin production and iron and copper metabolism with milk of low copper content. F. C. BRNG, E. M. SAURWEIN, and V. C. MYERS (J. Biol. Chem., 1934, 105, 343—354).—Rats rendered anaemic by a diet of milk containing 0.14 mg. of Cu per litre showed an increase in haemoglobin content (I) on oral administration of 0.5 mg. of Fe per day. Addition of 0.025 mg. of Cu per day as well restored (I) to the normal level. Intraperitoneal injection of Fe had the same effect, possibly due to increased retention of Cu.

C. G. A.

Specific catalytic action of copper in the oxidation of glutathione. A. QUARTAROLI (Annali Chim. Appl., 1934, 24, 225—226).—Whereas blood contains 1 part of Cu per 300—350 parts of Fe, haematin contains, contrary to Voegtlin *et al.* (A., 1931, 763; 1932, 77; this vol., 90), 124 mg. of Cu per kg. (A., 1932, 1182). The necessity of adding small proportions of Cu salts to Fe salts used to combat experimental anaemia is discussed.

T. H. P.

Gastro-intestinal studies. III. Determinations of enzymes on autopsy specimens from cases of pernicious anaemia and pellagra. O. M. HELMER, P. J. FOUTS, and L. G. ZERFAS (Arch. Int. Med., 1934, 53, 675—679).—Gastric mucosa taken *post mortem* from patients with pernicious anaemia contained no pepsin or rennin, whilst in cases of pellagra subnormal quantities were present. Neither disease was associated with decreased proteolytic, amylolytic, or lipolytic activity of the pancreas, whilst the intestinal mucosa was normal in respect of enterokinase action.

W. O. K.

Blood-calcium during consolidation of fractures. J. PERVES (Compt. rend. Soc. Biol., 1933, 114, 526—528).—The blood-Ca rises after bone fracture and returns to normal when consolidation is complete.

NUTR. ABS. (m)

Bones of native horses affected with osteomalacia. M. D. SUMULONG (Philippine J. Sci., 1934, 53, 141—157).—The wt. and ash content of the bones are diminished, the latter from 55.9 to 49.5%. The chief reduction is in CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$, and Na_2CO_3 .

H. G. R.

Relation between the physical character of food and dental caries in albino rats. C. A. LILLY and L. WILEY (J. Nutrition, 1934, 7, 463—472).—Appearance of caries in rats receiving standard rations containing coarse maize meal is related to the physical condition of the diet rather than to its Ca and P contents. Cooking or fine grinding prevented caries. Vitamin-D was without effect. A. G. P.

Calcium and cholesterol in blood and gall-bladder bile in cholelithiasis and cholecystitis. M. CATTANEO (Z. ges. exp. Med., 1933, 91, 683—688).—The cholesterol (I) concn. in bile (II) from obstructed gall-bladders was > in (II) obtained from a normal biliary tract. A high (I) val. indicates some obstruction, but a low val. does not necessarily signify the presence of gallstones. The serum-Ca is generally normal in cholelithiasis. In cholecystitis without gallstone formation both the (I) and Ca of (II) were increased. In cholecystitis with cholelithiasis no correlation was obtained between the increases of (I) in (II) and blood.

NUTR. ABS. (b)

Protein-bound sugar of blood and insulin. G. CARRIERE and P. MARTIN. **Protein-bound sugar and serum-proteins during insulin hypoglycæmia in normal and diabetic subjects.** G. CARRIERE, P. MARTIN, and CARBONNEL (Compt. rend. Soc. Biol., 1933, 114, 135—136, 265—266).—Administration of 15—45 units of insulin does not affect the level of the protein-bound sugar of whole blood or serum, nor are the proteins of serum affected.

NUTR. ABS. (m)

Metabolism of carbohydrate and fat and its relation to insulin: effects of high-carbohydrate-low-fat diet in diabetes. E. P. POULTON (Proc. Roy. Soc. Med., 1933, 26, 1591—1607).—Indirect calorimetry, involving calculations based on the Zuntz-Schumberg theory, is liable to serious errors. The heat produced appears to be \propto the CO_2 liberated, whilst under basal conditions there is a const. combustion ratio of carbohydrate and fat. Insulin increases combustion and stimulates conversion of carbohydrate into some less oxygenated substance.

NUTR. ABS. (m)

Variations in blood-potassium and -calcium in acute eczema and dermatitis. G. I. UMANSKY and A. P. STEPANOVA (Wien. klin. Woch., 1933, 46, 1262—1265).—An invariable increase in the blood-K and sometimes a decrease in the blood-Ca occur in dermatitis or acute eczema with cedema (I). The K tends to decrease and the Ca to increase with the disappearance of (I).

NUTR. ABS. (m)

Micro-incineration of the liver in Rift Valley fever. E. S. HORNING and G. M. FINDLAY (J. Roy. Microscop. Soc., 1934, 54, 9—17).—Incineration of the liver 24—30 hr. after infection with the virus of Rift Valley fever shows changes in the localisation of mineral salts. The ash of chromatin, nucleolus, and

inclusion body can be differentiated. The necrosis occurring in malignancy and CCl_4 poisoning is similar, as regards localisation of inorg. constituents of the tissue, to that which follows certain virus infections.

P. G. M.

Serum-proteins and chlorides in hepatic cedema. **Biochemical modifications after novasurol and hepatotherapy.** M. RAFFAELE (Arch. Farm. sperim., 1934, 57, 219—238).—Hepatic cedema is attended by a fall in serum-protein, inversion of the normal albumin-globulin ratio (I), and a rise in venous and capillary Cl' . Administration of novasurol or hepatotherapy, or both, brings (I) rapidly to the normal val. in both serum and ascites, and increases urinary Cl' excretion.

R. N. C.

Intermediary metabolism of carbohydrates, experimental hepatitis, and protective liver therapy. G. G. D'ANTONA (Riv. Patol. sper., 1933, 11, 354—380).—In rabbits with experimental liver lesions produced by tuberculin, injection of glucose has no protective action nor regenerative effect on the liver, kidneys, and spleen, and is actively harmful, since it increases fatty infiltration and has a deleterious action on the kidneys. The disappearance of the liver-glycogen is the result of the tuberculin poisoning.

NUTR. ABS. (m)

Enzymes in glycogen-storing disease. W. HERTZ (Klin. Woch., 1933, 12, 1725—1727).—The diastase of blood and urine is raised, blood-glycolysis is little affected, and the lipolytic activity of the blood-serum and liver is sometimes increased.

NUTR. ABS. (m)

Metabolism in glycogen-storing disease. W. HERTZ (Z. Kinderheilk., 1933, 55, 588—601).—In a dwarf child of 11 suffering from the disease the N exchange was not raised in spite of a high basal metabolic rate. There was no disturbance of NH_2 -acid metabolism, nor increased urobilin excretion, but the creatine-creatinine output was high. The condition is due, not to disordered liver function, but to exaggerated glycogen-storing power of the liver and other organs.

NUTR. ABS. (m)

Diagnostic significance of sodium chloride metabolism in liver disease. L. RÓSA (Orvosi Hetilap, 1933, 77, 1050—1051).—Normal 24-hr. urine contains ≤ 0.72 — 0.74% of NaCl . In the absence of acute infections and diabetes a lower concn. is characteristic for liver-disease.

NUTR. ABS. (b)

Origin and significance of tyrosinuria in liver disease. S. S. LICHTMAN (Arch. Int. Med., 1934, 53, 680—688).—Marked tyrosinuria (I) was found in acute yellow atrophy (II), whilst mild and transitory (I) occurred in subacute (II) and certain other diseases of the liver and bile passages.

W. O. K.

Creatinine in blood-serum and cerebrospinal fluid. R. B. MAYDELL (Z. ges. exp. Med., 1933, 91, 455—462).—In normal subjects the serum contains 1.6 mg. and the fluid 1.18 mg. of preformed creatinine (I) per 100 c.c. In chronic interstitial nephritis the (I) val. rises more slowly in the fluid than in the serum. Vals. > 4.0 mg. (serum) and 2.4 mg. (fluid) occur when there is tendency to uræmia; vals.

>14 and 5 mg. are obtained only in last stages of chronic nephritis and malignant nephrosclerosis.

NUTR. ABS. (m)

Lipin-protein equilibrium in serum of patients suffering from skin or lipaemic affections. A. SARTORY, R. SARTORY, J. MEYER, and J. CUENI (Compt. rend., 1934, 198, 1724—1726).—Total proteins (I) are unchanged in obesity, although the albumin (II)-globulin (III) ratio depends on the p_H . In hyperkeratosis, (II)/(III) is reversed in val., whilst in fatty dystrophy of the cornea the metabolism of fatty acids and cholesterol is abnormal. J. L. D.

Production of hypochloraemia in the dog with survival. J. BOTTIN (Compt. rend. Soc. Biol., 1933, 114, 1392—1394).—Death, following intestinal obstruction, is not due entirely, if at all, to hypochloraemia (I), since vals. for blood-Cl, approximating to that found in (I), have been obtained experimentally in the dog with survival.

NUTR. ABS. (m)

Organo-aciduria in pregnancy and physiological puerperium. F. P. DONEDDU (Arch. Farm. sperim., 1934, 57, 201—218).—The mean daily excretion of org. acids in the urine, equiv. to 330 c.c. of 0.1N, remains const. throughout the pregnancy period, but falls slowly during the first few days of puerperium.

R. N. C.

Effect of pregnancy and parturition on some blood and urinary constituents in the ewe. S. W. JOSLAND (New Zealand J. Sci. Tech., 1934, 15, 358—363).—During 2 months prior to and 6 weeks after parturition changes in serum-Ca and -Mg were insignificant, the inorg. P declined somewhat at or near parturition, whole blood-K varied irregularly, and -Na was slightly higher after parturition. Throughout the period the NH_3 - and total N in the urine varied considerably, the total P was approx. const., and protein, sugar, and $COMe_2$ were detectable only occasionally.

A. G. P.

Calcium metabolism and chronic rheumatism. F. COSTE, A. GRIGAUT, and P. CHARMANT (Compt. rend. Soc. Biol., 1933, 114, 895—897).—In arthritis deformans (I) the serum-Ca is 9.3—11.9 mg. per 100 c.c. No support is given to the view that parathyroid dysfunction is concerned with (I).

NUTR. ABS. (m)

Gastric tetany. R. KLINGNER (Z. ges. exp. Med., 1933, 92, 129—146).—Hypochloraemia occurs with increase of non-protein-N and alkali reserve. Serum-Ca increases. Parenteral administration of H_2O and NaCl leads to large retention of both with disappearance of the severe symptoms and return of blood constituents to normal.

NUTR. ABS. (m)

Blood-cholesterol and thyroid disease. III. Myxoedema and hypercholesterolaemia. L. M. HURXTHAL (Arch. Int. Med., 1934, 53, 762—781).—Thyroidectomy is frequently followed by hypercholesterolaemia (I) with or without myxoedema and a low metabolic rate. In the absence of other causative factors (I) suggests thyroid deficiency.

Inverted sugar tolerance curves in a case of Addison's disease. E. L. TURNER (Endocrinology, 1933, 17, 699—702).—Low blood-sugar (I) vals. in

Addison's disease have been recorded. In the case described, a series of (I) vals. after oral administration of glucose were < the fasting (I) val. (inversion curve). An intravenous glucose-tolerance test indicated that gastro-intestinal absorption was a factor.

NUTR. ABS. (b)

Hypoglycaemia due to intravenous insulin in endocrine disturbances. M. LABBE, A. ESCALIER, and P. UHRY (Compt. rend. Soc. Biol., 1933, 114, 890—892).—The hypoglycaemic response is normal in scleroderma, acromegaly, and diabetes insipidus (I) treated with pituitary extracts; it is enhanced in Recklinghausen's disease, exophthalmic goitre, and untreated (I). In a case of Addison's disease it was intense.

NUTR. ABS. (m)

Effect of toxæmia on tolerance for glucose and on the action of insulin. J. S. SWEENEY, N. BARSHOP, and L. C. LOBELLO (Arch. Int. Med., 1934, 53, 689—698).—The lowered sugar tolerance in rabbits resulting from diphtheria toxin is removed by giving a suitable quantity of insulin a short time before the glucose.

W. O. K.

Carbohydrate metabolism in pulmonary tuberculosis. S. SHIMIZU (Tohoku J. Exp. Med., 1933, 22, 132—148).—The blood-sugar level in pulmonary tuberculosis is not essentially abnormal, but may show wide variations in severe cases. Hyperglycaemia (I) may be due to secondary causes, e.g., loss of blood. Hypoglycaemia occurs only in the final stages of cachexia. Alimentary (I) tends to be prolonged.

NUTR. ABS. (b)

Metabolic rhythm, day and night, in the pigeon. E. BURCKARD, L. DONTCHEFF, and C. KAISER (Ann. Physiol. Physico-chim. biol., 1933, 9, 303—368).—The basal metabolic rate (I) in normal pigeons rises by 2.2% for each degree of fall in temp. from 30° to 20°; below 20° the increase is 3.3%. If ruffling of feathers be prevented, heat loss is increased and the increase in (I) is then 3.2% from 30° to 20° and 3.8% from 20° to 5°. The difference between day and night (I) is 15%.

NUTR. ABS. (m)

Fertilisation and temperature coefficients of oxygen consumption in eggs of *Arbacia punctulata*. B. B. RUBENSTEIN and R. W. GERARD (J. Gen. Physiol., 1934, 17, 677—685).—In a resting state the temp. coeff. Q_{10} is 4.1, but on fertilisation and on cytolysis this falls to 1.8 and 1.9, respectively. The factor causing increase in O_2 consumption is variable and depends on the temp. and on the species.

H. G. R.

Oxidation-reduction processes in muscular work. III. Glutathione. A. CHARIT and N. CHAUSTOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 26—29).—Stimulation of the gastrocnemius (dog) by an induction current for 15—60 min. causes a decrease in the reduced glutathione (I) content of arterial and (more so) venous (femoral) blood, and a corresponding increase in the oxidised glutathione content; a concomitant increase of (I) in the muscle tissue is observed.

J. W. B.

Oxidation-reduction processes in muscular work. IV. Ferric and ferrous compounds. A. CHARIT and A. KOSTIN (Compt. rend. Acad. Sci.

U.R.S.S., 1934, 2, 194—197).—During the stimulation of muscle the Fe^{III} content increases by $> 100\%$. Muscle activity is associated with the reaction $\text{Fe}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{III}}$, thus supporting Warburg's theory of the rôle of org. Fe compounds in muscle contraction.

F. O. H.

Chemical changes accompanying muscular activity and hyperthermia. II. Composition of the muscle, liver, and blood of normal dogs. J. HOUGET (Ann. Physiol. Physico-chim. biol., 1933, 9, 245—302).—Dogs kept for several weeks on identical diets do not show the same reserves in muscle, liver, or blood. H_2O , lipin, acid-sol. and total P show only slight, but other constituents may show large, individual variations. The composition is always characteristic for each tissue.

NUTR. ABS. (m)

Glycogen metabolism of muscle and neural influence thereon. I. Glycogen formation in denervated muscle. J. BAUM and E. PICHLER. II. **Glycogenolytical reflex.** J. BAUM, W. CHRISTEN, and E. PICHLER (Pflüger's Archiv, 1933, 233, 35—42, 43—50; Chem. Zentr., 1933, ii, 2850).—I. In winter the glycogen content (I) of a denervated frog-extremity is approx. $25\% >$ that of the normal portion. In summer a similar effect is obtained only by the simultaneous addition of insulin and glucose. After extirpation of the pancreas the increase is only 8% in denervated muscle and 16% in the dehepatised animal. The increase in (I) can be detected 4 hr. after the operation and reaches a max. in 24 hr.

II. After the removal of one gastrocnemius (I) the glycogen content of the other falls approx. 20% ; this fall persists after sympathicotomy (II). The glycogenolytical action of the sympathetic is directed straight to the muscle. The glycogenolytical reflex should occur more in the spinal nerves. Extirpation of (I) and (II) lead to a decrease in creatinephosphoric acid in the (I) of the other side.

L. S. T.

Glycogen metabolism of muscle and neural influence thereon. III. Proprioceptive glycogenolytical reflex. O. LOEWI and E. PICHLER (Pflüger's Archiv, 1933, 233, 51—56; Chem. Zentr., 1933, ii, 2850—2851).—The influence of strychnine convulsions on glycogenolysis is examined.

A. A. E.

Rôle of the adrenals in the resynthesis of muscle-glycogen after fatigue. R. G. DAMBROSI, F. L. LELOIR, and A. NOVELLI. **Rôle of the liver and pancreas in this resynthesis. Effect of section of the vagi or splanchnic nerves on this resynthesis in the dog. Rôle of the pancreas and the vagi in this resynthesis after fatigue in the cat.** R. G. DAMBROSI (Compt. rend. Soc. Biol., 1933, 114, 1219—1221, 1222—1224, 1224—1226, 1228—1230, 1230—1232).—In adrenalectomised dogs, the rate (I) of resynthesis of muscle-glycogen after fatigue is retarded. (I) is not increased by injection of glucose, but is made normal or above normal by injection of an extract of the adrenal cortex. In hepatectomised dogs, (I) varies with the level of the blood-sugar. Intravenous injection of glucose causes rapid resynthesis. In pancreatectomised dogs, (I) is little affected for a few hr. after the operation, but later is greatly retarded. Neither etherisation nor incomplete

pancreatectomy has this effect, which is also avoided after complete pancreatectomy by injection of insulin or grafting of pancreas in the neck. Resynthesis of muscle-glycogen after fatigue is unaffected in the dog by section of the vagi or of the splanchnics or of both together. In pancreatectomised cats (I) is retarded. Under chloralose, bilateral vagotomy does not cause diminution in (I), but Et_2O anaesthesia or respiratory troubles do so.

NUTR. ABS. (m)

Passage of glycogen through the haemochorial placenta. B. SZENDI (Z. Anat. Entw., 1933, 101, 791—798).—Glycogen (I) is supplied to the (rat) foetus not direct from the maternal blood-stream, but from the decidua where it is synthesised. The maternal placenta contains (I) cells (II) which make the (I) from the maternal blood-sugar. (II) pass over into the villi by means of the lymphatics as whole cells, after which (I) passes to the foetal blood.

NUTR. ABS. (m)

Blood-sugar equilibrium and gastric secretion. BAISSSET and BUGNARD. **Blood-sugar equilibrium and intestinal secretion.** A. BAISSSET. **Blood-sugar equilibrium in the depancreatized dog and in the normal dog following feeding.** BAISSSET, BUGNARD, and ROUZAUD. **Blood-sugar equilibrium following injection of glucose. Blood-sugar equilibrium and retention of sugar in tissues.** BASTIEN, BOUISSET, BUGNARD, and ROUZAUD. **Injection of glucose and retention in the liver.** BASTIEN, BOUISSET, and BUGNARD (Le Sang, 1933, 7, 875—881, 882—893, 894—901, 902—907, 908—913, 914—920, 921—932).—In dogs with oesophageal and gastric fistulae sham-fed with minced meat, blood-sugar rises with onset of gastric secretion (I) and attains a max. 1 hr. after the meal. The rise continues after the (I), returning to normal in about 3 hr. and is followed by hypoglycaemia (II). Where no (I) occurs (dogs drinking but refusing to eat) blood-sugar does not change. (I) and hyperglycaemia (III) are accompanied by a rise in blood- p_{H} and alkali reserve. In Pavlov pouch dogs (I) stimulates duodenal secretion with little change in blood-sugar (5 mg. per 100 c.c.). In gastrectomised dogs ingestion of HCl induces intestinal secretion and reduces blood-sugar. Injection of HCl into the duodenum in normal dogs also causes (II) of degree varying with the individual. A meal of potatoes causes (III) in dogs, varying from 15 to 80 mg. per 100 c.c., or may cause (II). A meal of meat causes little change, and of meat and potatoes together a variable (III). The largest increases in blood-sugar follow a meal of bread and milk. Alimentary (III) in depancreatized dogs following a meal of meat is much $>$ in normal dogs, but rapidly diminishes as in them. A regulatory mechanism, independent of the pancreas, is suggested, since blood-sugar equilibrium is re-established after pancreatectomy. Daily intravenous injection into unanaesthetised dogs of glucose in increasing amounts causes a rise in blood-sugar approx. \propto the amount injected, and a return to normal after an interval which also increases with the dose. The max. increase in blood-sugar is attained before completion of injection and is followed by a rapid fall with return to normal in 1-3 hr. After injection of glucose (1 g. per

rise in blood-sugar is greater in arterial than in venous blood at first, indicating retention in the tissues, but after about 45 min., venous blood-sugar is = or > arterial. In anaesthetised dogs exclusion of the liver by portal jugular anastomosis causes a variable (II), arterial blood-sugar falling more rapidly than venous with inversion after about 45 min. Following injection of 0.75 g. glucose per kg., the sugar rapidly disappears from the blood and there is again inversion of arterial and venous vals. The glucose stored following injection is more rapidly utilised by the normal than by the dog with exclusion of the liver, but in both cases blood-sugar returns to normal or below normal. Storage following injection is therefore independent of glycogen storage, although the utilisation of stored glucose is disturbed in absence of the liver.

NUTR. ABS. (m)

Assimilation of sugar in Eck fistula dogs. Blood-sugar after intravenous administration of sugar. S. LIVIERATO, M. VAGLIANO, and A. DERVENAGA (Compt. rend. Soc. Biol., 1933, 114, 462—464).—The glycaemic response of an Eck fistula dog to an intravenous injection of lactose or fructose is similar to that of a normal dog, but injection of glucose results in a hyperglycaemia > that found in the normal dog.

NUTR. ABS. (m)

Blood-sugar regulation after intravenous administration of large doses of glucose. M. FENICIA (Riv. Patol. sper., 1933, 11, 225—240).—After intravenous injection of massive doses of glucose into fasting dogs, the resultant hyperglycaemia rapidly disappears, due to an emergency fixation of the sugar by the tissues. Later, this sugar is discharged into the circulation, from which it is probably taken up by the liver.

NUTR. ABS. (b)

Carbohydrate metabolism. I. In the new-born. E. W. WINTER (Arch. Gynakol., 1933, 154, 354—373).—The mature new-born infant (I) has a physiological hypoglycaemia. The tolerance (II) of (I) to a single dose of glucose is normal, but a second dose, given about 90 min. after the first, results in a greater hyperglycaemia. This impairment of carbohydrate (II) during the early post-natal period may be due to a certain "unreadiness" of the infantile carbohydrate-regulating mechanism.

NUTR. ABS. (b)

Sugar metabolism in old age. Alimentary hyperglycaemia. J. NITZULESCU, I. ORNSTEIN, and M. SIBI (Compt. rend. Soc. Biol., 1933, 114, 1136—1138).—Determinations were made of blood-sugar (I) in fasting (aged) subjects after ingestion of 50 g. of glucose. Average vals. over a period of 3 hr. for each decade from 50 to 90 years are given. There was no progressive deviation of the (I) curve with increasing age, nor was glycosuria regularly found.

NUTR. ABS. (b)

Biological availability of soya-bean carbohydrate. W. H. ADOLPH and H. C. KAO (J. Nutrition, 1934, 7, 395—406).—Approx. 40% of the carbohydrate is utilisable by rats.

A. G. P.

dl-Lactic acid as nutritment. I. Assimilation toxicity in the rabbit. J. A. COLLAZO, J. PUYAL, and I. TORRES (Anal. Fis. Quim., 1933, 31, 684).—The metabolism of lactic acid is discussed.

Rabbits tolerate oral doses of 5—6 g. of Na lactate per kg. with slight dyspnoea. After administration the blood-lactic acid rises to 200—250 mg. per 100 c.c. and the blood-sugar increases simultaneously by as much as 50% of the initial val.

R. K. C.

Stimulating action of diet on production of glycogen from lactic acid in the liver. O. M. DOMANTOVITSCH (Problems of Nutrition, 1933, 2, 25—32).—In rats given special diets, followed, after an 18-hr. fast, by 0.2 g. of Na lactate (85% of which is absorbed), glycogen production (I) in the liver when meat is the chief food is > when it is wheat-protein or caseinogen. (I) is also stimulated by meat extract, lecithin, and PO_4''' .

NUTR. ABS. (m)

Production of liver-glycogen in the cat, under various conditions, following infusion of ammonium lactate. R. GRANT (J. Physiol., 1933, 80, 41—47).—Production of liver-glycogen (I) from NH_4 lactate occurs in the chloralosed cat with all organs intact, but is diminished or absent after splenectomy (II). After (II) infusion of acetylcholine with or after the lactate leads to an increase of (I) of the same order as that found in intact cats.

NUTR. ABS. (m)

Blood-lactic acid in man during rest. L. C. COOK and R. H. HURST (J. Physiol., 1933, 79, 443—454).—There are wide variations (I) in the same individual at different times under apparently identical conditions of bodily rest (II). During (II) the muscles supply no lactic acid (III) to the blood; activity of the sympathetic nervous system with consequent secretion of adrenaline is an unlikely source; the blood receives no demonstrable amount of (III) from the brain; glycolysis is the most probable source of the blood-(III) at rest. (I) during (II) are due to stimulation or depression of glycolytic activity.

NUTR. ABS. (m)

Glycolytic production of blood-lactate. C. L. EVANS, F. Y. HSU, and T. KOSAKA (J. Physiol., 1933, 80, 19—20r).—The rate of lactate formation in defibrinated blood perfused through ventilated lungs indicates that glycolysis is then 2 or 3 times as rapid as when blood is oxygenated by circulation *in vitro*. In the lung about 80% of the glucose lost is converted into lactic acid; in the oxygenator the conversion, which may be associated with haemolysis, is rather irregular.

NUTR. ABS. (m)

Ketosis in the phloridzinised rat. W. GOLDFARB, S. B. BARKER, and H. E. HIMWICH (J. Biol. Chem., 1934, 105, 283—286).—Unavoidable errors in the determination of the R.Q. made it impossible to conclude that the theoretical ketogenic-antiketogenic ratio of exactly 2:1 obtains in phloridzinised rats. The oxidation of keto-acids probably requires the simultaneous oxidation of antiketogenic substances.

A. E. O.

Ketosis in fasted and fat-fed rats. W. GOLDFARB, S. B. BARKER, and H. E. HIMWICH (J. Biol. Chem., 1934, 105, 287—290).—The rats excreted almost no ketonic substances (I) in a large majority of experiments. The non-protein R.Q. indicated that a mixture of fat and small amounts of preformed carbohydrate (II) was oxidised. Assuming a ketogenic-antiketogenic ratio of 2:1, and allowing for the (II)

oxidation and errors of method, the calc. and observed yields of (I) were in fair agreement. A. E. O.

Fasting ketosis of monkeys. I. T. E. FRIEDEMANN (J. Biol. Chem., 1934, 105, 335—341).—Fasting monkeys develop ketosis under conditions of metabolism similar to those producing ketosis in man.

C. G. A.

Chemical course of and physiological conditions for formation of ketonic substances from pyruvic acid. E. ANNAU (Z. physiol. Chem., 1934, 224, 141—149).—In the formation of COMe_2 from AcCO_2H in presence of H_2O_2 , 2 mols. of AcCO_2H probably condense to form parapyrucic acid, which, by decarboxylation and oxidation, then yields COMe_2 . The production of COMe_2 is increased by NH_3 and even by NH_4Cl . Oxidation in presence of liver-pulp shows the same effect. NH_3 probably also stimulates AcCO_2H formation in the liver, but has no action on fatty acid ketogenesis. In fasting the liver shows at first increased, later diminished, production of ketones, probably owing to more efficient breakdown of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{H}$ in prolonged hunger. The factors influencing ketogenesis are glycogen content and increased concn. of free NH_3 . Only the latter favours AcCO_2H production.

J. H. B.

Metabolism of neutral fat in central nervous system during embryonic development. A. HADJIOLOV and G. OUZOUNOV (Compt. rend. Soc. Biol., 1933, 114, 578—580).—Neutral fat, although not detectable histologically in the nervous system of adult fowls, can be detected therein during embryonic development.

NUTR. ABS. (m)

Influence of rations rich in phosphatides on the animal organism. A. TRAUTMANN (Z. Zucht., 1932, B, 24, 1—164; Bied. Zentr., 1934, A, 4, 339—340).—Soya-bean lecithin (I) was almost completely resorbed by rabbits, dogs, and pigs. The effects on the animals varied with their age and condition. Prolonged administration of small amounts of (I) to the very young favourably influenced live-wt. increases, but larger amounts retarded growth without notable ill-effects on general health. Long hair growth was induced in young pigs.

A. G. P.

Transformation of chlorophyll in the animal body. L. MARCHLEWSKI and W. URBANCZYK (Bull. Acad. Polonaise, 1933, A, 540—546).—The colouring matter from the air-dried excrement of silkworm larvae is shown, spectroscopically, to contain anhydro- β -phyllotaonin (I), (A., 1912, i, 641), max. absorption at 415.0 m μ , identical with Conant's phaeopurpurin 18 (A., 1930, 1299). A possible structure for (I) is suggested.

J. W. B.

Histolytic properties of regenerating tissue. V. N. ORECHOVITSCH and N. V. BROMLEI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 249—253).—Increases of approx. 100% in the residual N and $\text{NH}_2\text{-N}$ contents indicate that the regenerating tissue formed after amputation of a limb or tail of the axolotl or tadpole is the site of an increased protein degradation.

F. O. H.

Protein requirement in man. B. SUSSKIND (Z. Ver. deut. Zucker-Ind., 1934, 84, 341—356).—The presence of 1 g. of protein (I) per kg. of body-wt. in the

diet is not sufficient for the maintenance of normal condition, even when 70% of the (I) is of high biological val. Lack of (I) cannot be compensated by increasing the fat and carbohydrate contents of the diet.

P. G. M.

Synthesis and degradation of proteins in the laboratory and in metabolism. M. BERGMANN (Science, 1934, 79, 439—445).—A lecture. L. S. T.

Effect of heat on the biological value of meat protein. A. F. MORGAN and G. E. KERN (J. Nutrition, 1934, 7, 367—379).—Cooking of beef muscle or of horseflesh under atm. or increased pressure lowered the biological val. of the protein for maintenance of rats, the effect being rather more marked in the case of beef.

A. G. P.

Animal calorimetry. IX. Specific dynamic action of protein. X. Specific dynamic action of fat. Z. ASZÓDI and J. PELYI (Biochem. Z., 1934, 270, 389—418, 419—443).—IX. The sp. dynamic action (I) of protein (II) is dependent on the amount of (II) fed, due to its non-deposition and consequent immediate combustion. The amount of heat radiation by the organism is not in direct relationship with the O_2 utilisation after feeding (II).

X. No quant. relationship could be obtained between the (I) and the amount of fat ingested, due to its partial deposition. The amount of heat radiated, as before, does not synchronise with the O_2 utilisation.

P. W. C.

Specific dynamic action of the amino-acids, alanine and glycine. C. M. WILHELMJ (J. Nutrition, 1934, 7, 431—444).—When injected subcutaneously or intravenously into dogs alanine and glycine showed the same sp. dynamic action expressed as g.-cal. per millimol. of NH_2 -acid deaminised (0.2).

A. G. P.

Formation of ammonia from amino-acids in dog's liver *in vivo*. M. POLONOVSKI, P. BOULANGER, and G. BIZARD (Compt. rend., 1934, 198, 1815—1817).—Injection of glycine (I) or *dl*- $\text{NH}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (II) into the blood-stream of a dog causes immediate (2 min.) increase in the NH_3 in the renal vein (smaller increase in the artery), the effect of (II) being > that of (I) and much > that of natural *d*-(II). Hence natural NH_2 -acids, and especially their optical antipodes, are a source of urinary NH_3 . Injection of urea is without effect.

J. W. B.

Possible explanation of the function of glutathione in developmental growth. F. S. HAMMETT (Science, 1934, 79, 457).—Through cysteine glutathione accelerates cell proliferation, through glycine it accelerates protein reconstitution, and through glutamic acid it accelerates differentiation and consequent organisation.

L. S. T.

Effect of nutritional hypoproteinaemia on the electrolytic pattern and calcium concentration of serum. D. C. DARROW and M. K. CARY (J. Biol. Chem., 1934, 105, 327—334).—In dogs on protein-deficient diet there is no connexion between the serum-protein (I) and $-\text{Cl}'$, $-\text{HCO}_3'$, $-\text{K}$, or $-\text{Na}$, but (I) and serum-Ca are related by $\text{Ca} = 0.47 \times \text{protein} - 2.89$, Ca being expressed in milli-equiv. per litre and protein as %.

C. G. A.

Metabolism during growth. Variations with season and age. G. POPOVICIU, G. BENETATO, N. MUNTEANU, and M. SORESCU (Compt. rend. Soc. Biol., 1933, 114, 332—334).—In infants (up to 15 months) and adolescents (18—21 years) blood-lactic acid, -P, and to a certain extent -Ca, -K, and $-p_H$ decrease in Feb. and March, increase in Apr., and fall again in May. Glucose and total CO_2 increase in Feb. and March and decrease in Apr. Lactic acid decreases, whilst glucose increases with age.

NUTR. ABS. (m)

Mineral balance of the diet and its effect on chemical composition of the rat. L. EMERIQUE (Ann. Physiol. Physico-chim. biol., 1933, 9, 765—769).—When the Ca and K contents of a diet containing adequate amounts of vitamin or deficient in vitamin-A are varied the total Ca and K contents of rats are unaltered, but various ratios are changed.

NUTR. ABS. (m)

Comparative calcium and phosphorus retention of pigs on rations supplemented with limestone, bone meal, and "dicapho." J. M. RAMSBOTTOM (Iowa State Coll. J. Sci., 1933, 8, 221—223).—Pigs receiving rations which were adequate except for deficiencies in Ca and vitamin-D were given CaCO_3 , steamed bone meal, and commercial CaHPO_4 . No differences in retention of Ca and P were noted except when enough CaCO_3 was given to produce Ca : P = 2.13 : 1.

CH. ABS.

Calanus finmarchicus. IV. A. P. ORR. Seasonal changes in weight and chemical composition. V. S. M. MARSHALL, A. G. NICHOLLS, and A. P. ORR (J. Marine Biol. Assoc., 1934, 19, 613—627, 793—827).—IV. Seasonal fluctuations in wt. are recorded for Loch Fyne. Ash content 3.6%, chitin 3%. Fat and protein vary with dry wt.

V. Records from Loch Striven confirm the existence of three main breeding periods. The success of a brood depends on the presence of diatoms during the early stages.

L. D. G.

Consumption of calcium by plankton. L. H. N. COOPER (J. Marine Biol. Assoc., 1934, 19, 747—759).—The English Channel shows in summer a small difference in sp. alkalinity (excess base/chlorinity) between surface and bottom H_2O . This is attributed to removal of Ca from surface layers by plankton.

L. D. G.

Phosphorus and nitrogen in plankton. L. H. N. COOPER (J. Marine Biol. Assoc., 1934, 19, 755—759).—P is determined colorimetrically after digestion with H_2SO_4 and H_2O_2 , and N by a micro-Kjeldahl method.

L. D. G.

Fluctuations in the composition and structure bone and their bearing on endochondral ossification. S. E. POND (Anat. Rec., 1933, 57, No. 4, suppl., 64).—During growth, changes in the org. do not parallel changes in the inorg. constituents. The latter are affected by alterations in the circulatory fluids.

NUTR. ABS. (m)

Potassium equilibrium in muscle. W. O. FENN and D. M. COBB (J. Gen. Physiol., 1934, 17, 629—656).—The p_H of the inside of isolated muscle (I) is approx. that of the outside when first dissected,

but tends to follow the p_H of the surrounding medium (II). At each p_H there is a definite $[\text{K}']$ in (II) which is in diffusion equilibrium with $[\text{K}']$ in (I); this val. is least in the alkaline range so that $[\text{OH}'] \times [\text{K}']$ is const. The change in p_H in (I) is not equiv. to the diffusion of K^+ , which is not the only penetrating ion. The irritability of (I) is max. at a concn. of 0.02% of K and probably depends on the ratio of $[\text{K}']$ outside to that inside. Swelling of (I) occurs when injury allows both anions and cations to enter, without permitting protein anions to escape. An increase in CO_2 tension causes an increase in acidity in (II) > in (I) and leads to a loss in K^+ .

H. G. R.

Sodium in metabolism of rats. P. SCHOORL (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 239—245).—Diets low in Na cause poor growth (I) and uræmia. For young rats 0.2% of NaCl in the ration gives good (I). Fertility is not affected by lack of Na, but milk secretion is inhibited.

H. G. R.

Blood-chlorine on mixed diet and during fasting in the dog. Relation to corpuscle and plasma volume. J. BOTTIN (Compt. rend. Soc. Biol., 1933, 114, 1389—1391).—The blood-Cl of a dog fed on a mixed diet (bread, meat, potatoes, and NaCl) was remarkably const. from day to day. During a three weeks' fast, however, the val. fell proportionally to the fall in plasma vol., a rapid return to normal occurring with renewed feeding.

NUTR. ABS. (m)

Diffusion of carbon dioxide in tissues. C. I. WRIGHT (J. Gen. Physiol., 1934, 17, 657—676).—Methods are described for measuring the rate of diffusion of CO_2 in tissue-membranes, tissue-thickness, and the absorption coeff. of CO_2 in tissues; in all cases absorption was slower than in H_2O . The time of saturation with CO_2 is less in non-acidified tissues and the rate depends on CO_2 tension. In a steady state HCO_3^- has little effect on diffusion of CO_2 .

H. G. R.

Influence of various constituents of the diet on the ethyl alcohol content of the blood. E. M. P. WIDMARK (Biochem. Z., 1934, 270, 297—308).—When EtOH is administered together with food, a lower blood-EtOH concn. is obtained than when it is taken fasting. A systematic investigation with numerous foodstuffs shows that proteins and NH_2 -acids have a considerable and regular effect in decreasing absorption of EtOH, citric, malic, tartaric, phosphoric, and the higher fatty acids have an effect, but not so regular, whilst H_2O , fat, and carbohydrate are inactive.

P. W. C.

cycloPropane anaesthesia : gas concentrations, respiratory and electrocardiographic changes. M. H. SEEVERS, W. J. MEEK, E. A. ROVENSTINE, and J. A. STILES (J. Pharm. Exp. Ther., 1934, 51, 1—17).—As regards induction of, maintenance of and recovery from anaesthesia, cyclopropane is intermediate in effect between C_2H_4 and Et_2O , and in high concn. is sufficiently toxic to produce cardiac paralysis even under artificial respiration in presence of an adequate alveolar O_2 tension.

A. E. O.

Hyperazotæmia with chloropenia and reduction of alkali reserve. M. CHATRON (Bull. Soc.

Chim. biol., 1934, 16, 405—413).—Administration of NaHCO_3 and NaCl , given in consequence of the chemical findings in the blood and urine, caused much improvement in the condition of a patient who had been poisoned by inhalation of CCl_4 .

W. O. K.

[Pharmacology of] phenanthrene derivatives.

II. Effect of protecting the hydroxy-group of 2- and 3-hydroxyphenanthrene. N. B. EDDY (J. Pharm. Exp. Ther., 1934, 51, 75—84).—Conversion of OH into OMe, OEt, or OAc in hydroxyphenanthrenes results in a uniform decrease in activity, which is most pronounced with respect to the analgesic and general depressant actions of 3-hydroxyphenanthrene.

A. E. O.

Mode of action of anthraquinone purgatives in the cat. F. C. MACINTOSH (Proc. Nova Scotian Inst. Sci., 1931—1932, 18, 53—67).—Aloin has no effect on the motility of the small intestine. The higher of the contents of the colon explains the action of anthraquinone purgatives, which normally affect only the large intestine. The purgative action is due to increased peristalsis and, in smaller degree, to inhibition of absorption. Aloin acts on cats only when protein is fed.

P. G. M.

Action of diuretics on the gastro-intestinal canal. A. EBEL and H. MAUTNER (Arch. exp. Path. Pharm., 1934, 175, 128—145).—Subcutaneous injection of diuretics [caffeine, theophylline, novasurol (I)] into rats produces an increased secretion of gastric juice (II) with a high $[\text{Cl}']$. This action is inhibited by injection of chloretone, luminal, and, to a smaller extent, urethane and chloral hydrate, but not by veronal or somnifen. With (I) in dogs, removal of (II) through a gastric fistula inhibits the diuresis to an extent indicating that not only the loss of H_2O , but also that of Cl' and acid, must be concerned in the inhibition.

F. O. H.

Diuresis in the mouse. II. M. R. BONSMANN.

III. Quantitative study of the action of anti-diuretics. E. KLEMT (Arch. exp. Path. Pharm., 1934, 175, 322—327, 328—334).—II. Groups of mice are used for the investigation of diuretic action. Theophylline (I), strophanthin (II), and urea (III) produce a two- to four-fold increase in the vol. of urine within 4 hr. of administration. With (I) and (III), the diuretic dose is 14% and with (II) 50% of the min. lethal dose (IV).

III. The (IV) of urethane (V), codeine (VI), and chloral hydrate (VII) to mice is, respectively, 2.30, 0.25, and 0.75 g. per kg. body-wt. With a substance claimed to have a sp. anti-diuretic action, a dose of \times 5% of (IV) should reduce the vol. of urine by \leq 50%. Such a reduction requires 20% of (IV) of (VI) and (VII), whilst even 50% of that of (V) has no inhibitory action; tonephin and morphine are satisfactory, requiring, respectively, 0.03 and 2% of (IV). Interperitoneally injected 0.2% aq. NaCl in mice is absorbed within 1 hr.

F. O. H.

Diuresis. II. Evaluation of diuretic and anti-diuretic substances. W. BENTZ, H. MARX, and K. SCHNEIDER. III. Effect of diathermy of the pituitary region on the water threshold.

W. BENTZ and H. MARX (Arch. exp. Path. Pharm., 1934, 175, 165—168, 169—175).—II. The application of the method previously described (this vol., 216) is given.

III. Diathermic irradiation of the pituitary region of the brain of men and dogs produces a marked anti-diuretic action.

F. O. H.

Dependence of *Digitalis* action on its rate of combination with the heart. Distribution in non-cardiac tissues with various methods of injection. M. HAFERKORN and L. LENDLE (Arch. exp. Path. Pharm., 1934, 175, 248—264).—That the rapid disappearance of *Digitalis* glucosides (I) from the blood (II) is due to a combination with extra-cardiac tissue could not be confirmed (cf. A., 1928, 1400). No marked difference exists between the min. lethal dose to cats when (I) is administered intravenously or -arterially, by single or continuous dosage. For some min. after injection (I) are still present in (II); bleeding alleviates the toxic symptoms and yields (II) having an action on a heart-lung prep. typical of (I).

F. O. H.

[Physiological] action of thevetin, a cardiac glucoside of *Thevetia nerifolia*. K. K. CHEN and A. L. CHEN (J. Pharm. Exp. Ther., 1934, 51, 23—34).—Thevetin (I), the sole active constituent of be-still nuts (II), has a digitalis-like action on amphibian and mammalian hearts, its toxicity and potency each being $\frac{1}{2}$ that of ouabain. (II) kernels contain 3.6—4% of (I) as shown by physiological assay.

A. E. O.

Products of degradation of camphor, camphorquinone, and epicamphor in the animal organism.—See this vol., 658, 659.

"Vitacamphor." Pharmacological action of "vitacamphor," and the role played by its constituents, π - and p -oxycamphors. K. TANURA, G. KIHARA, and M. ISHIDATE (Proc. Imp. Acad. Tokyo, 1934, 10, 161—164).—The cardiostimulant action of π -oxycamphor (I) is $>$ of p -oxycamphor (II). The min. effective dose is $>$ that of vitacamphor (III), but $>$ corresponds with the amount of (I) in (III). The autoxidation of (I) is inhibited by (II), and the greater activity of (III) is considered to be due to the presence of both (I) and (II).

A. A. L.

Chronaxie and the action of local anaesthetics on sensory nerves. W. LAUBENDER and C. RAUFENBARTH (Arch. exp. Path. Pharm., 1934, 175, 113—127).—The changes in the chronaxie (I) and rheobase (II) of sensory nerve-fibres (indicated by the crossed extensor-reflex in the spinal frog) due to the anaesthetic action of cocaine, novocaine, percaïne, and pantocaine do not serve as a basis for a quant. method of determining their relative efficacy, yet indicate a certain differentiation in their action on (I) and (II).

F. O. H.

Influence of substitution in the benzene ring on the action of surface anaesthetics. F. BOEDECKER and H. LUDWIG (Arch. exp. Path. Pharm., 1934, 175, 307—312).—The effect of introducing various side-chains into the C_6H_5 ring of the compound $\text{OPh}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NEt}_2\cdot\text{HCl}$ on the anaesthetic action (I) on the rabbit's cornea was investigated. (I) is increased (up to $\times 100$) by alkyl in the o - or

p-position, the effect being proportional to the length of the chain. With unsaturated groups (which react differently from saturated), the position of the double linking is immaterial. Two allyl or propenyl groups have the same influence as one hexyl. MeO and BuO tend, respectively, to weaken and increase (I). Many *p*-derivatives have an inflammatory action which is independent of (I) and increases with saturation of the chain introduced; such compounds have a marked surface activity. F. O. H.

Action of aspirin and calcium-aspirin on growing bone. N. MUTCH (J. Pharm. Exp. Ther., 1934, 51, 112—126).—Relatively large doses of aspirin (I) given daily for a month to young rats did not cause any decalcification of the bone as judged by X-ray translucency. The observed broadening of the calcified zone in ossifying cartilage is due to the (I) mol. as a whole rather than to its acidic nature. Ca-aspirin (approx. composition, $[\text{C}_6\text{H}_4(\text{OAc})\text{CO}_2]_2\text{Ca} \cdot 4\text{H}_2\text{O} \cdot \frac{1}{3}\text{CaCl}_2$, prepared by pptn. from a conc. aq. solution of CaCl_2 , and quite stable when dry) contains absorbable Ca, and has a much less harmful action than (I) on growing bone. A. E. O.

Fixation of phenols by the tissues. A. D. MARENZI (Compt. rend. Soc. Biol., 1933, 114, 802—803).—The average total phenol content of rat tissues, determined by a modification of the method of Theis and Benedict, is as follows: liver 15.8, spleen 21.2, kidney 15.3, heart 12.4, lung 16.2, muscle 19.1 mg. per 100 g. and blood 1.8 mg. per 100 c.c. After injection of 2.5 mg. of phenol per kg., the blood content increases to 2.4 mg. in 5 min. and returns to basal level in 120 min., whilst the kidney content reaches a max. of 16.8 mg. in 60 min. Increase of conjugated phenols persists longer in the kidney, suggesting that they are fixed there. NUTR. ABS. (m)

Chemical constitution, pharmacological action, and enzymic activity. F. PIRRONE (Annali Chim. Appl., 1934, 24, 128—139).—Experiments with adrenaline, ephedrine, ephetone (*r*-ephedrine), tetrahydro- α , and β -naphthylamine show that increase in the intensity of the pharmacological action is accompanied by increase in the inhibiting effect on the velocity of alcoholic fermentation. T. H. P.

Hyperglycæmic action of amines. R. C. ANDERSON and K. K. CHEN (J. Amer. Pharm. Assoc., 1934, 23, 290—295).—With amines of the types $\text{Ph} \cdot \text{CH}_2 \cdot \text{NHR}'$, $\text{OH} \cdot \text{CHPh} \cdot \text{CHR} \cdot \text{NR}'\text{R}''$ (I), and (I) with OH and OAlk substituents *m* and *p* to the side-chain (some 40 studied in all), the hyperglycæmic action increases with the no. of C atoms in R', and R''. Only adrenaline and closely related compounds are active in very small doses, and raise the blood-sugar by subcutaneous injection. In general, there is little correlation between pressor and hyperglycæmic actions. A. E. O.

Increase of the toxicity of quinine on ultra-violet irradiation. V. V. ALPATOV and O. K. NASTIUKOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 238—243).—Ultra-violet irradiation increases the toxicity of aq. quinine hydrochloride to *Paramecium caudatum*. F. O. H.

[Pharmacological action of] morphine, codeine, and derivatives. IV. **Hydrogenated codeine isomerides.** N. B. EDDY and (in part) L. F. SMALL (J. Pharm. Exp. Ther., 1934, 51, 35—44; cf. A., 1932, 965).—Saturation of the double linking in ring III of codeine (I) and its isomerides causes a decrease in toxicity, in the augmenting effect on reflexes, and in convulsant action, but an increase in analgesic and respiratory effects. The order of effectiveness of the hydrogenated compounds (II) is not the same as that of (I) and its isomerides. Practically, dihydroisocodeine seems to be more important than the other (II); it is less toxic than (I), and its activity, especially in the production of analgesia, is much greater. A. E. O.

Physiological action of sarothamnine and genisteine. R. HAZARD (Compt. rend., 1934, 198, 1945—1947).—Sarothamnine (I), when injected into dogs, has a depressor action. It augments the vasoconstrictor (II) and hypertensor (III) effects of adrenaline (IV) by paralysis of the vagus, whilst suppressing the reflex bradycardia. Genisteine (V) has no depressor action, it increases (II) and (III) effects of (IV), but suppresses the vagal reflex effect. (I) and (V) suppress the action of acetylcholine and nicotine on the cardiac vagus. R. S. C.

Plant cholagogues. L. SCHINDEL (Arch. exp. Path. Pharm., 1934, 175, 313—321).—Addition of onions to the diet of dogs increases the amount and bile acid content of the bile. Fractionation of extracts yields an active concentrate sol. in H_2O and EtOH. A similar principle occurs in artichokes, but not in radishes. F. O. H.

Effect on blood-sugar of ligation of the portal vein and its branches in the dog. N. FIESSINGER and R. CATTAN (Compt. rend. Soc. Biol., 1933, 114, 483—486).—A deficiency of pancreatic and splenic hormones, general anæmia, and especially congestion of the abdominal veins are responsible for the sudden hyperglycæmia produced by this operation. NUTR. ABS. (m)

Disturbance of carbohydrate metabolism in stellate cell blockade. IRSIGLER (Arch. klin. Chirurg., 1933, 177, 708—715).—After poisoning the stellate cells (I) by intravenous injection of electrocolloidal Cu, there was, in fasting rabbits, an initial hyperglycæmia, followed by a progressive hypoglycæmia, unrelieved by glucose administration, resulting in convulsions and death. There is a close connexion between the liver cells (II) and (I); "blocking" (I) affects (II) and produces the same effect on carbohydrate metabolism as a true liver poison or hepatectomy. NUTR. ABS. (b)

Determination of arsenic [in urine] by Cribier's method.—See this vol., 745.

Detoxication of hydrogen cyanide. W. WIRTH and F. G. LAMMERHIRT (Biochem. Z., 1934, 270, 455—459).—Administration of $\text{Na}_2\text{S}_4\text{O}_6$ or NaNO_2 to an animal delays reaction to inspired HCN, and if the dose is sublethal assists in recovery, but if it is lethal, does not assist in keeping the animals alive. P. W. C.

Lactic acid in blood and tissues following intravenous injection of sodium hydrogen carbonate. J. HALDI (Amer. J. Physiol., 1933, 106, 134—144).—Following injection of NaHCO_3 , brain frozen immediately after decapitation has approx. the same lactic acid (I) content as a control brain, but after 5 and 10 min. incubation there is a slight increase. The kidney and muscle of animals receiving NaHCO_3 show a val. $>$ that of controls, but there is a relatively larger increase in the control kidney after incubation. NaHCO_3 invariably produces marked rise in blood-(I) within a few min., and there is increased excretion of (I) in the urine. NUTR. ABS. (m)

Effect of ammonium chloride on the adrena-line hyperglycaemia and hyperlacticaemia of rabbits. M. OHARA (Mitt. med. Akad. Kioto, 1933, 9, 443—454).—In normal rabbits simultaneous injection of 10% NH_4Cl with adrenaline increases the rise in blood-sugar and -lactic acid. In splanchnicotomised rabbits the NH_4Cl affects blood-sugar increase only slightly and appears to inhibit increase of -lactic acid. NUTR. ABS. (m)

Mechanism of the hyperglycaemia and high blood-lactic acid in the rabbit following ammonium chloride administration. M. OHARA (Mitt. med. Akad. Kioto, 1933, 9, 979—996).—Narcotisation with amytal reduces the effect of subcutaneous NH_4Cl injection. The rise of blood-sugar is $\frac{2}{3}$ of that found in normal rabbits and the rise in blood-lactic acid is small and variable. Narcotised and normal rabbits show an equal fall in alkali reserve. The modifications of the action of NH_4Cl following section of various nerves are described. NUTR. ABS. (m)

Action of potassium and other ions on the injury potential and action current in *Maia* nerve. S. L. COWAN (Proc. Roy. Soc., 1934, B, 115, 216—260).—The injury potential (I) of *Maia* nerves is 30 mv., which is depressed rapidly and reversibly by KCl. K, Rb, and Cs reduce the action current, but the two latter have little effect on (I). Ca lowers the effects of K, Rb, and Cs. C. G. A.

Influence of chronic fluorosis on vitamin-C in certain organs of the rat. P. H. PHILLIPS and C. Y. CHANG (J. Biol. Chem., 1934, 105, 405—410).—NaF in sufficient amount inhibits growth. Vitamin-C was increased in both the pituitary and adrenal glands, but not affected in the liver or kidney. H. G. R.

Action of harmful dusts. E. H. KETTLE (Bull. Inst. Min. Met., 1934, No. 357, 15 pp.).—A lecture.

Parasitism in heavy water of low concentration. E. J. LARSON and T. C. BARNES (Nature, 1934, 133, 873—874).—When kept in dil. heavy H_2O for long periods *Planaria maculata* (I) and *Phagocata gracilis* show a slower rate of shrinkage in body size probably owing to reduced enzymic hydrolysis. In more conc. heavy H_2O (1:213 H^2 ratio), (I) are rapidly parasitised by moulds. Moulds, chiefly saprophytic, also develop on seeds of *Aquilegia* in 0.47% H^2 cultures. L. S. T.

Physiological effect of trihydrol in liquid water. T. C. BARNES (Science, 1934, 79, 455—457).—A summary. L. S.

Radioactivity and metal-protein complexes. I. A. BENEDICENTI. II. G. RASTELLI. III. Biological action of normal and radioactive cobalt. A. GARELLO. IV. Fixation of cobalt in the lungs and its elimination by animals which inhale radium emanation. P. MASCHERPA. V. Effect of radium on cutaneous absorption of metals. A. AMBROGIO. VI. Effect of radium and its emanation on the metallisation of proteins. P. MASCHERPA (Arch. Sci. biol., 1933, 16, 421—422, 423—427, 428—432, 433—440, 441—451, 452—462; Chem. Zentr., 1933, ii, 2852).—II. Ra promotes the metallisation of protein. Radon acts similarly to RaBr_2 .

III. Radioactive Co is much more quickly fatal to the frog than normal Co, probably owing to quicker dissolution in the tissues and to a greater power of diffusion.

IV. Co administered intravenously to animals inhaling Rn is fixed only in small amounts by lung protein. Further inhalation of Rn leads to complete elimination of Co by the kidneys in 2 hr.

V. Ra irradiation promotes absorption of metals through the skin. The smallest Ra doses suffice.

VI. Co powder electrolytically treated with Ra or Rn is much more energetic in its metallising action on protein than is normal Co. Proteins with $p_H >$ the isoelectric p_H react most strongly. Radioactive Co is more poisonous than normal Co. L. S. T.

Mitogenetic radiation and bioluminescence. J. B. BATEMAN (Nature, 1934, 133, 860).—Critical. L. S. T.

Effect of ultra-violet light on blood-phosphorus in the fasting animal. R. DELLA GIUSTINA (Riv. Clin. Pediat., 1933, 31, 1205—1226).—Serum- PO_4 in rabbits on a low-P diet, after a fast of about 15 hr., is increased by ultra-violet irradiation. NUTR. ABS. (m)

Blood-cholesterol in man immediately after irradiation by infra-red rays, sunlight, and rays intermediate between ultra-violet and X-rays. S. MALCZYNSKI and J. LANKOSZ (Compt. rend. Soc. Biol., 1933, 114, 1126—1128).—Increase occurs usually 15 min. after irradiation. Normal vals. are reattained in 24 hr. NUTR. ABS. (m)

Effects of X-rays on *Planaria dorotocephala*. F. G. MESERVE and M. J. KENNEY (Science, 1934, 79, 408—409). L. S. T.

Cytochrome and the oxygen-carrying enzyme. O. WARBURG and E. NEGELEIN (Naturwiss., 1934, 22, 206—207).—The term "cytochrome" is to be reserved for the inert materials described by Keilin in 1925; it cannot be extended to the active O-carrying enzyme (cf. Keilin, this vol., 109, 452). R. K. C.

Cytochrome. E. HAAS (Naturwiss., 1934, 22, 207).—The absorptions of a suspension of bakers yeast at 550 m μ under aerobic and anaerobic conditions can be measured photo-electrically, and indicate the concn. of cytochrome (I). When HCl is added the rate of change into the Fe^{II} form of (I) corresponds with the rate of O_2 uptake in a respirometer. The O_2 taken up by the O-carrying enzyme

therefore reacts further in respiration only by way of the cytochrome-Fe.

R. K. C.

An absorption band in the yellow in baker's yeast. O. WARBURG and E. HAAS (Naturwiss., 1934, 22, 207).—A fully-oxygenated suspension of washed baker's yeast shows an absorption band at 583 m μ , which disappears when aeration ceases. This "respiratory" band is attributed to an O-additive product of a Fe^{II}-haemin compound. CO causes a shift to 590–600 m μ .

R. K. C.

Flavin respiration. T. WAGNER-JAUREGG, H. RAUEN, and E. F. MOLLER (Z. physiol. Chem., 1934, 224, 67–78).—In the dehydrogenation of glycerophosphoric acid, glyceraldehydophosphoric acid, and particularly succinic acid and PrCHO by rat-muscle and liver pulp, flavin acts as H acceptor. Malic and fumaric acids are inhibitors. Frog's muscle has a much slower action unless a liver extract (I) is added. Washed muscle is inactive even in presence of (I). Unwashed rat-muscle yields succino-dehydrogenase (II) solutions, which in presence of (I) can replace muscle. (I) is best obtained with 50% glycerol (III). The (III) extracts of various organs show decreasing activator-activity in the order liver, kidney, heart, testes, lung, spleen, brain, muscle. (II) activity is suppressed by CO and KCN. The ease of reduction of pyocyanine, flavin, and rosindulin-GG decreases in that order, following the oxidation-reduction potentials.

J. H. B.

Mechanism of the main respiration of pigeon's breast-muscle. B. GOZSY and A. SZENT-GYORGYI (Z. physiol. Chem., 1934, 224, 1–10).—Another co-enzyme in addition to co-dehydrase takes part in the respiration (I) of the minced breast-muscle of the pigeon. (I) is inhibited by malonate and maleate, but accelerated by succinate (II) or fumarate (III) without destruction of (II) or (III). (II) probably acts as catalyst of H transport.

J. H. B.

Oxidising enzymes in betel leaves (*Piper betel*).

BASU, M. C. NATH, and S. C. CHAKRAVARTY (J. Indian Chem. Soc., 1934, 11, 265–276).—2% p-C₆H₄(OH)₂ (I), leucine, and succinic acid at p_H about 5 are oxidised by the enzymes of betel juice (II) at 25° and 34.4°; temp. has little effect. MeCHO (III) has its optimum p_H of 6.2, and there is an appreciable temp. coeff. Lecithin accelerates the oxidation of linoleic and retards that of oleic acid. 0.002N-KCN retards oxidation of (I) and (III) to the extent of 75 and 45%, respectively (cf. A., 1929, 19). The catalase of (II) decomposes H₂O₂ at p_H 19). HCN retards its action.

J. L. D.

Liver enzymes. II. Aldehydease. L. REI-

and R. WETZEL (Z. physiol. Chem., 1934, 224, 116–186; cf. A., 1932, 303).—Stable dry preps. of aldehydease (I) are obtained by repeated pptn. of aq. liver extracts with COMe₂. Determinations of EtOH and EtCO₂H show that (I) produces quant. dismutation of EtCHO at p_H 7.8 under aerobic or anaerobic conditions.

J. H. B.

Decomposition of lactic acid by yeast enzymes.

HAHN and E. FISCHBACH (Z. Biol., 1934, 95, 163).—Lactic acid (I) when treated with yeast extract (II), purified by adsorption on Al(OH)₃, in

presence of methylene-blue (III) in vac. is converted into AcCO₂H and MeCHO. In presence of O₂ no disappearance of (I) occurs. (I), hexosediphosphoric acid, and citric acid strongly increase the O₂ uptake of (II) in the presence of (III); with (I) KCN lessens the increase by 50%. Muscle-extract and lactacidogen produced an increased O₂ uptake, independent of the presence of (III), which could be decreased by KCN to the extent of 70–80%.

H. D.

Lactic acid fermentation. E. AUBEL and E. SIMON (Compt. rend. Soc. Biol., 1933, 114, 905–907).—As dried yeast, COMe₂ extract of dog's muscle, and Thunberg's muscle extract (I) have no action on the system α -glycerophosphate (II)–AcCO₂H but produce from Mg hexose phosphate, AcCHO and lactic acid, it follows that, under the experimental conditions involved, AcCHO, not AcCO₂H, is the precursor of lactic acid. Although (I) contains (II) dehydrogenase, AcCO₂H reduction is not effected owing to the destruction of the Mg adenylyl pyrophosphate.

NUTR. ABS. (m)

Enzymic equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid. O. MEYERHOF and K. LOHMANN (Naturwiss., 1934, 22, 220).—Dihydroxyacetonephosphoric acid (I), formed from hexosediphosphoric acid (II) (this vol., 560), is identical with the synthetic acid (Kiessling, *ibid.*, 754). The equilibrium, (II) \rightleftharpoons 2 (I) in presence of enzyme, allows (II) to be prepared from synthetic (I), and the equilibrium mixture (III) can be obtained either from (II) or (I); the variation of (III) with temp. is identical, whether derived from (II), natural (I), or synthetic (I). Addition of KCN or NaHSO₃ disturbs the equilibrium, and the H sulphite compound of (I) can be obtained in 90% yield.

R. K. C.

Synthesis of a carbon chain by enzymes. V. Occurrence of carboligase in the animal organism. A. STEPANOV and A. KUSIN (Ber., 1934, 67, [B], 721–722; cf. A., 1931, 983).—The carboligase (I) content of the muscle of the dog is $\frac{1}{4}$ that of plants (*loc. cit.*). Traces of (I) are present in the liver. The universal occurrence of (I) in regions of carbohydrate synthesis justifies the assumption that it has a sp. part in the process.

H. W.

Synthesis of a carbon chain by enzymes. VI. Re-synthesis of glycogen in muscle. A. STEPANOV and A. KUSIN (Ber., 1934, 67, [B], 723–726).—In spite of autolysis of glycogen (I), the amount of (I) present after 24 hr. in a solution of K ketohydroxy-succinate (II) in H₂O at p_H 6.4 and 35° containing the striped muscle of the dog is nearly twice as great as in the absence of (II). The amount of monosaccharide (? glucose) is also increased.

H. W.

Amylosynthase. XIX, XX. T. MINAGAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 1198–1202, 1202–1206).—XIX. IsoLichenin (I) is present in *Alectoria ochroleuca*, *A. sulcata*, *A. japonica*, *Ramalina geniculata*, and *Usnea trichodea*, but not in *Cladonia bellidiflora*, *Gyrophora vellea*, *Lobaria pulmonaria*, *Parmelia tinctorum*, *Ramalina pollinalia*, *Usnea japonica*, and *U. montis*. Malt amylase or heating

with glycerol converts (I) into a product which does not give the I reaction and cannot be polymerised by amylosynthase (II). (I) closely resembles amylase.

XX. The action of (II) is retarded by $\text{Al}(\text{NO}_3)_3$, $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, AlCl_3 , and FeCl_3 . (II) is reactivated by $(\text{NH}_4)_2\text{SO}_4$. Following treatment with Ag, Cu, Hg, Zn, or Pt salts, (II) could not be reactivated. CH. ABS.

Fermentation of polysaccharides. E. THILO (Diss., Berlin, 1931; Bied. Zentr., 1934, A, 4, 446).—Tryptic digestion of protein renders it an energetic activator of amylase. The saccharification of cellulose by malt and snail extracts is examined. A. G. P.

Limits of degradation of starches by the action of salivary and pancreatic amylases. H. J. VONK and J. P. BRAAK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 188—193).—The action of salivary amylase (man) or pancreatic amylase (pig) on starch causes degradation far beyond the limit (36%) found by van Klinkenberg (A., 1932, 91, 1062; 1933, 92) for malt α -amylase, and the supposition that animal amylases attack only α -starch is untrue. R. K. C.

Influence of temperature on the stability of ptyalin. R. EGE (Z. physiol. Chem., 1934, 224, 129—140).—The temp. coeff. (Q_{10}) of ptyalin destruction varies with both temp. and p_{H} . Q_{10} is min. at low p_{H} , when the enzyme is least stable and very sensitive to change in p_{H} , and max. at low temp., where the stability is greatest. The Arrhenius const. A is more const.; it varies with reaction and is max. at the stability optimum. J. H. B.

Characteristics of intestinal lactase. F. A. CAJORI (Amer. J. Med. Sci., 1934, 187, 295).—A lactose-splitting enzyme is invariably present in aq. extracts of the mucosa of the duodenum and jejunum of adult dogs. The activity of intestinal lactase is max. at p_{H} 5.4—6; it is inhibited by glucose, but not by galactose. Aq. extracts of liver have one third of the lactase activity of intestinal mucosa extracts. CH. ABS.

Enzyme action. XLVII. Lipase action of serum. XLVIII. Lipase actions of horse serum. G. MCGUIRE and K. G. FALK (J. Biol. Chem., 1934, 105, 373—377, 378—389).—XLVII. Definite differences were found in the hydrolytic action of horse-, rat-, human, sheep-, and ox-serum (in order of descending activity) on different esters.

XLVIII. Horse-serum is suitable for the study of esterase actions and contains > one enzyme. Determinations of $[\text{H}^+]$ of serum should always be checked electrometrically owing to "protein error."

H. G. R.

Activation of papain by vitamin-C (ascorbic acid) or vitamin-C-iron. III. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1934, 224, 56—67; cf. this vol., 328).—When vitamin-C+Fe complex (I), papain (II), and substrate (III) are brought into contact, increased activity occurs only after some hr., but it is immediate if (II) is allowed to act on (I) for a time before (III) is supplied. Thiol activators neutralise the antiproteolytic action of heavy metals, (I) has no such effect. Witte's peptone is not hydrolysed by (II) in absence of vitamin-C

(IV), or better (I); gelatin-peptone is hydrolysed, but (IV) alone inhibits, whilst (I) accelerates the action. J. H. B.

X-Ray photographs of crystalline pepsin.—See this vol., 720.

Preparation of enzymically pure proteinase and determination of the influence of protaminase. L. WEIL (J. Biol. Chem., 1934, 105, 291—299).—Enzymically pure proteinase (I) was obtained by removal of protaminase (II) and carboxypolypeptidase from pig-pancreas extract by adsorption with $\text{Al}(\text{OH})_3\text{-C}_2$ and -A. Acid protone is used as substrate for the determination of (II). (II) is activated by enterokinase. Free NH_2 or CO_2H groups are not necessary for the activity of (I), substitution causing no inhibition. C. G. A.

Inactivation of pepsin, trypsin, and salivary amylase by proteases. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1934, 105, 411—414).—Pepsin and trypsin (I) can be reciprocally digested at the correct p_{H} . Erepsin does not digest (I) and salivary amylase is slowly inactivated by (I) and H_2S -papain. H. G. R.

Effect of decomposition products on enzymic proteolysis. E. DRESSLER (Diss., Berlin, 1931; Bied. Zentr., 1934, A, 4, 446—447).—The inhibitory action of decomp. products (I) on tryptic proteolysis is not observed if the concn. of enzyme is small relative to that of substrate and (I). The combination of enzyme and (I) is probably completely dissociated at low concn. Similar relationships were not apparent in the case of pepsin. A. G. P.

Action of oxidising and reducing agents on cathepsin. A. V. BLAGOVESTSCHENSKI and I. I. KORMAN (Biochem. Z., 1934, 270, 341—345).—Cysteine, O_2 , and H_2O_2 all inhibit the proteolytic action of cathepsin (from ripening seeds of *Vicia sativa*) on the globulin of sunflower seeds and favour the synthesis of material precipitable by $\text{CCl}_3\text{-CO.H}$.

Mechanism of the action of histozyme. F. P. MAZZA and L. PANNAIN (Atti R. Accad. Lincei, 1934, [vi], 19, 97—102).—Histozyme differs from carboxypeptidase by combining, not with the free CO_2H of the substrate, but with the N of the -CO.NH- . The difference between its activities towards aliphatic and aromatic acyl derivatives is probably due, not to the existence of two different enzymes, but to the varying velocities of the hydrolyses catalysed by the enzyme. This velocity is lower with the aromatic derivatives, and diminishes as the nucleus coupled with the NH_2 -acid becomes more electro-negative. T. H. P.

Antagonism of zinc and hydrocyanic acid in their action on peptidase activity. K. LINDERSTRÖM-LANG (Z. physiol. Chem., 1934, 224, 1—126).— Zn^{++} at low concn. ($< 3 \times 10^{-3}N$) activates peptidase, but higher concns. inhibit. HCN inhibits in all cases. Small amounts of Zn reverse the inhibition by HCN owing to combination, but larger amount inhibit; the curve thus shows a max. correspondence with $\text{Zn}(\text{CN})_4^{--}$. Addition of HCN to a solution inhibited by Zn increases the inhibition. J. H. B.

Proteolytic enzymes. III. a. Mode of action and specificity of dipeptidase. M. BERGMANN and L. ZERVAS. **b. Dipeptides with predominantly acid properties and their behaviour towards enzymes.** M. BERGMANN, L. ZERVAS, L. SALZMANN, and H. SCHLEICH. **c. Synthesis of dipeptides of lysine and their behaviour towards proteolytic enzymes.** **d. Dipeptides of epimeric glucosamic acids and their behaviour towards dipeptidase.** Configuration of *d*-glucosamine. M. BERGMANN, L. ZERVAS, H. RINKE, and H. SCHLEICH. **e. Synthesis of peptides of arginine.** M. BERGMANN, L. ZERVAS, and H. RINKE. **IV. Specificity and mode of action of so-called carboxy-polypeptidase.** M. BERGMANN, L. ZERVAS, and H. SCHLEICH (*Z. physiol. Chem.*, 1934, 224, 11—17, 17—26, 26—33, 33—39, 40—44, 45—51).—IIIa. Introductory. For hydrolysis of dipeptides (I) by dipeptidase (II) the necessary conditions are: the N of the peptide linking must bear H, the two adjacent C atoms (α and α') must bear H, and the α - and α' -C must show a definite configuration. If the imide form is the actual substrate, steric considerations, based on double linking and optical asymmetry, indicate that with (I) of the natural NH_2 -acids when the CO_2H and NH_2 are on the same side of the mol. plane the α - and α' -H atoms are on the other side of the flat (I) mol. and thus allow approach of (II) which is a necessary preliminary to fission.

b. Carbobenzyloxy-*l*-glutamic acid anhydride with *l*-tyrosine ester (I) gave, as *Et* ester, m.p. 176°, carbobenzyloxy-*l*-glutamyl-*l*-tyrosine, m.p. 185° (corr.), which on hydrogenation yielded glutamyl tyrosine (II), $[\alpha]_D^{20} + 30.1^\circ$ in $\text{H}_2\text{O} + 1$ mol. HCl . *O*-Acetyl-*N*-carbobenzyloxy-*l*-tyrosine, m.p. 120—121°, affords the acid chloride (III), m.p. 54°, which with (I) yields *O*-acetyl-*N*-carbobenzyloxy-*l*-tyrosyl-*l*-tyrosine *Et* ester, m.p. 160—161°, giving, by hydrolysis and hydrogenation, carbobenzyloxy-*l*-tyrosyl-*l*-tyrosine, m.p. 148° (corr.), and *l*-tyrosyl-*l*-tyrosine (IV), m.p. < 240°, $[\alpha]_D^{20} + 30.1^\circ$ in $\text{H}_2\text{O} + 1$ mol. of HCl . With Et_2 *l*-aspartate, (IV) gives *Et* *O*-acetyl-*N*-carbobenzyloxy-*l*-tyrosyl-*l*-aspartate, m.p. 144° (corr.), yielding *N*-carbobenzyloxy-*l*-tyrosyl-*l*-aspartic acid, and *l*-tyrosyl-*l*-aspartic acid (V), $[\alpha]_D^{20} + 20.4^\circ$ in $\text{H}_2\text{O} + 1$ mol. of HCl . Authentic β -*l*-asparagyl-*l*-tyrosine (VI), synthesised by way of *l*-(α -benzyl-*N*-carbobenzyloxyasparagyl)- β -*l*-tyrosine *Et* ester, m.p. 128°, and carbobenzyloxy-*l*-asparagyl- β -*l*-tyrosine (*Me*₂ ester, m.p. 136°), was identical with the alleged α - (A., 1932, 935), which was therefore actually the β -isomeride. (II) and (V) are, but (VI) is not, hydrolysed by dipeptidase (VII) (since the free NH_2 is not in the α -position); (IV) is the only known dipeptide hydrolysed by both (VII) and trypsin.

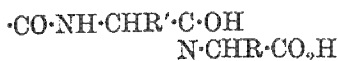
c. *l*-Lysyl-*l*-glutamic acid (I) yields a diphenylcarbamido-derivative, m.p. 144° (corr., decomp.), hydrolysed to *l*-lysinephenylcarbamidophenylhydantoin, m.p. 195° (corr.), $[\alpha]_D^{20} - 33.7^\circ$ in $\text{C}_5\text{H}_5\text{N}$, and *d*-glutamic acid hydrochloride, thus affording proof of its constitution. The following dipeptides were synthesised by the stages indicated. *l*-(ϵ -Benzoyl-lysyl)-*l*-glutamic acid (II), m.p. 220° (corr.) (decomp.), $[\alpha]_D^{20} + 14^\circ$ in $\text{H}_2\text{O} + \text{HCl}$: ϵ -benzoyl-*l*-lysine, m.p. 262° (corr.) (cf. lit.) — ϵ -benzoyl- α -carbobenzyloxy-*l*-

lysine, m.p. 99—100° —> hydrazide, m.p. 191° (corr.) —> azide —> *Et*₂ (ϵ -benzoyl- α -carbobenzyloxy-*l*-lysyl)-*l*-glutamate, m.p. 154° (corr.) — free acid, m.p. 173° (corr.) —> (II). *l*-Lysyl-*l*-aspartic acid (III) ($+ \text{H}_2\text{O}$), m.p. 161° (corr.) (decomp.), $[\alpha]_D^{20} + 23^\circ$ in H_2O : dicarbobenzyloxy-*l*-lysyl hydrazide —> azide —> *Et*₂ dicarbobenzyloxy-*l*-lysyl-*l*-aspartate, m.p. 142° (corr.) —> (III). *l*-Lysylglycine (IV) [sulphate, m.p. 207.5° (corr.), $[\alpha]_D^{20} + 30.0^\circ$ in H_2O]; dicarbobenzyloxy-*l*-lysine *Me* ester —> chloride —> dicarbobenzyloxy-*l*-glycine *Et* ester, m.p. 90°, —> free acid, m.p. 158—159° (corr.) —> (IV). Lysylglutamic acid liberates its total lysine-N (Van Slyke) in little > 5 min. All the dipeptides were hydrolysed by dipeptidase [(I) only very slowly]; they resisted aminopolypeptidase and trypsin.

d. The following dipeptides were synthesised by the steps indicated. *Et* benzylidene-*d*-glucosamate hydrochloride —> (carbobenzyloxyglycyl)benzylidene-*d*-glucosamic acid, m.p. 167—168° (corr.) [lactone, m.p. 197—198° (corr.)] —> glycyl-*d*-glucosamic acid (I), m.p. 179—180° (corr.), brown at 166°. Carbobenzyloxy-*l*-phenylalanine, m.p. 126—128° (corr.), $[\alpha]_D^{20} + 4.9^\circ$ in AcOH , —> acid chloride, m.p. 42°, —> *Et* (carbobenzyloxy-*l*-phenylalanyl)benzylidene-*d*-glucosamate, m.p. 173° (corr.), —> free acid, m.p. 157° (corr.), —> *l*-phenylalanylbenzylidene-*d*-glucosamic acid ($+ \text{H}_2\text{O}$), m.p. 166—167° (corr.) —> *l*-phenylalanyl-*d*-glucosamic acid (II), m.p. 182° (corr.), $[\alpha]_D^{20} + 40^\circ$ in H_2O . *epi*Glucosamic acid + carbobenzyloxyglycyl chloride —> carbobenzyloxyglycyl-*d*-epiglucosamic acid, m.p. 150—151° (corr.) —> glycyl-*d*-epiglucosamic acid (III), m.p. about 215°, $[\alpha]_D^{20} - 9^\circ$ in H_2O . (III) is, but (I) and (II) are not hydrolysed by dipeptidase. *d*-*epi*Glucosamic acid must therefore have the same configuration as the natural (*l*) NH_2 -acids, whilst *d*-glucosamic acid corresponds with the *d*- NH_2 -acids.

e. Hydrogenation of *l*-nitroarginine (I), m.p. 263° (corr.) (cf. lit.) [carbobenzyloxy-derivative, $+ \text{H}_2\text{O}$, m.p. 126° (corr.) (*Me* ester, m.p. 125°)], affords *l*-arginine. With carbobenzyloxyglycyl chloride, (I) gives carbobenzyloxyglycyl-*l*-nitroarginine, m.p. 145° (corr.), which on hydrogenation affords glycyl-*l*-arginine (II) (diflavinate, $+ \text{H}_2\text{O}$, decomp. about 220—225°, sulphate, $+ 2\text{H}_2\text{O}$). With arginine in place of (I) the yield of (II) is low.

IV. Methyl-*l*-tyrosine *Me* ester affords chloroacetyl-*N*-methyl-*l*-tyrosine *Me* ester, m.p. 108° (corr.), which on hydrolysis gives chloroacetyl-*N*-methyl-*l*-tyrosine (I), m.p. 135° (corr.), $[\alpha]_D^{20} - 97.7^\circ$ in H_2O . (I) in contrast with chloroacetyl-*l*-tyrosine is not hydrolysed by carboxypolypeptidase (II), indicating that the peptide-H is indispensable for (II) action. (II) reacts with the grouping (III), which is contrasted with the grouping (IV) necessary for dipeptidase action. The two enzymes are thus complementary. Most dipeptides are of type (IV); only the few which can exist in form (III), e.g., *l*-tyrosyl-*l*-tyrosine, are hydrolysed by (II)



(III.)



(IV.)

J. H. B.

Apparatus for determining the rate of carbon dioxide production during yeast fermentation. K. W. FRANKE and A. L. MOXON (J. Biol. Chem., 1934, 105, 415—418).—The apparatus automatically records the rate of CO_2 production. H. G. R.

Biochemistry of the pigments of red yeast. H. FINK and E. ZENGER (Woch. Brau., 1934, 51, 129—130).—Light or darkness had no appreciable effect on the growth of, or amount of pigment developed by, the red yeast investigated (cf. this vol., 562). The most favourable temp. was 20° , whilst growth and amount developed in air were $>$ in O_2 , the smallest vals. being obtained for each in N_2 . I. A. P.

Polyose of yeast membrane. I. L. ZECHMEISTER and G. TÓTH (Biochem. Z., 1934, 270, 309—316).—Pressed yeast (1 kg.) after digestion with alkali and acid gave a polyose (15 g.) containing 0.4% ash and 0.3—0.4% N, which on hydrolysis gave a 95% yield of glucose. If the hydrolysis is stopped when $2/3$ completed, a disaccharide can be separated as the osazone, m.p. 198° , $[\alpha]_D^{20} -75.3^\circ$ in EtOH. Hydrolysis of the methylated polyose gave 2:4:6-trimethyl-*D*-glucose. The polyose is therefore composed of a chain of glucose residues linked in the 1:3 positions. P. W. C.

Determination of ergosterol and total sterols in yeast. F. BILGER, W. HALDEN, and M. K. ZACHERL (Mikrochem., 1934, 15, 119—140).—Gravimetric and colorimetric methods for determination of total sterols are compared. Colorimetric determination by the Liebermann-Burchard reaction is most suitable; using CHCl_3 as solvent, it may be effected photometrically. Ergosterol may be approx. determined colorimetrically, but not photometrically, by means of the Rosenheim-Page reaction (cf. A., 1930, 951) in *trans*- but not in *cis*-[CHCl] $_2$. J. S. A.

Influence of organic dyes on cell and organ function. VI. Mechanism of absorption of dyes by yeast cells. F. AXMACHER and H. NARATH (Arch. exp. Path. Pharm., 1934, 175, 293—306; cf. A., 1933, 982).—The absorption of both basic [methylene-blue (I)] and acid dyes [trypan-blue (II)] by yeast cells (III) (living, dead, or lipin-free) varies asymptotically with time. With low concns. of (I) and (II) the amount of absorbed (II), but not that of (I), is related to the wt. of cells present; the variations with (I) are probably due to disturbances in the concn. of electrolytes (e.g., H^+). The bearing of ionic exchange and membrane-potentials and -equivs. on the absorption is discussed. The presence of gelatin or ovalbumin markedly inhibits absorption to an extent dependent on $[\text{H}^+]$. The diffusion of gases through a fluid membrane is inhibited to a varying extent by the presence of dyes. F. O. H.

Investigations in the region of high frequency. I. Biochemical action of ultra-short electromagnetic waves. F. PIRRONE (Atti R. Accad. Lincei, 1934, [vi], 19, 108—111).—Exposure of an H_2O suspension of brewers' yeast to the oscillations of a Hertz resonator capable of oscillating on the fundamental wave of λ 1.885 m. slightly accelerates subsequent fermentation of sucrose by the yeast. T. H. P.

Cholesterol and fermentations. E. MONTIGNIE (Bull. Soc. chim., 1933, [iv], 53, 1410—1411).—Cholesterol prevents fermentation of glucose by yeast, is fixed as lactate, m.p. 232 — 235° (decomp.), during lactic fermentation, and is changed into metacholesterol (I) by butyric fermentation. (I) is not changed into coprosterol by *B. coli* or faecal bacteria. R. S. C.

Influence of oxygen on the antitoxic action of cholesterol on saponins. B. S. LEVIN (Compt. rend., 1934, 198, 1812—1815).—Experiments at 60° on *Paramecium aurelia* on plates (free access of O_2) and in tubes (limited O_2) show that the inhibiting action of cholesterol (I) (concn. $1/1000$ — $1/32,000$) on the toxic effect of saponin (II) (same concn. limits) is notable even when aeration is unrestricted, but with certain concns. of (I)–(II) the degree of aeration is the more important factor. Since reduced (II) is less toxic, it is assumed that a restricted aeration is favourable to the reduction of (II). J. W. B.

Action of fungi on solutions of aldoses and other carbohydrates. IX. A. ANGELETTI and D. PONTE (Annali Chim. Appl., 1934, 24, 232—236; cf. A., 1933, 1206).—*Penicillium luteum-purpureogenum* and *P. crustaceum* (I) give small amounts of *D*-gluconic acid when grown in presence of dextrin. With (I) the reducing sugars formed are slightly $>$ those originally present, and remain const. for 3 months, the presence of a dextrinase in the mould being thus indicated. Only (I) gives *D*-gluconic acid with sol. starch. No other acids were detected. T. H. P.

Production of gluconic acid by submerged mould growth under increased air pressure. O. E. MAY, H. T. HERRICK, A. J. MOYER, and P. A. WELLS (Ind. Eng. Chem., 1934, 26, 575—578).—Increase of pressure increases the yield of gluconic acid (I) produced from glucose (200 c.c.; 20% solution) by *Penicillium chrysogenum* when growing totally immersed and aerated in presence of CaCO_3 (5 g.). At 30° and with the quantities stated 80—87% yields of (I) were obtained in 8 days. R. S. C.

Biochemistry of moulds. II. Metabolic product of *Aspergillus melleus*, Yukawa. E. NISHIKAWA (J. Agric. Chem. Soc. Japan, 1933, 9, 77—774). *Mellein*, $\text{C}_{10}\text{H}_{10}\text{O}_3$, m.p. 58° , $[\alpha]_D^{25} -108.15$ in CHCl_3 (NO_2 -derivative, m.p. 183 — 184° , $[\alpha]_D^{25} -171.59^\circ$ in CHCl_3), was isolated. CH. ABS.

Chemistry of mould tissue. III. Composition of certain moulds with special reference to their lipin content. L. M. PRUESS, E. C. EICHINGER, and W. H. PETERSON (Zentr. Bakt. Par., 1934, II, 89, 370—377).—On glucose-malt media the lipin content of a no. of moulds was $>$ and the protein content $<$ corresponding vals. on a glucose-inorg.-salt medium. The lipins contained free fatty acids (8—70% calc. as oleic acid) and phospholipins. Relationships are traced between the protein, lipin, and carbohydrate contents of *Aspergillus* species. A. G. W.

Nitrogen in *Aspergillus niger* in relation to the quantities of various salts in the culture solution. G. ROSSI and G. SCANDELLARI (Biochem. Terap. sperim., 1933, 19, 92—98; Chem. Zentr., 1934, 1,

559).—Aq. glucose containing NH_4NO_3 , K phosphate, and MgSO_4 is a good nutrient for *A. niger*. Absence of NO_3^- or PO_4^{3-} is injurious; MgSO_4 is desirable, but not essential. The presence of small quantities of MnSO_4 favours N fixation. A. A. E.

Proteolytic enzymes of *Aspergillus parasiticus*. M. J. JOHNSON (Z. physiol. Chem., 1934, 224, 163—175).—Aq. extracts of the dried mycelium of *A. parasiticus* grown on skim-milk-glucose medium contain the proteolytic enzymes proteinase (I), carboxy- (II) and amino-polypeptidase (III), and dipeptidase (IV). The culture solution contains much less (II), (III), and (IV), but more (I), than the mycelium. Partial separation of the enzymes was attained by adsorption methods. (III) was obtained practically free from (I), (II), and (IV) by COMe_2 pptn. and alternate adsorption on $\text{Al}(\text{OH})_3\text{-C}_v$ and $\text{Fe}(\text{OH})_3$ at p_H 4. Tri- and tetra-glycine are hydrolysed by yeast- and intestinal (III), but not by the mould-(III). J. H. B.

Phosphatase and phosphatase of *Rhizopus tritici*. F. HEMMI and N. TSUKITARI (J. Agric. Chem. Soc. Japan, 1933, 9, 1382—1393).—Phosphatase was not found; phosphatase may be present. CH. ABS.

***Rhizobium*. I. Effect of nitrogen source on oxygen consumption by *R. leguminosarum*,** Frank. R. H. WALKER, D. A. ANDERSON, and P. E. BROWN (Soil Sci., 1934, 37, 387—401).—Yeast extract increased the growth and O_2 consumption of cultures as compared with those on a N-free medium. Urea, alanine, NH_4Cl , and NaNO_3 had little or no effect. A. G. P.

Specific influence of acidity on nitrogen fixation by *Azotobacter*. D. BURK, H. LINEWEAVER, and C. K. HORNER (J. Bact., 1934, 27, 325—340).—Consumption of N_2 by *Azotobacter* declines from a max. at p_H 7.8 to zero at p_H 6.0. Within these limits the effect of acidity is reversible. Irreversible inactivation occurs only below p_H 5.0. The rate of consumption of fixed N (urea, NH_3 , NO_3^-) shows the same max., and a min. at approx. p_H 4.5, the change over the entire range being reversible. Relationships between O_2 consumption and p_H are of a similar character. The limiting val. (p_H 6.0) for fixation is not affected by differences in $[\text{Ca}^{++}]$, $[\text{Sr}^{++}]$, or N_2 pressure. The N-fixing system ("azotase") and the particular enzyme combining with N_2 ("nitrogenase") are discussed. A. G. P.

Bacteriological examination of soil on a plant-sociological basis. II. *Azotobacter chroococcum* in cultivated soils of the eastern area of the Neusiedlersee. H. WENZL (Zentr. Bakt. Par., 1934, II, 89, 353—369).—*A. chroococcum* (I) was present in all field and vineyard soils in use for > 20—30 years irrespective of their p_H or humus or CaCO_3 contents, but was less general in recently broken soils. Distribution of (I) in soils after inoculation was more rapid in highly org. loams of low CaCO_3 content than in sandy soils poor in humus and nutrients. A. G. P.

Metabolism of some nitrogen-fixing clostridia. W. H. WILLIS (Iowa State Coll. J. Sci., 1933, 8,

231—233).—Anaerobic N-fixing clostridia growing in N_2 on N-free media of initial p_H 6.5—9.5 produced 4.0—4.3 mg. of fixed N per 50 c.c. in 3 weeks; at p_H 5.0, 3.2 mg. were fixed. CaCl_2 and especially CaCO_3 promoted N fixation. If peptone, $(\text{NH}_4)_2\text{SO}_4$, or NaNO_3 was added to the medium glucose was utilised more rapidly, but little or no N was fixed. CH. ABS.

Relationship between the metabolic processes of micro-organisms and the oxido-reduction potential in the medium. I. Denitrifying bacteria. B. ELEMA, A. J. KLUYVER, and J. W. VAN DALFSEN (Biochem. Z., 1934, 270, 317—340).—A medium containing NO_3^- or NO_2^- and EtOH and sown with *Micrococcus denitrificans* under anaerobic conditions using a Au electrode gives reproducible potentials, a reversible oxido-reduction system being established. When actual denitrifying cells are present in a medium containing NO_2^- the potential vals. are dependent only on $[\text{H}^+]$, and when the NO_2^- has disappeared a considerable fall in potential occurs. The effects of H donators and KCN are investigated. P. W. C.

Physiological youth of a bacterial culture as evidenced by cell metabolism. H. H. WALKER, C. E. A. WINSLOW, E. HUNTINGDON, and M. G. MOONEY (J. Bact., 1934, 27, 303—324).—In peptone- H_2O media with or without aeration with CO_2 - and NH_3 -free air *E. coli* exhibits, between the end of the lag period and the beginning of the logarithmic increase (I), a period of high metabolic activity characterised by the rapid transference of $\text{NH}_3\text{-N}$ from cell to medium and increased CO_2 production. Addition of glucose to aerated media results in a somewhat more prompt initiation of (I) and some reduction in yield of NH_3 and CO_2 . The mechanism of these changes is discussed. A. G. P.

Actinomycosis. L. R. VAWTER (Cornell Vet., 1933, 23, 126—149).—Glucose (I), fructose (II), galactose (III), maltose (IV), sucrose (V), and mannitol (VI) were fermented in 1 day, lactose and raffinose (VII) in 4—10 days, and glycerol (VIII) in 14—21 days by various strains of *Actinobacillus*. With xylose (IX) fermentation was slight and irregular; dulcitol (X), inulin (XI), salicin (XII), and arabinose (XIII) were not fermented, and gelatin was not liquefied. Type I *Actinomyces* fermented (I)—(V) and (XII), but not (VI)—(XI) or (XIII). Type II *Actinomyces* may consist of > 1 species. *Corynebacterium pyogenes* resembles *Actinomyces* Type II; it ferments (IX), but not (XII). CH. ABS.

Action of lipolytic bacteria on simple triglycerides and natural fats. M. A. COLLINS (Iowa State Coll. J. Sci., 1933, 8, 187—189).—Bacterial hydrolysis of simple triglycerides becomes more difficult as the mol. wt. increases. Tristearin is unaffected. 159 cultures showed close agreement between lipolytic and proteolytic powers, but not all lipolytic bacteria (I) are proteolytic in litmus milk. (I) are present in ordinary milk, cream, and butter, but not in aseptically drawn milk or in salted butter. CH. ABS.

Influence of culture media on the biological properties of a cellulolytic bacterium. J. POCHON (Compt. rend., 1934, 198, 1808—1810).—After culture in its natural medium for 15 months *Plectridium cellulolyticum*, isolated from ox paunch, has undergone biological modification, and hydrolysis of cellulose (I) can then be effected in aerobic or anaerobic conditions in synthetic media [K, Mg, P, NH_4 salts of org. acids, proteins, and (I)], at p_{H} 8 (CaCO_3).

J. W. B.

Fermentation of glucose by variants of *B. paratyphosus*-B (type Schottmüller) which form no gas from glucose. A. TASMAN and A. W. POT (Biochem. Z., 1934, 270, 349—365).—The production of H_2 , CO_2 , AcOH , HCO_2H , EtOH , lactic and succinic acids by strains of typhoid and paratyphoid organisms is recorded. The typhoid strains effected the same type of reaction as the normal paratyphoid strains, except that the former could not, and the latter could, decompose formed AcOH into $\text{CO}_2 + \text{H}_2$. In those cases where AcOH accumulated, the fermentation was incomplete, only 48—73% of the glucose being metabolised.

P. W. C.

Effect of common salt on the growth of lactic streptococci in milk. F. H. McDOWALL and L. A. WHELAN (J. Dairy Res., 1933, 5, 42—45).—In concns. up to 2% NaCl stimulates, and at > 3% retards, the development of the organisms. Total inhibition is approached with > 6% NaCl .

A. G. P.

Pneumococcus variation. I. Variants characterised by rapid lysis and absence of normal growth under the routine method of cultivation. M. D. EATON (J. Bact., 1934, 27, 271—291).—Effects of temp., CO_2 , p_{H} , and O_2 tension of the growth and lysis of variant forms are examined. A. G. P.

Staphylococcus toxin. P. NÉLIS, J. J. BOUCKAERT, and E. PICARD (Ann. Inst. Pasteur, 1934, 52, 597—644).—A small quantity of glucose in the medium increases the production of the toxin (I), and successive cultures *in vitro* produce a more regular product without loss of toxicity. *In vivo*, (I) produces lesions in many organs with destruction of protoplasm, and death is caused after intravenous injection by cardiac insufficiency. (I) has no action on trypanosomes, and is destroyed by strong acids, cryptotoxic substances, Na oleate, etc. It is concluded that (I) is a single substance. H. G. R.

Clinical investigation of staphylococcal toxin, toxoid, and antitoxin. H. J. PARISH, R. A. Q. O'MEARA, and W. H. M. CLARK (Lancet, 1934, 226, 1054—1057).—Toxins (I) of various strains of *Staphylococcus* vary markedly in potency; light-coloured variants of *S. aureus* strains produce toxins which are more potent than the parent cultures. When rabbit corpuscles are used the combining power of (I) approximates to the hæmolytic val.

L. S. T.

Action of Timothy bacteria on *l*-phosphoglyceric acid. C. CATTANEO (Biochem. Z., 1934, 270, 382—385).—The biochemical conversion of *l*-phosphoglyceric acid into AcCO_2H , already effected by animal cells, lactic acid bacteria, and *B. coli*,

also occurs with acid-fast bacilli, the yield of AcCO_2H being 36% calc. in respect of the initial material or 100% in respect of the amount of ester dephosphorylated. P. W. C.

Lipins of tubercle bacilli. XXXVIII. Synthesis of phthiocol.—See this vol., 776.

Action of constituents of cod-liver oil on tubercle bacilli. P. A. COPPENS (Pharm. Weekblad, 1934, 71, 584—599).—Highly unsaturated fatty acids are chiefly responsible for changing the appearance of, and eventually killing, tubercle bacilli (I) in cod-liver oil suspension. Japanese wood oil has a similar but much less effective action. Vitamin-A and -D are ineffective. Active (I) contain a peroxidase. S. C.

Use of clarified honey in culture media. H. H. HALL and R. E. LOTHROP (J. Bact., 1934, 27, 349—355).—Flocculant matter appearing in honey-agar preps. is eliminated by preliminary warming of dil. honey (50°) with bentonite and subsequent filtration. Clarified honey is suitable for growth of sugar-tolerant yeasts. A. G. P.

Sealing wet preparations. J. E. BARNARD and F. V. WELCH (J. Roy. Microscop. Soc., 1934, 54, 29—31).—Convenient apparatus for sealing wet preps. (material containing virus bodies etc.) by means of paraffin wax or shellac-rosin mixture is described. P. G. M.

Quantitative bacteriological investigations. A. VAN ACKER (Natuurwetensch. Tijds., 1934, 16, 26—31).—Available methods of carrying out bacterial counts are described and discussed. The results obtained by the plate method are always < those given by the Thoma-Steiner method, but \propto the total no. of bacteria present. The latter method gives closely reproducible results and is trustworthy. H. F. G.

Polarographic analysis of bacterial culture solutions. J. KOŘÍNEK and J. BABIČKA (Zentr. Bakt. Par., 1934, II, 89, 497—501).—The formation of decomp. products of carbohydrates by bacteria is examined by means of the polarograph. A. G. P.

Fungi and fungicides. T. HARADA (Bull. Chem. Soc. Japan, 1934, 9, 186—191).—The fungicidal activity of a no. of chemicals towards *Tricophyton interdigitale*, *T. violaceum*, *Epidermophyton inguinale*, and *Aspergillus oryzae* (I) was investigated. HgI_2 , I, and HgCl_2 are the most potent, whilst (I) will grow in an 8% solution of NaOBz , and a 20% concn. of NaCl is required to prevent growth. $\text{CS}(\text{NH}_2)_2$ is toxic to the fungi, but harmless to human tissue. In some cases acidity alone is responsible for inhibition of growth. AcOH is more toxic than lactic acid. P. G. M.

Fungicidal quality of olive oil ozonide. T. HARADA (Bull. Chem. Soc. Japan, 1934, 9, 19—197).—The product obtained by passing O_3 into olive oil for 120—200 hr. became colourless on keeping for several days and contained 0.37—0.86% available O. It is more effective in destroying certain fungi than either H_2O_2 or NaOCl , and is suggested for use in the treatment of ringworm. P.

Toxic effect of sodium iodoacetate on trypanosomes. C. V. SMYTHE and L. REINER (Proc. Soc. Exp. Biol. Med., 1933, **31**, 289—292).—0.001M-CH₂I-CO₂Na (I) destroys a suspension of *T. equiperdum* (II) in 2—3 min. A 240-g. rat tolerates up to 0.2 c.c. of a 0.25M solution of (I); this dose in a rat injected with (II) clears the blood of (II) for 2—10 days. The toxicity of (I) for (II) is uninfluenced by cysteine or thioglycollate; a strain of (II) resistant to As was not resistant to (I). H. D.

Sterilising action of acids. IV. Unsaturated monobasic acids. V. Dibasic aliphatic acids. S. TETSUMOTO (J. Agric. Chem. Soc. Japan, 1933, **9**, 761—767, 1284—1293).—IV. Acrylic and crotonic acids have approx. equal sterilising powers at the same mol. concn. That of undecenoic acid and undecenoate is high. The sterilising action of unsaturated acids is generally > that of saturated acids in the same concn.

V. Of dibasic acids, H₂C₂O₄ has the strongest action. For C₂—C₃ the dibasic are stronger than the monobasic acids; for C₆ onwards the reverse holds. No relation was found between the no. of CO₂H groups and the sterilising action. CH. ABS.

Action of ultra-violet rays from a mercury lamp on the cells of *B. mycoides*, Fl. G. A. NADSON and E. A. STERN (Compt. rend. Acad. Sci. U.R.S.S., 1934, **2**, 51—56).—Irradiation of young cultures (24 hr.) of *B. mycoides* causes first the (reversible) formation of vacuoles, followed successively by (irreversible) dissociation of the lipoprotein plasma complex, granulation (fat drops) of the plasma and plasmolysis, the cells becoming irregular in shape, and finally forming aggregates of dead and dying bacteria. Similar, but slower, changes are produced by X-rays. J. W. B.

Distant action of metals on the structure and development of *Bacillus mycoides*, Fl. E. A. STERN and A. S. KRIVISKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, **2**, 254—258).—Retardation of growth and marked changes in morphology occur when cultures are near (approx. 1 mm. from) sheets of Pb, Au, Pt, or Mg; the extent of the action ∝ the at. no. of the metal, i.e., Pb > Pt, Au > Mg. F. O. H.

Biological action of metals at a distance. V. RIVERA (Atti R. Accad. Lincei, 1934, [vi], **19**, 432—436).—This action is regarded as due to secondary radiation acting either directly on the dividing cells or indirectly on the air of the chamber, possibly by producing ionisation. T. H. P.

Hormones and their chemical relations. E. C. DODDS (Lancet, 1934, **226**, 931—935, 987—992, 1048—1054).—Lectures. L. S. T.

Pupation of flies initiated by a hormone. G. FRAENKEL (Nature, 1934, **133**, 834).—Pupation in *Calliphora erythrocephala* is initiated by a hormone. L. S. T.

Substances affecting the circulation. I. Method. F. LANGE and I. DONOMAE (Arch. exp. Path. Pharm., 1934, **175**, 176—181).—A manometric method for the determination of the vol. of a section of isolated surviving artery and its application to the

study of vaso-constricting and -dilating substances are described. F. O. H.

Influence of the spleen on sulphur metabolism. K. IWABUCHI (Sei-i-kwai Med. J., 1933, **52**, No. 4, 59—83).—The spleen plays an important part in the S metabolism of dogs; its activity depresses S metabolism and its absence accelerates it. Injection of opostatin reduces the S metabolism accelerated by splenectomy. Adrenaline and oophormin accelerate S metabolism, especially of splenectomised animals. CH. ABS.

Effect of splenic substances on blood-cholesterol. E. SCHLIEPHAKE (Klin. Woch., 1933, **12**, 1936—1938).—Human serum-cholesterol (I) is usually increased by administration of the spleen hormone, prosplen, the increase being the greater the lower is the initial val. (I) is always increased initially by intravenous, but often decreased by intramuscular injection. NUTR. ABS. (m)

Functions of the adrenal cortex. F. A. HARTMAN (Ohio J. Sci., 1934, **34**, 4—8).—Cortin given to guinea-pigs on a diet deficient in vitamin-C delayed the onset of scurvy. The adrenal cortex contains cortilactin, necessary for milk production, as well as cortin, a general tissue hormone. CH. ABS.

Influence of adrenaline on blood-potassium. J. L. D'SILVA (J. Physiol., 1933, **80**, 7r).—Intravenous injection of 0.5 c.c. of 1:10,000 adrenaline into chloralosed cats causes an increase (up to 65%) in serum-K, the val. returning to normal after 15 min. The K enters the blood-stream from the tissues. NUTR. ABS. (m)

Adrenaline, lymphatic gland extracts, and the hyperglycaemic reaction. M. COPPO (Boll. Soc. ital. Biol. sperim., 1933, **6**, 378—381; Chem. Zentr., 1934, i, 560).—Thymus total extract causes hyperglycaemia (I) and diminishes or arrests adrenaline (I). Lymphatic gland extract behaves similarly. A. A. E.

Anterior pituitary hormones. VI. Deamination processes. R. AGNOLI (Boll. Soc. ital. Biol. sperim., 1933, **6**, 754—756; Chem. Zentr., 1934, i, 560).—Agnoli's lipid hormone and Zondek's prolan, but not "praephyson," intensify deamination. A. A. E.

Insulin and adrenaline. M. W. GOLDBLATT (J. Physiol., 1933, **79**, 286—300).—In the starving young rabbit, insulin (I) and adrenaline produce an increase in liver-glycogen (II). With (I) there is usually an increase in the total glycogen of the body with or without a decrease in muscle-glycogen (III). With adrenaline, in non-glycosuric doses, the increase in (II) is invariably accompanied by a decrease in (III) which may be similar in quantity; with larger doses, both (II) and (III) are diminished. Ergotamine (5 mg. intravenously) does not prevent these changes. CH₂I-CO₂Na (15 mg.) prevents accumulation of (II). Injection of (I) is not followed by a sufficient increase in blood-lactate to justify the belief that it causes production of (II) through adrenal secretion. NUTR. ABS. (m)

Effect of diet, insulin, and thyroxine on the adrenaline content of the adrenals. H. A. F. GOHAR (J. Physiol., 1933, **80**, 305—313).—In white

rats the adrenaline content (I) and wt. of the adrenals are unaffected by high-protein diet, but fat diet leads to a diminution of the abs. (I) and total wt. of the glands; the relative (I) per g. of gland is also slightly diminished. Carbohydrate diet also produces a diminution of the abs. (I); the wt. of the adrenals is diminished so that the relative (I) per g. of gland is increased. Starved rats also show diminution of (I) of the adrenals. Repeated administration of insulin in subconvulsive doses leads to increase in the wt. of the glands and of their (I). In convulsive doses there is a depletion of (I). This effect of insulin is produced through the nervous system as well as by peripheral action on the adrenals. Repeated injection of thyroxine also produces an increase in wt. and (I).

NUTR. ABS. (m)

Correlation between the action of insulin and adrenaline on muscle- and liver-glycogen. K. M. DAUD and H. A. F. GOHAR (J. Physiol., 1933, 80, 314—322).—Injection of convulsive doses of insulin into rats results in almost complete depletion of the liver-glycogen (I) and considerable diminution of the muscle-glycogen (II). In adrenalectomised animals, insulin causes a similar diminution in (I), but apparently has no effect on (II). Injection of adrenaline also causes depletion of (I) and considerably diminishes (II). The depletion of (I) is determined by the synergetic action of insulin and adrenaline, either of them alone giving the same result as both together, whilst the depletion of (II) is brought about by the insulin by acting indirectly through increased activity of the adrenal glands. A polarimetric method for determining small amounts of glycogen is described.

NUTR. ABS. (m)

Insulin and glycogen. III. F. RATHERY, S. GILBERT, and Y. LAURENT (Ann. Physiol. Physicochim. biol., 1932, 8, 492—593).—Insulin has a const. effect on blood-sugar and a variable effect on liver- and muscle-glycogen. Liver-glycogen in normal, starved, phloridzinised, or depancreatized dogs usually falls. Changes in liver are > those in muscle and are not related to those in muscle or in blood.

NUTR. ABS. (m)

Role of the pancreas in the tissue storage of glucose. A. BAISET, L. BOUISSET, L. BUGNARD, J. J. ROUZARD, and C. SOULA (Compt. rend. Soc. Biol., 1933, 114, 1308—1309).—The arterial and venous blood-sugar differences in the limbs of dogs, both normal and depancreatized, receiving glucose intravenously, indicate that the secretion of the pancreas permits storage of glucose in the tissues.

NUTR. ABS. (m)

Effect of insulin on blood-calcium. A. CABITTO (Riv. Clin. Pediat., 1933, 31, 1343—1350).—Insulin increases total blood-Ca and the increase seems to be directly related to the dose. Colloidal Ca is increased relatively more than ultrafilterable, which is increased only by doses of ≤ 1.5 —2 units per kg. Hence there is a % reduction in ultrafilterable and a relative increase in colloidal Ca. NUTR. ABS. (m)

Control of the insulin output of the pancreas. T. KOSAKA (J. Physiol., 1933, 79, 416—422).—Infusion of glucose into the pancreaticoduodenal artery of the decapitated cat is followed by a fall of

blood-sugar more rapid than that found when similar injections are made into the femoral artery or portal vein. The pancreas responds to hyperglycemia of its arterial supply by a liberation of insulin.

NUTR. ABS. (m)

Inactivation of insulin by normal and diabetic blood. P. T. BLACK (Brit. J. Exp. Path., 1933, 14, 318—322).—Insulin incubated with serum, laked red blood-cells, or cytolysed leucocytes, but not with heparinised whole blood or with intact red blood-cells or leucocytes, loses some of its power to lower the blood-sugar level. Blood from diabetics, including that from those resistant to insulin, does not differ in these respects from normal blood.

NUTR. ABS. (m)

Hypercalcemic action of intravenous injection of potassium chloride in thyroparathyroidectomised animals. J. T. RICO (Compt. rend. Soc. Biol., 1933, 114, 847—848).—When the injections are made a few hr. (but not several days) after removal of the glands a slight increase in serum-Ca results.

NUTR. ABS. (m)

Effect of parathyroidectomy on blood-calcium. R. GREGOIRE, LYONNET, and DELAVENNE (Le Sang, 1933, 7, 790—802).—In dogs, blood-Ca falls from 12.7 to 6.2 mg. per 100 c.c. in 48 hr. and returns to normal in a few weeks. The parathyroids are therefore not alone in their action on carbohydrate metabolism. Chloralose anaesthesia alone reduces blood-Ca by 20%.

NUTR. ABS. (m)

Effect of thyroxine on blood-calcium. C. ROSSO (Riv. Clin. Pediat., 1933, 31, 1351—1359).—Thyroxine always reduces blood-Ca after a slight initial rise. Changes in colloidal Ca closely follow those in total Ca, whilst ultrafilterable Ca shows a variable degree of reduction. In the first period (about 20 min.) ultrafilterable is changed into colloidal Ca.

NUTR. ABS. (m)

Effect of thyroidectomy and thyroid feeding on milk secretion and milk-fat production of cows. W. R. GRAHAM, jun. (J. Nutrition, 1934, 7, 407—429).—Thyroidectomy and also the removal of desiccated thyroid gland from the ration of thyroidectomised cows lowered the total milk and fat yields.

Non-thyroid substances with thyroid action. II. Influence of the fission products of artificially iodised protein (homothyroxine) on avian plumage and body-temperature of guinea-pigs. III. Physiologically active substances containing iodine from artificially iodised protein. ABELIN (Arch. exp. Path. Pharm., 1934, 175, 146—150, 151—155).—II. The I-containing products of the hydrolysis of iodised protein (homothyroxine) (cf. A., 1933, 1087) act similarly to thyroid preps. in causing moulting and depigmentation of tow feathers and in inhibiting the depression of the body temp. of guinea-pigs due to novocaine.

III. Hydrolysis of iodised caseinogen with aq. Ba(OH)₂ or NaOH followed by pptn. with HCl and extraction with BuOH yields a fraction containing up to 30% I and approx. 4% N which resembles thyroid gland preps. in its action on the basal

bolism of rats and thyroxine-containing fractions of thyroid proteins in its chemical properties.

F. O. H.

Relation of the pituitary gland to the action of insulin and adrenaline. A. B. CORKILL, H. P. MARKS, and W. E. WHITE (*J. Physiol.*, 1933, 80, 193—205).—After removal (I) of the pituitary, rabbits may develop spontaneous hypoglycæmia, and always show greater hypoglycæmic response to insulin, which is but little affected by injection of adrenaline (II) or vasopressin. There is generally also diminished response to (II) and increased sugar tolerance. Neither depletion of the liver-glycogen (III) nor deficient secretion of (II) is responsible for this abnormal sensitivity to insulin. (III) develops an unusual resistance to mobilisation by (II), possibly connected with the observed thyroid and adrenal cortex degeneration after (I).

NUTR. ABS. (m)

Pressor and insulin-antagonistic action of tonephin or pitressin and orasthin. H. SCHROEDER (*Klin. Woch.*, 1933, 12, 1766—1768; *Chem. Zentr.*, 1934, i, 560).—The pressor constituent of pituitary extract raises the blood-sugar (I) and is antagonistic to insulin. The component affecting the uterus has no action on (I).

A. A. E.

Effect of the pituitary gland on nitrogen metabolism. Y. TAKEUCHI and Y. TOKIZAKI (*Sei-i-kwai Med. J.*, 1933, 52, No. 3, 25—50).—Hypophysectomy in dogs produces a slight decrease in urinary non-protein-N, creatine, and creatinine, and blood-N, but an increase, followed by a decrease, in blood-non-protein-N. Daily injection of pituitrin into normal dogs causes a decrease in all except blood-N, and in blood-creatine and -creatinine; injection into hypophysectomised dogs causes an increase in all cases.

CH. ABS.

Depression of the basal metabolism of thyroidectomised guinea-pigs by anterior pituitary gland. W. SCHOEDEL (*Arch. exp. Path. Pharm.*, 1934, 175, 233—240).—Administration of anterior pituitary preps. (I) to thyroidectomised guinea-pigs (II) produces a diminution in the basal metabolism (III) which is not due to the thyroidectomy. Injection of muscle extracts or of deproteinised, heated (I) has no action on (III). With (II), the (III) of which has been increased by administration of thyroxine, the decrease of (III) by (I) is less evident. The mechanism is discussed.

F. O. H.

Separation of the hormone of the anterior pituitary gland related to fat metabolism from the thyrotropic hormone. K. J. ANSELMINO and F. HOFFMANN (*Arch. exp. Path. Pharm.*, 1934, 175, 335—338).—Ultrafiltration through collodion membranes of suitable extracts of anterior pituitary gland yields thyrotropic hormone (I) (residue) (A., 1933, 1337) and a hormone (II) (ultrafiltrate) which increases the blood-ketones of normal or thyroidectomised rats. Thus the action of (II) on fat metabolism, unlike the ketogenic action of (I), does not depend on the presence of the thyroid gland.

F. O. H.

Crystalline oestrus-producing hormone from rse (stallion) urine. V. DEULOFEU and J.

FERRARI (*Nature*, 1934, 133, 835).—Rhomboid plates, m.p. 254—255°, of high oestrogenic activity and apparently identical with the hormone of the urine of pregnant women, have been isolated from horse urine (cf. this vol., 567).

L. S. T.

Crystalline forms and m.p. of α -follicular hormone. A. KOFLER and A. HAUSCHILD (*Z. physiol. Chem.*, 1934, 224, 150—154).— α -Follicular hormone exists in three cryst. modifications, rhombic metastable (I), m.p. 254°, n_D 1.594, n_D 1.628, n_D 1.647; monoclinic metastable (II), m.p. 256°, n_D 1.520, n_D 1.642, n_D 1.690; and rhombic stable (III), m.p. 259°, n_D 1.512, n_D 1.619, n_D 1.692. (II) is obtained from a conc. solution in 20% EtOH, (I) on evaporation of MeOH solutions, (III) not from solution but from (I) and (II) at approx. the m.p.

J. H. B.

Substance from mammary adenocarcinomata of mice, which increases growth and accelerates genital development in young rats. H. DOBROVOLSKAIA-ZAVADSKAIA and P. ZEPHIROV (*Compt. rend.*, 1934, 198, 1950—1952).—An H₂O-sol., alkali-stable substance isolated from adenomatous growths in mice, when injected into young rats, increases the rate of growth and size of uterus and causes early oestrus.

R. S. C.

Relationship of blood-cholesterol to activity of sex glands. J. DIDRY (*Compt. rend. Soc. Biol.*, 1933, 114, 1080—1081).—Differences in serum-cholesterol in dogs following castration and ovariectomy are small and cannot be compared with the much larger variations following thyroidectomy.

NUTR. ABS. (m)

Effect of corpus luteum on blood-calcium in bitches with chronic parathyroid insufficiency. F. MATHIEU (*Compt. rend. Soc. Biol.*, 1933, 114, 1373—1374).—Corpus luteum injections cause a fall in blood-Ca.

NUTR. ABS. (m)

Blood-iodine after castration in bitches. M. FRANKE and L. PTASZEK (*Compt. rend. Soc. Biol.*, 1933, 114, 1129—1130).—In young bitches a transitory increase in blood-I occurs during the first week after oorectomy, followed by a fall. In old bitches there is an initial fall.

NUTR. ABS. (m)

Blood-iodine after castration in dogs. M. FRANKE and L. PTASZEK (*Compt. rend. Soc. Biol.*, 1933, 113, 1302—1303).—Six days after castration blood-I is considerably > before operation. The val. then falls and at 6 weeks is < pre-operative val.

NUTR. ABS. (m)

Formation of a substance which possesses the physiological action of the male hormone. W. DIRSCHERL and H. E. VOSS (*Naturwiss.*, 1934, 22, 315).—Hydrogenation of crude or cryst. samples of follicular hormone yields a product containing the male sex hormone (1 capon unit and 1 mouse unit in 25—100 $\times 10^{-6}$ g.). The original hormone contained 1 capon or mouse unit in 2 mg. (cf. A., 1933; 755).

W. O. K.

Active and inactive forms of the hormone promoting comb-growth. A. A. ADLER (*Nature*, 1934, 133, 798).—The hormone is present in the urine of men in an inactive form (I) which can be extracted

by means of BuOH. (I) is converted into an active form by boiling the extract with $\text{CCl}_3\cdot\text{CO}_2\text{H}$.

L. S. T.

A provitamin-A other than carotene? E. BOYLE (*Nature*, 1934, **133**, 798).—Spectrographic and colorimetric tests of a turbid concentrate after irradiation show that the chromogen responsible for the 565 m μ band is the precursor of the 575 m μ chromogen, which is either a vitamin-A purer than that of Carr and Jewell, or is a sterol with higher spectroscopic and colorimetric vals.

L. S. T.

Stability of carotene in olive oil. R. G. TURNER (*J. Biol. Chem.*, 1934, **105**, 443—454).—0.2% of carotene in olive oil or Et laurate together with a stabiliser (I) loses approx. 50% of its vitamin-A activity in 12 months. Light and temp. up to 37° have no effect on this inactivation, but cold prevents it. Without (I) complete destruction occurs in 3—4 months.

H. G. R.

Rich source of β -carotene. W. L. BROWN (*Science*, 1934, **79**, 481).—The Perfection pimento is a rich source of β -carotene, apparently free from α -carotene. Dried pimento shells contain 200—665 mg. per kg.

L. S. T.

Physico-chemical studies of complex organic molecules. I. Monochromatic irradiation. F. P. BOWDEN and C. P. SNOW. II. Absorption at low temperatures. F. P. BOWDEN and S. D. D. MORRIS (*Proc. Roy. Soc.*, 1934, **B**, **115**, 261—273, 274—278).—Radiations longer than 3130 Å. have no effect on calciferol (I), which is destroyed at 2650 and, less quickly, at 2537 Å. Ergosterol is converted into (I) at 2967 Å. Vitamin- B_1 has an absorption band at 2600 Å. Carotene irradiated at 2650 Å. gave the vitamin-A absorption band at 3280 Å.

II. The bands of β -carotene at liquid air temp. (I) narrow and shift to 4990, 4670, and 4350 Å. with a new band at 4060 Å. The main band of vitamin-A (II) shifts to 3350 Å. and new bands appear at 2900, 2770, 2580, 2510, and 2430 Å. Irradiated carotene, with an absorption band resembling that of (II) at room temp., shows bands at 3780, 3570, 3410, and 3210 Å. at (I); the two substances are thus not identical.

C. G. A.

Absorption spectra of α - and β -carotene and leaf-xanthophyll at room and liquid nitrogen temperatures. E. S. MILLER (*Plant Physiol.*, 1934, **9**, 179).—At the lower temp. of observations the absorption bands become narrower, but more distinct. The max. for carotenoids are moved 165—200 Å. towards the infra-red.

A. G. P.

Differences between biologically active substances before and after isolation from the raw materials in which they occur. H. I. WATERMAN and C. VAN VLODRUP (*Rec. trav. chim.*, 1934, **53**, 670—671).—Distillation of carotene (I) in red or colourless palm oil in a cathode vac. with internal condensation gives a distillate richer in (I). This does not occur with natural (II) or pre-conc. (i.e. extracted and fractionally frozen) (III) palm oil. The distillation residue from (II) contains an unaltered % of (I), that from (III) less. However, redistillation (which occurs without decomp.) of the distillate

from (II) causes concn. of (I) in the distillate. It is thus inferred that (I) does not occur entirely in the free state in (II).

R. S. C.

Absorption spectra in oil research. Distillation of palm oil. L. J. N. VAN DER HULST (*Rec. trav. chim.*, 1934, **53**, 672).—Quant. measurement of the absorption spectra shows that distillation of carotene (I) in palm oil (II) concentrates (I) into the distillate, but that this effect is very slight with natural (II) alone (cf. preceding abstract). Bleaching earth (Terrana "superior") absorbs carotene and other pigments from (II) in C_6H_{14} , giving an oil with a spectrum which from λ 220 to 500 m μ resembles that of a mixture of oleic and stearic acids.

R. S. C.

Determination of carotene in butter-fat. H. M. BARNETT (*J. Biol. Chem.*, 1934, **105**, 259—267).—A spectrophotometric method for the determination of the carotene (I) content of butter-fat (II) is based on transmittancies at different wave-lengths of varying amounts of (I) dissolved in (II).

A. E. O.

Influence of the nature and amount of proteins in the basal diet on avitaminosis-A. L. RANDOIN and S. QUEVILLE (*Compt. rend.*, 1934, **198**, 1942—1944).—Yeast and caseinogen (I) in the basal vitamin-A-free diet do not affect the onset of xerophthalmia. Large amounts of (I), however, prolong the periods of growth and survival.

R. S. C.

Vitamin-A and -D activity of egg yolks of different colour concentrations. B. BISBEY, V. APPLEBY, A. WEIS, and S. COVER (*Missouri Agric. Exp. Sta. Res. Bull.*, 1934, No. 205, 32 pp.).—Although some relationship exists between the growth of rats and the yolk colour of eggs used in feeding them, the vitamin-A activity of yolks cannot be explained on the basis of their carotenoid pigment contents, but is directly dependent on the hen's ration. Differences in yolk colour cannot be correlated with differences in vitamin-D content.

A. G. P.

Spectrographic evaluation of solutions of vitamin-D in fatty oils. II. L. FUCHS and Z. BECK (*Pharm. Presse*, 1933, **38**, 93—104; *Chem. Zentr.*, 1933, ii, 2867).—Vitamin-D (I) dissolved in olive oil can be isolated unchanged with the unsaponifiable fraction (II) and by methods previously described (this vol., 333) can be determined more simply than by animal tests. The extinctive power of (II) can be disregarded. Dissolution of (I) in sesame oil is unfavourable. The presence of white \bar{r} does not change the (I) in oil solutions.

L. S. T.

Biological comparison of vitamin-D from fish-liver-oils with that from irradiated ergosterol. O. DALMER, F. VON WERDER, and T. MOLL (*Z. physiol. Chem.*, 1934, **224**, 86—96).—Excessive doses of vitamin-D concentrates from halibut- and tunny-liver-oil from which most of the vitamin-A has been removed by maleic anhydride produce the same toxic symptoms in mice as overdoses of irradiated ergosterol or calciferol. The therapeutic indices are a so of the same order.

J. H. B.

Action of viosterol and parathormone. J. W. SPIES, R. H. WILSON, and J. A. STRINGHAM (*Chinese*

Med. J., 1934, 48, 352—372).—In thyroparathyroid-ectomised dogs viosterol (I) and parathormone (II) increase serum-Ca in amounts parallel to the muscular response to stimuli and to the urinary excretion of Ca. (I) produces a positive balance of Ca and P due to diminution of the faecal excretion being > the augmentation of urinary output, whereas (II) produces a negative balance due to the increase in urinary excretion.

H. G. R.

Mustard oil in subacute poisoning by vitamin-D. G. ORZECOWSKI and E. SCHREIBER (Arch. exp. Path. Pharm., 1934, 175, 265—283).—Crude mustard oil (I) has no influence on the changes (calcification etc.) in the arteries of rabbits due to administration of vitamin-D. Large doses of (I) do not influence the gaseous metabolism of rats, whilst during the loss in body-wt. preceding death in rabbits, the urinary excretion of neutral S attains pathological vals.

F. O. H.

Peroxidase reaction. XXXVIII. Relation between Arakawa's reaction and suitability of human milk. K. ASAKURA (Tohoku J. Exp. Med., 1932, 19, 275—281).—Mice fed on polished rice were protected from vitamin-B deficiency by milk which gave Arakawa's peroxidase reaction, but not by other milk.

CH. ABS.

Results of administration of large amounts of vitamin-B. G. BAGNACCI (Biochem. Terap. sperim., 1932, 19, 295—307; Bied. Zentr., 1934, A, 4, 344).—Considerable amounts of vitamin-B (up to 400 units) were not detrimental to the health of rats, mice, or pigeons.

A. G. P.

Vitamin-B₁ deficiency in carbohydrate-free diets and the behaviour of ethyl alcohol towards vitamin-B₁. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1933, 9, 1045—1048).—Addition of autoclaved yeast did not prevent vitamin-B₁ deficiency. Glucose accelerated, whilst EtOH delayed, the appearance of the symptoms.

CH. ABS.

[Isolation in] larger yields of crystalline anti-neuritic vitamin. R. R. WILLIAMS, R. E. WATERMAN, and J. C. KERESZTESY (J. Amer. Chem. Soc., 1934, 56, 1187—1191).—Details are given for the isolation of the vitamin (as hydrochloride) in a yield of about 5 g. per ton of rice polishings, i.e., about 25% of the amount originally present. The process gives consistent results.

H. B.

Vitamin-B₂. B. C. GUHA and P. N. CHAKRABORTY (J. Indian Chem. Soc., 1934, 11, 295—310; cf. this vol., 461).—Ox-liver extract (I) (prep. described) at p_H 1.2—11 is not freed completely from vitamin-B₂ (II) when shaken with C. MeOH-HCl is the best reagent for eluting (II). SiO₂ gel and AgBr, not BaSO₄, adsorb (II) (cf. A., 1931, 988), which is eluted by boiling HCl. (II) is not pptd. by saturated Cu(OAc)₂, HgCl₂, or Br. Fractional pptn. of (I) with EtOH only partial pptn. occurs; PrOH destroys the activity of (II). Many sugars, cytosine, and adened adenine and guanine contain no (II).

J. L. D.

Vitamin-B₂ potency of purified liver preparations. E. BRAND, R. WEST, and C. J. STUCKY

(Proc. Soc. Exp. Biol. Med., 1933, 30, 1382—1384).—Purified liver extracts, potent in pernicious anaemia, did not induce growth in rats deficient in vitamin-B₂.

CH. ABS.

Vitamin-B₂ in saké and saké-kasu (pressed cake). F. INUKAI, T. HIGASHI, and W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 113—118).—Saké and pressed cake are good sources of vitamin-B₂ (I), which may be obtained from acid MeOH extracts by adsorption on "acid earth." The (I) content of saké yeast is approx. the same as that of brewer's yeast. Neither of these products contains vitamin-B₁.

P. G. M.

Alkali-labile ring of lactoflavin. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 892—898).—Treatment of lumilactoflavin (I) with Ba(OH)₂-H₂O at 100°, acidification of the solution with AcOH extraction with CHCl₃, and treatment of the extract (II) with NaHCO₃ gives the acid (III) C₁₂H₁₂O₃N₂, m.p. 215° (corr.), yielding a sublimate, m.p. 173—174° (corr.), identical with that obtained by use of NaOH. (III) contains 1 active H (Zerevitinov), is titrated as a monobasic acid in presence of phenolphthalein, and gives a yellow Ag salt sparingly sol. in EtOH-CHCl₃. Na₂S₂O₄ decolorises the yellow solution in EtOH, but the colour is restored by air. Extraction of (II) with Na₂CO₃ gives a substance, partial decomp. 370° (red Ag salt); the colour of its solution darkens on addition of NaOH. Zn and HCl give a red intermediate. Reversible decolorisation is effected with difficulty by Na₂S₂O₄. Treatment of (II) with NaOH gives unchanged (I). Since 2H₂O are required for the alkaline hydrolysis of (I) the group which yields urea must belong to a ring system; this view is confirmed by the great stability of (I) towards HNO₂. Unsuccessful attempts at de-imination and acetylation indicate that both O atoms of (I) belong to the alkali-labile ring. 2 CO must therefore be involved, one of which appears as urea, whilst the other leads to CO₂H in (III). Treatment of the Ag salt of (I) with MeI yields a Me₁ derivative, sol. in NaOH, whereas (I) and Me₂SO₄ give a Me₂ compound, insol. in NaOH; both resemble (I) closely in colour and fluorescence.

H. W.

Dissociation constants of flavins. Relationship of p_H and fluorescence. R. KUHN and G. MORUZZI (Ber., 1934, 67, [B], 888—891).—The p_H -% of max. fluorescence graph of vitamin-B₂ (I) is the dissociation curve of an amphoteric electrolyte. In the broad region of optimum p_H brightness very exactly \propto pigment concn. The decrease in fluorescence on the acid and alkaline side can be used as a measure of the no. of electrically neutral mols. (Zwitterions) and the dissociation const. of (I) can be thereby determined with min. amounts of material. Similar observations are recorded with lumilactoflavin (II). With the porphyrins a min. of fluorescence is observed in the isoelectric region. Phosphorescence of lactoflavin or (II) could not be observed.

H. W.

Flavin potentials. [Reduction-oxidation behaviour and a colour reaction of lactoflavin (vitamin-B₂). Flavins as biological hydrogen acceptors.] K. G. STERN (Ber., 1934, 67, [B],

654—655).—In reply to Kuhn *et al.* (this vol., 461) and Wagner-Jauregg *et al.* (A., 1933, 1183), it is pointed out that the normal potential of cryst. hepato- and extensively purified malto- and uro-flavin at p_H 7 is about -0.2 volt, whereas that of pyocyanine at p_H 7.0 is -0.034 volt. H. W.

Lyochrome from urine (uroflavin). W. KOSCHARA (Ber., 1934, 67, [B], 761—766).—Fresh urine is agitated with "Floridin XXF" (I) and the solid is treated with 40% $C_6H_5N-H_2O$. The pigments are adsorbed from the eluate by pptn. with $Pb(OAc)_2$ and treatment of the filtrate with H_2S . The eluates are reddish-brown and fluoresce strongly in ultra-violet light. Saturation with $(NH_4)_2SO_4$ causes the appearance of the colour of lyochrome, but further purification of the pigments is not effected by use of $COMe_2$ or salts of heavy metals. Their separation is effected chromatographically using (I) with $MeOH-H_2O-C_6H_5N$ as developer, the addition of a small amount of $AcOH$ to the latter being particularly advantageous. Thus is obtained uroflavin (II), $C_{18}H_{22}O_7N_4$, m.p. 272° (decomp.) when slowly heated. (II) is identical in cryst. form and lyochrome character with lactoflavin *d* (III), m.p. $267-268^\circ$. A mixture of (II) and (III) has m.p. $267-268^\circ$. No differentiation is observed when a mixture of (II) and (III) is examined chromatographically. The formulæ of (II) and (III) are not sufficiently well established to afford trustworthy evidence, but the pigments are considered to be non-identical. H. W.

Vitamin-C. XI. Efficacy of vitamin-C and the manner in which it is supplied. XII. Vitamin-C in the liver and adrenal glands of cattle. XIII. Extraction of vitamin-C and solvents. XIV. Extraction of vitamin-C and p_H of the solution. T. MATSUOKA (J. Agric. Chem. Soc. Japan, 1933, 9, 1117—1123), 1124—1129, 1130—1136, 1136—1140).—XI. Effective doses are reported. XII. Adrenals are richer in vitamin-C than liver. Cryst. hexuronic acid was isolated.

XIII. Cabbage juice was evaporated under reduced pressure and dried over H_2SO_4 . Vitamin-C is sol. in $EtOH$ and $COMe_2$, but insol. in Et_2O and light petroleum.

XIV. The p_H of the solution had no effect on the solubility of vitamin-C in $EtOH$ and $COMe_2$.

CH. ABS.

Chinese citrus fruits. III. Composition of juices of several species of Chinese oranges and tangerines, and their vitamin-C content. P. P. T. SAH, T. S. MA, V. HOO, and H. H. LEI (J. Chinese Chem. Soc., 1934, 2, 73—83).—Kwan Cheng, a Canton orange, is richest in ascorbic acid.

J. L. D.

Vitamin-C content of Chinese green and red peppers. P. P. T. SAH and H. C. CHANG (J. Chinese Chem. Soc., 1934, 2, 84—85).—Judged by I titration, *Capsicum annuum* (green fruit) contains no vitamin-C (I), but the red fruit is rich in (I).

J. L. D.

Anti-pneumonia factor in fruits containing vitamin-C. H. VON EULER and M. MALMBERG (Naturwiss., 1934, 22, 205).—Lemon and red-currant juices contain a factor-I, not identical with ascorbic

acid, which aids recovery of guinea-pigs from pneumonia. R. K. C.

Significance of transpiration. H. F. CLEMENTS (Plant Physiol., 1934, 9, 165—172).—A discussion. A. G. P.

Chlorophyll production under various environmental conditions. G. B. ULVIN (Plant Physiol., 1934, 9, 59—81).—Leaves grown in continuous light contained more chlorophyll (I) per unit fresh or dry wt. or area than those grown in intermittent light. Maize plants showed markedly increased (I) formation following additions of 1 and 15 p.p.m. of Fe to the nutrient, but did not respond to addition of 1 p.p.m. of Mn. The % dry matter in leaves was directly proportional to the (I) content by wt. or area. Exposure to X-rays increased the amount of (I) in maize leaves. In sugar-cane receiving N as NO_3 , (I) production was > that in plants supplied with NH_3-N . A. G. P.

Causes of colour change in blue-green algæ. M. C. SARGENT (Proc. Nat. Acad. Sci., 1934, 20, 251—254).—A high intensity of light and a low Fe content of the medium cause a decrease in the chlorophyll in *Glæocapsa montana*. No complementary chromatic adaptation was observed. H. G. R.

Oxygen consumption of *Chlorella pyrenoidosa* as a function of temperature and oxygen tension. P. S. TANG and C. S. FRENCH (Chinese J. Physiol., 1933, 7, 353—377).—The variation of the rate of O₂ consumption (A) with O₂ tension (P) follows the equation $A = P/(K_1 + K_2P)$, where K_1 and K_2 are consts., the dependence of which on temp. is expressed by the equations of Arrhenius and van't Hoff. The vals. of μ and ΔH (apparent heats of activation and reaction, respectively) between 8° and 20° are approx. the same (20,000 g.-cal.), but of opposite sign, that for μ being positive. A. L.

Oxidation processes in the needles of *Picea excelsa* in winter. T. M. ZACHAROVA (Biochem. Z., 1934, 270, 281—290).—The C content and heat of combustion of pine needles (I) are less for (I) kept in the dark or from the depth of a wood, than for those in the light. The malic acid content of the (I) of a darkened branch increases from Nov. to Jan., and of an undarkened branch from Nov. to March, the total amount found being greater in the light. The $H_2C_2O_4$ content of (I) of a darkened branch increases continuously, but of the undarkened branch does not increase. P. W. C.

Time relations in effect of ethylene chlorohydrin in increasing and of ethyl alcohol in decreasing the respiration of potato tubers. L. P. MILLER (Contr. Boyce Thompson Inst., 1934, 6, 123—128).—The increased CO_2 production (I) from potato tubers following exposure to vapour of CH_2Cl-CH_2-OH (II) commences approx. 12 hr. after treatment and the reduction of (I) by $EtOH$, approx. 2 hr. after treatment. (II) and $EtOH$ applied simultaneously or alternately tend to counteract each other's effects. A. G. P.

Respiration and catalase activity in *Sauro-matum spadices*. A. W. H. VAN HERK and N. BADENHUIZEN (Proc. K. Akad. Wetensch. Amster-

dam, 1934, 37, 99—105).—The flower spikes of *S. guttatum* take up O_2 rapidly. The respiratory activity shows a broad optimum between p_H 6.6 and p_H 8, and is inhibited by the usual agents. Extracts show high catalase (I) activity (190—250 units per g.), which has an optimum val. at p_H 6.5—8 and is inhibited by HCN. The respiration of slices of tissue is accelerated by addition of (I), and the possible correlation of the two activities is discussed.

R. K. C.

Oxidase system of a non-browning yellow peach. Z. I. KERTESZ (New York State Agric. Exp. Sta. Tech. Bull., 1933, No. 219, 14 pp.).—Lack of discoloration in peach is not due to low activity of oxidising enzymes, but to deficiency or absence of pyrocatechol-tannin compounds which form an essential component of the oxidising system. A. G. P.

Determination of peroxidase activity. D. A. PACK (Ind. Eng. Chem. [Anal.], 1934, 6, 170—171).—The peroxidase activity of fruit juices is much greater if obtained by grinding with fine sand in H_2O or the buffer solution than by pressing, and if measured at the optimum p_H than at p_H 4.5. The optimum for pears is 6.2, and for strawberries, cauliflowers, asparagus, and potatoes between 6 and 7.

R. S. C.

Formation of cellulose membranes by microscopic particles of uniform size in linear arrangement. W. K. FARR and S. E. ECKERSON (Contr. Boyce Thompson Inst., 1934, 6, 189—203).—Fibrils of cell membranes from a no. of plants consist of particles of cellulose with a pectic covering arranged in a linear manner. A. G. P.

Red and brown algæ. T. DILLON and T. O TUAMA (Nature, 1934, 133, 837; cf. this vol., 571).—Cellulose has been obtained from *Laminaria* and converted into a sugar which gave phenylglucosazone but no insol. phenylhydrazone. L. S. T.

Acetyl and methoxyl content of pine-wood. E. HAGGLUND and O. SANDELIN (Svensk Kem. Tidskr., 1934, 46, 83—87).—Pine-wood (I) freed from lignin (II) by repeated treatment with Cl_2 and extraction with $COMe_2-C_5H_5N$ contained 0.80% OMe, OEt being probably absent. The OMe content of (I) is not wholly attributable to (II), but about one eighth associated with the 70% of carbohydrate (III). Of the Ac groups in (I), at least 60% are attached to (III). W. O. K.

Transformation of the methoxyl group in lignin in the process of decomposition of organic residues by micro-organisms. S. A. WAKSMAN

W. SMITH (J. Amer. Chem. Soc., 1934, 56, 25—1229).—Growth of *Agaricus campestris* on fresh or composted [which results in an increase of the amount of lignin (I) present] horse manure causes a decrease in the amount of (I); the OMe content of residual (I) is not appreciably altered, but the mol. is considerably modified. Prolonged decomp. of plant residues under aerobic and anaerobic conditions leads to an increase in (I): the OMe content of the residual acid-(I) is considerably reduced (especially in the latter case). Peat formation (decomp. of plant material under anaerobic conditions) is accompanied

by an accumulation of (I) and a decrease in OMe content [which characterises the gradual transformation of (I) into dark-coloured humus substances]. Sphagnum plants contain little OMe, but much uronic acid (II) (which is resistant to decomp.); anaerobic decomp. gives a type of peat which is rich in lignin-like complexes of low OMe and high (II) content.

H. B.

Formation of aromatic substances and terpenes in plants. T. WEEVERS (Pharm. Weekblad, 1934, 71, 621—630).—The formation of terpenes (I) in the plant is parallel with the formation of lignin. (I) may occur in certain plants as a result of pathological conditions, which bring about degeneration of the cells.

S. G.

Determination of pentosans in vegetable materials containing tannin. A. P. SAKOSTSCHIKOFF, W. I. IWANOWA, and A. M. KURENOWA (Ind. Eng. Chem. [Anal.], 1934, 6, 205—208).—Determination of pentosan (I) in cotton-seed hulls (II) by Tollens' method gives low results, the error increasing with increasing tannin content of (II). The real (I) is found by addition of the results obtained (i) on the aq. extract of (II) (after removal of tannins from the solution), (ii) on an acid extract of the residue from (i), and (iii) on the solid residue from (ii).

R. S. C.

Carbohydrates of the bulb of *Narcissus tazetta*, L., var. *chinensis*, Roem. UI. Enzymic hydrolysis of glucomannan. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1933, 9, 770—772).—When kept with *Eulota* extract for 3 days, glucomannan solution rapidly decreased in viscosity, affording a substance, m.p. 183° (decomp.), $[\alpha]_D^{25} +47.26^\circ$ (Ac derivative, m.p. 137°), which is not pptd. by $Ba(OH)_2$ or $Pb(OAc)_2$ and is hydrolysed by maltase but not by emulsin.

CH. ABS.

Methods of determining starch in plant tissues. F. E. DENNY (Contr. Boyce Thompson Inst., 1934, 6, 129—146).—To ensure conversion of potato-starch (I) completely into glucose by taka-diaxase (II) a suitable ratio of (II) : (I) must be used, p_H 3.0—5.0 must be maintained, and approx. 4 hr. contact allowed. Solutions of (II), free from reducing substances, of high amylolytic power and stable at room temp. for several weeks, may be obtained after dialysis in collodion sacs. Preliminary heating of (I) to 80° is sufficient to permit complete hydrolysis by (II). Determinations of (I) in the various organs of a no. of plants are recorded. Vals. of (I) obtained by the direct action of (II) on powdered plant tissue are > those resulting from extraction of (I) by $CaCl_2$, pptn. as the I-compound, removal of I and Ca, and treatment of the residue with (II). Decomp. of non-starchy substances in the former method is probable. The destruction of sugar under conditions required for the hydrolysis of starch does not occur unless the proportion of acid used is > twice the customary amount. A. G. P.

Determination of biologically important sugars in the presence of non-sugar reducing substances. O. LEHMANN (Diss., Leipzig, 1931; Bied. Zentr., 1934, A, 4, 364—365).—The Hagedorn-Jensen method is adapted to the determination of plant

sugars. Fermentation methods are utilised to separate hexoses from pentoses (the latter being determined by the furfuraldehyde method) and reducing sugars from non-sugar reducing substance in H_2O or Et_2O extracts of plant tissues.

A. G. P.

Determination of coumarin in plant material. I. J. DUNCAN and R. B. DUSTMAN (Ind. Eng. Chem. [Anal.], 1934, 6, 210—213).—Coumarin (I) is only slowly removed (completely in 120 hr.) by extraction (Soxhlet) of sweet clover (II) with Et_2O . Long heating of the solution, however, destroys some (I). The (I) content of (II) is determined by repeated distillation with steam in vac., removal of tannins etc. from the distillate by $Pb(OAc)_2$, and titration with $KMnO_4$. For comparative purposes four distillations suffice and the Pb treatment may be omitted.

R. S. C.

Colour reaction of chrysanthemum-monocarboxylic acid (hydrolysis product of pyrethrin I) and its detection in the urine excreted after administration of pyrethrins. M. AUDIFFREN (J. Pharm. Chim., 1934, [viii], 19, 535—536).—Chrysanthemum-monocarboxylic acid solution (1 c.c.), Deniges reagent (1 c.c.), and conc. H_2SO_4 (0.4—0.5 c.c., added rapidly without mixing) when mixed give an immediate red or rose changing to violet and green and a yellow ppt. after 24 hr. (sensitivity 1 : 100,000). The first fractions of the distillate from the urine of patients treated with pyrethrins give the reaction.

E. H. S.

Determination of the acids of plant tissue. III. **Determination of citric acid.** G. W. PUCHER, H. B. VICKERY, and C. S. LEAVENWORTH (Ind. Eng. Chem. [Anal.], 1934, 6, 190—193; cf. this vol., 572).—1—20 mg. of citric acid (I) is determined within $\pm 5\%$ by oxidation to $CHBr_2 \cdot CO \cdot CBr_3$ (II), debromination of the latter in light petroleum with aq. Na_2S , and titration of the liberated NaBr. Conversion of (I) into (II) is regularly about 90% under the conditions described.

R. S. C.

Localisation of fatty oils and starch in cells of cultivated beet. S. KOPUL-GOMOLYAKO (Nauk. Zapiski Tzuk. Prom., 1933, 10, No. 33, 91—100).—Differences in fat content between individual groups are not as great as among separate plants of the same group. The significance of the fatty oils is discussed. Starch is found only in the mangold group.

CH. ABS.

Constituents of tobacco. III. **Colouring matters of the flower.** I. K. YAMAFUJI (J. Agric. Chem. Soc. Japan, 1933, 9, 797—802).— $MeOH-HCl$ afforded an anthocyan (insol. picrate) affording an anthocyanidin and a monosaccharide. The residue, mixed with $CaCO_3$ and extracted with hot $EtOH$, afforded a flavone.

CH. ABS.

Gradient composition of rose shoots from tip to base. H. B. TUKEY and E. L. GREEN (Plant Physiol., 1934, 9, 157—163).—In 100-cm. shoots there was a rising gradient of H_2O , ash (I), and total N (II) and a falling gradient of starch (III) from base to tip. Shoots grown in high-N nutrients had more (I) and (II) and less (III) throughout their lengths than did those grown with less N. The distribution of starch in various stem tissues is examined.

A. G. P.

Two saponins from soya beans. K. OKAM and I. OHARA (J. Agric. Chem. Soc. Japan, 1933, 9, 1249—1258).—Sumiki's cryst. saponin (I), $C_{48-50}H_{77-81}O_{18}$, m.p. 225—227°, and an amorphous saponin (II), $C_{45-51}H_{79-83}O_{19}$, m.p. 216—218°, were obtained. On hydrolysis (I) affords a sapogenin, $C_{30-33}H_{48-52}O_9$, glycuronic acid (III), galactose (IV), and rhamnose (V); (II) affords a sapogenin, $C_{31-33}H_{50-54}O_9$, and (III), (IV), and (V). Five sapogenin isomerides, m.p. 201°, 235°, 239°, 260°, and 248—249°, were isolated according to the duration of hydrolysis. When heated with CuO or $PbCrO_4$, the saponins and sapogenins afford CH_4 and C_2H_6 . The saponins have no hæmolytic power. CH. ABS.

[Constituents of] *Ceanothus velutinus*. L. W. RICHARDS and E. V. LYNN (J. Amer. Pharm. Assoc., 1934, 28, 332—336).—The leaves of *C. velutinus* furnish 0.14—1.21% of an oil which consists chiefly of Et and cinnamyl cinnamates, together with salicyl-aldehyde, terpenes, and esters of an unidentified alcohol (diphenylurethane, m.p. 56°; phthalate, m.p. 204—205°) with cinnamic and probably valeric acids. The root bark furnishes 0.1% of an alkaloid, $C_{23}H_{29}O_4N_2$, m.p. 270° (decomp.) (unstable hydrochloride, decomp. 240°). The symptoms of a dermatitis caused by the leaves are described. A. E. O.

Constituents of native (Austrian) herbs. IV. J. ZELLNER (Arch. Pharm., 1934, 272, 601—607; cf. A., 1927, 598).—The rhizomes of *Petasites officinalis*, Moench, contain 2.5% of resins and small amounts of KCl, invert sugar (I), choline, terpenes, and a mixture (II), m.p. 132°, of sterols. Dry leaves of *Globularia nudicaulis*, L., contain ceryl alcohol (mainly in the fatty covering), (I), a mixture probably of stearic and palmitic acids, resin acids, lecithin, ? free choline, tannins, $BzOH$, a glucoside (? aucubin), possibly globularin, mannitol, (II), and a pectin-like carbohydrate.

R. S. C.

Chemical composition of *Daphne genkwa*. M. NAKAO and K. F. TSENG (J. Shanghai Sci. Inst., 1933, 1, 1—15).— $BzOH$, sitosterol, apigenin, m.p. 352° (Ac derivative of Me, ether, m.p. 199—200°), and a flavone, *genkwanin*, $C_{16}H_{12}O_5$ (I), m.p. 286° (Ac derivative, m.p. 196°; Bz derivative, m.p. 20°) were isolated from the flowers of *D. genkwa*, Sieb et Zucc. (I) with CH_2N_2 gives apigenin Me, ether, contains 1 OMe, and is not identical with acacetin. Fusion with KOH gives phloroglucinol $p-OH \cdot C_6H_4 \cdot CO_2H$, whilst with 50% KOH $p-C_6H_4 \cdot Ac$ (II) and phloroglucinol Me, ether are also obtained. (I) is therefore considered to be 4' : 5-dihydroxy-7-methoxyflavone.

A.

Constituents of be-still nuts, *Thevetia Neriiifolia*. K. K. CHEN and A. L. CHEN (J. Biol. Chem., 1934, 105, 231—240).— Et_2O extraction of the kernels of the nuts yields a fatty oil containing a *phytosterolin*, $C_{17}H_{35}O \cdot C_6H_{11}O_5$, m.p. 291—292.5° (corr., charring). $MeOH$ extraction of the defatted residue yields a mixture containing the following glucosides: *anona*, $C_{10}H_{18}O \cdot C_6H_{11}O_5$, softens at 94—95°, foams at m.p. 185° (decomp.); *kakilphin*, $C_{33}H_{63}O \cdot C_6H_{11}O_5$, m.p. 188.5—189° (corr.); *thevetin* (I), $C_{29}H_{46}O_{13}$, m.p. 188.5—189° (corr.).

m.p. 193° (corr.), $[\alpha]_D^{25} -62.5^\circ$ in MeOH. The digitalis-like action of (I) is $\frac{1}{8}$ that of ouabain.

A. E. O.

Soluble solids in the water-melon. L. R. TUCKER (Plant Physiol., 1934, 9, 181—182).—Refractometric observations of the distribution of sol. solids are recorded.

A. G. P.

Arsenic content of *Chondrus*. C. H. LAWALL and J. W. E. HARRISON (J. Amer. Pharm. Assoc., 1934, 23, 308—309).—Genuine unbleached or sun-bleached *Chondrus* contains As naturally, and its As content is > the tolerance for As in food products.

A. E. O.

Variation in the phosphorus content of maize meal used in rachitogenic diets. W. L. DAVIES (Analyst, 1934, 59, 340—341).—The % of H₂O, ash, and P in 9 samples of maize (I) are given, and the ratios 100P : ash and Ca : P (II) are calc. (II) varies from 2.8 to 4.8, indicating that analysis of (I) used in making up diets is necessary.

E. C. S.

Diurnal periodicity of mineral nutrition [in plants]. N. POTAPOV and N. J. STANKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 40—45).—Absorption of NO₃' and PO₄' by Indian corn (horse's tooth), kept without the sp. salt for 2 days prior to the test, in H₂O culture, increases rapidly after sunset and reaches a max. at night at a period coincident with that of greatest respiration intensity (by determination of H₂CO₃ in the medium), and decreases considerably during the day. The respiratory energy of the root cells is the main factor in the absorption of electrolytes.

J. W. B.

Influence of salts on development and sugar content of water-melons. I. D. ZNAMENSKI (Bull. Appl. Bot. Leningrad, 23, 297—319; Bied. Zentr., 1934, A, 4, 453).—Small additions of Na₂SO₄ or NaCl stimulated the growth of water-melons in pot cultures, Na₂SO₄ producing an increase in sugar content (notably fructose).

A. G. P.

Elements of mineral nutrition as factors changing the drought-resistance of plants. N. L. UDOLSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 45—48).—Addition of Na₂HPO₄ fertiliser (I) [+Ca(NO₃)₂] in dry soil (black earth) increases the H₂O-retaining capacity of the plasma, greatest receptivity to (I) being shown by *Pseudo-hostianum* 0303, of which the H₂O balance (at a subnormal level) and H₂O assimilation during drought are maintained by (I), no decrease in H₂O content during the hr. being observed. Conversely the yield of *Cœrulescens* 04972 was decreased in all experiments with fertilisers.

J. W. B.

Replacement of potassium by rubidium in *Nitzschia closterium*. F. A. STANBURY (J. Marine Biol. Assoc., 1934, 19, 931—937).—In this marine diatom Rb can partly but not entirely replace K. The ratio of P requirement to K requirement is 50 : 1.

L. D. G.

Classification of the chemical elements with respect to their functions in plant nutrition. R. THATCHER (Science, 1934, 79, 463—466; cf. A 1933, 101).—An attempt to correlate known or possible functions of the different elements in plant

nutrition with their general chemical properties. The groups proposed and discussed are : (I) H and O, energy exchange elements; (II) C, N, S, and P, energy storers; (III) Na, K, Ca, and Mg, translocation regulators; (IV) Mn, Fe (Co, Ni), Cu, and Zn, oxidation-reduction regulators; (V) B, Al, Si, As, Se; (VI) Cl, F (Br and I); (VII) Co and Ni; (VIII) Ge, Ga, and other rare elements.

L. S. T.

Factors affecting assimilation of ammonium- and nitrate-nitrogen particularly in tomato and apple. V. A. TIEDJENS (Plant Physiol., 1934, 9, 31—57; cf. B., 1933, 981).—Optimum assimilation of NO₃' by tomato and apple followed absorption from media having p_H 4.0. The corresponding optimum for NH₄' was p_H 5.0—6.5. Plants absorbed NH₄' unchanged, and protein synthesis continued immediately and more rapidly than when NO₃' was supplied. Direct relationships exist between the [NO₃'] of the medium and the growth produced, provided the reductase of the plant remains fully active. The [NH₄-N] necessary to produce a given growth was < the [NO₃-N]. Plants containing much available carbohydrate assimilated NH₄' the more readily. Feeding with NH₄-N resulted in the formation of more sol. org. N (I) in the plant than when an equal concn. of NO₃-N was used. (I) is directly correlated with [NH₄-N] in the medium. When both forms of N are present the relative rates of absorption are partly dependent on the p_H of the medium.

A. G. P.

Influence of hydrogen-ion concentration of the culture solution on absorption and assimilation of nitrate- and ammonium-nitrogen by peach trees grown in sand cultures. O. W. DAVIDSON and J. W. SHIVE (Soil Sci., 1934, 37, 357—385).—The rates of intake of N from solutions containing NH₄' or NO₃' as sole source of N are compared. Better growth occurred in NH₄' media at p_H 6 than at p_H 4 or 8, and in NO₃' media at p_H 4 than at p_H 6 or 8. NH₄' at p_H 6 and NO₃' at p_H 4 produced approx. the same effects. The rate of intake of N in each form followed the order of growth differences, but at favourable p_H NH₄'-N was absorbed more rapidly than NO₃'-N. Assimilation of NH₄' commenced in the roots (I) and reduction of NO₃' was almost completed in (I). Healthy growth and high production of plant-tissue are associated with low protein-N and high amide-, NH₂-, and humin-N in both stems (II) and (I), whereas basic N is low in (II) and high in (I).

A. G. P.

Influence of temperature on the physiological reaction of ammonium nitrate. P. STREBEYKO (Polish Agric. Forestal Ann., 1932, 28, 357—370).—The reaction (NH₄ : NO₃ taken up simultaneously by maize in H₂O cultures) is affected by p_H and temp. The higher is the temp. the greater is the amount of NO₄' absorbed, whilst the amount of NH₄' is const.

CH. ABS.

Nitrogen distribution in the leaf-proteins of Chinese cabbage during growth. H. C. KAO (Chinese J. Physiol., 1933, 7, 379—386).—The N content of the green leaves, the roots and stems, and the stalk decreases in this order, the vals. decreasing with age. Two protein fractions are prepared from the

leaves, one by coagulation of the expressed juice and the other by extraction of the pulp residue with aq. NaOH and pptn. with AcOH, and their N distribution is determined for different stages of growth.

A. L.

Isotopic fractionation of water by physiological processes. E. R. SMITH (Science, 1934, 79, 454—455; cf. this vol., 570).

L. S. T.

Isotopic carbon dioxide and oxygen in plants ? A. MOLDAVAN (Science, 1934, 79, 455).—CO₂ absorbed during photosynthesis (I) and O₂ absorbed during respiration (II) may differ isotopically from the O₂ rejected during (I) and the CO₂ rejected during (II).

L. S. T.

Hydrogen-ion concentration in relation to growth and ripening in fruits. J. S. CALDWELL (U.S. Dept. Agric. Tech. Bull., 1934, No. 403, 53 pp.).—In many fleshy fruits examined, the *p_H*, immediately after setting, remains high for a short period, corresponding with the stage of rapid cell division. Total solids are high at this stage. Subsequently there is a rapid increase in acidity and a heavy intake of H₂O, the period of max. active acidity coinciding with that of max. hydration of the fruit, and with a marked flattening in the growth (wt.) curve. Towards maturity acid production and H₂O content decline. Changes in H₂O absorption by the hydrophilic colloids of the fruit are probably controlled by the [H⁺] of the tissue fluids.

A. G. P.

Relation of "dark centre" to the composition of rutabagas. E. B. HOLLAND and C. P. JONES (J. Agric. Res., 1934, 48, 377—378).—The appearance of "dark centre" in roots is associated with a decreased % of carbohydrate which is partly replaced by pentosans and galactan.

A. G. P.

Plant injury caused by vapours of mercury and compounds of mercury. P. W. ZIMMERMANN and W. CROCKER (Contr. Boyce Thompson Inst., 1934, 6, 167—187).—Vapour containing Hg emanating from soil treated with various org. and inorg. Hg compounds injured many varieties of plants in the same greenhouse. In general the extent of the injury varied with the v.p. of Hg at any particular temp. Metallic Hg was detected in the air surrounding treated soil and also in leaves of plants enclosed in glass cases with a small amount of soil treated with HgCl₂.

A. G. P.

Effects of radiation from a quartz-mercury-vapour lamp on the mineral composition of plants. W. D. STEWART and J. M. ARTHUR (Contr. Boyce Thompson Inst., 1934, 6, 225—245).—Irradiation (I) increased the ash, Ca, and/or P content of soil-grown plants in relatively low but not in high light intensity. In 48—72 hr. after brief treatment (15—120 sec.) the above effects occurred in leaves, but stems showed a decline in ash and an increase in P. With prolonged treatment the general effect was apparent in both leaves and stems. Plants grown in sand-culture, with nutrients differing considerably from those in soil, were more sensitive to injury by (I), which caused changes in ash content even in plants grown in high light intensity. (I) had no

influence on the Mn or Mg of plants. The effective wave-lengths of ultra-violet light used were those inducing antirachitic effects and the activation of ergosterol. Cabbage, having no anti-rachitic effects even after (I), was not affected in mineral content by (I). Irradiated ergosterol in olive oil applied to the basal leaves of plants produced in them an increase in ash content.

A. G. P.

Effect of soft X-rays on germination of wheat seeds. H. M. BENEDICT and H. KERSTEN (Plant Physiol., 1934, 9, 173—178).—Brief irradiation resulted in increased diastatic activity and sugar content, both of which declined with prolonged treatment. Irradiated seeds probably cannot take in H₂O or utilise their additional sugar as readily as untreated controls.

A. G. P.

Virucidal action of high-frequency sound radiation. W. N. TAKAHASHI and R. J. CHRISTENSEN (Science, 1934, 79, 415—416).—Tobacco mosaic virus (I) is inactivated by high-frequency sound radiation. 2 hr. exposure to a frequency of 450,000 cycles per sec. inactivates (I) towards *Nicotiana glutinosa*.

L. S. T.

Plant immunity. K. T. SUCHORUKOV, E. GERBER, G. BARABANOVA, and N. BORODULINA (Sci. Mem. Univ. Saratov, 1933, 10, 106—118).—The reducing sugar and peroxidase content of cabbage leaves or juice infected with *Botrytis cinerea* (I) are <, and the catalase and NH₃ content are >, for healthy plants. (I) produces a sol. substance toxic to plant cells. No definite relationships are found between immunity to *Sclerotinia libertiana* and composition of carrot roots. *Fusarium nivium* does not possess proteolytic enzymes.

R. T.

Standardisation of biological products. P. BRUERE (Bull. Soc. Chim. biol., 1934, 16, 156—159).

A. L.

Improved gas analysis. R. MARGARIA (Biochem. Z., 1934, 270, 444—447).—A modification of the usual apparatus is described, the dead space between the CO₂- and O₂-absorption pipettes being eliminated.

C

Determination of cholesterol. II. Volumetric and gravimetric methods. A. S. RUIZ and I. TORRES (Anal. Fis. Quim., 1933, 31, 686—694; cf. A., 1933, 1063).—The gravimetric method of Szent-Gyorgyi is preferred (blood-cholesterol, average 144 mg. per 100 c.c.; recovery 100.2%). The volumetric method of Okey as modified by Turner is satisfactory, particularly for plant extracts. Bang's method gives a low recovery (66%) and is applicable only when neutral fats are simultaneously determined.

R. K. U.

Permanganate oxidation in the determination of iodine. B. GROAK (Biochem. Z., 1934, 270, 296).—A method is described whereby small amounts of I obtained by ashing org. material and extracting can be determined by Na₂S₂O₃ titration after oxidation with KMnO₄ to IO₃⁻; the excess of KMnO₄ being destroyed with NaNO₂, and of NaNO₂ with urea. The error with 1—2 × 10⁻⁶ g. of I is < ± 1%.

P. W. U.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1934.

General, Physical, and Inorganic Chemistry.

New band system in nitrogen. J. KAPLAN (Physical Rev., 1934, [ii], 45, 675—677).—Bands previously reported in the luminescence of solid N_2 and in the aurora have been photographed for the first time in the spectrum of gaseous N_2 . Measurements and data are revised and extended (cf. A., 1933, 205). The bands are attributed to vibrating N_2 mols. in the afterglow. N. M. B.

Temperatures indicated by intensity distributions in band spectra. O. S. DUFFENDACK, R. W. REVANS, and A. S. ROY (Physical Rev., 1934, [ii], 45, 807—814).—Distributions of intensity, other than those expected from the temp. of the gas, among the rotational and vibrational mol. states are reported and discussed for the negative bands of N_2^+ , alone and mixed with He, excited in low-voltage arcs. N. M. B.

Wave-lengths and term systems of the fluorine spectrum. F VII and F VI. B. EDLEN (Z. Physik, 1934, 89, 179—182). A. B. D. C.

Width of neon lines. E. LAU and J. JOHANNESSEN (Physikal. Z., 1934, 35, 457—460; cf. A., 1933, 991; this vol., 123).—Redetermination of the width of neon lines gives results 2—5 times as high as those of Schutz and Schillbach, but in agreement with those of Lau, Reichenheim, and Johannesson. A. J. M.

Measurement of intensity distribution and width of predissociation lines of the AlH molecule. L. FARKAS and S. LEVY (Z. Physik, 1934, 89, 256—258).—A reply to Burger and van Cittert (this vol., 344). A. B. D. C.

Infra-red spectrum of argon. R. M. WOODS and B. J. SPENCE (Physical Rev., 1934, [ii], 45, 669—670).—A special hot-cathode discharge tube for use up to 10 amp. is described. Data for 46 lines in the range 0.69—1.80 μ are tabulated. N. M. B.

Hyperfine structure of the resonance lines of potassium. D. A. JACKSON and H. KUHN (Nature, 1934, 134, 25—26). L. S. T.

Intensities of some multiplets of Fe II and Ti II in stellar spectra. C. T. ELVEY (Astrophys. J., 1934, 79, 263—270). L. S. T.

Absorption spectrum of diatomic arsenic. G. E. GIBSON and A. MACFARLANE (Nature, 1934, 133, 951).—Eighty absorption bands between 2200 and 2750 \AA . have been discovered in the spectrum of As, and can be assigned to the diat. mol. L. S. T.

Structure of singly-ionised selenium. S. G. MURTY and K. R. RAO (Current Sci., 1934, 2, 384).—Some of the abs. vals. of the energy states characteristic of Se II are recorded. L. S. T.

Isotope effect and quenching in the fluorescence of bromine. H. J. PLUMLEY (Physical Rev., 1934, [ii], 45, 678—684).—The fine structure of the resonance spectrum of Br_2 excited by the Hg green arc line has been photographed and interpreted. The fluorescence intensities were studied at $\lambda\lambda$ 6450, 6100, and 5660 as a function of the pressure, and are approx. 300 times weaker than for I_2 ; this is accounted for on the basis of less initial absorption and greater quenching, due to longer mean life of the mol. in the upper state. N. M. B.

Influence of electric field on the absorption spectrum of rubidium. N. T. ZE (Compt. rend., 1934, 198, 2156—2159).—The absorption of Rb vapour in parallel and perpendicular fields of 303 volts per cm. was measured. The intensities of the principal series lines diminished more rapidly than without a field, and the forbidden S - D and S - S lines were strongly enhanced. B. W. B.

Strontium II and barium II spectra. F. A. SAUNDERS, E. G. SCHNEIDER, and (MISS) E. BUCKINGHAM (Proc. Nat. Acad. Sci., 1934, 20, 291—296).—Full data for Sr II and Ba II, and new lines and terms for Ba II in the Lyman and Schumann region, are tabulated. Ba II shows anomalous reversal of relative intensity in the principal series pairs $6S$ - $7P$ and $6S$ - $8P$, as compared with $6S$ - $6P$, and also faintness and odd separation in the $5D$ - $5F$ group. N. M. B.

Nuclear spin of tin. S. TOLANSKY (Proc. Roy. Soc., 1934, A, 144, 574—587).—The fine structures of the visible lines of the Sn II spectrum have been analysed. The nuclear spin of the two main odd isotopes is $-1/2$, and $g(I)$ for these isotopes is -1.78 . L. L. B.

Absorption spectrum of the iodine atom. J. H. McLEOD (Physical Rev., 1934, [ii], 45, 802—804; cf. Turner, A., 1932, 1183).—Using a H or I discharge tube, the absorption of I dissociated by heating to 1000° was investigated in the range 2100—1400 \AA . The first source showed $\lambda\lambda$ 1830 and 1783 as absorption lines; the second source showed weakening by absorption in the heated I of $\lambda\lambda$ 1830, 1783, 1642, 1618, 1583, 1515, 1507, and 1422. N. M. B.

Hyperfine structure in the arc spectrum of xenon. E. G. JONES (Proc. Roy. Soc., 1934,

A, 144, 587—595).—16 lines in the region 4200—8800 Å. of the Xe I spectrum are complex, so that the lines of Xe I are not suitable as wave-length standards. The observed line structures are analysed, and the nuclear moments $I=0$ assigned to the even isotopes, $I=1/2$ to Xe¹²⁹, and $I=3/2$ to Xe¹³¹.

L. L. B.

Nuclear mechanical moment of lanthanum from hyperfine structure. O. E. ANDERSON (Physical Rev., 1934, [ii], 45, 685—688).—The hyperfine structure of the lines $\lambda\lambda$ 5212, 5234, and 6250 of La I has been photographed. The no. of components, intensity ratios, and interval spacing are in good agreement with the val. (7/2) for the nuclear mechanical moment.

N. M. B.

Spectrum of Ce III. P. N. KALIA (Current Sci., 1934, 2, 384).—A reply to criticism (this vol., 467).

L. S. T.

First spectrum of tantalum. C. C. KIESS and E. Z. STOWELL (Bur. Stand. J. Res., 1934, 12, 459—469).—Wave-length and intensity data are tabulated for > 2100 lines emitted by the arc in air between Ta electrodes in the range 10,300—2300 Å. Heads of an accompanying band spectrum, shaded towards the red and due to TaO₂, were measured. Ta is now identified in the sun by the 5997, 5944, and 5939 Å. lines.

N. M. B.

Spectral distribution of radiation from high- and low-pressure Hg arcs. B. T. BARNES (J. Opt. Soc. Amer., 1934, 24, 147—148).—Intensities of all the ultra-violet, visible, and infra-red lines easily measurable with a single spectro-radiometric apparatus are tabulated.

N. M. B.

Experimental demonstration of the existence of dipolar magnetic radiation. H. NIEWODNICZANSKI (Compt. rend., 1934, 198, 2159—2161).—Triplet Zeeman separation of the forbidden Pb I line, 4618 Å., confirms the view (cf. Physical Rev., 1934, 45, 64) that it consists of pure dipolar magnetic radiation.

B. W. B.

Comparison of continuous spectra of some stars of types A and B. Nocturnal proportions of O₃. D. BARBIER, D. CHALONGE, and É. VASSY (Compt. rend., 1934, 198, 2139—2142).—A spectrograph for study of atm. ultra-violet absorption is described. Comparison of stellar spectra with a distant continuous source enabled intensity- λ curves and also terrestrial [O₃] to be determined.

B. W. B.

Ionised argon in the spectrum of Upsilon Sagittarii. W. W. MORGAN (Science, 1934, 79, 454).

L. S. T.

B band of oxygen in the spectrum of Mars. W. S. ADAMS and T. DUNHAM, jun. (Astrophys. J., 1934, 79, 308—316).—The amount of O₂ in the atm. of Mars is probably < 0.1% of that in the earth's atm.

L. S. T.

Radiation of the night sky between 5000 and 8000 Å. J. CABANNES (Compt. rend., 1934, 198, 2132—2135; cf. this vol., 232; Sommer, A., 1933, 332).—H₂O and O₂ ($^1\Sigma \rightarrow ^3\Sigma$) bands are prominent.

B. W. B.

Intensities of magnetic dipole lines. J. BLATON (Z. Physik, 1934, 89, 155—165).—Selection rules and

intensity formulæ are derived for $^1S - ^3P$ and $^1D - ^3P$ transitions.

A. B. D. C.

Scattering of X-rays by cold-worked and by annealed beryllium. J. E. BOYD (Physical Rev., 1934, [ii], 45, 832—834).—Intensities of reflexion of Mo $K\alpha$ radiation by crystallographic planes in powdered Be were measured under various conditions of cold-working and annealing. At. structure factors showed no appreciable change. The mass absorption coeff. was 0.26.

N. M. B.

X-Ray emission spectra and chemical binding. III. $K_{\alpha_1\alpha_2}$ doublet of sulphur in various sulphides. O. LUNDQUIST (Z. Physik, 1934, 89, 273—276; cf. A., 1932, 1072).—Other sulphides investigated are MgS, Al₂S₃, CaS, FeS, NiS, Cu₂S, CdS, SnS₂, Sb₂S₃, and BaS. The doublet width is unchanged, but appreciable displacements are recorded.

A. B. D. C.

True absorption coefficients for the elements Au to Bi in the neighbourhood of the L-absorption edges. C. G. PATTEN (Physical Rev., 1934, [ii], 45, 662—666).—Using thin films of Tl, Pb, and Bi evaporated on very thin mica the L X-ray absorption spectra gave vals. $\propto \lambda^{2.56}$ for the true absorption coeffs. corresponding with the photo-electric absorption by the three types of L electrons.

N. M. B.

Mass-absorption coefficients for 16 elements and paraffin with monochromatic X-rays between 0.128 and 2.5 Å. K. GROSSKURTH (Ann. Physik, 1934, [v], 20, 197—232).—The mass-absorption coeffs. (μ/ρ) of paraffin and 16 elements were found with monochromatic X-rays (cf. A., 1931, 993). The coeff. follows the law $\tau = C\lambda^n$, C and n varying with the element. The classical mass-scattering coeffs. (σ_0/ρ) are for paraffin 0.18, C 0.16, Al and S 0.14. The val. is greater for the heavier elements.

A. J. M.

Fock-Dirac atom model and the existence of ionisation potentials. L. BRILLOUIN (J. Phys. Radium, 1934, [vii], 5, 185—192).—Mathematical. The Fock-Dirac atom is discussed in analogy with the Fermi-Thomas atom relative to the exchange term and its bearing on the evaluation of ionisation potentials.

N. M. B.

Thermionic work function and the slope and intercept of Richardson plots. J. A. BECKER and W. H. BRATTAIN (Physical Rev., 1934, [ii], 45, 694—705).—A crit. theoretical survey.

N. M. B.

Supposed relation between the work function and the electron potential in a metal. K. F. NIESSEN (Physica, 1934, 1, 623—626).—Frenkel's relation (A., 1928, 823) is criticised.

H. J. E.

Atomic work function of tungsten for potassium. R. C. EVANS (Proc. Roy. Soc., 1934, A, 145, 135—144).—The method developed for the measurement of the rate of evaporation of ions of the alkali metals from a hot W surface (A., 1933, 442) has been extended to investigate the rate of evaporation of atoms under the same conditions of very small surface concn. The val. 2.80 e.v. is derived for the at. work function, which in conjunction with the val. 2.43 e.v. for the positive-ion work function is in good agreement.

ment with the val. 2.73 volts required to close the Born cycle. L. L. B.

Scattering of a beam of potassium atoms in various gases. W. H. MAIS (Physical Rev., 1934, [ii], 45, 773—780).—The distribution of a narrow beam of neutral K atoms scattered by H_2 , He, Ne, N_2 , A, and CO_2 at low pressures was measured. The calc. effective collision radii were in good agreement with vals. based on the quantum theory of elastic sphere collisions in the case of H_2 and He, but for the other gases the experimental vals. were much larger, indicating the existence of considerable interat. forces. N. M. B.

Recording of electrons. O. GOCHE, P. MOLLET, and (Mlle.) J. CUDELL (Bull. Acad. roy. Belg., 1934, [v], 20, 447—456).—A survey of methods previously described (cf. A., 1932, 799; Henriot, A., 1932, 211) and their extension with improved apparatus to slow electrons. Carr's observations (cf. A., 1931, 278) are interpreted as due, not to a gaseous surface film, but to the deposition of atoms formed by ionisation due to the electron beam. N. M. B.

Behaviour of electrons in nitric oxide. V. A. BAILEY and J. M. SOMERVILLE (Phil. Mag., 1934, [vii], 17, 1169—1176; cf. A., 1930, 1081; 1932, 559; 1933, 109).—The relationships between the mean free path, probability of attachment, and the fractional energy loss of an electron on collision with NO (λ) indicate that an electron is more likely to remain attached the further it penetrates into the mol. The attachment of electrons is also influenced by the magnetic properties of the mol. The peak of the λ - u (electron velocity) curve corresponds with the first harmonic vibration absorption band, not, as with other gases, with the fundamental band. J. W. S.

Excitation of neon by electron impact. J. E. TAYLOR, R. WHIDDINGTON, and E. G. WOODROOFE (Proc. Leeds Phil. Soc., 1934, 2, 534—535).—Electrons of 120 e.v. are passed through Ne at a pressure of 0.01 mm. and the resulting beam is analysed with a magnetic field and spectroscopically. Three energy losses correspond with 16.76 ± 0.02 , 19.98 ± 0.04 , and 18.63 ± 0.04 volts with relative probabilities 16, 5, and 4, respectively, as indicated by the intensity of the spectrum. The normal state is $1s^2 2s^2 2p^6$, and the various excited states are shown. W. R. A.

Excitation of the nitrogen molecule by electron impact. J. E. ROBERTS (Proc. Leeds Phil. Soc., 1934, 2, 536—543).—Consideration of the excitation of diat. mols. by electrons from normal to higher electronic states raises two questions: (a) the most probable energy loss of the exciting electron and (b) the probability of excitation of vibrational levels near the most probable level. The $X \rightarrow a$ transition in N_2 is fully discussed. Potential energy curves are obtained from spectroscopic data and the Morse formula. W. R. A.

Least excitation potential of the nitrogen molecule. H. MAIER-LEIBNITZ and H. SPONER (Z. Physik, 1934, 89, 431—436).—Electron collision measurements give crit. potentials at 6.7, 7.2, and 8.0 volts. A. B. D. C.

Positive electrons: focussing of beams, measurement of charge-mass ratio, absorption, and conversion into light. J. THIBAUD (Physical Rev., 1934, [ii], 45, 781—787).—The "trochoid" method of concentrating and focussing weak electron beams to form sharp lines on a photographic plate, and the determination of e/m from the displacement of the beam by an imposed field, are described. The method is applied to the absorption of positive and negative electrons produced by γ -rays incident on Pb. Above a crit. thickness of absorber an imprint attributed to secondary X-rays or to the merging of positive and negative electrons and their conversion into photons is observed. Evidence of positive electrons proceeding directly from radioactive substances was found. N. M. B.

Photo-electric creation of positive and negative electrons. Y. NISHINA, S. TOMONAGA, and S. SAKATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 1—5, and Japan. J. Physics, 1934, 9, 21).—Mathematical. Calc. probability of the photo-electric creation of pair electrons agrees with that of Heitler (cf. this vol., 1927), but differs from the result of Oppenheimer (cf. Physical Rev., 1933, [ii], 44, 53). N. M. B.

Scattering of electrons in ionising collisions with gas atoms. C. B. O. MOHR and F. H. NICOLL (Proc. Roy. Soc., 1934, A, 144, 596—608).—Measurements have been made of the angular distribution of electrons which have lost different amounts of energy over and above that required for ionisation, in H_2 , He, N_2 , CH_4 , Ne, A, and Hg vapour. Curves are given for several incident energies < 300 volts. L. L. B.

Zero-angle energy losses in helium. R. L. WOMER (Physical Rev., 1934, [ii], 45, 689—693).—Using an electrostatic analyser for inelastic electron scattering at angle 0° and below 100 volts, four energy losses corresponding with transitions 1^1S-2^1P , 1^1S-3^1P , 1^1S-2^1S , and 1^1S-2^3S have been identified and investigated. N. M. B.

Energy spectrum of positive electrons from aluminium. L. MEITNER (Naturwiss., 1934, 22, 388—390).—The energy distribution of positive electrons emitted in the transmutation $_{13}Al^{27} + \alpha^4 \rightarrow _{15}P^{30} + n$, $_{15}P \rightarrow _{14}Si^{30} + e^+$, has been investigated. There is a continuous spectrum with max. frequency of occurrence at 800—1000 kv. and 1400—1500 kv. A. J. M.

Calcium isotopes and the problem of potassium. F. W. ASTON (Nature, 1934, 133, 869).—Using the purest materials the effect of K in the mass spectrum of Ca has been reduced to a negligible quantity; the line 41 disappears, and it is concluded that Ca^{41} does not exist, at least to 1 in 1000, in Ca. Mass nos. and abundances for Ca are 40, 42, 43, and 44, and 97, 0.8, 0.2, and 2.3, respectively. The mass spectra of Ca compounds from biotite used by Hevesy and from pegmatites used by Kendall are the same as that of ordinary Ca, hence the abnormal at. wts. reported (A., 1933, 658) are not due to Ca^{41} . The failure to detect Ca^{41} favours a more complex theory of the radioactive disintegration of K. L. S. T.

The new hydrogen. (LORD) RUTHERFORD (Proc. Roy. Inst., 1934, 28, 277—289).—A lecture.

Determination of isotopic masses from band spectra. R. DE L. KRONIG (*Physica*, 1934, **1**, 617—622).—The discrepancy between Bainbridge's and Holst and Hulthén's vals. for the mass of H^- (cf. *A.*, 1932, 1185; this vol., 472) is due to the assumed identity of the potential energy curves of the two isotopes of H. H. J. E.

Radioactive recoils by the Wilson apparatus. F. JOLIOT (*J. Phys. Radium*, 1934, [vii], 5, 219—224).—Using a new variable-pressure expansion apparatus the individual disintegration of radioactive atoms was observed and trajectories of recoils were measured. Anomalous collisions of recoil particles undergoing deviation exceeding that due to an elastic collision were found; the recoil particle appears to be activated at the moment of disintegration and gives up its activation energy as kinetic energy following an at. collision. N. M. B.

Distribution of Th-C'' in thallium salt solutions. I. J. ZIRKLER (*Z. Physik*, 1934, **89**, 439—442).—The distribution coeff. is given for active $TlNO_3$ and the non-active sulphate, and for active Tl_2SO_4 and the non-active perchlorate. The free interchange of the metal atom and the corresponding acid radicals was determined for Tl^+ compounds in aq. solutions. A. B. D. C.

Transmutation of hydrogen into neutron. D. D. IVANENKO (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **2**, 155—157).—Theoretical. W. R. A.

Ionisation by α -particles in gaseous mixtures. G. GLOCKLER and R. LIVINGSTON (*J. Physical Chem.*, 1934, **38**, 655—661; cf. *A.*, 1932, 671).—Range, stopping power, total ionisation relative to air, and the mol. ionisation are calc. for α -particles from Rn in spherical vessels. F. L. U.

Theory of β -radiation. G. BECK and K. SITTE (*Z. Physik*, 1934, **89**, 259—260).—Polemical, against Fermi (this vol., 579). A. B. D. C.

Transmutation effects observed with heavy hydrogen. M. L. E. OLIPHANT, P. HARTECK, and (LORD) RUTHERFORD (*Proc. Roy. Soc.*, 1934, **A**, 134, 692—703).—Compounds containing H^2 when bombarded by diplons yield two groups of particles in large nos., one of protons of 1.4–3 cm. range and one of singly-charged particles of 1–6 cm. range. The two groups contain an equal no. of particles. Reasons are given for supposing that the short-range group consists of nuclei of an isotope of H of mass 3.0151, the reaction being $H^2-H^2 \rightarrow He \rightarrow H^1-H^3$. The no. of particles emitted has been investigated as a function of the energy of the bombarding diplon, and the abs. yield for a pure diplon beam hitting a pure H^2 target is calc. to be about 1 in 10^6 at 10^5 volts. In the same bombardment neutrons are observed in large nos. Their energy is about 2×10^6 e.v., and they may arise from another method of disintegration of the unstable form of the He nucleus formed initially by the union of two diplons. This consists in the expulsion of a neutron and a He isotope of mass 3 in opposite directions ($H^2-H^2 \rightarrow He \rightarrow He^3-n^1$). L. L. B.

Experiments with high-velocity positive ions. III. Disintegration of lithium, boron, and carbon by heavy hydrogen ions. J. D. COCKCROFT

and E. T. S. WALTON (*Proc. Roy. Soc.*, 1934, **A**, 144, 704—720).—The disintegration of Li, B, and C, when bombarded by fast ions of H^2 , has been examined. Li gives a group of protons of 30.5 cm. range, interpreted as due to the transmutation of Li^6 to Li^7 . B gives proton groups of ranges 92, 58, and 31 cm., together with a continuous distribution of α -particles with ranges up to 15 cm. C gives a proton group of range 14 cm., probably due to the transformation of C^{12} into C^{13} . The emission of long-range protons always appears to be connected with the change of one isotope of an element into its next heavier isotope, the neutron being captured and the proton ejected. The emission of a 14-cm. group of protons from the heavier elements studied (Cu, Fe, Ag, W) is probably due to C atoms present on the surface as a thin film of grease. A smaller no. of 15-cm. protons are emitted from the heavy elements due to the disintegration of H^2 adsorbed on the surface. L. L. B.

New type of artificial β -radioactivity. A. J. ALICHANOW, A. J. ALICHANIAN, and B. S. DZELEPOW (*Nature*, 1934, **133**, 871—872).—The bombardment of Mg by α -rays of 6.3 cm. range from Ra-C' produces about four times as many negative (I) as positive electrons. The half-period of (I) is approx. 3 min. and the limit of their continuous spectrum is $> 2 \times 10^6$ e.v. The probable reactions for (I) are (i) ${}^{25}_{12}Mg - {}^4_2He^1 \rightarrow {}^{21}_{10}Al^{23} - {}^1_1H^1$; ${}^{23}_{13}Al^{25} \rightarrow {}^{22}_{14}Si^{23} + e^-$ or (ii) ${}^{26}_{12}Mg - {}^4_2He^1 \rightarrow {}^{22}_{13}Al^{25} - {}^1_1H^1$; ${}^{23}_{13}Al^{25} \rightarrow {}^{22}_{14}Si^{23} + e^-$. L. S. T.

Radioelements created by bombardment by neutrons. New types of radioactivity. (MME.) I. CURIE, F. JOLIOT, and P. PREISWERK (*Compt. rend.*, 1934, **198**, 2089—2091; cf. this vol., 234, 470).—Radioelements were obtained by irradiation of Ag, Si, Zn, I, and Fe with neutrons (n) of high energy, the results confirming Fermi's observations (this vol., 714). The approx. identical decay periods (2–3 min.) and identical max. β -ray energies (2.3×10^6 e.v.) given by the products of Mg- α -rays, Si- n , and P- n suggest that ${}^{23}_{13}Al^{25}$ is formed in all three cases. Secondary electrons with energies $> 5 \times 10^6$ e.v. were produced, probably from γ -rays, during decay of irradiated Si and P, indicating the transmutations: ${}^{23}_{13}Al^{25} = \beta - h\nu$ and ${}^{31}_{14}Si^{31} = {}^{31}_{15}P^{31} - \beta + h\nu$. Hence ${}^{27}_{13}Al^{27} - {}^0_1n^1$ and ${}^{31}_{14}Si^{31} = {}^{30}_{14}Si^{30} + {}^0_1n^1$ should be possible; the emission of n from irradiated P was confirmed. S and P also produced positrons possibly by materialisation of photons. The transition ${}^{31}_{15}P^{31} \rightarrow {}^0_1n^1 = {}^{31}_{16}S^{31} + {}^0_1n^1$ is also suggested, ${}^{31}_{16}S^{31}$ then emitting positrons. The production of negative protons may explain Fermi's reported element of at. no. 93. B. W. B.

Artificial disintegration. D. VAN DER VEEN (*Chem. Weekblad*, 1934, **31**, 383—388).—A review, with a full bibliography. H. F. G.

Spontaneous emission of neutrons by artificially-produced radioactive bodies. M. GOLDBABER (*Nature*, 1934, **134**, 25).—Theoretical. L. S. T.

Possible production of elements of atomic number higher than 92. E. FERMI (*Nature*, 1934, **133**, 898—899).—Th and U are strongly activated by neutron bombardment. Th activity shows at least

two periods, whilst for U the periods are approx. 10 sec., 40 sec., 13 min., and at least two more periods from 40 min. to 1 day. It is difficult to establish whether the periods represent successive or alternative processes of disintegration. The 13-min. activity is copptd. with MnO_2 after addition of a Mn salt to the irradiated U solution. It is apparently not due to isotopes of U, Pd, Th, Ac, Ra, Bi, or Pb; it may be an element of at. no. > 92 . L. S. T.

Relations involved in the disintegration of atoms by "non-capture" collisions. W. D. HARKINS and D. M. GANS (J. Amer. Chem. Soc., 1934, 56, 1420—1421).—The equations developed show that the disintegration of N nuclei by neutrons (I) involves the capture of (I). It appears that up to the present there is no authentic case of disintegration by collision without capture of the projectile. J. G. A. G.

Disintegration of α -particle. K. C. KAR and A. GANGULI (Current Sci., 1934, 2, 387; cf. this vol., 5).—A note. L. S. T.

Theory of β -disintegration. G. GAMOW (Physikal. Z., 1934, 35, 533—542).—A review of work up to May 20, 1934.

Nuclear changes in the atoms of radioactive substances. H. J. WATKINS (Phil. Mag., 1934, [vii], 17, 1176—1189; cf. A., 1933, 550).—The theory of Lande is extended to radioactive nuclei, which according to this view may contain neutrons, a proton, and α -particles, but no free electrons. Instability in the nucleus appears to be favoured by the presence of a proton, or of an odd no. of neutrons. J. W. S.

Production of showers by cosmic radiation. C. W. GILBERT (Proc. Roy. Soc., 1934, A, 144, 559—573).—The frequency of showers produced in Pb by the passage of cosmic radiation is proportional to the general cosmic radiation. Three types of radiation are needed to explain the experimental results: a primary radiation, a shower-producing radiation, and the shower particles. L. L. B.

Active nitrogen and the auroral spectrum. J. KAPLAN (Physical Rev., 1934, [ii], 46, 671—674).—A detailed account of work already noted (cf. this vol., 339, 823). N. M. B.

Excitation energy of metastable nitrogen. W. WEIZEL and H. FISCHER (Z. Physik, 1934, 89, 283—285).—Dispersion measurements give this energy for the $^3\Sigma$ term as 6.1 ± 0.5 volts. A. B. D. C.

Negative nuclear spins and a proposed negative proton. S. TOLANSKY (Nature, 1934, 134, 26).—The negative and positive nuclear spins of odd at. wt. atoms with even at. charges can be accounted for by postulating the existence of two types of nuclear neutrons: (i) proton+electron and (ii) negative proton+positron (cf. this vol., 826). L. S. T.

Exchange forces between neutrons and protons
Fermi's theory. I. TAMM (Nature, 1934, 133, 981).—Theoretical. Either Fermi's theory requires modification, or the origin of the forces between neutrons and protons does not lie in their transmutation considered in detail by Fermi. L. S. T.

Interaction of neutrons and protons. D. IWANENKO (Nature, 1934, 133, 981—982).—A discussion (cf. preceding abstract). L. S. T.

Neutrino hypothesis. E. FERMI (Z. Physik, 1934, 89, 522).—Polemical, against Beck and Sitte (this vol., 826). A. B. D. C.

Asymmetry of positive and negative β -spectra and the intrinsic mass of the neutrino or ergon. F. PERRIN (Compt. rend., 1934, 198, 2086—2088; cf. this vol., 127).—The ascription of zero mass to the neutrino is not invalidated by a consideration of nuclear field action during electron expulsion. B. W. B.

Quantum theory of the neutron. G. TEMPLE (Proc. Roy. Soc., 1934, A, 145, 344—358).—A theory of the neutron is developed from Dirac's wave equation without the use of any special assumptions. The second-order wave equation for the H atom is shown to possess two sets of solutions H and N, distinguished by their behaviour as $r \rightarrow 0$ (r being the distance of the electron from the proton). The H-solutions are the accepted wave functions of the H atom, the N-solutions those of the neutron. L. L. B.

Electron theory of metals. S. SCHUBIN and S. WONSOWSKY (Proc. Roy. Soc., 1934, A, 145, 159—180).—A modification of the Heisenberg scheme is worked out, which allows the electric and magnetic properties of metals to be treated simultaneously. L. L. B.

Numerical solution of Schrodinger's equation. G. E. KIMBALL and G. H. SHORTLEY (Physical Rev., 1934, [ii], 45, 815—820).—Mathematical. Solutions may be approximated to any desired accuracy by a difference equation over a lattice covering the region of integration. N. M. B.

Nuclear structure, γ -ray fission, and the expanding universe. A. C. BANERJI (Nature, 1934, 133, 984).—A discussion. L. S. T.

Atomic theory. J. TUTIN (Nature, 1934, 134, 23—24).—A reply to criticism. L. S. T.

Atomic theory. R. H. FOWLER (Nature, 1934, 134, 24—25).—Further criticism (cf. preceding abstract). L. S. T.

Equation of the photon. K. NIKOLSKY (Compt. rend., 1934, 198, 1901—1902). B. W. B.

Molecules in the sun and stars. H. N. RUSSELL (Astrophys. J., 1934, 79, 317—342).—Mol. const. derived mainly from band spectra have been collected for about thirty diat. mols. likely to occur in the sun and stars, and the dissociation const. calc. L. S. T.

Addition theorem for spherical harmonics and its application to space quantisation of atoms. H. HONL (Z. Physik, 1934, 89, 244—253). A. B. D. C.

Grating images. K. STREHL (Z. Physik, 1934, 89, 254—255).—Theoretical. A. B. D. C.

Factor 137 136 in quantum theory. (SIR) A. S. EDDINGTON (Nature, 1934, 133, 907). L. S. T.

Theory of the elementary particle. I. TAMM (Compt. rend. Acad. Sci., U.R.S.S., 1934, 2, 151—

155).—The val. of the magnetic spin moment of a proton in nuclear magnetons is discussed.

W. R. A.

Magnetic moment of the deuteron. I. ESTER-MANN and O. STERN (Nature, 1934, **133**, 911).—The val. obtained is 0.7 nuclear magneton (cf. A., 1933, 1226).

L. S. T.

Electronic energy bands in metals. J. C. SLATER (Physical Rev., 1934, [ii], **45**, 794—801).—Mathematical. The method of Wigner and Seitz (cf. A., 1933, 660) is extended to the computation of the excited bands of electrons in a metal.

N. M. B.

General and simple relation of molecular spectra to the electrons and electronic shells of the constituent atoms. H. DESLANDRES (Compt. rend., 1934, **198**, 2037—2041; cf. A., 1932, 791).—Conditions of electronic excitation of NaCl, NO, and CH₄ are deduced from their spectra (I). A general relationship exists between frequencies (II) of band heads of visible and ultra-violet electronic (I) and (II) of infra-red bands.

B. W. B.

Absorption of oxygen between 7000 and 3000 Å. L. HERMAN (Compt. rend., 1934, **198**, 2154—2156).—Absorption spectra of O₂ in a tube 100 m. long, at pressures up to 13 kg. per sq. cm., and of the setting sun, confirmed Janssen's observations (A., 1886, 749) and revealed new bands.

B. W. B.

Atmospheric ozone absorption in the visible spectrum. O. R. WULF, A. F. MOORE, and E. H. MELVIN (Astrophys. J., 1934, **79**, 270—272).

L. S. T.

Angstrom bands of CO. D. COSTER and F. BRONS (Physica, 1934, **1**, 634—648; cf. this vol., 237).—Perturbations in the vibrational levels $v=0, 1, 2, 3$, and 4 of the final $A^1\Pi$ state have been classified. The most probable dissociation energy of CO is 8.41 e.v.

H. J. E.

Afterglow of carbon dioxide. A. G. GAYDON (Nature, 1934, **133**, 984—985; cf. this vol., 8).—Further details of the spectrum of the afterglow produced by a modified method at higher pressures are given.

L. S. T.

Band spectrum of aluminium chloride. B. N. BHADURI and A. FOWLER (Proc. Roy. Soc., 1934, **A**, **145**, 321—336).—A band system extending from 2555 to 2810 Å., with its greatest intensity at 2610 Å., has been observed with high dispersion in vac. tubes containing AlCl vapour. Most of the bands are degraded towards the red, but there are two strong short sequences of bands of the same system which are shaded in the opposite direction. The main bands due to the mols. AlCl₃⁵⁵ are associated with bands due to AlCl₃⁵⁷.

L. L. B.

Absorption spectrum of SCl₂. R. K. ASUNDI and R. SAMUEL (Current Sci., 1934, **2**, 433—434).—The spectrum of SCl₂ vapour shows continuous absorption at approx. 4100 Å., a band system between 3400 and 2750 Å., and continuous absorption again between 2600 and 2400 Å., and from 2280 Å. onwards.

L. S. T.

Band systems of CdF. R. K. ASUNDI, R. SAMUEL, and M. Z. UDDIN (Current Sci., 1934, **2**, 429—430).—The arc spectrum of CdF shows a yellowish-green

band system between 5300 and 5550 Å. and an orange system between 6025 and 6300 Å.

L. S. T.

New band system of tin oxide. F. W. LOOMIS and T. F. WATSON (Physical Rev., 1934, [ii], **45**, 805—806).—Frequency and intensity data for a new band system of SnO in the region 2400—3100 Å. are tabulated.

N. M. B.

Absorption spectrum of mercuric sulphide. T. IREDALE and K. E. GIBSON (Nature, 1934, **133**, 985).—Evidence only of Hg vapour and of S₂ and, at higher pressures, S₈ has been obtained (cf. this vol., 237).

L. S. T.

Ultra-violet absorption of heavy water vapour. J. FRANCK and R. W. WOOD (Physical Rev., 1934, [ii], **45**, 667—668).—A comparison of the absorption spectrum of normal and heavy H₂O down to 1450 Å. shows that the long wave-length limit of the continuous absorption band is shifted towards shorter wave-lengths in the case of H₂O.

N. M. B.

Absorption spectra of some polyatomic molecules containing methyl and ethyl radicals. H. W. THOMPSON (J.C.S., 1934, 790—797).—The absorption spectrum of ZnMe₂ is continuous (threshold at about 2600 Å.). That of ZnEt₂ is continuous below about 2300 Å. with four pairs of superposed diffuse bands between 2396.5 and 2216 Å. PbEt₄ gave a system of seven groups of sharp bands, degraded to the red, between 2700 and 2200 Å. without an overlapping continuum.

H. J. E.

Auxochrome action. V. Action of the NH₂ group. VI. Of the OH and OMe groups. VII. Di-derivatives. M. HORIO (J. Soc. Chem. Ind. Japan, 1934, **37**, 284—285B, 285B, 285—288B).—V. 313 bands and lines have been observed in the ultra-violet vapour spectrum of NH₂Ph. The NH₂ group has a powerful effect, vals. for the electron displacement and energy of activation being much < for C₆H₅.

VI. The spectra of PhOH and PhOMe are similar to the above; the OH and OMe groups exert practically the same effect as NH₂ on the nuclear electrons.

VII. In the series for *o*-, *m*-, and *p*-C₆H₄Me·NH₂, the *o*- and *m*- are similar to NH₂Ph, but marked differences occur with *p*-C₆H₄Me·NH₂. Analogous results are obtained with the anisidines.

S. C.

Absorption spectra of aldehydes. C. P. SNOW and E. EASTWOOD (Nature, 1934, **133**, 908—909).—The ultra-violet absorption bands of a homologous series of aldehydes show vibrational structure probably due to a nuclear vibration $\begin{matrix} R \\ \diagup \\ H \end{matrix} C \rightarrow \leftarrow O$. Max. absorption is approx. const. at about 2900 Å. or 34,500 cm.⁻¹ The absorption spectrum of acetaldehyde shows several bands having a fine structure equal to those of the diat. gases in simplicity and sharpness.

L. S. T.

Optical absorption and fluorescence of benzene vapour in the ultra-violet. F. ALMASY and C. V. SHAPIRO (Z. physikal. Chem., 1934, **B**, **25**, 391—398).—The fluorescence spectrum and the long-wave part of the absorption spectrum coincide almost completely over the range 37,486—35,349 cm.⁻¹

R. C.

Spectrographic study of phloridzin and its derivatives. Ultra-violet spectra of phloretin, phlorin, and phloroglucinol. A. LAMBRECHTS (Compt. rend., 1934, 198, 1852—1854; cf. A., 1933, 336).—Absorption band max. were determined in EtOH (I) and in aq. solutions (II) of varied All the above compounds assumed keto-structures in (I) and showed reversible keto-enol tautomerism in (II). Tautomerism was most marked in phloroglucinol.

B. W. B.

Infra-red absorption of water from 2.5 μ to 6.5 μ E. K. PLYLER and C. J. CRAVEN (J. Chem. Physics, 1934, 2, 303—305).—New bands for liquid H₂O were observed at 3.30, 5.56, and 5.83 μ . The band at 4.7 μ contains several components. The position of max. absorption at about 3 μ changes with the cell thickness, due to differences in sharpness of the band components. The 6.15 μ band shows no such shift.

H. J. E.

Infra-red absorption of acid solutions. E. K. PLYLER and E. S. BARR (J. Chem. Physics, 1934, 2, 306—310).—Measurements were made on aq. HCl, HF, HBr, H₂SO₄, HNO₃, NaCl, and NaBr between 1.7 and 6.5 μ , and for aq. HCO₂H and BzOH between 5 and 6.5 μ . No bands were found for HCl and HBr at 3.5 μ and 3.8 μ , respectively, where there is strong absorption by gaseous HCl and HBr. For all the acid solutions a band was observed at about 5.5 μ , attributed to vibration of the acid mol. as a whole against the H₂O mol. through the acid H. A new band observed at 2.40 μ may be due to the same cause, or to H⁺ attached to H₂O.

H. J. E.

Photography of the second overtone of HCl at 1.19 μ under high dispersion. G. HERZBERG and J. W. T. SPINKS (Z. Physik, 1934, 89, 474—479).—Mol. consts. are deduced, and the isotope displacement agrees very well with the mass defect val.

A. B. D. C.

Nuclear vibrations of solid and liquid hydrogen chloride between 20° and 160° abs. G. HETNER (Z. Physik, 1934, 89, 234—243).—The 3.7 μ band is single in the liquid and β -solid form, but shows two max. 50 cm.⁻¹ apart in the α -form; the transition occurs near 38° abs. The α -form has a dielectric const. of 4.7, the β -form one of 14.6. At lower temp. the double band becomes very unsymmetrical.

A. B. D. C.

Broadening by collision damping of rotation-vibration lines of hydrogen chloride by foreign gases. W. GRASSE (Z. Physik, 1934, 89, 261—272).—Observations on the increase of absorption max. of the HCl 3.46 μ band are used to deduce effective radii of foreign gases; they are for He, H₂, A, N₂, and CO₂ 2.25, 2.97, 5.37, 6.68, and 10.15 Å., respectively.

A. B. D. C.

Structure of the molecule of nitrogen dioxide from a study of its infra-red absorption spectrum. G. B. B. M. SUTHERLAND (Proc. Roy. Soc., 1934, A, 145, 278—287; cf. A., 1933, 1102).—The infra-red absorption spectrum of NO₂ has been studied under high dispersion. Analysis of the data shows that the form of the mol. is triangular. The most probable vals. for the fundamental frequencies are 641, 1373,

and 1615 cm.⁻¹ The ONO angle lies between 55° and 58°.

L. L. B.

Investigations in the infra-red region of the spectrum. X. Asymmetrical molecule nitrosyl chloride. C. R. BAILEY and A. B. D. CASSIE (Proc. Roy. Soc., 1934, A, 145, 336—344).—Five bands have been isolated in the infra-red absorption spectrum of NOCl between 4 and 16 μ . Owing to the asymmetry of the mol., no resolution was obtained. The mol. has a vertical angle of 140°, and falls into the SO₂ class.

L. L. B.

Bands of "heavy" acetylene in the near infra-red. G. HERZBERG, F. PATAT, and J. W. T. SPINKS (Nature, 1934, 133, 951).—The infra-red spectrum of C₂H₂ prepared from CaC₂ and 93% H₂O shows four bands belonging to C₂HH², but none due to C₂H₂. The moment of inertia of C₂HH² in its lowest state is 27.90 $\times 10^{-40}$ g.-cm.² The C-C and C-H distances are 1.205 and 1.062 Å., respectively.

L. S. T.

Vibration spectra and structure of polyatomic molecules. R. TITEICA (Ann. Physique, 1934, [xi], 1, 533—621; cf. A., 1933, 337).—Data for infra-red and Raman spectra of the following substances in the gaseous form are tabulated: CH₂O, COMe₂, COEt₂, COMeEt, HCO₂Me, HCO₂Et, HCO₂Buⁿ, HCO₂Bu^s, isoamyl formate, MeOAc, EtOAc, PrOAc, BuOAc, EtCO₂Me, EtCO₂Et, Et₂O, and EtOH. From the results obtained mol. structures, interat. distances, angles between valency directions, and moments of inertia are deduced.

N. M. B.

Infra-red reflexion spectrum of silicates. C. SCHAEFER, F. MATOSI, and K. WIRTZ (Z. Physik, 1934, 89, 210—233).—Infra-red reflexion spectra between 8 and 22 μ are given for Be₂SiO₄, troostite, topaz, cyanite, albite, andalusite, titanite, almandine, vesuvian, beryl, aquamarine, heulandite, bronzite, diopside, hornblende, muscovite, klnochlore, apophyllite, and adularia. Two bands, one between 8 and 12 μ and the other between 17 and 20 μ , are ascribed to the SiO₄ group.

A. B. D. C.

Normal modes and frequencies of vibration of the regular plane hexagon model of the benzene molecule. E. B. WILSON, jun. (Physical Rev., 1934, [ii], 45, 706—714).—Mathematical. The 30 modes of vibration of the C₆H₆ hexagon are derived by Wigner's group theory method. From these the 20 vibration frequencies are calc. Selection rules for the Raman and infra-red spectra are listed.

N. M. B.

Raman effect for water in different states. I. R. RAO (Phil. Mag., 1934, [vii], 17, 1113—1134).—The infra-red absorption frequencies of the H₂O mol. are discussed with reference to the shape and dimensions of the mol. In the Raman spectra of H₂O in different states there is only one band at 3 μ , whilst there are two, at 2.66 and 6.26 μ , in the infra-red absorption spectra. Variations of Raman frequencies in different states are ascribed to mol. association.

J. W. S.

Modified scattering by crystalline HCl and HBr. D. CALLIHAN and E. O. SALANT (J. Chem. Physics, 1934, 2, 317—319).—HCl and HBr at just below the f.p. gave Raman lines 2784, 2480 cm.⁻¹,

respectively. The difference between these vals. and those for the gases is too large to be due entirely to Lorentz-Lorenz forces. The cryst. structure is non-ionic. H. J. E.

Raman spectra and molecular constants of the hexafluorides of sulphur, selenium, and tellurium. D. M. YOST, C. C. STEFFENS, and S. T. GROSS (J. Chem. Physics, 1934, 2, 311—316; cf. A., 1933, 466).—For liquid SF_6 , SeF_6 , and TeF_6 three Raman lines were observed in each case. For gaseous TeF_6 there were three, and for gaseous SF_6 and SeF_6 one. The no. of lines indicates regular octahedral mols. The frequencies were assigned to their modes of vibration. The free energy of formation of SF_6 (gas) at 25° is $-238,000$ g.-cal. H. J. E.

Valency angle of oxygen in methyl ether and ethylene oxide. N. G. PAI (Current Sci., 1934, 2, 386—387).—The valency angles in Me_2O and $(\text{CH}_2)_2\text{O}$ calc. from Raman frequencies are 102° and 64° , respectively. The smaller val. is due to the C-C linking. The permanent dipole moments of these two compounds support these vals. L. S. T.

Raman spectrum of ethyl alcohol. G. BOLLA (Z. Physik, 1934, 89, 513—521).—Raman displacements are bands of half width from 15 to 45 cm.^{-1} which show no fine structure with resolution of 1.4 cm.^{-1} . A band at 3360 cm.^{-1} of half width 240 cm.^{-1} is ascribed to the OH group. A. B. D. C.

Raman effect in di-iodoacetylene. G. GLOCKLER and C. MORRELL (J. Chem. Physics, 1934, 2, 349; cf. A., 1933, 1229).—Frequency shifts of 191, 310, 627, 688, and 2109 cm.^{-1} were observed. That due to the C-I vibration (627 cm.^{-1}) is about 100 cm.^{-1} > in the I-compounds of saturated hydrocarbons. The 2109 cm.^{-1} frequency shift indicates an acetylenic structure. H. J. E.

Raman spectra of benzene and hydrogen iodide in the liquid and solid state. H. EPSTEIN and W. STEINER (Nature, 1934, 133, 910—911).—With C_6H_6 , there is a small decrease in wave nos. in passing from the liquid to the solid state. The decreases in wave no. for HI in passing from the gaseous to the liquid and to the solid states are recorded. Liquid HI has a diffuse Raman line of complex structure. L. S. T.

Raman spectrum of thiophen, furan, and derivatives. G. B. BONINO and R. MANZONI-ANSIDEI (Z. physikal. Chem., 1934, B, 25, 327—347).—Raman spectra show that in thiophen, pyrrole, and furan there is only a plane of symmetry, or a binary axis of symmetry, olefinic C-C linkings are absent, and there are oscillations of the C-H linkings similar to those of C_6H_6 . Electronic formulae which agree with all the physical and chemical properties of these substances are proposed (cf. A., 1933, 886). There is resonance between an aromatic configuration and a configuration with ordinary double linkings. R. C.

Raman spectrum of some pyrrole derivatives. II. G. B. BONINO, R. MANZONI-ANSIDEI, and P. PRATESI (Z. physikal. Chem., 1934, B, 25, 348—362; cf. A., 1933, 886).—The spectra of various

derivatives are discussed in relation to structural problems. R. C.

Raman spectra of double linkings conjugated in a nucleus. R. TRUCHET and J. CHAPRON (Compt. rend., 1934, 198, 1934—1936).—*cyclopentadiene* and *dicyclopentadiene* were examined. Both include a strong line in the region $1400\text{—}1500\text{ \AA.}$ attributed to C-C in the conjugated system. Similar lines are given by pyrrole and thiophen (Venkateswaran, A., 1930, 1345) and furan (Bonino, see above). Bonino's objection to the Kekulé formula for C_6H_6 (*loc. cit.*) is therefore overruled. B. W. B.

Scattering of light by binary mixtures in the neighbourhood of the critical point of complete miscibility: measurement of depolarisation factor. A. ROUSSET (Compt. rend., 1934, 198, 2152—2154).—Depolarisation factors of $\text{H}_2\text{O}-\text{Bu}^\text{C}\text{CO}_2\text{H}$ and $\text{C}_6\text{H}_{14}-\text{PhNO}_2$ mixtures were measured and did not support Rocard's theory (A., 1928, 1310). It is suggested that superposed primary and secondary scattering is involved, completely and partly depolarised, respectively. B. W. B.

Rayleigh's law of scattering in the infra-red. A. H. PFUND (J. Opt. Soc. Amer., 1934, 24, 143—146).—Transmission measurements on transparent particles of ZnO and MgO dispersed in rubber show that Rayleigh's law is obeyed for the smallest particles of $0.088\text{ }\mu$ diameter, but not for larger particles. The effect of varying n of the surrounding medium agrees qualitatively with Rayleigh's formula. N. M. B.

Colour and crystal structure of precipitated cadmium sulphide. W. O. MILLIGAN (J. Physical Chem., 1934, 38, 797—800).—It is inferred from X-ray measurements that cubic $\beta\text{-CdS}$ or hexagonal $\alpha\text{-CdS}$ may each be yellow or red, depending on the conditions of pptn. The differences in colour are attributed to differences in particle size and nature of surface. All dry samples become orange on grinding. CdSO_4 and hot, acid $\text{Cd}(\text{NO}_3)_2$ give $\beta\text{-CdS}$; CdCl_2 , CdBr_2 , and CdI_2 give mainly $\alpha\text{-CdS}$. The lattice consts. agree with those of Ulrich and Zachariasen (A., 1926, 664). R. S. B.

Fluorescence of some pure substances. E. CANALS and P. PEYROT (Compt. rend., 1934, 198, 1992—1994).—The ratios of fluorescence intensity to mol. scattering were determined for H_2O and several org. liquids. Fluorescence was shown by H_2O (feeble), by all O-compounds (cf. A., 1925, ii, 1030), by cyclanes, cyclenes, and their derivatives, but not by all hydrocarbons. Intensities of fluorescence relative to H_2O are given in some cases (cf. this vol., 346). B. W. B.

Relationships between absorption and luminescence spectra in concentrated solutions of dyes. V. L. LEVSHIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 405—410; cf. A., 1931, 1351, 1353).—The mirror image correspondence between the absorption and luminescence spectra of rhodamine 6G solutions disappears at higher concn. when the increase in concn. is accompanied by a diminution in intensity of the luminescence. The symmetry tends to reappear, however, with rise of temp. The results are explained

by the association of the dye mols., and can be used to calculate the degree of association. J. W. S.

Electrical breakdown in liquids from negative to high positive pressures. W. FERRANT (Z. Physik, 1934, 89, 317—356).—Measurements up to 70 atm. show three regions: that of low pressure where breakdown potential is independent of pressure, that of 2—4 atm. where the pressure coeff. is high, and that above 15 atm. Breakdown potential under the v.p. alone is independent of temp. Examples discussed are oil and hexane. A. B. D. C.

Role of the unidirectional layer in rectification and in photo-electric phenomena. W. C. VAN GEEL (Physica, 1934, 1, 531—542).—Theoretical. H. J. E.

Anomalous electrical conductivity of thin metals. H. MURMANN (Z. Physik, 1934, 89, 426—430).—Optical transmission of the 404.7 mμ Hg line shows that anomalous electrical conductivity of very thin metal foils is not due to poor contact between neighbouring mol. groups. A. B. D. C.

Anomalous behaviour of dielectric liquids. W. JACKSON (J. Inst. Electr. Eng., 1934, 75, 93—110).—A résumé of recent work.

Dipole moments and physico-chemical properties. II. A. E. VAN ARKEL (Chem. Weekblad, 1934, 31, 264—267, 342—344).—A review, dealing especially with hydrate formation, the interaction of dipoles and ions, association of mols. in solution, and the formation of compounds such as polyiodides. H. F. G.

Dielectric constant of nitrogen up to 1000 atm. between 25° and 150°. A. MICHELS, A. JASPERS, and P. SANDERS (Physica, 1934, 1, 627—633; cf. A., 1932, 793).—Data are tabulated. No deviation from the Clausius-Mosotti relation was found. H. J. E.

Polarity of nitrogen tetroxide and nitrogen dioxide molecules. J. W. WILLIAMS, C. H. SCHWINGEL, and C. H. WYNNING (J. Amer. Chem. Soc., 1934, 56, 1427—1428).—The dielectric const. and d of equilibrium mixtures of N_2O_4 and NO_2 have been determined between 25° and 125°. In agreement with Zahn (A., 1933, 663) the dipole moment, μ , of NO_2 decreases with rise of temp., but contrary to Zahn, μ of N_2O_4 is approx. zero, since the mol. polarisation is independent of temp. and has a val. close to that required by the optical data of Cuthbertson (A., 1913, ii, 993). J. G. A. G.

Reactions relating to carbohydrates and polysaccharides. XLVII. Oxygen valency angle and structure of glucose and related compounds. J. S. ALLEN and H. HIBBERT (J. Amer. Chem. Soc., 1934, 56, 1398—1403).—A more detailed account of work previously reviewed (A., 1932, 1190; cf. *ibid.*, 1115). The electric moment ($\times 10^{18}$) and O valency angle are: $(CH_2)_5O$ 1.88, 70° (cf. Smyth and Walls, A., 1932, 984); propylene oxide, 1.88, 70°; $(CH_2)_3O$ 2.01, tetrahydrofuran —, 108° (cf. *loc. cit.*); tetrahydropyran 1.87, 93°; 2-hydroxy-2-dichloromethyl-3-dioxolan (glycol dichloroacetate), b.p. 106°/0.08 mm. [from $(CH_2)_2O$ and $CHCl_2 \cdot CO_2H$ in Et_2O at 0°], μ 3.5, about 90°; glycol chloroacetate 3.94, —. H. B.

Dipole moments of some aromatic compounds. G. M. BENNETT and S. GLASSTONE (Proc. Roy. Soc., 1934, A, 45, 71—80).—An analysis of the data for the dipole moments of p -substituted anisoles, phenols, Ph_2 ethers, and anilines leads to the conclusion that in all these compounds a deviation Δ from strict additivity of the linking moment occurs. The vals. of Δ , which is an additional moment operating along the axis of the C_6H_5 nucleus, are consistent with those to be expected on the basis of the electronic theory of aromatic reactivity. It is unsound to base computations of valency angles of O and S on dipole moment data. L. L. B.

Dipole moments of mono-substitution products of mesitylene. F. BROWN, J. M. A. DE BRUYNE, and P. GROSS (J. Amer. Chem. Soc., 1934, 56, 1291—1293).— d^{30} and n^{30} are recorded for the F, Cl, Br, and I monosubstitution products of mesitylene. d , n , and dielectric data are recorded for C_6H_6 and CCl_4 solutions, and the dipole moments, μ , of the mesitylene derivatives are: F- 1.36, Cl- 1.55, Br- 1.52, I- 1.42, NO_2 - 3.64, and OH- 1.36×10^{-18} e.s.u. PhF has 1.46. In general, these data are in good agreement with calc. vals. J. G. A. G.

Dielectric properties of acetylenic compounds. III. Substituted phenylacetylenes. M. M. OTTO and H. H. WENZKE (J. Amer. Chem. Soc., 1934, 56, 1314—1315).—The dipole moments of the following substituted phenylacetylenes are: p -Cl- 0.96, p -Br- 0.95, m -Cl- 1.38, m -Br- 1.35, o -Cl- 1.69, o -Br- 1.79, p -Et- 1.05, p -Me- 1.01, p -Pr²- 1.12, and p - NO_2 - 3.42×10^{-18} e.s.u., from which, with other data, it is inferred that the moment of $CPh:CH$ is 0.56 and is opposite in direction to that of $PhMe$. J. G. A. G.

Thermal and photochemical equilibria of the *cis-trans*-isomerides of dichloro- and dibromoethylene. [Dielectric constants.] A. R. OLSON and W. MARONEY (J. Amer. Chem. Soc., 1934, 56, 1320—1322).—The dielectric consts. of *cis*- and *trans*- $C_2H_2Cl_2$ (I) and *cis*- and *trans*- $C_2H_2Br_2$ (II) at 25° are 9.30, 2.35, 7.08, and 2.88, respectively. The heat of transition of (I) is 500 g.-cal. per mol. at 350° and that of (II) 340 at 150°. The extinction coeffs. of the vapours of (I) between 100° and 250° are recorded for the range 2302—2753 Å., and the ratio of the probability that an excited mol. will return to the *trans*-form to the probability that it will return to the *cis* on deactivation increases from 0.95 at 100° to 1.46 at 300°. The change of this ratio with change of temp. and wave-length is in accord with theory. J. G. A. G.

Variations in refractive index of benzene during intensive drying. J. J. MANLEY (Rec. trav. chim., 1934, 53, 785—791; cf. A., 1932, 323).—With progressive drying of C_6H_6 by P_2O_5 over a period of 2 years n increases, then passes through a stage during which it decreases, and finally increases again. An explanation in terms of polymerisation is attempted. The effect of P_2O_5 on boiling C_6H_6 in a few days is equiv. to that at room temp. for several years. E. S. H.

Rotatory dispersion measurements with phenylmethylcarbinol. W. BODENHEIMER and C. BRUHN (Z. physikal. Chem., 1934, B, 25, 319—326).—

Measurements have been made at 22° with the pure and dissolved substance from 3175 to 6560 Å. The dispersion curves of the pure substance and solutions in aliphatic alcohols are similar in position, but different from those of solutions in CCl_4 and C_6H_{14} . With increasing dilution the mol. rotation increases. These results are explained by Kuhn's theory of optical activity and the assumption of solvation in dil. solutions in alcohols. R. C.

[Rotatory polarisation of] certain compounds of tartramide and of tartramic acid. Y. K. HENG (Compt. rend., 1934, 198, 1985—1987).—Aq. tartramide (I) solutions gave $[\alpha]$ practically independent of concn. Vals. of $[\alpha]$ for various substances dissolved in aq. solutions of (I) or of tartramic acid (II) indicated the formation of the compounds $[\text{MoO}_3, 2\text{A}](\text{NH}_4)_2$ (cf. Darmois, A., 1932, i, 299); $\text{B}, \text{NH}_4\text{BO}_2$; B, NaBO_2 ; $[\text{CuO}, 4]\text{Na}_2$; $[\text{CuO}, 2\text{B}]\text{Na}_2$ (III) ($\text{A} = \text{C}_4\text{H}_7\text{O}_5\text{N}$, $\text{B} = \text{C}_4\text{H}_5\text{O}_4\text{N}_2$). (III) was strongly dichroic; ellipticity measurements are tabulated. $\text{Al}(\text{OH})_3$ was insol. in aq. (I) and gave a laevorotatory solution in aq. (II). B. W. B.

Optical rotatory power. A. R. CHAMBERS and H. G. RULE (Nature, 1934, 133, 910).—The optical activity of *d*-pinane (I), methylmenthane, and other non-polar solutes in numerous solvents is governed chiefly by the n of the solvent, supporting Boys' prediction (see below). $[\alpha]_D$ for (I) is practically unaltered when (I) is dissolved in CCl_4 , which has approx. the same n . L. S. T.

Optical rotatory power. I. Theoretical calculation for a molecule containing only isotropic refractive centres. II. Calculation of the rotatory power of a molecule containing four refractive radicals at the corner of an irregular tetrahedron. S. F. BOYS (Proc. Roy. Soc., 1934, A, 144, 655—675, 675—692).—I. Mathematical. A formula is derived by means of which the rotatory power of a mol. can be calc. Each atom is taken as a refractive centre, and the total rotatory power is the sum of the contributions from every possible combination of four atoms.

II. The formula is applied to the simplest type of optically active mol. Vals. of $[\alpha]_D$ are calc. for $\text{C}_5\text{H}_{11}\cdot\text{NH}_2$, $\text{C}_5\text{H}_{11}\cdot\text{OH}$, *sec.*- NH_2Bu , and *sec.*- BuOH , which agree in magnitude with those experimentally determined. A formula connecting the rotatory dispersion of a compound with that of the radicals contained in it is obtained. L. L. B.

Magneto-optical properties of hydrocarbons and their mixtures. Application to their identification. M. SCHERER (Chim. et Ind., 1934, 31, Spec. No., 383—400).—The magnetic rotatory power, dispersion, magnetic birefringence, and d of hydrocarbons from C_7H_{16} to $\text{C}_{16}\text{H}_{34}$, of the corresponding ethylenic hydrocarbons, and of a no. of C_6H_6 , cyclohexane, and cyclohexene hydrocarbons have been measured. Similar measurements have been made on numerous natural oils and products derived from them. In certain cases the composition of a mixture may be deduced from its magneto-optical properties. H. J. E.

Magnetic birefringence of gaseous oxygen and nitrogen and of aqueous chlorate solutions. A.

COTTON and T. BELLING (Compt. rend., 1934, 198, 1889—1893; cf. this vol., 132).—The magnetic birefringences of O_2 , N_2 (both at 100 atm.), H_2O , and NaClO_4 in aq. solution were respectively -4.05×10^{-4} , -0.33×10^{-14} , -0.14×10^{-14} , and -1.6×10^{-14} (cf. Chinchalkar, A., 1932, 1190). B. W. B.

Magneto-chemistry of rhenium: metallic and septavalent rhenium. N. PERAKIS and L. CAPATOS (Compt. rend., 1934, 198, 1905—1907).—The coeff. of magnetisation, χ , of Re , Re_2O_7 (I), and the per-rhenates (II) of K and NH_4 were determined. The val. for Re confirmed the previous determination (A., 1933, 340) and not that of Albrecht and Wedekind (A., 1931, 153). χ of (I) and of Re^{VII} were, respectively, -15.7×10^{-6} (per mol.) and 8.2×10^{-6} (per g.-atom). In every case χ was independent of temp. (-79° to 20°). The results for (II) indicated that XReO_4 cannot represent the mol. formulae of both per-rhenates. B. W. B.

Paramagnetism. II. Origin of the term "Δ" in paramagnetic salts. S. DATTA (Phil. Mag., 1934, [vii], 17, 1160—1168; cf. this vol., 350).—The temp. variation of χ has been determined for Co^{++} and Ni^{++} salts as powdered crystals of anhyd., hydrated, and other complex salts, and for solutions of CoCl_2 and NiCl_2 in different solvents. The vals. of the const. Δ in the Weiss formula are less for hydrated and complex salts than for the anhyd. salts; the sign of Δ also remains const. for the same anion, but varies with the state of aggregation. For solutions of NiCl_2 and CoCl_2 in acid and in EtOH , Δ varies with temp. The high vals. found for Δ in certain states of aggregation are attributed to interchange-interaction effect between the electrons attached to the paramagnetic atom and its halogen neighbours. J. W. S.

Paramagnetic rotatory power of dysprosium ethyl sulphate at very low temperatures. Paramagnetic saturation. J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Compt. rend., 1934, 198, 1849—1851).—The paramagnetic rotation of $\text{Ds}(\text{EtSO}_4)_3 \cdot 9\text{H}_2\text{O}$ was measured at 1.62° , 4.13° , 14.12° , and 20.35° abs.; it comprised two components, (a) independent of temp., and (b) a function of field strength/abs. temp. At 1.62° abs., saturation was attained in a field of 27,000 gauss. B. W. B.

Temperature and diamagnetism. I. Susceptibility of some aromatic liquids. S. S. BHATNAGAR, M. B. NEVGI, and M. L. KHANNA (Z. Physik, 1934, 89, 506—512).—Susceptibilities at 20° and 70° are given for C_6H_6 , PhNO_2 , PhCl , PhBr , $\text{I-C}_{10}\text{H}_7\text{Br}$, $\text{C}_5\text{H}_5\text{N}$, NH_2Ph , PhOMe , *p*-cymene, *m*-cresol, *m*- $\text{C}_6\text{H}_4\text{MeBr}$, and CH_2PhCl . A. B. D. C.

Electrostatic theory of ionic equilibria. II. Highest oxygen acids of metalloids. J. v. CHODAKOV (Z. physikal. Chem., 1934, B, 25, 37—390).—The theory previously developed (this vol., 254) is applied. The co-ordination no. for the addition of O to the metalloids of the third and fifth groups of the periodic system is shown to be four, and for the metalloids of the seventh group six or five. Unpolymerised antimononic acid must be H_2SbO_6 , agreeing with various experimental data. Sn^{IV} hydroxide is

H_3SnO_6 , the case with which two only of the H atoms are substituted being energetic and not constitutional. From dissociation consts. the chemical radius of the radicals PO_4 , AsO_4 , and SO_4 is calc. to be $\sim 3 \text{ \AA}$., and that of IO_6 , TeO_6 , and $\text{SbO}_6 \sim 3.2 \text{ \AA}$. It is found empirically that the radius of an ion of the inert gas type differs from that of the atom of the same element by approx. 0.75 \AA ., the atom being the larger or the smaller according as the ion is positive or negative, respectively. R. C.

Relations between isosterism and chemical character of acetylene, hydrogen cyanide, and derivatives. G. BAHR (Z. physikal. Chem., 1934, 168, 363—368).—There is striking chemical similarity between C_2H_2 , HCN, and their derivatives, which is closely connected with the fact that C_2H_2 and HCN are isosteric. The $\cdot\text{C}:\text{CH}$ radical has the properties of a pseudohalogen. R. C.

Structures of the metallic carbonyl and nitrosyl compounds. N. V. SIDGWICK and R. W. BAILEY (Proc. Roy. Soc., 1934, A, 144, 521—537).—For all carbonyls $\text{M}_x(\text{CO})_y$, if m is the at. no. of M, b that of the neutral inert gas, then $b - [(xm + 2y)/x] = x - 1$. When $x = 1$, M has effective at. no. of inert gas. Assuming that this is true when $x > 1$, M atoms must

be held together thus: $\overset{+}{\text{M}}:\overset{+}{\text{C}}:\overset{+}{\text{O}}:\overset{+}{\text{M}}$. Every M atom in the mol. is joined to every other through a linking of this kind. If the mol. contains 2M this is secured by joining them through a single CO; for 3, by placing them at the angular points of a triangle with a CO on each side; for 4, by placing them at those of a tetrahedron with a CO group on each edge. The crystal structures of $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ are compatible with this. Nearly all carbonyl derivatives follow these rules with the necessary modifications for these groups present. The structure of nitrosyl

compounds is $\overset{+}{\text{M}}:\overset{+}{\text{N}}:\overset{+}{\text{O}}$, corresponding with $\overset{+}{\text{M}}:\overset{+}{\text{C}}:\overset{+}{\text{O}}$, and the NO contributes 3 electrons to the effective at. no. of M, as CO contributes 2. On this hypothesis, the structures of most nitrosyl compounds are found to follow the same rules as the carbonyls. The similarity of the volatile compounds $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_3(\text{NO})$, and $\text{Fe}(\text{CO})_2(\text{NO})_2$ is explained, also the characteristic colour reaction of the nitroprussides with the sulphides. For a mol. $\text{M}_x(\text{CO})_y(\text{NO})_z$, the equation $b - [(xm + 2y + 3z)/x] = x - 1$ holds.

L. L. B.

Distances of the closest approach of atoms of rubidium, caesium, and barium. B. N. SEN (Current Sci., 1934, 2, 434).—Calc. vals. are Rb 4.56, Cs 5.7, and Ba 6.57 Å. L. S. T.

Simple modification of Morse's rule. C. H. D. CLARK (Nature, 1934, 133, 873).—For non-hydride diat. mols. of the period containing two completed K rings associated with each nucleus, the empirical modification is $\omega_e r_e^3 \sqrt{n} = 9.55 \times 10^{-21} \text{ cm}^2$, where ω_e and r_e are the equilibrium nuclear vibration frequency and separation, respectively, and n is the group no. equal to the no. of shared electrons, or total no. of valency electrons of the two separate atoms.

L. S. T.

Calculation of the lattice constant of potassium chloride. T. NEUGEBAUER and P. GOMBAS (Z.

Physik, 1934, 89, 480—496).—The lattice const. and energy are calc. from the polarisation energy of an ionic crystal and the van der Waals energy.

A. B. D. C.

Surface tension. A. FERGUSON (Proc. Roy. Inst., 1934, 28, 195—206).—A lecture.

Physical relationships amongst the hydrides of elements of the fifth group with special reference to association in these compounds. A. A. DURRANT, T. G. PEARSON, and P. L. ROBINSON (J.C.S., 1934, 730—735; cf. A., 1932, 454).— d and surface tensions of NH_3 , PH_3 , AsH_3 , and SbH_3 have been measured and their parachors deduced. The v.p. of AsH_3 and SbH_3 from 180.5° to 214.5° abs. and 212.7° to 255.9° abs., respectively, has been measured. These physical properties are discussed. AsH_3 and SbH_3 are normal liquids, PH_3 is somewhat associated, and NH_3 at its b.p. is largely bimol. H. J. E.

Volatile hydrides. I. Periodicity as a means of correcting and supplementing determined physical properties. II. The parachor, molar volume at absolute zero, and electronic structure and properties of compounds. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1934, 736—743).—I. In any group the m.p., b.p., mol. heats of vaporisation, and surface tensions vary directly with the period no. of the parent element, departures from linearity (e.g., with H_2O or NH_3) being due to association. Certain undetermined physical consts. are predicted.

II. The parachor of H in volatile hydrides varies from 10.28 in HF to 19.20 in BiH_3 , the variation being correlated with electronic structures of the atoms, and shown to accord with a hydrolytic mechanism of ionisation. In each periodic group the ratio $MV_{\text{b.p.}}/MV_0$ for the hydrides is const. ($MV_{\text{b.p.}}$, MV_0 are mol. vols. at the b.p. and 0° abs., respectively). H. J. E.

Parachor of hydrogen bromide. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1934, 880—881).—The surface tension and d of liquid HBr have been measured. The liquid is slightly associated. McIntosh and Steele's measurements (A., 1904, ii, 533) are not correct. H. J. E.

X-Ray wave-length from crystals and ruled gratings. A. E. RUARK (Physical Rev., 1934, [ii], 45, 827—831).—Crystal scale wave-lengths are supported by calculations of energies of photo-electrons ejected by X-rays from thin foils, and comparison with those calc. from wave-lengths of the incident rays and X-ray terms of the atoms in the foils, using wave-lengths measured with crystals and ruled gratings. N. M. B.

Calculation of intensity factors for the powder method of X-ray crystal analysis. F. C. BLAKE (J. Chem. Physics, 1934, 2, 320—330).—Theoretical. Calc. and observed vals. for wurtzite and sphalerite are compared. H. J. E.

State of ammonium salts at low temperatures. A. HETTICH (Z. physikal. Chem., 1934, 168, 353—362).— NH_4Cl exhibits below the discontinuity point at about -30° the Giebe-Scheibe effect, which supports the theory that the rotating NH_4 groups become frozen in at this point. There is a hysteresis

gap of 0.3° between the appearance and disappearance of the effect, corresponding with the gap observed in dilatometric investigation (cf. A., 1933, 1119). NH_4Br exhibits no Giebe-Scheibe effect down to liquid air temp., and becomes doubly-refracting at about -30° . With $(\text{NH}_4)_2\text{SO}_4$ the effect appears below -51° , and with RbNO_3 disappears at the temp. of transition to the cubic form. R. C.

Structural relations which must exist between two substances in order that one shall modify the crystal form of the other. L. ROYER (Compt. rend., 1934, 198, 1868—1870; cf. this vol., 249, 376).—Further examples are given. B. W. B.

Effect of a magnetic field on the linear rate of crystallisation. E. W. R. STEACIE and C. F. B. STEVENS (Canad. J. Res., 1934, 10, 483—485).—A magnetic field of about 5000 gauss had no effect on the linear rate of crystallisation of $\text{Na}_2\text{S}_2\text{O}_3$ from supersaturated solution. NiSO_4 showed a slightly increased rate. O. J. W.

Change in the elementary cell by directed forces. F. LIHL (Physikal. Z., 1934, 35, 460—468).—X-Ray examination of steel crystals indicates that the lattice undergoes change on the addition of foreign atoms, or when subjected to mechanical strain. The measurement of interference lines can give no information concerning a mean lattice parameter for alloyed or cold-worked substances. For such substances, this quantity has no physical meaning. A. J. M.

Transition of the cubic body-centred modification into the hexagonal close-packed modification of zirconium. W. G. BURGERS (Physica, 1934, 1, 561—586).—The transition from cubic to hexagonal Zr is shown, by X-ray measurements, to be due to a combination of shearing and dilatation processes parallel to definite crystallographic directions. H. J. E.

Perfection of quartz and other crystals and its relation to surface treatment. R. M. BOZORTH and F. E. HAWORTH (Physical Rev., 1934, [ii], 45, 821—826).—Rocking curve widths at half max. show that quartz is a perfect crystal, and that perfect specimens of Na K tartrate, fluorite, tourmaline, and pyrites might be found. Barite, rock-salt, gypsum, and crystals of Al, Fe, Ni, W, and permalloy are imperfect. The effect on perfection of etching permalloy and etching and grinding quartz surfaces was investigated. N. M. B.

Crystal structure of [high-temperature] α -silver iodide. L. W. STROCK (Z. physikal. Chem., 1934, B, 25, 441—459).— α -AgI crystallises in the cubic system with a_0 5.034 Å. and 2 mols. in the unit cell. The structure is of a new type and is outside the scope of the exact structure theory. It consists of a cubic body-centred I packing, with a distance I—I of 2.18 Å., in the 30 largest interstices of which 2 Ag⁺ are inserted at random. The Ag is thus contained like a liquid in the I lattice. The Ag—I co-ordination no. is 4, 3, and 2. This structure explains the electrolytic conduction and the self-diffusion of Ag⁺ in the lattice. R. C.

Diffraction of X-rays in glass. B. E. WARREN (Physical Rev., 1934, [ii], 45, 657—661).—Scattering

curves for vitreous SiO_2 and GeO_2 , obtained from X-ray diffraction patterns, are in good agreement with calculation. In vitreous SiO_2 each Si atom is tetrahedrally surrounded by four O atoms at a distance Si—O=1.60 Å., and each O is shared between two such tetrahedral groups. The resulting network repeats irregularly, but the presence of permanent neighbouring atoms justifies the term “amorphous solid” rather than “supercooled liquid” for glass. N. M. B.

Structure of 1:3:5-triphenylbenzene. I. B. ORELKIN and K. LONSDALE (Proc. Roy. Soc., 1934, A, 144, 630—642).— $\text{s-C}_6\text{H}_3\text{Ph}_3$ crystallises in the orthorhombic hemihedral class; space-group Pna (C_{2h}^2). The unit cell contains 4 mols. and has a 7.55, b 19.76, c 11.22 Å. The optical and magnetic properties of the crystal and the X-ray measurements show that the mol. approximates to the “layer-lattice” type. There are, in effect, twice as many C atoms in the crystal surface at one end of the polar axis as at the other end. L. L. B.

Influence of magnetic fields on scattering of X-rays by liquids. H. SIRK (Z. Physik, 1934, 89, 129—142).—A magnetic field of 4×10^4 gauss gave no indication of fibre structure in $\text{l-C}_{10}\text{H}_7\text{Cl}$, but showed particles containing 10^4 mols. A. B. D. C.

Structure of the fatty acid esters of cellulose. J. J. TRILLAT (J. Phys. Radium, 1934, [vii], 5, 207—215).—The propionate, butyrate, valerate, hexoate, heptoate, octoate, nonoate, decoate, palmitate, and stearate of cellulose have been investigated by X-ray examination of powder or of evaporated or deposited films. Lattice spacing increases regularly with the no. of C atoms; with increasing C chain length the esters pass from a cryst. to a mesomorphic form. The aliphatic chains attach perpendicularly to the principal valency-chain direction, and parallel to one another; the fatty acid character predominates increasingly with length of chain, tending to mask the cellulose character. N. M. B.

Mathematical treatment of a theory of rubber structure. T. R. GRIFFITH (Canad. J. Res., 1934, 10, 486—520).—The theory that the elasticity of rubber is due to the heat vibrations of very long chain mols., bound to one another at occasional points along their length, but able to move freely relatively to one another at all other points, has been considered. Assuming that the rubber mol. has a restricted rotation about the axis formed by joining two adjacent junction points, a stress-strain curve is derived which agrees approx. with the experimental curve. The following quantities have also been calc.: (1) the average distance between junction points, (2) length of the rubber mol., (3) the quantity of kinetic energy per c.c. causing the elastic effect, and (4) the min. quantity of S needed for vulcanisation, both for hard and for soft rubber. O. J. W.

Corniform crystals. E. ROSSMAN (J.S.C.I., 1934, 53, 135—137).—Corniform (horn-shaped) cryst. structures are occasionally observed at the surface of tung oil films which have been allowed to dry under abnormal conditions of intense illumination and retarded drying. They are truly cryst. and anisotropic when first formed, although they may become isotropic

on further oxidation. The peculiar curved shape is regarded as the resultant of crystal-lattice and surface-orienting forces acting simultaneously on large polar (asymmetric) mols. situated at the air-oil interface. Chemically, such crystals may consist of a peroxide of β -clæostearin. E. L.

Investigation of various forms of carbon by cathode-ray diffraction. M. MIWA (Sci. Rep. Tôhoku, 1934, 23, 242—257).—Amorphous C (I) is a fine form of graphite, the crystal lattice expanding in the direction of the principal axis as the grain size diminishes, in agreement with X-ray results. The magnetic susceptibility of (I) nearly \propto the grain size. H. S. P.

Electron diffraction by the oxides of nitrogen. L. R. MAXWELL, V. M. MOSLEY, and L. S. DEMING (J. Chem. Physics, 1934, 2, 331—336).— N_2O is a linear mol. with the end atoms separated by 2.38 ± 0.05 Å., agreeing with Wierl's val. (A., 1931, 665). NO_2 (at about 150°) gave no diffraction rings, indicating a triangular mol. with the N—O distance 1.15—1.3 Å. The N—N distance in N_2O_4 is 1.6—1.7 Å. N_2O_5 gave one diffraction ring, best explained by a symmetrical model $\text{O}_2\text{N}\cdot\text{O}\cdot\text{NO}_2$ with the N—O distance 1.3—1.4 Å. H. J. E.

Crystalline state of thin calcium fluoride films. W. G. BURGERS and C. J. DIPPEL (Physica, 1934, 1, 549—560; cf. A., 1931, 1226).—Thin transparent films of CaF_2 evaporated on to Cu or celluloid from a W filament coated with CaF_2 have been shown by electron diffraction to be cryst., with a random orientation of the crystallites in the first layers deposited. At thicknesses $> 0.1 \mu$ the outer layers are oriented with (111) planes parallel to the substratum for perpendicular incidence of the salt beam, or slightly inclined for oblique incidence. Heating to 400° in vac. does not change the diffraction pattern of the film. H. J. E.

Determination of crystal lattice constants by electron diffraction. N. A. SCHISCHAKOV and L. I. TATARINOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 164—168).—A cathode beam on passing between two convex specimens gives rise to double diffraction. A specimen of known lattice const. is used, together with another specimen of unknown lattice const. From the wave-length of the diffraction patterns vals. of the lattice const. are obtained with an accuracy equal to that of the X-ray method. W. R. A.

Lattice dimensions of zinc oxide. G. I. FINCH and H. WILMAN (J.C.S., 1934, 751—754).—For the close-packed hexagonal lattice of ZnO electron diffraction measurements gave a 3.258 ± 0.005 , c 5.239 ± 0.005 Å. H. J. E.

Diffraction of electrons by rubber. J. J. TRILLAT and H. MOTZ (Compt. rend., 1934, 198, 2147—2149).—Rubber films (order of thickness 1μ) extended by approx. 100% gave transmission patterns with 30—40-kv. electrons consisting of diffuse rings when thick or insufficiently stretched, or fine spots indicating lattice dimensions c 8.1, a 12.4 Å., the isoprene chains lying flat in the film surface. The change from diffuse rings to fine spots is attributed to

orientation of the isoprene chains by stretching (cf. this vol., 480). The spots disappeared in 24 hr.

B. W. B.

Behaviour of quartz crystals towards electric sparks. KREFT and STEINMETZ (Naturwiss., 1934, 22, 314—315).—In crystals with appreciable conductivity (e.g., NaCl), the electric spark passes through certain canals in the crystal. In non-conducting crystals, the discharge passes over the surface in definite lines. With l -quartz, the lines are the mirror images of those with d -quartz. A. J. M.

Change of resistance in a magnetic field. H. JONES and C. ZENER (Proc. Roy. Soc., 1934, A, 145, 268—277).—The theory of the change of resistance of a metal in a magnetic field is developed for an arbitrary lattice, assuming a const. time between electron collisions at all points on the surface of the Fermi distribution. The theory is applied to Li, with good agreement with the observations of Kapitza.

L. L. B.

State of the cerium atom inside the metallic lattice. R. I. JANUS and V. I. DROSHSHINA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 411—414).—The magnetic susceptibility of Ce has been measured over the temp. range -180.5° to 103.5° . The magnetic momentum is $11.4 M_B$ and remains const. over this temp. interval. Comparison with theoretical vals. corresponding with different states of the atom indicates that the metallic lattice consists either of Ce^+ or Ce^{++} ions, with the corresponding no. of free electrons. At temp. $< 6^\circ$ abs. Ce may be ferromagnetic. J. W. S.

New magnetic phenomenon : increasing paramagnetism superposed on diamagnetism in alloys with false Curie points. R. FORRER and (MLLE.) A. SERRES (Compt. rend., 1934, 198, 1903—1905; cf. A., 1932, 452; 1933, 1236).—The following series of alloys with false (i.e., discontinuous) Curie points, Θ , all showed const. diamagnetism at temp. $< \Theta$, and paramagnetism increasing with rise of temp. above Θ : β -brass, γ -brass, AgZn, and Ag_3Zn_8 . The magnitude of the paramagnetism was less as Θ was higher. B. W. B.

Ferromagnetic Curie point of thin films of electrolytically deposited nickel. S. PROCOPIU and T. FARCAS (Compt. rend., 1934, 198, 1983—1985). B. W. B.

(Magnetic) transformations of pyrrhotine and of ferrous sulphide. A. MICHEL and G. CHAUDRON (Compt. rend., 1934, 198, 1913—1915).—Temp.-magnetisation curves of pyrrhotine and pptd. FeS showed that transition occurred at 200° between a ferro-magnetic form stable at low temp., and a feebly magnetic high-temp. variety. B. W. B.

Paramagnetic rotatory power of siderite. J. BECQUEREL, W. J. DE HAAS, and J. VAN DEN HANDEL (Compt. rend., 1934, 198, 1987—1989). B. W. B.

Relation between magnetic susceptibility and elastic stress. Y. WATASE (Sci. Rep. Tôhoku, 1934, 23, 208—212).—The variation of the susceptibility has been measured under a homogeneous stress. H. S. P.

Abnormal permeability produced in a steel wire by loading. T. F. WALL (*Nature*, 1934, **133**, 949). L. S. T.

Variation of saturated magnetisation at low temperatures, $T^{3/2}$ law. P. WEISS (*Compt. rend.*, 1934, **198**, 1893—1895).—Experiments on magnetic saturation of Fe and Ni were undertaken to discriminate between the proposed laws involving functions of T^2 (Weiss and Forrer, A., 1929, 1369) and $T^{3/2}$ (Bloch, A., 1930, 673), respectively. A slight correction is necessary in the previously accepted vals. of the Fe magneton. B. W. B.

Optical and crystallographical properties of the alkali zinc uranyl acetates. H. INSLEY and F. W. GLAZE (*Bur. Stand. J. Res.*, 1934, **12**, 471—474).—The Li and Na salts are monoclinic and isomorphous, forming a series of solid solutions; the K salt is tetragonal. Refractive indices ± 0.002 are: Na salt, n_{Na} 1.475, γ_{Na} 1.480; Li salt, n_{Na} 1.495, γ_{Na} 1.503; K salt, n_{Na} 1.487, 1.477. N. M. B.

Elastic moduli and the variation with temperature of the principal Young's modulus of rock-salt between 78° and 273° abs. L. BALAMUTH (*Physical Rev.*, 1934, [ii], **45**, 715—720).—A new high-precision method is described, and data are given for rock-salt. N. M. B.

Mechanism of plastic deformation of single crystals of iron. N. AKULOV and S. RAEVSKI (*Ann. Physik*, 1934, [v], **20**, 113—117).—A single Fe crystal was submitted to pressure beyond the elastic limit in the (100) direction, and the characteristic patterns formed by Fe_2O_3 on the surface of the crystal (A., 1933, 213) were examined for the (010) face. There are periodic slips in the cleavage planes (100), (010), and (001). A. J. M.

Mesomerism and tautomerism. C. K. INGOLD (*Nature*, 1934, **133**, 946—947).—Theoretical. L. S. T.

Theory of m.p., recrystallisation and polymorphic transition temperatures. L. TARSCHISCH (*Physikal. Z.*, 1934, **35**, 469—471).—The theory indicates that for monat. regular cryst. substances the m.p. is a function of the at. distance. It is applied to solid solutions, and to the phenomenon of recrystallisation. A. J. M.

Theory of super-conductivity. R. SCHACHENMEIER (*Z. Physik*, 1934, **89**, 183—209; cf. A., 1932, 453). A. B. D. C.

Theory of thermo-magnetic and thermo-elastic phenomena. P. CHRAMOV and L. LVOVA (*Z. Physik*, 1934, **89**, 443—446). A. B. D. C.

Electrical resistance of platinum at low temperatures. W. J. DE HAAS and J. DE BOER (*Physica*, 1934, **1**, 609—616).—Data are recorded for the range 4—20° abs., disagreeing with vals. calc. from published formulæ. H. J. E.

Production of very low temperatures by the magnetic method: superconductivity of cadmium. N. KURTI and F. SIMON (*Nature*, 1934, **133**, 907—908).—Cd becomes a superconductor at approx. 0.6° abs. A temp. of 0.1° abs. has been reached by

this method using $Mn NH_4$ sulphate as the paramagnetic salt. L. S. T.

Melting ice. V. ALTBURG (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **2**, 168—170).—Ice formation in relation to geo-physical problems is considered.

The form of m.p.[—pressure] curves. G. TAMMANN and G. MORITZ (*Z. anorg. Chem.*, 1934, **218**, 60—64).—An interpolation formula connecting the vol. change on fusion with pressure is used in conjunction with the Clausius—Clapeyron equation. F. L. U.

F.p. of rhodium. W. F. ROESER and H. T. WENSEL (*Bur. Stand. J. Res.*, 1934, **12**, 519—526).—The f.p. of Rh is $1966^\circ \pm 3^\circ$. Modifications in the method of preparing pure Rh are described. H. J. E.

Direct determination of heat of condensation. I. Experiments with liquids not intensively dried. A. SMITS and D. CANNEGIETER (*Z. physikal. Chem.*, 1934, **168**, 391—410).—With a new type of apparatus, in which a const. temp. difference is maintained automatically between the calorimeter and a petroleum jacket surrounding it, heats of condensation of C_6H_6 , Br, and EtBr have been measured. R. C.

Thermochemical measurements on complex-forming amines and alcohols. W. HIEBER and A. WOERNER (*Z. Elektrochem.*, 1934, **40**, 252—256).—The following data (in g.-cal. per mol.) are recorded: heat of vaporisation, $C_2H_5(NH_2)_2$ 16,040 (0°), 11,200 (20°), C_5H_5N 10,180 (0°), 9710 (20°); heat of melting, $C_2H_4(NH_2)_2$ 4620, N_2H_4 1020. E. S. H.

Latent heat of fusion and ideal solubility of naphthalene. H. L. WARD (*J. Physical Chem.*, 1934, **38**, 761—769).—The latent heat of fusion, ΔH , of very pure $C_{10}H_8$ (m.p. 80.25—80.30°) is given by $\Delta H = 4090 + 9.23t - 0.0522t^2$ g.-cal. ($t = ^\circ C$). The ideal solubility has been calc. from ΔH , and agrees with data on the solubility in PhCl. R. S. C.

Calorimetric experiments on thallium. W. H. KEESOM and J. A. KOK (*Physica*, 1934, **1**, 595—608; cf. this vol., 589).—The at. heat of Tl has been measured from 1.969° to 2.404° abs. with and without an external magnetic field, but with persistent currents flowing. The cooling by adiabatic magnetic disturbance of the superconductive state (I) between 1.32° and 2.32° abs., and the at. heat of non-superconductive Tl at 1.310—1.425° abs. in a magnetic field > the threshold val. have been measured. The transition between (I) and the non-superconductive state is reversible. E.

Exact measurement of specific heats of solid substances at high temperatures. VI. Specific heats of vanadium, niobium, tantalum, and molybdenum. F. M. JAEGER and W. A. VEENSTRA (*Rec. trav. chim.*, 1934, **53**, 677—687; cf. this vol. 481).—The following revised true sp. heats are given. V $0.119795 + 0.18375 \times 10^{-4}t + 0.20457 \times 10^{-7}t^2 - 0.108004 \times 10^{-11}t^3$; Mo $0.061046 + 0.1232086 \times 10^{-4}t - 0.103636 \times 10^{-8}t^2$. E. S. H.

Purification and physical properties of organic compounds. V. The specific heats of solid and liquid phases at the f.p. as criteria

purity. E. L. SKAU (Bull. Soc. chim. Belg., 1934, 43, 287—298).—Whilst traces of impurities increase the sp. heat of a solid (C_p)_s in the neighbourhood of the f.p., the sp. heat of the liquid (C_p)_l is little affected; hence, if existing data near the f.p. afford negative vals. for Tammann's relation, $\alpha = (C_p)_l - (C_p)_s$, it is inferred that the substance is impure. This is confirmed by numerous cases. On the other hand, a substance affording a positive val. of α is not necessarily pure. J. G. A. G.

Specific heat of furan and ethyl ether vapours. W. H. JENNINGS and M. E. BIXLER (J. Physical Chem., 1934, 38, 747—751).—For furan vapour the sp. heat is given by C_p (molal at 1 atm.) = $14.2341 + 7.188 \times 10^{-2}t - 1.071 \times 10^{-4}t^2$ ($t = ^\circ\text{C}$), and varies from approx. 44° to 99° . For Et₂O at 1 atm. C_p (molal) = $23.3833 + 14.71 \times 10^{-2}t - 5.929 \times 10^{-4}t^2$. R. S. B.

Heat capacities of crystalline, glassy, and under-cooled liquid glucose. G. S. PARKS and S. B. THOMAS (J. Amer. Chem. Soc., 1934, 56, 1423).—The sp. heat of cryst. α -glucose (I) from -20° to the m.p. is given by C_p (g.-cal./g.) = $0.270 + 0.00092t$. L_f is 41.7 g.-cal. per g. at 141° (approx.). With rise of temp., the C_p of non-cryst. (I) has a sharp max. at $28-38^\circ$, and during cooling there is a rapid fall of C_p between 40° and 10° (cf. A., 1928, 1189). J. G. A. G.

Isotherms of nitrogen between 0° and 150° and at pressures from 20 to 80 atm. A. MICHELS, H. WOUTERS, and J. DE BOER (Physica, 1934, 1, 587—594; cf. A., 1929, 128).—Data are tabulated. H. J. E.

Beattie-Bridgman and Huang form of the equation of state. W. JACYNA, S. DEREWJANKIN, A. OBNORSKY, and T. PARFENTJEW (Z. Physik, 1934, 89, 370—372).—This formula (A., 1929, 252) is shown to be identical with that of Jakob and Plank (Physikal. Z., 1910, 11, 633). A. B. D. C.

Principle of Le Chatelier and Braun. M. PLANCK (Ann. Physik, 1934, [v], 20, 196).—Attention is directed to work overlooked by the author (cf. this vol., 589). A. J. M.

Thermal conductivity of air. T. H. LABY (Proc. Roy. Soc., 1934, A, 144, 494—495).—The parallel-plate and certain hot-wire methods for the determination of the conductivity of gases give concordant results. L. L. B.

Thermal conductivity of some gases at 0°C . W. G. KANNULINK and L. H. MARTIN (Proc. Roy. Soc., 1934, A, 144, 496—513).—Possible sources of error in hot-wire methods are discussed and the thermal conductivities of air, H₂, CO₂, O₂, CO, N₂O, He, Ne, and A have been measured by one of these methods. The const. ϵ in Maxwell's relation $k_0 = \epsilon \eta_0 c_v$ is calc. for the above gases. Vals. obtained for He, Ne, and A are in good agreement with Chapman's theoretical val. 2.5 for monat. gases. L. L. B.

Thermal expansion of aragonite and its atomic displacements by transformation into calcite between 450° and 490° in air. I. S. KÔZU and K. KANI (Proc. Imp. Acad. Tokyo, 1934, 10, 222—225).—Thermal expansion is very rapid between these temp. C. W. G.

Apparatus for measuring thermal conductivity of metals up to 600° . M. S. VAN DUSEN and S. M. SHELTON (Bur. Stand. J. Res., 1934, 12, 429—440).—The conductivity of the metal is compared directly or indirectly with that of Pb. Data are given for Ni, Zn, and Ni-Cr and other alloys. N. M. B.

Thermal conductivity of some irons and steels over the temperature range $100-500^\circ$. S. M. SHELTON (Bur. Stand. J. Res., 1934, 12, 441—450).—Data, by comparison with Pb, are given for 20 specimens of Fe, steel, Cr-Fe, and Cr-Ni-Fe alloys. N. M. B.

Viscosity and mol. wt. H. MARK (Chim. et Ind., 1934, 31, Spec. No., 788—791).—Vals. (3.7—8.1) of f (length/width of mol.) for hydrocarbons ($C_{22}-C_{53}$) calc. from the sp. viscosities of dil. solutions by the equation $\eta_{sp} = (2.5 + f^2/30)(v/V)$, where v and V are the vols. of the solute and solution, respectively, are $<$ those found by examination of the crystals ($10.2-22.8$). In solution the mols. are probably not straight, but curved or spiral with an effective length proportional to \sqrt{l} , and the above vals. agree approx. with this relation. A. G.

Kinetic theory of the viscosity of liquids. R. O. HERZOG and H. KUDAR (Physikal. Z., 1934, 35, 437—445).—The effect of the shape and dipole moment of mols. on viscosity is derived, and the equation is tested for various substances. A. J. M.

Electrostatic viscosity effect for liquids. R. O. HERZOG, H. KUDAR, and E. PAERSCH (Physikal. Z., 1934, 35, 446; cf. A., 1933, 1110).—The liquids were passed through a capillary tube having two Pt and two glass sides, an electric field being applied between the Pt sides. The viscosity of 13 liquids in a field of 110 volts was measured. There is no electrostatic effect with C₆H₁₄, CCl₄, and cyclohexane, but dipole liquids, with the exception of BuⁿI and decyl iodide, show an increase in viscosity. A. J. M.

Viscosity, heat conductivity, and diffusion of gas mixtures. XXV. Viscosity of xenon, and its mixtures with hydrogen and helium. M. TRAUTZ and R. HEBERLING. XXVI. Viscosity of propylene and β -butylene, and their mixtures with helium or hydrogen. M. TRAUTZ and I. HUSSEINI. XXVII. Viscosity of chlorine and hydrogen iodide. Test of the determination of η for corrosive gases. M. TRAUTZ and F. RUF. XXVIII. Viscosity of chlorine, nitric oxide, and nitrosyl chloride. Viscosity during the reaction $2\text{NO} + \text{Cl}_2 = 2\text{NOCl}$. M. TRAUTZ and A. FREYTAG (Ann. Physik, 1934, [v], 20, 118—120, 121—126, 127—134, 135—144).—XXV. The transpiration method was used with the pure gas from 289.7° to 550° abs., and on the mixtures at 293° , 400° , 500° , and 550° abs. XXVI. Data are given for temp. between 20° and 250° .

XXVII. The viscosities of gases which attack Hg, e.g., Cl₂ and HI, were determined by a method previously described (A., 1931, 1117), the results agreeing well with those obtained by others. A no. of mol. consts. were derived.

XXVIII. The method used for Cl₂ was also employed to find η for NO, the results agreeing with those

obtained by the transpiration method. The Maxwell and Enskog-Chapman diameters of the pure gas were determined. η for NOCl increases more rapidly than is indicated by theory. This is due to decomp. into NO and Cl₂. A. J. M.

Diffusion coefficients in gaseous systems. E. R. GILLILAND (Ind. Eng. Chem., 1934, 26, 681—685).—Diffusion coeffs. for mixtures of air with H₂O vapour, BuⁿOH, PhMe, *sec.*-BuOH, EtOAc, *sec.*-amyl alcohol, PhCl, NH₂Ph, Ph₂, Hg, and PrⁿOH have been determined, and these together with published data for other substances are expressed graphically and also by a modification of Maxwell's equation. D. K. M.

Dilute liquid amalgams of the alkaline earths with special reference to their electrical conductivity, viscosity, and density. G. R. PARANJPE and V. S. PATANKAR (J. Univ. Bombay, 1933, 2, 40—61).—Amalgams containing < 0.364 g. Ba (I), 0.4545 g. Sr (II), and 0.023 g. Ca (III), respectively, have been examined. The electrical conductivities and viscosities of (I) and (II) do not change with time. The conductivities of (II) and (III) increase uniformly with concn., but that of (I) decreases and shows discontinuities at 0.130, 0.225, and 0.325 g.-% Ba. The same vals. correspond with max. in the viscosity-concn. curve of (I), but the density decreases uniformly. The results are discussed in connexion with the theories of Skaupy and Lewis. R. S.

Gold-calcium alloys. F. WEIBKE and W. BARTELS (Z. anorg. Chem., 1934, 218, 241—248).—The thermal diagram shows the compounds Au₄Ca and Au₂Ca. A homogeneous mixed crystal phase is formed between 49 and 56 at.-% Ca. Au₂Ca and the solid solution occur in two modifications. Au₃Ca, AuCa_{1.33}, and AuCa₂ are formed by peritectic decomp. Microscopical observations on alloys up to 35 at.-% Ca confirm the results of thermal analysis. M. S. B.

System germanium-tellurium. W. KLEMM and G. FRISCHMUTH (Z. anorg. Chem., 1934, 218, 249—251).—The only compound formed is GeTe, incongruent m.p. 725±3°, d_{25}^{25} 6.20±0.02. Its existence is also confirmed by the X-ray diagram. GeTe is attacked to a small extent only by conc. HCl or H₂SO₄, NH₃, and H₂O₂, slowly by conc. HNO₃, and readily by aqua regia or a mixture of H₂O₂ and HCl. Comparisons are made with the corresponding Te compounds of Sn and Pb. M. S. B.

Kinetics and equilibrium diagram of the irreversible transformation in the iron-nickel system. U. DEHLINGER [with H. BUMM] (Z. Metallk., 1934, 26, 112—116).—On quenching the 29 : 71 Ni-Fe alloy in liquid air a purely martensitic structure is obtained, but X-ray examination shows the alloy to have a body-centred cubic lattice and not a tetragonal lattice like martensite. The quenched γ -phase has a hardness (H_B) of 145 and the α -phase produced from it by slip has H_B =270. Even on prolonged annealing at 1000° the α -phase is not completely converted into γ , but X-ray examination shows that the movement of the atoms in the lattice takes place along the same lines as in the $\alpha \rightarrow \gamma$ trans-

formation. The bearing of these factors on the equilibria in the Fe-Ni system is discussed.

A. R. P.

Liquid-vapour equilibria of mixtures of aromatic and non-aromatic hydrocarbons. IV. Mixtures of xylenes with non-aromatic hydrocarbons. M. MIZUTA (J. Soc. Chem. Ind. Japan, 1934, 37, 282B).—For mixtures of xylene and petrol (b.p. 120—150°) the v.p. are < those represented by the simple mixture rule. Xylene can be conc. in the liquid phase to any desired degree, but not so efficiently as C₆H₆ or PhMe. A. G.

Degree of dehydration of binary azeotropes. W. SWIENTOSLAWSKI (Compt. rend., 1934, 198, 2246—2247).—The b.p. of C₆H₆-EtOH, PhEt-EtOH, and CS₂-COMe₂ azeotropes are more sensitive to traces of H₂O than those of their constituent liquids. A differential ebullioscope will detect 10⁻⁵ to 3 × 10⁻⁶ g. H₂O, and suitable liquids can be dried to this extent by distillation. B. W. B.

Displacement of the azeotropic point of the ternary azeotrope C₆H₆-EtOH-H₂O as a function of pressure. W. SWIENTOSLAWSKI and B. KARPINSKI (Compt. rend., 1934, 198, 2166—2167).—Azeotropic data are tabulated for 1—19 atm.; vals. of dt/dp for the three corresponding binary azeotropes have also been determined. With increasing p , the % of C₆H₆ increases, that of H₂O decreases, and that of EtOH rises to a max. at 9.5 atm., and thereafter falls. B. W. B.

Liquid ammonia as solvent. II. Vapour pressures of solutions at 25°. H. HUNT and W. E. LARSEN (J. Physical Chem., 1934, 38, 801—807).—The v.p. of solutions of NH₄NO₃, NH₄Cl, NH₄Br, and NH₄I in liquid NH₃ at 25° has been determined over a wide range of concn. R. S. B.

Behaviour of the magnesium ion towards ammonia in aqueous solution. III. Solubility of certain salts in ammoniacal solution. IV. Equilibrium in ammoniacal magnesium salt solutions through the incomplete precipitation of magnesium hydroxide by ammonia. H. FREDHOLM (Z. anorg. Chem., 1934, 218, 225—234, 235—240).—III. The solubilities of 2-(C₁₀H₇·SO₃)₂Mg (I), Mg cinnamate (II), and MgC₂O₄ have been determined in aq. NH₃ of different concns. and the stability coeff. of the NH₃ complex has been calc. The changes in solubility due to changes in activity have been determined approx. by measuring the solubility of 2-(C₁₀H₇·SO₃)₂Ba and Ba(OBz)₂ in aq. NH₃ and of (I) and (II) in aq. MeOH which is physically similar to NH₃. The changes observed are negligible.

IV. The equilibrium $\text{Mg(OH)}_2 + 2\text{NH}_4^+ \rightleftharpoons \text{Mg} + 2\text{NH}_3 + 2\text{H}_2\text{O}$ has been investigated from both sides. The bearing of the results on the formation of complex NH₃ compounds is discussed. M. S. B.

Induced " solubility of ferric hydroxide and other hydroxides in alkali hydroxides in presence of chromic hydroxide. II. H. KNOCHE (Kolloid-Z., 1934, 67, 307—317; cf. this vol., 726).—When excess of alkali is added to a mixture of CrCl₃ and FeCl₃, both Fe(OH)₃ and Cr(OH)₃ are redissolved, giving a solution with colloid properties. The amount of Fe(OH)₃

peptised increases with the amount of alkali; KOH is more effective than NaOH. Dissolution does not occur when the Fe^{+++} content exceeds about 40%. Dry $\text{Fe}(\text{OH})_3$ is also peptised under the same conditions. When the amount of $\text{Fe}(\text{OH})_3$ is varied and the peptising liquid kept const., the observed behaviour is consistent with the phase rule. Alkali-free $\text{Cr}(\text{OH})_3$ sols have scarcely any peptising influence on $\text{Fe}(\text{OH})_3$. The active agent is probably the alkali chromite.

E. S. H.

Solubilities of organic oxygen compounds in sulphuric acid-water mixtures. L. P. HAMMETT and R. P. CHAPMAN (J. Amer. Chem. Soc., 1934, 56, 1282—1285).—The data refer to 0—90% H_2SO_4 at 25°. With increase of $[\text{H}_2\text{SO}_4]$, the solubilities at first decrease and then increase. The latter is not entirely due to ionisation or salt formation in the case of BzOH , $\text{CH}_3\text{Ph}\cdot\text{CO}_2\text{H}$, *o*- and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and $\text{C}_6\text{H}_5\text{PhBz}$ (I), since PhNO_2 , which is a weak electrolyte, exhibits similar phenomena. With BzOH a new phase appears with > 79% aq. H_2SO_4 and (I) affords an intensely yellow liquid with > 80% aq. H_2SO_4 . The other solutes do not exhibit changes of phase in the range investigated.

J. G. A. G.

Theory of absorption of gases by liquids flowing in thin layers. S. HATTA (J. Soc. Chem. Ind. Japan, 1934, 37, 275—277B).—The double-film theory of absorption applies only when both gas and liquid are in turbulent flow. The absorption when the liquid flow is stream-line is calc. with the aid of simplifying assumptions.

A. G.

Absorption of carbon dioxide by water flowing in a thin layer. S. HATTA and M. KATORI (J. Soc. Chem. Ind. Japan, 1934, 37, 280—282B).—The absorption of CO_2 by a flowing layer of H_2O agrees with the double-film theory when the flow is rapid. When the flow is slow and stream-line, the absorption is correctly expressed by the theoretical equations $C/C_s \propto \sqrt{x}$ and $C/C_s \propto (\sin \theta)^{1/6}$, in which C is the concn. of the outflowing H_2O , C_s the saturation concn., x the length of the surface, and θ its angle of slope.

A. G.

Vapour-binding power of active charcoal. IV. Dependence of the amount of bound vapour on the form of the charcoal layer. F. KROZIL and H. WEJROCH (Kolloid-Z., 1934, 67, 277—279; cf. this vol., 358).—The amount of bound vapour retained by Cafter the passage of an indifferent gas is independent of the form of the C layer.

E. S. H.

Absorption of hydrogen by nickel. J. SMITTENBERG (Nature, 1934, 133, 872).—Between 200° and 650° and pressures (p) up to 0.2 mm. there is no measurable adsorption of H_2 by thin Ni wire. Adsorption is appreciable, however, at higher p , and at const. temp. $\propto \sqrt{p}$. At const. p it increases with rise of temp. according to $\log a - A - B/T$. The calc. heat of absorption is somewhat < 3 kg.-cal. per g.-mol. of H_2 . Agreement with measurements (A., 1911, ii, 895) for thicker wire at higher temp. and p is good. L. S. T.

Absorptive power of palladium-boron alloys for hydrogen. A. SIEVERTS and K. BRUNING (Z. physikal. Chem., 1934, 168, 411—418).—Alloys with 2.5—16.6 at.-% B have been studied. Up to a B

content of 6.9 at.-% the alloys are homogeneous, whilst alloys with 13.8 and 16.6 at.-% are two-phase systems. The hardness is > that of Pd and increases with the proportion of B, rapidly at first and then more slowly. For all the alloys the absorptive power for H decreases with rising temp. At a given temp. the amount absorbed is approx. proportional to the square root of the pressure, except for alloys with 2.5 and 6.9 at.-% B below 500°. For an alloy with 2.5 at.-% B below 500° the isotherms resemble those for the system Pd-H. At 160—900° the absorption at 1 atm. passes through a max. at about 7 at.-% B. At 100° and 20° it falls continually with increasing % B.

R. C.

Coloured bromine adsorbates. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1934, 64, 114—122).—The following substances adsorb Br vapour to give more or less highly coloured products: $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (I), marble (3 varieties), fibrous Al_2O_3 , basic Al acetate, SiO_2 gel, $\text{Zr}(\text{OH})_4$, Sb_2O_3 (II), As_2O_3 (III), cotton, kapok, ramie, flax, and jute. A reaction occurs with (I), (II), (III), KI, CuI, S, keratin, and (probably) CsCl and RbCl. The remission curves of several of the products are given. MgO, ZnO, BeO, and basic Zn carbonate do not adsorb Br. The plant fibres behave more similarly towards Br than I (cf. this vol., 22, 358) in dry and moist atm.

H. B.

Adsorption of hydroxy- and amino-anthraquinones by cotton cellulose. K. BRASS and K. LAUER (Kolloid-Z., 1934, 67, 322—327).—Adsorption measurements in EtOH solution show the influence of the nature and position of the substituent groups. The following distribution coeffs. are recorded: 1-hydroxy- 1.88, 2-hydroxy- 1.29, homonuclear dihydroxy- 5.6—58.1, heteronuclear dihydroxy- 3.42—17.7, 1-amino- 70.0, 2-amino-anthraquinone 6.2.

E. S. H.

Surface tension and molecular volume of nitroglycerol. T. C. SUTTON and H. L. HARDEN (J. Physical Chem., 1934, 38, 779—781).—The surface tension of pure glyceryl trinitrate (I), determined by the bubble-pressure method, is 50.4 dynes per cm. at 20.5°; the same result is obtained by methods involving a stationary surface. From $d^{20}_5 = 1.595$ the parachor has been calc. to be 379.3 (mean), which agrees with the val. 378.9 derived from Sugden's consts. The parachors of (I) solutions in PhNO_2 have been determined and shown to be additive.

R. S. B.

Superficial properties of certain dyes. E. VELLINGER and R. DELION (Compt. rend., 1934, 198, 2084—2086).—The variation of the interfacial tension between 0.01% aq. bromothymol-blue (I) solutions and paraffin oil with the p_H of the solution suggests that the dissociation consts. of H_2O or of (I) are altered by differential adsorption of the ion and undissociated mol. of (I) at the interface.

B. W. B.

Study of adsorption at the benzene-sodium oleate solution interface. K. M. SEYMOUR, H. V. TARTAR, and K. A. WRIGHT (J. Physical Chem., 1934, 38, 839—851).—The adsorption of Na oleate at the aq. solution- C_6H_6 interface at 25° has been studied by dropping C_6H_6 through the aq. solution; the adsorption layer corresponds with 20—30 mols. calc. from

the gain of oleic acid and with 1—10 mols. calc. from gain of Na. Equilibrium and non-equilibrium solutions give similar results. R. S. B.

Laws of spreading of liquid drops on filter-paper. K. PROSAD and B. N. GHOSH (Current Sci., 1934, 2, 430).—The relations involved in the spreading of a single drop of liquid on filter-paper have been studied by experiments in a closed chamber containing saturated vapour. The velocity diminishes exponentially with the distance covered. L. S. T.

Mechanism of ascent of colloidal solutions in porous bodies. A. BOUTARIC (Compt. rend., 1934, 198, 2247—2250).—The height of ascent of the colloidal particles depends on their polarity relative to the wetted surface of the porous body, and is least when the signs are opposite. The surface tension of the intermicellary liquid is without effect. B. W. B.

Porosity determinations of dispersoids from the velocity of penetration of liquids. Z. V. VOLKOVA (Kolloid-Z., 1934, 67, 280—284).—An apparatus for measuring the penetration velocity of liquids in powders is described. The "mean penetration radius" r is defined as $-2l^2\eta/2t\sigma$, where l is the distance penetrated in time t . For a given powder r is const. for non-polar liquids, but is less for polar liquids, especially for H_2O . The decrease of r for polar liquids is ascribed to peptisation of the powder, orientation, or swelling. In the displacement of a non-polar liquid by H_2O the simple formula l^2/t is valid, as r for H_2O is very small. E. S. H.

Formation and properties of precipitates. Theory of coprecipitation. III. I. M. KOLTHOFF (Chem. Weekblad, 1934, 31, 395—400; cf. this vol., 727).—Imre's views on adsorption on crystal lattices are adversely criticised. Both Imre's and the author's experimental data lead to the conclusion that in the first stage the adsorbed ions displace ions of the same sign in the hydrated surface layer of the adsorbent; if of appropriate type these adsorbed ions may then exchange places with ions in the underlying lattice, but this is a relatively slow process. Paneth and Thimann's simple expression for calculating the sp. surface of ppts. from the adsorption of non-isotopic radioactive ions does not yield accurate results. H. F. G.

Structural changes taking place during the ageing of freshly formed precipitates. I. Ageing of lead sulphate precipitated at room temperature. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1934, 56, 1264—1269; cf. this vol., 594).—The sum of the external and internal surfaces of $PbSO_4$ freshly pptd. at room temp. from 0.1M- $Pb(NO_3)_2$ and 0.1M- K_2SO_4 is determined in terms of the adsorption of Th-B, and the magnitude of the external surface only is given by the adsorption of wool-violet. The crystals of the freshly formed ppt. are highly porous and all the Pb ions then behave as though present at the surface. An exceedingly rapid ageing occurs, resulting in the perfection of the internal structure of the pptd. crystals, and at the same time any adsorbed Th-B is incorporated. Growth of the crystals is evident only after long periods of ageing. The entire process is markedly

accelerated by digestion, especially in the presence of HNO_3 . J. G. A. G.

Liesegang rings. E. B. HUGHES (Biochem. J., 1934, 28, 1086—1106).—Occurrence of a ppt. in band formation during diffusion of one electrolyte into a solution of another of lower equiv. concn. is shown by experimental evidence to depend on: (1) the gradient of the concn. of the entering ion (I) and the resulting gradient on the ppt. front of the ion (II) contained in the medium; (2) removal of (II) by more (I) until diffusion of (I) again proceeds normally; (3) the rapid collection of the ppt. into a more closely defined zone; (4) the metastable solubility of the ppt.; (5) growth of the ppt. particles at the expense of the smallest. A theory of the formation of Liesegang rings is discussed. H. G. R.

Rhythmic precipitates. III. Effects of the presence of acids, alcohols, or amino-acids in gelatin jellies. T. ISEMURA (Bull. Chem. Soc. Japan, 1934, 9, 236—239).— $EtCO_2H$ and $PrCO_2H$ destroy the rhythmic bands of Ag_2CrO_4 in gelatin; hexoic and octoic acids give bands containing Ag soap. Alcohols increase, NH_2 -acids decrease, the no. of Ag_2CrO_4 bands. The formation of bands consisting entirely of Ag soap is also described. R. S. B.

Iridescence of old glasses. Formation of Liesegang strata by rhythmic precipitation of calcium carbonate in glass in contact with hydrogen carbonate solution. M. GUILLOT (Compt. rend., 1934, 198, 2093—2095).—The artificial production of iridescence (I) in glass is discussed. Contact with a no. of aq. solutions, particularly saturated $NaHCO_3$, at 15° , slowly produces (I) due to stratified $CaCO_3$ ptpn. B. W. B.

Equilibria at colloidal bounding phases in aqueous silicate systems. W. ERTTEL and H. E. SCHWIETE (Naturwiss., 1934, 22, 403—406).—The Donnan theory has been applied to the equilibria in aq. silicate systems in connexion with cements. A. J. M.

Statistical foundation of membrane equilibrium. A. GANGULI (Kolloid-Z., 1934, 67, 304—306).—Theoretical. E. S. H.

Exact thermodynamics of membrane equilibria. II. F. G. DONNAN (Z. physikal. Chem., 1934, 168, 369—380; cf. A., 1933, 127).—Equations are derived for the exchange equilibria of ions having charges of the same sign, the effect of non-diffusible non-electrolytes on the distribution of diffusible solutes, membrane potentials, and osmotic pressure. A new coeff., g , is introduced which can be regarded as a mean osmotic coeff. or mean activity index. R. C.

Colour and acid properties of α -naphtholphthalein. K. BUCH (Finska Kem. Medd., 1934, 43, 6—17).—Measurements have been made of the extinction curves of this indicator prepared by the method of Sorensen and Palitzsch, in 0.1N-HCl, 0.1N-NaOH, and some buffer solutions. By using light of two λ the curves for both the primary and secondary ions have been obtained. H. S. I.

Spectrophotometric investigation of α -naphtholphthalein. C. GUSTAFSSON (Finska Kem. Medd.,

1934, 43, 18—24).—The measurements made were similar to those in the preceding abstract, but the indicator was made by the method of Schulenburg.

H. S. P.

Osmometric investigations of dilute solutions of polymeric carbohydrates. V. State of solution of cellobiose and maltose octa-acetates in glacial acetic acid. M. ULMANN and K. HESS (Ber., 1934, 67, [B], 818—823; cf. A., 1933, 492).—Osmometric measurements show that maltose octa-acetate (I) in AcOH follows van 't Hoff's law down to the smallest concns. The osmotic pressure of solutions of cellobiose octa-acetate (II) in AcOH ($c > 0.5\%$) diminishes less rapidly than expected, and the decrease becomes \propto the concn. when $c \rightarrow 0.13\%$. The hypothesis that (II) forms a complex with AcOH which is appreciably dissociated at $c = > 0.5\%$ and completely dissociated at about $c = 0.1\%$ is supported by measurements of the conductivity of the solutions. The electrical behaviour of solutions of (I) and glucose penta-acetate in AcOH is normal.

H. W.

Dimensional relations in the theory of electrolytes. A correction. P. VAN RYSELBERGHE (J. Chem. Physics, 1934, 2, 350; cf. this vol., 25).

H. J. E.

Magnetic investigation of the mutual influence of potassium iodide and water in solution. H. CARRERA and H. FAHLENBRACH (Z. Physik, 1934, 89, 166—178).—Hydration of KI and depolymerisation of H_2O with increasing concn. of HI have been followed by measurements of magnetic susceptibility. The influence of temp. has also been studied; hydration at room temp. is small for all concns.

A. B. D. C.

Strong electrolytes as dispersion media. A. VOET (Rec. trav. chim., 1934, 53, 818—819).—Sols of metal sulphides, halides, etc. have been prepared by electro-dispersion in conc. H_2SO_4 , H_3PO_4 , saturated aq. KOAc, and other media. The particles appear to have no electrokinetic potential and exhibit spontaneous reversible coagulation.

E. S. H.

Preparation of colloid solutions by the silent electric discharge. S. MIYAMOTO (Kolloid-Z., 1934, 67, 284—288).—Compounds of Au, Ag, Pt, etc. are reduced by H_2 under the influence of the silent electrical discharge. The properties of hydrosols of Au, Ag, Pt, and of sols of Ag and Au in EtOH, Bu^iOH , and amyl alcohol, prepared in this way, are described.

E. S. H.

Mechanism of the formation of aurosols Au_F (Zsigmondy), and the part played by traces of sodium sulphide. R. WERNICKE and R. B. LOSSON (Anal. Assoc. Quim. Argentina, 1934, 22, 5—10).—Alkaline solutions of $HAuCl_4$, when boiled or kept in the cold for some hr., form colloidal particles which accelerate the reducing action of CH_2O . Traces of Na_2S in solutions of $HAuCl_4$ form colloidal particles u_2S_3 , which form aurosols by reduction with H_2O . Na_2S inhibits reduction by CH_2O of solutions in which $HAuCl_4$ has been completely converted into uO_2 , or when present in excess.

R. N. C.

Structure of colloidal particles. III. Electrochemical properties of atacamite. I. N. PUTILOVA. IV. Electrochemical study of atacamite

sols. A. A. MOROZOV (J. Gen. Chem. Russ., 1934, 4, 80—85, 86—103).—III. The concn. of $Cu(OAc)_2$ (I) in the intermicellar fluid (II) of saturated atacamite (III) sols is 0.00288%. The fall in conductivity, κ , of (III) sols on dilution with H_2O is $<$ that found on similar dilution of (II), pointing to passage of (I) from (III) to (II) on dilution. The micellar wt. of (III) in its saturated sols in presence of excess of (I) is approx. 150,000, and the constitution of the micelle is $[[Cu(OH)_2Cu^+]OH \cdot Cl]_{292} \{Cu(OAc)_2\}_{22} Cu^{++}]_5$. The fall in κ of (III) sols when diluted with 0.001*N*-(I) is explained by peptisation of (III), with adsorption of (I) on the fresh surfaces formed.

IV. The κ of (I)-NaCl solutions falls at first rapidly, and then more slowly, corresponding with the formation of particles of (III), and their subsequent aggregation. (III) sols are reversibly coagulated by $> 0.08N$ -NaCl, and irreversibly by 0.00025*N*- Na_2SO_4 . In presence of excess of NaCl the structure of the micelles of (III) is

$n[Cu([OH]_2Cu)_3]Cl_2, xCuCl_2, mCu^{++}2mCl$. R. T.

Concept of "eucolloids." W. OSTWALD (Kolloid-Z., 1934, 67, 330—333).—A discussion of nomenclature.

E. S. H.

Rates of coagulation. I. Autocatalysis and sol purity. F. C. HILDEBRAND and C. H. SORUM (J. Physical Chem., 1934, 38, 809—816).—The coagulation-time curves of highly purified Fe_2O_3 sols in the presence of NaCl, Na_2SO_4 , and Na_3PO_4 have been determined, and show no induction period and no autocatalytic character. The rate corresponds with the second order.

R. S. B.

Ionic interchange in sulphur sols. III. Mechanism of coagulation. T. R. BOLAM and J. J. MUIR (J.C.S., 1934, 754—766; cf. A., 1933, 1011).—The influence of temp., presence of EtOH, nature of cation and anion, acidity, and sol concn. on the ionic interchange and the coagulation vals. of salts has been examined. The coagulative action of a salt is closely related to the replacing capacity of the cation. It is supposed that coagulation is due to diminution of the actual charge on the S surface by the formation of non-ionised mols. or complexes between the coagulating cations and the micellar polythionic anions. H_2SO_4 is adsorbed on colloidal S, but the stability is not increased.

R. S.

Nature and amount of non-diffusible calcium in protein sols. D. M. GREENBERG (J. Biol. Chem., 1934, 105, 511—513).—The results of Eversole *et al.* (this vol., 253) are criticised on the ground that the Ca electrode used is untrustworthy.

H. D.

Nature and amount of non-diffusible calcium in protein sols. W. G. EVERSOLE (J. Biol. Chem., 1934, 105, 515—518).—A reply to Greenberg (preceding abstract).

H. D.

Osmotic pressure of serum-albumin. W. PAULI and P. FENT (Kolloid-Z., 1934, 67, 288—304).—A modification of the apparatus of Krogh and Nakazawa (A., 1927, 1104) is described; the procedure enables accurate vals. of osmotic pressure P to be obtained with 0.4 c.c. of liquid. For highly-purified, electrolyte-free, non-crystallised serum-albumin P is a linear function of concn.; the mol.

wt. derived is 59,000. In presence of 0.125*N*-KCl the *P*-concn. curve shows a pronounced upward bend.

E. S. H.

Denaturation of proteins. XIV. Titration curves of natural and heat-denatured ovalbumin. C. Y. CHOU and H. WU (Chinese J. Physiol., 1934, 8, 145—152).—Aq. re-cryst. (I) and denatured (II) (by heating at 90—95° for 30 min. at p_H 7) ovalbumin were treated with varying amounts of standard HCl and NaOH and the amounts of bound acid and base determined. The data indicate an isoelectric point (III) of 4.75 for (I) and of approx. p_H 4.80 for (II). The titration curve for (II) has an inflexion at (III) and deviates from the curve of (I) on the acid side between (III) and p_H 3 and on the alkaline side between (III) and p_H 8; thus denaturation of aq. (I) at p_H 7 gives aq. (II) of p_H 7.25. The curves are compared with those previously obtained (cf. A., 1929, 459, 508; 1932, 181).

F. O. H.

Colloidal behaviour of sericin. I. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 207—221).—The solubility in H₂O at t° of sericin prepared from silk is given by $S = A t^K$, where A and K are consts.; K changes at 60° and 90°. According to viscosity (η) data the mol. wt. of sericin in various batches varies from 4026 to 2382. Owing to gelatinisation η changes with time. The effect on η of the addition of acids and salts, and of variation in temp. is recorded. Results for different batches are correlated with the wt. of raw silk reeled per hr.

R. S. B.

Lyophilic colloids. III. Solvation of cellulose acetate. S. M. LIEPATOV and Z. A. PREOBRAZENSKAJA. **IV. Hydration of the various fractions of gelatin.** S. M. LIEPATOV and I. N. PUTILOVA (J. Gen. Chem. Russ., 1934, 4, 59—72, 73—79).—III. Measurements of the osmotic pressure and viscosity, and of their temp. coeff., of cellulose acetate (I) sols in MeOAc suggest that of the total quantity of solvent bound with (I), >20% is chemically combined. The large increase in the vol. of the disperse phase points to considerable solvation, chiefly due to osmotic imbibition by the micelles. The identical heat of dissolution of samples of (I) of high and low mol. wt. supports the view that intramolecular chemical combination with the solvent takes place.

IV. Osmometric measurements of gelatin (II) sols indicate that the mol. wt. of the fraction (III) of (II) which is insol. in cold H₂O falls from 141,000 to 32,000, whilst that of the sol. fraction (IV) decreases from 44,700 to 26,500 as the temp. rises from 20° to 40°. Hydration appears to be absent at 40°. The heat of imbibition of (III) is equal to that of dissolution of (IV), pointing to chemical combination of approx. 0.18 g. of H₂O per g. of (II).

R. T.

Lyophilic colloids. XXI. Coacervation. I. Simple coacervation of gelatin sols. L. W. J. HOLLEMAN, H. G. B. DE JONG, and R. S. T. MODDERMAN (Kolloid-Beih., 1934, 39, 334—420; cf. this vol., 27).—A comprehensive survey of published and new work on coacervation is made, with particular reference to the systems (a) gelatin-H₂O-Na₂SO₄ at 50°, (b) gelatin-H₂O-EtOH at 50°, and (c) gelatin-H₂O-resorcinol at 45°. The composition of the co-existing liquid layers has been determined,

adsorption measurements have been made with gels and coacervates, and the mechanism of the processes preceding coacervation is examined. Viscosity determinations show that coacervation occurs when the viscosity val. of the dispersed material is reduced to about one half. The upper liquid layer is never free from colloid, although its concn. may be very low. The kinetics and theory of coacervation are discussed.

E. S. H.

Diffusion of electrolytes in silica gel. W. A. PATRICK and B. W. ALLAN (J. Physical Chem., 1934, 38, 771—778).—(a) Methods of prep. of gels of silicic acid impregnated with salts are described. On dialysis salts are retained more tenaciously by gels containing a large excess of HCl. (b) Discs of SiO₂ gel, which can be dried without shattering, have been prepared, and the rates of diffusion through them of salt solutions have been determined. The diffusion of salt is diminished by the presence of HCl, and the diffusion of HCl is increased by the presence of salts, which is in accord with the experiments (a).

R. S. B.

Effect of non-electrolytes on diffusion in gelatin gels. L. FRIEDMAN and W. N. SHEARER (J. Amer. Chem. Soc., 1934, 56, 1323—1324; cf. A., 1930, 693).—The rate of diffusion (I) of CO(NH₂)₂ (II) into 3% gelatin gel at 5° rises to sp. max. with increasing concn. of glycerol, sucrose, (II), MeOH, and glucose and then falls below the initial val. with 0.08—0.18*M* non-electrolyte. It appears that the non-electrolytes accelerate (I) by enlarging the pore size owing to decreased hydration of the solid phase and retard (I) by increasing the viscosity of the medium.

Action of electric current on fields of diffusion in colloidal gels. J. SWYNGEDAUF (Compt. rend., 1934, 198, 2098—2100).—Gelatin or gelose films 2—3 mm. thick spread on glass were cut into three segments by two parallel channels, and an e.m.f. was applied to the two outer segments. The channels were filled with various electrolytes and the swelling or contraction of the films was studied at various p_H vals. (cf. Veil, A., 1932, 226).

B. W. B.

Influence of lipins on the elasticity of gelatin gels. P. BAMBERGER (Biochem. Z., 1934, 270, 366—377).—The effect on the elasticity of pure ash-free gelatin of [H⁺], neutral salts, and lipins is investigated. The vals. in the neighbourhood of the isoelectric point show a flat max., displacement of p_H to 3.8 or 6.9 resulting in a sharp fall. Cl⁻ and I⁻, lecithin, and Na taurocholate also decrease, whilst SO₄²⁻ increases, the elastic properties, and cholesterol antagonises the effect of lecithin. The results are discussed in relation to changes in muscle contraction (cf. A., 1933, 1318).

P. W. C.

Inhibitive power of gelatin. B. N. DESAI and B. M. NAIK (J. Univ. Bombay, 1933, 2, No. 2, 90—110; cf. this vol., 598).—The inhibitive power (I) of gelatin is a min. at p_H 5.75 with respect to Ag₂CrO₄. Changes in (I) and in the gold nos. of hydrolysed or electro-dialysed gelatin are due to changes in p_H . (I) decreases with p_H for AgI, but is a max. at p_H 7.1 for PbI₂. In all cases, the plot of log. gelatin concn. against log. time of inhibition is a straight line.

R. S.

Rhythmic cracking of silica gels in contact with hypertonic solutions. W. G. EVERSOLE and E. W. DOUGHTY (J. Amer. Chem. Soc., 1934, 56, 1263).—Two types of cracks develop in rectangular cells. Type (i) consists of a main cleavage plane parallel to the two faces of the cell and small lateral cracks perpendicular to this plane. In type (ii), the main cleavage has a wave form and lateral cracks are absent. In cylindrical cells, type (ii) only occurs.

J. G. A. G.

Complex relations in lyophilic colloidal systems. V. Auto-complex flocculation of carrageen mucilage sol. VI. Auto-complex flocculation of linseed mucilage sols and examples of auto-complex fibrils. H. G. B. DE JONG and P. VAN DER LINDE (Rec. trav. chim., 1934, 53, 737—746, 747—759; cf. this vol., 731).—V. The coagulation effected by neutral salts in aq. and aq.-COMe₂ solutions is similar to the auto-complex coacervation described for other negatively-charged hydrophilic colloids, although the coagula do not possess a coacervate nature and are formed of fibrillar elements.

VI. Similar coagulation phenomena are observed in the action of neutral salts on linseed sols in aq. and aq.-COMe₂ solutions. In certain circumstances the separation of fibrils can be observed; it is probable, therefore, that the "amorphous" coagula are also fibrillar.

E. S. H.

Plant colloids. XXXVI. Preparation and degree of dispersion of erythro-substances from potato starch. XXXVII. Particle size of amyloses and their degradation products [formed] by acetylation, heating, and ageing. M. SAMEC and L. KNOP. XXXVIII. Roast dextrins. M. SAMEC and M. FORSTER (Kolloid-Beih., 1934, 39, 421—437, 438—463, 464—468).—XXXVI. The degree of dispersion of several erythro-products obtained in different ways from starch has been determined by measurements of diffusion and osmotic pressure. The products are polydisperse and the mean mol. wt. varies between 1700 and 534,000. Since all these substances are coloured red by I, there is no relation between this reaction towards I and the mol. wt.

XXXVII. Acetylation and subsequent deacetylation has little effect on some amyloses, whilst in certain amyloses the mol. wt. is reduced, although not to the limit of crystalloid dimensions. When amylose is heated in C₁₀H₈ at < 285° the products resemble the original substance in general properties, but the mol. wt. decreases as the duration of heating is prolonged. The products formed at 305° have greater reducing power and behave differently towards I.

XXXVIII. The degradation products of amylose form larger particles on ageing, but do not revert to the original substance. The viscosity and degree of hydration are lower.

E. S. H.

Plant colloids. XXXIX. Thread-drawing power of starch solutions. M. SAMEC and B. BUDANKO (Kolloid-Z., 1934, 67, 258—264; cf. this 637).—Thread-drawing power (I) is observed fairly conc. starch solutions and in amylopectin fractions, but not in amylose solutions. The length

of the thread decreases with rising temp. and increases with increasing concn. up to a certain val. The (I) of amylopectin varies with the kind of starch used and is highest in the most strongly hydrated forms; (I) is increased simultaneously with the degree of hydration by adding alkali. Amyloses exhibit (I) when combined with EtOH and NaOH. The factors involved are association and solvation. E. S. H.

Physical chemistry of starch and bread-making. XV. Sharp lower temperature limit of peptisation and its variability for the individual granules of a sample of starch. J. R. KATZ and E. A. HANSON. XVI. Repeptisation of retrogressed starch paste (in relation to the organised structure of the starch granule). J. R. KATZ and J. C. DERKSEN. XVII. Attempts to render the organised structure of the starch grain microscopically visible, particularly in lintnerised starch. E. A. HANSON and J. R. KATZ (Z. physikal. Chem., 1934, 168, 321—333, 334—338, 339—352; cf. this vol., 145).—XV. In the peptisation of starch with H₂O there is a well-defined lower temp. limit, *T*, below which peptisation does not occur even with much H₂O. In a sample of starch, *T* varies from one granule to another, and is the lower the smaller is the size of the granule. The frequency curve of *T* is characteristic of the sample, and the mean val. of *T* depends on the variety of starch. Apparently each granule has an organised structure which opposes swelling in peptisation and must be broken down for dispersion to occur. At 20° there are considerable differences between the amounts of Congo-red adsorbed from very dil. aq. solution by various starches. If the starch is previously heated the adsorption increases, apparently running parallel with the no. of granules which have become isotropic; even below *T* the granules have been changed by heating.

XVI. Starch which has been peptised and then retrogressed undergoes repeptisation at a much lower temp. than the native starch. Peptisation probably consists in conversion into a more voluminous and highly hydrated phase and the breakdown of the organised structure of the granule, which resists swelling.

XVII. Maceration experiments with aq. HCl at room temp. have shown that the starch granule consists of doubly-refracting, approx. isodiametric, cryst. blocks of about 1 μ in size disposed in tangential layers and also exhibiting a radial arrangement. The spaces between these units are occupied by another substance, perhaps amylopectin. The granules, of potato starch at least, also have an external membrane. R. C.

Equilibria between hydrocarbons. VI. A. A. VEDENSKI and S. G. VINNIKOVA. VII. A. V. FROST (J. Gen. Chem. Russ., 1934, 4, 120—123, 124—131).—VI. The equilibrium consts. for C₂H₄+H₂ C₂H₆ have been determined at 510° (Pd catalyst) and at 500° (Cr₂O₃ catalyst).

VII. The sp. heat, entropy, and ϕ' -potential of C₂H₄ and C₂H₆ calc. from spectroscopic data are in good agreement with the experimental vals. R. T.

Equilibrium between carbon monoxide, hydrogen, formaldehyde, and methyl alcohol. II. Reaction CO + 2H₂ CH₃OH. R. H. NEWTON

and B. F. DODGE (J. Amer. Chem. Soc., 1934, 56, 1287—1291; cf. this vol., 146).—The equilibrium has been studied by a dynamic method with Cu-Zn catalysts at 225°, 250°, and 275° and 3 atm. The products are essentially H₂O and MeOH. The data accord with $\log_{10} K_p = 3724/T - 9.1293 \log_{10} T + 0.00308T + 13.412$, which is based on thermal data.

J. G. A. G.

Colour and nature of iodine solutions in different solvents. E. CHIRNOAGA and (Mlle.) E. CHIRNOAGA (Z. anorg. Chem., 1934, 218, 273—300).—Observations on the dialysis of solutions of I in KI show that these are kryptocolloidal, containing I in the form of amicrons invisible in the ultramicroscope. The adsorption of I' by I has been determined and the rate of cataphoresis measured. The violet solutions only are true solutions of I and the change from violet to brown is accompanied by a change of structure resulting in a colloidal solution containing numerous micelles. By the action of alkaloids, especially quinine and cinchonine, on the violet solution, a brown colloidal solution containing numerous ultramicros is obtained. Irradiation by ultra-violet light produces a similar effect which is reversed when the radiation ceases.

M. S. B.

Hydrolysis of iodine monochloride. F. A. PHILBRICK (J. Amer. Chem. Soc., 1934, 56, 1257—1259).—The hydrolytic equilibrium represented by $5\text{ICl}_2' + 3\text{H}_2\text{O} \rightleftharpoons 2\text{I}_2 + \text{IO}_3' + 6\text{H}^+ + 10\text{Cl}'$ has been examined in < 0.07*N* solution at 25°. In chloride solution, I monochloride is present chiefly as ICl_2' which dissociates into I' and Cl' with increasing dilution. This dissociation is negligible in conc. HCl.

J. G. A. G.

Displacement of selenium by sulphur. M. LEMARCHANDS and M. BRUTEL (Bull. Soc. chim., 1934, [v], 1, 388—390).—S displaces Se from SeO₂ dissolved in H₂SO₄: $2\text{S} + 3\text{SeO}_2 \rightleftharpoons 3\text{Se} + 2\text{SO}_3$. The reaction is too slow to be observed below 87°. At 100° the reaction reaches equilibrium in < 50 min., giving a green solution of Se in H₂SO₄. With rising temp. the equilibrium moves to the left, the reaction from left to right being exothermic. The heat of reaction of S on SeO₂, as calc. from thermochemical data, is approx. 18,800 g.-cal., and from van 't Hoff's relation it is 16,000 g.-cal. between 100° and 130°. No replacement of Se by S in Na₂SeO₃ has been observed.

M. S. B.

Electron-sharing ability of organic radicals.

VII. Dissociation constants of organic acids and amines in water, methanol, and ethanol. L. D. GOODHUE and R. M. HIXON (J. Amer. Chem. Soc., 1934, 56, 1329—1333).—Measurements have been made in MeOH at 25° by methods analogous to those used for aq. solutions (a vac. tube potentiometer arrangement is used to eliminate the high internal resistance). pK_a and pK_b vals. are: AcOH 9.34, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ 9.33, BzOH 9.12, $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{H}$ 8.74, $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ 8.57, NH_2Bu^+ 4.92, $o\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\cdot\text{NH}_2$ 6.61, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ 10.0, NH_2Ph 10.53, $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ 12.14, and 2-cyclohexyl- 4.89, 2-benzyl- 5.42, 2-*p*-tolyl- 5.68, and 2-phenyl- 5.83, -pyrrolidines. Calc. vals. for RCO₂H and NH₂R in H₂O, MeOH, and EtOH agree generally with the

determined vals. (above; Goldschmidt *et al.*, A., 1922, ii, 135; 1924, ii, 825; 1926, 577).

H. B.

Influence of sugars on the dissociation of boric acid. F. J. BERENSCHTEIN and L. N. AJZENBERG (Ukrain. Chem. J., 1933, 8, 307—315).—Fructose (I) has practically the same effect as mannitol in augmenting the dissociation of H₃BO₃ (II); the magnitude of the effect is greatest with 2 mols. of (I) per mol. of (II), and increases with the concn. Sucrose has no action, whilst that of maltose, lactose, glucose, erythritol, and galactose increases in the order given, being, however, considerably < that of (I).

R. T.

Molecular size and phase distribution. III. J. N. BRÖNSTED and P. COLMANT (Z. physikal. Chem., 1934, 168, 381—390; cf. A., 1931, 1119, 1221).—Equations are derived for the activity coeffs. of the components of binary mixtures of non-electrolytes. These have been tested by v.-p. measurements for binary mixtures of Buⁿ-valerate and Buⁿ-sebacate with C₆H₆ and PrBr.

R. C.

Activity. The cell Pb amalgam|PbSO₄|CuSO₄|Cu amalgam. A. LEBETTRE (J. Chim. phys., 1934, 31, 348—360).—The amalgam in each case consists of two phases and the e.m.f. remains const. so long as [Pb] lies between 2 and 6% and [Cu] between 3 and 5%. For concns. of CuSO₄ < 0.01*M*, Debye's theory, as modified by La Mer and others, is applicable. Experimental verification is not possible below 0.001*M* because the solubility of PbSO₄ then becomes important. The ionic radius is approx. 2.4 Å., but increases slightly with rise of temp. The results verify Quintin's conclusions (A., 1933, 468, 781).

M. S. B.

Free energy of formation of lead amalgams. C. S. HOYT and G. STEGEMAN (J. Physical Chem., 1934, 38, 753—759).—From measurements of the e.m.f. of cells Pb|PbSO₄|ZnSO₄|PbSO₄|PbHg (satd.) and PbHg (unsatd.)|PbSO₄|ZnSO₄|PbSO₄|PbHg (satd.), the free energy of formation of Pb amalgams, and the activities of Pb and Hg, up to a mol. fraction of approx. 0.5, have been computed. The amalgam is saturated at 0.0142 mole fraction Pb, and all amalgams between this concn. and 0.66 have the same potential (same solid phase present). The heat of dissolution of Pb in unsaturated amalgams has been calc. from the temp. coeff. of the e.m.f.

R. S. B.

Thermodynamic properties of fused salt solutions. VIII. Lead chloride in silver chloride. E. J. SALSTROM (J. Amer. Chem. Soc., 1934, 56, 1272—1275).—The e.m.f. of the cell Ag(s)|0.0—0.9 mol. fraction PbCl₂ in AgCl(l)|Cl₂(g) has been determined in the range 460—620°, and vals. of the activity, activity coeff., free energy and heat of formation, and partial mol. free energy are calc. for 500° and 600°. The activity of AgCl is in accord with Raoult's law in the range studied. The density of equimol. mixtures in the range 428—576° is given by $5.547 - 0.00128t$ and the contraction on mixing is < 0.2% at 500°.

J. G. A. G.

Free energy change in the reaction between nitrogen peroxide and solid potassium chloride. C. W. WHITTAKER and F. O. LUNDSTROM (J. Amer. Chem. Soc., 1934, 56, 1323).—The most recent data

lead to -6042 and -5502 g.-cal. for the free energy change in the reaction $\text{KCl}(s) + 2\text{NO}_2(g) = \text{KNO}_3(s) + \text{NOCl}(g)$. J. G. A. G.

Lattice energies of ferrous halides and the nature of the radical $\text{Fe}^{\text{II}}(\text{CO})_4$. W. HIEBER and E. LEVY (Z. Elektrochem., 1934, 40, 291—295; cf. this vol., 734).—Theoretical. In the $\text{Fe}(\text{CO})_4$ halides the entry of CO does not appreciably affect the state of polarisation of the halogen atoms. The observed gradation of stability from Cl to I is adequately accounted for by lattice expansion.

F. L. U.

Heats of dilution of salts. (Mlle.) M. QUINTIN (Compt. rend., 1934, 198, 1856—1858).—An expression is derived for the mol. heats of dilution (I) of an electrolyte in terms of the temp. coeff. of e.m.f. and applied to the case of CuSO_4 (cf. A., 1933, 468, 781; this vol., 367). Vals. of partial and integral (I) are tabulated and compared with theoretical and calorimetrically determined vals.

B. W. B.

Thermal dissociation of certain oxides and peroxides. VI. Rubidium and caesium peroxides. M. BLUMENTHAL (Rocz. Chem., 1934, 14, 233—238).—Data for the oxides Rb_2O_2 , m.p. 570° , Rb_2O_3 , m.p. 489° , Rb_2O_4 , m.p. 412° , Cs_2O_2 , m.p. 594° , Cs_2O_3 , m.p. 502° , and Cs_2O_4 , m.p. 432° , indicate that the reactions $2\text{M}_2\text{O}_4 \rightleftharpoons \text{O}_2 + 2\text{M}_2\text{O}_3$ and $2\text{M}_2\text{O}_2 \rightleftharpoons \text{O}_2 + 2\text{M}_2\text{O}$ are reversible only within certain temp. limits, above which association does not take place. R. T.

Thermal analysis of picrates. III. T. TUCHOLSKI (Rocz. Chem., 1934, 14, 259—267).—Dehydration, fusion, and explosion temp. of the picrates of Cr, Mn, Fe^{II} , Fe^{III} , Co, and Ni are recorded. The following hydrates are indicated: $\text{Cr}_2\text{H}_2\text{O}$, $\text{Co}_8\text{H}_2\text{O}$, $\text{Ni}_4\text{H}_2\text{O}$, Fe^{II}_4 and $5\text{H}_2\text{O}$, $\text{Fe}^{\text{III}}_2\text{H}_2\text{O}$. The hydrates Co_5 and $9.5\text{H}_2\text{O}$, Ni_2 , 8, and $9.5\text{H}_2\text{O}$, and $\text{Fe}^{\text{II}}_2\text{H}_2\text{O}$, recorded by other authors, are not confirmed.

R. T.

System methyl thiocyanate-cobalt thiocyanate. J. GILLIS and A. DE SWEEMER (Natuurwetensch. Tijds., 1934, 16, 44—46).—The system shows a eutectic at -61.2° and 21.9% $\text{Co}(\text{CNS})_2$, and a compound $2\text{MeCNS} \cdot \text{Co}(\text{CNS})_2$ which is stable in contact with saturated solution up to about 38° , and forms greenish-blue crystals which evolve MeCNS when exposed to the air.

H. F. G.

Thermal analysis of mixtures containing trinitrotrimethylenetriamine. T. URBAŃSKI and I. RABEK-GAWROŃSKA (Rocz. Chem., 1934, 14, 239—245).—Neither solutions nor compounds are formed in the systems trinitrotrimethylenetriamine- $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$, $-p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, $-1\text{-C}_{10}\text{H}_7 \cdot \text{NO}_2$, $-m\text{-C}_6\text{H}_4(\text{NO}_2)_2$, $-s\text{-C}_6\text{H}_3(\text{NO}_2)_3$, $-C_6\text{H}_3(\text{NO}_2)_3 \cdot \text{OH}$, tetryl, $\text{NPh}_2 \cdot \text{CO} \cdot \text{N}(\text{Et})_2$, $\text{NPh}_2 \cdot \text{CO} \cdot \text{NMe}_2$, camphor, and NHPh_2 .

R. T.

System water-ether-alcohol. I. Freezing points. II. Densities at 0° . A. LALANDE (Bull. Soc. chim., 1934, [v], 1, 236—242).—Data are tabulated. No compound is formed between 0° and -125° .

D. R. D.

X-Ray study of the system nickel-oxygen-water. E. OTT and R. W. CAIRNS (Z. Elektrochem.,

1934, 40, 286; cf. A., 1933, 352).—A reply to criticisms by Le Blanc and Möbius (*ibid.*, 1013). The new lines observed relate to $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. F. L. U.

Heterogeneous equilibrium in ternary systems composed of organic compounds. T. ASAHINA (Bull. Chem. Soc. Japan, 1934, 9, 222—235).—Phase diagrams are given for the system $\beta\text{-C}_{10}\text{H}_7\text{OH}$ -methylenedioxybenzylideneacetophenone-picric acid.

R. S. B.

Reciprocal salt pair $\text{NH}_4\text{NO}_3 + \text{KCl}$ $\text{KNO}_3 + \text{NH}_4\text{Cl}$ at -10° and -15° . I. KRITSCHESKI and E. GOLDMANN (Z. anorg. Chem., 1934, 218, 253—254).—Equilibrium diagrams indicate that the prep. of KNO_3 from NH_4NO_3 and KCl at temp. below -10° is not technically practicable.

M. S. B.

Field of saturation with regard to potassium and sodium chloride in quinary sea-salt systems.

III. D. LANGAUER and W. OLPINSKI (Rocz. Chem., 1934, 14, 246—249).—Data at 83° and 95° are given for solutions saturated with respect to NaCl and KCl, and containing various proportions of MgCl_2 and MgSO_4 .

R. T.

Conductivities of dilute sulphuric acid solutions in anhydrous acetic acid [at 25°]. B. V. WEIDNER, A. W. HUTCHISON, and G. C. CHANDLER (J. Amer. Chem. Soc., 1934, 56, 1285—1287).—Anhyd. AcOH with sp. conductivity as low as 0.40×10^{-8} mho has been prepared. The mol. conductance of $0.35\text{—}0.059\text{M}$ H_2SO_4 in anhyd. AcOH is independent of the conductivity of the AcOH except at high dilutions (cf. A., 1933, 230).

J. G. A. G.

Iron complexes. II. Electrical conductivity of the system $n\text{FeCl}_3 \cdot m\text{H}_3\text{AsO}_4 \cdot x\text{H}_2\text{O}$. B. RICCA and R. LAMONICA (Gazzetta, 1934, 64, 294—296).—Conductivity data indicate the formation of the strong acid $\text{H}_3[\text{FeCl}_3(\text{AsO}_4)]'''$, the Ag salt of which has been isolated by pptn.

D. R. D.

Anhydrous hydrazine as an ionising medium for electrolytes and non-electrolytes. II. Behaviour of aromatic nitro-compounds and typical half-electrolytes. P. WALDEN [with H. HILGERT] (Z. physikal. Chem., 1934, 198, 419—467; cf. A., 1933, 907).—Conductivity measurements have been made at dilutions up to ~ 5000 litres for aromatic NO_2 -compounds, carboxylic acids, and phenols. The NO_2 -compounds form strongly coloured, highly conducting solutions, which obey Kohlrausch's square-root law and have conductivity-dilution curves similar to those of typical salts. The colour of the dil. solution is usually the same as that of the solid mol. compounds formed by the NO_2 -compound with aromatic amines. The vals. of λ_∞ for NO_2 -, $(\text{NO}_2)_2$ -, and $(\text{NO}_2)_3$ -compounds are approx. in the ratio 1 : 2 : 3, and approximate to those for the mono-, di-, and tri-carboxylic acids, respectively. Transport experiments show that the coloured ion is an anion and contains the NO_2 -compound. The process of ionisation apparently consists in the transfer of an electron from solvent to solute: $\text{ArNO}_2 + \text{N}_2\text{H}_4 \rightleftharpoons \text{ArNO}_2 \cdot \text{N}_2\text{H}_4 \rightleftharpoons \text{ArNO}_2' + \text{N}_2\text{H}_4'$, the solvate being formed by a semipolar linking effected by juxtaposition of NO_2 and the amino-residue. In solutions of carboxylic acids and phenols the ionisation is

$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}'$, $\text{H}^+ + \text{N}_2\text{H}_4 \rightleftharpoons \text{N}_2\text{H}_5^+$. The electrolytic character of NO_2 -compounds dissolved in N_2H_4 may be increased by substitution, e.g., of aromatic H by OMe or CO_2Me , to an extent which depends on the position of the substituent. R. C.

Platinum electrode. A. FRUMKIN and A. SCHLIGIN (Compt. rend. Acad. Sci., U.R.S.S., 1934, 2, 173—179).—Polarisation and adsorption data for Pt electrodes in H_2SO_4 are recorded and discussed. W. R. A.

Electrode capacity in the presence of foreign ions and the electrocapillary capacity of mercury. N. THON (Compt. rend., 1934, 198, 2149—2151; cf. this vol., 718).—A discussion of the effects of ions other than those of the electrode metal. The difference between the a.-c. electrode capacity of Hg and that deduced from (static) electrocapillary curves is attributed to hindrance of dipole orientation in the double layer. B. W. B.

Diffusion potentials between solutions of hydrogen and potassium chlorides. V. ČUPR (J. Chim. phys., 1934, 31, 326—347).—An apparatus for the determination of diffusion potentials is described. Quinhydrone electrodes are used and corr. for salt effect. The activity of H^+ in dil. HCl increases with the concn. of KCl, independently of the concn. of HCl when this is $< 1.0N$. HCl thus appears to be completely dissociated at these concns. and the diffusion potentials (I) between aq. HCl of different concns. below $1.0N$ can be calc. from Nernst's formula. Taking this into consideration, and neglecting (I) between aq. KCl of different concns., (I) between aq. HCl containing KCl may be calc. M. S. B.

Electrometric behaviour of thallium elements. L. W. ÖHOLM (Finska Kem. Medd., 1934, 43, 25—44).—Investigations have been made of Tl elements of the type $\text{Tl}|\text{Tl}^I$ salt, Hg^I salt|Hg, the negative pole being a rod of Tl for the SO_4^{--} and Cl^- cells and 55% Tl for the Br^- and I^- cells. Measurements over long intervals and at different temp. show that the e.m.f. tends to diminish with time and that the temp. coeffs. are positive. The differences in the heats of formation of the corresponding Tl^I and Hg^I salts are deduced and agree with thermal measurements. H. S. P.

Potentiometric study of photo-flavin. K. G. STERN (Biochem. J., 1934, 28, 949—964).—Photohepatoflavin (I) is a perfectly reversible redox system with a normal potential of -0.227 volt at $p_{\text{H}} 7.0$. At low p_{H} vals. there is a break in the titration curves, indicating that the oxidation takes place in two steps, the intermediate probably being a semiquinone. (I) appears to be identical with Warburg's photo-yeast-flavin. It is suggested that photoflavin is related to the alloxazine structure. C. G. A.

Polarographic studies with the dropping mercury cathode. XXXIX. Electro-reduction of some alkaloids. J. PECH. XL. Lowering of the hydrogen over-potential by some organic substances. P. HERASYMENKO and I. ŠLENDYK (Coll. Czech. Chem. Comm., 1934, 6, 190—202, 204—210).—XXXIX. The H overvoltage (I) in acid solutions is catalytically lowered 0.2 — 0.3 volt in

presence of the quinoline alkaloids (II), whilst *iso*-quinoline alkaloids (codeine, morphine) increase (I). In presence of NH_4^+ , H^+ is discharged catalytically in solutions of (II) about 0.4 volt more positive than NH_4^+ .

XI. The catalytic lowering of the H overvoltage by (II) is perceptible in high dilutions. With increasing voltage the "catalytic" current reaches a steady val., and normal deposition of H occurs. The effect is attributed to a reduction product of (II). J. S. A.

Electrolytic properties of hydrogen. I. Hydrogen as an anodic depolariser. II. Effect of anodic polarisation of the platinum electrodes. J. A. V. BUTLER and G. ARMSTRONG (J.C.S., 1934, 743—750).— H_2 liberated in the cathodic polarisation of bright Pt electrodes in H_2 -saturated solutions with small currents passes into the Pt. The H_2 in solution behaves similarly without cathodic treatment, but the process is slow. During subsequent anodic polarisation, there is a change at $e_{\text{H}} = +0.5$ volt, which is attributed to ionic dissolution of the H_2 contained in the Pt. No depolarisation effects could be traced to the H_2 of the solution. Successive anodic polarisations of a bright Pt electrode to $+1.26$ volts, when adsorption of O_2 begins, produces depolarisation at the reversible H_2 potential. The effect is increased by stirring. Such an activated electrode is reversible and the cathodic current-voltage curve is linear. It is suggested that the thermionic work function of the Pt is reduced, and the adsorption and subsequent ionisation of H_2 facilitated by the anodic treatment, probably during the formation or reduction of the O_2 film. R. S.

Historical development of passivity research and critical discussion of different passivity theories. W. MACHU (Oesterr. Chem.-Ztg., 1934, 37, 109—112).

Activation energy of unimolecular reactions. H. GERSHINOWITZ and O. K. RICE (J. Chem. Physics, 1934, 2, 273—282).—Using the principle of microscopic reversibility, unimol. decomp. are considered from the point of view of the reverse reaction, which is a bimol. association. An explicit expression for the activation energy in terms of the energy of reaction and the thermal properties of the mols. is obtained. The calculation of the rate const. as a function of the pressure is discussed. N. M. B.

I. Determination of speed of flames and the temperature distribution in a spherical bomb from time-pressure explosion records. II. Determination of heat capacity of explosive gases. III. Heat capacity of gaseous ozone. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1934, 2, 283—290, 291—293, 294—295).—I. By the method described, flame speed can be evaluated at any moment during its progress from the centre of the bomb outwards, as well as the temp. in the unburned phase, the temp. immediately behind the flame front, the temp. gradient from the latter point to the centre, and the pressure in the bomb. The vol. occupied by the products for a given burned fraction can be found before and after expansion, and when combustion is complete. Data are tabulated for O_2 -

O₃ mixtures. The temp. gradient does not affect the sp. heat results as calc. from the final temp. found from the max. pressure by means of the gas laws (cf. A., 1933, 343, 350, 368).

II. An application of the method given above to the determination of heat capacity up to several hundred degrees is given. The method is applicable to easily decomposed gases and to CO₂ at high and low temp.

III. Using the above method the heat capacity of O₃ in the range 300—476° abs. is 10.94 g.-cal. per mol., against the val. 10.39 obtained from band spectra. Causes of the discrepancy are discussed. N. M. B.

Kinetics of reactions of heavy hydrogen. H. W. MELVILLE (Nature, 1934, 133, 947).—With excess H₂ at room temp. H¹ and H² atoms produced photochemically react with O₂ at the same speed. With excess of O₂ there is a difference due solely to collision frequency factors between the Hg atoms and the H₁, H¹H², H₂, and O₂ mols. In the hydrogenation of C₂H₂ and of N₂O and in the reduction of CuO by atoms there is no difference in the rate of reaction of the two isotopes. CuO is reduced at different speeds with H₁ and H₂, the separation decreasing with a rise in temp. In the H₂-O₂ reaction where chains are propagated separation occurs at higher temp.; at 339° with a 2:1 mixture at 5 mm. pressure, the rate of reaction for a 66% H₂ mixture is 1.26:1, falling to 1.10:1 at 421°. In the H₂-N₂O and H₂-C₂H₂ reactions no separation occurs. The results show that H¹ and H² atoms react at the same speeds in the gas phase, but where the determination of rate involves a mol. or interaction of an adsorbed atom on a surface, the greater reactivity of H₂ is due mainly to the difference in zero point energies of H₁ and H₂.

L. S. T.

Synthesis of tetradeuteromethane. H. C. UREY and D. PRICE (J. Chem. Physics, 1934, 2, 300).—The ratio of the velocities of the reactions of H₂O and H₂O with Al₄C₃ is approx. 23:1.

N. M. B.

Para-ortho-hydrogen conversion by the hydrogen iodide reaction and by iodine atoms. E. J. ROSENBAUM and T. R. HOGNESS (J. Chem. Physics, 1934, 2, 267—272).—From the rate of conversion, determined in presence of equilibrium concns. of HI and I₂, velocity coeffs. and collision efficiencies for the conversion by I atoms are calc., in agreement with Wigner's theoretical equation (cf. A., 1933, 1257).

N. M. B.

Explosion of CS₂-NO mixtures. III. J. A. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1934, 53, 760—768; cf. A., 1933, 355, 910).—A method for measuring the intensity of light as a factor of time during the explosion is described. The max. intensity is attained after about 1—2×10⁻² sec., depending on the conditions. In the mixture S₂:NO=1:2.25 at 14 cm. total pressure the velocity of propagation is about 3 m. per sec.

E. S. H.

Thermal decomposition of gaseous methyl iodide. E. W. R. STEACIE and R. D. McDONALD (Canad. J. Res., 1934, 10, 591).—The reaction proceeds at a measurable rate above 450°, but is too complicated to give any trustworthy data on the kinetics.

W

Homogeneous unimolecular decomposition of gaseous alkyl nitrites. II. Decomposition of ethyl nitrite. E. W. R. STEACIE and G. T. SHAW (J. Chem. Physics, 1934, 2, 345—348).—The thermal decomp. is homogeneous and of the first order between 190° and 240° and at pressures down to 5 cm. The main reaction is EtNO₂=NO+0.5MeCHO+0.5EtOH. The reaction rate is given by $k=1.39 \times 10^{14} e^{-37,700/RT}$ sec.⁻¹

H. J. E.

Induction periods in chemical reactions. Action of phosphorous acid on alkali bromate and iodate. P. NEOGI, B. N. SEN, and A. MUKHERJEE (J.C.S., 1934, 767—769).—The influence of concn. and temp., and the effect of the addition of alcohols, HCl, Na₂S₂O₃, S sol, and salts, on the induction period of the reduction of alkali bromates and iodates by H₃PO₃ have been determined. The reaction is homogeneous.

R. S. B.

Kinetic study of hydrolysis of esters by water. I, II. A. KIRRMANN (Bull. Soc. chim., 1934, [v], 1, 247—254, 254—259).—Hydrolysis of allyl pyruvate (I), Et pyruvate (II), allylidene acetate (III), and propylidene acetate (IV) proceeds in two concurrent ways, one unimol. and spontaneous (velocity coeff. k), the other with a velocity $\propto [H^+]$ (proportionality const. b). At 25°, for (I), $k=0.062$, $b=8$; for (II), $k=0.025$, $b=10$; for (III), $k=0.010$, $b=8$; and for (IV), $k=0.004$, $b=7$, the units being g.-mols., litres, and hr. These results support the view that an alkoxyl rather than an alkyl group is eliminated.

D. R. D.

Mechanism of substitution reactions. A. R. OLSON and F. A. LONG (J. Amer. Chem. Soc., 1934, 56, 1294—1299; cf. this vol., 35).—Assuming that *l*-chloro- (I) and *l*-bromo-succinic (II) acids have the same configuration and that configurative inversion occurs at every substitution, the following velocity coeffs. at 50° have been determined in aq. 2*N*-H⁺ solution using 0.178*M*-*l*-(I) and *l*-(II); (1) *l*-(II)=fumaric acid + H⁺ + Br⁻ 0.0000305 (g.-mol. per litre, min.), (2) *l*-(II)+Br⁻=*d*-(II)+Br⁻ 0.00164, (3) *l*-(I)+Cl⁻=*d*-(I)+Cl⁻ 0.0000106, (4) *l*-(I)+Br⁻=*d*-(II)+Cl⁻ 0.000047 and (5) *l*-(II)+Cl⁻=*d*-(I)+Br⁻ 0.000233. Within experimental error (approx. 1%) replacement without inversion does not occur.

J. G. A. G.

Chlorinated fatty acid soap. I. Neutralisation and substitution of chlorostearic acid by alkali. II. Surface tension of aqueous chlorostearic acid soap solutions. Y. TANAKA, R. KOBAYASHI, and T. TAKAYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 197B, 197—198B).—I. The rate of reaction between a chlorostearic acid (I) and alkali depends on the rate of substitution, as neutralisation of CO₂H is very rapid, and is given by $dz/dt=k(a-z)^4$, where a is the initial concn. of (I) and z that of chlorohydroxystearic acid (II) at time t ; $k=1.84$ —2.2 for (I) containing 33% of Cl, reacting at the b.p.

II. The surface tension of 0.25% aq. solutions of the Na salts of (I) and (II), containing varying amounts of Cl and OH, ranges from about 48.5 to 53 dynes per cm. at 22° (cf. 62.3 for 0.25% aq. Na stearate).

E. L.

Velocity of the reaction between sodium chloroacetate and sodium hydroxide. H. M. DAWSON and W. LOWSON (Proc. Leeds Phil. Soc.,

1934, 2, 544—548; cf. A., 1933, 1276).—Using equiv. quantities of reactants the reaction is bimol. In experiments at 25° in which the $\text{CH}_2\text{Cl}\cdot\text{CO}_2'$ was present in excess, k remained practically const. until 70% NaOH had been used, and then increased appreciably. On addition of NaCl the initial vals. of k were increased from 1.10 to 1.48×10^{-4} , but again an increase was observed when 70% NaOH had disappeared. The latter stages of the reaction cannot be represented by $\text{CH}_2\text{Cl}\cdot\text{CO}_2' + \text{OH}' \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2' + \text{Cl}'$. Available data for the hydrolysis of $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Na}$ (Dawson and Dyson, A., 1933, 234) suggest that reactions between $\text{CH}_2\text{Cl}\cdot\text{CO}_2'$ and H_2O , pairs of $\text{CH}_2\text{Cl}\cdot\text{CO}_2'$, and $\text{CH}_2\text{Cl}\cdot\text{CO}_2'$ and $\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2'$ play an important role when $[\text{OH}']$ is small. W. R. A.

Kinetics of the alkaline hydrolysis of the halogen-substituted acetates. H. M. DAWSON and E. R. PROCK (J.C.S., 1934, 778—783).—The velocity, v , of hydrolysis of $\text{CH}_2\text{X}\cdot\text{CO}_2\text{Na}$ ($\text{X}=\text{Cl}$ or Br) by NaOH at 45° is given by $v=v_A+v_B+v_C$
 $k_A[\text{CH}_2\text{X}\cdot\text{CO}_2'] + k_B[\text{CH}_2\text{X}\cdot\text{CO}_2'] + k_C[\text{CH}_2\text{X}\cdot\text{CO}_2']^2 + k_D[\text{CH}_2\text{X}\cdot\text{CO}_2'] + k_E[\text{CH}_2\text{X}\cdot\text{CO}_2']^2 + k_F[\text{CH}_2\text{X}\cdot\text{CO}_2']^2 + k_G[\text{CH}_2(\text{OH})\cdot\text{CO}_2']$,
 where $-k_D$ are const. Departures from the bimol. formula $v=v_A$ were observed and successfully interpreted for the late stages of hydrolysis in the absence of excess of alkali and for the initial stages with equiv. reactants. R. S. B.

Dilatometric studies in the hydrolysis of the 2:5-diketopiperazines and polypeptides. I. Alkaline hydrolysis of glycine and alanine anhydrides. M. SRINIVASAN and M. SREENIVASAYA (J. Biol. Chem., 1934, 105, 563—570).—Alkaline hydrolysis of glycine (I) and alanine (II) anhydrides is accompanied by an increase in vol. which is not in accordance with the NH_2 liberated; the divergence increases with the concn. of the alkali. Hydrolysis of (I) by $>0.01N$ -alkali is accompanied by a disruption of the resulting dipeptide which does not occur in the case of (II). H. G. R.

Velocity of detonation of solid explosives. R. SCHWOB (Compt. rend., 1934, 198, 1990—1992).—The expression $V=1/(m-n)$ (V =velocity of detonation, Δ =charge density, m and n are const.) is derived. Application to Friederich's results (B., 1933, 493) for four nitrated explosives gives agreement to approx. $\pm 2\%$ for Δ 0.25—1.5. B. W. B.

Initiation of the detonation wave in solid explosives. W. E. GARNER (J.C.S., 1934, 720—722).—A study of the rate of decomp. of solid PbN_6 shows that the simultaneous decomp. of two adjacent mols. is an event possessing a probability of the same order as that of detonation, whereas simultaneous decomp. of >2 adjacent mols. has a smaller probability. The no. of mols. forming a detonation centre cannot, therefore, exceed two. The character of the reaction interface in the detonating solid determines the rapidity with which the detonation wave is set up; e.g., Hg fulminate gives a diffuse interface, whereas that of PbN_6 is quite sharp, in agreement with their sp. explosive properties. A chain theory of the thermal decomp. of solid explosives is supported, and it is suggested that detonation occurs when two reaction chains intersect. O. J. W.

Calculation of heterogeneous reaction rates. [Decomposition of ammonia.] R. E. BURK (J. Amer. Chem. Soc., 1934, 56, 1279—1282).—The observed energy of activation of the decomp. of NH_3 (47,000—48,000 g.-cal. per mol.) at 1260—1480° abs. on W filaments "aged" at 2400° abs. for 1 hr. in vac. is consistent with the decomp. occurring uniformly on the dodecahedral faces of the W (A., 1933, 1098), and at such a rate that almost every vibration of the underlying W atoms with the requisite energy of activation leads to reaction. The effects of various factors not included in the calculation are considered. J. G. A. G.

Diatomaceous earth; equilibrium and rate of reaction in the system hydrated lime-diatomaceous silica-water. A. B. CUMMINS and L. B. MILLER (Ind. Eng. Chem., 1934, 26, 688—693).—Diatomite (I) reacts with $\text{Ca}(\text{OH})_2$ more rapidly than other forms of SiO_2 , the liquid phase containing at equilibrium $\text{CaO}:\text{SiO}_2=2:3$, whilst the limit composition of the solid is $5\text{CaO}\cdot 6\text{SiO}_2\cdot x\text{H}_2\text{O}$. The initial rate of reaction (II) depends on the fineness, heat treatment, etc., and approx. \propto the vol. of the flocculated SiO_2 . Concrete made with (I) shows improved workability, roughly proportional to (II). J. S. A.

Action of nitric acid on tin. G. S. KASBEKAR and A. R. NORMAND (J. Univ. Bombay, 1933, 2, No. 2, 111—122).—Analytical data are given showing the influence of $[\text{HNO}_3]$, temp., and $[\text{Sn}]$ on the reaction velocity and products. The amounts of Sn^{+++} and N_2 formed are in linear relationship and increase with $[\text{HNO}_3]$ and rise of temp. R. S.

Influence of gelatin on the rate of dissolution of zinc. N. JERMOLENKO (Z. anorg. Chem., 1934, 218, 255—256).—Addition of a small quantity of gelatin, up to approx. 0.3%, greatly reduces the rate of dissolution of Zn in H_2SO_4 , but further additions have very little effect. Gum arabic has a similar action. The action is not due to a diminution in the rate of diffusion, but probably to the formation of an adsorption layer of gelatin on the surface of the Zn.

Catalytic decomposition of hydrogen peroxide in an acid chlorine-chloride solution. II. Steady state function at 0—25°. B. MAKOWER (J. Amer. Chem. Soc., 1934, 56, 1315—1319; cf. this vol., 152).—The $[\text{Cl}_2]$ when the net reaction is $2\text{H}_2\text{O}_2=\text{O}_2+2\text{H}_2\text{O}$ in 2.84—5.25M-HCl at 25° has been determined by a distribution method. The vals. of the steady state function $R=[\text{Cl}_2]/[\text{H}']^2[\text{Cl}']^2$ are in close accord at corresponding $[\text{HCl}]$ with vals. calc. from the relation $R=k_1/k_2$ (I), where k_1 and k_2 are, respectively, the independently determined sp. rates of the reactions $\text{H}_2\text{O}_2+2\text{H}'+2\text{Cl}'=\text{Cl}_2+2\text{H}_2\text{O}$ (II) and $\text{H}_2\text{O}_2+\text{Cl}_2=\text{O}_2+2\text{H}'+2\text{Cl}'$ (III). Vals. of k_2 and R between 0° and 25° using 3.84M-HCl and other data (*loc. cit.*) show that the directly determined temp. coeff. of R is equal to that calc. by (I) from independently determined vals. of k_1 and k_2 , thus supporting the mechanism proposed. The heats of activation of (II) and (III) are $21,000$ and $13,700 \pm 300$ g.-cal., respectively. J. G. A. G.

Polymerisation products in concentrated hydrogen peroxide. E. H. RIESENFELD (Z. anorg.

Chem., 1934, 218, 257—266).—The velocity of the H_2O_2 - KMnO_4 reaction at first increases with increasing $[\text{H}_2\text{O}_2]$, then falls, and finally rises again. The position of the max. and min. on the reaction velocity curve depends only on $[\text{H}_2\text{O}_2]$, so that the anomaly is due to the H_2O_2 mol. and not to the other reactants. H_2SO_4 accelerates the reaction at the max. and delays it at the min., whilst Mn^{++} catalyses the reaction strongly at the max. and less strongly at the min. It is concluded that H_2O_4 only is present in solutions of concn. > 500 milli-equiv. per litre, and H_2O_2 only at concn. < 5 milli-equiv., the two mol. species being in equilibrium at intermediate concns.

M. S. B.

Catalysis of peroxide oxidations by ferrous ions. J. D. STIRLING (Biochem. J., 1934, 28, 1048—1062).—Experiments on the oxidation of tartaric acid, glucose, and inositol (I) indicate that production of Fe^{+++} is a necessary preliminary to catalysis, the catalyst being actually a derivative of Fe^{+++} . Regeneration of Fe^{++} is a side-reaction due to reduction of Fe^{+++} by oxidation products, and with HCO_2H , the oxidation products of which are not further oxidisable, does not take place. It is probable that the Fe^{+++} compound initially formed can donate O_2 without change of valency. Oxidation is most favourably carried out by adding the requisite amount of H_2O_2 to a solution of the substrate (II) containing a trace of Fe^{++} . Formation of an ionisable complex of O_2 donor+ (II) probably takes place. The first oxidation product of (I) gives a blue colour with Fe^{+++} .

A. E. O.

Deactivation of chemically activated oxalic acid. K. WEBER (Z. physikal. Chem., 1934, B, 25, 363—371; cf. A., 1933, 792).—The reducing action of $\text{H}_2\text{C}_2\text{O}_4$ activated with KMnO_4 on HgCl_2 is decreased considerably by the presence of phenols or vat dyes, the reactivity of the $\text{H}_2\text{C}_2\text{O}_4$ decreasing exponentially with increasing concn. of foreign substance (I). The inhibiting action of (I) is the more pronounced the more positive is its normal reduction-oxidation potential. (I) undergoes no detectable chemical change. Baur's sensitisation-desensitisation theory (A., 1932, 578) affords a satisfactory explanation of these observations.

R. C.

Catalytic influences in three-carbon tautomerism. III. Review of possible mechanisms, and further examination of catalysis by alkoxides. IV. Tautomeric changes of unsaturated acids at high temperatures. R. P. LINSTEAD and E. G. NOBLE. **V. Acid catalysis in ketones and esters.** G. A. R. KON and K. S. NARGUND (J.C.S., 1934, 610—614, 614—623, 623—629; cf. A., 1931, 438).—III. Three-C tautomeric changes can proceed by at least three different mechanisms: (1) intramol., (2) removal of the mobile H by negative ions, (3) reversible addition of catalyst mols. The role of alkoxide ions in changes of type (2) is discussed in the light of new experimental evidence.

IV. The reversible interconversion of Δ^a - and Δ^b -unsaturated acids at their b.p. (cf. A., 1930, 1162) has been studied in the case of *n*-hexenoic, -pentenoic, and -butenoic acids in the pure state and in solution. In inert org. solvents the tautomeric change is inde-

pendent of the environment provided there is no secondary decomp. In aq. solution the change is greatly accelerated by inorg. substances. The effect of alkalis has been studied in detail.

V. The action of alcoholic mineral acids has been examined on the two equilibria involving the four isomeric homomesitones: $\text{CMeEt}:\text{CH}:\text{COEt}$ (I) $\text{CHMe}:\text{CMe}:\text{CH}:\text{COEt}$ (II) and $\text{CMeEt}:\text{CMe}:\text{COMe}$ (III)

$\text{CHMe}:\text{CMe}:\text{CMe}:\text{COMe}$ (IV). The order of catalytic activity is $\text{HCl} > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4$. The mobility of (III) and (IV) is much $<$ that of (I) and (II). In the latter pair the point of equilibrium is considerably nearer the Δ^b -side than the val. (67% Δ^a -) found with alkaline catalysts. Displacement of equilibrium towards the Δ^a -form was also observed in esters, viz., cyclopentylidene-, α -methylcyclopentylidene-, and cyclohexylidene-acetic, and 3-methylpentenoic esters. The hexenoic esters are not isomerised at all in acid solution. The interconversion of esters with $\text{EtOH}:\text{HCl}$ is complete only with very conc. acid. The simple ionic explanation of isomeric change is not supported.

O. J. W.

Catalytic hydrogenation of organic halogen derivatives. M. MLADENOVIC (Bull. Soc. Chim. Yougoslav., 1933, 4, 187—196).—Monobromo- α -elemolic and -elemonic acid yield dihydro- α -elemolic and -elemonic acid on hydrogenation (Pd-black). The velocity of hydrogenation of aryl halides is greater in alkaline than in neutral media.

R. T.

Organic catalysts. IX. Structure specificity of esterase models. W. LANGENBECK and J. BALTES (Ber., 1934, 67, [B], 1204—1209).—The rate of hydrolysis of Et H succinate (I), Et H malonate, and acetylmandelic acid is not influenced by the presence of benzoylcarbinol (II), which accelerates the hydrolysis of Et H adipate. The specificity of the org. catalyst is quite different from that of OH' and is identical with that of esterase. ω -Hydroxyacetophenone-4-carboxylic acid (III), m.p. 248—250° (decomp.), accelerates the hydrolysis of EtHSO_4 , but is less sp. than (II), since it causes slow but distinct hydrolysis of (I). Since restriction of the hydrolysis of $\text{Pr}:\text{CO}_2\text{Me}$ by glycollanilide is not caused by the presence of (I), it appears that, as in the case of esterase, there is no union of substrate and catalyst. The active group of esterases is alcoholic OH and the enzymes are therefore main valency catalysts. Similarly, carboxylase is a main valency catalyst with active NH_2 .

4-Aminoacetophenone is converted into the corresponding nitrile, hydrolysed by boiling H_2SO_4 (1 : 1) to acetophenone-4-carboxylic acid, m.p. 205°, whence (Br in AcOH) ω -bromoacetophenone-4-carboxylic acid, m.p. 220—221°, and (III) are obtained.

H. W.

Optical activity in relation to tautomeric change. IV. Comparison of the rates of racemisation and of bromination of a ketone. C. K. INGOLD and C. L. WILSON (J.C.S., 1934, 773—777).—In accordance with theoretical predictions, the unimol. velocity coeffs. of racemisation and bromination of 2-o-carboxybenzylindan-1-one in 16*N*-AcOH in presence of 0—0.4*N*-HBr at 25° are identical.

R. S. B.

Active oxides. LXXIV. System zinc oxide-cupric oxide as a catalyst of the decomposition of methyl alcohol. O. KOSTELITZ and G. F. HUTTIG (Kolloid-Z., 1934, 67, 265—277; cf. this vol., 606).—The yields of H_2 , CO, CO_2 , CH_4 , C_2H_4 , HCO_2H , CH_2O , and HCO_2Me obtained in the decomp. of MeOH over pastilles of different ZnO-CuO catalysts at 270°, 300°, and 320° have been determined. The results are not in accordance with the simple mixture rule. With rising temp. the yields of CO_2 , CH_4 , and CH_2O increase, whilst those of HCO_2H and HCO_2Me decrease. The kinetics of the process have been investigated. E. S. H.

Active oxides. LXXV. Active intermediate stages between an oxide mixture and the [resulting] chemical compound. G. F. HUTTIG, D. ZINKER, and H. KITTEL (Z. Elektrochem., 1934, 40, 306—313; cf. this vol., 371, 490).—The systems ZnO- Fe_2O_3 , BeO- Fe_2O_3 , CaO- Fe_2O_3 , MgO- Cr_2O_3 , and MgO- Al_2O_3 have been studied with respect to their catalytic activity in promoting the reaction $2CO + O_2 = 2CO_2$ as a function of the temp. of heating of the oxide mixture. Well-defined max. of activity are found corresponding with the formation of active intermediate forms. F. L. U.

Active oxides. LXVI. Methods and results of structure determination of active zinc oxides. G. F. HUTTIG [with, in part, H. SCHWARZER, O. HNEVKOWSKY, W. NESTLER, H. KITTEL, and O. KOSTELITZ] (Kolloid-Beih., 1934, 39, 277—333; cf. A., 1933, 774).—A summary of published work and new experiments on the prep. of active ZnO from ZnC_2O_4 , $ZnCO_3$, and $Zn(NO_3)_2$, the kinetics of the reactions, X-ray examination of structure, d , sorptive power for MeOH and for dye solutions, microscopical examination, sedimentation analysis, solubility, magnetic susceptibility, sp. heats, energy content, fluorescence, and catalytic properties. The characteristic properties of the different forms of active ZnO are not due to modifications in crystal structure, to space-lattice distortions, or to the presence of an amorphous component; the chief factors are (a) peculiarities in the pore systems, (b) faults in the crystals, and (c) the distribution of the different crystal planes in the total surface.

E. S. H.

Kinetics of reaction between nitrous oxide and hydrogen at a silver surface. [Decomposition of nitrous oxide.] A. F. BENTON and C. M. THACKER (J. Amer. Chem. Soc., 1934, 56, 1300—1304).—In flow experiments at 60—180°, the rate of formation of H_2O , using 9—109 mm. N_2O and 17—111 mm. H_2 , at a Ag catalyst reduced at 100°, is independent of $[N_2O]$, increased by rise of $[H_2]$, and retarded by H_2O which is strongly adsorbed. The temp. coeff. indicates an energy of activation of 13 kg.-cal. The reaction involves a primary decomp. of N_2O followed by interaction of H_2 with the adsorbed O. N_2O alone is decomposed by the catalyst at 60°, and in static experiments at 160° the N_2O is not appreciably adsorbed as such, but slowly decomposes into N_2 and an adsorbed O atom, which may react with another N_2O mol. to give gaseous O_2 and N_2 . The

O atoms (or possibly oxides of N) inhibit the ordinary activated adsorption of O_2 . J. G. A. G.

Mode of action of catalyst mixtures in decomposition of nitrous oxide. III. G. M. SCHWAB and H. SCHULTES. IV. G. M. SCHWAB and R. STAEGER (Z. physikal. Chem., 1934, B, 25, 411—417, 418—440; cf. A., 1932, 689).—III. The catalysis of the decomp. by oxides and binary mixtures of oxides has been studied. The activity of a CuO- TiO_2 mixture is additively constituted of those of the constituents, whilst BeO reduces the activity of CdO slightly and that of CuO considerably. For CuO-CdO and CuO- Al_2O_3 mixtures the heat of activation is $>$ that for either component, yet the catalytic activity is $>$ corresponds with additivity.

IV. The decomp. on CuO is retarded by O_2 , and, at lower temp., by N_2O also. The heat of activation on a CuO- Al_2O_3 catalyst is $>$ on CuO by about 3 kg.-cal., and N_2O and O_2 are adsorbed in comparable amounts at all the temp. studied. Cr_2O_3 reduces the activity of CuO considerably. The high activity of the CuO- Al_2O_3 catalyst is ascribed to the formation of a spinel on which the adsorption d is especially high. R. C.

Catalytic action of Japanese acid earth. XI. Relation between catalytic activity and adsorption. K. ISHIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 180—181B).—The conversion of $C_{10}H_8$ into $\beta\beta'$ -dinaphthyl by heating with Japanese acid earth at 300° is promoted by O-containing substances such as H_2O and alcohols, and poisoned by nitrogenous substances. The adsorption of H_2O and MeCN by the earth was studied, and it is probable that H_2O is able to displace MeCN. A. G.

Catalytic decomposition of sodium amalgam. I. A. S. FORKIN and M. A. RABINOVITSCH. II. P. B. SHIVOTINSKI and A. P. MASCHOVETZ. III. A. P. MASCHOVETZ and P. B. SHIVOTINSKI (Ukrain. Chem. J., 1933, 8, 355—365, 366—371, 372—380).—I. Decomp. of Hg-Na (I) by aq. NaOH is catalysed by reduced Fe, V, W, Ni, Mn, and by alloys of Fe with V, W, Si, Mo, Ti, Zr, and B, as well as by salts of V and W. Cast Fe has only a feeble action. Anhyd. EtOH reacts with (I) in presence of the above catalysts.

II. Inactivation of Fe-Si catalyst (II) is due to the covering of its surface with a suspension of Fe in Hg; (II) can be reactivated by shaking in an atm. of H_2 . The activity of (II) falls with increasing Si content from 12 to 52%.

III. A continuous process for the electrolytic prep. of NaOH from NaCl, involving the catalytic decomp. of (I) in a side chamber, is described. R. T.

Change of chemical reactivity and catalytic activity of silica on loosening its lattice with ferric oxide. J. A. HEDVALL, R. HEDIN, and S. LJUNGKVIST (Z. Elektrochem., 1934, 40, 300—302; cf. A., 1931, 582).—Cristobalite containing 0.24% Fe_2O_3 in solid solution reacts with $CaCO_3$ at about 50° lower than when pure. When used as a catalyst in the thermal decomp. of EtOH to C_2H_4 , the soln. produces the same effect at 380° as does the pure substance at 460°. It has 0.1 of the catalytic

activity of Pt-asbestos in promoting the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$, pure SiO_2 being inactive.

F. L. U.

Catalysts for ammonia synthesis.—See B., 1934, 623.

Catalysts for conversion of carbon monoxide.—See B., 1934, 611.

Interaction of carbon monoxide and steam over iron catalysts. B. G. SIMEK and R. KASSLER (Chim. et Ind., 1934, 31, Spec. No., 330—337).—The part played by secondary reactions in the conversion of CO and H_2O into CO_2 and H_2 has been studied. As catalysts a reduced alumino-ferric contact and cast-Fe filings were used, both being activated by K_2CO_3 . At 500° reduction of the oxide catalyst by CO stopped before the liberation of Fe. Fe formed by the reduction of the catalyst by H_2 was re-oxidised by H_2O at 500° to a definite equilibrium ratio of $\text{H}_2 : \text{H}_2\text{O}$ in the gaseous phase. Some C deposition occurred when CO was passed over the catalyst at 500° , and it is concluded that the main reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ probably proceeds in stages, $2\text{CO} \rightarrow \text{C} + \text{CO}$, and $\text{C} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. The amount of conversion passed through a max. as the rate of passage of the gases over the catalyst was increased, the rate giving max. conversion varying with the temp. The presence of H_2S adversely affected the conversion.

A. B. M.

Catalytic hydrogenation of simple molecules by light and heavy hydrogen. H. W. MELVILLE (J.C.S., 1934, 797—805).—The kinetics of reaction of H_2 , and of $\text{H}:\text{H}^2$ mixtures, with O_2 , N_2O , and C_2H_4 , and of H_2 with CO, have been studied on Ni wire at $100\text{--}300^\circ$ at pressures $1\text{--}760$ mm. H^1 reacts with N_2O and O_2 from 160° to 250° about twice as fast as H_2 , a difference attributable to the different zero point energies of $\text{Ni}-\text{H}^1$ and $\text{Ni}-\text{H}^2$; a similar variation with C_2H_4 cannot be given a quant. interpretation. It is inferred that the rate is controlled by the rate of migration of adsorbed H^1 or H^2 to adsorbed O atoms. Measurements on the Hg-photosensitised reaction between H^1 or H^2 and N_2O give almost equal rates for H^1 and H^2 , since the atoms are free and considerations of zero point energy do not enter.

R. S. B.

Catalytic properties of electrolytically deposited smooth layers of platinum metals. I. I. SHUKOV, A. A. GLAGOLEVA, and V. I. STRUKOVA (J. Gen. Chem. Russ., 1934, 4, 9—12).—The velocity of decomp. of H_2O_2 in presence of Au foil covered with Pt- or Ir-black is the same as for smooth layers of the metals, whilst Rh-black is approx. twice, and Pd-black 10 times, as active as in smooth layers.

R. T.

Reactions of pyrogenous condensation. I. Kinetics of condensation of benzene. G. I. KRASNOKUTSKI and M. S. NEMTZOV (J. Gen. Chem. Russ., 1934, 4, 132—144).— Ph_2 in 0.5% yield is obtained by heating C_6H_6 in presence of Fe at 470° , and in 0.46% yield with Ni catalyst. The catalytic action of brass, Al, Cu, and Cr is considerably < that of Fe or Ni. The reaction is one of zero order in presence of Fe, and of the first order with Ni. The temp. coeff. of the reaction for the interval $450\text{--}460^\circ$ is 2.63 for active C, and about 2 for metallic

catalysts. Dihydrodiphenyl is not a reaction product. The velocity of formation of $\text{C}_6\text{H}_4\text{Ph}_2$ is < that of Ph_2 . Condensation is practically inhibited by high pressures of H_2 .

R. T.

Catalytic reduction of organic halogen compounds; 5-bromo-5-alkylbarbituric acids. G. K. HUGHES, A. K. MACBETH, and S. W. PENNYCUICK (J.C.S., 1934, 769—773).—The unimol. velocity coeffs., k , for the reduction of 5-bromo-5-alkylbarbituric acids by EtOH in excess in presence of colloidal Pt have been determined at 30° . The variation of k with change in alkyl group is small, except in the case of the Pr^s acid, for which k is abnormally large. k is not \propto the concn. of EtOH , and is abnormal for variation in the concn. of Pt. Colloidal W gives a slower rate than Pt.

R. S. B.

Catalysis in the pyrolysis of hydrocarbons. T. S. WHEELER (J. Univ. Bombay, 1933, 2, No. 2, 123—124).—Theoretical. It is suggested that catalytic activity is due to the presence of loosely-bound electrons at the surface.

R. S.

Catalytic hydrogenation of aromatic hydrocarbons in solution in presence of nickel-black.—See this vol., 877.

Catalytic conversion of acetylene and acetaldehyde into acetone.—See B., 1934, 567.

Catalytic preparation of butaldehyde and butyl alcohol from acetaldehyde.—See B., 1934, 567.

Surface reaction between acetylene and iodine. C. P. ELLIS (J.C.S., 1934, 726—727).—Crystals of I kept in C_2H_2 for 2—3 days at 25° are converted into acetylene di-iodide. The rate of the reaction depends to some extent on the nature of the surface of the vessel used, but not to so marked a degree as in the reaction between C_2H_4 and I.

O. J. W.

Energetics of catalysis. III. Poisoning coefficients of hydrogenation processes. E. B. MAXTED and V. STONE (J.C.S., 1934, 672—674; cf. this vol., 262).—The poisoning coeff., α , is a const. for the hydrogenation on a Pt catalyst of COPhMe , PhNO_2 , C_6H_6 , and oleic acid, using Hg^{++} ions as poison, and of COPhMe and C_6H_6 using CS_2 as poison. The vals. of α are approx. 2 and 8 for Hg^{++} and CS_2 , respectively.

O. J. W.

Depolymerisation of triisobutene.—See this vol., 864.

Separation of the hydrogen isotopes by electrolysis. I. B. TOPLEY and H. EYRING (J. Chem. Physics, 1934, 2, 217—230).—From the calc. equilibrium consts. of the reactions $\text{H}_2\text{O} + 2\text{H}^2 = \text{H}_2\text{O} + 2\text{H}$ and $\text{H}_2\text{O} + \text{H}_2^3\text{O} = 2\text{HH}^3\text{O}$ an expression is obtained for the electrolytic separation coeff., valid when zero-point energy and tunnelling are negligible in the activated state. The change of this coeff. with increase in concn. of H^- is calc. Experimental vals., in the range 7.6—2.8, were determined for the separation coeff. at cathodes of Pb, Pt, Pt (black), Pt (activated), W, Fe, Ni, Cu, Ag, Hg, and Ga.

N. M. B.

Continuous-flow methods of concentrating deuterium. L. C. ANDERSON, J. O. HALFORD, and J. R. BATES (J. Chem. Physics, 1934, 2, 342—344).—

H₂O is passed from an 8-litre Mariotte bottle through a no. of cells with Ni cathode and Fe anode arranged in series, and operated on the 110- or 220-volt supply. A method of recovering the gases evolved in electrolysis of partly heavy H₂O by combustion on Pt-asbestos is described. H. J. E.

Preparation of deuterium oxide by electrolysis of water. K. SCHWARZ, L. KUCHLER, and H. STEINER (Z. Electrochem., 1934, 40, 298—299).—Apparatus and procedure for preparing H₂O by the electrolysis of 0.8N-NaOH are described. F. L. U.

Electrodeposition of tin from sodium stannate solutions with the use of insoluble anodes.—See B., 1934, 583.

Electrolytic separation of tantalum from aqueous solutions. N. ISGARISCHEV and A. F. PREDE (Z. Elektrochem., 1934, 40, 295—297; cf. A., 1933, 681).—Cathodic deposition of Ta is possible from acid solutions containing glucose, K salicylate, or resorcinol, provided no diaphragm is used. The current yield is $\geq 0.16\%$. F. L. U.

Electrolysis of sodium nitrate in liquid ammonia solution. N. KAMEYAMA and H. MORI (J. Soc. Chem. Ind. Japan, 1934, 34, 167—168B).—NaNO₃ when electrolysed in liquid NH₃ at -40° to -47° with Pt electrodes at c.d. 0.1 amp. per sq. cm. gives N₂ at the anode and NaNO₂ with a little NaOH and H₂ at the cathode. The reaction is $3\text{NaNO}_3 + 2\text{NH}_3 = 3\text{NaNO}_2 + \text{N}_2 + 3\text{H}_2\text{O}$. R. S. B.

Reduction of oxygen to hydrogen peroxide by the irradiation of its aqueous solution with X-rays. FRICKE (J. Chem. Physics, 1934, 2, 240).—O₂ dissolved in H₂O yields H₂O₂ on irradiation with X-rays, the amount of H₂O₂ being independent of the O₂ pressure and falling to approx. 50% of its val. in acid solution at $p_{\text{H}} > 8$. H. J. E.

Colour changes in light and darkness of ammonium thiocyanate solutions. B. S. V. R. RAO (J.C.S., 1934, 880—881).—The colour changes undergone by conc. aq. NH₄CNS in light and darkness are due to reversible oxidation and reduction processes associated with the presence of Fe as impurity. R. S. B.

Errors in the photographic method of comparing light intensities. J. T. LAY and I. C. CORNOG (J. Opt. Soc. Amer., 1934, 24, 149—154).—The causes and magnitudes of errors due to variations in density over the plate caused by its irregular structure and uneven development were investigated. N. M. B.

Photographic sensitivity after the Herschel effect. J. M. BLAIR (J. Opt. Soc. Amer., 1934, 24, 155—156).—An emulsion when exposed to white and then to red light fully regains its original sensitivity. N. M. B.

Photographic inversion due to simultaneous action of two different radiations. V. DOLEJŠEK and A. NĚMEJCOVÁ (Compt. rend., 1934, 198, 2081—2082; cf. A., 1932, 29).—Inversion was produced when photographic plates were exposed successively to two different radiations in the following orders: X-W, C-W, X-H, C-H, C-X (X=X-rays, W=white

light, C=cathode-rays, H=heat rays). In all except the last case, it was essential to expose to the shorter λ first. The effects were not due to solarisation. B. W. B.

Influence of anti-oxygens on the sensitivity of photographic emulsions. A. CHARRIOU and (Mlle.) S. VALETTE (Compt. rend., 1934, 198, 2078—2080; cf. B., 1933, 333).—The following fluorescence-suppressing anti-oxygens decreased sensitivity (I) and contrast when incorporated in an emulsion: resorcinol, guaiacol, PhOH, NH₂Ph, Na salicylate, and PhNO₂. NHPH₂ reduced (I) only. In all cases the effects were $<$ those produced by KI. B. W. B.

Reaction produced by light of very short wavelength. F. PALMER, jun. (J. Chem. Physics, 1934, 2, 296—297).—Light from a capillary discharge tube containing H₂ at 1—2 mm. pressure, when passed through a fluorite window into air at atm. pressure, causes the formation of a film of unknown nature on the outside of the window. N. M. B.

Catalysis of acetylene polymerisation in ultra-violet light by mercury vapour. F. TOUL (Coll. Czech. Chem. Comm., 1934, 6, 162—189).—Pure C₂H₂ (prep. described) does not polymerise in sunlight either alone, when mixed with N₂, or in presence of Hg. Slow polymerisation takes place in ultra-violet light even in the purest C₂H₂, the reaction being catalysed by Hg vapour, with which an equilibrium is reached when approx. 10% of the C₂H₂ has polymerised. This reaction is not due to photosensitisation, and is still observed with a source not containing the Hg lines. Pure dry C₂H₂ after irradiation with cathode rays causes condensation of H₂O when mixed with undried C₂H₂ up to 60 min. after exposure. No effects were observed on exposure to X-rays. Some properties of the polymeride are described. A. A. L.

Primary photochemical reactions. IV. Decomposition of methyl ethyl ketone and methyl butyl ketone. R. G. W. NORRISH and M. E. S. APPLEYARD (J.C.S., 1934, 874—880).—Light of λ 2200—3000 Å. decomposes (1) COMeEt giving (a) (70—80%) $\frac{1}{2}(\text{C}_2\text{H}_6 + \text{C}_2\text{H}_8 + \text{C}_4\text{H}_{10}) + \text{CO}$ and (b) (20—25%) C₂H₄ + MeCHO, (2) COMeBu giving COMe₂ + CHMe₂CH₂. It is inferred that (a) occurs by the formation of free radicals. The mechanism by which the energy of the chromophoric group (CO) is transferred to the other groups is discussed. R. S. B.

Photochemical studies. XVII. Chlorination of chlorobenzene; a comparison with benzene. E. J. HART and W. A. NOYES, jun. (J. Amer. Chem. Soc., 1934, 56, 1305—1310; cf. this vol., 40).—The gas-phase photochemical chlorination of PhCl proceeds by short reaction chains, and initially the rate of reaction of Cl₂ is proportional to a power of the light intensity between 0.5 and 1.0. The ratio of substitution to addition increases from 1 to > 1 as the ratio of Cl₂ used to initial pressure of PhCl is increased (cf. C₆H₆, *loc. cit.*), and the relation is independent of temp. between 25° and 35°, but in the purely thermal reaction substitution dominates and the rate $\propto [\text{Cl}_2][\text{PhCl}]$ and is increased by surface.

The rate of addition of Cl_2 to $p\text{-C}_6\text{H}_4\text{Cl}_2$ is slightly < to PhCl . Some intermediate substances have been isolated and the final product is C_6Cl_{12} . The mechanism of the reaction is discussed. J. G. A. G.

Electrometric measurement of Röntgen energy. N. WATERMAN and H. LIMBURG (Phil. Mag., 1934, [vii], 17, 1144—1150; cf. A., 1933, 1020).—The electrochemical effects of X-rays consist of an electrode effect and a secondary process. The former depends quantitatively on the energy received by the system and can be utilised for its measurement. An apparatus for this purpose, utilising the reducing action of X-rays on methylene-blue, is described. J. W. S.

Periodic system of the elements and its gaps. I. NODDACK (Angew. Chem., 1934, 47, 301—305).—A crit. review of the lit. indicates that the elements with at. nos. 61 (a rare-earth metal), 85 (*eka-I*), and 87 (*eka-Cs*) have not yet been discovered. Attempts by the author to concentrate *eka-Cs* by crystallisation of Cs alum and $3\text{CsCl} \cdot 2\text{SbCl}_3$ from numerous sources, and detect it by means of X-ray or infra-red spectra have been unsuccessful. The possible reasons for the non-existence or rarity of these elements and of elements heavier than U are discussed. Possible developments in the conception of the periodic system, due to the discovery of the neutron, the positron, and isotopes (particularly H^2), are considered. D. R. D.

Natural separation of the isotopes of hydrogen. I. Concentration of deuterium in benzene, kerosene, and honey. M. DOLE (J. Chem. Physics, 1934, 2, 337—341; cf. this vol., 613).—Methods of combustion, purification of H_2O , and measurement of d are described. H. J. E.

Increase of the percentage of diplogen in water during very slow evaporation. T. TUCHOLSKI (Nature, 1934, 134, 29).—Evaporation of 25 litres of H_2O to approx. 600 c.c. over a period of three years gave H_2O of d^4 1.0016 corresponding with 1.65% H_2O . Slow evaporation is more effective than boiling. L. S. T.

Isotopic exchange between H_2O and C_2H_2 . L. H. REYERSON and S. YUSTER (J. Amer. Chem. Soc., 1934, 56, 1426—1427).—Isotopic exchange was not detected between C_2H_2 and 18.5% H_2O alone or in presence of H_3PO_4 , but exchange occurs in presence of NaOH , thus confirming the acidic nature of C_2H_2 . J. G. A. G.

Reaction of atomic hydrogen with metallic copper. F. A. McMAHON and P. L. ROBINSON (J.C.S., 1934, 854—855).—At. H passed at the rate of 0.5 litre per hr. over Cu which has been oxidised and reduced, or roughened, gives a black Cu^1 hydride sol. in 70% HCl in absence of air. R. S. B.

Action of aqueous solutions of cupric sulphate on copper oxide. O. BINDER (Compt. rend., 1934, 198, 2167—2169).—The basic salt produced by the action of aq. CuSO_4 on CuO , $3\text{CuO} \cdot \text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, NiO , $\text{Ni}(\text{OH})_2$, or NiCO_3 was shown by analysis, X-ray spectrum, and paramagnetic susceptibility ($\chi = 11.5 \times 10^{-6}$ at 17°) to be $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$ in all cases, and not to contain admixed $\text{Cu}(\text{OH})_2$ (cf. this 376). B. W. B.

Silver silicate. B. BOGITCH (Compt. rend., 1934, 198, 1928—1929).—Various oxidising, neutral, and reducing gases were bubbled through a melt of soda-glass and AgNO_3 . The effects on the resultant glass are described. Ag silicate appears to be formed, and is readily reduced to colloidal Ag. B. W. B.

Mechanism of oxidation of alloys of magnesium at high temperatures. R. DELAVAUULT (Compt. rend., 1934, 198, 1929—1932; cf. following abstract).—Microscopical study during heating in air of etched surfaces of Mg alloyed with 0.2—10% of Na, Te, Ca, Zn, Cd, Al, Pb, Sn, Bi, Si, Cu, or Ag showed that oxidation commences at grain boundaries, at which rapidly attacked protuberances of liquid metal are formed. Similar results were obtained with Ca. B. W. B.

Superficial oxidation of molten metals. R. DELAVAUULT (Bull. Soc. chim., 1934, [v], 1, 419—424).—The behaviour of Mg, Al, and alloys of Mg and Al on oxidation in air is in agreement with Pilling and Bedworth's theory according to which the oxide of a metal forms a protective coating preventing further oxidation only when Wd/wD is > 1 , W and w being mol. wts. and D and d densities of oxide and metal, respectively. The presence of BF_3 in the air results in the formation of a temporarily protective layer of MgF_2 on Mg for which the ratio is > 1 . The same probably applies to the presence of SiF_4 . The possible practical application in the prep. of alloys of Mg is discussed. M. S. B.

Hydrated calcium sulphatoaluminate and calcium chloroaluminate. J. LEFOL (Compt. rend., 1934, 198, 1858—1860; cf. this vol., 31).—Thermal analysis showed: (i) $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$ rapidly loses H_2O on heating, forming a heptahydrate stable at 145° and decomposed at higher temp.; free CaSO_4 is not liberated; (ii) $\text{Al}_2\text{O}_3 \cdot 3\text{CaO} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ (I) is stable to 120° and forms a hexahydrate at 175° which is stable to 280° . At temp. $> 100^\circ$ (I) decomposes to $\text{CaCl}_2 + \text{Al}_2\text{O}_3 \cdot 3\text{CaO}$. B. W. B.

Celite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) of Portland cement. S. NAGAI and G. SAWAYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 264—267b).—A mixture $4\text{CaO} : \text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ readily forms $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ at 1250° . A mixture $5\text{CaO} : \text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ (or $3\text{CaO} \cdot \text{Al}_2\text{O}_3 : 2\text{CaO} \cdot \text{Fe}_2\text{O}_3$) forms $2\text{CaO} \cdot \text{Fe}_2\text{O}_3 + 6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$ (I) at $1400\text{—}1420^\circ$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{I}$ at $1250\text{—}1370^\circ$. (I) is probably a mixture of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ and the eutectic (CaO 47, Al_2O_3 53%) between $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. J. A. S.

Reactions between nitrogen dioxide and sulphur dioxide in the condensed phase. E. TERRES and M. CONSTANTINESCU (Angew. Chem., 1934, 47, 470—471).— NO_2 is absorbed by SO_2 at -70° . The m.p.-composition curve indicates a eutectic containing 6% NO_2 . Probably SO_2NO_2 is formed, which is converted by a slight temp. rise into SO_3NO , from which $(\text{SO}_3)_2\text{N}_2\text{O}_3$ is also formed. A. G.

Reactions of oxides of nitrogen and of sulphur. Nitrosulphonic acid anhydride and its reversible conversion into nitrosylsulphuric acid anhydride. E. TERRES and M. CONSTANTINESCU

(Angew. Chem., 1934, 47, 468—470).—The reaction $\text{SO}_2 + 2\text{NO} = \text{SO}_3 + \text{N}_2\text{O}$ is reversible. The formation of NO begins at 550° and increases with rising temp.; it never exceeds 1% of the mixture because the decomp. of N_2O is much more rapid than its oxidation. N_2O is formed from NO and SO_2 only in presence of Pt and at 250 — 470° , with a max. at 350 — 400° . Crystals of the composition SO_3NO are formed at the inlet end of the reaction tube, and may also be produced from SO_3 and NO at 90° and from SO_2 and NO_2 . SO_3NO melts at 93° with formation of $(\text{SO}_3)_2\text{N}_2\text{O}_3$. A. G.

Nitrosoamine. R. SCHWARZ and H. GIESE (Ber., 1934, 67, [B], 1108—1115).— N_2O_3 and NH_3 at its m.p. form a red compound (I) regarded as *nitrosoamine*; $\text{N}_2\text{O}_3 + 2\text{NH}_3 = 2\text{NH}_2\cdot\text{NO} + \text{NH}_4\text{NO}_2$. With $\text{H}(\text{NO})\text{SO}_4$ the total reaction is: $5\text{H}(\text{NO})\text{SO}_4 + 15\text{NH}_3 = 2\text{NH}_4\text{NO}_2 + 3\text{N}_2 + 5(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$, and the intermediate changes are: $\text{H}(\text{NO})\text{SO}_4 + 3\text{NH}_3 = (\text{I}) + (\text{NH}_4)_2\text{SO}_4$, $4(\text{I}) = 2\text{NH}_4\text{NO}_2 + 2\text{N}_2$; $(\text{I}) = \text{N}_2 + \text{H}_2\text{O}$. (I) is also formed from $(\text{NO})\text{ClO}_4$ and NOCl . The formulation of (I) is strengthened by the observations that NHPHMe and N_2O_3 at -5° yield $\text{NHPHMe}\cdot\text{NO}$ and that (I) and KNO result from the action of NO under pressure on KNH_2 in solid NH_3 : $\text{KNH}_2 + 2\text{NO} = \text{KNO} + (\text{I})$. (I) cannot be obtained in any solvent other than liquid NH_3 , from which it cannot be separated owing to decomp. into NH_4NO_2 and N_2 , also obtained in NH_3 - H_2O . (I) unites with H_2O to give NH_4NO_2 . NaNH_2 at -40° reacts with dil. NOCl vapour: $3\text{NaNH}_2 + 2\text{NOCl} = 2\text{NaCl} + \text{NaNO}_2 + 2\text{NH}_3 + \text{N}_2$. Nitrous esters do not react with anhyd. liquid or gaseous NH_3 ; with KNH_2 in NH_3 change occurs: $2\text{RNO}_2 + \text{KNH}_2 = \text{R}_2\text{O} + \text{KNO}_2 + \text{N}_2 + \text{H}_2\text{O}$. NH_2Cl does not react with liquid NH_3 or with KNO suspended therein. $\text{NH}_2\cdot\text{SO}_3\text{H}$ does not react with KNO_3 in liquid NH_3 ; $\text{H}(\text{NO})\text{SO}_4$ and KNH_2 afford $\text{NH}_2\cdot\text{SO}_3\text{K}$ and KNO_2 . The possible structures of (I) are discussed. H

Hydration of phosphoric anhydride. A. TRAVERS and Y. K. CHU (Compt. rend., 1934 198, 2169—2171).—Addition of P_2O_5 to ice- H_2O did not give dimetaphosphoric acid, $\text{H}_2\text{P}_2\text{O}_6$ (I) (cf. Réchid, A., 1933, 475), as chief product, local overheating causing hydration or polymerisation. With special precautions, P_2O_5 + an ethereal solution of either H_2O or of anhyd. H_3PO_4 gave a mixture of (I) and its polymeride (II), readily hydrated to pvro- (III) and ortho- (IV) -phosphoric acids, respectively. (I) may be separated from admixture with (II) (III), and (IV) by pptn. of Pb salts of the last three in dil. NaOH solution. B B

The two forms of phosphorous acid. R. DOLIQUE and A. GRANGIENS (Bull. Soc. chim., 1934, [v], 1, 380—387).—A detailed account of work already noted (A., 1933, 1129).

Dimetaphosphoric acid. A. TRAVERS and Y. K. CHU (Compt. rend., 1934, 198, 2100—2102).—Na dimetaphosphate, $\text{Na}_2\text{P}_2\text{O}_6$, prepared by Pascal and Réchid's method (A., 1933, 475), always contains $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$. The following modification of Knorre's method (A., 1900, ii, 651) is satisfactory. A mixture of 5 parts $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ + 1 part NH_4NO_3 + 1 part

NH_4Cl is heated in vac. at 250° for 8 hr.; crystallisation of the product from H_2O gives pure, birefringent $\text{Na}_2\text{P}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$ (I), mol. wt. 65 (extrapolated from cryoscopic data; cf. $\text{Na}_2\text{P}_2\text{O}_6$, 68). Dimetaphosphoric acid (II), prepared by the action of H_2S on PbP_2O_6 , did not coagulate albumin (III) and was slowly hydrolysed by cold H_2O to $\text{H}_4\text{P}_2\text{O}_7$. (I) after heating for 2 hr. at 900° and treatment with AcOH gave a polymeride of (II) (mol. wt. 338) which coagulated (III). The latter is a property of highly polymerised metaphosphoric acids. B. W. B.

Structure of hypophosphoric acid. P. NYLEN and O. STELLING (Z. anorg. Chem., 1934, 218, 301—303).—Blaser and Halpern's experiments (this vol., 43) do not bring any important evidence against the authors' formula for hypophosphoric acid (A., 1933, 664) and their formula does not account for the properties of the acid. M. S. B.

Oxidation of phosphoformic acid by bromine and permanganate. P. NYLEN (Z. anorg. Chem., 1934, 218, 304—306).—Oxidation by Br takes place quantitatively and rapidly between p_H 4 and 11.2. In neutral solution it is practically instantaneous. A no. of other acids, e.g., phosphoacetic, β -phosphopropionic, methanediphosphonic, arsinoacetic, and dithionic acids are resistant to Br. Et phosphite is slightly attacked. Oxidation by KMnO_4 takes place rapidly at room temp. with the employment of approx. 93% of the KMnO_4 theoretically required. As with $\text{H}_2\text{C}_2\text{O}_4$, there is an induction period. The results support the structural formula $\text{CO}_2\text{H}\cdot\text{PO}(\text{OH})_2$. M. S. B.

Wet-way preparation of antimony iododisulphide. F. FRANÇOIS (Compt. rend., 1934, 198, 1994—1996).— SbSI , prepared by long shaking of mixed aq. solutions of SbI_3 , HI, and H_2S , or of Sb_2S_3 + aq. HI, was a red cryst. powder, m.p. 392° , unattacked by H_2O or H_2S . Sb cannot be determined by pptn. with H_2S from solutions containing HI. B. W. B.

Preparation of sodium bismuthate. I. VACHROMEY (Zavod. Lab., 1934, 3, 269).—100 g. of $\text{Bi}(\text{OH})_3\cdot\text{NO}_3$ are dissolved in 200 g. of NaOH at red heat, after which 20 g. of Na_2O_2 are added. The melt is leached with 1500 c.c. of H_2O , and the insol. residue of NaBiO_3 is collected, washed, and dried at 100 — 105° during 16 hr. R. T.

Complex bismuth oxalates. S. ŠKRAMOVSKY (Coll. Czech. Chem. Comm., 1934, 6, 145—162; cf. A., 1930, 1008).—The course of dehydration of the double oxalates of Bi, and of $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 5, 6, 7$, and $8\text{H}_2\text{O}$, shows them to be derived by substitution from aquo-oxalato-complexes of 4- or 6-co-ordinate Bi, some polynuclear, containing $-\text{C}_2\text{O}_4-$ bridges. The following compounds were prepared: $\text{LiBi}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$; $\text{NH}_4\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot \text{NO}_3 \cdot 3$ and $1\text{H}_2\text{O}$; $(\text{NH}_4)_2\text{Bi}_2(\text{C}_2\text{O}_4)_3(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and anhyd.; $(\text{NH}_4)_2\text{Bi}(\text{C}_2\text{O}_4)_2\text{F} \cdot 2\text{H}_2\text{O}$; $(\text{NH}_4)_2\text{Bi}_2(\text{C}_2\text{O}_4)_5\text{Cl} \cdot 8$ and $2\text{H}_2\text{O}$; $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 5$ and $8\text{H}_2\text{O}$; $(\text{NH}_4)_2\text{Bi}_4(\text{C}_2\text{O}_4)_7 \cdot 11\text{H}_2\text{O}$. J. S. A.

Purification of half a gram of protoactinium. (element 91). G. GRAVE and H. KADING (Naturwiss., 1934, 22, 386—388).—The working up of 5.5

tons of pitchblende residues after extraction of Ra is described.

A. J. M.

Isotopic composition of oxygen made by the fractionation of liquid air and oxygen of ordinary air. E. R. SMITH (J. Chem. Physics, 1934, 2, 298).—Increase in d of H_2O prepared from the fractionation specimen of O_2 was 2.2 ± 0.5 p.p.m., indicating the presence of 2 in 10^5 more atoms of O^{18} than O^{16} .

N. M. B.

Reactions of inorganic compounds with liquid hydrogen sulphide. H. F. GUEST (Iowa State Coll. J. Sci., 1933, 8, 197—198).—CaO forms CaS and Ca(OH)SH; CaC_2 forms CaS and $Ca(SH)_2$; C_2H_2 forms a little CHMeS; dry SO_2 at $> -68^\circ$ reacts with explosive violence; $VOCl_3$ forms $VSCl_3$ and $VCl_3(OH)SH$; Na_2S and CS_2 in H_2S form Na_2CS_3 ; $POCl_3$ oxidises H_2S slowly; in $EtOH-H_2S+CS_2$, NH_3 forms $NH_4S(NH_2)CS$.

CH. ABS.

Formation of pyrosulphate by treatment of sulphur trioxide with aqueous sulphate solutions. P. BAUMGARTEN (Ber., 1934, 67, [B], 1100—1104).—Introduction of SO_3 vapour under precise conditions into aq. alkali sulphate at $5-10^\circ$ and immediate treatment of the solution with C_5H_5N yields 1-pyridinium-sulphonic acid identified as glutacondialdehydedianil hydrochloride. With H_2O the reaction is scarcely observed and the formation of pyrosulphate is postulated. Similar results are observed in presence of $CO_3^{''}$, ClO_4' , and particularly of $PO_4^{'''}$, but not of Cl' .

H. W.

Reaction of sulphur trioxide with ammonia in aqueous solution and the chemical composition of the so-called "sulphur trioxide fog." P. BAUMGARTEN and A. H. KRUMMACHER (Ber., 1934, 67, [B], 1257—1260).—The main product of the action of SO_3 as vapour mixed with air on 25% NH_3 at about -15° is $(NH_4)N(SO_3NH_4)_2$ accompanied by $(NH_4)_2SO_4$ and minor amounts of $NH_2 \cdot SO_3 \cdot NH_4$. With $C_5H_5N \cdot H_2O$, SO_3 vapour yields pyridiniumsulphonic acid, converted by alkali into *enol*-glutacondialdehyde, recognised by its yellowish-brown colour, or, more readily, by the production of the intensely red dianil hydrochloride after subsequent addition of NH_2Ph and HCl. Application of this test to "sulphur trioxide fog" shows the latter to contain only H_2SO_4 particles unless the fog has been in contact with H_2O or aq. solutions for only a very short time.

H. W.

Uranyl salts. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 410—411).— $UO_2(NO_3)_2$ reacts with the following substances in aq. solution: $NHPh \cdot NH_2$, forming hydrated U_3O_8 ; $(CH_2)_6N_4$, giving $(NH_4)_2UO_4 \cdot H_2O$; antipyrine, forming *uranyl antipyrine nitrate*, $C_{11}H_{12}ON_2 \cdot UO_2(NO_3)_2 \cdot 10H_2O$, as a yellow ppt. sol. in warm H_2O ; $(CH_2)_4(NH)_2$, forming *uranyl-piperazine*, $(CH_2)_4N_2 \cdot UO_2 \cdot 2H_2O$, as a yellow ppt. insol. in boiling H_2O and sol. in cold acids; K xanthate, giving a brown coloration; K guaiacolsulphonate (I), giving a blood-red coloration in the cold and, after evaporation, a reddish-brown, cryst., deliquescent mass containing a mixture of (I) and UO_2 guaiacol-sulphonate; thiosinamine, with formation of NH_3 and C_3H_5SCN .

M. S. B.

Reduction of polonium in solution. M. GUILLLOT and M. HAISSINSKY (Compt. rend., 1934, 198, 1911

1913).—The existence of Po^{III} and Po^{IV} (cf. A., 1931, 591, 697, and Joliot, A., 1930, 713) is confirmed by the effects of reducing agents (N_2H_4 , NH_2OH , $H_2C_2O_4$, and H_2O_2 in acid solution) on the crit. deposition potential. Metallic Po was pptd. by CH_2O in alkaline solution and by H_3PO_3 or $Na_2S_2O_4$. Electrolytic deposition was suppressed by $NaNO_2$ in HNO_3 solution. B. W. B.

Recovering radium-D and polonium. T. BJERGE (Z. Physik, 1934, 89, 277—282).—The radioactive layer of used emanation tubes may be recovered by etching.

A. B. D. C.

New fluorides. O. RUFF [with A. BRAIDA, W. KWASNIK, and M. GIESE] (Angew. Chem., 1934, 47, 480).—A review of Ruff's work on I, Re, Ag, Cu, and Au fluorides.

D. R. D.

ψ -Halogens. XXIV. Reaction of metallic sulphates with iodine in concentrated sulphuric acid. L. BIRCKENBACH and J. GOUBEAU [with H. G. KRALL] (Ber., 1934, 67, [B], 917—927; cf. A., 1933, 1281).—I is slightly sol. in conc. H_2SO_4 with a pale pink colour unaffected by anhyd. $CuSO_4$, $PbSO_4$, $FeSO_4$, $NiSO_4$, $ZnSO_4$, K_2SO_4 and Na_2SO_4 . I, Ag_2SO_4 , and H_2SO_4 give a reddish-violet solution in which I : $Ag = 1 : 4-5$ for solutions very dil. in Ag and $= 1 : 1.8$ in saturated solution. The relationship oxidation val. : total I $= 1 : 1$ and the absence of AgI exclude the possibility of the presence of I_2SO_4 or analogous mixed ψ -halogen, and the existence of adducts $I_2[Ag_2SO_4]_3$ or $I_2[AgHSO_4]_6$ is assumed. Addition of C_6H_6 to the solution causes almost immediate disappearance of the colour and formation of AgI , but the production of PhI is gradual, indicating that the reactive I_2SO_4 is not immediately present. I, H_2SO_4 , and $HgSO_4$ or Hg_2SO_4 yield brown solutions, Hg_2SO_4 being first oxidised by I. The relationship oxidising power : total I exceeds $1 : 1$, indicating $HgSO_4 + 2I_2 \rightleftharpoons HgI_2 + I_2SO_4$. At the commencement of the change the ratio (max.) is $3 : 1$, rapidly declining to $2 : 1$ and ultimately becoming const. at $1.25 : 1$. Similar brown solutions are obtained from I, conc. H_2SO_4 , and KIO_3 , MnO_2 , KIO_4 , and $KMnO_4$. Treatment of I- $HgSO_4$ - H_2SO_4 mixtures with C_6H_6 causes immediate separation of I and production of p - $C_6H_4I_2$ with a little PhI (possibly $C_6H_6 + I_2SO_4 + 3I_2 \rightarrow C_6H_4I_2 + H_2SO_4 + 3I_2$). An analogous change occurs with I- H_2SO_4 and AgI , PbI_2 , or HgI_2 , leading to complete separation of I with production of only a pale pink solution; possibly $2HgI_2 + I_2SO_4 + 3I_2 \rightarrow HgI_2 \cdot HgSO_4 + 5I_2$.

H. W.

Sublimed iron. W. KROLL (Z. Elektrochem., 1934, 40, 303—306).—An Fe crucible was sublimed in a high vac. at $1100-1200^\circ$ at the rate of 0.054 g. per sq. cm. per hr. The sublimate was examined microscopically, spectrographically, and chemically. There was more Mn and less C in the sublimate than in the crucible, and approx. the same proportion of other impurities.

F. L. U.

Complex salts of tervalent rhodium with 2 : 2'-dipyridyl. F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 284—290).— 6.5 g. of finely-powdered $RhCl_3 \cdot 4H_2O$, added to 15 g. of boiling dipyridyl (dipy), heated for 10 min., and then heated on the H_2O -bath, with addition of some H_2O and

EtOH, for several hr. yields a solution which on cooling deposits the pale yellow *compound*, $[\text{Rh}(\text{dipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ (I). If the mother-liquor is extracted with Et₂O and conc. on the H₂O-bath addition of EtOH ppts. the almost colourless *compound* $[\text{Rh}(\text{dipy})_3]\text{Cl}_3\cdot 3\text{H}_2\text{O}$ (II), which crystallises in rhombic-pyramidal form isomorphous with $[\text{Co}(\text{dipy})_3]\text{Cl}_3\cdot 2\text{H}_2\text{O}$. Traces of a *compound*, probably $[\text{Rh}_2(\text{dipy})_3\text{Cl}_6]$, are also obtained. If 9 g. of $\text{Na}_3\text{RhCl}_6\cdot 12\text{H}_2\text{O}$ be dissolved in 40 c.c. of H₂O and heated on the H₂O-bath with 6 g. of dipyrldyl in EtOH, (I) and (II) are formed, but the yield of (I) is 37 times that of (II). In presence of H₂O partial hydrolysis of (I) occurs, yielding the *compounds* $[\text{Rh}(\text{dipy})(\text{H}_2\text{O})_4]\text{Cl}_3$, $[\text{Rh}(\text{dipy})(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}$, $[\text{Rh}(\text{dipy})(\text{H}_2\text{O})_3\text{Cl}]\text{Cl}_2$, and $[\text{Rh}(\text{dipy})(\text{H}_2\text{O})\text{Cl}_3]$, according to the conditions of hydrolysis. When Na_3RhCl_6 is treated with an equiv. amount of AgNO_3 , and the Ag_3RhCl_6 obtained treated with the calc. amount of BaCl_2 , red crystals of $\text{Ba}_3(\text{RhCl}_6)_2\cdot 7\text{H}_2\text{O}$ are obtained on evaporation. These when treated with the calc. quantity of dipyrldyl sulphate give a brownish-red solution which on evaporation in vac. yields reddish-brown needles of the *compound* $[\text{Rh}_2(\text{dipy})_2\text{Cl}_6]\cdot 3\text{H}_2\text{O}$. J. W. S.

Direct oxidation of platinum under pressure. P. LAFITTE and P. GRANDADAM (Compt. rend., 1934, 198, 1925—1927).—The oxidation of heated Pt was studied at high pressures of O₂. Wire was superficially oxidised at 300—500° and 50—200 kg. per sq. cm. In 6 hr. at the optimum temp., 455°, sponge increased in wt. by 2.1% at 40 atm. and 7.37% at 150 atm. At 450° and 150 atm. Pt-black increased by 13.94% (cf. 8.19% O in PtO and 16.4% in PtO₂), *d* decreasing to 11.1; PtO₂, isolated from the product (I) by washing with aqua regia, was a blue powder, *d* 10.2, stable to 350°, and reduced by H₂ at room temp. (I) also contained PtO. B. W. B.

Stromholm's [platinum] triamminesulphite. I. I. TSCHERNIAEV and A. M. RUBINSCHTEIN (Compt. rend. Acad. Soc., U.R.S.S., 1934, 2, 179—184).—On oxidising $\text{Pt}(\text{NH}_3)_3\text{SO}_3$ the SO₃ undergoes oxidation first, whilst simultaneously NH₃ is eliminated. The transition from triammino-sulphite to -chloride cannot be accomplished. The solubilities at 25° of $\text{Pt}(\text{NH}_3)_3\text{SO}_3$ in H₂O and 0.1*N*-acids and NaOH have been determined. W. R. A.

Quantitative spectral analysis of gas mixtures. F. KLAUER (Ann. Physik, 1934, [v], 20, 145—160).—The spectroscopic detection of H₂ in He and A, and of He and A in H₂, was investigated by examination of the high-frequency glow discharge of the gas mixtures. Such a method is suitable for the determination of these gases in admixture. A high degree of sensitivity cannot be claimed for the detection of H₂ in these mixtures, a result in contrast with that of earlier workers, whose gas probably contained hydrocarbons. A. J. M.

Cadmium sulphate as a basis for acidimetry. S. E. Q. ASHLEY and G. A. HULETT (J. Amer. Chem. Soc., 1934, 56, 1275—1278).—Clear crystals of $\text{CdSO}_4\cdot \frac{8}{3}\text{H}_2\text{O}$ (I) have a highly uniform composition; by removing at a Hg cathode the Cd from an aq. solution containing a known wt. of (I), standard aq.

H₂SO₄ is obtained. This solution is as trustworthy a standard as aq. HCl of const. b.p., BzOH, and K phthalate. J. G. A. G.

Micro-determination of heavy water. P. GOLD-FINGER and L. SCHEEPERS (Compt. rend., 1934, 198, 1916—1918).—A micro-flotation method (cf. Lewis and Macdonald, A., 1933, 894) requiring 0.1—0.2 c.c. of H₂O is described. Flotation temp. were reproducible to $\pm 0.05^\circ$. B. W. B.

New mode of expression of analytical data for mineral waters. L. NENADOVIĆ (Bull. Soc. Chim. Yougoslav., 1933, 4, 221—226).—Graphical and other methods of presenting analytical results are proposed. R. T.

Determination of water in liquid sulphur dioxide.—See B., 1934, 624.

Photometric micro-analysis of drinking and service water. X. Determination of sulphate. XI. Determination of lead.—See B., 1934, 654.

Chronometric catalytic method for determining micro-quantities of iodine. E. B. SANDELL and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1934, 56, 1426).—The reaction between H₃AsO₃ and $\text{Ce}(\text{SO}_4)_2$ in aq. H₂SO₄ is greatly accelerated by traces of I', the rate being approx. $\propto [\text{I}']$ when other factors are const. Thus, the time required for the yellow colour of Ce^{IV} to disappear, or with *o*-phenanthroline-FeSO₄ as indicator, the pink colour to appear, is inversely \propto the wt. of I. Alkali chlorides and bromides and other salts have only small effects and by a special procedure 0.01—1 micro-g. of I at a dilution of 1 : 10⁷ is determined to within 20%. Micro-quantities of Os may be determined similarly. The test appears to be sp. for I, Os, and presumably Ru. J. G. A. G.

Determination of iodide by photometric titration. S. HIRANO (J. Soc. Chem. Ind. Japan, 1934, 37, 177—178B).—I' may be determined by photometric titration with IO₃⁻; at the end-point the [I] is a max. and there is a sharp max. in the optical density. A. G.

Determination of iodine in hard drinking waters. J. STRAUB (Z. anal. Chem., 1934, 97, 259—262).—In the determination of I by von Fellenberg's method, no formation of $\text{Ca}(\text{IO}_3)_2$ could be detected with hard H₂O, but repeated extraction with EtOH is necessary for quant. removal of I'. J. S. A.

Determination of fluorine in silicate rocks, waters, etc. O. HACKL (Z. anal. Chem., 1934, 97, 254—258).—To the neutralised solution of the rock, after fusion and treatment with $(\text{NH}_4)_2\text{CO}_3$, are added H₂O₂ and 1—10 c.c. of aq. $\text{Ti}(\text{SO}_4)_2$ (1 mg. TiO₂ per c.c.), then H₂SO₄. The comparison solution is treated identically, and standard aq. NaF added until a colour match is obtained. J.

Mindalev's volumetric method of determination of sulphate. C. B. MEDINSKI, V. L. NIKOPOLSKAJA, and M. D. TRUSOV (Zavod. Lab., 1934, 3, 230—231).—Mindalev's method (A., 1929, 162) gives untrustworthy results in presence of Ca⁺⁺ and Cl⁻, or at > 25°, and is unsuitable for factory practice. R. T.

Kjeldahl method. III. Further comparisons of selenium with mercury and with copper ca a-

lysts. R. A. OSBORN and A. KRASNITZ (J. Assoc. Off. Agric. Chem., 1934, 17, 339—342; cf. A., 1933, 520).—HgO alone and HgO+Se are equally effective catalysts, giving 25% saving of time when compared with Se alone or Se+CuSO₄. When the digestion period is extended the danger of loss of N increases in the order: HgO, Se, HgO+Se. The danger can be obviated by using larger amounts of H₂SO₄.

E. C. S.

Detection of phosphoric acid in hydrogen peroxide solutions.—See B., 1934, 572.

Determination of carbon dioxide using the Geissler-Vorišek apparatus. J. VORIŠEK (Chem. Listy, 1934, 28, 116—118).—Modifications of the Geissler apparatus are described, and the use of a citric acid-HCl mixture is recommended for expulsion of CO₂ from carbonates.

R. T.

Continuous determination of carbonate-caustic ratio in a carbon dioxide absorption system.—See B., 1934, 623.

Determination of carbon monoxide. R. GOUBAU and J. ECKHOUT (Natuurwetensch. Tijds., 1934, 16, 117—130).—The CO content of a gas mixture containing 0.001% CO may be determined by a spectrophotometric method in which the λ at which the absorption curve of a solution of hæmoglobin (I) intersects that of a solution of Congo-red (II) is compared with the corresponding point of intersection for solutions of carboxyhæmoglobin (III) and (II). The solution of (II) must be buffered to prevent change of colour with time. Under specified conditions, the observed point of intersection ranges from 5243 Å. for solutions of 100% (III) to 5415 Å. for solutions of 100% (I). The error depends on the degree of refinement of the λ reading, but should be $\pm 2\%$.

H. F. G.

Lawrence Smith method for the determination of alkalis in rocks. W. VAN TONGEREN (Z. anorg. Chem., 1934, 218, 252).—The powdered rock is ground still more finely under EtOH, NH₄Cl moistened with EtOH is added, and the mixing with CaCO₃ is carried out under EtOH.

M. S. B.

Determination of sodium by means of uranyl magnesium acetate. I. I. NAZAROV and L. P. BANINA (Zavod. Lab., 1934, 3, 226—229).—Kahane's method (A., 1930, 726), with minor modifications, gives trustworthy results.

R. T.

Rapid determination of silver in argentiferous galena.—See B., 1934, 582.

Rapid identification of silver cyanide in presence of silver halides. E. V. ZAPPI and A. MANINI (Anal. Asoc. Quim. Argentina, 1934, 22, 21—23). A sample of the ppt. is treated with Hg₂(NO₃)₂; AgCN (I) is blackened, but Ag halides (II) are unaffected. (I), if present, is destroyed by boiling the remainder of the ppt. with HNO₃ before testing for (II). R. N. C.

Indifferent electrodes. I. Potentiometric titration of calcium. C. A. NIERSTRASZ and H. J. C. TENDELOO (Rec. trav. chim., 1934, 53, 792—797). Electrodes of the type M₁, CuC₂O₄, CaC₂O₄ (where M₁=Au, or Pt) are satisfactory for titrating Ca with (NH₄)₂C₂O₄. Electrodes of Au and Pt, or Ag and Pt,

using CuC₂O₄ in both cases, are still more satisfactory for Ca(NO₃)₂. Cl' does not interfere. E. S. H.

Separation of beryllium from iron by means of "cupferron." A. TETTAMANZI (L'Ind. Chimica, 1934, 9, 752—755).—The solution is acidified with conc. HCl and treated with excess of clear, fresh 6% cupferron solution. After 15—20 min., the Fe ppt. is collected, with the help of gentle suction, on a tared filter supported on a Pt cone and washed 4—5 times with dil. HCl (5 c.c. conc. HCl+100 c.c. H₂O), 2—3 times with dil. NH₃ (1 vol. conc. NH₃+1 vol. H₂O), and 4—5 times with H₂O. The ppt. and paper are dried in a Pt crucible for 30 min. at 100—105°, heated gently, and later strongly, and weighed. Any Cu is pptd. with the Fe.

T. H. P.

Volumetric determination of zinc. A. CHIAROTINO (L'Ind. Chimica, 1934, 9, 468—470).—Disadvantages of the method based on the reaction between ZnS and AgCl are discussed. In the method recommended, the Zn (0.1 g.) is pptd. as ZnS in the usual manner; the washed ppt. is heated on the H₂O-bath for a few min. with 50 c.c. of H₂O and an excess of HgCl₂, and the HgS is allowed to settle after a few drops of dil. H₂SO₄ have been added. The filtered solution is treated with HNO₃ and 0.1N-AgNO₃, and titrated with NH₄CNS.

H. F. G.

Quantitative spectral analysis. II. R. BRECKROT and A. MEVIS (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 99—119).—Data for the determination of Cd, Sn, Zn, Al, Ba, Ca, Mg, Ge, and Au are given.

C. W. G.

Indirect potentiometric determination of cadmium. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 97, 263—266).—[Cd(CNS)₂(C₅H₅N)₂] is pptd. quantitatively by addition of excess of 0.1N-KCNS+C₅H₅N. An aliquot portion of the liquid is neutralised with HNO₃ (Me.-orange), and excess of CNS' titrated back potentiometrically with AgNO₃.

J. S. A.

Gravimetric determination of thallium as cobaltinitrite and its separation from other metals. S. NISHIKU (J. Soc. Chem. Ind. Japan, 1934, 37, 180B).—The reagent is prepared by mixing equal vols. of solutions containing 28.6 g. of Co(NO₃)₂ and 50 c.c. of 50% HCO₂H in 500 c.c. and 180 g. of NaNO₂ in 500 c.c., respectively, and after heating at 30—40° is added to the Tl solution containing 5% HCO₂H and heated at Tl—50°. The scarlet ppt. is collected in a glass filter, dried at 120°, and weighed; it contains 64.67% Tl.

A. G.

Separation of thallium as bromide by means of ether. I. WADA and R. ISHII (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 135—148).—Tl may be separated from the alkali, alkaline-earth, rare-earth, and Pt-group metals, also Cu, Zn, Cd, Hg, Al, Ga, In, Ti, Zr, Pb, Th, V, Sb, Bi, Cr, Mo, Te, U, Mn, Fe, Co, and Ni, by extracting with Et₂O in presence of N-HBr. Au, which also passes into the Et₂O, may be separated by heating the extract with H₂O, and adding successively 2 c.c. of 10% NH₄OH, HCl, 2 c.c. of 10% KCN, 2 c.c. of 2N-KOH, and 1 c.c. of 5% KI for 100 mg. of Au and 100 mg. of Tl; the Au remains in solution.

R. S. B.

Titrimetric determination of copper. E. BOYE (Ber., 1934, 67, [B], 1119—1121).—The sol. Cu salt (0.1—0.2 g.) is dissolved in about 75 c.c. of H_2O slightly acid with H_2SO_4 or HCl and 25 c.c. of $MeOH$ are added. The solution is heated to boiling in a stream of N_2 or CO_2 , which is continued until the end of the titration. $(NH_4OH)_2.H_2SO_4$ (0.5—1 g.) is added in small portions until reduction is complete, as shown by the decolorisation of the solution. The liquid is cooled to about 15—20° and titrated with 0.5*N*- $KCNs$ in presence of Fe^{III} alum. H. W.

Quantitative spectral analysis of "pure" metals. R. BRECKPOT (Natuurwetensch. Tijds., 1934, 16, 139—143).—In electro-refined Cu (99.94—99.975%) very few of the impurities can be determined directly. By recourse to co-pptn. on suitable substances $[MnO_2, Fe(OH)_3]$, 0.01 mg. of As and Sb and 0.001 mg. of Bi can be determined in 10 mg. of Cu. Since CuS adsorbs Sb_2S_3 , separation by the sulphide method is not satisfactory; the MnO_2 ppt. should be washed as free as possible from Cu, the residual Cu determined colorimetrically, and sufficient Cu added to yield a total of 100 mg., which can then be examined spectrographically. Alkaline-earth metals in Al should be co-pptd. with Fe carbonate from a solution in $NaOH$; traces (10⁻⁴%) of Ba may be so determined. The method may be applied to the determination of traces of Ba etc. dissolved from glassware, and of Pb in H_2O . H. F. G.

Use of sodium diethyldithiocarbamate in the determination of minute amounts of copper. H. W. MOSELEY, A. G. ROHWER, and M. C. MOORE (Science, 1934, 79, 507—508).—The addition of gum tragacanth or gelatin prevents the turbidity which often occurs. Details of a modified method (cf. A., 1930, 53) for the microcolorimetric determination of Cu using Na diethyldithiocarbamate are given.

L. S. T.

Colorimetric determination of small quantities of copper in presence of iron. A. CASTIGLIONI (Z. anal. Chem., 1934, 97, 270—273).—By boiling an aq. HCl solution with $Na_2S_2O_4$, $Cu + CuS$ is pptd. The ppt. is dissolved in HNO_3 , excess of aq. NH_3 added, and then $(NH_4)_2S$. Colloidal CuS is pptd., and may be determined colorimetrically. J. S. A.

Microchemical reaction of mercurous mercury. S. AUGUSTI (Gazzetta, 1934, 64, 322—324).—1 drop of the solution is evaporated cautiously to dryness on a microscope slide. After cooling, 1 drop of dil. aq. $KCNs$ or NH_4CNS and one of aq. $Co(NO_3)_2$ or $CoSO_4$, or 1 drop of aq. $K_4[Co(CNS)_6]$, is added. Blue crystals of $Hg_4[Co(CNS)_6]$ indicate the presence of Hg^{II} . 0.6×10^{-6} g. may be detected, using a magnification of 300 diameters. Cu^{II} , Pb^{II} , Bi^{III} , OH' , NH_3 , and large quantities of NO_3' and Cl' interfere. D. R. D.

Analysis of mercuriammonium compounds. S. AUGUSTI (Gazzetta, 1934, 64, 324—334).—Published methods are reviewed, the author's results with various Hg_2N^I salts being quoted. D. R. D.

Volumetric determination of mercuric chloride. M. RAGNO (Annali Chim. Appl., 1934, 24, 270—272).— $HgCl_2$ in sublimate tablets may be determined

volumetrically in accordance with the reactions: (1) $2KMnO_4 + 5K_2SnCl_4 + 2H_2O + 16HCl = 5SnCl_4 + 12KCl + 2MnCl_2 + 18H_2O$, and (2) $HgCl_2 + K_2SnCl_4 + 2H_2O = Hg + 2KCl + SnCl_4 + 2H_2O$; $NaHCO_3$ is added to give an atm. of CO_2 to prevent oxidation of the K_2SnCl_4 . Results to within about $\pm 0.1\%$ are recorded. T. H. P.

Determination of aluminium in spring waters. V. GAZZI (Annali Chim. Appl., 1934, 24, 226—229).—Chemical analysis of natural H_2O often indicates amounts of Al greatly in excess of the true amounts. The val. of spectrographic analysis is emphasised. T. H. P.

Separation of aluminium from nickel and cobalt by hydrazine carbonate. A. JLEK and J. VREŠT'AL (Chem. Listy, 1934, 28, 113—115).—4 c.c. of 50% aq. $N_2H_4.H_2CO_3$ are added to 200 c.c. of solution, containing > 0.1 g. each of Al, Ni, and Co, the solution is filtered after heating for 1 hr. at 100°, and the ppt. is washed with 1% aq. NH_4NO_3 , and dissolved in HNO_3 , excess of which is removed by evaporation. The pptn. is repeated, and the ppt. is ignited, and weighed as Al_2O_3 . Ni and Co are determined in the united filtrates by the ordinary procedures. R. T.

Acidimetric titration in presence of manganous salts. P. MARANGONI (Boll. Chim. Farm., 1934, 73, 361—363).—Free acid in a solution containing Mn^{II} salt cannot be determined by titration with $NaOH$ in presence of Me-orange, Me-red, etc., owing to decolorisation of the indicator, unless NH_4Cl is added. Titration with Na_2CO_3 needs no such addition (cf. Perret and Krawczynski, A., 1932, 1220). T. H. P.

Modified thiocyanate procedure for the determination of small quantities of iron. H. A. DANIEL and H. J. HARPER (J. Assoc. Off. Agric. Chem., 1934, 17, 286—290).—The isoamyl alcohol modification of the CNS' method (B., 1932, 78) is untrustworthy owing to fading of the coloration at all temp., and to the undesirable colours introduced by Ca salts. The colour does not fade in dil. aq. HNO_3 , but fades in presence of HCl or H_2SO_4 . Ca does not interfere when present as $Ca(NO_3)_2$. A procedure for the determination of Fe in forage and grain is outlined. E. C. S.

p-n-Butylphenylarsinic acid as a reagent for determining iron. K. A. CRAIG and G. C. CHAND-LEE (J. Amer. Chem. Soc., 1934, 56, 1278—1279; cf. A., 1933, 1263).—0.75 g. of reagent in 100 c.c. of H_2O at 80—90° is added slowly to > 70 mg. of Fe in 200 c.c. of $> 0.4N$ - HCl , HNO_3 , or H_2SO_4 at $< 100^\circ$. After digestion (30 min.), the cold ppt. is washed with 0.02*N*- HCl and ignited to Fe_2O_3 . In this way, Fe is separated quantitatively from Ni, Zn, Co, Mn, Cu, Cd, K, Al, Mg, Ca, Be, La, Er, Nd, V, Cr (repptn. necessary), and Ti (special procedure). F' , PO_4 , tartrate, citrate, Zr, Sn, Ti, Th, U, and Ce interfere.

Quantitative optical spectral analysis. W. SEITH and E. HOFER (Z. Elektrochem., 1934, 40, 313—322; cf. A., 1932, 1195).—Tables are given for the determination of Ni in Pb, Pb in Sn, Mg in Pb, and Ca in Pb by the method of homologous pairs. A photometric method, devised for Cu in Pb, Pb in Cd, and Cu in Pb, yields reproducible results. F. L. C.

Colorimetric determination of tungsten. F. A. FERJANTSCHITSCH (Zavod. Lab., 1934, 3, 301—303).—0.1 g. of mineral (containing 0.02—1% WO_3) is ignited, treated with HF to eliminate SiO_2 , the residue is fused with 0.5 g. of Na_2CO_3 , MnO_4^{2-} in the solution of the melt is reduced with EtOH, the solution is filtered, and the filtrate is evaporated to dryness. The residue is dissolved in 3 c.c. of H_2O , 10 drops of 25% KCNS, H_2O to 5 c.c., 4 c.c. of conc. HCl, and a few drops of 0.75% TiCl_3 in 50% HCl are added, and H_2O to 10 c.c. The coloration obtained is compared with that given by standard aq. Na_2WO_4 . R. T.

Separation of tin by nitric acid and contamination of stannic oxide by accompanying metals. W. TILK and R. HOLTJE (Z. anorg. Chem., 1934, 218, 314—320).—A systematic study has been made of the amounts of Cu, Pb, Zn, Ni, and Fe retained by SnO_2 in the quant. analysis of Sn alloys when Sn is separated by repeated evaporation with HNO_3 . M. S. B.

Solutions of bivalent vanadium salts as reducing agents in potentiometric analysis. K. MAASS (Z. anal. Chem., 1934, 97, 241—253).—Acid VCl_2 or VSO_4 solutions maintain a stable titre in the absence of air. Titration is best effected at 90—100°, using a Pt indicator electrode. Fe^{3+} , Cu^{2+} in HCl and AcOH, and Ag^+ oxidise V^{II} to V^{IV} , which is reduced by further V^{II} to V^{III} , giving two potential increments (equal if the reagent contains no V^{III}). Cu^+ in H_2SO_4 solution oxidises to V^{III} only, as do VO^{2+} salts. CrO_4^{2-} , MnO_4^- , etc. oxidise to V^V , which is reduced by further reagent giving three increments. Simultaneous determination of Fe^{2+} and Cu or VO (in HCl), or of Ag and Fe^{2+} or Cu (in H_2SO_4) is possible. Addition of inert salts (e.g., NaCl, Na_2SO_4 , NaOAc) frequently sharpens the end-point. J. S. A.

Determination of small amounts of bismuth, antimony, tin, and molybdenum in copper.—See B., 1934, 630.

Rapid separation of gold and silver from cyanide and chloride solutions. M. MLADENOVIC and V. STAJIC (Bull. Soc. Chim. Yougoslav., 1933, 4, 207—209).—10—50 c.c. of solution are diluted to 500 c.c., 20 c.c. of 10% $\text{Pb}(\text{OAc})_2$ or CuSO_4 are added, the temp. is raised to 50°, and aq. Na_2S is added to complete pptn. R. T.

Determination of gold by photometric titration. S. HIRANO (J. Soc. Chem. Ind. Japan, 1934, 37, 178—179B).—Au may be determined photometrically by reduction with SnCl_2 , a break in the curve corresponding with complete formation of purple of Cassius. Cu, Pb, and small amounts of Fe do not interfere. A. G.

Registering apparatus for studying reactions at regularly varied temperatures. P. VALLET (Compt. rend., 1934, 198, 1860—1863).—Guichard's method (A., 1925, ii, 559) has been modified to give simultaneous automatic records of wt. and temp. during thermal analysis. The results obtained with several hydrated salts are described. B. W. B.

Electric furnace for micro-Kjeldahl digestions similar purposes. S. J. FOLLEY (Biochem. J., 1934, 28, 890—891). F. O. H.

Preventing overheating of oil-baths. H. LEVIN and R. LANARI (Ind. Eng. Chem., 1934, 26, 696).—Melting of a fusible alloy strip immersed in the bath breaks the heating current if overheating occurs. J. S. A.

Automatic registration of rapidly proceeding thermal processes. J. I. LEVANDO (Zavod. Lab., 1934, 3, 316—325).—Apparatus and methods for the thermal analysis of steels are described. R. T.

Cathode-ray furnace. F. TROMBE (Bull. Soc. chim., 1934, [v], 1, 262—266).—A simple and efficient furnace is described. D. R. D.

Gas blowpipe with electric preheating. A. A. GUNTZ (Bull. Soc. chim., 1934, [v], 1, 259—262).—By preheating the gas and air, hard glasses may be easily worked without O_2 . An apparatus is figured. D. R. D.

Measurement of slow variations in the refractive index of solids. A. BIOT (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 93—99).—The substance studied is placed between the collimator and the telescope of a spectrometer, and the movement of the fringes produced is measured photographically. C. W. G.

Conversion of photographic sensitivity scales. J. A. M. VAN LIEMPT (Rec. trav. chim., 1934, 53, 816—817).—Conversion formulæ for the Scheiner, Hurter and Driffeld, and DIN systems are given. E. S. H.

Combined light and electron microscope, its properties and use. W. KNECHT (Ann. Physik, 1934, [v], 20, 161—182).—An arrangement of apparatus for combining in the same tube a light- (I), magnetic- (II), and electron-microscope (III) for the study of cathode images is described. (II) and (III) appear to be equally suitable. Combinations of electrical and magnetic lenses were investigated. Images formed by (III) show many details not observed in (I), particularly phenomena occurring in the interface between metal and oxide paste of an oxide cathode. A. J. M.

Permeability of glasses to ultra-violet light, measured by fluorescence. P. W. DANKWORT and E. JURGENS (Arch. Pharm., 1934, 272, 713—715).—Apparatus for determination of the absorption of ultra-violet light of different λ by glass, using a fluorescent screen or a camera, is described. R. S. C.

Broad-range vacuum spectrograph for the extreme ultra-violet. K. T. COMPTON and J. C. BOYCE (Rev. Sci. Instr., 1934, [ii], 5, 218—224).—A 2-m. focus normal-incidence instrument, covering on one plate the range zero order—first order of λ 2500, is described. Dispersion is 4.27 Å. per mm., and the body is exhausted to 2×10^{-5} mm. pressure. N. M. B.

Apparatus for the examination of fluorescent materials, particularly for television receivers. M. VON ARDENNE (Angew. Chem., 1934, 47, 483—484).—The properties which a substance should possess in order to be suitable for use on the fluorescent screens of television receivers are listed. It is important that it should fluoresce intensely and with a pleasing colour and that the luminescence should not

persist for > 0.04 sec. after irradiation has ceased. An apparatus for testing these points under standardised conditions is described. D. R. D.

Objective colorimeter. A. H. W. ATEN, N. GALEMA, and C. A. GOETHALS (Chem. Weekblad, 1934, 31, 258—264).—A simple form of apparatus in which the light intensity is determined by means of a Se cell and a millivoltmeter is described. Concns. may be determined to within 0.25% if special precautions are taken, or rapidly to within 2.5% if certain refinements are omitted. H. F. G.

Precipitation of silver chloride. I. Photronic nephelometer. C. H. GREENE (J. Amer. Chem. Soc., 1934, 56, 1269—1272).—The apparatus consists of a Weston photonic cell for determining the light from a standard source scattered by suspensions prepared under carefully controlled conditions. The reproducibility of the opalescence of AgCl suspensions made from dil. AgNO₃ and excess of HCl increases with increase of [HCl] and added HNO₃. J. G. A. G.

Methods of focussing in analysis of crystalline powders and in spectrography of X- and γ -rays. H. HULUBEI (Compt. rend., 1934, 198, 2164—2166; cf. this vol., 163).—A discussion and suggested modifications of the author's method. B. W. B.

Influence of polarisation on the effects of selenium electrolytic photo-cells. R. AUDUBERT and J. ROULLEAU (Compt. rend., 1934, 198, 1907—1909; cf. this vol., 584).—Photo-potential (I)-polarisation potential (II) curves for polarised Se/Pt electrolytic photo-cells were determined for a range of λ and light intensities. The results support the proposed electronic mechanism (*loc. cit.*). The sign of (II) was reversed at high vals. of (I), due to photo-electronic penetration of the Se-Pt boundary. Se functions as an inert polarisable electrode. B. W. B.

Constancy of the selenium unidirectional-layer photo-cell. L. BERGMANN (Physikal. Z., 1934, 35, 450—452).—The conclusion of Grundmann and Kassner (this vol., 276) that these cells are unsuitable for meteorological work is too general. The newer and more sensitive cells give const. results, not varying with age or duration of illumination. For very strong illumination the use of a shutter is recommended. A. J. M.

Boundary-layer photo-electric cells. (MME.) ROY-POCHON (Compt. rend., 1934, 198, 2083—2084).—Practically non-rectifying Se cells, giving linear photo-current-light intensity curves, have been constructed. The differences between the properties of such cells and of highly rectifying Se cells indicate that the photo-electric effect is independent of rectification. B. W. B.

Fluorine generation cell. K. G. DENBIGH and R. WHYTLOW-GRAY (J.S.C.I., 1934, 53, 139—140r).—The cell is made of Cu and has a specially wide exit tube and a high diaphragm vessel to eliminate blocking up. The efficiency is 80% at 15 amp. The C fluorides (formed by attack of the graphite anode) are removed by passage through liquid air. A cement compound of CaF₂ and water-glass is described.

Conductivity recorder. S. KAMBARA and M. MATSUI (J. Soc. Chem. Ind. Japan, 1934, 34, 158—159B).—A conductivity recorder operating on a.c. suitable for industry is described. R. S. B.

Simple heavy-current resistance. F. A. CUNNOLD and M. MILFORD (J. Sci. Instr., 1934, 11, 199).—A C rod is supported axially in an insulated Fe tube through which H₂O is flowing. C. W. G.

High-intensity mass-spectrometer. W. R. SMYTHE, L. H. RUMBAUGH, and S. S. WEST (Physical Rev., 1934, [ii], 45, 724—727).—An instrument, in which a new type of magnetic lens focusses on a slit all the positive ions of a given mass from an extended source, is described. Almost complete separation of the K isotopes, and the collection of samples of Li⁶ and Li⁷, have been carried out. N. M. B.

Significant vapour-pressure considerations of the Van Slyke manometric method of gas analysis. M. SHEPHERD (Bur. Stand. J. Res., 1934, 12, 551—566).—Van Slyke's C correction changes with temp. Modifications of the apparatus and method are suggested. H. J. E.

Apparatus for the study of chemical reactions under mechanical pressure. K. C. BEESON and J. B. KERSHAW (J. Assoc. Off. Agric. Chem., 1934, 17, 320—323). E. C. S.

Source of error in chemical measurements of high precision which depend on the use of compressed oxygen. I. L. J. P. KEFFLER (J. Amer. Chem. Soc., 1934, 56, 1259—1262).—The apparent val. of the H₂O equiv. of the calorimetric bomb decreases as the pressure of O₂ in a cylinder of commercial gas, from which the bomb is filled, gradually falls. The effect is attributed to the more rapid effusion through the valve of the O₂ as compared with the traces of combustible impurities. J. G. A. G.

Direct-reading manometer for low pressures. F. TROMBE (Bull. Soc. chim., 1934, [v], 1, 408—410).—The apparatus is not subject to the errors of the McLeod gauge in the presence of vapours liquefiable at the temp. of measurement. It can be used for the measurement of small v.p. and low pressures between 0.001 and 1 mm. M. S. B.

Spring tubing in high-vacuum technique. F. DURAU (Z. Physik, 1934, 89, 152—154). A. B. D. C.

High-vacuum lubricant-free metal valve. High-vacuum lubricant-free metal seals and joints. F. DURAU (Z. Physik, 1934, 89, 143—147, 148—151). A. B. D. C.

Wilson apparatus for variable pressures. F. JOLIOT (J. Phys. Radium, 1934, [vii], 5, 216—218). An apparatus in which the pressure in the expansion chamber can be varied from 1 cm. to several atm. is described. N. M. B.

Determination of the volume of dielectric bodies suspended or deposited in an electrolyte by the method of two tubes. A. SLAWINSKI (Bull. Soc. Chim. biol., 1934, 16, 448—460).—A description of the technique of the author's method (A., 1919, 1142) of determining suspension concns. A. L.

Water-tight "lead-in" to an enclosed chamber, suitable for ordinary temperatures. W. F. COPE (J. Sci. Instr., 1934, 11, 198—199).—Rubber rings on the tubes are squeezed between the counter-sunk faces of two brass plates. C. W. G.

Pressure measurements by photographic determination of the levels attained by liquids in tubes. A. FORTIER (Compt. rend., 1934, 198, 2142—2144).—Oblique upward illumination of the meniscus of a transparent liquid produces two real, curvilinear images, < 0.01 mm. wide, which may be photographed directly for continuous record.

B. W. B.

Continuous extractor for liquids heavier or lighter than the solvent. E. A. GAUTHIER and B. ROSSI (Annali Chim. Appl., 1934, 24, 257—259).—In this apparatus solvents heavier and lighter than the liquid to be extracted may be used successively.

T. H. P.

Improvements in the Dufton-Crismer fractionating column. O. MILLER (Bull. Soc. chim. Belg., 1934, 43, 279—286).—The efficiency of the column is increased (1) by progressively increasing the distance between the turns of the spiral from 2.5 mm. as the column is descended, and (2) by winding the column with an electrically heated wire and varying the current so that the column is always on the point of flooding.

J. G. A. G.

Dependence of velocity of filtration on the chemical and colloidal properties of the impurities. R. KOPPEN (Arch. Pharm., 1934, 272, 698—700).—Lactose does not prevent oxidation of metals during the prep. of colloidal solutions by friction. Membranes which give similar speeds of filtration for H₂O may behave differently towards all except very stable colloids, owing to large variations in the size of the particles.

R. S. C.

Solvents for micro-mol. wt. determinations according to the method of mol. depression of m.p. for the practice of organic chemistry. J. PRMSCH (Ber., 1934, 67, [B], 1115—1119).—Suitable

alcoholic and ketonic solvents of m.p. about 100° are *tetrahydro- α -dicyclopentadien-3-ol*, b.p. 118°/12 mm., m.p. 85°, $E=49$ [obtained by hydrogenation (Pd-BaSO₄-anhyd. EtOH) of dihydro- α -dicyclopentadien-3-ol], *tetrahydro- α -dicyclopentadien-3-one*, m.p. 101°, $E=56.8$, and dihydro- α -dicyclopentadien-3-one, m.p. 53°, $E=92$.

H. W.

Limiting gas-density method for mol. wts. R. T. BIRGE and F. A. JENKINS (J. Chem. Physics, 1934, 2, 167—183).—Methods of reducing available data are examined critically; the most satisfactory methods are applied to data for MeCl and NH₃ and discrepancies of previous results are discussed.

N. M. B.

Easy method of removing adhering rubber tubing and stoppers from laboratory glassware. L. SKAZIN (Canad. J. Res., 1934, 10, 592).—The rubber is softened by allowing steam to circulate inside the glassware.

O. J. W.

Periodicities of precipitation [studied] by the two-drop method. (MLLE.) S. VEIL (Compt. rend., 1934, 198, 1854—1856).—The advantages of studying periodic pptn. by interaction between two drops of solutions placed in proximity on gelatin are discussed (cf. A., 1933, 224).

B. W. B.

Collecting spilled mercury. C. V. BOYS (Nature, 1934, 134, 29).—Hg spilled on a smooth surface can be collected into one mass by sprinkling with H₂O.

L. S. T.

Chart for [determining] logarithmic mean. S. HATTA (J. Soc. Chem. Ind. Japan, 1934, 37, 165—166B).—A nomograph is given for reading the logarithmic mean of two nos. from one no. and their ratio.

A. G.

Muhammad Ibn Umail: an early Muslim alchemist. E. J. HOLMYARD (Nature, 1934, 133, 937—938).

L. S. T.

Early history of Mendeleeff's periodic law. B. N. MENSCHUTKIN (Nature, 1934, 133, 946).

L. S. T.

Geochemistry.

Density of Dead Sea water. R. J. CLARK and F. L. WARREN (Nature, 1934, 134, 29).—No difference in d could be detected between H₂O from the Dead Sea and redistilled H₂O, by two methods in which the uncertainty is approx. 1 in 10⁵.

L. S. T.

Mineral water of the Chief Spring in Krymca. S. JURKOWSKI (Arch. Chem. Farm., 1934, 1, 81—92).—The analytical data obtained are practically identical with those found by Schultes in 1807.

R. T.

Water of some lakes of the Kurgan forest steppe. A. V. GOLOVIN (Trav. inst. rech. biol. Perm, 1932, No. 3—4, 61—75).—Chemical differences are recorded. Most of the lakes fall into groups I and III of Palmer's classification. As the lake passes from "youth" to "maturity" it shows an increase in dry residue, and in alkali and Cl concn., and a decrease in [Ca⁺⁺] and [CO₃⁼⁼].

CH. ABS.

Physical tests and properties of oil and gas sands. G. H. FANCHER, J. A. LEWIS, and K. B. BARNES (Penn. State Coll. Min. Ind. Exp. Sta. Tech. Paper, 1933, No. 4).—Petrographic examination, screen analysis, and porosity and permeability tests are described and discussed.

CH. ABS.

Physical characteristics of oil sands. G. H. FANCHER, J. A. LEWIS, and K. B. BARNES (Penn. State Coll. Min. Ind. Exp. Sta. Bull., 1933, 12, 65—171).—Porosity and permeability determinations are described and data for 130 sands are recorded. No consistent relationship was found between porosity, permeability, and screen analysis.

CH. ABS.

Berthierite from Kisbanya, Carpathians. V. ZSIVNY and L. ZOMBORY (Min. Mag., 1934, 23, 566—568).—This rare mineral, previously known from two localities in old Hungary, also occurs at Kisbanya in

comitat Szatmar (now Chiuzbaia in Satu Mare, Romania), as bundles of needles with stibnite and rhombohedral carbonates. Analysis agrees closely with FeSb_2S_4 , but d 4.65 is higher than previously recorded for the mineral. L. J. S.

Zeolites. VII. "Clinoptilolite," a silica-rich variety of heulandite. M. H. HEV and F. A. BANNISTER (Min. Mag., 1934, 23, 556—559).—The "mordenite" from Wyoming described by Pirsson (1890) has been named "clinoptilolite" by Schaller (A., 1932, 1228). X-Ray examination of the original material shows that it bears no relation to either mordenite or ptilolite, the structure being that of heulandite with a replacement of CaAl by NaSi in the unit cell formula $\text{Na}_x\text{Ca}_y\text{Al}_{x+y}\text{Si}_{36-(x+2y)}\text{O}_{72}\cdot 24\text{H}_2\text{O}$. L. J. S.

Zoning in plagioclase feldspar. J. PHEMISTER (Min. Mag., 1934, 23, 541—555).—Feldspar phenocrysts in Scottish basalts show several types of zoning: (a) normal, proceeding outwards from more basic to more acid plagioclase; (b) simple reverse; and (c) oscillatory, which may be oscillatory-normal or oscillatory-reverse. The alternating composition of the thin zones is possibly the result of lack of balance between rate of growth of the crystal and rate of diffusion from the surrounding magma. Recurrence of calcic plagioclase in the inner part of main zones is explained as the result of irruption of hot magma into the crystallising liquid, probably consequent on eruption of lava at higher levels. L. J. S.

Zoned associations of antigorite, talc, actinolite, chlorite, and biotite in Unst, Shetland Islands. H. H. READ (Min. Mag., 1934, 23, 519—540).—Large spheroidal bodies up to 20 ft. across occurring in garnet-staurolite-kyanite-gneisses consist in the interior of antigorite followed outwards by successive zones of talc, actinolite, chlorite, and biotite. An intrusion of peridotite into pelitic sediments was followed by intense metamorphism separating the former into smaller masses and converting the latter into gneisses. Fluids from later granitic intrusions were then supposed to give rise to differences in composition in the successive zones of the balls, this further metamorphism being accompanied by a transfer of material on a considerable scale. L. J. S.

Diminution in the density of quartz on grinding. G. TAMMANN and G. MORITZ (Z. anorg. Chem., 1934, 218, 267—272).—The d of quartz (I) may be reduced by grinding by as much as 10%. The X-ray diagram shows no marked change in crystal structure and the phenomenon is attributed to the formation in (I) of hollow channels which do not reach the surface. By the same process the d of cristobalite (II), and also of (I) glass, is, on the contrary, increased by approx. 2%. The transition of both (I) and (II) is prevented by grinding. M. S. B.

Structure of kaolin. II. Refractiveness of the aluminosilicate nucleus of kaolin and its derivatives. M. DOMINIKIEWICZ (Arch. Chem. Farm., 1934, 1, 115—119; cf. A., 1933, 37).—The view that kaolin (I) is the Na_6 salt of the hexabasic acid, $\text{H}_{12}\text{Al}_6\text{Si}_6\text{O}_{27}$ (II) is supported by the following: (I), on fusion with Na_2CO_3 , yields the Na_{12} salt (III)

of (II), which on heating with H_2O at 180° regenerates (I), crystallising as $4(\text{I})\cdot 3\text{H}_2\text{O}$ (IV). (IV) and (III) yield the corresponding Ag_6 (V) and Ag_{12} (VI) salts on prolonged heating with aq. AgNO_3 . Dehydrated (I), $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}$, does not react with AgNO_3 , whence it follows that $\text{H}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ is a stronger acid than (II), in which 6 H atoms are combined with Si, and 6 with Al. (V) yields the corresponding K_6 salt on heating with aq. KCl , and $\text{H}_{10}(\text{NH}_4)_2\text{Al}_6\text{Si}_6\text{O}_{27}$ with aq. NH_4Cl , whilst (VI) affords on heating with aq. NaCl successively $\text{Ag}_3\text{Na}_3\text{Al}_6\text{Si}_6\text{O}_{27}$ and $\text{H}_3\text{Ag}_3\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{27}$. R. T.

Superficial alteration of copper deposits and prospecting. F. BLONDEL (Chim. et Ind., 1934, 31, Spec. No., 295—305).—In general Cu deposits exhibit three zones, (a) an oxidation zone, where most of the minerals are oxidised and where the seam is usually impoverished, (b) a cementation zone, lying below a and generally enriched in sulphides, and (c) lower still, a zone of primary minerals. The character and extent of the first two zones are discussed. A. B. M.

Geochemistry of manganese in West Siberia. P. I. LEBEDEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 422—427).—The Mn contents of different types of rocks from Oirotia have been determined and are discussed with reference to the development of Mn ore deposits. J. W. S.

Physico-chemical properties of Japanese acid clay. X. Formula of crystalline aluminium silicate. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 272—275B; cf. this vol., 628).—Natural clays of the type $\text{Al}_2\text{O}_3\cdot 8\text{SiO}_2\cdot \text{H}_2\text{O}$ yielded, after treatment with dil. alkali, an insol. residue, $\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$. The SiO_2 obtained from the alkaline solution was highly active (oil decolorising). The less acid clays (Al_2O_3 : 4—5 SiO_2) have a similar constitution and after treatment with H_2SO_4 are more active than the natural more acid clays. J. A. S.

Change of inner structure of siliceous materials by heat treatments. I. X-Ray study of natural minerals. T. NAKAI and Y. FUKAMI (J. Soc. Chem. Ind. Japan, 1934, 37, 283—284B).—Analyses and structures of chalcedony, flint, jasper, opal, and diatomaceous earth are given. The effect of impurities on the rate of inversion of quartz at high temp. was studied. J. A. S.

Limestones of Canada. Their occurrence and characteristics. II. Maritime Province. M. F. GOUDGE (Canada Dept. Mines, Mines Branch, No 742, 186 pp.).

Chemical composition of rocks at Dinantien, Belgium. (MLLE.) Y. CALLEBAUT (Ann. Soc. Sci. Bruxelles, 1934, B, 54, 128—146).—Analyses are given. C. W. G.

Gold-bearing rock on Olkhon Island and the genesis of the brown iron ore and manganese ore deposits in the Olkhon region. L. KOTELNIKOV (Bull. Acad. Sci. U.R.S.S., 1934, 2, 209—214).—Analyses are given. C. W. G.

Occurrence of mercury. A. STOCK and F. CUCUEL (Naturwiss., 1934, 22, 390—393).—The development of analytical methods capable of detecting quantities of Hg of the order of 0.001 mg. has made

it possible to indicate the presence of traces of Hg in many minerals, waters, and animal and vegetable matter. The view is expressed that traces of Hg are to be found in everything. A. J. M.

Relation between P_2O_5 and insoluble residue of Chibin apatite-nepheline deposits dissolved in aqua regia. S. N. ROZANOV and E. N. ISAKOV (Zavod. Lab., 1934, 3, 310—314).—A linear relationship exists between P_2O_5 content and that of substances insol. in aqua regia; the vals. for P_2O_5 calc. on this basis are in good agreement with those given by direct determination of P. R. T.

Composition of Moravian igneous rocks. K. PRECLIK (Tsch. Min. Petr. Mitt., 1934, 45, 269—332).—Many analyses are given of rocks of various types from Moravia and Czech Silesia, and these are compared on diagrams with analyses of rocks from Bohemia and Austria. L. J. S.

Rocks from the Lieser gorge on the Drave. H. HERITSCH (Tsch. Min. Petr. Mitt., 1934, 45, 333—348).—Descriptions with chemical analyses of amphibolite, eclogite, and garnet-gneiss are given. L. J. S.

"Chess-board" albite in pegmatite from the Lieser gorge, Carinthia. K. SCHOKLITSCH (Tsch. Min. Petr. Mitt., 1934, 45, 349—354).—Analysis shows albite 63.9% and quartz 34.1%, which form an oriented intergrowth. The albite is a secondary replacement of microcline. L. J. S.

Cause of the red coloration of acid lavas. F. ANGEL and H. GAMERITH (Tsch. Min. Petr. Mitt., 1934, 45, 355—358).—Analysis is given of a soda-liparite

from Bulgaria. The red colour of the rock is due to hydrothermal alteration. L. J. S.

New meteoric stone from Silverton, New South Wales. L. J. SPENCER (Min. Mag., 1934, 23, 569—572).—A stone of 350.7 g., showing on the surface a well-marked oriented flow of fused material, probably dates from the time (1883) of the discovery of the mineral deposits in the Broken Hill district. It is a white hypersthene-olivine-chondrite with a small amount of metallic Ni-Fe. L. J. S.

Soil survey of north Shropshire. I. Geography, geology, parent materials, soils. W. M. DAVIES and G. OWEN (Empire J. Exp. Agric., 1934, 2, 178—188).—Descriptive. A. G. P.

Characteristics of brown earths. T. SEKI (J. Sci. Soil and Manure, Japan, 1934, 8, No. 1; Proc. Internat. Soc. Soil Sci., 1934, 9, 111).—Brown earth soils of grassland and forest types are described and their classification is discussed. A. G. P.

Nature of the vegetal substances constituting coal, as shown by microscopic examination in reflected light. A. DUPARQUE (Chim. et Ind., 1934, 31, Spec. No., 279—285; cf. A., 1931, 818, 931).—Petrographic examination of the coals of Northern France permits them to be classified as follows: (a) "cutin" coals rich in spores and cuticle; these are bituminous coals of > 26% volatile matter content, (b) lignituous coals containing woody tissue and sclerenchyma; these belong in general to the class of coking coals of > 18% and < 26% volatile matter content, (c) cellulosic coals consisting principally of amorphous colloidal substances derived from the disintegration of cellulosic material; these are anthracites. A. B. M.

Organic Chemistry.

Robinson's electronic theories of organic chemistry. (1) W. A. NOYES. (2) R. ROBINSON (Chem. and Ind., 1934, 559—562, 562—563).—A discussion.

Stability of organic compounds in the gaseous or vapour state towards impact of potassium ions. O. SCHMIDT (Ber., 1934, 67, [B], 1145—1152).—Comparison of the behaviour of gases and vapours of inorg. and org. substances towards K ions with a velocity corresponding with 25 and 200 volts shows that the energy losses on impact of K with the scarcely deformable atom of Hg and the rare gases increase with decreasing wt. of the disrupted gas particle. With the paraffin hydrocarbons the loss of energy increases with chain length and hence with mol. wt., showing that more energy is absorbed by the mol. as its size increases, with consequent diminution of stability. As in cracking, the hydrocarbons with longer are less stable than those with shorter chain. Similar but less marked phenomena are observed with C_2H_4 and $CH_2:CMe_2$, since the double linking in $CH_2:CMe_2$ strengthens the neighbouring C-C unions. C_2H_2 , CO, CO_2 , and MeCl are stable, NH_3 is very unstable. H. W.

Thermal decomposition of organic compounds from the viewpoint of free radicals.

VIII. Comparison of thermal and electrical decomposition of organic compounds into free radicals. F. O. RICE and F. R. WHALEY (J. Amer. Chem. Soc., 1934, 56, 1311—1313).—The following compounds decompose at 800—1000° at low pressures (method: A., 1932, 1108; cf. A., 1933, 1270; this vol., 276) into fragments which remove Sb (and usually Pb) mirrors at varying rates: C_2H_6 , C_3H_8 , C_4H_{10} , $CHMe_3$, C_7H_{16} , gasoline, Et_2O , $EtCHO$, C_3H_6 , $AcOH$, $EtOAc$, $EtCO_2Et$, Et maleate, Bu^oOH , and NMe_3 ; C_2H_4 does not give active fragments. X-Ray powder photographs of the $HgRBr$ obtained by combination of the fragments from C_4H_{10} with Hg and subsequent treatment with $EtOH-HgBr_2$ indicate the formation of Me and Et at about 850° and Me only at about 950°. When $n-C_4H_{10}$, $n-C_7H_{16}$, C_2H_4 , $MeOH$, $EtOH$, $MeCHO$, $AcOH$, and $COMe_2$ are passed through a discharge tube, fragments are formed which remove Sb or Pb (but not Zn or Cd) mirrors and have a half-life of $0.7-2.1 \times 10^{-3}$ sec. It is shown by the above method that $COMe_2$ gives Me; the product from $n-C_4H_{10}$ could not be identified. Pr could not be detected in any of the decomp. products examined. H. B.

[Chlorination of paraffins.] H. B. HASS and P. WEBER (Ber., 1934, 67, [B], 974—975).—Reasons are

advanced for considering that the "isoamyl chlorides" of Wertyporoch (A., 1933, 590) are derivatives of *n*-pentane. The b.p. of γ - and β -chloropentane are 97.1—97.4°/760 mm. and 96.6—96.8°/760 mm., respectively. H. W.

Decomposition of aliphatic and alicyclic hydrocarbons by aluminium chloride. K. H. BAUER and U. TOMA (Ber., 1934, 67, [B], 1135—1138).—When heated with 25% of its wt. of AlCl_3 , octadecane, b.p. 181—187°/15 mm., m.p. 28°, gives 23% of C, 3.3% of condensation products, 13% of non-condensable gases (CO_2 1.3%; H_2 13.6%; gaseous hydrocarbons 85%), and 60% of volatile liquids, b.p. 20—175°, I val. 0. Under similar conditions, hexatriacontane, m.p. 76°, affords 24% of C, 30.0% of heavy oils, b.p. >450°, and 33% of volatile liquids, b.p. 20—175°; the gases consist of CO_2 0.5%, H_2 14.3%, and hydrocarbons 85%. Octahydroanthracene at 175—320° yields 36% of C, 10.0% of heavy oils, and 53.3% of volatile liquids, b.p. 90—350°; the gases contain 2.3% of CO_2 , 54.0% of H_2 , and 43.6% of hydrocarbons. H. W.

Peroxide effect in addition of reagents to unsaturated compounds. M. S. KHARASCH and M. C. McNAB (J. Amer. Chem. Soc., 1934, 56, 1425).—A reply to Sherrill *et al.* (this vol., 630). Previous work (A., 1933, 805) on the addition of HBr to C_3H_6 is confirmed. H. B.

Thermal preparation of ethylene hydrocarbons from alcohols. W. TREIBS (Ber., 1934, 67, [B], 942—943; cf. A., 1928, 68; Ssakmin, this vol., 508).—The catalytic activity of unglazed porcelain is considerably < that of amorphous Al_2O_3 , but is sufficient to lead to the production of ethylenic hydrocarbons in good yield from the alcohols at the temp. indicated for work in tubes and autoclaves, respectively: Et (450°); Pr^a (450°); Pr^b (400°); Bu (450°), *n*- C_8H_{17} (475°; 300°); linalyl (400°; 250°); cyclohexyl (400°; 300°). Borneol, isoborneol, and fenchyl alcohol (450°, 250°; 400°, 200°; 400°, 200°) yield camphene (I) and liquid isomerides also produced from (I). Menthol (400°, 250°) yields menthene. At 500° alcohols and phenols with the Pr^a group commence to lose C_3H_6 . H. W.

[Laboratory preparation of pure ethylene and propylene.] V. N. IPATIEV (Ber., 1934, 67, [B], 1061).—A question of priority (cf. Ssakmin, this vol., 508). H. W.

Polymerisation of isobutene. H. I. WATERMAN, J. OVER, and A. J. TULLENERS (Rec. trav. chim., 1934, 53, 699—702).—*iso*Butene and AlCl_3 in C_5H_{12} at -78° to 16° give mixtures of olefinic (I) and cyclic products of mol. wt. 132—4800, (I) having the lower mol. wts. Physical consts. are given for products obtained at -35° and 16°, before and after hydrogenation. Lower temp. produce products of higher mol. wt. Reaction is often explosive at -78°, the products at this temp. being highly viscous. R. S. C.

Reaction of *n*- and *iso*-pentenes with hydrogen chloride and aluminium chloride at low temperatures. J. J. LEENDERTSE, A. J. TULLENERS, and H. I. WATERMAN (Rec. trav. chim., 1934, 53,

715—724).—Pentan- γ -ol with active Al_2O_3 at 380—400° gives an 81% yield of *n*- Δ^8 -pentene (I). *n*- Δ^2 -Pentene (II) could not be satisfactorily obtained from *n*-amyl alcohol under similar conditions, owing to cracking and isomerisation to (I); its prep. (impure) from allyl bromide and MgEtBr is modified. At -80° (II) and CH_3CHPr^s (III) do not react with HCl alone, (I) reacts slowly, and $\text{CHMe}:\text{CHEt}$ (IV) and $\text{CHMe}:\text{CMe}_2$ (V) give rapidly CMe_2EtCl . (I), (III), (IV), and (V) with HCl and AlCl_3 at -80° give rapidly $\text{C}_5\text{H}_{11}\text{Cl}$ and a mixture of chlorides derived from polymerisation products. (I), (II), and (III) polymerise only slowly, (IV) and (V) rapidly in presence of AlCl_3 alone at -80°. R. S. C.

Action of chlorine on isoprene. W. J. JONES and H. G. WILLIAMS (J.C.S., 1923, 829—835).—Pure isoprene (I), b.p. 33.9—34.3°/760 mm. (improved prep. through the sulphone described), with 1 mol. of Cl_2 in CCl_4 in a freezing mixture, affords α -chloro- β -methylbutadiene, b.p. 50.4°/100 mm. (38%) [purified through α -chloro- β -methyl- Δ^8 -butene-1:4-sulphone, m.p. 73° (corr.), obtained by treatment with liquid SO_2 ; affords 1-chloro-2-methyl-1:4:4a:9a-tetrahydroanthraquinone, m.p. 146° (corr.), with α -naphthaquinone in N_2 at 80°] {polymerises to approx. $[(\text{C}_5\text{H}_7\text{Cl}_2\text{O})_x]$ on keeping}, $\alpha\delta$ -dichloro- β -methyl- Δ^8 -butene (II) (45%), b.p. 56°/10 mm. (CH_2ClAc and $\text{CH}_2\text{Cl}\cdot\text{CHO}$, oxidised to $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, by ozonolysis), a small amount (6%) of a Cl_2 -compound of lower b.p., and residue (11%). Oxidation of (II) with $\text{KMnO}_4\text{--H}_2\text{O--COME}_2$ at -5° gives $\alpha\delta$ -dichloro- β -methylbutane- $\beta\gamma$ -diol, m.p. 106.5° (corr.); with Zn and boiling EtOH it regenerates (I). J. W. B.

Isomeric transformation of hydrocarbons of the diallyl series in presence of silicates. S. V. LEBEDEV and J. M. SLOBODIN (J. Gen. Chem. Russ., 1934, 4, 23—30).— $\text{CH}_2:\text{CMe}$, and Br yield a mixture of $\alpha\beta\gamma$ - and $\alpha\alpha\beta$ -tribromoisobutane; the former affords diisobutenyl (I) on treatment with Mg, and the latter diisocrotyl (II). (I), on passing over floridin at 205°, is converted partly into (II), the equilibrium mixture containing 20—25% of (I) and 75—80% of (II). The equilibrium mixture obtained similarly from diallyl (III) contains 42% of di-propenyl (IV) and 58% of (III). Part of (II) and (IV) undergoes conversion into polymerides under the above conditions. R. T.

Polymerisation. XIV. Depolymerisation of triisobutene. S. V. LEBEDEV and I. A. LIVSCHITZ (J. Gen. Chem. Russ., 1934, 4, 13—22).—99% of $(\text{C}_4\text{H}_8)_3$ is dissociated at >50° in presence of active silicate (floridin) to afford $(\text{C}_4\text{H}_8)_2$ (I) and C_4H_8 (II), whilst 0.5—1% is converted into isobutane. Part of (I) is polymerised under these conditions to $(\text{C}_4\text{H}_8)_4$ and higher polymerides. The (I) obtained is identical with that formed by polymerisation of (II). R. T.

Organo-alkali compounds. XI. Mechanism of polymerisation of unsaturated hydrocarbons by alkali metals and alkali metal alkyls. K. ZIEGLER, P. DERSCH, and H. WOLLTHAN. XII. "Catalysis" of polymerisation of unsaturated hydrocarbons by organo-alkali compounds. K. ZIEGLER and L. JAKOB. XIII. Primary reaction

products of alkali metals on butadienes. K. ZIEGLER, L. JAKOB, H. WOLLTHAN, and A. WENZ (Annalen, 1934, 511, 13—44, 45—63, 64—88).—XI. (cf. A., 1928, 404; 1929, 1091.) Exclusive 1:4-addition of 1 mol. of an alkali metal alkyl to 1 mol. of butadiene (I) occurs; with >1 mol. of (I), some 1:2-addition also occurs. The possibility of allyl tautomerism between the 1:2- and 1:4-adducts [and its relation to the further addition of (I)] is discussed. (I) (approx 1.5 mols.) and CKPhMe₂ (II) (1 mol.) in Et₂O give (after decomp. with H₂O) (mainly) ϵ -phenyl- ϵ -methyl- Δ^8 -hexene (III), b.p. 224—226°, 102°/13 mm.; hydrocarbons, CPhMe₂·[C₄H₆]_nH (IV), with $n=2$, b.p. 90°/0.2 mm., 146—148°/10 mm., $n=3$, b.p. 189—192°/10 mm., and $n=4$, b.p. 130—170°/0.2 mm., are also formed. (III) is oxidised (O₃) to MeCHO, β -phenylisovaleraldehyde (V), b.p. 115—116°/11 mm. (semicarbazone, m.p. 123.5—124.5°; p -nitrophenylhydrazine, m.p. 135°), and β -phenylisovaleric acid (VI), m.p. 59—60°. (IV, $n=2$) similarly gives (mainly) resin and small amounts of MeCHO and (V); oxidation (CrO₃, AcOH, conc. H₂SO₄) affords (·CH₂·CO₂H)₂ (VII) and unidentified oily acid. Oxidation (O₃ followed by CrO₃) of (IV, $n=3$) gives (VI) and (VII); (VII) is also obtained by similar oxidation of a polymeride from (I) (100 mols.) and (II) (1 mol.). Isoprene (VIII) and (II) (1:1) afford (by 1:4-addition in both possible ways) a mixture, b.p. 117°/13 mm., of ϵ -phenyl- $\beta\epsilon$ - and - $\gamma\delta$ -dimethyl- Δ^8 -hexenes, since ozonolysis gives MeCHO, COMe₂, (V), and β -phenylisobutyl Me ketone (IX) (semicarbazone, m.p. 164°). Oxidation (O₃ followed by Ag₂O) of a polymeride from 6 mols. of (VIII) affords HCO₂H, AcOH, lævulic acid, (V), (VII), (IX), and acetonylacetone. Ozonolysis is considered to be unsatisfactory; CH₂O (which could not be detected) is probably formed and then condenses with other fission products to give resins.

LiCH₂Ph and (I) (4 mols.) afford (after decomp. with aq. NH₄Cl) a product which is a mixture containing phenylparaffins, Ph·[CH₂]_{4n+1}H; fractionation gives (with some difficulty) α -phenylpentane, b.p. 81°/10 mm. [p-Ac derivative, b.p. 146—148°/10 mm. (semicarbazone, m.p. 185°), obtained using AcCl and AlCl₃ in CS₂], α -phenylnonane, b.p. 146°/14 mm. [p-Ac derivative, b.p. 190°/10 mm. (semicarbazone, m.p. 172°)], α -phenyltridecane, b.p. 188—189.5°/10 mm. [p-Ac derivative, b.p. 177°/0.4 mm., m.p. 35° (semicarbazone, m.p. 168°)], and α -phenylheptadecane, m.p. 38° [p-Ac derivative, m.p. 53° (semicarbazone, m.p. 158—161°)]. 1:4-Addition is not proved to be exclusive, since substances other than the above are also formed. The above hydrocarbons are also synthesised: COCl·[CH₂]_{4n}H + C₆H₆ + AlCl₃ → CPh·[CH₂]_{4n}H, and thence by reduction (Wolff-Kishner) of the semicarbazones to Ph·[CH₂]_{4n+1}H. Tridecoic acid is prepared by dehydration and subsequent oxidation (cf. Skraup, A., 1928, 882) of β -phenyltridecylcarbinol, m.p. 43° (from MgPhBr and Me myristate). The semicarbazones of Ph dodecyl and hexadecyl ketones have m.p. 101° and 87.5°, respectively. Reduction (H₂, Pd-BaSO₄, EtOAc) of the product from LiBu (1 mol.) and (I) (3 mols.) does not give fully saturated material; reduction with Raney Ni at 130—140° and 180 atm. affords a mixture

of paraffins, C_{4n}H_{8n+2} (from which n -octane is isolable), which appears to contain branched-chain compounds (formed by 1:2-addition). Thus, the dodecane fraction has a b.p. < that of n -dodecane. An artificial mixture of n -paraffins (above; $n=2-9$) could not be separated sharply by fractional distillation.

XII. Polymerisation of butadiene (I) and styrene (II) is "catalysed" by CMAr₃, CHMAR₂, and CMAr₂Alph (M=alkali metal). (I) is unaffected by the Na or Li derivatives of fluorene, indene, phenylindene, and 1:3-diphenylindene, whilst $\Delta^{\alpha\gamma}$ -penta-diene and $\beta\gamma$ -dimethylbutadiene are, in general, unaffected by any of the above alkali compounds. Prolonged interaction of (I) (0.1 mol.) and CHPh₃ (0.1 mol.) in presence of Et₂O-CNaPh₃ gives resinous material; practically all the CHPh₃ is recovered. Very slow passage of (I) (4 mols.) during 38 days into CHPh₃+CNaPh₃ in Et₂O results in the addition of about 70% of the CHPh₃:CNaPh₃+CH₂:CH:CH:CH₂

→ CPh₃·CH₂CH:CH·CH₂Na — CNaPh₃+CPh₃·CH₂·CH:CHMe. Passage of (I) into CHPh₃+CNaPh₃ in N₂ at 130—140° results in the addition of >90% of the CHPh₃; distillation of the reaction mixture gives a triphenylpentene (III), b.p. 162°/0.2 mm., m.p. 115°, and a little $\alpha\alpha\alpha$ -triphenyl- Δ^{γ} -pentene (IV), m.p. 83° [oxidised (CrO₃, AcOH) to CPh₃·CH₂·CO₂H]. The former reaction mixture similarly affords a triphenylpentene (V), m.p. 124°. (IV) and a little (V) are also obtained from (I), dicyclohexylamine, and CNaPh₃. (III), (IV), and (V) are all reduced to $\alpha\alpha\alpha$ -triphenylpentane, m.p. 61.5°. Addition of CHPh₃ to (II) can be effected in presence of CNaPh₃ at 130—140°. (I) does not react with fluorene and its Na derivative at 140°. The amount of CHPh₃ in mixtures containing neutral resin is determined (accuracy 3—5%) by successive treatment with CKPhMe₂ (VI), dicyclohexylamine [which removes excess of (VI), but has practically no action on the CKPh₃ now present], CO₂, and dil. H₂SO₄; the resultant CPh₃·CO₂H is dried and titrated with (VI) in Et₂O.

XIII. When a 0.5M-Et₂O solution of butadiene (I) is shaken with "mol." Na (2 atoms) the resulting solution contains only a small amount of combined Na. $\Delta^{\alpha\gamma}$ -Pentadiene (II) and $\beta\gamma$ -dimethylbutadiene (III) similarly give solutions which are 0.01 and 0.006 N, respectively, in alkali. Hydrolysis of the resultant products affords undistillable resinous oils. (II) and Na in presence of CHPh₃ give CNaPh₃ (0.17N; theory 0.8N); decomp. of the reaction mixture with EtOH and repeated further treatment with (II) afford pentene and products, H[C₅H₈]_nH ($n=2$ to 6—7). (III) similarly gives CNaPh₃ (0.55N; theory 0.8N); CMe₂·CMe₂ (IV) and hydrocarbons, C₁₂H₂₂, b.p. 81—83°/14 mm., and C₁₈H₃₂, b.p. 156.5°/14 mm., are isolable (as above). In presence of fluorene, the adduct from Na and a butadiene reacts rapidly to give Na fluorenyl. Analogous results are obtained with amines (NHET₂, dicyclohexylamine, NHPPhEt, NH₂Ph); ready addition of 2 H to the diolefine occurs [thus, (III) gives (IV)]; C₁₀H₈ affords 1:4-dihydronaphthalene. Octadiene, b.p. 120°, is obtained from (I), Li, CPh₂·CH:CH₂Ph, and NHPPhEt

in Et_2O , whilst (I), Li, and 2-dimethylaminofluorene in Et_2O give octadiene and some dodecatriene, b.p. 90–95°/15 mm. When 0.5*M*- Et_2O solutions of (I), (II), (III), and isoprene are shaken with finely-divided Li, the resulting solutions are 0.03, 0.27, 0.5, and 0.24*N*, respectively, in alkali. The product from (I) is hydrolysed (H_2O) to a high-mol. resin. Decolorisation of the solution from (II) with MeOH and further addition of (II) give pentene and condensation products $\text{H}[\text{C}_5\text{H}_8]_n\text{H}$ ($n=2-5$). (III) similarly affords a little (IV), (mainly) a bimol. product, b.p. 78°/8 mm., and some higher polymerides; the intermediate $\text{CH}_2\text{Li}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CH}_2\text{Li}$ reacts rapidly with a second mol. of (III), but subsequent addition of (III) to the new complex is slow. Thus, the orange-red solution from Li and (III) treated with (III) gives (after 45 min.) a yellow solution [hydrolysis (H_2O) of which affords no (IV)]; the major part of the (III) has not reacted [complete disappearance of the (III) is found after 18–24 hr.]. No evidence has been obtained indicating the formation of radical-like intermediates. H. B.

Preparation of pure *n*- Δ^8 -octene. H. I. WATERMAN and W. J. C. DE KOK (Rec. trav. chim., 1934, 53, 725–729).—The consts. of *n*- Δ^8 -octene, prepared from $n\text{-C}_8\text{H}_{11}\cdot\text{MgBr}$ and allyl bromide, reported by Whitmore *et al.* (A., 1933, 1033), are confirmed. R. S. C.

Isomerisation of olefines. I. Conversion of *tert*-butyl-, *as*-methylisopropyl-, and tetramethyl-ethylene into equilibrium mixtures of the three olefines. K. C. LAUGHLIN, C. W. NASH, and F. C. WHITMORE (J. Amer. Chem. Soc., 1934, 56, 1395–1396).—Essentially the same mixture of $\text{CMe}_2\cdot\text{CMe}_2$, $\text{CH}_2\cdot\text{CMePr}^s$, and $\text{CH}_2\cdot\text{CHBu}^t$ is obtained when each olefine is passed over P_2O_5 on SiO_2 gel at 300°, as is formed by similar dehydration of $\text{CHMeBu}^t\cdot\text{OH}$ (A., 1933, 1140). The possible changes involved are discussed. H. B.

Catalysis of acetylene polymerisation in ultra-violet light.—See this vol., 852.

Surface reaction between acetylene and iodine.—See this vol., 851.

Chlorination of solid paraffins. II. Molecular volumes of chloroparaffins and chlorostearic acids. III. Lowering of m.p. by chlorination. Y. TANAKA, R. KOBAYASHI, and I. NISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 208–209B, 209B).—II. The mol. vol. of chlorinated *n*-paraffins (m.p. 46–51°) and of chlorinated stearic acids are directly \propto the Cl content.

III. In the above cases chlorination produces a marked lowering of m.p. (to –37° for 44% chlorinated stearic acid) and increase in η . H. A. P.

Action of inorganic bases on *sec*- and *tert*-butyl bromides. H. E. FRENCH, W. H. McSHAN, and W. W. JOHLER (J. Amer. Chem. Soc., 1934, 56, 1346–1348).— C_4H_8 is obtained in 13–47% yield from *sec*-BuBr and AgOH (I), KOH, NaOH, $\text{Ca}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$ in aq. solution or suspension at 30–60°; the amount produced is approx. \propto to the concn. of dissolved hydroxide [except for (I)]. The yield of C_4H_8 from BuBr varies from 0 [(I) at 30°] to 2.2%. H. B.

Hydrolysis of tertiary aliphatic halides. I. H. M. WOODBURN and F. C. WHITMORE (J. Amer. Chem. Soc., 1934, 56, 1394–1395).—The ease of hydrolysis of BuCl (I), *tert*-amyl chloride (II) and bromide, CMeBu_2Cl , and CBu_3Cl with hot H_2O or aq. Na_2CO_3 decreases with increase in mol. wt. (probably owing to decreased solubility); olefines are formed exclusively. The rate of hydrolysis of (I) and (II) decreases in the order $\text{H}_2\text{O} > 5\%$, $\text{Na}_2\text{CO}_3 > 40\%$ Na_2CO_3 , and is thus dependent on the solubility in the hydrolysis medium. Hydrolysis with cold H_2O or cold aq. NaOH gives olefine and some *tert*-alcohol. CR_3Hal are more resistant to hydrolysis than is usually supposed. H. B.

Optical rotation and atomic dimension. D. H. BRAUNS (J. Amer. Chem. Soc., 1934, 56, 1421–1422).— α -Chloro-, $[\text{M}]_D^{20} + 179^\circ$, α -bromo-, (I), $[\text{M}]^{20} + 610.1^\circ$, and α -iodo-, $[\text{M}]^{20} + 1124.7^\circ$, β -methylbutanes are prepared from (–)- β -methylbutyl alcohol and HHal; α -fluoro- β -methylbutane, $[\text{M}]_D^{20} - 799.1^\circ$, is obtained from (I) and AgF. The differences in the above vals. are \propto to the differences in at. diameter (cf. A., 1925, ii, 633), but not to the differences in at. wt. (Guye's hypothesis). H. B.

Mechanism of the condensation of nitromethane with formaldehyde and preparation of nitroethanol. I. M. GORSKI and S. P. MAKAROV (Ber., 1934, 67, [B], 996–1000).—Interaction of CH_2O (I) with MeNO_2 (II) in presence of K_2CO_3 with or without EtOH involves the equilibria, $(\text{I}) + (\text{II}) \rightarrow \text{NO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (III) $\rightleftharpoons \text{NO}_2\cdot\text{CH}(\text{CH}_2\cdot\text{OH})_2$ (IV) $\rightleftharpoons \text{NO}_2\cdot\text{C}(\text{CH}_2\cdot\text{OH})_3$ (V). Conditions are described for the prep. of (III), b.p. 89–90°/4 mm., (IV) b.p. 157–158°/7 mm., m.p. 58–59°, and (V), m.p. 159°. H. W.

Electrochemical oxidation of α -glycols. E. TOMMILA (Ann. Acad. Sci. Fennicae, 1934, 39, 3–65).—Electrochemical oxidation of ethylene, propylene, and phenylethylene glycols and of pinacol in alkaline and acid solution under varying conditions has been examined. Two reactions may take place with a smooth Pt anode, either oxidation of the OH group to an OH-aldehyde or -ketone, or the breaking down of the mol. into two aldehyde or ketone mols., the latter reaction being more pronounced at higher potentials. With a platinised anode, two interconvertible products are obtained, the oxidation being facilitated by the catalytic effect of the anode metal. F. R. S.

Determination of butane- $\beta\gamma$ -diol. C. MATIGNON, H. MOUREU, and M. DODE (Bull. Soc. chim., 1934, [v], 1, 411–419; cf. A., 1933, i, 1041).—Butane- $\beta\gamma$ -diol (1 mol.) with Br- H_2O (8–10 mols.) at 100 during 3 min. affords OH-CHMe-Ac (I) (76.5% yield), oxidised to Ac_2 , which is determined as Ni dimethylglyoxime. The yield of (I) is not much influenced by temp. or the quantity of Br- H_2O . J. L. D.

Plant pigments. LXI. Products of the action of magnesium alkyl salts on esters of dihydrobixin. I. P. KARRER and F. RUBEL (Helv. Chem. Acta, 1934, 17, 773–774).—Dihydrobixin Me ester (I) is converted by MgMeI into $\alpha\alpha\phi\phi$ -tetramethyl-dihydrobixinol, m.p. 166–167°, the visible absorption spectrum of which scarcely differs from that of ().

(I) does not readily lose H_2O . The term "bixinol" is used to denote the primary alcohol obtained by replacing the $2\text{CO}_2\text{H}$ of bixin by $2\text{CH}_2\text{OH}$. H. W.

Olefinic ethyl ethers of α -glycols. D. BARDAN (Bull. Soc. chim., 1934, [v], 1, 368—370; cf. A., 1932, 143).—Interaction of γ -ethoxy- β -methylheptan- β -ol (cf. this vol., 754) with P_2O_5 in boiling $\text{C}_5\text{H}_5\text{N}$ during 2 hr. affords γ -ethoxy- β -methyl- Δ^8 -heptene, b. p. 107—109°/42 mm. The following are prepared similarly: δ -ethoxy- γ -ethyl- Δ^7 -octene, b. p. 119—121°/34 mm.; ϵ -ethoxy- δ -n-propyl- Δ^6 -nonene, b. p. 132—136°/21 mm.; ethoxy- ϵ -n-butyl- Δ^5 -decene, b. p. 149—153°/17.5 mm.; δ -ethoxy- γ -ethyl- Δ^7 -decene, b. p. 120—126°/21 mm.; ϵ -ethoxy- δ -n-propyl- Δ^6 -nonene, b. p. 155—159°/22 mm.; and ζ -ethoxy- ϵ -n-butyl- Δ^5 -dodecene, b. p. 174—179°/20—19.5 mm. 20% H_2SO_4 de-ethylates these compounds to ketones. J. L. D.

Ether-like compounds. XIII. Hydrolysis of acylalkyl formals. M. H. PALOMAA and V. JAAKKOLA (Ber., 1934, 67, [B], 949—954; cf. this vol., 625).—The rates of hydrolysis of acylalkyl formals measured at 15°, 25°, and 35°, are tabulated. In general, the temp. coeff. increases as the rate of ester hydrolysis decreases, and with increasing complexity approximates to but does not reach that of acetal hydrolysis. The following observations appear new: CH_2OMe *n*-butyrate, b. p. 151—152°; CH_2OMe β -methoxypropionate, b. p. 88.0—88.4°/18 mm.; CH_2OEt *n*-butyrate, b. p. 166°; CH_2OEt β -methoxypropionate, b. p. 95°/15 mm.; $\text{CH}_2\text{OPr}^\beta$ acetate, b. p. 134—135°; CH_2OPr propionate, b. p. 154—155°; CH_2OPr *n*-butyrate, b. p. 171—172°; $\text{CH}_2\text{OPr}^\beta$ β -methoxypropionate, b. p. 105°/20 mm.; Pr^β methoxyacetate, b. p. 148°; Pr^β β -methoxypropionate, b. p. 67—68°/21 mm. H. W.

Preparation of ketals of alkylacetylenes with methyl alcohol. D. B. KILLIAN, G. F. HENNION, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 1384—1385).— CHMe(OMe)_2 , b. p. 64—65°, and β -dimethoxy-propane, b. p. 78—80°/747 mm., -butane, b. p. 48—50°/100 mm., -pentane, b. p. 30—31°/15 mm., -neizane, b. p. 58—60°/30 mm., and -heptane (I), b. p. 74—75°/27 mm., are prepared from CR:CH ($\text{R} = \text{H}-\text{C}_5\text{H}_{11}$) and MeOH by the method previously described (this vol., 759). (I) is hydrolysed (dil. acid) to *Me n*-amyl ketone. Ketals are not obtained from ROH other than MeOH . H. B.

α -Hydroxy-acetals of high mol. wt. and aldehydes derived from them. M. ROTBART (Ann. Chim., 1934, [xi], 1, 439—514).—The Na derivatives of aliphatic and cycloparaffin alcohols are best prepared by "mol." Na in PhMe , but CH_2PhOH (I) is partly hydrogenated by this method. CH_2PhOK is obtained by distillation of (I) in vac. with KOH-EtOH . The Na (or K) derivatives with $\text{CH}_2\text{BrCH(OEt)}_2$, best in an autoclave at 170—180°, give *alkyloxycetals*, $\text{R}\cdot\text{CH}_2\cdot\text{CH(OEt)}_2$, in which $\text{R} = \text{n-octyl}$ (II), b. p. 122°/5 mm., α -methyl-*n*-heptyl (III), b. p. 131—132°/14 mm., *n*-decyl (IV), b. p. 159—160°/14 mm., *n*-lauryl (V), b. p. 150—151°/3 mm., *myristyl* (VI), m. p. 25°, b. p. 161—162°/2 mm., cetyl (VII), m. p. 37°, b. p. 192—194°/1 mm., cyclohexyl (VIII), b. p. 115°/12 mm., 2- (IX), b. p. 124—126°/18 mm., 3- (X), b. p. 121°/12 mm., and 4-methylcyclohexyl (XI), b. p.

125—126°/12 mm., Ph , b. p. 136—138°/16 mm., CH_2Ph (XII), b. p. 143°/12 mm., $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$ (XIII), b. p. 179°/16 mm., $\text{CH}_2\text{Ph}\cdot\text{CH}_2$ (XIV), b. p. 126—128°/3 mm., $\text{CHPhMe}\cdot\text{CH}_2$ (XV), b. p. 130—132°/5 mm., CHPhMe (XVI), b. p. 138—140°/14 mm., CPhMe_2 (XVII), b. p. 150—152°/16 mm., and $\text{CH}_2\text{Ph}\cdot\text{CMe}_2$ (XVIII), b. p. 115—118°/2 mm. Similarly are prepared $\alpha\alpha$ -dimethoxy- (XIX), b. p. 138—140°/15 mm., and $\alpha\alpha$ -di-*n*-propoxy-ethyl *n*-octyl ether (XX), b. p. 163—165°/15 mm., from $\text{CH}_2\text{BrCH(OMe)}_2$, b. p. 49.5—50.5°/15 mm., and $\text{CH}_2\text{BrCH(OPr}^\alpha)_2$, b. p. 89.5—90.5°/13 mm. By hydrolysis with about 30% aq. $\text{H}_2\text{SO}_4\text{-AcOH}$ (unless otherwise stated) were obtained the corresponding α -alkyloxycetals [m. p. (block) of the semicarbazones being stated in parentheses], in which $\text{R} =$ (II), b. p. 111—113°/18 mm. (98.5—99°), (III), b. p. 98—99.5°/15 mm. (78.5—79.5°), (IV), b. p. 133—135°/15 mm., m. p. 19.5—20° (103—104°), (V), m. p. 18°, b. p. 118—119°/3 mm. (108°), (VI), m. p. 36°, b. p. 138—140°/4 mm. (97°), (VII), m. p. 47° (102°), (VIII) (by 1% H_2SO_4), b. p. 71°/14 mm. (175°), (IX) (bv 1% H_2SO_4), b. p. 85—88°/12 mm. (152—152.5°), (X) (bv 1% H_2SO_4), b. p. 84—86°/14 mm. (175°), (XI) (by 1% H_2SO_4), b. p. 98—100°/19 mm. (187—188°), Ph (bv 1—5% H_2SO_4), b. p. 101—103°/15 mm. (145°), (XII) (by 1% H_2SO_4), b. p. 109—111°/11 mm. (119°), (XIII) (only by 4—5% H_2SO_4 ; poor yield), b. p. 157—160°/15 mm. (160—160.5°), (XIV) (by 7% H_2SO_4), b. p. 120—122°/15 mm. (88—88.5°), and (XV) (by 5% H_2SO_4), b. p. 134—136°/16 mm. (89—89.5°). (XIX) and (XX) are smoothly hydrolysed by 15 and 25% H_2SO_4 , respectively. The aldehydes in which $\text{R} =$ (XVI), (XVII), and (XVIII) could not be obtained, since even very dil. H_2SO_4 hydrolysed the alkoxy-group. The analogous substances, *p*-anisyl-methyl Et ether [prepared in 78% yield from $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ and NaOEt at 160—200° (autoclave)], b. p. 111—113°/11 mm., and $\text{CHPhMe}\cdot\text{OEt}$, are hydrolysed by hot 5 and 1% aq. $\text{H}_2\text{SO}_4\text{-AcOH}$, respectively. The semicarbazones are analysed by Veibel's method (A., 1927, 1172), which must be modified by addition of MeOH for aliphatic compounds. The aldehydes are best obtained from the semicarbazones by distillation in steam from 2—5% aq. H_2SO_4 . R. S. C.

Reaction of dialkyl sulphates with $\text{OR}\cdot\text{MgBr}$ compounds. A. C. COPE (J. Amer. Chem. Soc., 1934, 56, 1342—1346).—The reaction $2\text{OR}\cdot\text{MgBr} + 2\text{R}'\cdot\text{SO}_4 = \text{Mg(OR)}_2 + 2\text{R}'\cdot\text{Br} + \text{Mg(R}'\text{SO}_4)_2$, occurs with $\text{R}' = \text{Me}$ or Et and $\text{R} = \text{Ph}$, Bu^α , CHPh_2 , CPh_3 , and $\text{CO}_2\text{Et}\cdot\text{C(CHPh}_2)_2\cdot\text{C(OEt)}$. Evidence is given showing that the equilibrium $2\text{OR}\cdot\text{MgBr} \rightleftharpoons \text{Mg(OR)}_2 + \text{MgBr}_2$ exists in solution; treatment with $\text{R}'\cdot\text{SO}_4$ causes the change, $\text{MgBr}_2 + 2\text{R}'\cdot\text{SO}_4 \rightarrow 2\text{R}'\cdot\text{Br} + \text{Mg(R}'\text{SO}_4)_2$, to occur. Thus, $\text{Me}\cdot\text{SO}_4$ and $\text{CO}_2\text{Et}\cdot\text{C(CHPh}_2)_2\cdot\text{C(OEt)}\cdot\text{OMgBr}$ [from $\text{CHPh}_2\cdot\text{CH(CO}_2\text{Et)}_2$ and MgPhBr] in C_6H_6 give MeBr , $\text{Mg(MeSO}_4)_2$, and $[\text{CO}_2\text{Et}\cdot\text{C(CHPh}_2)_2\cdot\text{C(OEt)}\cdot\text{O}]_2\text{Mg}$ [which reacts further with Me_2SO_4 in C_6H_6 or PhMe at higher temp. to give $\text{CHPh}_2\cdot\text{CMe(CO}_2\text{Et)}_2$ and $\text{Mg(MeSO}_4)_2$]. The production of Bu^αI from $n\text{-C}_6\text{H}_{13}\text{Me}\cdot\text{SO}_3\text{Bu}^\alpha$ and $\text{OEt}\cdot\text{MgI}$ or $\text{OPh}\cdot\text{MgI}$ (Gilman and Heck, A., 1928, 1124) is explained: $2\text{OR}\cdot\text{MgI} +$

$2C_6H_4Me \cdot SO_3Bu \rightarrow Mg(OR)_2 + 2BuI + Mg(SO_3 \cdot C_6H_4Me)_2$. The following appear to be new: $Mg(MeSO_4)_2$; $Mg(EtSO_4)_2$; *Et benzhydrylmethylmalonate*, b.p. 180—182°/2 mm., m.p. 41—42°.

H. B.

Electron-sharing ability of organic radicals.

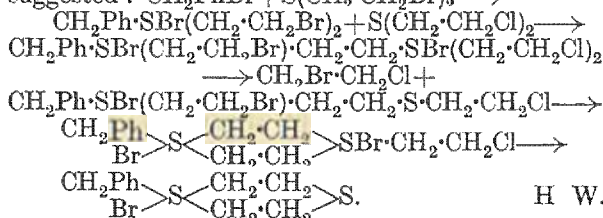
VIII. Condensation of mercaptans with chloral.

I. B. JOHNS and R. M. HIXON (J. Amer. Chem. Soc., 1934, 56, 1333—1336).—The equilibrium consts. for the reaction $CCl_3 \cdot CHO + RSH \rightarrow CCl_3 \cdot CH(OH) \cdot SR$ ($R = Et, Bu, CH_2Ph, Ph, p-C_6H_4Me, p-C_6H_4Cl$) are calc. from f.-p. data; reaction is carried out in presence of C_6H_6 and a trace of HCl (catalyst). The consts. [and those for the reaction $2HgRI \rightarrow HgR_2 + HgI_2$ (A., 1930, 1526)] are expressed as mathematical functions of the electron-sharing abilities of R . A new type of f.-p. apparatus is described.

H. B.

Unusual reaction of 3,3'-dichlorodiethyl sulphide with halogen compounds. C. D. NENITZESCU and N. SCARLATESCU (Ber., 1934, 67, [B], 1142—1144).— MeI and $(CH_2Cl \cdot CH_2)_2S$ (I) in boiling $EtOH$ afford $(CH_2I \cdot CH_2)_2S$, m.p. 62°, and *dithian methiodide*, $S < \begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{smallmatrix} > S < \begin{smallmatrix} Me \\ | \\ I \end{smallmatrix}$, m.p. 174°, also obtained from

$(CH_2Br \cdot CH_2)_2S$. Similarly, (I) and CH_2PhBr yield dithian benzylbromide, m.p. 146° [also obtained from $(CH_2Br \cdot CH_2)_2S$], and $CH_2Cl \cdot CH_2Br$. $(OEt \cdot CH_2 \cdot CH_2)_2S$ and MeI do not react at low temp., but at 100—110° give dithian dimethiodide. The following scheme is suggested: $CH_2PhBr + S(CH_2 \cdot CH_2Br)_2 \rightarrow$



H. W.

β -isoButyl sulphide. O. HINSBERG (J. pr. Chem., 1934, [ii], 140, 65—68; cf. A., 1929, 1269).— Bu^i_2S with 70% $HClO_4$ at 100° gives the *perchlorate* (I) $(Bu^i_2S)_2 \cdot HClO_4$ of the β -form (II) (*picrate*, m.p. 79°), converted by warm aq. KOH into a mixture, b.p. 167—168°/735 mm., of (II) (93%) and the α -form (III), distinguished and separated by the fact that only (II) gives (I) with $HClO_4$ in cold $CHCl_3$. By this method the relative amounts of conversion of (I) into (III) under various conditions are determined. Both forms on oxidation give the same sulphone. J. W. B.

Preparation and salts of cetylsulphonic acid.

B. FLASCHENTRAGER and G. WANNSCHAFF (Ber., 1934, 67, [B], 1121—1124).—Interaction of cetyl alcohol and PBr_5 in boiling C_6H_6 and treatment of the product with H_2O gives a semi-solid mass, the liquid portion of which at 22° gives pure cetyl bromide, m.p. 15° after softening at 13.5°. Cetyl mercaptan (I), b.p. 123—128°/0.5 mm., m.p. 18°, is obtained in 85% yield from cetyl iodide and $NaHS$ in abs. $EtOH$ at 40—45°. Addition of (I) in $COMe_2$ to $KMnO_4$ in boiling $COMe_2$ leads to *di- β -cetylthiolpropane*, m.p. 53° (yield 29%), and *K cetylsulphonate* (II) (29.4%). Oxidation of (I) with $KMnO_4$ at 100° affords (II) (60%) and *dicetyl disulphide*, m.p. 50° (27.6%). *Ba, Pb, Li, Na, and NH₄ cetylsulphonates* are described.

H. W.

Mechanism of ester condensations. G. V. TSCHELINCEV (Ber., 1934, 67, [B], 955—963).—The schemes of Claisen and Scheibler are criticised in detail and the following is suggested: $EtOAc + CH_3C(ONa) \cdot OEt \rightarrow OEt \cdot CMe(OH) \cdot CH_3C(ONa) \cdot OEt \rightarrow COMe \cdot CH_3C(ONa) \cdot OEt + EtOH$. The new scheme enables condensations of $(CH_2)_2O$, epichlorohydrin, etc. with the Na derivatives of $CH_2(CO_2Et)_2$, $CH_2Ac \cdot CO_2Et$, and $CH_2Bz \cdot CO_2Et$ to be included. The necessity for the presence of a trace of $EtOH$ is explained by the scheme, $EtOAc + EtONa \rightarrow OEt \cdot C(CH_3) \cdot ONa + EtOH$. Scheibler's observation of the production of keten acetals (I) and salts is due to a side reaction, $EtOBz + CH_2 \cdot C(OK) \cdot OEt \rightarrow KOBz + CH_2 \cdot C(OEt)_2$, whilst the formation of (I) by the decomp. of the intermediate products of the $EtOAc$ condensation by H_2O is explained by the scheme: $CHAc \cdot C(ONa) \cdot OEt + EtOAc \rightarrow CHAc \cdot C(OEt)_2$ (II) $+ NaOAc$; (II) $+ NaOEt \rightarrow ONa \cdot CMe \cdot C(OEt)_2$ (III) $+ EtOH$; (III) $+ H_2O \rightarrow NaOAc + CH_2 \cdot C(OEt)_2$. The scheme is applied to the explanation of many condensations previously unexplained or explained with difficulty.

H. W.

Production of acetyl chloride by action of phosphoryl chloride on acetic acid. Y. KATO, S. FUJINO, and S. KIKUCHI (J. Soc. Chem. Ind. Japan, 1934, 37, 170—171B).— $AcCl$ is formed according to $2AcOH + POCl_3 = 2AcCl + HPO_3 + HCl$ if the HCl and $AcCl$ formed are continuously removed by distillation.

Nitroso-compounds. II. Reduction of derivatives of α -nitrosoisobutyric acid to the corresponding azoxy-compounds. J. G. ASTON and G. T. PARKER (J. Amer. Chem. Soc., 1934, 56, 1387—1388; cf. A., 1932, 602).—Bimol. α -nitrosoisobutyronitrile is reduced ($SnCl_2$, conc. HCl) to α -azoyisobutyronitrile (I), m.p. 37° (18% yield), whilst bimol. *Et* α -nitrosoisobutyrate similarly gives 42% of *Et* α -azoyisobutyrate, b.p. 142—144°/12 mm., 155—157°/20 mm. (free acid, m.p. 128—129°), also prepared from (I) and $EtOH \cdot HCl$ and by oxidation (method: Jolles, A., 1931, 1152) of *Et* α -azoisobutyrate.

H. B.

Structure of acids obtained by oxidation of triisobutene. II. α -Acid of Conant and Wheeland. F. C. WHITMORE and C. D. WILSON (J. Amer. Chem. Soc., 1934, 56, 1397; cf. this vol., 755).—The α -acid, $C_{12}H_{24}O_2$, m.p. 89°, of Conant and Wheeland (A., 1933, 804) is *dineopentylacetic acid* (I); the chloride, b.p. 78—79°/4 mm., and NaN_3 in $PhMe$ give [after hydrolysis (HCl)] *dineopentylcarbinyamine* (*hydrochloride*, m.p. 239—240°; *Ac* derivative, m.p. 134.5°), which with HNO_3 affords *dineopentylcarbinol*. The mechanism of formation of (I) from *as*-dineopentylethylene is discussed.

H. B.

General interpretation of fatty acid analyses by the ester fractionation method. T. P. MILDITCH (Biochem. J., 1934, 28, 779—785).—Discussion of methods and of results.

W. O. K.

Catalytic influences in three-carbon tautomerism, III—V.—See this vol., 849.

Esterification of binary mixtures of fatty acids. Y. TOYAMA, T. ISHIKAWA, and G. AKIYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 193—195B).—Analysis of

the products obtained by esterification of binary mixtures of stearic, oleic, lauric, and behenic acids by EtOH, isoamyl alcohol, or glycerol in the presence of HCl shows that the acids have entered evenly into reaction, each in proportion to its concn. E. L.

Constituents of the triglycerides formed by esterification of the equimolecular mixture of stearic and oleic acids. T. TSUCHIYA and G. AKIYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 195B).—Oxidation by the Hilditch method showed that the neutral product of the esterification of a mixture of 3 mols. each of stearic and oleic acids with 1 mol. of glycerol in the presence of HCl at 225–230° contained 20% of tristearin; oxidation products corresponding with distearo-, steardi-, and tri-olein were almost certainly formed, but could not be isolated. E. L.

Polymerisation of fatty oils. IV. Constitution of "dried" linseed and perilla oils. A. STEGER and J. VAN LOON (Rec. trav. chim., 1934, 53, 769–778; cf. B., 1934, 107).—Linseed and perilla oils, heated at 285° and 300°, respectively, contain all the glycerol as glycerides. By distillation of the Et esters prepared from the products it is shown that "polymerisation" is a gradual process accompanied by formation of products of lower sap. val., that the linolenic esters polymerise less readily than the linoleic esters, and that the portion non-volatile in a high vac. is completely polymerised. R. S. C.

Raman effect and problems of constitution. V. Keto-enolic tautomerism in β -ketonic esters. K. W. F. KOHLRAUSCH and A. PONGRATZ (Ber., 1934, 67, [B], 976–989).—Raman spectra are recorded for the following compounds: HCO_2Et , $(\text{CO}_2\text{Et})_2$, $\text{CH}_2(\text{CO}_2\text{Et})_2$, $\text{CHMe}(\text{CO}_2\text{Et})_2$, $\text{CMe}_2(\text{CO}_2\text{Et})_2$, $\text{CH}(\text{CO}_2\text{Et})_3$, $\text{C}(\text{CO}_2\text{Et})_4$, $\text{CAcMe}_2\cdot\text{CO}_2\text{Et}$, $\text{CHAcMe}\cdot\text{CO}_2\text{Et}$, $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, $\text{OEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, AcCO_2Et , PhMe , NH_2Ph , CHMe_3 , NH_2Pr^3 , MeOAc , $\text{NH}_2\cdot\text{CO}_2\text{Me}$, EtOAc , $\text{NH}_2\cdot\text{CO}_2\text{Et}$, COMe_2 , NH_2Ac , COMeEt , $\text{NH}_2\cdot\text{COEt}$. The data are discussed in their relationships to keto-enolic desmotropy. H. W.

Complex bismuth oxalates.—See this vol., 854.

Oxidation of fatty dibasic acids and of lævulic acid by hydrogen peroxide in presence of a cupric salt. A. P. PONSFORD and I. SMEDLEY-MACLEAN (Biochem. J., 1934, 28, 892–897).—Glutaric (I), adipic (II), suberic (III), and lævulic acid (IV) are readily oxidised by H_2O_2 at 60° in presence of Cu^{++} yielding succinic acid, CO_2 , etc. (I) produces small amounts of COMe_2 indicating β -keto-oxidation; similarly (II) affords (IV). With both (I) and (IV), CO_2 is liberated during the steam distillation of the oxidation product, indicating the presence of unstable intermediates. With (III), α -, β -, and γ -hydroxy-suberic acids appear to be produced, hydroxypimelic acids being possible intermediates. Traces of $[\text{CH}_2\text{Ac}]_2$ indicate a partial $\beta\beta$ -keto-oxidation, whilst small amounts of monoketosuberic acid and other keto-derivatives are detectable. F. O. H.

Preparation and synthetic application of magnesiomalonyl ester. H. LUND (Ber., 1934, 67, [B], 935–938).—Inception of the action between Mg and EtOH is effected by CCl_4 or less advantageously by

CHCl_3 or $\text{C}_2\text{H}_2\text{Cl}_4$, which appear to be partly hydrogenated. (CCl_4 can also be used in the prep. of anhyd. EtOH by Mg, since the products distil with the first few c.c. of EtOH.) The prep. from Mg, EtOH, $\text{CH}_2(\text{CO}_2\text{Et})_2$, and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ of Et_4 propane- $\alpha\beta\gamma$ -tetracarboxylate and from Mg, EtOH- Et_2O , $\text{CH}_2(\text{CO}_2\text{Et})_2$, and BzCl or AcCl of Et_2 benzoylmalonate (Mg derivative) and Et_2 acetylmalonate is described. $\text{CH}(\text{CO}_2\text{Et})_3$ is obtained by use of ClCO_2Et . H. W.

Polarimetric study of beryllium tartrates. J. L. DELSAL (Compt. rend., 1934, 198, 2076–2078).—Electrometric and polarimetric examination of the solutions obtained by dissolution of varying molecular proportions of $\text{Be}(\text{OH})_2$ (I) in solutions of tartaric acid and its Na H salt (II), indicates the formation of only

one complex, $\text{Be} \begin{matrix} \text{O}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{Be}\cdot\text{OH} \\ \text{O}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{Be}\cdot\text{OH} \end{matrix} [\alpha]_D -173.5^\circ$ (isolated), and the Na derivative,

$\text{Be} \begin{matrix} \text{O}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{Na} \\ \text{O}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{Be}\cdot\text{OH} \end{matrix} [\alpha]_D -214^\circ$, obtained only by the action of (I) on (II). J. W. B.

Isomerism in chloralides. N. M. SHAH and R. L. ALIMCHANDANI (Current Sci., 1934, 2, 383–384; cf. this vol., 301).—*d*- and *r*-Tartaric and lactic acid each give two chloralides on condensation with $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ in presence of H_2SO_4 . The m.p. are 162° and 175°, 160° and 215°, 62° and b.p. 212°, respectively. L. S. T.

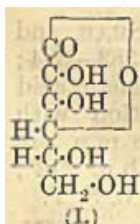
Selenium dioxide. New oxidising agent. IV. Preparation and properties of ethyl ketohydroxy-succinate. S. ASTIN and H. L. RILEY (J.C.S., 1934, 844–848).—Et *d*-tartrate (3 mol.) heated with SeO_2 (1 mol.) at 120–130° gives CO_2 , complex organo-Se compounds, and a 16% yield of Et *d*-ketohydroxy-succinate, m.p. 98–99° (105–106° after drying over P_2O_5), $[\alpha]_D^{25} +14^\circ$ in H_2O , -15.6° in EtOH (no reaction in $[\text{CH}_2\cdot\text{OH}]_2$ or dioxan), hydrolysed by KOH to $\text{H}_2\text{C}_2\text{O}_4$, EtOH, CO_2 , and a little $[\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}]_2$, and by HCl to a mixture of *d*- and meso-tartaric acid; it gives osazones of $[\text{CO}\cdot\text{CO}_2\text{Et}]_2$ with $\text{NHPh}\cdot\text{NH}_2\cdot\text{AcOH}$. Its relationships to the two forms of Et dihydroxymaleate (probably *cis* and *trans*; Fenton, J.C.S., 1896, 69, 546) are discussed. Similar oxidation of Bu and amyl tartrates gives unidentified decomp. products, and Me fumarate is the only solid product isolated when the Me ester is employed. Similar oxidation of $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ gives only a trace of AcCO_2Et and, possibly, $\text{CHO}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ (I) or $\text{CHO}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Et}$, since with $\text{NHPh}\cdot\text{NH}_2$, the bisphenylhydrazone of (I) is obtained. J. W. B.

Synthesis of vitamin-C. F. MICHEEL, K. KRAFT, and W. LOHMANN (Z. physiol. Chem., 1934, 225, 13–27).—With 40% aq. NaOH in absence of O_2 , α -keto-d-gluconic acid undergoes conversion (44%) into a substance (I) reducing I on acidification. With dil. alkali the yield is less and also decreases on dilution of the conc. alkaline mixture. On keeping in acid solution, the yield of (I) falls to a const. val. of 6%. With Me_2SO_4 -aq. NaOH, (I) yields a syrup which, after treatment with CH_2N_2 and MeI and Ag_2O , contains 52% of OMe. Ozonisation then yields $\text{H}_2\text{C}_2\text{O}_4$. The product is evidently a methylated dienol ($\Delta^2:3$). *l*-Sorbitol prepared from sorbitol by *Bact. xylinum* was

converted into the osazone, which afforded the osone (II) with PhCHO and AcOH. With Br (II) gave *l*-sorburonic acid (III) [$\text{Na} (+\text{H}_2\text{O})$, m.p. 145° (decomp.), $[\alpha]_D^{20} -23.6$ in H_2O , and *brucine* ($+\text{H}_2\text{O}$), m.p. 146° (decomp.) salts]. Treatment of (III) with conc. aq. NaOH afforded ascorbic acid (IV), identical with the natural (IV). (IV) is recovered unchanged from conc. aq. NaOH. J. H. B.

Behaviour of ascorbic acid towards nitrate and nitrite. P. KARRER and H. BENDAS (Helv. Chim. Acta, 1934, 17, 743—745).—At p_{H} 6.0, 7.0, or 9.3, ascorbic acid (I) does not appear to reduce KNO_3 to KNO_2 in boiling H_2O . In acidic or neutral, but not in alkaline, solution KNO_3 is reduced by (I) to NO. In presence of NH_4Cl , NO is liberated from alkaline solution. Most marked evolution of NO occurs in the vicinity of the neutral point. H. W.

Preparation of isovitamin-C (*d*-araboascorbic acid). II. K. MAURER and B. SCHIEDT (Ber., 1934, 67, [B], 1239—1241).—Mo α -ketogluconate (prep. from diisopropylidene-fructose described) is converted by NaOMe-MeOH into *Na isoascorbate*. *isoAscorbic acid* (I), m.p. 168°, $[\alpha]_D^{20} -21.95^\circ$ in H_2O , in chemical properties closely resembles ascorbic acid (II). It is oxidised by 2I to the neutral diketone, $[\alpha]_D^{20} +92.5^\circ$ in H_2O , reduced by H_2S to (I). Its antiscorbutic action is approx. 0.05 of that of (III). It is an excellent photographic developer. H. W.



Synthesis of a lactosecarboxylic acid (5- β -*d*-galactosido- α -*d*-glucoheptonic acid). R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 1390—1391).—Application of the modified Kiliani reaction (this vol., 757) to lactose gives 5- β -*d*-galactosido- α -*d*-glucoheptonic acid, m.p. 185—186° (all m.p. are corr.), $[\alpha]_D^{20} +11.2^\circ$ in H_2O {*quinine*, m.p. 169—170° (decomp.), $[\alpha]_D^{20} -71.9^\circ$ in H_2O , and *brucine*, m.p. 172—173° (decomp.), $[\alpha]_D^{20} -7.6^\circ$ in H_2O , salts}, hydrolysed (2% H_2SO_4) to *d*-galactose and α -*d*-glucoheptonic acid {*brucine* salt, m.p. 155° (decomp.), $[\alpha]_D^{20} -18.4^\circ$ in H_2O }. H. B.

Alkylthiol- and alkylsulphonyl-carboxylic acids. A. MELLANDER (Svensk Kem. Tidskr., 1934, 46, 99—108).—The SMe-acids are obtained from the SH-acids by Me_2SO_4 and NaOH. SET-acids are derived from the halogeno-acids and EtSH in alkaline solution. Oxidation of SAlk- to SO_2Alk -acids is effected by KMnO_4 in neutral or slightly alkaline solution. The following compounds are described: methylthiolacetic acid, b.p. 107° (corr.)/9.5 mm.; methylsulphonylacetic acid, m.p. 114.5—115.5° (corr.), converted by Br into $\alpha\alpha$ -dibromodimethylsulphone, r.p. 65.5—66.5° (corr.); α -methylthiolpropionic acid, b.p. 104—104.5° (corr.)/8 mm.; α -methylsulphonylpropionic acid, m.p. 96—97.2°, whence α -bromo- α -methylsulphonylpropionic acid, m.p. 172.5—173.5° (corr.); α -ethylthiolpropionic acid, b.p. 113.7—113.8°/8 mm.; α -ethylsulphonylpropionic acid, m.p. 62.0—63.2° (corr.), whence α -bromo- α -ethylsulphonylpropionic acid, m.p. 96.0—96.5° (corr.). Optical and affinity consts. of the compounds are recorded. H. W.

Reaction between ethyl α -bromoisobutyrate and sodium sulphide in alcoholic solution. E. LARSSON and K. JONSSON (Ber., 1934, 67, [B], 1263—1270).—The action of NaSH on Et α -bromoisobutyrate (I) in EtOH leads to *thio*- $\alpha\beta'$ -diisobutyric acid (H) ($+\text{H}_2\text{O}$), m.p. 153°, *thio*- $\alpha\alpha'$ -diisobutyric acid (III), m.p. 142°, and *thio*- $\beta\beta'$ -diisobutyric acid (IV), m.p. 115°. (I) appears to behave as if containing the β -Br-compound, which is not appreciably present in the initial material. The constitution of the acids is decided mainly by consideration of their dissociation consts. and the behaviour of the corresponding SO-acids towards HCl, whereby it is considered that fission occurs thus: $\text{CH}_2\text{R}\cdot\text{SO}\cdot\text{R}' \longrightarrow \text{OH}\cdot\text{CHR}\cdot\text{SR}' \longrightarrow \text{R}\cdot\text{CHO}+\text{R}'\cdot\text{SH}$, and hence is contingent on the presence of H attached to C. (II) is also obtained from (I) and $\text{SNa}\cdot\text{CMe}_2\cdot\text{CO}_2\text{Na}$ in abs. EtOH. It is oxidised by $\text{Br}\cdot\text{H}_2\text{O}$ to *sulphonyl*- $\alpha\beta'$ -diisobutyric acid, m.p. 193°, and by 30% H_2O_2 in CMe_2 at 0° to *thionyl*- $\alpha\beta'$ -diisobutyric acid, m.p. 103° ($+\text{H}_2\text{O}$, m.p. 100—101°), which is converted by HCl into α -dithiodiisobutyric acid (V) and passes when distilled into (V), $\text{Pr}^2\text{CO}_2\text{H}$, and methacrylic acid. (III) is isolated from the reaction mixture after removal of (II) as the K salt. It is oxidised by Br to *sulphonyl*- $\alpha\alpha'$ -diisobutyric acid, m.p. 190°, and by H_2O_2 to *thionyl*- $\alpha\alpha'$ -diisobutyric acid, which is stable towards HCl. (IV) is oxidised to *sulphonyl*- $\beta\beta'$ -diisobutyric acid, m.p. 141°, and *thionyl*- $\beta\beta'$ -diisobutyric acid, m.p. 128° (decomp.), unstable towards HCl. H. W.

[Polyoxymethylenes.] H. STAUDINGER (Ber., 1934, 67, [B], 948).—A reply to Hess (this vol., 493). H. W.

Comparison of the viscosity properties of synthetic and natural highly-polymerised compounds. I. SAKURADA (Ber., 1934, 67, [B], 1045—1051).—The viscosity data of a no. of synthetic and natural polymerides are separated into two components (a =form and charge factor, ϕ =sp. vol.) according to the author's formula $c/\eta_{\text{sp}}=100/a\phi-c/a$ (cf. A., 1933, 901). With synthetic polymerides (polystyrene and polymeric ω -hydroxydecoic acids) a increases regularly and almost linearly with $\log [100(\eta_{\text{sp}}/c)_{\text{lim. } c=0}]$, whereas with cellulose nitrates and caoutchouc (I) it is independent of the viscosity. There exists, therefore, a fundamental difference between the viscosity properties of natural and synthetic polymerides, and Staudinger's viscosity rule is not applicable to substances such as cellulose, starch, and (I). H. W.

Action of Grignard reagent on $\alpha\beta$ -unsaturated aldehydes. P. G. STEVENS (J. Amer. Chem. Soc., 1934, 56, 1425).— MgBu^nCl and crotonaldehyde give approx. equal amounts (about 25%) of $\text{CHMe}\cdot\text{CH}\cdot\text{CHBu}^n\cdot\text{OH}$ and $\beta\gamma\gamma$ -trimethylvaleraldehyde (semicarbazone, m.p. 166°). $\beta\gamma\gamma$ -Trimethylvaleramide has m.p. 163—164°. Me $\beta\gamma\gamma$ -trimethyl- Δ^2 -pentenoate (ozonolysis product, CMeBu^n) is obtained from Me α -bromo- $\beta\gamma\gamma$ -trimethylvalerate and NPhEt_2 . Some 1:4-addition also occurs with MgEtBr , MgPr^nBr , and MgPr^2Br . H. B.

Oxidation of citronellal. H. I. WATERMAN and E. B. ELSBACH (Rec. trav. chim., 1934, 53, 730—736).—Analysis of the gaseous and liquid products

formed when citronellal autoxidises in a closed system shows that 1 mol. of CO_2 is formed for each mol. of peroxide formed and that little citronellic acid is produced. The main product is a viscous, unstable C_9 peroxide, isolated by distillation in a cathode vac.

R. S. C.

Dialkyl ketones derived from ethoxy-compounds of high mol. wt. D. BARDAN (Bull. Soc. chim., 1934, [v], 1, 370—373; cf. A., 1932, 368).— γ -Ethoxy- β -methyl- Δ^8 -heptene with 20% H_2SO_4 at 140—145° during 3—5 hr. affords COPr^nBu^n , b.p. 158—160° (cf. A., 1915, i, 497). The following are prepared similarly: γ -ethyloctan- δ -one, b.p. 122—125°/38 mm.; δ -n-propylnonan- ϵ -one, b.p. 142—144°/29 mm.; ϵ -n-butyldecan- ζ -one, b.p. 155—158°/23 mm.; γ -ethyldecan- δ -one, b.p. 132—134°/23 mm.; δ -n-propylundecan- ϵ -one, b.p. 157—162°/25—26 mm., and ϵ -n-butylidodecan- ζ -one, b.p. 180—183°/24 mm. These ketones do not afford oximes, semicarbazones, or H sulphite compounds.

J. L. D.

Keto-ethers. I. [Alkyl] methoxymethyl ketones. H. R. HENZE and N. E. RIGLER (J. Amer. Chem. Soc., 1934, 56, 1350—1351).— $\text{OMe}\cdot\text{CH}_2\cdot\text{COR}$, where R is Me, b.p. 114.6°/746 mm. (all b.p. are corr.), Et, b.p. 133—133.6°/757 mm. (lit. about 130°), Pr^n , b.p. 152—153°/745 mm. (lit. 142—150°), Pr^i , b.p. 143.5—145°/748 mm., Bu^n , b.p. 167—169°/744 mm., Bu^i , b.p. 163—164°/751 mm., sec.-Bu, b.p. 164°/757 mm., Bu^t , b.p. 158—159°/743 mm., n-amyl, b.p. 191—191.5°/753 mm., and isoamyl, b.p. 185—186°/752 mm., are prepared from $\text{OMe}\cdot\text{CH}_2\cdot\text{CN}$ and the requisite Grignard reagent. They give unstable liquid phenylhydrazones and reduce Fehling's and Tollens' reagents in the hot.

H. B.

Reactions of carbohydrates [with diazobenzenesulphonic acid and alkali]. L. EKKERT (Pharm. Zentr., 1934, 75, 407—409).—Colour reactions of 13 carbohydrates are given. E. H. S.

Derivatives of xylose. G. J. ROBERTSON and T. H. SPEEDIE (J.C.S., 1934, 824—829).— γ -Methylxyloside (prep. with β -compound described) with $\text{HCl}\cdot\text{COMe}_2$ at room temp. gives its 3:5-isopropylidene derivative (I), b.p. 102—107°/0.1 mm., $[\alpha]_D^{+17.3}$ in CHCl_3 , converted by $\text{MeI}\cdot\text{Ag}_2\text{O}$ into its 2-Me derivative, b.p. 77°/0.07 mm., $[\alpha]_D^{+24.6}$ in CHCl_3 , hydrolysed by boiling $\text{N}\cdot\text{H}_2\text{C}_2\text{O}_4$ to 2-methylxylose, m.p. 132—133°, $[\alpha]_D^{-23.9}$ to $+35.9$ in 20 hr. in H_2O , the Ac_3 derivative, m.p. 95°, $[\alpha]_D^{-2.2}$ in CHCl_3 (probably a mixture of α - and β -forms), of which is converted by $\text{HBr}\cdot\text{AcOH}$ and $\text{Ag}_2\text{CO}_3\cdot\text{MeOH}$ into 2-methyl- β -methylxyloside 3:4-diacetate, m.p. 78—79°, $[\alpha]_D^{-38.1}$ in CHCl_3 , hydrolysed to 2-methyl- β -methylxyloside, m.p. 111—112°, $[\alpha]_D^{-67.7}$ in CHCl_3 (3:4-di-p-toluenesulphonyl derivative, m.p. 123°, $[\alpha]_D^{-16}$ in CHCl_3). With $\text{BzCl}\cdot\text{C}_5\text{H}_5\text{N}$ at 0° (I) affords its 2-Bz derivative, hydrolysed by boiling 1% $\text{HCl}\cdot\text{MeOH}$ to methylxyloside 2-benzoate, methylated (Purdie) to its 3:4-Me₂ derivative, debenzoylated ($\text{NaOMe}\cdot\text{MeOH}$) 3:4-dimethylmethylxyloside, b.p. 110—115°/0.2 mm., hydrolysed to 3:4-dimethylxylose (II), $[\alpha]_D^{+24.9}$ to $+20.5$ in 5 hr. in H_2O (syrupy osazone). (II) does not condense with 1% $\text{MeOH}\cdot\text{HCl}$, but its Bz derivative with $\text{HBr}\cdot\text{AcOH}$ followed by $\text{Ag}_2\text{CO}_3\cdot\text{MeOH}$ and debenzoylation affords 3:4-dimethyl- β -

methylxyloside, m.p. 89—90°, $[\alpha]_D^{-82.2}$ in CHCl_3 (2-p-toluenesulphonyl derivative, m.p. 105°, $[\alpha]_D^{-34.8}$ in CHCl_3). β -Methylxyloside with CPh_3Cl gives a syrupy 3-CPh₃ derivative, from which by acetylation and hydrolysis is obtained β -methylxyloside 2:4-diacetate, the 3-nitrate, m.p. 120—121° (by CHCl_3 -fuming HNO_3), of which with 33% $\text{NHMe}_2\cdot\text{EtOH}$ and methylation gives the 3-nitrate (a syrup) of 2:4-dimethyl- β -methylxyloside, b.p. 100—105°/0.06 mm., m.p. 60—61°, $[\alpha]_D^{-82.4}$ in CHCl_3 (3-p-toluenesulphonyl derivative, m.p. 88°, $[\alpha]_D^{-58.9}$ in CHCl_3), which is obtained by treatment with 5% $\text{Na}\cdot\text{Hg}$ in $\text{H}_2\text{O}\cdot\text{EtOH}\cdot\text{AcOH}$. 2:3-Dimethylxylose (from xylan) gives its β -methylxyloside, b.p. 90—95°/0.03 mm., $[\alpha]_D^{-5.8}$ in CHCl_3 (4-p-toluenesulphonyl derivative, m.p. 56—59°, $[\alpha]_D^{-8.8}$ in CHCl_3). All b.p. are bath temp.

J. W. B.

Munson-Walker method for reducing sugars. R. F. JACKSON (J. Assoc. Off. Agric. Chem., 1934, 17, 293—301; cf. A., 1906, ii, 634).—Direct weighing of Cu_2O is untrustworthy and tedious. $\text{Na}_2\text{S}_2\text{O}_3$ titration is slightly more exact than the electrometric $\text{K}_2\text{Cr}_2\text{O}_7$ method, but is less convenient, but both are more trustworthy than KMnO_4 titration. Standardisation of the time required for filtration of the Cu_2O ppt. is as important as standardisation of the conditions of boiling.

E. C. S.

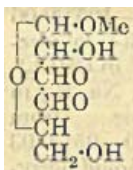
Natural interconversion of isomeric sugars. G. J. ROBERTSON and J. W. H. OLDHAM (Nature, 1934, 133, 871).—The hydrolysis of p-toluenesulphonyl derivatives of methylglucosides falls into two main groups according as the original substance contains one or two p-C₆H₄Me·SO₂ residues in neighbouring positions. When Walden inversion (I) occurs it is accompanied by anhydro-formation, which may be a necessary precursor to it. This supports Robinson's view that (I) within the sugar mol. is the agency for natural interconversion of simple sugars. L. S. T.

Relationships of isomeric d-glucoses and d-glucosephenylhydrazones. G. H. STEMPEL, jun. (J. Amer. Chem. Soc., 1934, 56, 1351—1355).—The mutarotation of α -d-glucosephenylhydrazone (I), m.p. 160°, $[\alpha]_D^{25}$ —87° (initial) \rightarrow —52.5° (const.) in H_2O (convenient prep. given), is not unimol.; at least 3 substances are involved in the equilibrium. Hydrolysis (aq. $\text{H}_2\text{C}_2\text{O}_4$ at 30°) of (I) is pseudo-unimol.; an increase in the velocity coeff. towards the end of the reaction is ascribed to the adsorption of d-glucose on $\text{NHPh}\cdot\text{NH}_2$ oxalate (pptd. towards the end of the reaction). Information concerning the structures of d-glucosephenylhydrazones and their relationships to the isomeric d-glucoses cannot be obtained from studies of hydrolysis (cf. Frérejacque, A., 1925, i, 635). The reactions of α - (I) and β - (II) -d-glucose with $\text{NHPh}\cdot\text{NH}_2$ in aq. EtOH are followed polarimetrically; (I) reacts more rapidly than (II) [probably owing to the presence of a trace of catalyst in the (I) used, since in presence of 0.0073M-HCl the rates are identical]. Strong acids catalyse hydrazone but not osazone formation.

H. B.

Oxidation of glucose and derivatives of glucose with periodic acid. P. KARRER and K. PFAEHLER (Helv. Chim. Acta, 1934, 17, 766—771).—Oxidation of

glucose (I) by HIO_4 gives only approx. 1 mol. of CH_2O when 6 mols. of HIO_4 are used. With 1 mol. only about 0.03 mol. of CH_2O results, showing that main fission of (I) is not between C_5 and C_6 , but at some other position of the mol., and that the production of large amounts of CH_2O is a secondary process. If the oxidation of (I) by HIO_4 (mol. ratio 1 : 5) is interrupted after 10, 30, and 60 min., the corresponding amounts of formaldehyde are a trace, 0.33 mol., and 0.46 mol. respectively. Methylglucoside does not yield CH_2O even when an excess of HIO_4 is used, possibly owing to formation of (II). Mannosephenylhydrazone and HIO_4 yield only 0.35 mol. of CH_2O . Glucosephenylosazone and HIO_4 (1 : 3) in 50% EtOH readily yield 4-benzeneazo-1-phenylpyrazol-5-one, m.p. 150°, fission occurring between C_3 and C_4 .



(II.)

EtOH readily yield 4-benzeneazo-1-phenylpyrazol-5-one, m.p. 150°, fission occurring between C_3 and C_4 .

H. W.

Carbohydrates. IV. Peculiar behaviour of the 2-hydroxyl group in the glucose molecule. T. LIESER and E. LECKZYCK (Annalen, 1934, 511, 137—140).—Glucosediethylmercaptal (I) does not appear to yield a xanthate. Treatment of (I) with Ag_2O and much MeI yields 2-methylglucosediethylmercaptal in 51.4% yield. Attempts to substitute a solvent for the large excess of MeI proved unsatisfactory, whereas 2-methylglucosediethylmercaptal (II), m.p. 193—194° (corr.), is obtained in 13.2% yield in CHCl_3 and in 55.1% yield in abs. MeOH. Attempts to methylate the Et_2 and $(\text{CH}_2\text{Ph})_2$ mercaptals of galactose, arabinose, or rhamnose or xylosediethylmercaptal, m.p. 77.5—78° [Bz_4 derivative, m.p. 170° (corr.)], were unsuccessful. (II) could not be caused to react with acetobromoglucose.

H. W.

Acyl migration in the sugar group. L. VON VARGHA (Ber., 1934, 67, [B], 1223—1229).—The 6-triphenylmethylisopropylideneglucose 3-acetate (I) of Josephson is converted by Ag_2O and MeI into 6-triphenylmethyl-3-methyl-1:2-isopropylideneglucosfuranose 5-acetate (II), m.p. 155°, $[\alpha]_D^{20}$ -37.0° in CHCl_3 (in poor yield due to loss of CPh_3 with production of $\text{CPh}_3\cdot\text{OMe}$), also obtained by the successive action of CPh_3Cl and Ac_2O in $\text{C}_5\text{H}_5\text{N}$ on 3-methylisopropylideneglucose. (II) is converted by $\text{NaOH}\cdot\text{MeOH}$ into 6-triphenylmethyl-3-methyl-1:2-isopropylideneglucosfuranose, m.p. (indef.) 60°, $[\alpha]_D^{20}$ -38.6° in CHCl_3 , hydrolysed by AcOH to 3-methyl- α -glucose, m.p. 167—168°, $[\alpha]_D^{20}$ (equil.) +55.5° in H_2O {phenylosazone, m.p. 176—177°, $[\alpha]_D^{20}$ (equil.) -41.6° in EtOH}. The point at which acyl wanders is discussed, and it is suggested that (I) is a mixture of the 3- and 5-acetate. Diisopropylideneglucose in $\text{C}_6\text{H}_6\cdot\text{C}_5\text{H}_5\text{N}$ is transformed by COCl_2 in C_6H_6 or PhMe into di(diisopropylideneglucose) 3:3'-carbonate (III), m.p. 149°, $[\alpha]_D^{20}$ -50.8° in CHCl_3 , which affords a tetra-acetate, m.p. 104° after softening, $[\alpha]_D^{20}$ +7.62° in CHCl_3 , and is re-converted by COMe_2 and anhyd. CuSO_4 into (III). In H_2O , MeOH, EtOH, $\text{C}_5\text{H}_5\text{N}$, or dioxan (III) readily undergoes intramolecular transformation into 1:2-isopropylideneglucosfuranose 5:6-carbonate and 1:2-isopropylideneglucosfuranose. The probability that acyl migration is accompanied by intermediate production of orthocarbonic esters is

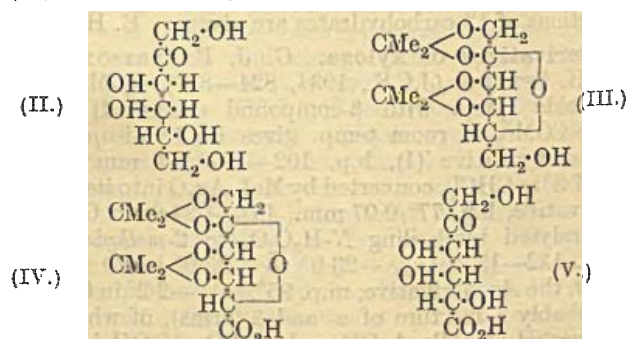
strengthened by the observation that the transformation of (III) is independent of the solvent and hindered by acids which retard the production of orthocarbonates.

H. W.

Preparation of methylglucosides of methylated glucoses. J. W. H. OLDHAM (J. Amer. Chem. Soc., 1934, 56, 1360—1362).—The methylglucoses are benzoated (BzCl , $\text{C}_5\text{H}_5\text{N}$) and the resulting benzoates converted by $\text{HBr}\cdot\text{AcOH}$ in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$ into bromomethylglucose benzoates; these and $\text{MeOH} + \text{Ag}_2\text{CO}_3$ give the corresponding methylglucosides, which are then debenzoylated. *o*-Methyl-2-methylglucoside, m.p. 97—98°, $[\alpha]_D^{20}$ -37.5° in H_2O (tribenzoate, m.p. 119—120°, $[\alpha]_D^{20}$ -40.4° in CHCl_3), β -methyl-3-methylglucoside, $[\alpha]_D^{20}$ -26.6° in H_2O (tribenzoate, m.p. 125—126°, $[\alpha]_D^{20}$ +14.7° in CHCl_3), β -methyl-2:3-dimethylglucoside, m.p. 62—64°, $[\alpha]_D^{20}$ -47.8° in CHCl_3 (dibenzoate, m.p. 99—101°, $[\alpha]_D^{20}$ -8.2° in CHCl_3), and β -methyl-2:3:6-, m.p. 59—60°, $[\alpha]_D^{20}$ -47.5° in CHCl_3 , and -2:4:6-, m.p. 70—71°, $[\alpha]_D^{20}$ -27.4° in CHCl_3 . -trimethylglucosides are thus prepared. β -2- and β -3-Methylglucose tetra-benzoates have m.p. 169—170°, $[\alpha]_D^{20}$ -6.2° in CHCl_3 , and m.p. 198—199°, $[\alpha]_D^{20}$ +3.6° in CHCl_3 , respectively.

H. B.

d-Tagatose, diacetone-*d*-tagatose [*d*-tagatose diisopropylidene ether], and *d*-tagaturonic acid. T. REICHSTEIN and W. BOSSHARD (Helv. Chim. Acta, 1934, 17, 753—761).—Anhyd. *d*-galactose (I) is heated in $\text{C}_5\text{H}_5\text{N}$ at 145°, the solvent is removed, and the bulk of unchanged (I) is pptd. by addition of EtOH to a solution of the residue in H_2O . Remaining (I) is removed by fermentation, thus leading to the isolation of tagatose (II), m.p. 131—132° (corr.), $[\alpha]_D^{20}$ -2.3° in H_2O . *d*-Sorbosose does not appear to be produced, but the formation of talose is probable. (II) is converted by COMe_2 and conc. H_2SO_4 at room

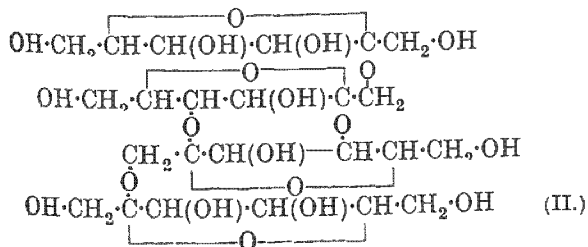


temp. into diisopropylidenetagatose (III), m.p. 65—66°, $[\alpha]_D^{20}$ +81.5° in COMe_2 , +71.8° in H_2O , oxidised by alkaline KMnO_4 to *d*-diisopropylidenetagaturonic acid (IV), m.p. about 118—121° (corr.) in capillary, m.p. 102—103° under the microscope (also +0.5 H_2O , m.p. 117—121° in capillary, m.p. 98—99° under the microscope, $[\alpha]_D^{18}$ +33.5° in COMe_2). (IV) is hydrolysed by boiling H_2O to *d*-tagaturonic acid (V), 106—108°, $[\alpha]_D^{20}$ -12.55° (equilibrium val.) {*Me* ester (VI), $[\alpha]_D^{20}$ about +13° in MeOH}. The constitution of (V) follows from its reduction to *l*-galactonic and *d*-altronic acid. Short treatment of (VI) with NaOMe gives very small amounts of substances which reduce I in acid solution. H. W.

Carbohydrates. II. Xanthate reaction of mono- and di-saccharides. III. Xanthate reactions of polymeric carbohydrates with exception of cellulose. T. LIESER and A. HACKL (Annalen, 1934, 511, 121—127, 128—136; cf. A., 1932, 718).—II. Cu^I methylglucosidyl xanthate (improved prep.) is readily decomposed by dil. NaOH with formation of β -methylglucoside. With dil. AgNO_3 the Ba salt affords *Ag methylglucosidyl xanthate*, transformed by excess of MeI at room temp. into *Me methylglucosidyl xanthate*, m.p. $67-68^\circ$ (corr.), and by MeOH-I into the *dixanthate*, $\text{C}_{16}\text{H}_{26}\text{O}_{12}\text{S}_2$; *Me₂ xanthate* is described. Glucosephenylhydrazone and methylgalactoside afford the compounds $\text{C}_{13}\text{H}_{17}\text{O}_5\text{N}_2\text{SCu}$ and $\text{C}_8\text{H}_{13}\text{O}_6\text{S}_2\text{Cu}$, respectively, whereas fructose gives the substance, $\text{C}_7\text{H}_{10}\text{O}_6\text{S}_2\text{Cu}_2$. The compounds, $\text{C}_{14}\text{H}_{20}\text{O}_{11}\text{S}_4\text{Cu}_2$, from maltose, lactose, and cellobiose, respectively, are sol. in H_2O , from which they are pptd. by MeOH . Since sucrose and raffinose give the substances $\text{C}_{13}\text{H}_{21}\text{O}_{11}\text{S}_2\text{Cu}$ and $\text{C}_{20}\text{H}_{30}\text{O}_{16}\text{S}_4\text{Cu}_2$, respectively, it appears that the fructosidic portions of the higher sugars are incapable of xanthate formation.

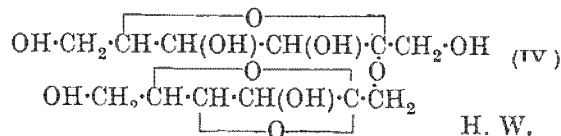
III. Starch, glycogen (I), lichenin, mannan, inulin, and xylan yield xanthates with concns. of alkali < are required by cellulose. With the possible exception of (I), xanthate formation increases with concn. of alkali to an optimum, after which it declines. The optimal composition of the xanthates, with the exception of (I), indicates the relationship $2C_6H_{10}O_5 : CS_2$ as with cellulose (II). Since this apparent ratio for (II) depends on a micellar surface reaction, it follows that the investigated polymerides with the exception of (I) have a micellar structure, and that on the average nearly as many sugar anhydride chains are situated on the surface of the micelles as in the interior.

Fructose anhydrides. XIV. Constitution of irisin. II. H. H. SCHLUBACH, H. KNOOP, and M. Y. LIU (Annalen, 1934, 511, 140—151; cf. A., 1933, 938).—Interruption of the hydrolysis of irisin (I) by $N\text{-H}_2\text{SO}_4$ at 20° at the point at which the greatest difference exists between reducing power and $[\alpha]_D$ of the products discloses the complete disappearance of (I). The bulk of the fructose is readily removed from the product by treatment of the H_2O solution with EtOH, the remainder by acetylation and subsequent hydrolysis, whereby *di-irisin* (II),



$[\alpha]_D - 36.6^\circ$, mol. wt. 642 (Ac derivative, $[\alpha]_D^{20} -$ in AcOH), is obtained. Marked difference exists in the period of semi-hydrolysis of (II) as judged re-actometrically and polarimetrically, so that an intermediate product (III) is formed on the way to fructose. Treatment of (II) containing a small amount of (III) with $\text{MeSO}_3\text{-NaOH}$ and $\text{Ag}_2\text{O-Mel}$

leads to a non-distillable *methyl-di-irisan*, $[\alpha]_D^{20}$ -48.3° in CHCl_3 , -50.1° in COMe_2 , hydrolysed to equiv. amounts of tetra- and di-methylfructose and a *tri-methylfructose*, b.p. $93.5^\circ/0.06$ mm., $[\alpha]_D^{20}$ -12.7° to -45.6° in H_2O , $+13.1^\circ$ to $+10.1^\circ$ in CHCl_3 , which is not the 3:4:6-derivative and contains OMe in position 1, since (with loss of OMe) it affords a *phenylosazone*, $\text{C}_{20}\text{H}_{26}\text{O}_4\text{N}_4$. The dimethylfructose yields an osazone without loss of OMe, and hence contains a free OH at 1. Irisan, the fundamental substance of (I), is therefore (IV).



State of solution of cellobiose and maltose octa-acetates in acetic acid.—See this vol., 841.

Synthesis of *p*-aminophenyl- β -glucosides of maltose, lactose, cellobiose, and gentiobiose. F. H. BABERS and W. F. GOEBEL (J. Biol. Chem., 1934, 105, 473—479).—The method adopted in every case was to treat the acetobromo-compound of the sugar with p -OH-C₆H₄-NO₂ and NaOH in aq. COMe₂, deacetylate, and reduce the resulting *p*-NO₂-compound with H₂-PtO₂ in MeOH. The following are described: β -*p*-nitrophenyl-lactoside, m.p. 258—260° (darkens 250°), $[\alpha]_D^{25}$ -74.2° in H₂O [*Ac*- derivative, m.p. 132—133° (corr.), $[\alpha]_D^{25}$ -35.4° in CHCl₃], -maltoside, m.p. 221°, $[\alpha]_D^{25}$ +6° in MeOH [*Ac*- derivative, m.p. 175—176° (corr.), $[\alpha]_D^{25}$ +33.8° in CHCl₃], -gentiobioside, m.p. 221—223°, $[\alpha]_D^{25}$ -105.2° in 50% MeOH [*Ac*₇ derivative, m.p. 215—216° (corr.), $[\alpha]_D^{25}$ -47.35° in CHCl₃], and -cellobioside, m.p. 255—256° (decomp., darkens 245°), $[\alpha]_D^{25}$ -85.1° in 40% MeOH (*Ac*- derivative, m.p. 234—235°); β -*p*-aminophenyl-lactoside, m.p. 233° (decomp.), $[\alpha]_D^{25}$ -36.4° in H₂O, -maltoside, m.p. 91—92° (corr.), $[\alpha]_D^{25}$ +35.3° in 50% MeOH, -gentiobioside, m.p. 237—238° (decomp.), $[\alpha]_D^{24}$ -79.8° in H₂O, and -cellobioside, m.p. 245° (decomp.), $[\alpha]_D^{25}$ -52.9° in 50% MeOH. H. A. P.

Glucosides of *Digitalis lanata*. C. MANNICH (Helv. Chim. Acta, 1934, 17, 789—790).—The strongest evidence that the author's glucoside II is composed of genuine glucosides and is practically identical with the total digilanid prep. of Stoll and Kreis rests in the observation that it cannot be separated into differing components by careful crystallisation from EtOH. Decomp. products poor in sugar or free from Ac do not form isomorphous series with the genuine glucosides (cf. this vol., 636). H. W.

Glucosides of *Digitalis lanata*. A. STOLL and W. KREIS (Helv. Chim. Acta, 1934, **17**, 790—794).—A reply to Mannich (preceding abstract). H. W.

Colouring matter of the seed-coat of *Abrus precatorius*, Linn. (scarlet variety). N. GHATAK (Current Sci., 1934, 2, 380, and Bull. Acad. Sci. Agra and Oudh, 1933, 3, 69-74).—Gallic acid and an anthocyanin, now named *abranin* (I), have been isolated from the seed-coat of *A. precatorius*. *Abranin chloride*, m.p. 178-179° (sintering), isomerises readily in H₂O, EtOH, etc., and yields glucose on

hydrolysis. The *picrate* melts at 149—150°. (I) is a monoglucoside. L. S. T.

Sterol glucosides. O. GISVOLD (J. Amer. Pharm. Assoc., 1934, 23, 402—404).—A no. of sterol glucosides were synthesised by the method of Power and Salway (J.C.S., 1913, 103, 399). The following appear to be new: *stigmasterylglucoside*, m.p. 299°; *phytosterylglucoside*, m.p. 293°. A. E. O.

Highly-polymerised compounds. XCIX. Structure of highly-polymerised compounds and the law of viscosity. H. STAUDINGER (Ber., 1934, 67, [B], 1242—1256).—A statement of the author's views on the macro-mol. structure of highly-polymerised compounds, the determination of the mol. wt. of such substances from measurements of viscosity, the form of the mols., and the origin of the term "eucolloid." H. W.

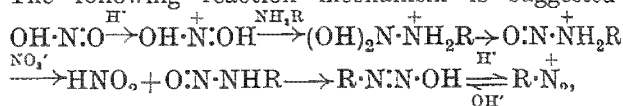
Morphology and chemistry of organic high-molecular natural products. K. HESS (Naturwiss., 1934, 22, 469—476).—A lecture.

Degradation of starch by phosphoric acid, glycerol, and acetic anhydride and sulphuric acid (acetolysis). R. SUTRA (Compt. rend., 1934, 198, 1863—1865).—H₂O-sol. potato or maize starch (I) dissolves slowly in 85% H₃PO₄ at room temp. α of these solutions (II) is about the same as that of aq. solutions, does not change at room temp., but decreases rapidly at 100° owing to degradation and hydrolysis. Addition of EtOH ppts. a non-reducing product (III), which is obtained free from acid by washing with EtOH and Et₂O. (II) gives with I a blue colour, changed by heat successively to violet, red, and colourless. (III) is thus a dextrin, similar to that obtained by glycerol at 200° (results recorded in the lit. are confirmed) or by Ac₂O—H₂SO₄. The results are in agreement with Haworth's formula for (I). R. S. C.

Soziodolic acid as precipitant for bases. D. ACKERMANN (Z. physiol. Chem., 1934, 225, 46—48).—Soziodolic acid (2 : 6-di-iodophenol-4-sulphonic acid) (I) affords cryst. salts with many bases and NH₂-acids. The base is regenerated (as hydrochloride) by BaCl₂, which ppts. the Ba salt of (I) (solubility 0.158 g. in 100 c.c. at 16°). Salts of the following were prepared: spermine A₄B, decomp. 244—246°; putrescine, A₂B (+2H₂O), decomp. 250°; histamine, A₂B, decomp. 241°; cadaverine, A₂B, decomp. 242°; creatinine, AB, decomp. 229—231°; *D*-arginine, AB, decomp. 213—214°; guanidine, AB, decomp. 247—249°; *L*-histidine, AB, decomp. 207—208°; glycinebetaine, AB, decomp. 223—224°; lysine, A₂B, decomp. 234—235°; glucosamine, AB, decomp. 181—182°, carbamide, AB, decomp. 208°; choline, AB, decomp. 180°. Solubilities are given. J. H. B.

Decomposition of the nitrites of some primary amines. D. W. ADAMSON and J. KENNER (J.C.S., 1934, S38—S44).—The relative proportions of the products of decomp. of *n*-amyl- (I) (*picrate*, m.p. 138—138.5°), -hexyl- (*picrate*, m.p. 126.5°), -heptyl-, -octyl-, (II), -nonyl-, and -decyl- (*picrate*, m.p. 118—118.5°), -amine with HNO₃ (NH₂R, HCl + AgNO₃, filtered and thermal decomp. of solution) are, respectively, alcohol: 50.0, 50.5, 48.3, 46.3, 48.5, and 50.0;

olefine: 30.1, 28.0, 25.4, 24.4, 24.4, and 27.4; nitroso-*sec*.-amine: 1.9, 2.5, 5.3, 5.5, 9.0, and 15.3; unchanged NH₂R: 1.7, 1.5, 0.8, 4.5, 1.0, and 1.1; and NH₂R, HCl, 0.7, 1.0, 0.5, 0.8, 0.5, and 1.4%. The proportion of *sec*.-alcohol formed decreases rapidly as the series is ascended [58% for NH₂Pr^a, approx. 33% for (I), 5% in (II), and none in the higher members]. The following reaction mechanism is suggested:



whence olefines are formed by Ingold's mechanism and primary and *sec*.-alcohols by decomp. of the onium cation and attack of OH' at the α- or β-carbon atom. The correlation of such reactions with the pinacol and Wagner-Meerwein changes is fully discussed. The following new derivatives were prepared as reference compounds: α-naphthylurethanes of *n*-, m.p. 65.5°, and *sec*.-amyl, m.p. 74.5°, *n*-, m.p. 59°, and *sec*.-hexyl, m.p. 60.5°, *sec*.-heptyl, m.p. 54°, *sec*.-octyl, m.p. 62.5°, *n*-, m.p. 65.5°, and *sec*.-nonyl, m.p. 55.5°, *n*-, m.p. 73°, and *sec*.-decyl, m.p. 69°, α-, m.p. 106°, and β-phenylethyl, m.p. 117°, alcohols: the αβ-dibromides of C₇H₁₄, b.p. 99.5°/10 mm., C₈H₁₆, b.p. 123°/14 mm., and C₉H₁₈, b.p. 133.5°/12 mm.; slightly impure *picrates* of diheptyl-, m.p. 117—120°, di-octyl-, m.p. 110—110.5°, dinonyl-, m.p. 106—108°, didecyl-, m.p. 115°, and di-β-phenylethyl-, m.p. 153°, -amines. Similar decomp. of CH₂Ph·CH₂·NH₂ (III) affords CH₂Ph·CH₂·OH, 49.1, CH₂·CHPh, 4.8, (CH₂Ph·CH₂)₂N·NO, 14.1, unchanged (III) 5.2, and its hydrochloride, 9.4%. J. W. B.

Reaction of chloroamines with zinc alkyls. G. H. COLEMAN, H. P. ANDERSON, and J. L. HERMANSON (J. Amer. Chem. Soc., 1934, 56, 1381—1382). The nos. quoted after the following pairs of reactants are the yields of primary and *sec*.-amines, respectively, when reaction is carried out in Et₂O (the nos. in parentheses are the respective yields in light petroleum): NMeCl₂ + ZnEt₂, 78, 17 (44, 46); NEtCl₂ + ZnEt₂, 71, 17 (49, 42); NBu^aCl₂, 76, 18 (57, 43); dichloroisamylamine + ZnEt₂, 78, 16 (52, 41); NBu^aCl₂ + ZnPr^a, 61, 24. NBu^aCl and ZnEt₂ in Et₂O give 71% of *sec*.- and 1.5% of *tert*.-amine. NEt₂Cl and ZnEt₂ in light petroleum afford 70% of *sec*.- and 1.8% of *tert*.-amine. H. B.

Factors governing the instability of carbon to nitrogen linking. I. Instability of the carbon to nitrogen linking in substituted methylamines. M. S. KHARASCH and L. B. HOWARD (J. Amer. Chem. Soc., 1934, 56, 1370—1373).—NH₂Bu^a, CPhMe₂·NH₂ (?), and CPh₂·Me·NH₂ (?) are unaffected by 0.05*N*-HCl at 100° for 50—100 hr.; CPh₂·NH₂ (I) is hydrolysed to the extent of 18% after 15 min. and 50% after 90 min. (I) is unaffected by heating in at 150° (sealed tube) for 24 hr. or at 250° for 1. r. Similar hydrolysis of 2 : 1-OH·C₁₀H₆·CHR·NH₂ (o, C₁₀H₇·OH, R·CHO, and NH₄Cl) occurs with increasing ease when R is CH₂Ph·CH₂, Ph, *p*- to *y*, anisyl (free amine not isolable). CH₂Ph·CH₂·CHO, and EtOH·NH₃ give the γ-phenyl-propylidene derivative (II), m.p. 103 (lit.), of 2-hydroxy-α-naphthyl-β-phenylethyl^{me} *y* crystals).

amine (III), m.p. 108° (hydrochloride, m.p. 205—210°); (III) is obtained from (II) by hydrolysis with 20% HCl. The *p*-methylbenzylidene derivative, m.p. 149°, of *p*-tolyl-2-hydroxy- α -naphthylmethylamine, m.p. 109.5° [hydrochloride, m.p. 195—220° (decomp.)], is similarly prepared using *p*-C₆H₄Me·CHO. Anisyl-2-hydroxy- α -naphthylmethylamine is not obtained by hydrolysis (20% HCl) of its anisylidene derivative, m.p. 181°; *p*-OMe·C₆H₄·CHO, β -C₁₀H₇·OH, NH₄Cl, and anisylidenediphenyl ether, m.p. 206°, are formed. The stability of the above amine hydrochlorides towards 20% HCl is attributed to (i) their insolubility and (ii) decrease in electronegativity of the NH₂ on conversion into NH₄Cl. H. B.

Laboratory method for the preparation of unsymmetrical β -diethylaminoethylamine. W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 401—402).—A modification of the method of Ristenpart (A., 1897, i, 46). Condensation of β -bromoethylphthalimide and NHEt₂ in boiling PhMe for 12 hr. followed by hydrolysis of the product with 20% HCl and extraction of the amine with Pr^oOH leads to β -diethylaminoethylamine in 61% yield. A. E. O.

Preparation of diaminobutanes. III. $\beta\gamma$ -Diaminobutane. E. STRACK and H. SCHWANEBERG (Ber., 1934, 67, [B], 1006—1011; cf. this vol., 283).— $\beta\gamma$ -Diaminobutane [*r* (I) : meso (II) = 4 : 1] is obtained in 92% yield by catalytic reduction of dimethylglyoxime (Pd) at room temp. in very dil. solution in MeOH. (I) is resolved into its optical isomerides as the H tartrate from EtOH, the resolution being completed by pptn. of the hydrochlorides from EtOH by Et₂O. The following derivatives are described: hydrochlorides, (II), decomp. 325°, (I), m.p. 253—254° after softening at 250°; (+), m.p. 238—239° after softening at 236°, [α]_D²⁰ -12.1° in H₂O, (-), m.p. 238—239° after softening at 236°, [α]_D²⁰ +12.1° in H₂O; sulphates, (II), +1.5H₂O, m.p. > 320°, (I), m.p. > 320°; platinichlorides, (I), (II), (+), (-), decomp. about 300°; aurichlorides, (II), decomp. 239—240° after softening at 234°, (I) + 2H₂O, decomp. 239—240° after softening at about 230°, (+) and (-) + 2H₂O, decomp. 245—246° after softening at 235°; compounds, C₄H₁₂N₂(HgCl₂)₂, (II), m.p. 152°, (I), m.p. 179° after softening at 172° and darkening at 176°, (+) and (-), m.p. 179°; C₄H₁₂N₂HgCl₂ (II), m.p. 166°, (I), m.p. 188°, (+) and (-), m.p. 195°, all dependent greatly on mode of heating; C₄H₁₂N₂(HgCl₂)₆, (II), (I), (+), and (-), m.p. about 190° (decomp.) after softening at 170—180°; picrates, (II), decomp. 275° after darkening at 265°, (I) + 2H₂O, decomp. 250° after softening at 247°, (+) and (-), + 2H₂O, decomp. 248°; picrolonates, (II), (I), (+), and (-) + H₂O, all decomp. 265—270°; Bz₂ derivatives, (II), m.p. 298°, (I), m.p. 251°, (+) and (-), m.p. 214°; di-*m*-nitrobenzoyl compounds, (II), m.p. 325°, (I), m.p. 245°, (+) and (-), m.p. 272°. H. W.

Synthesis of monoacyl derivatives of aliphatic diamines. J. VON BRAUN and W. PINKERNELLE [with, in part, H. HARTMANN] (Ber., 1934, 67, [B], 1056—1060).— ϵ -Iodoamylbenzamide is converted by AgNO₃ in Et₂O into α -nitro- ϵ -benzamidopentane (I),

m.p. 76° (yield 45%), and a non-cryst., non-distillable material transformed by boiling MeOH into ϵ -benzamido-*n*-amyl alcohol in small yield. (I) is readily reduced by SnCl₂ to α -amino- ϵ -benzamidopentane, b.p. 180—185°/0.1 mm. (hydrochloride, m.p. 145°; picrate, m.p. 163°), which is not thus readily isolated and is best obtained by treatment of (I) with H₂ (Pd in MeOH). $\alpha\epsilon$ -Dibenzamido-*n*-pentane, m.p. 132°, is transformed by warm Ac₂O into α -acetamido- ϵ -benzamido-*n*-pentane, m.p. 119°. δ -Iodobutylbenzamide from δ -chlorobutylbenzamide (improved prep.) is converted by successive treatment with AgNO₃, boiling MeOH, and H₂ (Pd-MeOH) into δ -benzamidobutyl alcohol, b.p. 180—200°/0.3 mm. (slight decomp.), m.p. 71—73°, and α -amino- δ -benzamidobutane, b.p. 176—178°/0.1 mm. (hydrochloride, m.p. 167°; platinichloride, decomp. 213°; picrate, m.p. 168—170°). α -Acetamido- δ -benzamidobutane has m.p. 143°. γ -Nitropropylphthalimide (III), b.p. 184—185°/0.1 mm., is converted by NaOH into *o*-carboxybenz- γ -nitropropylamide, m.p. 119°, converted by Br and alkali into *o*-carboxybenz- $\gamma\gamma$ -dibromo- γ -nitropropylamide, m.p. 147°. (III) is not satisfactorily reduced by Sn and HCl, but is converted by H₂ into crude phthalyltrimethylenediamine [hydrochloride, m.p. 171°; platinichloride, m.p. 239° (decomp.); aurichloride, m.p. 294—296°; Ac derivative, m.p. 256°]. H. W.

Methylcholines and analogous substances. I. R. HUNT. II. R. R. RENSHAW and F. I. LAWRENCE (J. Pharm. Exp. Ther., 1934, 51, 237—255, 255—262).—I. Earlier work on choline esters is discussed (cf. A., 1929, 349, 468). Some claims of Simonart (A., 1932, 1284) are refuted.

II. That Menge's alleged "acetyl- α -methylcholine" [actually synthesised by Karrer (A., 1922, i, 813)] is acetyl- β -methylcholine is confirmed (A., 1912, i, 949; 1925, i, 1502; 1932, 257). The β -derivative, m.p. 148—149° (corr.), is prepared by a modification of Menge's method or by treating [CH₂]₃O (1 mol.) with AcBr (1 mol.) at low temp. to give α -bromo- β -acetoxypropane, which is condensed with NMe₃ at 45—50° under pressure, the cryst. product being acetylated and fractionally recrystallised from COMe₂. F. O. H.

Reactions of tri(hydroxyethyl)amine. E. JAFFE (L'Ind. Chimica, 1934, 9, 750—752).—Reactions with H₃PO₄, phosphates, molybdates, vanadates, Hg⁺+I, H₃BO₃, and Fe⁺⁺⁺ are described (cf. A., 1933, 246). T. H. P.

Reactions of ethylurethane. L. EKKERT (Pharm. Zentr., 1934, 75, 406—407).—Colour reactions with PhN₂SO₃H, *m*-C₆H₄(OH)₂-H₂SO₄, *m*-C₆H₄(NO₂)₂-NaOH, and MeCHO-H₂SO₄ and Jacquemin's and Schuster's reactions are described. E. H. S.

Alkaline hydrolysis of glycine and alanine anhydrides.—See this vol., 848.

Marasmin. E. SPATH and J. ZELLNER (Monatsh., 1934, 64, 123—124).—Marasmin (A., 1929, 108) is shown to be an impure specimen of (mainly) *l*- and some *dl*-leucine. H. B.

Long dipole. R. KUHN and F. GIRAL (Ber., 1934, 67, [B], 1130—1132).—*cyclo*Pentadecanoneisoxime is converted by fuming HCl at 150° into ξ -aminopentadecanoic acid semihydrochloride, $2\text{NH}_2\cdot[\text{CH}_2]_{14}\cdot\text{CO}_2\text{H}\cdot\text{HCl}$, m.p. 165—165.5°, transformed by repeated crystallisation from EtOH—conc. HCl into the *monohydrochloride* (I), m.p. 131—132°. (I), KOH, and Me_2SO_4 yield the corresponding *betaine* (II), $\text{C}_{18}\text{H}_{37}\text{O}_2\text{N}_2\cdot 3\text{H}_2\text{O}$, m.p. 259.5—260° [*platinichloride*, m.p. 214° (corr.); *aurichloride*, m.p. 120°]. The dipole moment of (II) is unusually high.

H. W.

Synthesis of phosphoric esters of hydroxy-amino-acids. II. *dl*-Serinephosphoric acid. P. A. LEVENE and A. SCHMULLER (J. Biol. Chem., 1934, 105, 547—562).—*dl*-Serine- β -phosphoric acid (I) is synthesised by action of POCl_3 on benzylidene-serine Ba salt in presence of MgO and hydrolysis of the product, $\text{C}_{20}\text{H}_{39}\text{O}_6\text{N}_2\text{P}_2\text{Mg}_3$, with 10% HCl. It is also obtained by action of H_3PO_4 and P_2O_5 on serine (II), and its anhydride is similarly obtained from serine anhydride. With EtPO_3 in CHCl_3 at the b.p. (II) gives a diphosphoric acid (isolated as Ba salt; cf. A., 1911, i, 705). With CH_2O and $\text{Ba}(\text{OH})_2$ (II) gives a salt $(\text{C}_4\text{H}_6\text{O}_3\text{N})_2\text{Ba}$, apparently of the *N*- $\text{CH}_2\cdot\text{OH}$ derivative, but the corresponding free acid in aq. solution does not give (I) with POCl_3 and MgO. The Me ester of (I) with CH_2O gives *substances*, $\text{C}_{11}\text{H}_{18}\text{O}_6\text{N}_2$, m.p. 137°, possibly $\text{CH}_2[\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{N}\cdot\text{CH}_2)\cdot\text{CO}_2\text{Me}]_2$, and b.p. 164—168/0.9 mm.; the latter may be an oxazole. α -Bromo- β -hydroxypropionic acid (III) is converted by P_2O_5 and H_3PO_4 into a *phosphate* (isolated as Ba salt, $\text{C}_6\text{H}_6\text{O}_{12}\text{Br}_2\text{P}_2\text{Ba}_3\cdot 2\text{H}_2\text{O}$), which, however, gives a complex mixture with NH_3 under various conditions. $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$ similarly gives a *phosphate* (Ba salt) with POCl_3 , but this could not be hydrolysed without loss of H_3PO_4 . The Me ester, b.p. 94—98°/9 mm. (MeOH; CH_2N_2 failed), of (III) is converted by NaN_3 in MeOH into *Me* β -azido- α -hydroxypropionate, b.p. 102—104°/9 mm., which is reduced by H_2 -PtO₂ to *isoserine*; apparently an ethylene oxide ring is formed intermediately and is opened by HN_3 in the same way as by NH_3 . The $(\text{CO}_2\cdot\text{CH}_2\cdot\text{Ph})$ derivative of (II), m.p. 94°, is described.

H. A. P.

Guanido-acids and guanidopeptides. J. KAPFHAMMER and H. MÜLLER (Z. Physiol. Chem., 1934, 225, 1—12).—Guanido-compounds of NH_2 -acids and peptides were prepared by an improved method using *O*-methylisocarbamide base (I) prepared from the hydrochloride in MeOH solution. The following derivatives were obtained. *l*-Cystine (with *S*-ethylisothiocarbamide) $\rightarrow \alpha$ -*diguanido*- β -*dithiodipropionic acid*, decomp. < 200°; *dl*-serine $\rightarrow \beta$ -*hydroxy*- α -*guanidopropionic acid*, decomp. about 200°; *dl*-phenylalanine $\rightarrow \beta$ -*phenyl*- α -*guanidopropionic acid*, decomp. < 200°; *l*-hydroxyproline \rightarrow *iminoamino*-*N*-*methylhydroxypyrrolidinecarboxylic acid* (+ H_2O) (II), m.p. 240° [with 2 mols. of Reinecke acid (III) \rightarrow salt, m.p. 160°]; *l*-proline \rightarrow *iminoamino*-*N*-*methylpyrrolidinecarboxylic acid* (+ H_2O) (IV), decomp. 236—242° [with 2 mols. of (III) \rightarrow salt, decomp. 198°]; *l*-tryptophan $\rightarrow \alpha$ -*guanido*- β -*indolylpropionic acid*, decomp. 225—230°; *d*-glutamic acid $\rightarrow \alpha$ -*guanido*-

glutaric acid, decomp. 155—160° [salt of (I), decomp. 150—160°]; glycyl-*d*-alanine \rightarrow *guanidoacetylalanyl*, decomp. 220—225°; *dl*-alanylglycine \rightarrow *guanido*-*dl*-*propionylglycine*, decomp. > 235; glycyl-*dl*-phenylalanine \rightarrow *guanidoacetyl*-*dl*-phenylalanine, decomp. 225—230°; glycyl-*l*-leucine \rightarrow *guanidoacetyl*-*l*-leucine, decomp. 215°. All the derivatives give the Ac₂ reaction, and all except (II) and (IV) the reaction with α - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ and NaOCl.

J. H. B.

Formamide. P. L. MAGILL (Ind. Eng. Chem., 1934, 26, 611—614).—Small-scale methods of prep. and properties of $\text{HCO}\cdot\text{NH}_2$ (I) are reviewed. A mechanism for the reaction between (I), NH_2Ph , and S is suggested. Glass and Al are the most satisfactory materials for the storage of (I). D. K. M.

Spontaneous resolution of *dl*-dilactyldiamide in aqueous solution. P. VIÈLES (Compt. rend., 1934, 198, 2102—2104).—Spontaneous evaporation of a saturated solution of *dl*-dilactyldiamide (A., 1932, 253) above 34—35.5° (transition temp.) affords crystals of the *d*- and *l*-forms, m.p. 208°, but below this temp. the racemate + $2\text{H}_2\text{O}$ separates. Separation is best effected by seeding a supersaturated solution, at 40°, with the *d*-form, which causes rapid crystallisation of this form, and subsequent seeding of the mother-liquor, which contains a large excess of the enantiomorph, with the *l*-form.

J. W. B.

Reaction between hydroferrocyanic acid and ethyl alcohol. F. HOLZL and J. KRAKORA (Monatsh., 1934, 64, 97—105).— $\text{H}_4\text{Fe}(\text{CN})_6$ (I) (the etherate (cf. von Baeyer and Villiger, A., 1902, i, 355) is formulated as the oxonium compound $[\text{Fe}(\text{CN})_6]\text{H}[\text{Et}\cdot\text{OH}]_3$ and abs. EtOH at 100° (sealed tube) for 15 hr. in absence of light give the complex $[(\text{CN})_2\cdot\text{Fe}(\text{OH})_2]_2\cdot(\text{CN})_2\cdot\text{Fe}(\text{OH})_2\cdot(\text{CN})_2\cdot\text{Fe}(\text{OH})_2\cdot(\text{CN})_2\cdot\text{Fe}(\text{OH})_2(\text{CNEt})_2\cdot(\text{CN})_2$, which is a very weak acid (titration curve given). The reaction between (I) and EtOH at about 98° is followed titrimetrically and potentiometrically; after 8—10 hr. a stable dibasic acid (or equiv. amounts of two monobasic acids) is produced.

H. B.

Cyanogen bromide and anhydrous hydrocyanic acid. K. H. SLOTTA (Ber., 1934, 67, [B], 1028—1030).—Precise directions are given for the laboratory prep. of CNBr (I) from Br, H_2O , and NaCN in 90% yield and of HCN (II) from H_2SO_4 , H_2O , FeSO_4 , and NaCN in almost quant. yield. (I) can easily be preserved unchanged if colourless, but rapidly polymerises if discoloured. (II) is stabilised by addition of a little conc. HCl.

H. W.

Organic compounds of mercury. IX. Reaction of mercuric chloride with ethyl diazoacetate. A. N. NESMEJANOV and G. S. POWCH (Ber., 1934, 67, [B], 971—974; cf. this vol., 313).— $\text{NH}_2\text{Me}\cdot\text{HCl}$, HgCl_2 , and *isoamyl* nitrite in MeOH do not react; addition of Cu powder induces diazotisation and decomp. of the diazonium compound with production of $\text{CH}_3\text{Cl}\cdot\text{HgCl}$, m.p. 130°, in small yield. $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ and HgCl_2 react vigorously with production of $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ and complex Hg compounds, from which the substance $\text{Hg}[\text{Cl}(\text{HgCl})\cdot\text{CO}_2\text{Et}]_2$ is

isolated by repeated dissolution in C_2H_5N and pptn. with $EtOH$. H. W.

Organic compounds of gold. III. Monoethylgold dibromide (monoethylgold dibromide). A. BURAWOY and C. S. GIBSON (J.C.S., 1934, 860—864).

—Diethylmonobromogold (I), $Et_2Au\begin{smallmatrix} \nearrow Br \\ \searrow Br \end{smallmatrix} AuEt_2$ (A., 1931, 1316), is best prepared by the action of $MgEtBr$ on pyridino-trichloro- or -tribromo-gold in $C_2H_5N-Et_2O$ in a freezing mixture. With Br in CCl_4 (I) affords monoethylgold dibromide (II) (monoethylauric dibromide of J.C.S., 1907, 91, 2064), probably $Br_2Au\begin{smallmatrix} \nearrow Br \\ \searrow Br \end{smallmatrix} AuEt_2$. Quant. decomp. of (II) — $2AuBr + 2EtBr$ occurs at room temp. and at 80—85°. Contrary to Kharasch *et al.* (A., 1931, 1043) (II) does not dissolve in C_6H_6 , but affords (I) and brominated C_6H_6 , and, in general, (II) is decomposed by readily brominated or oxidised solvents (Et_2O , $EtOH$, $COMe_2$, also ligrom and H_2O) to give (I) with pptn. of $AuBr$ and/or Au , bromination or oxidation of the solvent being due to the action of $AuBr_3$. Co-ordination compounds of the type $[Et_2BrAuQ]Br$ (Q =a diamine) could not be obtained, and with $[-CH_2NH_2]_2$ (II) gives only $[Au.en]_2Br_3$ and $[AuEt.en]Br$, the latter giving (I) on acidification.

J. W. B.

Thermal decomposition of cyclopentane and methylcyclopentane. B. A. KASANSKI and A. F. PLATE (Ber., 1934, 67, [B], 1023—1028).—The liquid products of the thermal decomp. of cyclopentane at 650° in SiO_2 tubes are mainly unchanged (I) containing a little cyclopentadiene. The gaseous products consist of C_2H_4 and $CHMe:CH_2$ (II) (together 73%), H_2 , saturated hydrocarbons (III), and traces of diolefines. Methylcyclopentane gives mainly (II) with some $CH_2:CMc_2$ (IV), and a higher % of (III) (? CH_4). The gases from cyclohexane contain much more H_2 and saturated hydrocarbons; the unsaturated portion is almost exclusively C_2H_4 containing very little (III) and about 6% of (IV).

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Biological and chemical nomenclature for the carotenoids. L. S. PALMER (Science, 1934, 79, 488—490).—A discussion, and a scheme of new generic and chemical names. L. S. T.

Mechanism of formation of aromatic hydrocarbons by pyrolysis. (a) E. N. HAGUE and R. V. WHEELER. (b) H. P. A. GROLL (Ind. Eng. Chem., 1934, 26, 697, 697—698).—(a) A reply to Groll (B., 1933, 691). The yield of aromatic compounds (I) in gals. per cu. ft. of olefines increases as the series is ascended. C_2H_4 , not C_3H_6 , is the essential intermediate in the formation of (I); a wt. conversion of 65% of C_2H_4 has been obtained at 750° against 42% of C_3H_6 and butylene (II). A mechanism for the formation of C_6H_6 is suggested. Hydroaromatic compounds, e.g., cyclohexene (III), are thought to be the forerunners of (I). The primary reaction of C_2H_4 is polymerisation to (II), which yields butadiene (IV) and C_4H_6 . (IV) may react with (1) C_2H_4 to give (III) and thence C_6H_6 , (2) C_3H_6 to give methylcyclohexenes and thence $PhMe$, (3) Δ^{α} -(II) to give $PhEt$ and thence $CHPh:CH_2$, (4) Δ^{β} -(II) to give dimethyl-

cyclohexenes and *o*-xylene. It is not confirmed that above 500° C_3H_6 prevails increasingly over (II) in the products obtained in the heat treatment of C_2H_4 .

(b) A reply to the above. C_2H_2 is always formed when C_3H_6 etc. is cracked in the vapour phase. The yields of (I) from the pyrolysis of C_nH_{2n} are better represented by Groll's than by Hague and Wheeler's equation. It is doubtful if (III) is an essential intermediate to (I), since it does not form (I) more readily than any other olefine. D. K. M.

Hydrogenation of aromatic hydrocarbons in solution at room temperature in presence of nickel-black. R. TRUFFAULT (Bull. Soc. chim., 1934, [v], 1, 206—223; cf. Brochet, A., 1914, i, 645).— C_6H_6 (I) is reduced to C_6H_{12} by H_2 and a Ni (II) or, better, a Ni-3% Cr (III) catalyst, at room temp. and pressure without solvent. Reduction is also effected in C_6H_{12} and C_6H_{14} solution, but not in $AcOH$, Ac_2O , or $EtOH$. Thiophen present in commercial C_6H_6 greatly retards reduction, but cryoscopic (I) is sufficiently pure. Except with very small amounts of (III) H_2 absorption is approx. \propto amount of (III), and almost independent of the amount of (I). The kinetics are complicated, the reaction order being <1 . Similar but slower reduction of $PhMe$ (IV) and of *m*- and *p*-xylene occurs. The velocity of reduction of (I) is trebled by a temp. rise from 20° to 50° (optimum), and that of (IV) is doubled by rise from 20° to 70—80° (optimum), above which temp. the high v.p. of the hydrocarbon rapidly decreases the velocity. The optimum reduction temp. for the prep. of (II) is 220—225°, for Ni-Mg (3—9%), 350° [less efficient than (II)], and for (III), 300° [1.5—2 times as efficient as (II)]. In C_6H_{12} or C_6H_{14} complete reduction of $C_{10}H_8$, fluorene, CH_2Ph_2 , and Ph_2 (8 hr. at 50°) with (III) is effected, but is slower than that of (I).

J. W. B.

Catalytic hydrogenation of aromatic hydrocarbons in solution in presence of nickel-black and phosphoric oxide. R. TRUFFAULT (Bull. Soc. chim., 1934, [v], 1, 391—406).—Interaction of C_6H_6 with H_2 in presence of Ni-black (I) and P_2O_5 at room temp. affords cyclohexane (II), together with phenylcyclohexane, which is further reduced to cyclohexylcyclohexane (III). $PhMe$ gives analogous results. P_2O_5 diminishes the initial activity of (I); the activity of the catalyst diminishes rapidly after the second day. 1:2-Dibromocyclohexane with Na isoamyloxide in isoamyl alcohol affords the diisoamyloxy-cyclohexane (IV), b.p. 206°/750 mm., and cyclohexadiene [also formed from (IV) with $KHSO_4$], which with P_2O_5 gives a resin (polymeride) which absorbs H_2 in presence of (I). cyclohexene (V) in (II) containing (I) and P_2O_5 with H_2 affords 2-cyclohexyl- Δ^1 -cyclohexene, b.p. 237° (cf. A., 1911, i, 473). (V) in boiling C_6H_6 containing P_2O_5 affords an oil, b.p. 106—107°/13 mm., hydrogenated to (III).

J. L. D.

Photochemical chlorination of chlorobenzene.—See this vol., 852.

Bromination of benzene. J. B. MENKE (Chem. Weekblad, 1934, 31, 344—345).—When Br , C_6H_6 , and $FeCl_3 \cdot 6H_2O$ are heated together, $PhBr$ is formed with evolution of HBr and HCl . $FeSO_4 \cdot 7H_2O$ is also

active, but with $\text{Fe}(\text{NO}_3)_3$ ($\text{H}_2\text{O}=30-40\%$) the reaction does not occur. Anhyd. $\text{Fe}_2(\text{SO}_4)_3$ is active, but cryst. K Fe^{III} sulphate is inert, although addition of K_2SO_4 to hydrated $\text{Fe}_2(\text{SO}_4)_3$ does not diminish the activity of the latter. Nitrates and nitrites inhibit the reaction. H. F. G.

Fluorination of organic substances with free fluorine. K. FREDENHAGEN and G. CADENBACH (Ber., 1934, 67, [B], 928—935).—The apparatus consists of a glass cylinder which can be rotated around a horizontal axis and externally cooled. F_2 , obtained by electrolysis of molten KHF_2 (modified method), is introduced through a Cu tube closed at the end and provided with numerous fine openings. The choice of experimental conditions is dictated by the v.d. of the material. If this is sufficiently high, fluorination is effected in the gas phase; dilution with 15 vols. of N_2 is essential to avoid risk of inflammation, and F does not enter the org. mol. If the Cu tube is greatly roughened and has many fine orifices the proportion of N_2 can be greatly reduced and addition or substitution occurs. A similar effect is not produced if glass is substituted for Cu. The action is enhanced by wrapping the tube in wire gauze, Cu, Ag, and Fe appearing equally effective. If the v.p. is not sufficiently high, the gas is allowed to play on the surface of the liquid. Rotation of the vessel, delivery of F_2 through a long tube, and initial dilution with N_2 prevent inflammation; subsequently the indifferent gas in the tube serves as diluent. Substances the m.p. of which is too high to permit safe manipulation may be dissolved in CCl_4 or AcOH . The fluorination of C_6H_6 , PhMe, C_{10}H_8 , $n\text{-C}_6\text{H}_{14}$, amylene, dipentene, palmitic acid, $\text{C}_5\text{H}_5\text{N}$, PhOH, cresol, thymol, menthol, coumarin, geraniol, paraffin oil, petroleum, ligroin, tar oil, linseed oil, and various ethereal oils is described as far as concerns the % of F in the products. H. W.

Migration of bromine during side-chain chlorination of bromotoluenes. F. ASINGER (Monatsh., 1934, 64, 153—160).—Chlorination of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{MeBr}$ gives crude products which analyse (Cl+Br) correctly for $\text{C}_6\text{H}_4\text{Br}\cdot\text{CH}_2\text{Cl}$ (I), but are mixtures of (I) and $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Br}$, since hydrolysis (aq. EtOH-KOH) affords Cl' and Br'. The following reactions probably occur: $\text{C}_6\text{H}_4\text{MeBr} + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_4\text{MeCl} + \text{ClBr} \rightarrow \text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Br} + \text{HCl}$. 3 : 5- $\text{C}_6\text{H}_3\text{MeBr}_2$ gives a similar mixture; the product obtained by crystallisation from EtOH in about 30% yield has m.p. 80° and contains 63% Br (indicating the presence of some 3 : 5- $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{CH}_2\text{Br}$). Similar results are obtained on dichlorination. Cl and Br in CHArCl_2 are determined by hydrolysis with conc. H_2SO_4 at $100-140^\circ$; HCl and HBr (+Br) are removed in N_2 or CO_2 and absorbed in dil. NaHSO_3 . H. B.

Nitration of chloro-*p*-xylene. H. WAHL (Compt. rend., 1934, 198, 2105—2107).—From the fraction, b.p. $170-175^\circ/15\text{ mm.}$, obtained from the products of nitration of chloro-*p*-xylene after isolation of 2-chloro-*p*-tolualdehyde (I) (this vol., 772), is obtained 2-chloro-5-nitro-*p*-tolualdehyde (II), m.p. 100° [oxime, m.p. 145° (corr.); phenylhydrazone, m.p. 228° (corr., decomp.); semicarbazone, m.p. 310° (corr., decomp.)], the constitution of which is proved by its

identity with the nitration product of (I), its oxidation (KMnO_4) to the corresponding benzoic acid, and its conversion by $\text{NaOH}\cdot\text{COMe}_2$ into 5 : 5'-dichloro-6 : 6'-dimethylindigotin. The mother-liquor from (II) affords a phenylhydrazone, m.p. 145° , of an isomeric aldehyde. The nitration products of *p*-xylene contain *p*-tolualdehyde and its 3- NO_2 -derivative.

J. W. B.

Volume effects of alkyl groups in aromatic compounds. III. Dinitration of 3-chloro- and 3-bromo-*p*-cymene. IV. Dinitration of 2-chloro-*p*-cymene. S. N. GANGULY and R. J. W. LE FEVRE (J.C.S., 1934, 848—852, 852—854).—III. Mononitration of 3-chloro- or 3-bromo-*p*-cymene gives the 6- NO_2 -derivative (Fileti *et al.*, A., 1889, 493), the constitution being confirmed by replacement of the halogen by piperidine (I). Dinitration (HNO_3 , *d* 1.5, at -5° , or HNO_3 , *d* 1.43, + $\text{H}_2\text{SO}_4 < 10^\circ$) gives the 2 : 6-(NO_2)₂-derivative (II), converted by (I) into 2 : 6-dinitro-3-piperidino-*p*-cymene (III), m.p. $123-124^\circ$ [identical with a specimen prepared by successive action of PCl_5 and (I) on 2 : 6-dinitrothymol]. The supposed isomeric (NO_2)₂-derivative, m.p. 80° (Cl) and 94° (Br) (*loc. cit.*), is (II) contaminated with the ketone (IV) resulting from oxidation of Pr^s to Ac. $m\text{-C}_6\text{H}_4\text{ClMe}$ with $\text{AcCl}\cdot\text{AlCl}_3$ gives 2-chloro-4-methylacetophenone [oxidised by $\text{KMnO}_4\text{-NaOH}$ to 3-chloro-4-acetylbenzoic acid, m.p. 228° , further oxidised to chloroterephthalic acid (III)], converted by HNO_3 (*d* 1.5) at -10° into its 3 : 5-(NO_2)₂-derivative (IV), m.p. $91-92^\circ$, which with (I) affords 3 : 5-dinitro-2-piperidino-4-methylacetophenone, m.p. $108-109^\circ$, which can also be isolated by the action of (I) on the crude dinitration product (II).

IV. Nitration of pure 2-chlorocymene (by the Sandmeyer reaction from 2-cymidine) with HNO_3 (*d* 1.5), or HNO_3 -oleum, $< 0^\circ$, gives 2-chloro-3 : 5-dinitrocymene [converted by (I) into 3 : 5-dinitro-2-piperidinocymene (A., 1933, 1153)], and no trace of the compound (V), m.p. $88-89^\circ$, obtained by Lubs *et al.* (A., 1920, i, 153). (V) may be (IV) resulting from the presence of some 3-chlorocymene in the sample previously used, or 3-chloro-2 : 6-dinitro-4-methylacetophenone, m.p. $97-98^\circ$ (3-piperidino-derivative, m.p. $113-114^\circ$), synthesised by nitration (HNO_3 , *d* 1.5, $< 0^\circ$) of 3-chloro-4-methylacetophenone (VI) (by the Sandmeyer reaction on the 3- NH_2 -compound). (VI) is oxidised by $\text{KMnO}_4\text{-NaOH}$ successively to 2-chloro-4-acetylbenzoic acid, m.p. 228° , and (III).

J. W. B.

Comparison of the activating effect of the sulphone and nitro-group. H. R. TODD and R. L. SHRINER (J. Amer. Chem. Soc., 1934, 56, 1382—1384).— $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SO}_2\text{Na}$ (the acids are prepared from the diazonium sulphates, SO_2 , and Cu-bronze) and $\text{EtOH}\cdot\text{MeI}$ give *o*-, m.p. 90° , *m*-, m.p. 106° , and *p*-, m.p. 96° , -chlorophenyl Me sulphones. The reactivity of Cl towards $\text{EtOH}\cdot\text{NaOEt}$ is $o > p > m$; the $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ show much greater activity ($p > o > m$). The NO_2 -group has a much greater activating effect than $\cdot\text{SO}_2\text{Me}$. The dipole moment ($\text{SO}_2 > \text{NO}_2$) is not an index of activating power.

H. B.

Stereochemical studies. I. Racemisation of optically active sulphinic esters. K. ZIEGLER and

A. WENZ (Annalen, 1934, 511, 109—120).—When freshly distilled (—)- β -octyl (I) and menthyl *p*-toluenesulphates are kept in a high vac., the rotations do not alter during several months. In presence of air or O_2 the rotation alters after a short time, acid formation occurs, and O_2 is absorbed; with absolutely dry O_2 , there is an induction period of about 100 hr. The rotations of mixtures of (—)- β -octanol (II) and (I) do not change over a long period in absence of air; addition of *p*- $C_6H_4Me\cdot SO_3H$ (III) causes a rapid alteration [the velocity depends on the concns. of (II) and (III)] at room temp. Addition of (III) to (I) causes a relatively slow change of rotation. The strong catalytic action of (II)+(III) is ascribed to ester interchange. The velocity of mutarotation of (I) (in $CHCl_3$) catalysed by (II)+(III) is similar to, but differs slightly (in the expected manner) from, that of Et *p*-toluenesulphate (IV) catalysed by (III) + EtOH. Comparison of the rate of "autoracemisation" of (IV) with the catalytic racemisation [(II)+(III)] indicates that the former is explained (cf. Phillips, A., 1926, 159) by the formation of decomp. products (assuming that ester interchange occurs simultaneously). Indications of a true autoracemisation of toluenesulphinic esters at room temp. are not observed. H. B.

Convenient synthesis of durene and penta-methylbenzene from crude xylene. J. VON BRAUN and J. NEILLES (Ber., 1934, 67, [B], 1094—1099; cf. A., 1933, 1283).—When heated with conc. HCl and CH_2O at 60—70° in a current of HCl, *p*-xylene affords 2-chloromethyl-, b.p. 100—103°/12 mm. (oxidised by HNO_3 to trimellitic acid), *di*-2 : 5-chloromethyl- (I), m.p. 133° (whence pyromellitic acid), and *di*-2 : 3-chloromethyl-, m.p. 68—70° (whence mellophanic acid), -xylene. (I) is transformed by KOAc in AcOH into *di*-2 : 5-acetoxymethyl-, m.p. 65°, which affords *di*-2 : 5-hydroxymethyl-, m.p. 160°, and thence *di*-2 : 5-bromomethyl-, m.p. 160°, -*p*-xylene. Similarly, *m*-xylene gives 4-chloromethyl-, b.p. 100—105°/14 mm. (oxidised to trimellitic acid), *di*-4 : 6-chloromethyl- (II), m.p. 99° (whence pyromellitic acid), and *di*-2 : 4-chloromethyl-, m.p. 58—60° (whence mellophanic acid), -*m*-xylene. (II) gives non-cryst. 6-acetoxymethyl-, hydrolysed to *di*-4 : 6-hydroxymethyl-, m.p. 151°, whence *di*-4 : 6-bromomethyl-, m.p. 111°, -*m*-xylene. *o*-Xylene is converted into a mixture of 3- and 4-chloromethyl-, and *di*-4 : 5-chloromethyl- (III), m.p. 105—106°, -*o*-xylene. (III) gives non-cryst. *di*-4 : 5-acetoxymethyl-, *di*-4 : 5-hydroxymethyl-, m.p. 99°, and *di*-5 : 5-bromomethyl-, m.p. 120°, -*o*-xylene. Treatment of crude xylene (IV) with CH_2O and conc. HCl (2 : 5 by wt.) at 70° for 7 hr. and then with 2 parts of CH_2O and HCl for 12 hr., followed by reduction and distillation, gives a fraction from which, after crystallisation from EtOH, durene, m.p. 80°, is obtained in 45% yield. Similar treatment of (IV) followed by reduction and re-treatment gives a trimethyldi(chloromethyl)benzene, m.p. 121, converted by 2*N*-NaOH into C_6HMe_5 , m.p. 47—49. H. W.

Mechanism of chemical reactions. V. Importance of molecular compounds in catalytic hydrogenations. K. KINDLER, E. BRANDT, and

E. GEHLHAAR (Annalen, 1934, 511, 209—212).—Catalytic hydrogenation (Pd sponge) of $CHPh\cdot CH\cdot NO_2$ occurs rapidly in $AcOH-H_2SO_4$ yielding, $CH_2Ph\cdot CH_2\cdot NH_2$ (I) in 84% yield. In absence of H_2SO_4 H_2 is absorbed much more slowly and (I) is produced only in traces. The formation of an intermediate product $CHPh\cdot CH\cdot N(O)\cdot O\cdots H_2SO_4$ is postulated. The reduction of Me phenylacetoxycetate to $CH_2Ph\cdot CO_2Me$ is similarly facilitated greatly by H_2SO_4 . H. W.

Highly polymerised compounds. XCIII. Rupture of the thread molecules of polystyrene. XCIV. An insoluble polystyrene. H. STAUBINGER and W. HEUER (Ber., 1934, 67, [B], 1159—1164, 1164—1172).—XCIII. Prolonged trituration of polystyrenes, mol. wt. 470,000 and 163,000, respectively, and periodic determination of $\eta_{sp.}$ of the products in tetrahydronaphthalene (I) shows that the process is accompanied by progressive degradation of the mol. to a mean mol. wt. of about 103,000, after which change ceases. It therefore appears probable that mechanical accompanies oxidative degradation during the grinding of caoutchouc. Similar degradation is observed when polystyrenes of mol. wt. 610,000 and 440,000 dissolved in (I) are forced repeatedly through fine Pb orifices; the change proceeds to mean mol. wt. about 350,000. A polymeride, mol. wt. 300,000, is stable under these conditions. Similar changes of viscosity have been observed in solutions of serum.

XCIV. A technical, monomeric styrene passed at 60—100° into a polystyrene glass, insol. in all media and swelling to a limited extent according to the nature of the medium with which it was brought into contact (this was usually accompanied by dissolution of small amounts of material of mean mol. wt. 60,000). The unusual behaviour is traced to the presence of very small amounts of *p*-divinylbenzene (I). Polymerised products containing 1% of (I) are insol. and swell little; with > 0.01% of (I) the swelling properties are very marked, but the material contains considerable amounts of sol. polymerides. Polymerides with unlimited ability to swell have therefore thread mols., whereas the completely insol. materials which scarcely swell have 3-dimensional mols. Materials with limited ability to swell are composed of thread mols. united at a few places to 3-dimensional mols. The effect of solvent on the swelling power of insol. polystyrenes is examined. Solvents with comparatively little action (EtOAc, BuOAc, cyclohexane) are considered to cause solvation only of the Ph group, whereas "good solvents" (C_6H_6 , CS_2 , $CHCl_3$) also cause solvation of the paraffin chain. This conception is strengthened by the observed parallelism between swelling of the insol. polystyrenes in different media, viscosity of soluble polystyrenes in the same media, and precipitability of such polystyrenes from solution by MeOH. Good solvents which cause marked solvation also cause marked swelling and high viscosity. The conversion of sol. into insol. caoutchouc by traces of O_2 or light is attributed to the union of thread mols. by O-bridges or direct C-C unions. Similar processes occur during vulcanisation by S or S_2Cl_2 . The irregularities observed in the polymerisation of butadiene to

butadiene-caoutchouc are ascribed to the possibility of union in the $\alpha\beta$ - as well as in the $\alpha\delta$ -positions.

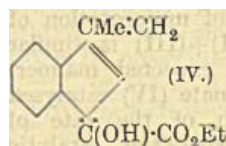
H. W.

Preparation and properties of substituted phenylacetylenes and mercury di(phenylacetylenyls). M. M. OTTO (J. Amer. Chem. Soc., 1934, 56, 1393—1394).—*p*-Methyl-, b.p. 65—67°/18 mm., *p*-ethyl-, b.p. 72—74°/16 mm. (*Hg* derivative, m.p. 142—143°), *p*-isopropyl-, b.p. 79—81°/12 mm. (*Hg* derivative, m.p. 109—110°), *p*-chloro-, m.p. 43·5—44° (*Hg* derivative, m.p. 221—222°), *p*-bromo-, m.p. 63·5—63·7° (*Hg* derivative, m.p. 256—257°), and *o*-, b.p. 92—93°/20 mm. (*Hg* derivative, m.p. 184—185°), and *m*-bromo-, b.p. 85—86°/16 mm. (*Hg* derivative, m.p. 143—144°), -phenylacetylenes are prepared thus: $\text{COMeAr} + \text{PCl}_5 \rightarrow \text{CArCl} \cdot \text{CH}_2 \rightarrow \text{CAr} \cdot \text{CH}$. *o*-, b.p. 71°/18 mm. (*Hg* derivative, m.p. 213—214°), and *m*-Chlorophenylacetylene, b.p. 64—65°/12 mm. (*Hg* derivative, m.p. 138—139°), are prepared from *o*-, m.p. 131—132°, and *m*-, m.p. 140—141°, -chlorophenylpropionic acid, respectively. *o*- and *m*-Bromophenylpropionic acids have m.p. 118—119° and 135—136°, respectively. H. B.

Organo-alkali compounds. XIV. Lithium phenyl and fulvenes. K. ZIEGLER and W. SCHAFER (Annalen, 1934, 511, 101—109).—Dimethylfulvene and LiPh in Et_2O give 1-lithio-1-phenylisopropylcyclopentadiene (the hydrolysis product resinifies easily), addition occurring across the extracyclic double linking. 1-isoPropylideneindene and LiPh afford 1-lithio-1-phenylisopropylindene, which with MeI gives a hydrocarbon, $\text{C}_{19}\text{H}_{20}$, b.p. 116—117°/0·3 mm., and with $\text{OMe} \cdot \text{CH}_2\text{Cl}$ affords an ether, $\text{C}_{26}\text{H}_{22}\text{O}$ [1 (or 3)-phenylisopropyl-1-methoxymethylindene], b.p. 155—158°/0·66 mm. 1-Lithio-1-benzhydrylindene (?), from benzylideneindene and LiPh, is hydrolysed (H_2O) to 3-benzhydrylindene (Courtot, A., 1915, i, 392), whilst 9-lithio-9-benzhydrylfluorene (from benzylidenefluorene) is hydrolysed (H_2O) to 9-benzhydrylfluorene. Di(diphenylene)ethylene and $\text{Et}_2\text{O} \cdot \text{LiPh}$ give α -lithio- β -phenyl- $\alpha\beta$ -di(diphenylene)-ethane (I), hydrolysed (H_2O) to α -phenyl- $\alpha\beta$ -di(diphenylene)ethane, m.p. 275° (sealed tube in N_2) (previous softening), which decomposes when distilled in a vac. to 9-phenylfluorene. α -Phenyl- $\alpha\beta$ -di(diphenylene)propane, m.p. 161°, is prepared from (I) and MeI. (I) and I in N_2 give the free radical β -phenyl- $\alpha\beta$ -di(diphenylene)ethyl, bluish-black, which dissolves in C_6H_6 to a KMnO_4 -coloured solution (becoming reddish-brown in air). H. B.

Tautomerism of methylated fulvenes. K. ZIEGLER and F. CROSSMANN (Annalen, 1934, 511, 89—101).—9-Ethylidenefluorene, PhCHO , and KOEt in $\text{Et}_2\text{O} \cdot \text{EtOH}$ give 9-cinnamylidenefluorene; 9-*p*-methoxycinnamylidenefluorene, m.p. 142—143° (cf. Kliegl *et al.*, A., 1930, 1031), is similarly obtained using *p*- $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ (I). 3-Methyl-1-isopropylideneindene, b.p. 144—148°/11 mm., m.p. 48—49° (from 3-methylindene, COMe_2 , and 27—28% $\text{MeOH} \cdot \text{KOH}$), and (I) similarly afford 1- α -methyl-*p*-methoxycinnamylidene-3-methylindene, m.p. 152·5°; 3-phenyl-1-isopropylideneindene, m.p. 99·5—100°, gives 3-phenyl-1- α -methyl-*p*-methoxycinnamylideneindene, m.p. 150—152°. Cryst. condensation products could not

be obtained from 1-isopropylideneindene (II), b. dimethylfulvene (III), (I), and $\text{Et}_2\text{O} \cdot \text{EtOH} \cdot \text{KO}$ afford 2(or 3)-anisylidene-1-isopropenylcyclopentadiene, m.p. 122°, reduced (H_2 , $\text{Pd} \cdot \text{BaSO}_4$, EtOH) to 2-3-*p*-methoxybenzyl-1-isopropylcyclopentane, b.p. 175°/13 mm., which is demethylated ($\text{HI} \cdot \text{AcOH}$) to 2(or 3)-*p*-hydroxybenzyl-1-isopropylcyclopentane, b.p. 135—137°/0·15 mm., m.p. 59—60°. (III) thus reacts with (I) as an isopropenylcyclopentadiene; this is established by the synthesis of β -anisylethylmethylfulvene (from cyclopentadiene,



$\text{p} \cdot \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, and $\text{EtOH} \cdot \text{NaOE}$ which is reduced to the *Me ether*, b.p. 178—179°/mm., of γ -cyclopentyl- α -anisylbutane, b.p. 137°/0·075 mm. $\text{Et}_2\text{C}_2\text{O}$, (I) and $\text{Et}_2\text{O} \cdot \text{EtOH} \cdot \text{KOEt}$ the unstable isopropenyl es (IV), reduced (as above) to 3-isopropyl- α -hydrindylglycolla b.p. 145—147°/0·3—0·4 mm. m.p. 66—67°, also obtained by reduction of the ester, m.p. 110—111°, of 1-oxalo-3-isopropylindene [prepared from isopropylindene (Thiele and Mer A., 1918, i, 484) and $\text{Et}_2\text{C}_2\text{O}_4$ by Thiele's method (A., 1901, i, 76)]. Alternative structures are suggested for the compound obtained by Thiele and Balho (A., 1906, i, 639) from (III) and COMe_2 . H. B.

Isomerisation of decahydronaphthalene. V. N. CHADSHINOV (Ukrain. Chem. J., 1933, 333—346).—Tetrahydronaphthalene (I) is converted into *trans*-decahydronaphthalene (II) at 430—440 atm. H_2 , in presence of MoS_3 catalyst, which also catalyses further transformation of (II) into methylhydride and dimethyldicyclooctane, to an extent increasing with rise in temp. Hydrogenation of (I) does not take place with initial H_2 pressures of 70 atm. R. T.

Action of magnesium on dibromonaphthalenes. J. SALKIND [with V. SERGEEV, L. LEVIN, and A. EGOROV] (Ber., 1934, 67, [B], 1031—1036).—Decomp. of the product from Mg and 2- $\text{C}_{10}\text{H}_7\text{Br}$ in presence of air with H_2O yields β - $\text{C}_{10}\text{H}_7 \cdot \text{OH}$ and some C_{10}H_8 ; β - $\text{C}_{10}\text{H}_7 \cdot \text{CO}_2\text{H}$ cannot be obtained from by CO_2 . In H_2 , a considerably increased yield of C_{10}H_8 and moderately good yield of β - $\text{C}_{10}\text{H}_7 \cdot \text{CO}_2$ result. Air has no appreciable influence in the prep. of 1- $\text{C}_{10}\text{H}_7 \cdot \text{MgBr}$. 1:4- $\text{C}_{10}\text{H}_8\text{Br}_2$ (I) and 1:2 (1:2) react readily initially, then slowly until 80% of the Mg has entered into change. The product is converted by H_2O into C_{10}H_8 (35—50%), 1- $\text{C}_{10}\text{H}_7 \cdot \text{H}$ (31—25%), and resinous products with unchanged (I). The product derived from (I) and Mg (1:1) is converted by CO_2 into 4-bromo- α -naphthoic acid (II), m.p. 220° (77%), and C_{10}H_8 (9%); 1- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ (III) could not be isolated. The product from (I) and Mg (1:2) and CO_2 contains (50%), but not (III). 1:5- $\text{C}_{10}\text{H}_8\text{Br}_2$ (IV) reacts with 93·5% of Mg (ratio 1:2), forms very small amounts of condensation products, and after treatment with CO_2 gives 1:5- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ (V) in almost theoretical yield. The product from (IV) and (1:1) when treated with CO_2 affords unchanged (IV), much (V), and little 5-bromo- α -naphthoic acid. 1:2- $\text{C}_{10}\text{H}_8\text{Br}_2$ (VI) reacts with difficulty, but ultimately

ately 75.5% of the Mg enters into change. Mainly resinous condensation products result, which with H_2O yield C_{10}H_8 and a little $1\text{-C}_{10}\text{H}_7\text{-Br}$ and with CO_2 give traces of $1:2\text{-C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$, a little C_{10}H_8 and $1\text{-C}_{10}\text{H}_7\text{Br}$. As in (VI), the $\beta\text{-Br}$ in $1:6\text{-}$ and $1:7\text{-C}_{10}\text{H}_6\text{Br}_2$ appears the more reactive. H. W.

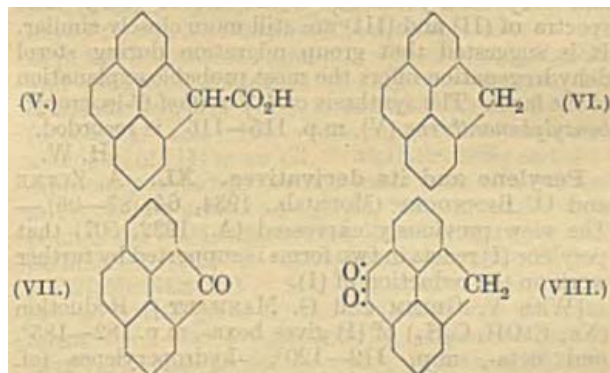
Sensitiveness of aromatic nitro-compounds to light. III and IV. *peri*-Derivatives of 1-nitronaphthalene. R. E. STEIGER (Helv. Chim. Acta, 1934, 17, 701—703, 794—803).—III. Mainly a historical résumé.

IV. The following 1-nitronaphthalene-8-derivatives have been prepared: -sulphonyl chloride, decomp. 167.5° (corr.); -sulphonamide, m.p. $190.5\text{—}191.5^\circ$ (corr.); -sulphonmethylamide, m.p. $195.5\text{—}196^\circ$ (corr.); -sulphondimethylamide, m.p. $151.5\text{—}152.5^\circ$ (corr.); -sulphonethylamide, m.p. $127.5\text{—}128.5^\circ$ (corr.); -sulphondiethylamide, m.p. $115\text{—}116^\circ$ (corr.); -sulphonanilide, m.p. $178.0\text{—}178.5^\circ$ (corr.); -sulphonmethylanilide, m.p. $177.5\text{—}178.0^\circ$ (corr.); -sulphonethylanilide, m.p. $170\text{—}171^\circ$ (corr.). Me, m.p. $124\text{—}125^\circ$ (corr.), Et, m.p. $123.5\text{—}124^\circ$ (corr.) after softening at 123° , Ph, m.p. $132.5\text{—}133.5^\circ$ (corr.), and NH_3Ph , decomp. $226\text{—}229^\circ$ (corr.) after darkening at 221° (corr.), 1-nitronaphthalene-8-sulphonate are described. H. W.

Fluoranthene and its derivatives. V. Substitution relationships of 1-phenylnaphthalene. J. VON BRAUN and E. ANTON [with G. MANZ] (Ber., 1934, 67, [B], 1051—1056; cf. A., 1932, 847).—1- $\text{C}_{10}\text{H}_7\text{Ph}$ (I), b.p. $187\text{—}189/12$ mm., is smoothly obtained by heating 1-phenyldihydronaphthalene with S. The products derived from treatment with Br obstinately retain halogen, whilst purely thermal dehydrogenation is accompanied by isomerisation to the 2-derivative. The position of NO_2 in 4-nitrophenylnaphthalene is confirmed by reduction of the NH_2 -compound (II) obtained therefrom ($\text{Na} + \text{C}_5\text{H}_{11}\text{OH}$) to 4-amino-1-phenyl-5:6:7:8-tetrahydronaphthalene, b.p. $180\text{—}185/0.5$ mm. (hydrochloride, decomp. about 235° ; Ac derivative, m.p. 198°), which can be diazotised. (II) is diazotised with difficulty and is more readily converted into 4-hydroxy-1-phenylnaphthalene (III), m.p. 140° , by treatment with 0.1N-HCl at 210° . (I) is scarcely affected by conc. H_2SO_4 at 100° , but is transformed by acid containing 20% of SO_3 at 50° into 1-phenylnaphthalene-4-sulphonic acid (IV), m.p. 167° (Na salt; corresponding anilide, m.p. 167°), which is almost the sole product of the action. Fusion of (IV) with KOH at $260\text{—}300^\circ$ leads to (III). (I) is converted by BzCl and AlCl_3 in CS_2 at $15\text{—}20^\circ$ almost exclusively into 4-benzoyl-1-phenylnaphthalene, b.p. $225\text{—}228/0.3$ mm. (oxime, m.p. 177°), which passes when heated with NaOH-CaO at 270° into a little C_6H_6 , much BzOH , and a small amount of 1-phenylnaphthalene-4-carboxylic acid (V), m.p. 172° . (V) is obtained synthetically by converting 4:1- $\text{C}_{10}\text{H}_6\text{BrPh}$ by CuCN at 270° into 4-cyano-1-phenylnaphthalene, m.p. $114\text{—}115^\circ$, which is hydrolysed by conc. HCl at 140° . 1-Keto-1:2:3:4-tetrahydronaphthalene (VI) and $p\text{-C}_6\text{H}_4\text{Me-MgBr}$ yield $p\text{-tolylidihydronaphthalene}$, b.p. $185\text{—}188/14$ mm., m.p. 48° , dehydrogenated by S at 250° , but not

smoothly by Br, to 1- $p\text{-tolyl}$ naphthalene, b.p. $192\text{—}195/14$ mm., m.p. 53° , which affords $o\text{-4'}$ -toluoylbenzoic acid, m.p. 118° , when oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ ($=30$) in AcOH . (VI) and $p\text{-C}_6\text{H}_4\text{Br-MgBr}$ lead to 1- $p\text{-bromophenyl}$ dihydronaphthalene, b.p. $215/14$ mm., m.p. 98° , incompletely dehydrogenated by S and converted by Br in CS_2 into the dibromide $\text{C}_{16}\text{H}_{12}\text{Br}_2$, b.p. $220/14$ mm., m.p. 104° , which does not lose HBr completely when heated with $\text{KOH-EtOH-H}_2\text{O}$. The product is transformed by CuCN at 270° in N_2 into 1-phenylnaphthalene-4'-nitrile, b.p. $230\text{—}240/14$ mm., m.p. $73\text{—}77^\circ$, whence 1-phenylnaphthalene-4'-carboxylic acid, m.p. 229° . The double attachment of the C_6H_6 in fluoranthene appears to impart to it an enhanced reactivity in comparison with (I). H. W.

New hydrocarbons from the anthracene oil of coal tar. O. KRUBER (Ber., 1934, 67, [B], 1000—1005).—Technical anthracene residues, b.p. $345\text{—}375^\circ$, after removal of 6% of acid and 10% of basic components are distilled under diminished pressure. The distillates deposit 20—25% of carbazole and its homologues. The fraction (I), b.p. $361\text{—}370^\circ$, thus prepared when treated with Na at 135° and subsequently with CO_2 affords 1:2:3:4-tetrahydrofluoranthene-1-carboxylic acid (II), m.p. $188\text{—}189^\circ$ (Et ester, m.p. 104° , b.p. $224\text{—}226/15$ mm.), which passes when superheated into 1:2:3:4-tetrahydrofluoranthene (III). (II) could not be obtained from fluoranthene (IV), Na, and CO_2 in presence of $\text{C}_{10}\text{H}_7\text{Me}$, or Ph_2 . Passage of (I) over heated PbO , leads to (IV). The prep. of (II) from (III) by means of MgEtBr followed by CO_2 in boiling NPhMe , is described. Similar treatment of a fraction, b.p. $350\text{—}360^\circ$, leads to phenanthrylene-4:5-acetic acid (V), m.p. 253° (decomp.), which passes above its

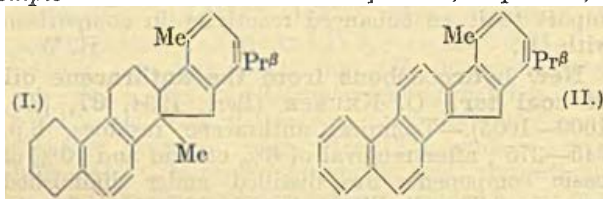


m.p. into phenanthrylene-4:5-methane (VI), m.p. 116° [picrate, m.p. 166° ; condensation product with $(\text{COEt})_2$, m.p. $91\text{—}92^\circ$; CHPh derivative, m.p. 108°]. (VI) is oxidised by $\text{Na}_2\text{Cr}_2\text{O}_7$ in AcOH to phenanthrylene-4:5-ketone (VII), m.p. 170° , or, under somewhat modified conditions, to 9:10-diketophenanthrylene-4:5-methane (VIII), m.p. $240\text{—}241^\circ$ [converted by $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ into the compound $\text{C}_{21}\text{H}_{12}\text{N}_2$, m.p. 261°]. Further oxidation of (VII) leads to 9:10-diketophenanthrylene-4:5-ketone, m.p. $286\text{—}287^\circ$ (azine, $\text{C}_{21}\text{H}_{10}\text{ON}_2$, m.p. 328°), and fluorenone-4:5-dicarboxylic acid (IX), m.p. 285° (decomp.) [anhydride, m.p. 253°]. (IX) is transformed when heated with CaO into fluorenone. When fused with

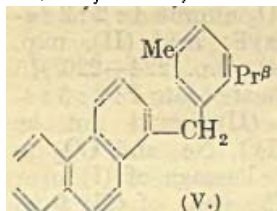
KOH (VII) affords *phenanthrene-4-carboxylic acid*, m.p. 170—171°, transformed by CaO into phenanthrene.

H. W.

Pentacyclic aromatic hydrocarbon from cholesterol. J. W. COOK, C. L. HEWETT, W. V. MAYNEORD, and (Miss) E. ROE (Chem. and Ind., 1934, 569—570).—The Grignard compound from β -5-tetrahydronaphthylethyl chloride condenses with 2 : 7-dimethyl-4-isopropylhydrindone to give 4-methyl-3- β -5'-tetrahydronaphthylethyl-7-isopropylindene, cyclised in almost theoretical yield to the hydrocarbon (I), which is dehydrogenated with loss of Me to 5-methyl-8-isopropyl-2' : 1'-naphtha-1 : 2-fluorene (II), m.p. 198° (complex with 2 : 7-dinitroanthraquinone, m.p. 261°).



(II) is not identical with Diels' hydrocarbon (III) from cholesterol. It is readily oxidised to a golden-orange ketone, which, like that derived from (III), gives an



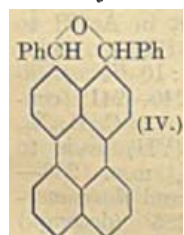
intense purple solution in conc. H_2SO_4 . A similar colour is given by 2' : 1'-naphtha-1 : 2-fluorenone, m.p. 208°, the first product of the oxidation of 2' : 1'-naphtha-1 : 2-fluorene (IV), m.p. 327—328° (complex with 2 : 7-dinitroanthraquinone, m.p.

250°), but not by fluorenone or 1 : 2-benzofluorenone. The absorption curve of (IV) is intermediate in character between those of phenanthrene and picene and very closely analogous to that of (III). The spectra of (II) and (III) are still more closely similar. It is suggested that group migration during sterol dehydrogenation offers the most probable explanation of the facts. The synthesis of 4-3'-methyl-6'-isopropylbenzylphenanthrene (V), m.p. 115—116°, is recorded.

H. W.

Perylene and its derivatives. XL. A. ZINKE and O. BENNDORF (Monatsh., 1934, 64, 87—96).—The view previously expressed (A., 1932, 507) that perylene (I) reacts in two forms is supported by further work on the reduction of (I).

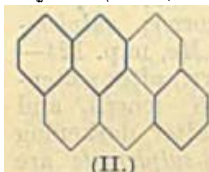
[With V. GRIMM and G. MANHART.] Reduction (Na, EtOH, C_6H_6) of (I) gives hexa-, m.p. 182—185°, and octa-, m.p. 119—120°, -hydroperylenes (cf. *loc. cit.*; A., 1920, i, 541). 3 : 9-Dibenzoylperylene (II) [dioxime (III), m.p. 336° (darkens at 300°)] is similarly reduced to an octahydro-derivative, m.p. 276°, which with NH_2OH gives (probably) a little (III). Reduction (Na, amyl alcohol) of (II) affords 3 : 9-dibenzyl-octahydroperylene, m.p. 154°, which when distilled over Cu in N_2 gives (I) and PhMe; 3 : 9-dianisoylperylene is similarly reduced to 3 : 9-di-*p*-methoxybenzyl-octahydroperylene, m.p. 195°. 3 : 4-Dibenzoylperylene is reduced (H_2 , Pt-C, AcOH) to (probably) the compound (IV), m.p. 289—291°. H. B.



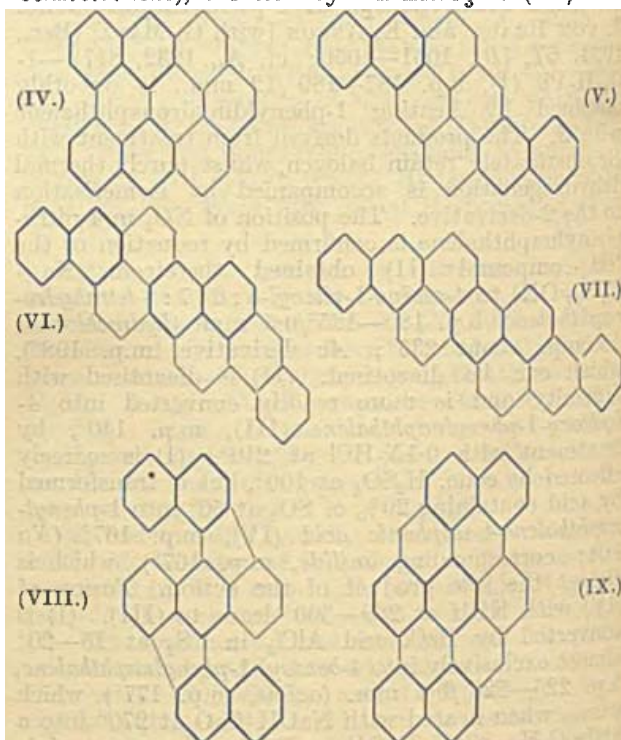
[Diradical formula of rubene and the constitution of its dissociable peroxide.] C. DUFRAISSE (Ber., 1934, 67, [B], 1021—1023).—Mainly a reply to Schönberg (this vol., 643). The constitutions assigned to rubene (I) and its oxide are not new, and the reaction mechanisms, although plausible, are devoid of experimental foundation. The structure assigned to the isomerisation product of oxyrubene is probably incorrect, since the substance cannot be reduced to (I).

H. W.

Aromatic parent hydrocarbons of anthanthrone, anthdianthrone (2 : 3 : 4 : 5-dibenzocoronene-1 : 6-quinone), pyranthrone or amphi-isopyranthrone, violanthrone, isoviolanthrone, 1 : 2 : 3 : 7 : 8 : 9-dinaphthacoronene-4 : 10-quinone, and dibenzrubicene. R. SCHOLL and K. MEYER (Ber., 1934, 67, [B], 1229—1235).—Anthanthrone (I) or a halogenated derivative is converted by HI (*d* 1.7) and red P at 190—200° and subsequent dehydrogenation by sublimation through Cu at 500°/20 mm. into anthanthrene (II), m.p. 257°, reconverted into (I) by CrO_3 in boiling AcOH.



Similar treatment transforms mesoanthrodianthrone (III) into anthrodianthrone (IV) (2 : 3 : 4 : 5-vic.-diperi-dibenzocoronene), oxidised by dil. HNO_3 to (III). Di-

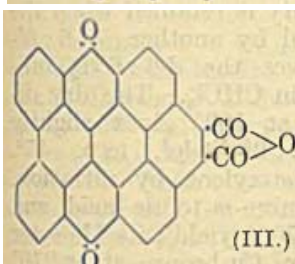
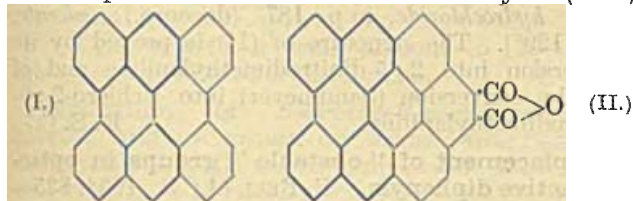


hydropyranthrone and Cu powder at 400°/20 mm. in CO_2 afford pyranthrone (V). Violanthrone, H^+ (*d* 1.7), and red P at 220° afford tetrahydroviolanthrone, converted by Cu powder at 450°/25 mm. in CO_2 into violanthrene (VI). Tetrahydroisoviolanthrene and isoviolanthrene (VII) are obtained similarly. The lactone of 9 : 10-dihydroxy-9 : 10-di- α -naphthyl-*v*. dihydroanthracene-1 : 5-dicarboxylic acid is converted

by sublimation with Zn dust at $500^{\circ}/20$ mm. in H_2 into dibenzorubicene (VIII). Reduction of 1:2:3-7:8:9-dinaphthocoronene-4:10-quinone with HI (d 1.7) and red P at 180 – 190° and treatment of the H-compound with Cu powder at $500^{\circ}/1$ mm. in H_2 leads to 1:2:3-7:8:9-dinaphthocoronene (IX).

H. W.

Blue aromatic parent hydrocarbon of mesonaphthodanthrone and its conversion by maleic anhydride into anthrodianthrene. R. SCHOLL and K. MEYER (Ber., 1934, 67, [B], 1236–1238).—mesoNaphthodanthrone is transformed by HI (d 1.7)



and red P at 200° into hexahydromesonaphthodanthrene, which passes when heated with Cu at $500^{\circ}/20$ mm. in H_2 into mesonaphthodanthrone (I). Treatment with maleic anhydride in boiling $PhNO_2$ transforms (I) into 2:3-4:5-dibenzocoronene-9:10-dicarboxylic anhydride

(II). Oxidation of (II) with H_2SO_4 - CrO_3 yields 2:3-4:5-dibenzocoronene-1:6-quinone-9:10-dicarboxylic anhydride (mesoanthrodicarboxylic anhydride) (III), whereas distillation with soda-lime at $500^{\circ}/1$ mm. in H_2 gives 2:3-4:5-dibenzocoronene (mesoanthrodianthrene).

H. W.

Preparation of aniline and aromatic amines by the contact method. SCHIPOV (Ukrain. Chem. J., 1933, 8, 347–354).— NH_2Ph is obtained in 6% yields by passing C_6H_6 vapour and NH_3 over Fe_2O_3 at 620° . The reaction is not catalytic, as the Fe_2O_3 undergoes reduction successively to FeO and Fe .

R. T.

Introduction of the thiocyno-group into organic compounds. H. P. KAUFMANN and K. KUHLER (Ber., 1934, 67, [B], 944–948).—Treatment of suitable materials in org. solvents with $Cu(CNS)_2$ leads to the introduction of CNS : $2Cu(CNS)_2 + RH - 2CuCNS + RSCN + HSCN$ and $2Cu(CNS)_2 + \cdot CH:CH = 2CuCNS + \cdot CH(SCN) \cdot CH(SCN) \cdot$. Reaction can be effected in H_2O and in presence of acids if hydrolysis of SCN is repressed by org. solvents. Reduction of the crude products leads to mercaptans, and treatment of them with alkali affords disulphides. Aromatic amines with substituted p -positions give 2-aminobenzo-thiazoles. Intimate mixtures of $NaCNS$ and hydrated Cu salts afford pastes of $Cu(CNS)_2$ to which the react-
ing substance may be added in the presence of little, if any, solvent. Alternatively, substance and Cu^{II} salt (I) may be mixed and added to the thiocyanate (II) or substance and (II) may be added to (I). The following examples are cited: p -thiocyanoaniline from NH_2Ph ; 1:2- $CNS \cdot C_{10}H_6 \cdot NH_2$ from β - $C_{10}H_7 \cdot NH_2$; 4:2- $CNS \cdot C_{10}H_6 \cdot OH$ from β - $C_{10}H_7 \cdot OH$;

$\mu\nu$ -dithiocyanobenzenic from erucic acid; 2-amino-6-methylbenzthiazole from p - $C_6H_4Me \cdot NH_2$; 6-chloro-2-aminobenzenethiazole from p - $C_6H_4Cl \cdot NH_2$; 2-amino-6-ethoxybenzthiazole from p - $OEt \cdot C_6H_4 \cdot NH_2$; 2-aminonaphthathiazole from α - $C_{10}H_7 \cdot NH_2$; Et 2-aminobenzenethiazole-6-carboxylate from anæsthesin; 4:4'-bis-(1-phenyl-2:3-dimethyl-5-pyrazolonyl) disulphide from antipyrine.

H. W.

Simplified preparation of anilides. R. C. SHAH and R. K. DESHPANDE (J. Univ. Bombay, 1933, 2, Pt. 2, 125–127).—To the crude mixture of acid chloride and $POCl_3$ obtained by the action of PCl_5 (1 mol.) on the acid (1 mol.), C_6H_5N , $NPhMe_2$, or $NPhEt_2$ (2 mols.) is added. The amine (1.25–1.5 mols.) is added and the product treated with dil. HCl , dil. $NaOH$, and H_2O . The yields of recryst. product obtained by applying the method to the prep. of many acyl derivatives of aromatic amines are given.

H. N. R.

So-called hexa-alkyltriaminodibenzoylbenzenes of Michler. A. WAHL (Bull. Soc. chim., 1934, [v], 1, 244–246).—The product obtained when $COCl_2$ is passed into $NPhMe_2$ at 190° is $CO(NPhMe)_2$ ($MeCl$ being evolved), and not $NMe_2 \cdot C_6H_3(CO \cdot C_6H_4 \cdot NMe_2)_2$ as stated by Michler *et al.* (A., 1877, ii, 233). Similarly $NPhEt_2$ and $NPhBu^a_2$ afford $CO(NPhEt)_2$ and $CO(NPhBu^a)_2$. A little $CO \cdot NPh$ is formed as a by-product.

J. W. B.

Constitution and reactions of thiocarbonyl tetrachloride. I. Reaction with arylamines. J. M. CONOLLY and G. M. DYSON (J.C.S., 1934, 822–824).— $CSCl_4$ (I) and p - $C_6H_4Me \cdot NH_2$ in Et_2O with aq. Na_2CO_3 at 30° give p -toluidinodichloromethylchlorothiols (II), m.p. 73° , which with cold KOH - $EtOH$ - Et_2O gives 2:2:5:5-tetrachloro-1:4-di- p -tolyl-1:2:4:5-tetrahydro-3:6-dithiapyrazine (III), m.p. 142.5° (violent decomp.). The Ph , p - $C_6H_4 \cdot OMe$, and p - C_6H_4Cl analogues of (II) are oils, but give compounds of type (III), m.p. 145.5° (decomp.), 113° (decomp.), and 160° (decomp.). The m -2-xylyl analogue of (II) is an oil. s - $C_6H_2Br_3 \cdot NH_2$ and 3:5-dibromo- p -toluidine do not react with (I), whereas m -2-xylylidine and 2:4- $C_6H_3Cl_2 \cdot NH_2$ give the compounds [as (II)], which with KOH - $EtOH$ give thiocarbimides. (II) is hydrolysed by hot H_2O to p - $C_6H_4Me \cdot NCS$ (IV), HCl (I), and p - $C_6H_4Me \cdot NH_2$ (V), with HCl gives (I) and (V), and with dil. alkali forms (IV) and p - $C_6H_4Me \cdot SCN$, whence it follows that (II) contains the grouping $R \cdot N \cdot C$. (III) with HCl in Et_2O gives 3-chloro- p -toluidine (by way of p - $C_6H_4Me \cdot NHCl$) and trichloromethylthiol, b.p. $125^{\circ}/15$ mm. (Hg salt; oxidised by air to a substance, m.p. 96° , probably the disulphide; gives chloropierin with fuming HNO_3 ; gives SCl_2 and a cryst. solid when heated at atm. pressure; gives H_2 with Na), and with HBr - Et_2O affords (V) and an oil, probably $CCl_2Br \cdot SBr$. The parachor of (I) agrees better with the formula $CCl_2 \cdot SCl_2$ (A) than with $CCl_3 \cdot SCl$, and (A) is confirmed by the above reactions, published data, and by the discovery of $CSCl_2$ as an intermediate product in the reaction of (I) with K_2SO_3 , which is best formulated: $(I) + K_2SO_3 + H_2O \longrightarrow CSCl_2 + K_2SO_4 + 2HCl$; $2HCl + K_2SO_3 \longrightarrow KHSO_3 +$

alkylresorcinol \rightarrow (III), were used. The PhOH-coeffs. (towards *S. aureus* at 20° using 5–8% EtOH solutions) of the above are 6, 45, 240, 625, and 665, respectively (*n*-hexylresorcinol = 60). *Chlororesorcinol* Bu^a, b.p. 128–134°/1 mm., *n*-amyl, b.p. 140–150°/3 mm., *n*-hexyl, b.p. 152–162°/2 mm., *n*-heptyl, b.p. 173–183°/5 mm., and *n*-octyl, b.p. 184–187°/4–5 mm., *ethers*, prepared from (I) and alkyl bromide in EtOH–NaOEt, have PhOH-coeffs. of 50, 100, 250, 200, and 65, respectively; against *B. typhosus*, they have practically the same (much smaller) activity as (III). H. B.

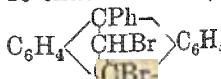
Substitution products of 2'-nitro- and 2':4'-dinitro-2-methoxydiphenyl ethers. H. A. SCARBOROUGH and J. L. SWEETEN (J.C.S., 1934, 867–869).—The presence of two NO₂-groups prevents bromination of 2-methoxydiphenyl ethers and further nitration is controlled by the OMe-group. Trinitro-derivatives cannot be prepared by direct nitration of the mononitro-ethers. Guaiacol, KOH, and *o*-C₆H₄Cl·NO₂ (I) at 150° give 2'-nitro-2-methoxydiphenyl ether (II), m.p. 69°, which with SO₂Cl₂ gives the 5-Cl-derivative (III), m.p. 91°. Cl₂ in AcOH with (II), (III), or 4-chloro-2'-nitro-2-methoxydiphenyl ether (IV), m.p. 79° [obtained from (I), 4-chloroguaiacol, and KOH at 200°], gives the 4:5-Cl₂-derivative (V), m.p. 98°, of (II), also obtained from (I) and 4:5-dichloroguaiacol. (V) with Cl₂ (excess) in AcOH in light yields the *x*:4:5-Cl₃-derivative, m.p. 107°. The 4-, m.p. 77°, and 5-Br-, m.p. 90°, and 4:5-Br₂-derivatives, m.p. 112°, of (II) were prepared by all the methods used for the Cl-analogues, excepting that the dibrominations were effected at 90°. (I) and 4-nitroguaiacol give the 4-NO₂-derivative, m.p. 105°, of (II), and 2:4-C₆H₃Cl(NO₂)₂ and guaiacol give the 4'-NO₂-derivative (VI), m.p. 92°. Similar condensations give the 4-Cl- (VII), m.p. 116°, 4:5-Cl₂- (VIII), m.p. 144°, 4-Br-, m.p. 132°, 5-Br-, m.p. 140° (prepared at 90° in EtOH) [also obtained from (VI) and Br–AcOH], and 4:5-Br₂-derivatives, m.p. 165°, of (II), and the 5-NO₂- (IX), m.p. 115°, 4:4'-(NO₂)₂-, m.p. 138° (prepared in EtOH at 90°), 4':5-(NO₂)₂- (X), m.p. 161° (prepared in hot EtOH), and 3:4':5-(NO₂)₃-derivatives (XI), m.p. 174° (prepared in hot EtOH), of (II). (VI) and SO₂Cl₂ give 5-chloro-2':4'-dinitro-2-methoxydiphenyl ether, m.p. 117°, which with Cl₂ in warm AcOH gives (VIII), also obtained by chlorination of (VII). (II) with HNO₃ (*d* 1.4) at <30° gives (IX), whilst (VI) gives similarly (X). However, HNO₃ (*d* 1.5), first at <30° and then at 100°, yields (XI) from (II), (IX), (VI), (X), or 4'-nitro- or 4':5-dinitro-2-methoxydiphenyl ether. R. S. C.

Organic sulphides. C. LEFEVRE and C. DESGREZ (Compt. rend., 1934, 198, 1791–1793; cf. this vol., 766).—By fusion of the appropriate C₆H₆ derivative with S, glycerol, and PbCO₃ are obtained: *di*-*p*-amino-, m.p. 106° (with the sulphide), *di*-*p*-hydroxy-, m.p. 116° (with the sulphide, m.p. 95°), and *di*-2:4-dihydroxy- (and sulphide) -phenyl disulphide. Similar sulphides are obtained from pyrogallol, guaiacol, C₁₀H₇·OH, borneol, salicylic and gallic acids. No action occurs with only COR, CO₂H, CO·NH₂, SO₂, or SO₂·NH₂ group in the C₆H₆ ring. J. W. B.

[**Synthesis of mescaline.**] K. H. SLOTTA and G. SZYSZKA (Ber., 1934, 67, [B], 1106–1108).—A comment on the publication of Hahn and Wassmuth (this vol., 647). H. W.

[**Synthesis of mescaline.**] G. HAHN (Ber., 1934, 67, [B], 1210–1211).—A reply to Slotta *et al.* (preceding abstract). H. W.

Reversible transformation of benzoylmethylcarbinol and acetylphenylcarbinol. Keto-anol tautomerism. A. E. FAVORSKI and (MME.) T. I. TEMNIKOVA (Compt. rend., 1934, 198, 1998–2000).—CHMeBz·OH (I) or CHPhAc·OH (II) with MgMeBr give the same mixture, m.p. 35–44°, b.p. 154.5–155°, of *glycols*, OH·CMePh·CHMe·OH and OH·CHPh·CMe·OH. With MgPhBr, however, (II) gives only OH·CHPh·CPhMe·OH (III), whereas (I) gives (III) and OH·CPh·CHMe·OH (fractions melting between 45° and 97.5°). With BzCl both (I) and (II) give mixtures of Bz derivatives of (I), m.p. 108–109°, and of (II), m.p. 51.5–52.5°. (I) and (II) thus have separate existence, but often react (*e.g.*, as above and with semicarbazide and PhCNO) as isomerides. The change, which involves two H, is called keto-anol or keto-carbinol tautomerism. R. S. C.

1:3-Diphenylindan-1-ol and its derivatives. C. DUFRAISSE and L. ENDERLIN (Bull. Soc. chim., 1934, [v], 1, 267–280).—With MgPhBr 3-phenyl- α -hydrindone affords 1:3-diphenylhydrinden-1-ol, dimorphous, m.p. 85° and (stable form) m.p. 93–94° (*Me ether*, m.p. 127°, by cold 1% MeOH–H₂SO₄), readily dehydrated by most dehydrating agents to 1:3-diphenylindene (I), dimorphous, m.p. 68–69° (Ziegler *et al.*, A., 1925, i, 131) and 85° (*nitrosochloride*, decomp. 84–85°, instantaneous fusion on block, 160°). In agreement with Weiss *et al.* (A., 1927, 970) (I) gives its Br₂ additive compound (II), m.p. 140° (block) (*loc. cit.*, m.p. 92–96°) (oxidised to C₆H₄Bz₂ and reduced to the indane), but with excess of Br in Et₂O is obtained a stable compound (III), m.p. 118–119°, which gives only resins on oxidation with CrO₃–AcOH, or reduction with Fe–AcOH, and is probably 10-bromo-9-phenyl-9:10-endobromomethylene-9:10-dihydroanthracene, 

With Br in CS₂ (II) or (III) affords a Br₃-derivative, probably C₂₁H₁₃Br₃·H₂O, decomp. 156–157° (bath), m.p. 216° (block). J. W. B.

(a) **Action of selenious anhydride on cholesterol.** (b) **Various methods for nitration of cholesterol.** E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 290–291, 291–292).—(a) By heating cholesterol (I) and SeO₂ at 180–200°, or in EtOH at 0°, only metacholesterol (II) and unchanged (I) are obtained, no oxidation to cholestenone being detected. No transformation of (I) occurs in sunlight in presence of light-sensitive substances such as UO₂(NO₃)₂, AgNO₃, HgO, HgI₂, or CHI₃.

(b) With conc. HNO₃–AcOH (I) affords a (NO₂)₂-derivative, m.p. 120–121°, but in AcOH with HNO₃–H₂SO₄ is obtained a compound, m.p. 112° (post Liebermann reaction: Br₂ additive compound), converted by KOH–EtOH into (II) and KOAc. When

shaken with an emulsion of HNO_3 in EtOH , Et_2O , C_6H_6 , PhNO_2 , or COMe_2 , (I) gives its ψ -nitrosite.

J. W. B.

Irradiation products of ergosterol. H. LETTRÉ (Annalen, 1934, 511, 280—291).—Under conditions in which cholesterol and ergosterol (I) give cryst. products, dehydrogenation of vitamin-D with Se at 320° gives only liquids from which no cryst. picrates could be obtained. Tachysterol acetate-citraconic anhydride compound is reduced by H_2 -Pd in EtOAc to its H_2 -derivative, m.p. 155 — 156° , $[\alpha]_D^{25} + 79.7^\circ$ in CHCl_3 (since no $\text{CHMePr}^{\text{ac}}\text{CHO}$ is obtained on ozonolysis, the side-chain double linking has been reduced), further reduced in AcOH-EtOAc to the H_4 -derivative; m.p. 134 — 135° , $[\alpha]_D^{25} + 18.4^\circ$ in CHCl_3 , converted by heating with EtOH-NaOH and reprecipn. with H_2O into an amorphous substance, $\text{C}_{25}\text{H}_{56}\text{O}_4$, not yet characterised. Analytical data and determination of the no. of double linkings in these derivatives and comparison with dehydroergosterol $\text{C}_{28}\text{H}_{42}\text{O}$ (which it most resembles) show that tachysterol (II) is $\text{C}_{28}\text{H}_{44}\text{O}$. In the isomeric (I) there are four rings and three double linkings, but in (II) there are three rings and four double linkings, and structures obtained by opening the C_{10} - C_9 linking in (I) with H -migration are suggested.

J. W. B.

Dehydrogenation of neoergosterol with platinum. H. HONIGMANN (Annalen, 1934, 511, 292—301).—Dehydrogenation of neoergosterol (I) with Pt-black in CO_2 at 250 — 300° gives a phenol (II), $\text{C}_{27}\text{H}_{36}\text{O}_2\text{H}_2\text{O}$, m.p. indef. 140° [Ac derivative, m.p. 150° , $[\alpha]_D^{25} + 46.8^\circ$ in CHCl_3 , absorption max. $280\text{ m}\mu$; 3:5-dinitrobenzoate, m.p. 207 — 208° ; Me ether, m.p. 114° , $[\alpha]_D^{25} + 26.7^\circ$ in CHCl_3 (by $\text{NaOH-Me}_2\text{SO}_4$), absorption spectrum resembles that of (II)]. Since such dehydrogenation is sp. for 6-hydroaromatic rings containing no quaternary C, the three double linkings in (I), and hence the two in ergosterol, must be in ring B (cf. Windaus *et al.*, this vol., 768). α -Ergosterol, which has Me at C_{10} , is unchanged under these dehydrogenation conditions.

J. W. B.

Phenyltrimethylglycerol and chlorohydrins of tetrasubstituted glycerols. H. RAVIER (Compt. rend., 1934, 198, 1787—1788).— MgPhBr (I) reacts with CMe_2CHAc , or MgMeBr with CMe_2CHBz , to give β -phenyl- δ -methyl- Δ^7 -n-penten- β -ol, b.p. 95 — $96^\circ/9\text{ mm.}$, converted by $\text{H}_2\text{C}_6\text{O}_4$ into β -phenyl- δ -methyl- Δ^7 -n-pentadiene, b.p. 77 — $80^\circ/10\text{ mm.}$, and by HOCl into γ -chloro- β -phenyl- δ -methyl- Δ^7 -n-pentene, b.p. 115 — $117^\circ/9\text{ mm.}$ (I) and $\text{OH}\cdot\text{CMe}_2\cdot\text{CHClAc}$ (II) afford γ -chloro- β -phenyl- δ -methyl-n-pentane- $\beta\delta$ -diol, m.p. 91° , hydrolysed with difficulty to β -phenyl- δ -methyl-n-pentane- $\beta\gamma\delta$ -triol, m.p. 74° , which is best obtained from (I) and $\text{OH}\cdot\text{CMe}_2\cdot\text{CHAc}\cdot\text{OH}$. With the appropriate MgRBr (II) affords γ -chloro- $\beta\delta$ -dimethyl-n-heptane- $\beta\delta$ -diol, b.p. 119 — $120^\circ/10\text{ mm.}$, and n-octane- $\beta\delta$ -diol, b.p. 129 — $130^\circ/9\text{ mm.}$ (also by HOCl addition to the corresponding Δ^8 -unsaturated alcohols). MgEtBr and corresponding Δ^8 -unsaturated alcohols. MgEtBr and $\text{OH}\cdot\text{CMe}_2\cdot\text{CHCl}\cdot\text{CO}_2\text{Et}$ afford γ -chloro- β -methyl- δ -ethyl-n-hexane- $\beta\delta$ -diol, b.p. 119 — $123^\circ/10\text{ mm.}$, m.p. 78° , hydrolysed by K_2CO_3 to the corresponding $\beta\gamma\delta$ -triol, m.p. 91° and giving the glycidate with K in dry Et_2O .

J. W. B.

Electrolyses with *p*-toluic and hexahydro-*p*-toluic (*p*-methylcyclohexanecarboxylic) acid. F. FICHTER and C. SIMON (Helv. Chim. Acta, 1934, 17, 717—725).—Electrolysis of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{K}$ in $\text{MeOH-H}_2\text{O}$ at a Pt wire anode leads to evolution of CO_2 in small amount and production of $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{Me}$, m.p. 33° , by a side reaction. Electrolysis of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ (I) in $0.2N\text{-H}_2\text{SO}_4\text{-COMe}_2$ at 75° with PbO_2 anode and rotating Pb cathode yields mainly $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ in 12.05% yield. Dark resinous compounds and oily products (derived from COMe_2) are formed in less amount and small quantities of toluquinol, m.p. 125° , (?) 2:5-dihydroxy-*p*-toluic acid, m.p. 210 — 212° , α -methylsuccinic acid, m.p. 108 — 110° , and trioxymethylene are isolated. (I) appears incapable of undergoing the Kolbe synthesis. *p*-Methylcyclohexyl bromide, Mg, and CO_2 yield 4:4'-dimethyldicyclohexyl (III), b.p. 127 — $132^\circ/15\text{ mm.}$, 4-methyl- Δ^1 -cyclohexene (III'), and a mixture of acids hydrolysed by conc. HCl to *trans*-hexahydro-*p*-toluic acid (IV), m.p. 107.5 — 108.5° (Ca salt + $5\text{H}_2\text{O}$), in 3—4% yield. Electrolysis of a mixture of (IV) and its K salt in H_2O between Pt electrodes affords (III), 4-methylcyclohexanone, 4-methylcyclohexanol, possibly (II), di-*p*-methylcyclohexyl ether, b.p. 83 — $86^\circ/0.7\text{ mm.}$, and 4-methylcyclohexyl 4-methylcyclohexylcarboxylate, b.p. 86 — $90^\circ/0.7\text{ mm.}$

H. W.

Catalytic hydrogenation of hydroxybenzoic acids in aqueous solution. N. L. EDSON (J.S.C.I., 1934, 53, 138—139T).—Catalytic hydrogenation (PtO_2) in aq. solution results as follows: *p*-hydroxybenzoic acid gives hexahydrobenzoic acid (I) (75—80%) together with *trans*-4-hydroxycyclohexane-1-carboxylic acid, but no *cis*-acid or lactone; *m*-hydroxybenzoic acid yields (I) (60%) together with a residue (m.p. 107 — 110°) believed to be a mixture of *cis*- and *trans*- H_6 -derivatives; salicylic acid forms hexahydrosalicylic acid, and a small quantity of (I) (10—15%). It is suggested that (I) arises during the intermediate formation and subsequent cleavage of a lactone ring.

Replacement of phosphorus pentachloride by thionyl chloride in the preparation of imidochlorides. J. VON BRAUN and W. PINKERLE (Ber., 1934, 67, [B], 1218—1220).—The use of COCl_2 in place of PCl_5 causes very smooth conversion of NBzMe_2 into $\text{CPhCl}_2\cdot\text{NMe}_2$, but its general use in the laboratory is not advised. For amides of aromatic acids, SOCl_2 is a nearly ideal chlorinating agent, reaction being cleaner than with PCl_5 , since analogues of the complex by-products containing P are not produced. With amides of aliphatic acids, SOCl_2 is less suitable. Amides derived from $\alpha\beta$ -unsaturated acids yield non-volatile materials containing S, probably formed by addition of SOCl_2 to the double linking. Simple amides, such as NHAcPh , give poorly cryst. materials containing S, possibly arising from addition of SOCl_2 to the chlorovinyl base arising by displacement of H in the imidochloride primarily formed. The following examples are cited: NHBzPh to $\text{CPhCl}_2\cdot\text{NPh}$ in 100% yield; NHBzMe to $\text{CPhCl}_2\cdot\text{NMe}$; NBzMe_2 to $\text{CPhCl}_2\cdot\text{NET}$; NBzPhMe

to CPhCl:NPh . SOCl_2 is particularly valuable for the conversion of $[\text{CH}_2]_4(\text{NHBz})_2$ into $\text{CH}_2\text{Cl}[\text{CH}_2]_3\text{NHBz}$ and analogous reactions.

Addition of halogens to benzene derivatives.

II. Addition of chlorine to benzoyl chloride.

III. Addition of chlorine to benzoic acid.

T. VAN DER LINDEN (Rec. trav. chim., 1934, 53, 703—714, 779—784; cf. this vol., 293).—II. BzCl and Cl_2 (6 atoms) in sunlight slowly give a mixture (mixed crystals) (I), m.p. 153° , of equal parts of δ -1:2:3:4:5:6-hexachlorocyclohexanecarboxyl chloride (II), m.p. 158 — 159° , and β -1:2:3:4:5:6:4'-heptachlorocyclohexanecarboxyl chloride (III), m.p. 143.5 — 144.5° , a γ -isomeride, m.p. 112 — 113° , of (II), an α -isomeride, m.p. 162° , of (III), and an oil, which after treatment with dil. KOH and distillation in steam yields a little 1:2:4:5- $\text{C}_6\text{H}_2\text{Cl}_4$ (IV), an oil, b.p. 93 — $98/0.1$ mm., three isomeric hexachlorocyclohexenes (V), m.p. 144° , b.p. 107 — $127/0.15$ mm., m.p. 71° , and 103 — 104° , respectively, a mixture, m.p. 223.5 — 225° , of $\text{C}_6\text{H}_4\text{Cl}_2\text{CO}_2\text{H}$ and $\text{OH}\cdot\text{C}_6\text{H}_4\text{Cl}_2\text{CO}_2\text{H}$ or of $\text{OH}\cdot\text{C}_6\text{H}_5\text{Cl}_2\text{CO}_2\text{H}$ and $\text{C}_6\text{H}_5\text{Cl}_2\text{CO}_2\text{H}$, the acid (VI) of (III), m.p. 277° , and ϵ -benzoic acid hexachloride (VII), m.p. 247° . (I) is inseparable by sublimation ($150^\circ/18$ mm.) or distillation in steam, and is hydrolysed by hot aq. org. solvents to a mixture of (VI) and a δ -isomeride (VIII), m.p. 247° , of (VII). (VI), (VII), and the γ -isomeride (IX) of (VII) with PCl_5 give the corresponding acid chlorides, but (IX) gives with PCl_5 a little and with SOCl_2 mainly the anhydride, $+\text{C}_6\text{H}_6$ and anhyd., m.p. 253° . The polychlorinated acid chlorides distil unchanged in steam. (V) is stable under the conditions used for isolation of (IV), whence it follows that (V) and (IV) are formed by loss of HCl and CO_2 from different acids.

III. BzOH and Cl_2 (6 atoms) in sunlight give the γ - (I), m.p. 237° , and β - (II) -hexachloride, m.p. 245° (rapid) or 220° (slow heating), a pentachlorocyclohexanecarboxylic acid (III), m.p. 217.5 — 218.5° [also obtained from (I) by heat or boiling H_2O], and a mixture which, when distilled in steam, yields (I), (II), the α -isomeride, 1:2:4:5-tetra-, penta-, and hexa-chlorobenzene, and (III). The formation of chlorobenzenes indicates that some Cl - and Cl_3 -acids are formed. Benzoic acid hexachlorides decompose slightly below the m.p. exactly as in boiling H_2O .

R. S. C.

Action of cold or warm sulphuric acid on aromatic esters. J. B. SENDERENS (Compt. rend., 1934, 198, 1827—1830).—The times for complete hydrolysis by cold H_2SO_4 are: EtOBz 12, $o\text{-C}_6\text{H}_4(\text{CO}_2\text{Et})_2$ 12, Pr^oOBz >15 , $\text{OBz}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr}^o$ >15 days, and $\text{C}_6\text{H}_4\text{MeCO}_2\text{Et}$ and Pr^oOBz immediate. Hydrolysis is immediate at 80° . $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Et}$, $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, and $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Pr}^o$ are rapidly hydrolysed and slowly sulphonated in the cold, but rapidly sulphonated at 80° . $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ and 2:4- $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ are rapidly sulphonated in the cold.

R. S. C.

5-Amino- and 5-nitro-diphenyl-2-carboxylic acid and 5-nitro-2-cyanodiphenyl.—See B., 1934,

Synthesis of *l*- α -naphthylmercapturic acid. H. R. ING, M. C. BOURNE, and L. YOUNG (Biochem. J., 1934, 28, 809—810).—The product from $\alpha\text{-C}_{10}\text{H}_7\text{NH}_2$ and *d*-acetylcysteine was heated in H_2O containing EtOH in presence of Cu -bronze powder to yield $\text{C}_{10}\text{H}_7\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NHAc})\cdot\text{CO}_2\text{H}$, m.p. 170.5 — 171° , identical with the compound found in rabbit's urine after C_{10}H_8 feeding (see this vol., 922). W. O. K.

Decomposition of α -keto-acids. C. D. HURD and H. R. RATERINK (J. Amer. Chem. Soc., 1934, 56, 1348—1350).— BzCO_2H decomposes at about 270° (method: A., 1933, 607) to CO (19%), CO_2 (49%), PhCHO (15—25%), and BzOH (35—45%); at 500° (flow method), a 62% yield of PhCHO is obtained. $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ gives (at 250 — 280°) CO (57—66%), CO_2 (44%), H_2O , and $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ (30—43%); $\text{CH}_2\text{Ph}\cdot\text{CHO}$ could not be isolated. H. B.

Haloform reaction. XIII. Trihalogenomethylketonic acids of mesitylene series. R. JOHNSON and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1417—1419).—3-Acetyl-2:4:6-trimethylphenyl styryl ketone, m.p. 95 — 96° [from diacetomesitylene (I), PhCHO , and aq. EtOH-NaOH], is oxidised (O_3 in CCl_4 , followed by alkaline H_2O_2) to 3-acetyl-2:4:6-trimethylbenzoic acid, m.p. 144 — 145° , which with cold aq. NaOH gives 3-trichloroacetyl- (II), m.p. 148 — 149° , and 3-tribromoacetyl- (III), m.p. 189° (decomp.), -2:4:6-trimethylbenzoic acid. (II) and (III) can be titrated with alkali (end-point not permanent); they are cleaved rapidly by warm aq. NaOH to 2:4:6-trimethylisophthalic acid (IV), m.p. 289° (corr.; decomp.) (lit. 283°), also prepared by oxidation of *dicinnamoylmesitylene*, m.p. 134 — 135° [from (I), PhCHO , and aq. EtOH-NaOH]. (III) shaken with 10% NaOH for about 15 hr. gives CBr_4 and 3-dibromoacetyl-2:4:6-trimethylbenzoic acid (V), m.p. 173.5 — 174.5° ; the following reactions occur: $\text{C}_6\text{HMe}_3(\text{CO}_2\text{H})_3 + \text{CHBr}_3 \leftarrow \text{CBr}_3\cdot\text{CO}\cdot\text{C}_6\text{HMe}_3\cdot\text{CO}_2\text{H} \rightarrow (\text{V}) + \text{NaOBr}$; $\text{CHBr}_3 + \text{NaOBr} \rightarrow \text{CBr}_4$. (V) and alkaline NaOBr give (IV) and CBr_4 . H. B.

Synthesis of acetoarylcboxylic acids. F. FEIST (Ber., 1934, 67, [B], 938—943; cf. A., 1932, 851).— $p\text{-C}_6\text{H}_4\text{MeAc}$ is converted by Cl_2 at 100 — 110° in presence of ultra-violet light into *p*-trichloroacetyl-trichloromethylbenzene, m.p. 38° , converted in EtOH by insufficiency of 2N-NaOH into *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ and trichloroacetylbenzoic acid (I), m.p. 193° , by protracted ebullition with MeOH into *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Me})_2$, and by restricted action of boiling MeOH into *p*-trichloroacetylbenzoate (II), m.p. 60 — 62° , and its methylate (III), $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{OMe})\cdot\text{CCl}_3$, m.p. 138.5 — 140.5° . (II) and (III) are transformed by H_2 in presence of Pd-CaCO_3 or Pd-BaSO_4 , respectively, into *p*- $\text{C}_6\text{H}_4\text{Ac}\cdot\text{CO}_2\text{Me}$, m.p. 94° (acid, m.p. 200°). *Me* 4-trichloroacetyl-3-trichloromethylbenzoate is most readily hydrolysed by $\text{H}_2\text{SO}_4\text{-AcOH}$ giving trichloroacetylisophthalic acid in addition to 16 products described (*loc. cit.*). Attempts to determine the basicity of (I) by use of NH_3 led to $p\text{-CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$. H. W.

Stereomutation and absorption of β -amsyl acrylic acids. (MLLE.) R. M. DA COSTA (Comp. rend., 1934, 198, 1996—1998).—Ultra-violet light

changes β -anisyl-, β -anisyl- α - (I) and β -methyl-acrylic acids (best if present as Na salts) into the corresponding *allo-acids*, m.p. 65° (30%), 113° (30%), and 110° (35% yield), respectively. (I) is unchanged by conc. H_2SO_4 at -10° , but the corresponding *allo-acid* gives 6-methoxy-2-methylindone, m.p. 142°, thus proving the *cis*-structure of the *allo-acids*. The absorption spectra of the two series are closely similar, but those of the *allo-acids* are slightly weaker and displaced towards the ultra-violet. R. S. C.

1:6-Reduction of cyclic β -bromobenzoyl-crotonic ester. R. E. LUTZ (J. Amer. Chem. Soc., 1934, 56, 1378—1381).— γ -Methoxy- γ -*p*-bromophenyl- β -methyl- γ -crotonolactone (cyclic Me β -*p*-bromobenzoylcrotonate) (I) (this vol., 406) is reduced (Zn dust, AcOH at 50—55°) to γ -methoxy- γ -*p*-bromophenyl- β -methyl- Δ^2 -butenoic acid (the enol Me ether of β -*p*-bromobenzoylbutyric acid) (II), m.p. 122.5° (corr.) (ozonolysis products, *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}_2\text{Me}$ and $\text{CH}_3\text{Ac}\cdot\text{CO}_2\text{H}$). Reduction (Zn dust, boiling AcOH) of (I) gives γ -methoxy- γ -*p*-bromophenyl- β -methyl- γ -butyrolactone (cyclic Me β -*p*-bromobenzoylbutyrate), m.p. 98° (corr.) [also obtained when (II) is boiled with AcOH], converted by $\text{MeOH}\cdot\text{H}_2\text{SO}_4$ into Me β -*p*-bromobenzoylbutyrate. The formation of (II) from (I) is considered to involve 1:6-addition of H_2 (i.e., to $\text{C}=\text{O}$ and $>\text{O}$) giving $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{OMe})\cdot\text{CMe}\cdot\text{CH}\cdot\text{C}(\text{OH})_2$, which then re-arranges. H. B.

***cis*- and *trans*-1:2-Dimethylcyclopropane-1:2-dicarboxylic acid.** K. VON AUWERS and O. UNGEMACH (Annalen, 1934, 511, 152—168).—The condensation product from Me_2 pyrocinchonate and CH_3N_2 is decomposed by superheating, the ester hydrolysed by HCl, and the mixture of acids thus obtained is treated with AcCl, whereby *cis*-1:2-dimethylcyclopropane-1:2-dicarboxylic acid (I), m.p. 115—117°, is converted into the anhydride (II), b.p. 113—115°/9 mm., m.p. 54—56°, from which it is regenerated by H_2O . *trans*-1:2-Dimethylcyclopropane-1:2-dicarboxylic acid (III), m.p. 230—231°, is obtained similarly from the pyrazoline derived from Me_2 dimethylfumarate and CH_3N_2 . Unlike (I), (III) reacts with difficulty with AcCl, by which it is converted into a non-cryst. polymeric anhydride (IV) slowly re-transformed by H_2O into (III). When heated in vac., (IV) passes into γ -methyl- α -methylene-glutaric anhydride, b.p. 135—136°/9 mm., m.p. 60° [corresponding acid (V), m.p. 107°; monoanilide, m.p. 164—164.5°]. Reduction of (V) by Na-Hg affords a mixture of $\alpha\alpha'$ -dimethylglutaric acids (monoanilide, m.p. 157°). Attempts to isomerise (I) by HCl gave partly unsaturated products formed by fission of the cyclopropane ring. Similar difficulties were met in the use of AcCl for the isomerisation of (III), which could be effected in some degree by use of Ac_2O . Treatment of (II) with NH_2Ph in C_6H_6 leads to *cis*-1:2-dimethylcyclopropanecarboxylanilic acid (VI), m.p. 139—140° when rapidly heated, hydrolysed by NaOH to (I) and NH_2Ph , transformed by NH_2Ph at 100° into the dianilide or, under other conditions, into the corresponding anil, m.p. 131—132°, obtained also from (VI) and AcCl. With NH_2Ph in C_6H_6 (III) gives *trans*-1:2-dimethylcyclopropane-1:2-dianilide

(VII), m.p. 266—267°, accompanied by the *trans-anilic acid*, m.p. 195—196°. Excess of NH_2Ph at 100° or its b.p. transforms (III) into (VII) exclusively. (III) is unaffected by heating at 220—230° or by protracted warming with AcCl. The following derivatives are prepared analogously: *cis*-*p*-toluidic acid, m.p. 149—150°; *cis*-*p*-tolil, m.p. 120—121°; *trans*-*p*-toluidic acid, m.p. 200°; *trans*-*di*-*p*-toluidide, m.p. 275—276°. The dissociation consts. of (I) and (III) have been measured at 25°. H. W.

Synthesis in the santene series; complete synthesis of santenic acid. G. KOMPPA and W. ROHRMANN (Ber., 1934, 67, [B], 828—829).—Catalytic reduction of dehydro- π -apocamphoric acid (Skita) yields isosantenic acid (I) and a non-separated mixture of isomeric santenic acids. (I) is transformed into *Et*, bromoisosantenate, b.p. 147—149°/7 mm., converted by hot quinoline into *Et*, dehydrosantenate, b.p. 133—135°/7 mm., which is hydrolysed to a dehydrosantenic acid (II), m.p. 168—169°, identical with that obtained by Aschan from bromosantenic acid. Catalytic reduction of (II) affords mainly *cis*-isosantenic acid with smaller amounts of *cis*- and *trans*-santenic acid. H. W.

Derivatives of salicylic acid. VII. Interaction of thionyl chloride with esters of aromatic hydroxy-acids in presence of finely-divided copper. II. Synthesis of thio-ether of 4-methoxysalicylic acid and related compounds. N. W. HIRWE, G. V. JADHAV, and Y. M. CHAKHRADEO (J. Univ. Bombay, 1933, 2, No. 2, 128—131).—Treatment of Me 4-methoxysalicylate with SOCl_2 and Cu powder gives the Me_2 ester (I) of *bis*-(4-hydroxy-2-methoxy-5-carboxyphenyl) sulphide (II), m.p. 226° [by hydrolysis of (I) with aq. NaOH] [Na_2 (+ H_2O), K_2 (+ $2\text{H}_2\text{O}$), Ca (+ $4\text{H}_2\text{O}$), and Ba (+ $4\text{H}_2\text{O}$) salts; diamide, m.p. 187°; Ac_2 derivative, m.p. 162°; Bz_2 derivative, m.p. 185°]. The constitution of (II) is confirmed by nitration with dil. HNO_3 to 5-nitro-4-methoxysalicylic acid, m.p. 232°. The mechanism of the formation of (I) is discussed. H. N. R.

Action of sulphuric acid in the cold and at slightly raised temperatures on aromatic acids and their esters. J. B. SENDRENS (Compt. rend., 1934, 198, 1655—1658; cf. A., 1928, 881).— BzOH , $o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$, and $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ are unaffected by conc. H_2SO_4 at room temp. and at 80°. $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{H}$ and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ give sulphonic acids slowly at room temp. and rapidly at 80°, whilst $2\text{:}4\text{-C}_6\text{H}_3\text{Me}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is immediately sulphonated as it dissolves. $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is sulphonated in the nucleus at room temp. after some hr. J. L. D.

Aluminium sulphonates and aluminosulphonic acids of the aromatic series, and their application to certain syntheses. M. DOMINIKIEWICZ (Arch. Chem. Farm., 1934, 1, 93—108).—The Al salts of 1:3- and 1:4- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})\cdot\text{SO}_3\text{H}$, 1:4:3- and 1:2:5- $\text{C}_6\text{H}_3(\text{CO}_2\text{H})(\text{OH})\cdot\text{SO}_3\text{H}$, 2:3:5- and 2:3:7- $\text{C}_{10}\text{H}_5(\text{CO}_2\text{H})(\text{OH})\cdot\text{SO}_3\text{H}$ are prepared by adding the theoretical amount of $\text{Al}_2(\text{SO}_4)_3$ to the aq. Ba salts, filtering, evaporating the filtrate to dryness, dissolving in EtOH, and again evaporating. The above salts are readily sol. in H_2O , EtOH, and AcOH, and are

not decomposed by dil. alkalis. $\text{Hg}(\text{OAc})_2$ and $\text{Al}[\text{I} : 2 : 5\text{-C}_6\text{H}_3(\text{CO}_2\text{H})(\text{OH})\text{-SO}_3]_3$ give the corresponding 3-acetoxymercuri-derivative, sparingly sol. in H_2O . R. T.

Preparation of phthalimide. C. L. TSENG and M. HU (Sci. Quart. Nat. Univ. Peking, 1934, 4, 191—235).—A survey of existing methods. W. R. B.

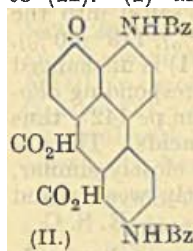
Influence of *o*-, *m*-, and *p*-substituents in organomagnesium carboxylates containing a labile hydrogen on their reaction with Grignard reagents. D. IVANOV and G. POHENITCHNY (Bull. Soc. chim., 1934, [v], 1, 223—233).—The effect of the nature of the group Ar in $\text{CH}_2\text{Ar}\cdot\text{CO}_2\text{MgCl}$ in determining whether the product of its interaction with RMgX gives (1) an arylmalonic acid (A., 1931, 483) or (2) a β -hydroxy- $\alpha\beta$ -triarylbutyric acid (*ibid.*, 726) has been studied. (1) is the main reaction when $\text{Ar} = o$ -, *m*-, or *p*- $\text{C}_6\text{H}_4\text{Me}$, or *p*- $\text{C}_6\text{H}_4\text{Pr}^s$ (group *a*), *o*-, (*b*) and *m*-, (*c*) - $\text{C}_6\text{H}_4\text{Br}$ or - $\text{C}_6\text{H}_4\text{Cl}$, and α - or β - C_{10}H_7 (*d*), and $\text{R} = \text{alkyl}$, *o*- $\text{C}_6\text{H}_4\text{Me}$ or α - C_{10}H_7 ; $\text{Ar} = \alpha$ - C_{10}H_7 and $\text{R} = \text{Ph}$, *m*- or *p*- $\text{C}_6\text{H}_4\text{Me}$, and *p*- $\text{C}_6\text{H}_4\text{Br}$; and thus from appropriate pairs are obtained *o*-, m.p. 139—140° (decomp.), *m*-, m.p. 130—131° (decomp.), and *p*-tolyl-, m.p. 143.5—144.5° (decomp.), *p*-isopropyl-, m.p. 143.5° (decomp.), *o*-, m.p. 124—125° (decomp.), and *m*-bromo-, m.p. 125.5—126.5°, and *m*-chloro-, m.p. 127—128° (decomp.), -phenyl-, and - α -, m.p. 151° (decomp.), and - β -naphthyl-, m.p. 148° (decomp.), -malonic acid. (2) is the main reaction when $\text{Ar} =$ group (*a*), *m*- $\text{C}_6\text{H}_4\text{Br}$, or β - C_{10}H_7 , and $\text{R} = \text{Ph}$, *m*- and *p*- $\text{C}_6\text{H}_4\text{Me}$, or *p*- $\text{C}_6\text{H}_4\text{Br}$, and thus are obtained the following -butyric acids: β -hydroxy- $\alpha\gamma$ -di-*o*-tolyl- β -*m*-tolyl-, m.p. 147—148.5°, - $\alpha\gamma$ -di-*o*-tolyl- β -*p*-tolyl-, m.p. 138°; - β -phenyl- $\alpha\gamma$ -di-*o*-, m.p. 145—146°, -di-*m*-, m.p. 137.5—138°, and -di-*p*-tolyl-, m.p. 172—173°; - $\alpha\beta\gamma$ -tri-*m*-tolyl-, m.p. 135—136°; - $\alpha\gamma$ -di-*m*-tolyl- β -*p*-tolyl-, m.p. 139—140°; - $\alpha\gamma$ -di-*p*-tolyl- β -*m*-tolyl-, m.p. 162—163°; - $\alpha\beta\gamma$ -tri-*p*-tolyl-, m.p. 174—175°; - β -*m*-tolyl- $\alpha\gamma$ -di-*p*-isopropylphenyl-, m.p. 139—140°; - β -*p*-tolyl- $\alpha\gamma$ -di-*p*-isopropylphenyl-, m.p. 158—159°; - β -phenyl- $\alpha\gamma$ -di-*p*-isopropylphenyl-, m.p. 162—163°; - $\alpha\gamma$ -di-*m*-bromophenyl- β -*m*-, m.p. 142.5—143.5°, and - β -*p*-tolyl-, m.p. 142—143°; - β -phenyl- $\alpha\gamma$ -di-*m*-bromophenyl-, m.p. 157.5—158.5°; - β -phenyl- $\alpha\gamma$ -di-*m*-chlorophenyl-, - β -phenyl- $\alpha\gamma$ -di- β -naphthyl-, m.p. 165.5—166.5° (decomposed by 20% NaOH to β - $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and *Ph* β -naphthylmethyl ketone, m.p. 122°), -butyric acid. From COPh_2 are obtained β -hydroxy- $\beta\beta$ -diphenyl- α -*m*-chlorophenyl-, m.p. 161.5°, and - $\alpha\alpha$ -diphenyl- α - β -naphthyl-, m.p. 163—164°, -propionic acid. J. W. B.

Perylene and its derivatives. XLI. Position of the substituents in dinitroperylene. K. FUNKE and G. P. YPSILANTI (Monatsh., 1934, 64, 143—152).—3:10-Dibenzamidoperylene (I) is oxidised (aq. CrO_3) to 6-benzamido-Bz-1-benzamido-1:9-benzanthrone(2)-5:10-dicarboxylic acid (II) (converted by distillation with Zn dust into benzanthrene) and 3:10-dibenzamidoperylene-4:9-quinone (III) (quinol dibenzoate). The production of (II) from (I) establishes the constitution of 3:10-dinitroperylene [from which (I) is prepared]. (III) is best prepared from (I) and HNO_3 (*d* 1.1); it is oxidised (MnO_2 , conc. H_2SO_4)

to (II). (I) and HNO_3 (*d* 1.4) in AcOH at 100° give a nitro-3:10-dibenzamidoperylene-4:9-quinone (IV) [reduced (alkaline $\text{Na}_2\text{S}_2\text{O}_4$) to the NH_2 -derivative], whilst (I) and boiling HNO_3 (*d* 1.4) afford a dinitro-3:10-dibenzamidoperylene-4:9-quinone [corresponding (NH_2)₂-derivative], also prepared from (III) and (IV). 3:10-Di-*p*-chlorobenzamidoperylene and HNO_3 (*d* 1.32) give a nitro-3:10-di-*p*-chlorobenzamidoperylene-4:9-quinone. H. B.

Characteristics of opianic and hemipinic acid. V. M. RODIONOV and T. A. ABLETZOVA (Ukrain. Chem. J., 1933, 8, 316—321).—Hemipinic acid (I) can be separated from opianic acid (II) by pptn. as the Ca salt. Good yields of meconine and (I) are obtained by boiling (II) during 3 hr. with 35% KOH . R. T.

Action of acetic anhydride and sodium acetate on the anhydrides of β -arylglutaconic acids. Formation of glutaconylacetic acids. D. B. LIMAYE and V. M. BHAVE (J. Univ. Bombay, 1933, 2, No. 2, 82—89).— β -Arylglutaconic anhydrides condense in their enolic form, $\text{CH} \begin{smallmatrix} \text{CHR}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH})\cdot\text{O} \end{smallmatrix} \text{CO}$, with Ac_2O and NaOAc to give β -arylglutaconylacetic acids (I), $\text{CH} \begin{smallmatrix} \text{CR}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH})\cdot\text{O} \end{smallmatrix} \text{C}\cdot\text{CH}\cdot\text{CO}_2\text{H}$. Treatment of (I) with aq. NaOH causes ring-fission with production of γ -acetyl- β -aryl- Δ^2 -butenoic acids, $\text{CHAc}\cdot\text{CR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (II). (I) is normally accompanied by the lactone $\text{CH}_2 \begin{smallmatrix} \text{CR}\cdot\text{CH} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{O} \end{smallmatrix} \text{C}\cdot\text{CH}_2$ (III), which may also be obtained from (I) and aq. HCl . (II) is decarboxylated when heated above its m.p. to yield the corresponding ketone, $\text{CHAc}\cdot\text{CRMe}$ (IV). (II) may also be reduced with Na-Hg , yielding the saturated keto-acid, $\text{CH}_2\text{Ac}\cdot\text{CHR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (V). The following are described: β -*p*-anisyl-, m.p. 132° (gives *p*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ with aq. NaOH); β -(4-methoxy-3-methylphenyl)-, m.p. 189°; β -(2-methoxy-*o*-methylphenyl)-, m.p. 129°; β -phenyl-, m.p. 115°; β -(2-methoxy-4-methylphenyl)-, m.p. 138°; β -*o*-anisyl-, m.p. 116°; -glutaconylacetic acids [as (I)]. γ -Acetyl- β -*p*-anisyl-, m.p. 125° (decomp.) [semicarbazone, m.p. 155° (decomp.)]; phenylhydrazones, m.p. 165°; oxime, m.p. 190° (decomp.)]; β -(4-methoxy-3-methylphenyl)-, m.p. 146° (semicarbazone, m.p. 155°; phenylhydrazones, m.p. 165°); β -(2-methoxy-5-methylphenyl)-, m.p. 98° (semicarbazone, m.p. 152°; phenylhydrazones, m.p. 122°), and - β -phenyl-, m.p. 109° (semicarbazone, m.p. 152°; phenylhydrazones, m.p. 145°), - Δ^2 -butenoic acids [as (II)]. Anisyl-, m.p. 112°, β -(4-methoxy-3-methylphenyl)-, m.p. 95°; β -phenyl-, m.p. 96°, -methyleneglutaconides [as (III)]. 4-Methoxy-, m.p. 48° (semicarbazone, m.p. 193°; phenylhydrazones, m.p. 70°; oxime, m.p. 107°; oxidised to *p*-methoxy- β -methylcinnamic acid); 4-methoxy-3-methyl-, b.p. 145—150°/5 mm. (semicarbazone, m.p. 205°; oxime, m.p. 100°; oxidised to 4-methoxy-3-methyl- β -methylcinnamic acid, m.p. 145°); and 2-methoxy-5-methyl-, b.p. 135°/5 mm. (semicarbazone m.p. 200°), - β -methylstyryl Me ketone [as (IV)]. γ -Acetyl

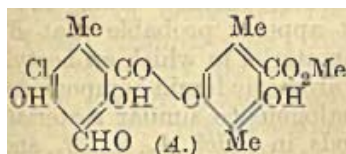


β -anisyl-, m.p. 104° (semicarbazone, m.p. 190°; oxime, m.p. 169°; Et ester, b.p. 190—195°/5 mm.); - β -(4-methoxy-3-methylphenyl)-, m.p. 72° (semicarbazone, m.p. 178°); - β -(2-methoxy-5-methylphenyl)-, m.p. 98° (semicarbazone, m.p. 199°), and - β -phenyl-, m.p. 85° (semicarbazone, m.p. 175°), -butyric acids [as (V)].

H. N. R.

Chlorine-containing lichen substance. I, II. G. KOLLER and K. POPL (Monatsh., 1934, 64, 106—113, 126—130).—I. The atranorin extracted (Et₂O) from *Pseudevernia furfuracea*, L., contains Cl and on acetolysis (AcOH at 140—150°) gives Me β -orcinolcarboxylate, atranol, and an aldehyde (I), C₈H₇O₃Cl, m.p. 143° [m-bromoanil, m.p. 228° (vac.) (decomp.)]. Reduction (H₂, Pd-C, EtOH) of (I) gives β -orcinol (II) and 2-chloro-3:5-dihydroxy-p-xylene, m.p. 88—89° [reduced (HI in CO₂) to (II)]. The Me₂ ether, m.p. 78° (Me₂SO₄), of (I) is oxidised (alkaline KMnO₄) to an acid (III), C₁₀H₁₁O₄Cl, m.p. 158°, reduced (H₂, Pd-C, aq. NaOAc) to p-orseilic acid Me₂ ether (IV). (I) appears to be 2-chloro-3:5-dihydroxy-p-tolualdehyde.

II. Chloro-p-orseilic acid Me₂ ether, m.p. 157—158° (Me ester, m.p. 71—72°), from (IV) and Cl₂-H₂O, is identical with (III) (above). Details are given for the isolation and purification of chloroatranorin (A), m.p. 208° (vac.), which on acetolysis (AcOH at 150°) gives (I). Alcoholic (MeOH at 155°) of (A) affords Me



β -orcinolcarboxylate and Me chlorohaematommate (6-chloro-3:5-dihydroxy-4-aldehyde-o-toluate), m.p. 90°.

H. B.

Lichen substances. XXXVIII. Protocetraric acid and its alkyl ethers. Y. ASAHINA and Y. TANASE. XXXIX. Norstictic acid, a new lichen acid, and occurrence of d-arabitol in lichens. Y. ASAHINA and M. YANAGITA. XL. Occurrence of volemitol in lichens. Y. ASAHINA and M. KAGITANI. XLI. Constitution of physodic acid (I). Y. ASAHINA and H. NOGAMI (Ber., 1934, 67, [B], 766—773, 799—803, 804—805, 805—811).

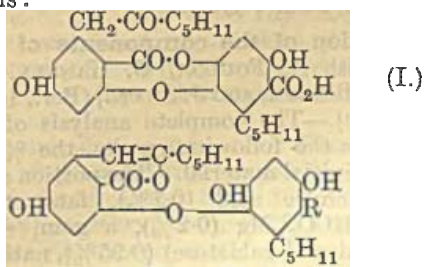
—XXXVIII. Successive extraction of the thalli of *Parmelia Zollingeri*, Hepp, with boiling Et₂O and COMe₂ yields atranorin, m.p. 196°, lecanoric acid, m.p. 180° (decomp.) [Me ester Me₃ ether, m.p. 147°], mannitol, and considerable amounts of protocetraric acid (I), decomp. 245—250° after darkening at about 220° [Ac₅ derivative (II) m.p. 113°]. Hydrogenation of (I) (Pd-C) affords hypoprotocetraric acid (III), decomp. 241° after darkening at 220°, best identified by conversion by CH₂N₂ into Me hypoprotocetrarate Me₂ ether (IV), m.p. 170°. Mild treatment of (IV) with KOH-MeOH leads to a compound, C₁₈H₁₄O₄(OMe)₄ (due to opening of lactone ring), transformed by CH₂N₂ in COMe₂ into the Me₅ derivative of hypoprotocetraric acid hydrate, C₁₈H₁₃O₃(OMe)₅, m.p. 115—116°. (I) or fumarprotocetraric acid and Pr^oOH at 100° afford protocetraric acid Pr^o ether, decomp. 240° after darkening at 200°, hydrogenated (Pd-C in AcOH) to (III) and converted by Ac₂O containing a little conc. H₂SO₄

into (II). The Bu^o, m.p. 178—179° (decomp.), isoamyl, m.p. 173° (decomp.), and CH₃Ph, m.p. 201° (decomp.) after darkening at 198°, ethers of (I) are prepared similarly and undergo similar transformations.

XXXIX. Extraction of the thalli of *Lobaria pulmonaria* from Sakhalin with Et₂O and COMe₂ and treatment of the extracts with NH₂Ph in COMe₂ leads to the isolation of gyrophoric acid, m.p. 228° (decomp.) (Ac₄ derivative, m.p. 228°), and norstictidiamil, m.p. about 265° (decomp.) after softening at about 240°, hydrolysed by conc. HCl in COMe₂ at room temp. to norstictic acid (I), C₁₈H₁₂O₉, decomp. 283° after darkening at 240° (penta-acetate, m.p. 212°). Catalytic hydrogenation (Pd-C in AcOH) converts (I) into hyposalazic acid, decomp. 280° after darkening at 240° (Me ester Me₂ ether, m.p. 164°). The COMe₂ extract (see above) contains d-arabitol (II), m.p. 103°, [α]_D²⁰ +7.82° in saturated Na₂B₄O₇ (penta-acetate, m.p. 76°). l- and r-Arabitol penta-acetate have m.p. 76° and 95°, respectively. (II) is also obtained from *L. pulmonaria* from Central Japan and from *Ramalina geniculata*. Extraction of *R. scopulorum* (Retz), Nyl, leads to the isolation of usnic acid, (II), and salazic acid.

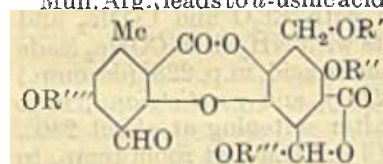
XL. Volemitol, m.p. 153.5° [(CHPh)₃ derivative, m.p. 222—223°], is obtained from *Dermatocarpon miniatum* and *Primula officinalis*, Jacq.

XLI. Extraction of the thalli of *Parmelia physodes* with Et₂O leads to atranorin and physodic acid (I), C₂₆H₃₀O₈, m.p. 205°. (I) does not contain OMe, gives a monoxime, m.p. 209—210°, and an Ac₂ derivative (II), m.p. 153—155.5°. Treatment with CH₂N₂ affords successively the Me₁ ester, m.p. 156—157°, Me₁ ester Me₁ ether (III), m.p. 117—119°, and Me₁ ester Me₃ ether (IV), m.p. 123—125°. In presence of bromothymol-blue and phenolphthalein (I) neutralises I and 2 equivs. of KOH, respectively, indicating thus the presence of a highly sensitive lactone ring. Dissolution of (I) in cold KOH followed by immediate acidification of the solution leads to isophysodic acid (V), m.p. 191—192°, converted by short treatment with CH₂N₂ into the Me ester, m.p. 197°, and by prolonged action into (IV). CH₂N₂ transforms (II) successively into Me diacetylphysodate, m.p. 114—115°, and its non-cryst. Me₁ ether. When boiled with HCO₂H or with quinoline and Cu-bronze (I) or (V) loses CO₂ and yields physodone (VI), C₂₅H₃₀O₆, m.p. 198—199°, which does not react with NH₂OH and gives an amorphous product with CH₂N₂. Fusion of (I) with KOH gives n-hexoic acid, orcinol, and n-amylresorcinol. (III) with KMnO₄ yields olivetonide Me₁ ether, m.p. 57°. The transformations of (I), (V), and (VI) are readily explained by the following constitutions:



(V; R=CO₂H.) (VI; R=H.) H. W.

Lichen substances. XLII. Components of certain *Usnea* types with special consideration of compounds of the salazic acid group (II). Y. ASAHINA and T. TUKAMOTO (Ber., 1934, 67, [B], 963—971).—Extraction of *Usnea articulata* v. *asperula*, Müll. Arg., leads to *d*-usnic acid, m.p. 203°, $[\alpha]_D^{25} + 483^\circ$ in



(A.)

CHCl_3 , salazic acid α -Me ether (I) [A ; $R' = \text{Me}$; $R'' = R''' = R'''' = \text{H}$], m.p. 210° (decomp.), and salazic acid β -Me ether (II) [A ; $R' = \text{Me}$; $R'' = R''' = R'''' = \text{H}$], m.p. 250—252° (decomp.) after becoming discoloured at 240°. (I) is transformed by H_2 (Pd-C in AcOH) into hyposalazic acid, decomp. about 280° (Me ester Me_2 ether, m.p. 165°). (I) affords a *dianil* $\text{C}_{31}\text{H}_{21}\text{O}_8\text{N}_2$, m.p. 169° (decomp.), and is converted by Ac_2O containing a trace of conc. H_2SO_4 into an amorphous material. (II) yields a *penta-acetate*, m.p. 228° (decomp.), and a *dianil*, m.p. 231° (decomp.). Dry distillation of (II) gives *atranel* Me_1 ether, m.p. 78°, whilst reduction (Pd-C) affords hypostictic acid, m.p. 264° (decomp.) after darkening at 240°. Treatment of salazic acid (III) with CH_2N_2 in COMe_2 - Et_2O yields *Me salazate* (A ; $R'' = \text{Me}$; $R' = R'' = R''' = \text{H}$), m.p. 229° [acetate, m.p. 103—104°; *monoanil*, $\text{C}_{25}\text{H}_{19}\text{O}_8\text{N}$, m.p. 218—219° (decomp.)], transformed by H_2 (Pd-C-AcOH) into *Me hyposalazate*, m.p. 273°. Treatment of (III) with boiling AcOH gives α -acetylsalazic acid, decomp. 275—276° after darkening at about 220°. *Triacetylhyposalazic acid* has m.p. 234° (slight decomp.). Possibly the salazic acid Me ether (A , 1933, 1161) is A ($R'' = \text{Me}$; $R' = R'' = R''' = \text{H}$), but the material does not appear homogeneous. Extraction of *U. japonica*, Wain, leads to usnic acid, norstictic acid, m.p. 284—285° (decomp.) after becoming discoloured at 260° (*penta-acetate*, m.p. 212°; *dianil*, decomp. 260—262° after becoming discoloured at 240°), reduced and methylated to trimethylhyposalazic acid, m.p. 165°; and (III). H. W.

Ring change by deamination of 2-aminocycloparaffin alcohols. M. ГОРЧУХ and M. МОУСЕРОН (Compt. rend., 1934, 198, 2000—2002).—The H oxalate and H tartrate of 2-aminocyclohexanol and NaNO_2 at 0° give NH_4NO_2 and cyclopentanealdehyde (80% yield), b.p. 42—43°/18 mm. (NaHSO_3 -compound; *semicarbazone*, m.p. 123—124°; with HNO_3 gives $\text{CO}_2\text{H} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$). 2-Aminocycloheptanol gives similarly cyclohexanealdehyde (*semicarbazone*, m.p. 167—168°; oxidised to adipic acid), but 2-aminocyclopentanol forms N_2 , cyclopentane 1:2-oxide, b.p. 102—103°, and *trans*-cyclohexane-1:2-diol (unchanged by COMe_2 -HCl). R. S. C.

Separation of the components of lignin. H. PAULY [with A. FOULON, O. HANSEN, O. HABERSTROH, H. BAILON, and J. SEXTL] (Ber., 1934, 67, [B], 1177—1199).—The complete analysis of winter rye straw gives the following results, the % being calc. on the dry initial material. The portion sol. in MeOH contains cerotic acid (0.7%), fats etc. (0.23%), $\text{HCO}_2\text{K} + (\text{HCO}_2)_2\text{Mg}$ (0.2%), a gum, sol. in H_2O , (uronic acid and galactose) (0.95%), native lignin A_1 (0.36%), and native lignin A_2 (0.74%). Extraction

of the residue with cold, 1.5% NaOH removes a fraction containing $(\text{HCO}_2)_2\text{Ca}$ (0.9%), AcOH (from Ac) (1.3%), pentoses (due to hydrolysis) (2.8%), alkali-lignin B_1 (1.54%), alkali-lignin B_2 (4.67%), and xylan (11.59%). Treatment of the residue with 85% AcOH containing 0.3% of H_2SO_4 gives 18.55% of substances sol. in H_2O with 85% of monoses (xylose, methyl pentose, glucose, mannose, galactose), 3.22% of lignol C_1 , 4.68% of lignol C_2 , and 3.50% of lignol C_3 . Residual cellulose amounts to 38.56%. The separation of A_1 from A_2 depends mainly on the difference in solubility in CHCl_3 . A_1 has m.p. about 160° after softening at 100° and shrinking strongly at 140°, I val. 40.4%, $[\alpha]_D^{25} \pm 0^\circ$ in AcOH. It dissolves readily in dil. NaOH. It does not reduce Fehling's solution before or after hydrolysis. A_2 has m.p. >250° after softening at 190°, I val. 22.4%; in general phenolic and lignin properties it closely resembles A_1 , from which it differs in composition, mol. wt., and solubility. B_1 and B_2 are separated from one another mainly by CHCl_3 . B_1 is non-cryst., has m.p. 120° after softening at 102°, $[\alpha]_D^{25} \pm 0^\circ$ in AcOH, and gives the usual colour reactions of lignins. B_2 softens at about 190°, but does not melt at a higher temp. Apart from mol. wt. and m.p., the differences between B_1 and B_2 are less marked than those between A_1 and A_2 . It appears probable that A_1 and B_2 are derived from material in which an acetyl-xylan is esterified by the aromatic lignin components. C_1 , C_2 , and C_3 appear analogous to similar materials isolated from various woods, in which A_1 , A_2 , B_1 , and B_2 are not present. The term "lignol" is applied to the phenolic components of difficultly produced lignins completely free from polysaccharides. The C_1 fraction from all sources is characterised by solubility in C_6H_6 , C_2 by solubility in CHCl_3 , whereas C_3 is generally sol. in AcOH, fatty acids, etc., but not in C_6H_6 or CHCl_3 . C_1 fractions have low m.p. (about 90°), whereas the m.p. of C_2 fractions are higher and C_3 fractions cannot be melted. All are optically inactive and non-cryst. They do not contain Ac. They give all the colour and other reactions of lignin and behave as typical phenol derivatives. The mol. wt. of fraction C_2 from any given source is double that of fraction C_1 , but individual vals. of the mol. wt. of fraction C_1 or C_2 from various sources differ greatly. Fraction C_3 exhibits very high mol. wt. It therefore appears incorrect to consider a single lignin in nature or a single fundamental unit from which all lignins are derived. The widely varying yields of vanillin obtained by oxidising lignins of differing origin with CrO_3 -AcOH or by oxidising C_1 , C_2 , and C_3 are explicable only by assuming a differing structure; this view is supported by the I vals. The supposed presence of piperonyl residues in lignin is negated by the complete absence of piperonal from the products of large-scale oxidation which yielded several hundred g. of vanillin.

The examination of the absorption of I from 0.1A-I-KI at 15—20° in absence of light shows that no action is observed in 10—14 days with eugenol, $\text{CHPh}:\text{CH}:\text{CH}_2:\text{OH}$, coniferin, coniferaldehyde, fumaric acid, styryl Me ketone, *p*-hydroxystyryl Me ketone, $\text{CO}(\text{CH}:\text{CHPh})_2$, dipiperonylideneacetone, cinnamylidene-acetophenone, -benzylideneacetone, -acrylic

acid, -pyruvic acid, -lævulic acid, piperic acid, piperin, and furfuraerylic acid. Almost exactly 2 atoms are added by isoprene, isoprenedicarboxylic acid, limonene, terpinene, cyclopentadiene, pinene, indene, and kawaic acid, whereas menthene, phellandrene, dicyclopentadiene, and caoutchouc absorb < 2 atoms. It is shown that the action of I on lignin is strictly chemical and additive. The method consists in allowing the finely-divided material to remain in contact with at least twice the requisite amount of 0.1N-I for 4—5 days. The method is well suited for purposes of comparison, but the exact point of addition is not obvious and the presence of conjugated double linkings is suggested.

H. W.

Nitration of phenacyl chloride and bromide. C. BARKENBUS and J. P. CLEMENTS (J. Amer. Chem. Soc., 1934, 56, 1369—1370).—The % of m -NO₂-derivative formed during nitration (no details given) of C₆H₅Me, C₆H₅·CH₂Cl (I), and C₆H₅·CH₂Br is 65.5, 68.5, and 69.4, respectively; determinations are made (essentially) by Yabroff and Porter's modification (A., 1932, 511) of Flurschein and Holmes' method (A., 1928, 403). m -Nitrophenacyl chloride, m.p. 100.5—102°, is obtained in 77% yield from (I) and HNO₃ (d 1.5) in cold 96% H₂SO₄.

H. B.

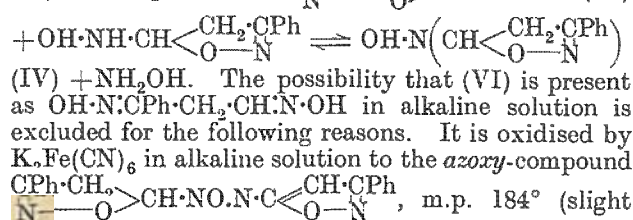
Action of Grignard reagents on ketoximes. J. HOCH (Compt. rend., 1934, 198, 1865—1868).—C₆H₅Et·N·OH (I) and MgPhBr (5 mols.) give a little NH₂Ph, (usually) α -hydroxylamino- α -diphenylpropane (II), m.p. 103° (hydrochloride, m.p. 258°; Bz derivative, m.p. 189°), and α -diphenylpropane- α -imine (III), $\text{C}_6\text{H}_5\text{CH}=\text{NCHMe}$, m.p. 74° (hydrochloride, m.p. 170—

175°; phenylurethane, m.p. 149°). The structures of (II) and (III) are based on the following reactions and on non-identity with the products expected to result from addition of Ph to N in (I). (III) is shown by spectral analysis to be saturated, gives CHPh₂·CHMe·NH₂ with Na·EtOH, does not react with NH₂OH or semicarbazide, and with hot 20% HCl yields CHAcPh₂ (by isomerisation to the ketimine and subsequent hydrolysis). The formation of NH₂Ph is explained by addition of some Ph to N yielding MgBr·C₆H₅Et·NPh·OMgBr, which hydrolyses to C₆H₅Et·NPh, and finally NH₂Ph and C₆H₅Et. MgEtBr gives only γ -ethylpentane- β -imine (60% yield), b.p. 102°/13 mm. (hydrochloride, m.p. 180—185°; phenylurethane, m.p. 11°; picrate, +C₆H₅, m.p. 135—136°), stable to HCl. R. S. C.

Hydroxylamine derivatives of hydroxymethylacetophenone. K. VON AUWERS and H. WUNDERLING (Ber., 1934, 67, [B], 1062—1077).—The spectrochemical behaviour of benzoylacetaldoxime (I) excludes the possibility that it has the structure CHBz·CH·NH·OH, but the sp. exaltations are low for a true oxime. (I) is converted into 5-phenylisooxazole (II) by AcCl or by acidification of its alkaline solutions by mineral acids, but not by AcOH. (II) is the main product formed when (I) is distilled in vac. (I) is transformed by PCl₅ into (II) and CH₂Bz·CN (III), whereas (III) is exclusively obtained when an alkaline solution of (I) is preserved. It is not considered that a fundamental difference exists in the mode of withdrawal of H₂O from (I) by acid and

alkali. Dissolution of (I) in cold Ac₂O and removal of the excess of anhydride gives the Ac₁ derivative, transformed by distillation in vac. or treatment with Ac₂O at 100° into a mixture of (II) and (III), whereas (III) is the sole product of hydrolysis by cold NaOH·H₂O. An Ac₂ derivative, m.p. 114—115°, is described. (I) is therefore A (R=H) and the monoximes of CH₂BzAc and CH₂Bz₂ for similar reasons are as A, with R=Me and Ph, respectively. (III), b.p. 160°/10 mm. (prep. from CH₂BzCl described), is converted by boiling Ac₂O into β -acetoxycinnamonnitrile, b.p. 170—171°/10 mm.

The "sesquioxime" (IV) of hydroxymethylacetophenone is converted by hot alkali into 3-phenylisooxazole (V) and 5-amino-3-phenylisooxazole. At room temp., 5-hydroxylamino-3-phenylisooxazoline (VI), m.p. 108—109° (sulphate), is formed; it slowly reduces cold Fehling's solution and AgNO₃·EtOH and passes when treated with dil. HCl at 15—20°, with AcOH, or boiling H₂O into (IV). The reactions may be represented:



The possibility that (VI) is present as OH·N·C₆H₅·CH₂·CH·N·OH in alkaline solution is excluded for the following reasons. It is oxidised by K₂Fe(CN)₆ in alkaline solution to the azoxy-compound $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{N}-\text{O}-\text{N} \cdot \text{C} \left\langle \begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_5 \\ \text{O}-\text{N} \end{array} \right\rangle$, m.p. 184° (slight decomp.), thus resembling NHPH·OH. All the replaceable H atoms of oximes or hydroxylamino-oximes can be substituted by Ac by means of Ac₂O and Ac attached to O, but not to N, is removed by cold MeOH·KOH, giving N -Ac derivatives which yield a characteristic red colour with FeCl₃. (VI) yields a non-cryst. Ac₂ derivative from which a N -Ac compound, m.p. 172—174°, is obtained. With BzCl it affords a monobenzoate (VII), m.p. 136—137°, an ON·Bz₂ compound (VIII), m.p. 157—158°, and a N -Bz₁ derivative, m.p. 175—176°. Since (VII) and (VIII) are obtained by the Schotten-Baumann and C₅H₅N methods, (VI) must contain ·NH·OH and its ring remain intact in alkaline solution. (VI) is transformed by warm BzCl into dibenzhydroxamic acid and (V). Attempts to prepare benzoylacetaldedioxime by the action of an excess of NH₂OH and alkali on hydroxymethylacetophenone (IX) led to (VI) in good yield. The action of NH₂OH on the condensation product of (IX) and NHPHMe gives the hydroxylamino-oxime OH·N·C₆H₅·CH₂·CH(NH·OH)·NPhMe, m.p. 107°. The following compounds are incidentally described: the Ac₂ derivative of benzylideneacetophenone-hydroxylamino-oxime, converted by KOH·MeOH into the N -Ac₁ compound, m.p. (indef.) 80°; Ac₃ and N -Ac₁ compounds of crotonylbenzenehydroxylamino-oximine; Ac₂ derivative of benzoylacetonedioxime.

H. W.

Phenanthrene derivatives. I. Reactions of magnesium 9-phenanthryl bromide. W. E. BACHMANN (J. Amer. Chem. Soc., 1934, 56, 1363—1367).—Mg 9-phenanthryl bromide (I) and PhCN in Et₂O·C₆H₆ give 9-benzoylphenanthrene, m.p. 89.5—90° (cf Willgerodt and Albert, A., 1911, i, 882), also pre-

pared from 9-cyanophenanthrene and MgPhBr and by the action of PhCHO on the $\cdot\text{OMgBr}$ derivative of phenyl-9-phenanthrylcarbinol (II), m.p. 139.5—140.5° [from (I) and PhCHO]. Reduction (I, red P, AcOH) of (II) affords 9-benzylphenanthrene, m.p. 153—154° (cf. *loc. cit.*), also obtained from (I) and CH_2PhCl . The following are prepared from the compounds quoted in parentheses and (I): o-tolyl 9-phenanthryl ketone, m.p. 88—90° ($\text{o-C}_6\text{H}_4\text{Me}\cdot\text{CN}$), which when heated at the b.p. for 45 min. and then distilled at atm. pressure gives 1:2:3:4-dibenzanthracene, m.p. 200—202° (lit. 196—197°); 9-methylphenanthrene, m.p. 90—91° (MeI); diphenyl-9-phenanthrylmethane (III), m.p. 175—176° (CHBrPh_2); 9-phenanthryldiphenylenemethane (IV), m.p. 197—198° (9-bromofluorene); 9-phenanthrylcarbinol, m.p. 149° (CH_2O); 9-phenanthrylmethylcarbinol, m.p. 134—135° (MeCHO); diphenyl-9-phenanthrylcarbinol (V), m.p. 173—174° (COPh_2); 9-phenanthryldiphenylenecarbinol (VI), m.p. 189° (fluorenone); phenanthrene-9-carboxylic acid, m.p. 251—252° (CO_2), and its Et ester, m.p. 58° (ClCO_2Et); di-9-phenanthryl, m.p. 184—185° (CuCl_2), and 9-hydroxyphenanthrene, m.p. 144—146° (O_2). (I) exhibits chemiluminescence when exposed to air. Reduction ($\text{HI}\cdot\text{AcOH}$) of (V) gives (III) and 9-phenyl-1:2:3:4-dibenzfluorene [also obtained by dehydration ($\text{AcOH}\cdot\text{conc. H}_2\text{SO}_4$) of (V)]. (VI) is similarly reduced to (IV). H. B.

Unsaturated ketones from deoxybilianic and isodeoxybilianic acid. T. SHIMIZU and T. KAZUNO (*Z. physiol. Chem.*, 1934, 224, 155—159).—Distillation of isodeoxybilianic acid yields an oil, which on hydrogenation (PtO_2) adds H_2 and gives a ketone, $\text{C}_{22}\text{H}_{34}\text{O}$, m.p. 133—134°, $[\alpha]_D^{25} -96.8^\circ$ in EtOH. Distillation of deoxybilianic acid gives a cryst. ketone, $\text{C}_{22}\text{H}_{32}\text{O}$, m.p. 153°, $[\alpha]_D^{25} +110.8^\circ$ in EtOH, which on hydrogenation affords the ketone (I), $\text{C}_{22}\text{H}_{34}\text{O}$, m.p. 136°, $[\alpha]_D^{25} +182.7^\circ$ in EtOH, identical with Wieland's product from Borsche's ketone, m.p. 144° (A., 1924, i, 1201; 1925, i, 1066). With Br in AcOH , (I) gives a bromoketone (II), $\text{C}_{22}\text{H}_{32}\text{OBr}$, m.p. 161°, $[\alpha]_D^{25} +15.5^\circ$ in EtOH. In $\text{C}_2\text{H}_5\text{N}$, (II) yields an unsaturated ketone (III), $\text{C}_{22}\text{H}_{32}\text{O}$, m.p. 107°, oxidised by KMnO_4 in AcOH to a hydroxydiketone, $\text{C}_{22}\text{H}_{32}\text{O}_3$, m.p. 170—173°. The Br in (II) must be at C_5 , the double linking in (III) between C_π and C_α . J. H. B.

Condensation of cyclopentanone with phenolic aldehydes. B. SAMDAHL and B. HANSEN (*J. Pharm. Chim.*, 1934, [viii], 19, 573—578; cf. A., 1928, 523; 1930, 343).—In presence of HCl phenolic aldehydes condense with cyclopentanone to give 2:5-dibenzylidene compounds. These may be used as indicators, being greenish-yellow in acid and orange or red in alkaline solution. The following are described, the p_H range of the colour change being given in brackets: 2:5-divanillylidene-, m.p. 214—215° [7.4—9.8]; 2:5-di-4-hydroxy-3-ethoxybenzylidene-, m.p. 188—189° (decomp.) [7.8—9.8]; 2:5-di-5-bromovanillylidene-, m.p. 268—269° (decomp.) [7.0—8.1]; 2:5-di-5-nitrovanillylidene-, m.p. 292—294° (decomp.) [insol.]; and 2:5-di-3:4-dihydroxybenzylidene-cyclopentanone, m.p. 274—275° [6.6—6.8—11.6]. H. N. R.

Allyl rearrangements in indene series. C. F. KOELSCH (*J. Amer. Chem. Soc.*, 1934, 56, 1337—1339).—1-Hydroxy-1:2-diphenyl-3-p-tolylindene (I), m.p. 175—177° [from 2-phenyl-3-p-tolylindone (II) and MgPhBr in $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$], and 1-hydroxy-2:3-diphenyl-1-p-tolylindene [from 2:3-diphenylindone and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ (III)] are converted by $\text{MeOH}\cdot\text{H}_2\text{SO}_4$ into the same Me ether (IV), m.p. 206—207° [probably that of (I)]. 2:3-Diphenyl- α -hydrindone, m.p. 100—101° (from $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{COCl}$ and AlCl_3 in C_6H_6), and (III) give 1-hydroxy-2:3-diphenyl-1-p-tolylhydrindene, m.p. 171—173°, dehydrated ($\text{AcOH}\cdot\text{H}_2\text{SO}_4$) to 1:2-diphenyl-3-p-tolylindene (V), m.p. 116—117°. 2-Phenyl-3-p-tolyl- α -hydrindone [by reduction (Zn dust, AcOH) of (II)] and MgPhBr afford 1-hydroxy-1:2-diphenyl-3-p-tolylhydrindene, m.p. 140—160° (? mixture of stereoisomerides), similarly dehydrated to 2:3-diphenyl-1-p-tolylindene (VI), m.p. 154—156°. (IV) is cleaved by 40% Na-Hg in Et_2O to a mixture of approx. equal amounts of (V) and (VI). The Na derivative from (V) or (VI) and 40% Na-Hg is hydrolysed to the same mixture of (V) and (VI). (V) undergoes 90% conversion into (VI) when boiled with a 5% solution of KOH in 90% EtOH. The anion present in solutions of the metal derivatives of (V) and (VI) is labile; the structure is fixed only after addition of H^+ . Contrary to Earl and Wilson (A., 1932, 382), 9-phenyl-9:10-dihydrophenanthrene-10-carboxylic acid could not be obtained from $\text{CHBrPh}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, C_6H_6 , and AlCl_3 ; $\text{CHPh}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ results under varying conditions. H. B.

Preparation of 2-hydroxyfluorenone. R. PATRIZIETTI (*Anal. Asoc. Quím. Argentina*, 1934, 22, 24—27).—The method of Diels is modified, the solution of diazofluorenone being filtered into boiling aq. AcOH . The yield is increased to 80%.

R. N. C.

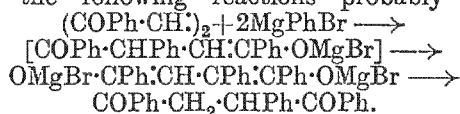
Poly-membered ring systems. III. m- and p-Ring closure in benzene series. K. ZIEGLER and A. LUTTRINGHAUS (*Annalen*, 1934, 511, 1—12; cf. A., 1933, 951; this vol., 195).—Crude resorcinol di- ζ -bromohexyl ether [from $m\text{-C}_6\text{H}_4(\text{ONa})_2$ and an excess of α , α -dibromohexane in EtOH], KCN , KI , and a little CuSO_4 in aq. EtOH give resorcinol di- ζ -cyano-hexyl ether, b.p. 238°/0.04 mm., m.p. 53—54°, converted by treatment with NaNPhAlk in Et_2O (*loc. cit.*) and subsequently with H_2O into resorcinol 7-imino-8-cyano-1:13-tridecamethylene ether,

$m\text{-C}_6\text{H}_4\text{<}\begin{matrix} \text{O}[\text{CH}_2]_6\text{C}\cdot\text{NH} \\ \text{O}[\text{CH}_2]_6\text{CH}\cdot\text{CN} \end{matrix}$ m.p. 97° (53.0% yield), which is hydrolysed ($2N\text{-H}_2\text{SO}_4$ in CHCl_3) to resorcinol 7-keto-8-cyano-1:13-tridecamethylene ether, m.p. 93. Quinol di- ζ -cyano-hexyl ether, m.p. 84—88° (the crude di- ζ -bromohexyl ether has m.p. 91—95°), is similarly converted into quinol 7-imino-8-cyano-1:13-tridecamethylene ether (I), m.p. 138—139° (52% yield); the corresponding keto-nitrile (II) undergoes ready autoxidation in MeOH and air to HCN and the $p\text{-CO}_2\text{H}\cdot[\text{CH}_2]_5\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$, m.p. 13 (Me_2 ester, m.p. 68°). More energetic hydrolysis (aq. H_2SO_4 in CO_2) of (I) gives [after removal of (II) by autoxidation and subsequent extraction with alkali] quinol 7-keto-1:13-tridecamethylene ether, m.p. 58—59° (semicarbazone, m.p. 124—126°).

$m\text{-C}_6\text{H}_4(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, obtained by reduction (H_2 , Pd-BaSO_4 , H_2O) of the NH_4 salt of $m\text{-C}_6\text{H}_4(\text{CH}:\text{CH}\cdot\text{CO}_2\text{H})_2$ [from $m\text{-C}_6\text{H}_4(\text{CHO})_2$ and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ at $45\text{--}50^\circ$], is converted through the chloride and amide into *m-di-β-cyanoethylbenzene*, b.p. $165\text{--}169^\circ/0.1\text{ mm.}$, which with NaNPhAlk gives much resin and a compound, $(\text{C}_{12}\text{H}_{12}\text{N}_2)_2$, m.p. $266\text{--}268^\circ$. Hydrolysis (aq. H_2SO_4 in CO_2) of this affords the diketone

$m\text{-C}_6\text{H}_4\langle\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\rangle\text{C}_6\text{H}_4\text{-}m$, m.p. $116\text{--}117.5^\circ$ (*disemicarbazone*, decomp. 274°). Attention is directed to the possibility of optical isomerism in polymembered ring ethers of 1:5- and 2:6- $\text{C}_{10}\text{H}_8(\text{OH})_2$ and 2:6-disubstituted quinols. H. B.

Action of magnesium phenyl bromide on dibenzoyl ethylene. R. E. LUTZ and W. R. TYSON (J. Amer. Chem. Soc., 1934, 56, 1341—1342).—Addition of $[\text{CHBz}]_2$ (I) to $\text{Et}_2\text{O-MgPhBr}$ (II) gives 60—65% of $\alpha\beta$ -dibenzoyl- α -phenylethane (III), about 5% of high-melting secondary product (A), and resin; the following reactions probably occur:



Addition of (II) to (I) gives a little or no (III) and 70—85% of (A); (A) is freed from Mg and Br with difficulty and has m.p. $145\text{--}200^\circ$ (fractional crystallisation has yielded a substance, $\text{C}_{38}\text{H}_{28}\text{O}_3$, m.p. $272\text{--}274^\circ$). MgMeI and (I) give (mainly) non-cryst. products and traces of two isomeric compounds, $\text{C}_{18}\text{H}_{20}\text{O}$, m.p. 170° and $215\text{--}216^\circ$. $\alpha\beta$ -Di-2:4:6-trimethylbenzoyl-, m.p. 137° (corr.), and $\alpha\beta$ -di-*p*-bromobenzoyl-, m.p. 160° (corr.), α -phenylethanes are prepared [as (III)] from (II) and $\alpha\beta$ -di-2:4:6-trimethylbenzoyl- and -*p*-bromobenzoyl-ethylene, respectively. H. B.

Derivatives of 9-hydroxy-9-phenyl-10-anthrone. F. F. BLICKE and R. D. SWISHER (J. Amer. Chem. Soc., 1934, 56, 1406—1408; cf. A., 1932, 617).—2-*o*-Methoxybenzylbenzoic acid and $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ (3:1 by vol.) at 50° give 4-methoxy-9-anthrone, m.p. $134\text{--}135^\circ$, oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, AcOH) to 1-methoxyanthraquinone. MgPhBr (3 equiv.) and 2-, 3-, and 4-methoxy-9-anthrone give 2-, m.p. $94\text{--}96^\circ$, 3-, m.p. $106\text{--}108^\circ$, and 4-, m.p. $164\text{--}166^\circ$, -methoxy-9-phenylanthracene, respectively, oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, AcOH) to 9-hydroxy-2-, m.p. $183\text{--}185^\circ$, -3- (I), m.p. $177\text{--}178^\circ$, and -4-, m.p. $228\text{--}230^\circ$, -methoxy-9-phenyl-10-anthrone, respectively, which are methylated (MeOH-HCl) to 2:9-, m.p. $115\text{--}117^\circ$, 3:9-, m.p. $142\text{--}144^\circ$, and 4:9-, m.p. $194\text{--}195^\circ$, -dimethoxy-9-phenyl-10-anthrone, respectively. 4':4''-Dimethoxydiphenylphthalein and SOCl_2 in C_6H_6 give 4'-methoxy-2-anisoylbenzophenone and a trace of (probably) 2:5-dianisyl-3:4-benzofuran; 4'-methoxydiphenylphthalein (II) similarly affords (I) and 9-hydroxy-9-anisyl-10-anthrone (III). (II) is converted by conc. H_2SO_4 into (probably) 2-phenyl-5-anisylbenzofuran, amorphous, which is oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, AcOH) to 2-anisoylbenzophenone and (III). H. B.

Condensation of 3:4-methylenedioxy-styryl methyl ketone with nitrobenzaldehydes. W.

KRASZEWSKI and K. GOŁĘBICKI (Rocz. Chem., 1934, 14, 203—206).—The products of condensation of 3:4-methylenedioxy-styryl Me ketone with the isomeric nitrobenzaldehydes are: *o*-, m.p. 154° (4-*Br*-derivative, m.p. $138\text{--}140^\circ$; phenylhydrazone, m.p. $88\text{--}89^\circ$), converted on recrystallising from H_2O into β -hydroxy- β -*o*-nitrophenylethyl 3:4-methylenedioxy-styryl ketone, m.p. 118° [*Bz*, m.p. 130° , and 2-*Br*-derivative, m.p. 90° (decomp.); semicarbazone, m.p. 191°]; *m*-, m.p. 188° (4-*Br*-derivative, m.p. 155° ; phenylhydrazone, m.p. 170°), and *p*-nitro-styryl 3:4-methylenedioxy-styryl ketone, m.p. $189\text{--}190^\circ$ (4-*Br*-derivative, m.p. 142° ; phenylhydrazone, m.p. 165°). R. T.

Highly activated carbonyl group. Dimesityl tetraketone. A. R. GRAY and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1367—1369; cf. this vol., 525).—Mesitylglyoxal (*loc. cit.*) and EtOH-KCN give γ -hydroxy- $\alpha\beta\delta$ -triketo- $\alpha\delta$ -di-2:4:6-trimethylphenylbutane (I), m.p. $188.5\text{--}189.5^\circ$, oxidised (conc. HNO_3) to di-2:4:6-trimethylphenyl tetraketone (II), $(\text{C}_6\text{H}_2\text{Me}_3\text{CO}\cdot\text{CO})_2$, m.p. $133\text{--}134^\circ$, red. (II) gives an unstable hydrate and is reduced by $\text{NHPh}\cdot\text{NH}_2$ in EtOH to (I). (II) undergoes fission when treated with warm 20% KOH ; CO_2 , mesityl-glycollic and -glyoxylic acids, and an unidentified compound, m.p. $112.5\text{--}113.5^\circ$, are isolated on acidification. Attempted prep. of derivatives with $\text{NH}_2\cdot\text{OH}$, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, and $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ has been unsuccessful (owing to the alkaline reaction medium). H. B.

Reduction of acenaphthenequinone by Clemmensen's method. H. GOLDSTEIN and W. GLAUSER (Helv. Chim. Acta, 1934, 17, 788—789).—Acenaphthenequinone is reduced by Zn-Hg and boiling 20% HCl to acenaphthene in about 35% yield. Similarly, 3-methoxyacenaphthenequinone affords 3-methoxyacenaphthene, m.p. 65.5° , in about 25% yield. H. W.

Application of the electronic theory to organic compounds. VI. Isomerism of sulpho-derivatives of anthracene and anthraquinone. A. M. BERKENGEIM and M. P. ZNAMENSKAJA (J. Gen. Chem. Russ., 1934, 4, 31—58).— SO_3H groups are replaced by H on hydrolysis with 75% H_2SO_4 or on reduction with 2% Na-Hg , whilst $\text{O}\cdot\text{SO}_2\text{H}$ groups are unaffected by these reagents. This rule is verified for anthraquinone-1- and -2-mono- and -1:5-, -1:8-, -2:7-, and -2:6-di-sulphonic acids, and for anthracene-1:8-, -2:7-, and -2:6-disulphonic acids. Apparent deviations from the rule are ascribed to impurities, to erroneously allocated orientation (thus, the 1:5-acid is supposed, on the basis of the results of hydrolysis, to be in reality 1:6-), or to isomeric transformation at the temp. of hydrolysis. R. T.

Derivatives of anthraquinone. III. Amino-methylantraquinones. IV. Dichloroanthraquinones. M. HAYASHI and A. NAKAYAMA (J. Soc. Chem. Ind. Japan, 1934, 37, 238—239B, 239—240B).—III. Interaction of 4-nitrophthalic anhydride, excess of PhMe , and AlCl_3 at $75\text{--}78^\circ$ gives 4-nitro-, m.p. $217\text{--}218^\circ$, and 5-nitro-2-*p*-toluoylbenzoic acid, m.p. $190\text{--}191^\circ$, which are reduced to 4-amino- (I), m.p. 224° (*Ac* derivative, m.p. 244°), and 5-amino-2-*p*-toluoylbenzoic acid (II), m.p. $181.5\text{--}182^\circ$ (de-

comp.) (*Ac* derivative, m.p. 220—221°). (I) is cyclised by conc. H_2SO_4 at 100° to *aminomethylantraquinone-A* (III), m.p. 281—281.5°, which is converted (Sandmeyer) into the corresponding *Cl*-compound, m.p. 228.5—229.5°. Under the same conditions (II) gives a mixture apparently containing some (III).

IV. Chloroaminoanthraquinone-*A* (cf. A., 1933, 612) is converted by Sandmeyer's reaction into 2 : 6-dichloroanthraquinone, m.p. 287.5—288°; chloroaminoanthraquinone-*B* (*loc. cit.*) similarly gives 2 : 7-dichloroanthraquinone, m.p. 230.5—231°. Absorption curves of all the above in EtOH are given.

H. A. P.

Mechanism of the asymmetric catalytic racemisation of amygdalin. I. A. SMITH (Ber., 1934, 67, [B], 1307—1317).—The action of KOH-MeOH on amygdalin (I) is similar to its action on Fischer's glucoside, and hence is restricted to the aglucone portion of the mol. The first phase of the change, which is complete in a few min. and is accompanied by a slight increase in levorotation, involves a catalytic racemisation. At the end of this phase CN is intact and hydrolysis by conc. HCl yields a nearly inactive mandelic acid. The second phase, which requires about 1 day for completion, is accompanied by diminution of levorotation. The product does not contain OMe and does not give the carmine-red coloration with H_2SO_4 characteristic of CN-CHPh-OH. Hydrolysis with conc. HCl gives OH-CHPh-CO₂H (II) with moderately high + rotation, whereas similar hydrolysis of (I) yields the homogeneous *l*-acid and hydrolysis with H_2SO_4 removes the gentiobiose residue, leading thus to optically pure (+)-mandelonitrile. The product of the second phase when treated with H_2SO_4 gives OH-CHPh-CO₂Me (III), $[\alpha]_D^{15} +33.2^\circ$ in CO_2Me_2 (the pure ester has $[\alpha]_D +121^\circ$). The second phase is considered to be associated with the addition of MeOH to CN giving an imino-ether. Since reaction occurs under the influence of the optically active gentiobiose group, a preferential production of the compound from neoamygdalin (IV) is assumed. The residue consists of (IV) with an excess of (I), and since each component is very sensitive to alkali, the mixture is rapidly transformed into isoamygdalin. In the third phase, which requires about 1 month for completion, the levorotation increases; OMe is already present in the mol. Hydrolysis with HCl yields nearly inactive (II), whereas treatment with H_2SO_4 affords almost inactive (III) and (II). In this phase reaction is considered to consist in the slow, catalytic racemisation of the imino-ether or Me ester. Confirmation of this view is found in the observation that a third phase does not exist in the action of NH_3 -MeOH on (I); at the end of the second phase hydrolysis with H_2SO_4 gives (III), $[\alpha]_D^{15} +43.3^\circ$ in CO_2Me_2 , and (II), $[\alpha]_D^{15} +70.1^\circ$ in H_2O . Treatment of (I) with KOH-MeOH for about 1 day and of the product with Ac_2O in $\text{C}_6\text{H}_5\text{N}$ affords *Me hepta-acetylamygdalate*, m.p. 202—203.5°, $[\alpha]_D^{20} -66.4^\circ$, $[\alpha]_{3461}^{20} -78.4^\circ$ in CHCl_3 , and *Me hepta-acetylneoamygdalate*, m.p. 187—189, $[\alpha]_{3461}^{20} -6.6^\circ$ in CHCl_3 .

H. W.

Cerebronic acid. Reply to Levene and Yang. E. KLENK (J. Biol. Chem., 1934, 105, 467—468; cf. this vol., 78).—Polemical. The view is restated that

lignoceric acid obtained by Levene and Yang by oxidation of cerebronic acid (I) is present as an impurity in the (I).

H. A. P.

Dehydrogenation of gitogenin. W. A. JACOBS and J. C. E. SIMPSON (J. Amer. Chem. Soc., 1934, 56, 1424—1425).—Dehydrogenation (Se) of gitogenin gives the same ketone, $\text{C}_8\text{H}_{16}\text{O}$ (semicarbazone, m.p. 144.5—145°) (cf. Ruzicka and van Veen, A., 1929, 1305), and hydrocarbon, m.p. 123.5—124° (not depressed by Diels' hydrocarbon, $\text{C}_{18}\text{H}_{16}$), as are obtained from sarsapogenin (I). (I), the *Digitalis* saponins, and the cardiac aglucones appear to be alicyclic derivatives of the sterol and bile acid ring-system.

H. B.

Sarsapogenin and gitogenin. W. A. JACOBS and J. C. E. SIMPSON (J. Biol. Chem., 1934, 105, 481—510).—Dehydrogenation of sarsapogenin (I) with Se at 230—240° gives a ketone, $\text{C}_8\text{H}_{16}\text{O}$ (semicarbazone, m.p. 143—144°), which is not necessarily *Me isohexyl* ketone (semicarbazone, m.p. 153—154°), as stated by Ruzicka and van Veen (A., 1929, 1305), and methylcyclopentanophenanthrene, m.p. 123.5—124°; it therefore probably contains a nuclear structure similar to that of cholesterol. With AcOH-HCl (I) gives a *CO*-compound, $\text{C}_8\text{H}_{14}\text{O}_3$ (semicarbazone, m.p. 119.5—120°), which appears to be unsaturated $[\text{C}(\text{NO}_2)_4]$. A similar result is obtained with gitogenin.

H. A. P.

Saponins and saponins. I. Echinocystic acid. I. BERGSTEINSSON and C. R. NOLLER (J. Amer. Chem. Soc., 1934, 56, 1403—1405).—Successive extraction of the root of *Echinocystis fabacea* with MeOH, 50% MeOH, and MeOH and evaporation of the combined extracts to dryness gives the crude saponin, hydrolysed (aq. MeOH-HCl at 60°) to the saponin (*echinocystic acid*) (I), $\text{C}_{30}\text{H}_{48}\text{O}_4$, m.p. 305—312° (corr.; decomp.), $[\alpha]_{546}^{25} +40.6^\circ$ in 95% EtOH [*diacetate* (II), m.p. 272—275° (corr.); *Me* ester, m.p. 213—215° (*diacetate*, m.p. 200—201°)]. The rate of hydrolysis (EtOH-KOH) of (II) indicates the occurrence of primary and sec. OH groups in (I). (I) and (II) give a yellow colour with $\text{C}(\text{NO}_2)_4$ in CCl_4 ; neither could be reduced (H_2 , PtO_2 , AcOH).

H. B.

Plant pigments. LX. Astacin. II. P. KARRER and L. LOEWE (Helv. Chim. Acta, 1934, 17, 745—747).—Astacin (I) is $\text{C}_{40}\text{H}_{48}\text{O}_4$ and its *Ac* derivative is $\text{C}_{40}\text{H}_{46}\text{O}_4\text{Ac}_2$. (I) yields a *dioxime*, $\text{C}_{40}\text{H}_{50}\text{O}_4\text{N}_2$, which contains four active H (Zerevitinov). (I) evolves little CH_4 when treated with MgMeI in $\text{C}_6\text{H}_5\text{N}$. Catalytic hydrogenation of (I) discloses the presence of thirteen active double linkings, two of which are due to enolisation; this is in accord with the established presence of 2 OH in perhydroastacin. The 4 CO of (I) are present in pairs, since (I) and *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ yield a *diphenazine* derivative, $\text{C}_{50}\text{H}_{56}\text{N}_4$. (I) is therefore 4 : 5 : 4' : 5' - or 5 : 6 : 5' : 6' - tetraketo- β -carotene.

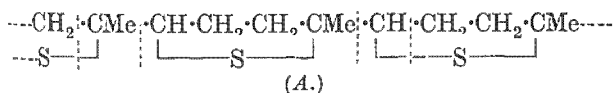
H. W.

Modified rubbers. IV. Oxidation of rubber with aqueous hydrogen peroxide-acetic acid mixtures. G. F. BLOOMFIELD and E. H. FARMER (J.S.C.I., 1934, 53, 121—125t).—The oxidation of rubber with H_2O_2 in presence of AcOH and H_2O yields partly-acetylated OH-acids of considerable mol. wt. By varying the proportions of reagents in the

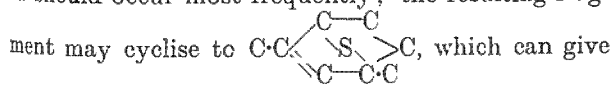
oxidation the proportion of OAc groups entering the mols. of the rubber may be regulated. Since the oxidation product (*A*) closely resembles those resulting from AcO_2H oxidation of rubber, it is inferred that oxidation proceeds through the intermediate agency of AcO_2H . The influence of proportion of reagents, temp., catalysts, etc. on the oxidation is studied. *A* can undergo further acetylation (free OH groups); its saponification gives a OH-acid (*B*) which can be reacylated to yield a material similar to *A*. The composition of *B* appears to remain const. in spite of considerable changes in the proportions of reagents used in the formation of *A* or when the AcOH in the oxidising mixture is replaced, e.g., by HCO_2H .

Natural and synthetic rubber. XIII. Mol. wt. of sol-rubber. T. MIDGLEY, jun., A. L. HENNE, A. F. SHEPARD, and M. W. RENOLL. **XIV.** Structural formula for ebonite. T. MIDGLEY, jun., A. L. HENNE, and A. F. SHEPARD (J. Amer. Chem. Soc., 1934, 56, 1325—1326, 1326—1328).—XIII. A solution of sol-rubber (I) (B., 1931, 853; 1933, 200), tetramethylthiuram disulphide, and a little Zn stearate in C_6H_6 is evaporated at room temp. in a high vac. and the resulting skin heated at 100° (bath) until approx. 0.06% S is combined. Repeated fractional pptn. of the product from $\text{EtOH}-\text{C}_6\text{H}_6$ gives fractions containing 0.058 ± 0.003 , 0.116 ± 0.003 , and $0.179 \pm 0.003\%$ S. Assuming that these are mono-, di-, and tri-sulphur derivatives (RS , RS_2 , RS_3), the mol. wt. of (I) is about 54,000.

XIV. The structure (*A*) assigned to ebonite explains



the production (B., 1932, 902) of the following pyrolysis products: 2-methylthiophen (by fission at *bc*), 2-methyl-5-ethylthiophen (fission at *ac*), 2:3-dimethylthiophen (fission at *bd*; migration of Me). Fission at *ad* should occur most frequently; the resulting frag-



rise to $m\text{-C}_6\text{H}_4\text{Me}_2$ (loss of H_2S) or 2:4-dimethylthiophen (loss of 2C).

H. B.

Citronellol and rhodinol. ANGLA (Compt. rend., 1934, 198, 2241—2244).—*d*-Citronellol (I) and *l*-rhodinol from the Bourbon geranium (II) and from the Algerian geranium (III) are isolated with BzCl (cf.

1896, i, 445) to give (cf. A., 1928, 1113) mixtures containing 45% of the α - and 55% of the β -form. (I) and (II) have the same numerical rotatory dispersion; and (III) has a higher val. The results of Lagneau (cf.

1934, 301) are untrustworthy because his measurements were carried out on commercial samples of (I) and (II), which contain the α - and β -forms in varying proportions. His vals. for rhodinol from the rose (isolated as above) agree with the vals. now obtained.

Pyrolysis of carveol. J. DÈUVRE (Bull. Soc. chim., 1934, [v], 1, 198—206).—Pyrolysis of *d*-carveol (I) [from *d*-carvone and $\text{Al}(\text{OPr}^i)_3$ or $\text{Al}(\text{OBu}^n)_3$] at $560/170$ mm. affords uncondensed (-75°) gaseous products 10%, Δ^8 -butene, MeCHO 0.5%, isoprene

6%, tiglaldehyde 5% [2:4-dinitrophenylhydrazones, m.p. 222° (block)], a mixture of hydrocarbons, b.p. $55\text{--}90^\circ/40$ mm., 10% (probably containing $\text{C}_{10}\text{H}_{14}$ or $\text{C}_{10}\text{H}_{16}$), a C_{10} aldehyde, b.p. $88\text{--}92^\circ/15$ mm., 5% (probably $\text{CH}_2\text{:CMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{CHO}$), a ketone fraction, b.p. $98\text{--}109^\circ/15$ mm., 15%, unchanged (I) 40%, and a viscous residue 3%.

J. W. B.

Synthesis of myrtenol and myrtenal. G. DUPONT, W. ZACHAREWICZ, and R. DULOU (Compt. rend., 1934, 198, 1699—1701; cf. A., 1933, 1166).—Pinene with SeO_2 in boiling EtOH during 4 hr. does not afford verbenol and verbenone, but myrtenol (I), b.p. $106\text{--}108^\circ/14$ mm., $[\alpha]_D +44.11^\circ$ [phthalate, *d*- or *l*-form, m.p. $114\text{--}115^\circ$; *dl*-form, m.p. $120\text{--}120.5^\circ$], which is oxidised (CrO_3) to (II); and reduced ($\text{H}_2\text{--Pt}$) to myrtanol (III), b.p. $113\text{--}114^\circ/14$ mm., and myrtenal (II), b.p. $99\text{--}100^\circ/15$ mm., $[\alpha]_D +14.75^\circ$ [semicarbazone, *d*- or *l*-form, m.p. 225° and 216° (two forms), *dl*-form, m.p. 206° ; oxime, *d*- or *l*-form, m.p. $70.5\text{--}71.5^\circ$, *dl*-form, m.p. 101°], which gives *d*-pinic acid (*dl*-form, m.p. $101\text{--}102.5^\circ$) with KMnO_4 , is reduced ($\text{H}_2\text{--Pd}$) to myrtanal (semicarbazone, m.p. 155°) and by $\text{H}_2\text{--Pt}$ to (III). Interaction of *d*-pinene with Co acetate and O_2 during 24 hr. affords *d*-verbenone (IV) (oxime, m.p. 163° ; semicarbazone, m.p. $206\text{--}207^\circ$), oxidised by KMnO_4 to *d*-pinonic acid, m.p. $130\text{--}131^\circ$. Raman spectra measurements show (I), (II), and (IV) to be different.

J. L. D.

10-Hydroxycamphor and its derivatives. Y. ASAHINA and M. ISHIDATE [with T. SANO] (Ber., 1934, 67, [B], 1202—1204).—*d*-Ketopinonic acid is converted by CH_2N_2 into *Me d*-ketopininate, b.p. $137^\circ/16$ mm., m.p. $45\text{--}46^\circ$ [semicarbazone (I), m.p. 216°]. (I) is transformed by Na-EtOH and subsequent hydrolysis with HCl into *d*-10-hydroxycamphor (II), m.p. 220° , $[\alpha]_D^{25} +48.6^\circ$ in EtOH [semicarbazone (III), m.p. 200° (decomp.); *d*-10-acetoxycamphor, b.p. $148^\circ/16$ mm.]. (II) with $\text{Na}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 affords the corresponding aldehyde, m.p. $210\text{--}213^\circ$, readily oxidised by air. (III) with NaOEt-EtOH at $160\text{--}180^\circ$ gives 10-hydroxycamphor (ω -borneol), m.p. $200\text{--}201^\circ$, $[\alpha]_D \pm 0^\circ$, oxidised to the aldehyde, m.p. $187\text{--}189^\circ$ (semicarbazone, $\text{C}_{11}\text{H}_{19}\text{ON}_3$, m.p. $220\text{--}221^\circ$).

H. W.

Diterpene oxides of the resin of Dacrydium Colensoi. I. J. R. HOSKING and C. W. BRANDT (Ber., 1934, 67, [B], 1173—1177).—Extraction of the wood of *D. Colensoi* with boiling C_6H_6 yields 7% of brown resin containing 10% of acidic products, mainly resin acids, and 90% of neutral material, not volatile with steam. Distillation of the neutral portion under diminished pressure gives manoyl oxide (I), $\text{C}_{20}\text{H}_{34}\text{O}$, b.p. $135\text{--}137^\circ/0.3$ mm., m.p. 29° , $[\alpha]_D^{25} +19.6^\circ$ in abs. EtOH , ketomanoyl oxide (II), $\text{C}_{20}\text{H}_{32}\text{O}_2$, b.p. $174\text{--}178^\circ/0.5$ mm., m.p. $76\text{--}77^\circ$, $[\alpha]_D^{25} +440.4^\circ$ in abs. EtOH , and a trihydroxyditerpene oxide (III), $\text{C}_{20}\text{H}_{32}\text{O}_4$, m.p. $208\text{--}209^\circ$, $[\alpha]_D^{25} -12.5^\circ$ in EtOH . (I) is unsaturated and is hydrogenated (PtO_2 in EtOAc at $15\text{--}20^\circ$ or AcOH at 50°) to dihydromanoyl oxide, b.p. $148^\circ/0.2$ mm., m.p. 19° . (I) does not react with $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, $\text{NHPh}\cdot\text{NH}_2$, or NH_2OH . It cannot be acetylated. OH and OMe are absent. It remains unchanged when heated with Na. (II)

affords an *oxime*, m.p. 146—147°, and a *semicarbazone*, m.p. 135°; it is hydrogenated (PtO₂ in EtOAc) to *dihydroketomanoyl oxide*, m.p. 89—90°. (II) forms the main component of the cryst. deposit found in the wood. (III) contains 3 OH (Zerevitinov) and yields an *Ac₃* derivative. It is hydrogenated (PtO₂ in EtOH and EtOAc) to a *H₂*-derivative, m.p. 211°. H. W.

Hydrogenation of a mixture of two α -ethylenic aldehydes. WIEMANN (Compt. rend., 1934, 198, 2263—2264; cf. A., 1933, 255).—Furfuraldehyde (I) with Zn—Cu—H₂ in AcOH affords some furfuryl alcohol, resins, and products which distil with decomp. Equimol. quantities of (I) and crotonaldehyde give dipropenyl glycol (10%) and *furfurylpropenyl glycol*, b.p. 125°/2.8 mm. (*phenylurethanes*, m.p. 222—223°, and much below 222°, respectively). (I) (3 mols.) and acetaldehyde (4 mols.) afford divinyl glycol (15%) and *furfurylvinyl glycol* (40%), b.p. 115—116°/3 mm. (*phenylurethanes*, m.p. 189° and 116—118°).

Condensations of furan derivatives. III. Condensation of furfuraldehyde with acetone in acid and alkaline media. Determination of small quantities of furfuraldehyde. V. V. TSCHELINCEV and E. K. NIKITIN (Bull. Soc. chim., 1934, [v], 1, 184—189).—The orange colour formed when solutions of furfuraldehyde (I) are condensed with excess of COMe₂ in 50% H₂SO₄ at 50° α concn. of (I), but when condensation is effected with *N*-KOH at 20°, the colour obtained by subsequent addition of 50% H₂SO₄ α [concn.]² of (I). Details of colorimetric methods for the determination of (I) based on these reactions are given, sensitivity being 0.001%.

J. W. B.

strepto- and heterocyclo-Polymethine dyes from furfuraldehyde and their vinylenic homologues. W. KONIG [with K. HEY, F. SCHULZE, E. SILBERKWEIT, and K. TRAUTMANN] (Ber., 1934, 67, [B], 1274—1296).—Azomethine salts could not be obtained from the aldehydes

$\begin{array}{c} \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{CH} - \text{O} \end{array} > \text{C} \cdot [\text{CH} \cdot \text{CH}]_n \cdot \text{CHO}$ (I) ($n=0, 1, 2$, or 3) and *sec.* bases. Addition of HClO₄ to the Schiff's base derived from (I) and primary aromatic amines yields azomethine perchlorates

$\begin{array}{c} \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{CH} - \text{O} \end{array} > \text{C} \cdot [\text{CH} \cdot \text{CH}]_n \cdot \text{CH} \cdot \text{NR} \cdot \text{Ar} \mid \text{X}^-$, the stability of

which increases with increase of n . When $n=1, 2$, and 3, respectively, the colours of the salts are yellow to red, red to bluish-red, and violet or, in solution, orange-yellow, orange-red, and dark ruby-red. *Furfurylidene-p-anisidine*, m.p. 68°, yields a *perchlorate*, m.p. 156°. The azomethine *perchlorates* from 2-*streptovinyl*enefurfuraldehyde (I; $n=1$) and the requisite bases are as follows: from NH₂Ph, m.p. 184°; from *p*-OMe·C₆H₄·NH₂, m.p. 211° (Schiff's base, m.p. 70°); from *p*-OMe·C₆H₄·NHMe, m.p. 191°; from tetrahydroquinoline (II), decomp. 177°; from 2-methyldihydroindole (III), m.p. 223°. From 2-*streptodivinylenefurfuraldehyde* (I; $n=2$) azomethine *perchlorates* are obtained by use of the bases: NH₂Ph, decomp. 167°; *p*-OMe·C₆H₄·NH₂, decomp. 179° (Schiff's base, m.p. 102°); from NHPhMe, m.p. 159°; from *p*-OMe·C₆H₄·NHMe, decomp. 180°; from (II),

m.p. 165°; from tetrahydro-*p*-toluquinoline (IV), m.p. 196°; from thallin, m.p. 191°; from (III), m.p. 199°. From 2-*streptotrivinylenefurfuraldehyde* (I; $n=3$) and *p*-OMe·C₆H₄·NH₂ or (IV) are derived *perchlorates*, m.p. 198° and m.p. 189°, respectively. Treatment of (I) with 2 mols. of a *sec.* amine in little MeOH and with 1 mol. of HClO₄ or HBr in EtOH leads to dyes of the type

$[\text{Ar} \cdot \text{NR} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}(\text{OH}) \cdot [\text{CH} \cdot \text{CH}]_n \cdot \text{CH} \cdot \text{N} \cdot \text{ArR}] \text{X}^-$.

The following compounds, in which $n=0$, are described: Ar=Ph, R=Me, X=ClO₄, m.p. 104°; Ar=

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄, m.p. 159° Ar=

OMe·C₆H₃ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄, indef. m.p.; Ar=

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{N} \end{array} > \text{CHMe}$, X=ClO₄, m.p. 185°; the anhydro-

bases, $\text{O} < \begin{array}{c} \text{CH}(\text{N} \cdot \text{ArR}) - \text{CH} \\ | \quad | \\ \text{C} : \text{CH} \cdot \text{N} \cdot \text{ArR} \end{array} > \text{CH}$ or $\text{O} < \begin{array}{c} \text{CH} \cdot \text{N} \cdot \text{ArR} \\ | \quad | \\ \text{C} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{N} \cdot \text{ArR} \end{array} >$

from (IV) and (III) have m.p. 131° and m.p. 139°, respectively. Analogous compounds in which $n=2$ are

described: Ar=C₆H₄ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$ X=ClO₄, m.p. 141°;

Ar=C₆H₃Me < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄, m.p. 139°; Ar=

OMe·C₆H₅ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄, m.p. 119°; Ar=

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{N} \end{array} > \text{CHMe}$, X=ClO₄, m.p. 149°. Acetyl-

ation of the furfuraldehyde dyes and their vinylenic homologues is effected with warm Ac₂O, with AcCl usually in the cold, less frequently in the warm, or by treatment with Ac₂O or AcCl (BzCl) in C₅H₅N with good cooling, the last-described process being most generally applicable. The following compounds are described derived from

$[\text{Ar} \cdot \text{NH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}(\text{OAc}) \cdot [\text{CH} \cdot \text{CH}]_n \cdot \text{CH} \cdot \text{N} \cdot \text{ArR}] \text{X}^-$:

$n=0$ Ar=Ph, R=Me, X=ClO₄ decomp. 168°; Ar=

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄, decomp. 142°; Ar=

$\text{C} \text{H} \text{Me} < \begin{array}{c} \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$ X=ClO₄, ill-defined m.p.; Ar=

OMe·C₆H₃ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄, ill-defined m.p.; Ar=

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{N} \end{array} > \text{CHMe}$, X=ClO₄, ill-defined m.p.; $n=1$:

Ar=Ph, R=Me, X=ClO₄, decomp. 108°; Ar=Ph,

R=Et, X=ClO₄, m.p. 170°;

Ar=C₆H₄ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄,

decomp. 181°; Ar=OMe·C₆H₄ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄,

decomp. 196° Ar=C₆H₄ < $\begin{array}{c} \text{CH}_2 \\ | \\ \text{N} \end{array} > \text{CHMe}$, X=ClO₄,

decomp. > 200°; Ar=C₆H₄ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=Cl

(Bz in place of Ac); $n=2$: Ar=

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH}_2 \end{array} >$, X=ClO₄, m.p. 175°; Ar=

OMe·C₆H₂ < $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{N} - \text{CH} \end{array} >$, X=ClO₄, m.p. 174° Ar=

$\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ | \\ \text{N} \end{array} > \text{CHMe}$, X=ClO₄, m.p. 185°. The opti-

cal properties of the dyes are described in detail.

W

Dibenzfuran. [Diphenylene oxide.] I. Sulphonation. H. GILMAN, E. W. SMITH, and H. J. OATFIELD. **II. Metalation.** H. GILMAN and R. V. YOUNG (J. Amer. Chem. Soc., 1934, 56, 1412—1414, 1415—1416).—I. Diphenylene oxide (I) and ClSO_3H in CCl_4 at about 25° give the 3-sulphonic acid (II), decomp. $> 300^\circ$ (Ba salt); the *sulphonyl chloride*, m.p. 140° , is reduced (Zn dust, H_2O followed by NaOH and Na_2CO_3) to *Na diphenylene oxide-3-sulphinate*, which with aq. HgCl_2 affords 3-chloromercuridiphenylene oxide (III), m.p. $236.5\text{--}237^\circ$, also obtained from Mg 3-dibenzfuryl bromide and HgCl_2 in Et_2O . (III) is converted (usual methods) into 3-bromo and 3-iodo-diphenylene oxide. Disulphonation (conc. H_2SO_4) of (I) or further sulphonation (conc. H_2SO_4) of (II) gives the 3:6-disulphonic acid; the *disulphonyl chloride*, m.p. 219° , is reduced (as above) to *Na diphenylene oxide-3:6-disulphinate*, which is then converted into 3:6-di(chloromercuri)-, and thence into 3:6-dibromo- and 3:6-di-iodo-diphenylene oxide.

II. $\text{Hg}(\text{OAc})_2$ and (I) at 150° give 1-acetoxy-mercuridiphenylene oxide, m.p. $199\text{--}200^\circ$, converted into 1-chloromercuri-, m.p. $235\text{--}238^\circ$, and 1-iodo-diphenylene oxide, m.p. $71\text{--}72^\circ$ [the Grignard reagent and CO , afford diphenylene oxide-1-carboxylic acid (IV), m.p. $208\text{--}209^\circ$]. (I) with $\text{Et}_2\text{O-LiMe}$, $\text{Na} + \text{HgBu}_2$ in light petroleum, and Na-K alloy in light petroleum gives the 1-Li, 1-Na, and 1-K derivative, respectively; treatment with CO_2 affords (IV) in each case.

H. B.

Natural coumarins. XIII. Synthesis of angelicin (from *Angelica archangelica*). E. SPATH and M. PAILER (Ber., 1934, 67, [B], 1212—1213; cf. this vol., 779).—*Na umbelliferone* is converted by $\text{CH}_2\text{Br-CH}(\text{OEt})_2$ in xylene at $175\text{--}180^\circ$ into angelicin and almost homogeneous umbelliferone Et ether.

H. W.

Synthesis of 7-methoxy-8-isoamylcoumarin (dihydro-osthol). H. L. HALLER and F. ACREE, jun. (J. Amer. Chem. Soc., 1934, 56, 1389—1390).—2:6-Dihydroxyisoamylbenzene (tetrahydrotubanol), malic acid, and conc. H_2SO_4 at $70\text{--}80^\circ$ and then at $130\text{--}140^\circ$ give 7-hydroxy-8-isoamylcoumarin (I), m.p. $104\text{--}106^\circ$, methylated (CH_3N_2) to the *Me ether*, m.p. $104\text{--}106^\circ$ (cf. Spath *et al.*, this vol. 416). Tetrahydrotubal acid similarly affords 7-hydroxy-8-isoamylcoumarin-6-carboxylic acid, m.p. $224\text{--}225^\circ$ (Ac derivative, m.p. $113\text{--}175^\circ$), decarboxylated (Cu-bronze, quinoline) to (I) in poor yield.

H. B.

Synthesis of anthocyanins. R. ROBINSON (Ber., 1934, 67, [A], 85—105).—Mainly a lecture. [With J. RESUGGAN.] The following synthesis of cyanin is cited as an example of successful operation in the absence of protective groups. 3:4-Dihydroxy- β -glucosidoxyacetophenone (I), m.p. 158° , is obtained in 70% yield by hydrolysing its Ac derivative with $\text{Ba}(\text{OH})_2$. O^2 - β -Glucosidyl- (II), m.p. 192° (decomp.) after softening at 170° , and O^2O^4 -di- β -glucosidyl-, m.p. 164° (decomp.), -phloroglucinaldehyde are prepared similarly. A mixture of (I) and (II) is dried at 150° *in vac.* and dissolved in EtOAc containing $\text{Hg}(\text{ClO}_4)_2$. The solution is saturated with HCl and preserved at 0° , thereby giving cyanin chloride.

Synthesis of anthocyanins. XVIII. Cyanidin 3-xyloside and 3:7- and 5:7-diglucosides. R. H. MACDOWELL, R. ROBINSON, and A. R. TODD. **XIX. 5-Glucosidylapigeninidin**, believed to be identical with gesnerin, an anthocyanin of *Gesnera fulgens*. (MRS.) G. M. ROBINSON, R. ROBINSON, and A. R. TODD. **XX. Synthesis of malvidin 3-galactoside and its probable occurrence as a natural anthocyanin.** (MISS) J. C. BELL and R. ROBINSON (J.C.S., 1934, 806—809, 809—812, 813—818).—XVIII. ω -O-Triacetyl- β -xylosidoxy-3:4-diacetoxyacetophenone (I), m.p. 162° , prepared from ω -hydroxy-3:4-diacetoxyacetophenone and triacetyl- α -xylosidyl bromide, with HCl and 2-O-benzoylphloroglucinaldehyde followed by picric acid, gives 3- β -xylosidylcyanidin picrate. The chloride could not be obtained owing to hydrolysis to cyanidin chloride. The xyloside shows similar colour reactions to chrysanthemum. (I) and HCl with 2-O-benzoyl-4-tetra-acetylglucosidylphloroglucinaldehyde affords cyanidin chloride 3-xyloside 7-glucoside ($+3\text{H}_2\text{O}$), whilst ω -O-tetra-acetyl- β -glucosidoxy-3:4-diacetoxyacetophenone similarly yields cyanidin chloride 3:7-di- β -glucoside ($+5.5\text{H}_2\text{O}$). ω -3:4-Trihydroxyacetophenone and 2:4-di-(O-tetra-acetyl- β -glucosidyl)-phloroglucinaldehyde give the flavylium salt, hydrolysed to cyanidin chloride 5:7-di- β -glucoside ($+2\text{H}_2\text{O}$). The 3:7- and 5:7-diglucosides are readily distinguished from cyanin, especially by the colour reactions.

XIX. 2-O-Benzoylphloroglucinaldehyde (II), 4-hydroxyacetophenone, and HCl give benzoylapigeninidin chloride, decomp. 203° , debenzoylated to apigeninidin chloride, identical with the product obtained by demethylation of acacetinidin chloride (cf. Pratt *et al.*, A., 1927, 1083; Asahina and Inibuse, A., 1928, 1256). 2-O-Tetra-acetyl- β -glucosidylphloroglucinaldehyde (III) and 4-hydroxyacetophenone afford 7:4'-dihydroxy-5-O-tetra-acetyl- β -glucosidoxyflavylium chloride ($+2\text{H}_2\text{O}$), hydrolysed to 5- β -glucosidylapigeninidin chloride ($+8\text{H}_2\text{O}$). Acetovanillone and (III) yield 7:4'-dihydroxy-3'-methoxy-5- β -glucosidoxyflavylium chloride (3'-methoxygesnerin chloride) ($+2\text{H}_2\text{O}$), hydrolysed to a diglucoside ($+1.5\text{H}_2\text{O}$), which resembles gesnerin chloride in many of its properties. The second anthocyanin isolated from natural gesnerin is probably 3':5'-dimethoxygesnerin.

XX. ω -Hydroxy-4-acetoxy-3:5-dimethoxyacetophenone, O-tetra-acetyl- α -galactosidyl bromide, and Ag_2O give ω -O-diacetyl- β -galactosidoxy-4-acetoxy-3:5-dimethoxyacetophenone, which with (II) forms a flavylium salt. This salt with picric acid yields 3- β -galactosidylmalvidin picrate ($+2\text{H}_2\text{O}$), which is converted into malvidin chloride 3-galactoside (IV). (IV) behaves similarly to cœnin in colour reaction, but differs in distribution numbers. A re-examination of cyclamin and cœnin has shown them to be identical. Primulin from *P. sinensis* and (IV) are identical. ω -Hydroxy-4-acetoxy-3:5-dimethoxyacetophenone, triacetylxylosidyl bromide, and Ag_2O give ω -O-triacetyl- β -xylosidoxy-4-acetoxy-3:5-dimethoxyacetophenone, which with (II) forms a flavylium salt and 5-O-benzoyl-4'-O-acetylmalvidin chloride. The flavylium salt is hydrolysed to malvidin chloride 3-xyloside, which readily decomposes.

F. R. S.

E. S. CHOTINSKI, B. Z. AMITIN, and D. A. KORNIENKO. (b) Distillation of ammonium mucate. E. S. CHOTINSKI and V. S. BOGOMOLOV (Ukrain. Chem. J., 1933, 8, 297—303, 304—306).—(a) Chiefly pyrrole (I) is obtained by the destructive distillation of NH_4 mucate (II), with pyrrole-2-carboxylamide (III) as a secondary product, whilst with NH_4 mucamate (IV), (III) is the principal product.

(b) The yield of (I) from (II) increases, and that of (III) diminishes, when the distillation is performed rapidly; slow heating has the opposite effect. It follows that (III) is produced from (IV), which is formed from (II) during the reaction. R. T.

1-Phenylpiperidine-4-carboxylic acid. V. PRELOG and V. HANOUSEK (Coll. Czech. Chem. Comm., 1934, 6, 225—230).— α -Dibromopentane- γ -carboxylic acid heated with NH_2Ph gives 1-phenyl-3-(8-phenyl-aminoethyl)pyrrolidone, m.p. 128—129° (hydrobromide, m.p. 182—183°), and the anilide, m.p. 210°, of 1-phenylpiperidine-4-carboxylic acid (I), m.p. 131° [hydrobromide, m.p. 218—219°; picrate, m.p. 207° (decomp.)]. The methiodide, decomp. 180°, of (I) gives a betaine, m.p. 266°, converted by heat into the Me ester, m.p. 46°, of (I). A. A. L.

Synthesis of the two isomeric N-methylconicines. R. LUKES and (MME.) M. SMETACKOVA (Coll. Czech. Chem. Comm., 1934, 6, 231—240).—N-Methylpiperidone with $\text{MgPr}^\beta\text{Br}$ gives 1-methyl-2:2-dipropylpiperidine, b.p. 102—103°/9 mm. [isolated as the picrate, m.p. 163—164°; aurichloride, m.p. 162—164°; platinichloride, m.p. 220—222° (decomp.)], and N-methyl- γ -coniceine, b.p. 182°/760 mm., 72°/10 mm. [hydrochloride (+ H_2O), m.p. 89°; aurichloride, m.p. 80°; perchlorate, m.p. 130—133°; picrate, m.p. 170—171°]. The latter is reduced electrolytically or with H, and colloidal Pd to N-methylconicine (platinichloride, m.p. 197°; picrate, m.p. 112—114°), which is resolved by crystallisation of the H tartrate. The d-base has $[\alpha]_D^{25} +82.4^\circ$ (hydrochloride, m.p. 192—193°, $[\alpha]_D^{25} +27.8^\circ$; hydrobromide of the l-base, m.p. 188—191° $[\alpha]_D^{25} -21.9^\circ$). Physical consts. of the bases are recorded. A. A. L.

Action of Grignard reagents on 4-diphenylpiperidinomethyl ketone and on N-methylcinchotoxine. (Miss) B. R. CARPENTER and E. E. TURNER (J.C.S., 1934, 869—872).— $\text{Ph}_2\text{CH}_2\text{Br}\cdot\text{COBr}$, and AlCl_3 afford 4-diphenyl CH_2Br ketone (I), m.p. 126—127°, which with NPhMe_2 gives phenyl-4-phenylphenacyldimethylammonium bromide, m.p. 144—145°. (I) is also obtained by bromination of 4-diphenyl Me ketone, and is different from 4'-bromo-4-diphenyl Me ketone, m.p. 131°, from AlCl_3 and 4-bromodiphenyl. 4-Diphenyl Pr^β ketone, m.p. 61—62° (lit. 56°; p-nitrophenylhydrazone, m.p. 143—144°), is brominated to the α -Br-compound, m.p. 99—100°, obtained by Friedel-Crafts reaction, whilst the Bu^β ketone, m.p. 77—78° (lit. 63°), gives the α -Br-compound, m.p. 131—132°. 4-Phenylacetyl-4'-acetyldiphenyl has m.p. 118—119°. Ph 4-diphenyl ketone and MgMeI give phenyl-4-diphenylmethylcarbinol, m.p. 102—103°. 4-Diphenyl Me ketone and $\text{MgPr}^\beta\text{I}$ yield 4-diphenylmethylisopropylcarbinol, m.p. 63—64°. $\text{Ph}_2\text{CH}_2\text{Cl}\cdot\text{COCl}$, and AlCl_3 give 4:4'-di(chloroacetyl)diphenyl, m.p. 226—227°, which with $\text{C}_5\text{H}_{11}\text{N}$ gives

4:4'-di(piperidinoacetyl)diphenyl, m.p. 143—144°. 4-Diphenylpiperidinomethyl ketone, m.p. 93—94° (methiodide, m.p. 184—185°), obtained from the bromomethyl ketone, with MgMeI affords 4-diphenylmethylpiperidinomethylcarbinol, m.p. 89—90° (methiodide, m.p. 186—187°). N-Methylcinchotoxine does not react with MgPhBr or MgMeI , and hence tends to avoid the ketonic structure. F. R. S.

3-Quinolylazo-2:6-diaminopyridine and its derivatives. M. M. KATZNELSON and I. L. KNUNIANZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 415—418).—Diazotisation of 8-aminoquinoline and coupling with 2:6-diaminopyridine (I) yields 3-(8'-quinolylazo)-2:6-diaminopyridine, m.p. 191—193° (hydrochloride), unaccompanied by any bisazo-compound. 3-(6'-Methoxy-8'-quinolylazo)-2:6-diaminopyridine, m.p. 168°, is similarly obtained from 8-amino-6-methoxyquinoline and (I). H. N. R.

Substituted amides of pyridinecarboxylic acids. E. GRYSZKIEWICZ-TROCHIMOWSKI (Arch. Chem. Farm., 1934, 1, 65—71).—Nicotinoyl chloride condenses with 2-aminopyridine in C_6H_6 in presence of $\text{C}_5\text{H}_5\text{N}$ to yield the 2-pyridylamide, m.p. 138—139°, with d-2-aminocamphor in Et_2O to yield the d-2-camphorylamide, m.p. 144—145°, and with d-bornylethylamine (without solvent) to afford the 2-d-N-ethyl-bornylamide, m.p. 89—90°, of nicotinic acid. The bis-N-diethylamide of pyridine-2:6-dicarboxylic acid, m.p. 122—123°, is prepared from NHET_2 and isocinchomeronyl chloride. R. T.

Ease of formation of cyclic imines. II. G. SALOMON (Helv. Chim. Acta, 1934, 17, 851—862).—Conditions favourable for the synthesis of poly-membered cyclic imines are examined in connexion with possible side changes which are detected by kinetic measurements. The velocity coeffs. of the formation of hexamethylenimine (I) have been measured between 37° and 58° and the proportion of multimol. reactions calc. from the relationship of rate of reaction to initial concn. Undisturbed ring closure occurs in $\times 0.005M$ solution. Examination of the readiness of formation of hexadecamethyleneimine in alkaline BuOH is complicated by the side changes caused by an involved relationship to p_H in these media. Comparison of the heats of activation and reaction consts. of the formation of (I) and $[\text{CH}_2]_2\text{NH}$ shows that the poor yields frequently observed in the synthesis of (I) are due essentially to the insolubility of $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\cdot\text{NH}_2$ in H_2O , and not to smaller ease of formation. The readiness of production of cyclic imines in solution depends mainly on the spatial structure of the rings and the thermodynamically caused, chemical relationship between halogenoalkylamine and solvent. H. n.

Poly-membered heterocyclic compounds. III. Preparation of hexamethyleneimine and hexadecamethyleneimine from the aliphatic bromamines. L. RUZICKA, G. SALOMON, and K. MEYER (Helv. Chim. Acta, 1934, 17, 882—886).— $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HBr}$ and NaOH in much at 50° and then at 80° yield hexamethylenimine, 1:130°/723 mm., in 50% yield.

[With M. HURBIN.] α -Dibromohexadecane at 1

o -C₆H₄(CO)₂NK at 170—180° give *phthal- π -bromohexadecylimide*, m.p. 74°, hydrolysed to *π -bromohexadecylamine hydrobromide* (I), m.p. 165°. In H₂O, (I) does not appear to yield hexadecamethyleneimine (*picrolonate*, m.p. 208—210°), which is obtained by means of NaOH in BuOH. These and other polymembered, cyclic imines have the characteristic odour of musk.

H. W.

Synthesis of isatin. M. DOMINIKIEWICZ and M. KLEWSKA (Arch. Chem. Farm., 1934, 1, 71—81).—In the Sandmeyer synthesis of isatin from NPh·C(S·NHR) (R=*p*-tolyl and 1-C₁₀H₇), of the two possible isomerides of the nitriles only NPh·C(CN)·NHR is obtained, and of the thioamides (I) only NPh·C(CS·NH₂)·NHR, whilst when R=*p*-C₆H₄Br the corresponding compounds are NPh·C(CN)·N·C₆H₄Br and NPh·C(CS·NH₂)·N·C₆H₄Br (II). (I) yield the anils of 4-methyl- and 1:2-benzo-isatin on heating with H₂SO₄, whilst (II) affords the *p*-bromoanil of isatin. The substance NPh·C(CS·NH₂)·NH·C₁₀H₇, m.p. 122—123°, is prepared by heating the corresponding nitrile with NH₄ polysulphide at 32° (96 hr.).

R. T.

Condensation of 2-chlorolepidine with anthranilic acid. P. K. BOSE (Current Sci., 1934, 2, 430—431).—Previous views (A., 1932, 66) of the mechanism of the condensation are maintained.

L. S. T.

Syntheses in the hydroaromatic series. XX. Addition of acetylenedicarboxylic esters to hydrazobenzene. O. DIELS and J. REESE (Annalen, 1934, 511, 168—182).—[NHPH₂ (I) and [C·CO₂Me]₂ (II) in boiling MeOH afford the adduct (III), CO₂Me·C(NHPH·NHPH)·CH·CO₂Me, m.p. 138°, which passes in hot AcOH containing dil. HNO₃ into benzidine nitrate and *Me* 1:2-diphenylpyrazol-5-one-3-carboxylate (IV), m.p. 137—138°, obtained directly from (I) and (II) in warm AcOH. Treatment of (III) with KOH·MeOH at 100° leads to 1:2-diphenylpyrazol-5-one-3-carboxylic acid (V), decomp. about 205°. Condensation of (I) with Et₂C₂O₄ at 140° and hydrolysis of the product gives (V), transformed by boiling Ac₂O into 1:2-diphenylpyrazol-5-one, m.p. 130°. In boiling xylene (III) is converted into *Me*₂ indole-2:3-dicarboxylate, m.p. 114°, hydrolysed by boiling conc. HCl to *Me* *H* indole-2:3-dicarboxylate, m.p. 256°, and transformed by 30% KOH into indole-2-carboxylic acid, m.p. 203—204° (*Me* ester, m.p. 152°), which loses CO₂ above its m.p. and gives indole. When heated above its m.p. or in boiling C₆H₅N or NPhMe₂, (III) passes into *Me* 3-anilino-2-hydroxyquinoline-4-carboxylate, m.p. 224—225° (*Ac* derivative, m.p. 276°), hydrolysed by 20% KOH to 3-anilino-2-hydroxyquinoline-4-carboxylic acid (VI), m.p. 257° (*Ac* derivative, m.p. >345°), which gives 3-anilino-2-hydroxyquinoline (VII), m.p. 219—220° (*Ac* derivative, m.p. 272°), when heated. (VI) or (VII) is converted by prolonged boiling with conc. HCl·AcOH into 2:3-dihydroxyquinoline, m.p. 258° (*Ac* derivative, m.p. 214°).

H. W.

Nitration of aryloxy-2- and -4-methylquinolines. **Synthesis of substances having possible antimalarial action.** (Miss) R. M. MURRAY and E. E. TURNER (J.C.S., 1934, 856—860)—KOPh and

2-chloro-4-methylquinoline at 190° give 2-phenoxy-4-methylquinoline, m.p. 51° [*methiodide*, m.p. 220° (decomp.); stable to piperidine (I) at 195°], which with HNO₃ (*d* 1.5) and AcOH at 50° gives 2-(4'-nitrophenoxy)-4-methylquinoline, m.p. 140—141° (corr.) [gives with (I) at 170—180° 2-hydroxy-4-methylquinoline and *p*-nitrophenylpiperidine], reduced by Fe·EtOH·HCl to the 4'-NH₂-compound, m.p. 135° (acetylacetone anil, m.p. 109°, hydrolysed by conc. H₂SO₄ at 100°). *m*-NO₂·C₆H₄·OK and 2-chlorolepidine (II) yield 2-(3'-nitrophenoxy)-4-methylquinoline, m.p. 152°, reduced to the 3'-NH₂-compound, m.p. 170—171° [acetylacetone anil, m.p. 81°, gives with H₂SO₄ at 100° 5- or 7-(4'-methyl-2'-quinolinoxy)-2:4-dimethylquinoline, m.p. 173°]. 2-*p*-Tolyloxy-4-methylquinoline (III), m.p. 60°, similarly prepared [*methiodide*, m.p. 197—198° (decomp.)], with KNO₃·H₂SO₄ at <−5° gives the 3'-NO₂-derivative (IV), m.p. 121°, also obtained from 2-nitro-*p*-cresol and (II), stable to (I) at 160°; the 2'-NO₂-derivative, m.p. 148° (prepared from 3-nitro-*p*-cresol) [gives a gum with (I) at 160°], with HNO₃ (*d* 1.5) at 60—70° gives the 2':5'-(NO₂)₂-derivative, m.p. 186°, reduced to the 2':5'-(NH₂)₂-derivative, m.p. 204°. (IV) is reduced to the 3'-NH₂-derivative, m.p. 174°, the acetylacetone anil of which, m.p. 139—140°, is hydrolysed by H₂SO₄. (III) with HNO₃ under certain conditions gives 2-(2':3':5'[?]-trinitro-4'-methylphenoxy)-4-methylquinoline, m.p. 315°. Quinol Me ether leads to 2-(4'-methoxyphenoxy)-4-methylquinoline, m.p. 103° (corr.) [*methiodide*, m.p. 182° (decomp.; corr.)], the 3'-NO₂-derivative, m.p. 112—113° (corr.), of which is reduced to the 3'-NH₂-derivative, m.p. 138—139° (corr.) (*salicylidene* derivative, m.p. 127—128°; acetylacetone anil, m.p. 115—116°, hydrolysed by H₂SO₄), and with NH₃·EtOH at 170—180° affords the 3'-nitro-4'-amino-compound, m.p. 156°. Similarly are obtained 2-(4'-ethoxyphenoxy)-4-methylquinoline, m.p. 90—91° [*methiodide*, m.p. 185—186° (decomp.) after sintering at 130—131°], 4-phenoxy-2-methylquinoline (VI), m.p. 73° [*methiodide*, m.p. 210° (decomp.); 4'-NO₂, m.p. 177° [reacts normally with (I) at 170—180°], and 4'-NH₂-derivative, m.p. 168°], the 3'-NO₂-derivative of (VI) (from *m*-NO₂·C₆H₄·OH), m.p. 135—136°, and the corresponding 3'-NH₂-compound, m.p. 101—102°, the acetylacetone anil of which gives 5- or 7-(2'-methyl-4'-quinolinoxy)-2:4-dimethylquinoline, m.p. 194—195°; 4-*p*-tolyloxy-2-methylquinoline, m.p. 89—90° [*methiodide*, m.p. 207—208° (decomp.) after sintering at 204°; 3'-, m.p. 163°, and 2'-NO₂, m.p. 134—135°, and 3'-NH₂-derivative, m.p. 98—99°], 4-(4'-methoxyphenoxy)-2-methylquinoline, m.p. 168° [*methiodide*, m.p. 225—226° (decomp.) after sintering at 223°; 3'-NO₂, m.p. 205—206°, and 3'-NH₂-derivative, m.p. 171—172°].

R. S. C.

Structure and synthesis of new anti-malarials.

I. Plasmoquin. **III. Atebrin.**—See B., 1934, 650.

Nitro- and amino-derivatives of acridone. N. S. DROZDOV and S. S. DROZDOV (J. Gen. Chem. Russ., 1934, 4, 1—8).—2-Nitro- and 2-amino-acridone are obtained in good yield by heating the corresponding substituted diphenylaminocarboxylic acids or their salts with POCl₃. 2:4-Dinitrodiphenylamine-

2'-carboxylic acid (I) yields similarly 2:4-dinitro-acridone, whilst its K salt affords the acid chloride of (I), together with its *lactam*, m.p. 224°. R. T.

Monochloroacridine and acridone. N. S. DROZDOV (J. Gen. Chem. Russ., 1934, 4, 117—119).—Acridone is obtained by heating diphenylamine-2-carboxylic acid in xylene with the theoretical amount of POCl₃, in presence of a 300% excess of which the product is chloroacridine. R. T.

Preparation of cystinehydantoin. W. C. HESS (J. Amer. Chem. Soc., 1934, 56, 1421).—Cystine (I) and KNCO in dil. HCl give *cystinehydantoin*, C₈H₁₀O₄N₄S₂, decomp. from 310°, which is readily decomposed by alkalis, gives a negative Sullivan reaction for (I), and behaves as (I) in the Okuda (A., 1926, 190) and Folin-Marenzi (A., 1929, 1093) methods of determination of (I). H. B.

5-β-Ethyl-substituted derivatives of barbituric acid. E. F. ROSENBERG, R. F. KNEELAND, and G. S. SKINNER (J. Amer. Chem. Soc., 1934, 56, 1339—1340).—*Et n-butyl-β-bromoethyl-* (I), b.p. 127—128°/0.5 mm., and *isoamyl-β-bromoethyl-* (II), b.p. 145—147°/2 mm., *-malonates* are prepared from CNaR(CO₂Et)₂ and (CH₂Br)₂ in Et₂O or C₆H₆; *Et isoamyl-β-chloroethylmalonate* (III), b.p. 132°/1 mm., is similarly obtained using CH₂Cl·CH₂I. *Et isoamyl-β-dimethylaminoethyl-*, b.p. 152—154°/10 mm. (*hydrochloride*, m.p. 78°) [from (III) and EtOH·NHMe₂ at 100°], *isoamyl-β-diethylaminoethyl-*, b.p. 141°/1 mm. [from (II) and EtOH·NHMe₂ at 100°], and *n-butyl-β-dimethylaminoethyl-malonate*, b.p. 115°/3 mm. [*hydrochloride*, m.p. 137—138° (corr.)] [from (I) and EtOH·NHMe₂ at room temp.], are described. *5-n-Butyl-α-β-dimethylaminoethyl-*, m.p. 118—119° [*hydrochloride*, m.p. 244—245° (corr.)], and *5-isoamyl-α-β-dimethylaminoethyl-barbituric acid*, m.p. 115—116° (sealed tube) [*hydrochloride*, m.p. 277—280° (sealed tube)], are prepared by a slight modification of the usual procedure. When (II) is distilled slowly at about 20 mm., *α-carbethoxy-α-isoamyl-γ-butyrolactone*, b.p. 165—166.5°/18 mm., is formed; with CO(NH₂)₂ and EtOH·NaOEt, this gives *α-isoamyl-5-β-hydroxy-ethylbarbituric acid*, m.p. 177.5—178° (corr.).

H. B.

Enolisation of ψ-uric acid. H. BILTZ and L. LOEWE (Ber., 1934, 67, [B], 1199—1202).—Treatment of ψ-uric acid (I) or its 1-Me ether (II) with CH₂N₂ leads to the *Me ether of enol-1:3-dimethyl-ψ-uric acid*, decomp. 210° after reddening and softening at about 200°, converted by conc. HCl at 100° into 1:3-dimethyluric acid. (II) and CHMeN₂ give the *Et ether of enol-methyl-ψ-uric acid*, m.p. 205° (decomp.), or, if reaction is prolonged, the *Et ether of enol-methyl-ethyl-ψ-uric acid*, m.p. 230° after reddening at 210°, decomp. 232—234°. Reasons are advanced for considering that the conversion of (I) into uric acid does not proceed through the enols. H. W.

Mono-N-arylpiperazines and their derivatives. V. PRELOG and Z. BLÁZEK (Coll. Czech. Chem. Comm., 1934, 6, 211—224).—The following are obtained by methods previously described (this vol., 196; in some cases MeOH is replaced by Bu^oOH): the *monohydrobromides* of *N-p-bromo-*, m.p. 239° (decomp.) {base,

m.p. 98.5° [*Ac derivative*, m.p. 129°, and its *hydrochloride*, m.p. 215—220° (decomp.)]} (yield 52%), *-m-*, m.p. 255°, and *-p-nitro-* (I), m.p. > 290° (*dihydrobromide*, m.p. > 290°; *base*, m.p. 135°), *-o-* (II), m.p. 242.5° (yield 90%), and *-p-hydroxy-phenyl-* (III), m.p. 219° (yield 70%), *-p-tolyl-*, m.p. 242° (*base*, m.p. 32—33°, b.p. 112°/1 mm.) (yield 85%), *-α-*, m.p. > 290° (*hydrochloride*), and *-β-naphthyl-piperazine*, decomp. 280° (*base*, m.p. 78°), *Et p-piperazinebenzoate*, m.p. 188.5° (*hydrobromide* of acid, m.p. > 300°), *ββ'-di-o-*, m.p. 188—189° (yield 12%), and *-p-toluidino-*, m.p. 245° (yield 6%), and *-α-naphthylamino-diethylamine*, m.p. 216—217° (yield 8.5%); and the *dihydrobromides* of *N-o-*, m.p. > 290°, and *-m-amino-phenyl-*, decomp. 305° (*base*, m.p. 179—180°), and *-o-tolyl-piperazine*, m.p. 278° (yield 40%), and *-p-phenylenedipiperazine*, m.p. > 300° (*tetrahydrobromide*, m.p. > 300°; colour reaction described) (I) is reduced to the *dihydrobromide*, m.p. > 290°, of the NH₂-compound, m.p. 126° (colour reaction described). Hydrolysis of (II) and (III) with 48% HBr gives the *dihydrobromides* of *N-o-*, m.p. 289—290° (decomp.), and *-p-hydroxyphenylpiperazine*, decomp. 275°. A. A. L.

Uranyl [antipyrine and piperazine] salts—See this vol., 855.

Pyrimidines. CXLII. Acetylation of 2-keto-tetra- and -hexa-hydropyrimidines. K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1934, 56, 1374—1377).—*Et 2-keto-4-phenyl-6-methyl-1:2:3:4-tetrahydropyrimidine-5-carboxylate* (I) is acetylated (Ac₂O) to (probably) the 1-*Ac derivative*, m.p. 175.5—177° (not obtainable from NHAc·CO·NH₂, PhCHO, and CH₂Ac·CO₂Et), which is readily hydrolysed (EtOH·HCl) to (I) and is converted by POCl₃ into (I). *Et 2-keto-4-phenyl-1:6- and -3:6-dimethyl-1:2:3:4-tetrahydropyrimidine-5-carboxylate* similarly afford the 3-*Ac*, m.p. 108—109.5°, and 1-*Ac*, m.p. 164.5—166°, derivative, respectively, showing that both the 1- and 3-NH groups are sufficiently basic for reaction. The increased basicity of *Et 2-keto-4-phenyl-6-methylhexahydropyrimidine-5-carboxylate* is manifested by its (partial) solubility in dil. HCl and the formation of its 1:3-*Ac₂ derivative*, m.p. 101.5—102.5°. *2-Keto-5-phenyl-4-benzyl-1:2:3:4-tetrahydropyrimidine* also gives the 1:3-*Ac₂ derivative*, m.p. 104.5—105°; the increased basicity is ascribed to the absence of a 6-substituent and the displacement of Ph at C₄. *2-Keto-4:6-diphenyl-4-methyl-1:2:3:4-tetrahydropyrimidine* (II) (A., 1933, 1059) affords (probably) the 3-*Ac derivative*, m.p. 182—183°, thus favouring the constitution assigned (*loc. cit.*) to (II). H.

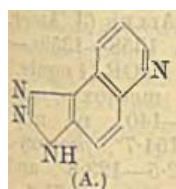
Change of 2:4:6-trinitrobenzylideneaniline into an indazolone derivative. S. SECAREANU and I. LUPAS (Bull. Soc. chim., 1933, [iv], 1436—1442).—2:4:6-Trinitrobenzylideneaniline and Na₂CO₃ in hot EtOH give 4:6-dinitro-*N-oxy-2-phenyl-indazolone*, C₆H₂(NO₂)₂ < $\begin{matrix} \text{C(OH)} \\ \text{NO} \end{matrix}$ > NPh, m.p. 252 [Na salt, m.p. about 240° (decomp.)], the *Ag salt*, decomp. about 250°, of which with EtI gives the corresponding 3-ethoxy-compound, m.p. 148°.

Isomerism of 4:6-dinitrobenzylideneaniline. S. SECAREANU and I. LUPAS (Bull. Soc. chim., 1934, [v], 1, 373—380).—2:4-(NO₂)₂C₆H₃N:CHPh with Na₂CO₃ in boiling EtOH affords 6-nitro-3-hydroxy-2-phenylindazole, m.p. about 260° (Ac derivative, m.p. 190—191°; Bz derivative, m.p. 171°), together with 6-nitro-3-hydroxy-2-phenylindazole 1-oxide, m.p. 166—167° (Ag salt; OEt-derivative, m.p. 64—65°), but less easily than does the corresponding 2:4:6-(NO₂)₃-compound (cf. preceding abstract). o-NO₂·C₆H₄·N:CHPh does not undergo similar rearrangements. J. L. D.

Vasicin and peganin. K. S. NARANG and J. N. RAY (Current Sci., 1934, 2, 388—390).—Evidence against the identity of vasicin and peganin and against the structure given by Spath and Nikatwitz (this vol., 310) to the latter is discussed. L. S. T.

2:4:6-Trinitrobenzylideneaniline. S. SECAREANU and I. LUPAS (J. pr. Chem., 1934, [ii], 140, 90—96).—Extension of the previously described reaction (this vol., 308) to the 2:4:6-trinitrobenzylidene derivatives of *m*-NO₂·C₆H₄·NH₂, m.p. 160—161°, *o*-, m.p. 143°, and *p*-NH₂·C₆H₄·CO₂H, m.p. 204° (lit. 147°), and *p*-NH₂·C₆H₄·OEt, affords the following 4:6-dinitro-2-hydroxy-1:3-diaryl(R)benztriazolines: R = *m*-C₆H₄·NO₂, m.p. 263°, *o*-, m.p. > 280°, and *p*-C₆H₄·CO₂H, m.p. > 340°, *p*-C₆H₄·OEt, m.p. 197°, and CH₂Ph, m.p. 224° [no (NO₂)₃-benzylidene derivative obtained], together, in the last case, with a substance, C₂₀H₂₄O₉N₈, m.p. > 300° (structures suggested). Their more strongly basic character prevents the similar reaction with alkyamines. J. W. B.

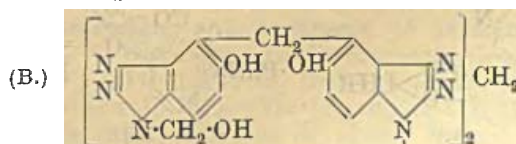
Azimido- and N-methylazimido-benzene derivatives. K. FRIES, H. GUTERBOCK, and H. KUHN (Annalen, 1934, 511, 213—240).—5-Amino-1:2:3-benztriazole (I) [by reduction of the 5-NO₂-compound with H₂-Ni-Co-Cu at 80°/80 atm.; Ac₂ (II), m.p. 184°, and Ac, m.p. 240°, derivatives; benzeneazo-compound, m.p. 207° (Ac derivative, m.p. 243°)] is converted by the Skraup synthesis into 5:6-triazolo-



quinoline (A), m.p. 260°, and by diazotisation into 5-hydroxy-1:2:3-benztriazole (III), m.p. 228° (decomp.) [Ac₂ derivative (IV), sinters 115°, m.p. 127°], which with Br-AcOH affords its 4-Br-derivative, m.p. 230° (decomp.), converted by AcOH-HNO₃ (d 1.51)

into 4-nitro-5-hydroxy-1:2:3-benztriazole, m.p. 236° (decomp.). With Cl₂ (II) in AcOH-NaOAc gives the 5-Ac derivative, m.p. 281° (decomp.), of 4-chloro-5-amino-1:2:3-benztriazole, m.p. 218°, obtained by aq. EtOH-HCl hydrolysis. (III) in AcOH with Cl₂ affords its 4-Cl-derivative (V), m.p. 246° (decomp.), further converted by Cl₂ in AcOH-NaOAc at 0° into 4:4-dichloro-5-keto-4:5-dihydro-1:2:3-benztriazole, m.p. 132° (decomp.) (hydrochloride, decomp. 72°), reduced by SnCl₂-AcOH to (V). With NaNO₂-H₂SO₄ at 0° (III) gives its 4-NO-derivative, explodes > 360°, reduced (SnCl₂-HCl) to the 4-NH₂-compound, m.p. 217° (decomp.). Diazotisation of 6-amino-1-methyl-1:2:3-benztriazole (Brady *et al.*, A. 1931, 239; best obtained by catalytic reduction of the 6-NO₂-compound) affords the 6-OH-derivative

(VI), m.p. 151°, which condenses with 40% CH₂O in EtOH-NaOAc to di-(6-hydroxy-1-methyl-1:2:3-benztriazole-7-methane, sinters 230°, m.p. 242° (Ac₂ derivative, m.p. 236°). With Br-AcOH (VI) gives its 7-Br-derivative, m.p. 159°, converted by CHCl₃-HNO₃ (d 1.52), through the nitro-bromo-ketone, into 6:7-diketo-, decomp. > 100°, and by Br-AcOH-NaOAc into 7:7-dibromo-6-keto- (VII), m.p. 117—119°, -1-methyl-6:7-dihydro-1:2:3-benztriazole. (VII) is converted by heating in AcOH—few drops conc. HCl into 5:7-dibromo-6-hydroxy-1-methyl-1:2:3-benztriazole, m.p. 222° (decomp.). With H₂SO₄-HNO₃ (d 1.4) at < 30°, 1:2:3-benztriazole (VIII) gives its 4-NO₂-derivative (IX) (Borsche *et al.*, A., 1911, i, 329), reduced (H₂-Ni-Co-Cu at 100°/80 atm.) to the 4-NH₂-compound (X), m.p. 149° [Ac, m.p. 241°, and Ac₂, m.p. 174°, derivatives; benzeneazo-compound, m.p. 244° (Ac₂ derivative, m.p. 284°)], converted by diazotisation into the 4-OH-compound, m.p. 216°, which with Br-AcOH affords its 5:7-Br₂-derivative, explodes when heated. Passage of Cl₂ into (X) in AcOH-fuming HCl and subsequent reduction (SnCl₂-AcOH) of the ketochloride gives 5:6:7-trichloro-4-hydroxy-1:2:3-benztriazole, decomp. > 280°, converted by HNO₃ (d 1.4) into 6:7-dichloro-4:5-diketo-4:5-dihydro-1:2:3-benztriazole. With HNO₃-H₂SO₄ 1-methyl-1:2:3-benztriazole gives its 7-NO₂-derivative (XI), m.p. 203°, the isomeric 4-NO₂-derivative, sinters 163°, m.p. 173°, being obtained by Me₂SO₄ from the tautomeric (IX). Catalytic reduction of (XI) gives the corresponding 7-NH₂-compound, m.p. 121° [4-benzeneazo-compound, m.p. 246° (Ac derivative, m.p. 223°), and, under certain coupling conditions, its 4-(1'-methyl-1':2':3'-benztriazole-4'-)azo-compound, m.p. 291°]. The corresponding 4-amino-1-methyl derivative with Cl₂ in AcOH-conc. HCl affords 4:4:5:6:6-pentachloro-7-keto-1-methyl-4:5:6:7-tetrahydro-, m.p. 176° (decomp.), reduced (SnCl₂-AcOH) to 4:6-dichloro-7-hydroxy-1-methyl-, m.p. 273° (decomp.), converted by HNO₃ (d 1.4) into 4-chloro-6:7-diketo-1-methyl-6:7-dihydro-, m.p. 187—188°, which with boiling EtOH-NH₂Ph gives 4-anilo-6-hydroxy-7-keto-1-methyl-4:7-dihydro-, m.p. 219—221°, -1:2:3-benztriazole. In EtOH-NaOAc, or 2N-HCl, (VIII) condenses with 40% CH₂O to give its 1-hydroxymethyl derivative, m.p. 148° (decomp.) [5-NO₂-derivative, m.p. 133—136° (decomp.), obtained similarly], (III) similarly giving its 1-hydroxymethyl derivative, m.p. 187° (decomp.) [giving (IV) with AcCl-C₅H₅N-CHCl₃], isomerised by 2N-NaOH to the 4-hydroxymethyl derivative, explodes on heating (Ac₂ derivative, m.p. 135°), but when condensation is effected in EtOH-aq. NaOH, the 1:4-di(hydroxymethyl) derivative, decomp. 327°, is obtained, whereas in 2N-NaOH the product is di-(5-hydroxy-1-hydroxymethyl-1:2:3-benztriazole-4-methane, decomp. 316—317° (Ac₄ derivative, m.p. 202°),



converted by long boiling with H₂O into the compound C₂₅H₂₄O₆N₁₂, darkens 280°, decomp. 360° (Ac-

Pr^i , Bu^i , *n*- and *iso*-amyl, hexyl, Ph, $p\text{-OH}\cdot\text{C}_6\text{H}_4$, and $\text{C}_2\text{H}_4\text{Ph}$ ethers were unsuccessful. H. B.

Chlorophyll-b. H. FISCHER and S. BREITNER (Annalen, 1934, 511, 183—202).—Rhodin-*g*-oxime (I) is smoothly converted by $\text{Na}_2\text{CO}_3\text{-C}_5\text{H}_5\text{N}$ into pyrophæophorbide-*b*-oxime (II) and, similarly, rhodin-*g* ester into pyrophæophorbide-*b* (III) thus establishing the presence of the isocyclic ring in chlorophyll-*b* and of $\text{N}\cdot\text{OH}$ in the same positions in (I) and (II). Rhodinporphyrin-*g* Me. ester is transformed by AcOH-HBr at 45–50° into phæoporphyrin-*b*₄ (Me ester, m.p. 262°). Rhodinporphyrin-*g* is converted by protracted heating with HCO_2H into rhodinporphyrin-*g*₅ (IV) (Me ester, $\text{C}_{35}\text{H}_{38}\text{O}_5\text{N}_4$, m.p. 264°). Energetic degradation of (IV) with alkali leads to phyllo- and rhodo-porphyrin. The oxime of (IV) has m.p. 263°. Rhodin-*g* and HCO_2H at 80° give *neorhodinporphyrin-g*₃ (V), $\text{C}_{32}\text{H}_{32}\text{O}_3\text{N}_4$ (Me ester, m.p. 243°, and its oxime, m.p. 245°), and a substance converted by CH_2N_2 into the Me ester $\text{C}_{33}\text{H}_{36}\text{O}_4\text{N}_4$, m.p. 239° (oxime, m.p. 255°). Boiling 20% HCl transforms (V) into a compound (Me ester $\text{C}_{33}\text{H}_{36}\text{O}_4\text{N}_4$, m.p. 232°). Subjection of the Fe salt of (V) to the keto-

MANN (Helv. Chim. Acta, 1934, 17, 837—851).—Methylphæophorbide-*a*-oxime (I) in $\text{C}_5\text{H}_5\text{N}$ is converted by short treatment with boiling KOH-MeOH into *pyrophæophorbin-a-oxime* (II), m.p. > 280°, which very closely resembles (I) in colour and absorption spectrum. (II) is readily transformed by HCl-MeOH at room temp. into the Me ester, softens at 310° (corr.), and is hydrolysed by HCl containing Et_2O to *pyrophæophorbin-a*, $\text{C}_{33}\text{H}_{36}\text{O}_3\text{N}_4$, m.p. 235° (corr.). Similarly, methylphæophorbide-*b*-dioxime (III) is hydrolysed by alkali to *pyrophæophorbin-b-dioxime* (IV), the colour and spectrum of which in $\text{Et}_2\text{O-C}_5\text{H}_5\text{N}$ are closely similar to those of (III). With cold HCl-MeOH (IV) yields the Me₂ ether, softens at 315° (corr.), and is transformed by $\text{HCl-Et}_2\text{O}$ into *pyrophæophorbin-b-monoxime* (II) [Me ester, m.p. (indef.) 207° (corr.)]. Protracted acid hydrolysis of (IV) leads to *pyrophæophorbin-b*, which closely resembles phæophorbide-*b* in colour and spectrum. H. W.

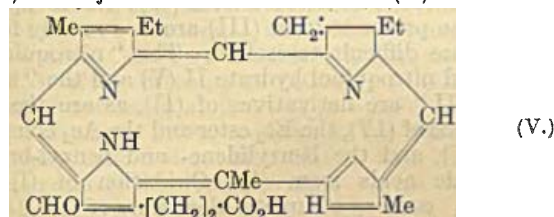
Bile pigments. VI. Biliverdin, uteroverdin, and oocyan. R. LEMBERG (Biochem. J., 1934, 28, 978—987; cf. A., 1932, 627, 1266).—Improved preps. are described for biliverdin (I), mesobiliverdin (II), and their Me₂ esters. (I) forms the first (green) stage of the Gmelin reaction. The formula $\text{C}_{33}\text{H}_{34}\text{O}_6\text{N}_4$ for (I) is confirmed. The Me₂ ester of (I) crystallises in two forms, one from prep. of pure bilirubin (III) and the other from natural (I) (oocyan and uteroverdin) and from (III) mother-liquors. Crystallographic investigation shows that the two forms are not structurally different substances. Cryst. *monochlorides* are obtained from (I) (green needles), (II) (green needles), (I) Me₂ ester and (II) Me₂ ester (m.p. 175—176°, sinters). The ester of (II) gives complex salts with Zn and Cu, the Zn salt lacking the typical fluorescence of pyrrole pigment Zn complexes. A formula for (I) is suggested. C. G. A.

Alkaloids of Anabasis aphylla. VIII. Products of the oxidation of anabesine. G. MENSCHIKOV, M. LOSSIK, and A. OREKHOV (Ber., 1934, 67, [B], 1157—1158).—Benzoylanabesine in boiling H_2O is oxidised by KMnO_4 to δ -benzamido- δ -3-pyridyl-*n*-valeric acid (I), m.p. 145—146°, $[\alpha]_D^{20} \pm 0^\circ$, hydrolysed by 12*N*- HCl to δ -amino- δ -3-pyridyl-*n*-valeric acid dihydrochloride (II), m.p. 172°, which gives the corresponding lactam (III), $\text{C}_{10}\text{H}_{12}\text{ON}_2$, m.p. 147—147.5°, when heated at 160°. The physiological activity of (I), (II), or (III) is < that of anabesine. H. W.

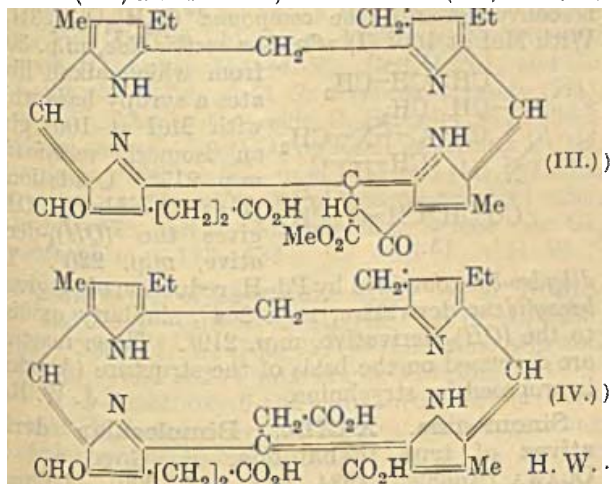
[Yohimbine.] G. BARGER (Ber., 1934, 67, [B], 1124—1125).—A comment on the publication of Hahn *et al.* (this vol., 667). H. W.

[Yohimbine.] G. HAHN (Ber., 1934, 67, [B], 1211).—A reply to Barger (see above). H. W.

Constitution and synthesis of salsoline. E. SPATH, A. OREKHOV, and F. KUFFNER (Ber., 1934, 67, [B], 1214—1217; cf. Orekhov *et al.*, A., 1933, 727; this vol., 787).—The identity of *ON*-dimethylsalsoline with carnegine is placed beyond doubt. *iso*Vanillin, CH_2PhCl , and KOH in boiling EtOH afford *isovanillin benzyl ether*, m.p. 62—63°, transformed by MeNO_2 and KOH in EtOH at 0—10° into



reaction gives a new porphyrin (Me₂ ester $\text{C}_{34}\text{H}_{36}\text{O}_4\text{N}_4$, m.p. 205°), which does not contain CO. The presence of CH is established by its production from rhodin-*g*, its catalytic reduction to phylloporphyrin, and its oxidation to citraconimide, thus indicating the structure given for (V). Rhodin-*g* Me₃ ester and $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ give a product which is hydrolysed and re-esterified (CH_2N_2) to a Me₂ tetracarboxylate 231°, in which CO is intact. Since (I) reacts similarly, the CH_2 group is involved. Under like conditions, *neorhodinporphyrin-g*₃ Me ester and $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ afford the Me ester $\text{C}_{36}\text{H}_{38}\text{O}_5\text{N}_4$, m.p. 230°. (III) and rhodin-*g* are therefore (III) and (VI).



Chlorophyll. VIII. Pyrophæophorbins-a and -b and their oximes. A. STOLL and E. WIEDE-

α -nitro- β -3-benzoyloxy-4-methoxyphenylethylene (I), m.p. 129—130°. (I) is reduced by Zn dust and AcOH in EtOH to 3-benzoyloxy-4-methoxyphenylacetaldoxime, m.p. 120—122°, converted by Na-Hg in AcOH-EtOH into β -3-benzoyloxy-4-methoxyphenylethylamine, m.p. 43—44° (picrate, m.p. 144—146°). The Ac derivative, m.p. 128—128.5°, of the base is transformed by P_2O_5 in boiling PhMe and subsequent reduction with Sn and HCl into 6-hydroxy-7-methoxy-1-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 223—224° (vac.), identical with natural salsoline. In like sequence vanillin benzyl ether is transformed successively into α -nitro- β -4-benzoyloxy-3-methoxyphenylethylene, m.p. 122—123°, 4-benzoyloxy-3-methoxyphenylacetaldoxime, β -4-benzoyloxy-3-methoxyphenylethylamine, m.p. 68—70° [picrate, m.p. 174—176° (vac.)]; Bz derivative, m.p. 134—135°, acet- β -4-benzoyloxy-3-methoxyphenylethylamide, m.p. 116—117°, and 7-hydroxy-6-methoxy-1-methyl-1:2:3:4-tetrahydroisoquinoline, m.p. 174—176° (vac.). H. W.

Rotatory dispersion of the quinine salts of the Codex. E. CANALS, M. MOUSSERON, and S. PERROTET (J. Pharm. Chim., 1934, [viii], 19, 578—589).— $[\alpha]_{570}^{20}$, $[\alpha]_{561}^{20}$, and are tabulated for the basic valerate, hydrobromide, hydrochloride, and formate and the neutral sulphate, hydrobromide, and hydrochloride of quinine. The val. of $[\alpha]$ depends mainly on the p_H of the solution; this also influences the rotatory dispersion, which conforms to Drude's expression. H. N. R.

Separation of *d*- and *dl*-lupanines. J. F. COUCH (J. Amer. Chem. Soc., 1934, 56, 1423—1424).—The mixture, b.p. 220—226°/12 mm., m.p. 67—81° (softens at 40°), $[\alpha]_D^{20} +32.02^\circ$ in EtOH, of *d*- (I) and *dl*- (II) -lupanine, obtained from white lupin seeds, is extracted four times with warm light petroleum. Recrystallisation of the insol. material from COMe₂ gives (II). Crude (I), obtained by cooling the extract, is purified through the *d*-camphorsulphonate and hydroiodide. H. B.

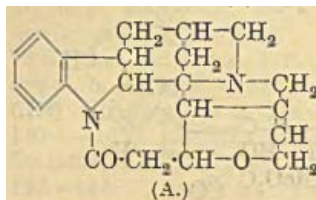
Alkaloids of *Convolvulus pseudocantabricus*. II. A. OREKHOV and R. KONOVALOVA (Ber., 1934, 67, [B], 1153—1156).—The crushed seeds are moistened with 25% NH₃ and percolated with C₆H₆. The solution is extracted with 10% HCl which is made alkaline with NH₃ and extracted with CHCl₃. The dried extract is evaporated and the residual crude alkaloids are transformed into their hydrochlorides, which are separated by 96% EtOH into (mainly) convolvine hydrochloride and convolvamine hydrochloride, m.p. 237—239°. Convolvamine (I), C₁₇H₂₃O₄N, has m.p. 114—115°, $[\alpha]_D^{20} \pm 0^\circ$ [picrate, m.p. 263—264° (decomp.)]; platinichloride, m.p. 216—217°; aurichloride, m.p. 201—202°; methiodide, m.p. 257—259°. (I) is hydrolysed by boiling KOH-EtOH to 3:4-(OMe)₂C₆H₃-CO₂H (II) and tropine (III) and hence is veratroyltropeine. Its synthesis from veratroyl chloride and (III) in boiling PhMe is recorded. Convolvine is also an alkamine ester and affords (II) when hydrolysed. H. W.

Ring closure of (–)-norprotolaudanosine to (–)-tetrahydroprotoberberine and configuration of bases of the type of tetrahydroberberine. W. LIETHE (Ber., 1934, 67, [B], 1261—1263).—*dl*-1-

Benzyltetrahydroisoquinoline is resolved into its optical antipodes by NH₄ *d*- α -bromocamphor- π -sulphonate in very dil. AcOH. (–)-1-Benzyltetrahydroisoquinoline (I) has $[\alpha]_D^{20} -72^\circ$ in C₆H₆, -44° in MeOH (*d*- α -bromocamphor- π -sulphonate, m.p. 173°; hydrochloride, m.p. 192°, $[\alpha]_D^{20} -45^\circ$ in H₂O). (I) is converted by successive action of HCO₂H at 200° and P₂O₅ in boiling tetrahydronaphthalene into (–)-tetrahydroprotoberberine. The steric relationship of bases of the type of tetrahydroberberine to laudanoline is thus established and the validity of the optical methods of determining configuration of this class of substances is confirmed. H. W.

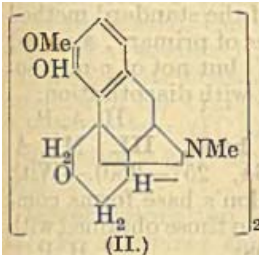
Strychnos alkaloids. LXXX. So-called "brucinesulphonic acid II." H. LEUCHS (Ber., 1934, 67, [B], 1082—1085).—Specimens of brucinesulphonic acid II (I), forming apparently homogeneous, rectangular leaflets, when treated with boiling 80% EtOH yield brucinesulphonic acid IV (II) in 40% yield, and a mixture of (II) and brucinesulphonic acid III (III) gives the crystals of (I). Re-examination of the products obtained from (I) proves them to be derived from (II); this is expected, since the products from (III) are less readily formed and more difficult to isolate. The "nitroquinone" (IV) and nitroquinol hydrate II (V) and the "aminoquinol II" are derivatives of (II), as are the semicarbazone of (IV), the Et₃ ester and the Ac₃ compound from (V), and the benzylidene- and benzyl-brucinesulphonic acids from (I). Oxidation of (I) with KMnO₄ causes complete decomp. of (II), while leaving (III) intact. H. W.

Strychnine. II. Constitution of strychnine and of Tafel's base. M. KOTAKE and T. MITSUWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 119—134).—Tafel's base C₂₄H₃₀O₃N₂ (I), m.p. 156° [benzylidene derivative (II), m.p. 168°], obtained from methylstrychnine and NaOEt-EtOH, and the similar base C₂₃H₂₅O₃N₂ (III) (benzylidene derivative, m.p. 210°) formed when NaOMe-MeOH is used, with 6*N*-HCl on a H₂O-bath afford the same compound C₂₂H₂₅O₂N₂Cl.H₂O (IV), m.p. 265—268°, and with 6*N*-HNO₃, (I) gives the compound C₂₂H₂₃O₄N₂, m.p. 212—213°. With conc. KOH (IV) is converted into the compound C₂₂H₂₄O₃N₂.3H₂O. With MeI at 100° (I) affords a methiodide, m.p. 304°, from which alkali liberates a syrupy base which with MeI at 100° gives an isomeric methiodide, m.p. 217°. Oxidation of (II) with KMnO₄-COMe₂ gives the (OH)₄-derivative, m.p. 226°. The dihydro-base obtained by Pd-H₂ reduction of (I) gives benzylidene derivative, m.p. 204°, similarly oxidised to the (OH)₂-derivative, m.p. 219°. These reactions are discussed on the basis of the structure (A) which is proposed for strychnine. J. W.



Sinomenine. XXXIX. Bimolecular derivatives of true thebaine. K. GOTO and T. OGAWA (Annalen, 1934, 511, 202—209).—1-Bromothebaine, m.p. 196°, $[\alpha]_D^{20} -52.0^\circ$ in EtOH (from thebaine), $[\alpha]_D^{20} -53.7^\circ$ (from codeine) is obtained

by the action of Br on thebainone (I) in AcOH. The *methiodide*, m.p. 200° (decomp.), and *oxime*, m.p. 235° (decomp.) (*hydrochloride*, m.p. 261°), are described. Pschorr's "S-free ketone," $[\alpha]_D^{25} -45.7^\circ$



in EtOH, or Schopf's "true thebainone," $[\alpha]_D^{25} -46.5^\circ$ in EtOH, is reduced by Na-Hg to *di-8:8'-dihydrothebainone* (II), m.p. 303°, $[\alpha]_D^{25} +15.9^\circ$ in MeOH-CHCl₃ [*methiodide*, m.p. 310° (decomp.); non-cryst. *semicarbazone*, m.p. 283° (decomp.)]. Admixture with an equal amount of its optical antipode affords *dl-di-8:8'-dihydrothebainone*, m.p. 307°. (I) is transformed by AuCl₃ in dil. HCl into *di-1:1'-thebainone* (II), decomp. (indef.) 265° after softening at 210°, $[\alpha]_D^{25} -219.8^\circ$ in MeOH-CHCl₃ [*hydrochloride*, m.p. 295°; *methiodide*, m.p. 250° (decomp.); non-cryst. *oxime*, decomp. > 298°]. *Di-1:1'-dihydrothebainone*, large prisms, m.p. 235°, or short prisms, m.p. 258°, $[\alpha]_D^{25} -159.8^\circ$ in EtOH, is obtained by hydrogenation (Pd) of (II) or by oxidation of dihydrothebainone with AgNO₃; the *methiodide*, m.p. 278° (decomp.), and *oxime*, decomp. 287°, are described. *Di-1:1'-demethoxydihydrosinomenine*, m.p. 255° after softening at 210° or (+COMe₂) m.p. 235° after softening at 200°, $[\alpha]_D^{25} +158.5^\circ$ in EtOH (*methiodide*, m.p. 278°), is obtained by treatment of tetrahydrosinomenine with NaOH and Na-Hg or of demethoxydihydrosinomenine with AgNO₃. *dl-Di-1:1'-dihydrothebainone* has m.p. 334°.

H. W.

Organic compounds of germanium. III. H. BAUER and K. BURSCHKIES (Ber., 1934, 67, [B], 1041—1045; cf. A., 1933, 1062).—Prolonged interaction of MgPhBr and GeCl₄ in Et₂O-C₆H₆ leads to GePh₄, m.p. 229—230°, and Ge₂Ph₆ (I), m.p. 336—337°, whilst less highly phenylated compounds cannot be isolated. (I) is also obtained from MgPhBr and GeBr₄ if the reaction is protracted (cf. Morgan *et al.*, A., 1925, i, 1197). Similarly *p*-C₆H₄Me-MgBr and GeCl₄ afford Ge(*p*-C₆H₄Me)₄, m.p. 226°, and *germanium hexa-p-tolyl*, m.p. 345°, obtained in better yield from *p*-C₆H₄MeBr, Na, and GeCl₄ in boiling Et₂O. GeCl₄ and CH₃Ph-MgCl in Et₂O-C₆H₆ give Ge(CH₂Ph)₄, m.p. 110°, and *Ge tribenzyl chloride* (II), m.p. 154—155°. Ge(CH₂Ph)₄ and Br in boiling C₂H₄Br₂ yield *Ge tribenzyl bromide* (III), m.p. 145°, whence the *oxide*, C₄₂H₄₂OGe₂, m.p. 134—135°, by means of AgNO₃ or KOH in boiling EtOH, *fluoride*, m.p. 96°, *iodide*, m.p. 141°, and (II). (III) is converted by MgEtI in Et₂O into *Ge tribenzyl ethyl*, m.p. 56—57°, and by Na in boiling xylene into *Ge₂ hexabenzyl*, m.p. 183—184°.

H. W.

Mercuration of hemipinic acid. V. M. RODIONOV and T. A. ABLETZOVA (Ukrain. Chem. J., 1933, 8, 322—332; cf. A., 1933, 729).—Hemipinic acid and Hg(OAc)₂ yield a 2:1 mixture of 3:4-dimethoxy-2- and 2:3-dimethoxy-6-anhydrohydroxymercuribenzic acid (I), together with *o*-veratric acid, originating from the hydrolysis of (I).

R. T.

Preparation of mixed organo-magnesium compounds. V. GRIGNARD (Compt. rend., 1934,

198, 2217—2220).—Grignard's method (this vol., 327) gives better results than that of Urien (*ibid.*, 640) as regards the ease of formation of organo-Mg compounds from bromoveratrole, *p*-C₆H₄Br₂, *p*-C₆H₄Br-CH₂Br, and C₆BrMe₅. Both methods give the same yield with C₆Me₅-CH₂Br because the Br is labile. Double decomp. (cf. A., 1932, 41) is insufficient to explain these reactions.

J. L. D.

Aromatic organo-zinc compounds. K. A. KOZESCHKOV, A. N. NESMEJANOV, and V. I. POTROSOV (Ber., 1934, 67, [B], 1138—1142).—The following compounds are obtained by heating the requisite Hg diaryl with Zn wool in xylene in CO₂. The liquid is decanted from pptd. Hg and cooled, when the Zn diaryl separates and is preserved in CO₂: ZnPh₂, m.p. 107°; Zn *di-p-fluorophenyl*, m.p. 135—136°; Zn *di-p-chlorophenyl*, m.p. 212—214°, which does not increase in wt. when covered with Et₂O which is allowed to evaporate and affords Sn(C₆H₄Cl)₄, m.p. 200°, when treated with SnBr₄ in boiling xylene; Zn *di-o-tolyl*, m.p. 207—210°; Zn *di-p-dimethylaminophenyl*, m.p. 135—137°; Zn *di-β-naphthyl*, m.p. 184—186°. Under similar conditions, Zn and Hg(α-C₁₀H₇)₂ do not appear to interact. Reaction between Zn and Hg(*p*-C₆H₄Br)₂ does not occur appreciably in boiling xylene, whereas at 220—230° complex change takes place without yielding organo-Zn compounds, which, similarly, are not obtained from Hg(*p*-C₆H₄I)₂ at 200—250°. Zn and Hg(C₆H₄·CO₂Et-*p*)₂ do not react at 200—210°. Zn and Hg(CH₂Ph)₂ in boiling xylene or at 110° afford [CH₂Ph]₂.

H. W.

Titration curves of proteins.—See this vol., 842.

Salting-out of amino-acids from protein hydrolysates. I. Isolation of tyrosine, leucine, and methionine. E. M. HILL and W. ROBSON (Biochem. J., 1934, 28, 1008—1013).—A simple procedure is described for the isolation from caseinogen hydrolysates (I), and from ovalbumin, of tyrosine (II), methionine (III), and leucine (IV). The yields of (II) and (III) compare favourably with those obtained by other methods. (II) slowly separates when an aq. solution of the residue from the evaporation of (I) is brought to *p*_H 2.4 by addition of NaOH and decolorised by C. The mother-liquor after separation of (II) is brought to *p*_H 6.0 and evaporated until NaCl begins to separate; (III) and (IV) also separate on cooling and float near the surface. (III) is separated from (IV) by formation of an insol. Hg complex (V) with Hg(OAc)₂ in 3% AcOH. To obtain max. pptn. of (V), saturated NaCl solution must later be added. (V) is decomposed by H₂S, and the liberated (III) is isolated by evaporation and crystallising from EtOH-C₅H₅N at *p*_H 6.0. (IV) can readily be isolated after removal of Hg from the filtrate from (V). Curves are given showing the solubility of (III) in H₂O and in saturated aq. NaCl; the latter does not exhibit dissymmetry as does the corresponding curve for (IV). The isoelectric point of (III) is at *p*_H 6.

A. E. O.

Autoclave splitting of blood albumin with 2% phosphoric acid. V. S. SADIKOV and D. P. MALIUGA (Compt. rend. Accad. Sci. U.R.S.S., 1934, 2, 418—421).—H₃PO₄ has a weaker effect on

albumin than have other mineral acids, 6 hr. in an autoclave at 180° being necessary with 2% acid. Treatment of 1500 g. of white blood albumin yielded 30 g. of a substance (I), $C_{17}H_{29}O_3N_3$, m.p. (recryst.) 271.5°; it is optically inactive and contains no NH_2 or CO_2H groups. Hydrolysis with conc. HCl yields 2 mols. of leucine and 1 mol. of proline. (I) is represented as $OH \cdot C \cdot NH \cdot C(CH_2Pr^{\beta}) \cdot C(OH) \cdot N \cdot CH_2 > CH_2$.
 $C(CH_2Pr^{\beta}) \cdot NH \cdot C(OH) = C \cdot CH_2 > CH_2$.

H. N. R.

Simplified Dennstedt method of elementary analysis without the secondary oxygen supply. E. YAMAGUCHI (J. Soc. Chem. Ind. Japan, 1934, 34, 206B).—2—8 mg. of substance are gently heated in a stream of O_2 . Combustion occurs on a Pt tube filled with Pt wire contained in a SiO_2 tube.

R. S. B.

Chromic acid method for determining organic carbon. J. W. WHITE and F. J. HOLBEN (J. Assoc. Off. Agric. Chem., 1934, 17, 334—336).—Improvements of the original method (A., 1925, ii, 240) are described.

E. C. S.

Determination of sulphur in organic compounds by oxidation with perchloric acid. E. KAHANE and M. KAHANE (Bull. Soc. chim., 1934, [v], 1, 280—290).—The substance (0.1—0.2 g.) is heated with 0.5 c.c. of 10% aq. I_2O_5 and 2 c.c. of a mixture of $HClO_4$ (d 1.61, 2 parts) and HNO_3 (d 1.39, 1 part). Any escaping H_2S is trapped in bulbs containing some of the I_2O_5 solution. The oxidised residue and the contents of the bulbs are combined, evaporated to fuming, reduced with $N_2H_4 \cdot 2HCl$, and S is determined as $BaSO_4$.

D. R. D.

Micro-volumetric determination of sulphur and chlorine in organic compounds with the use of an assay balance. D. W. COWIE and D. T. GIBSON (Analyst, 1934, 59, 388—391).—Improvements in Pregl's method for determining S, and modifications enabling simultaneous determination of halogens to be made, are described.

E. C. S.

Determination of arsenic in organic compounds. E. KAHANE (Bull. Soc. chim., 1934, [v], 1, 190—198).—The substance (0.3—0.4 g.) is oxidised with 5 c.c. of a mixture of H_2SO_4 (d 1.81, 7 parts), $HClO_4$ (d 1.61, 2 parts), and HNO_3 (d 1.39, 1 part). After oxidation the liquid is evaporated to fuming, and contains the As as arsenate which is determined by standard processes.

D. R. D.

Colorimetric method for the determination of N-acetylglucosamine and N-acetylchondrosamine. W. T. J. MORGAN and L. A. ELSON (Biochem. J., 1934, 28, 988—995).—The method of Zuckerkandl and Messiner-Klebermass (A., 1931, 1081) is modified by the use of 0.5N- Na_2CO_3 and a glacial AcOH solution of $p-NMe_2 \cdot C_6H_4 \cdot CHO$ to give an accuracy of 1—2%.

C. G. A.

Determination of aromatic amines. I. Use of potassium bromide in [nitrite] titration. S. UENO and H. SEKIGUCHI. II. Determination of mixed primary, sec., and tert. arylamines. S. UENO, S. KANESAKA, and H. SEKIGUCHI (J. Soc. Chem. Ind. Japan, 1934, 37, 235—236B, 236—237B).—

NH_2Ph , the toluidines, aminophenols, and their ethers, are rapidly and accurately determined by titration with $NaNO_2$ in acid solution in presence of KBr.

II. The above modification of the standard method is equally applicable to mixtures of primary, sec., and tert. arylamines, formation of *N*- but not of *p*-nitrosoamine being accelerated equally with diazotisation.

H. A. P.

Behaviour of Millon's base. III. M. A. SCHWARZ (Gazzetta, 1934, 64, 257—260).—With $CHPhCl_2$ and with $CPhCl_3$ Millon's base forms compounds analogous, respectively, to those obtained with $BzCl$ and CH_2PhCl (A., 1931, 808).

T. H. P.

Tetrachlorophthalimide as a reagent in qualitative organic analysis. C. G. F. ALLEN and R. V. V. NICHOLLS (J. Amer. Chem. Soc., 1934, 56, 1409—1410).—Tetrachlorophthalimide, m.p. 336—337° [from $C_6Cl_4(CO)_2O$ and $(NH_4)_2CO_3$], and $MeOH-KOH$ in dioxan give the K derivative (I) [the Na derivative, prepared similarly, is less reactive than (I)], which reacts with alkyl halides and halogeno-esters, -ketones, -ethers, and -hydriens at 200° (in sealed tube if b.p. of halide is < 140°) to give cryst. *N*-substituted derivatives. The following are described: *Me* (II), m.p. 210—211°; *Et*, m.p. 192—193°; *Bu*, m.p. 153—154°; *n*-, m.p. 145—146°, and *iso*-, m.p. 170—171°; *-amyl*; *n-hexyl*, m.p. 150—151°; *n-heptyl*, m.p. 145—146°; *n-hexadecyl*, m.p. 129—130°; *carbo-n-butoxy*, m.p. 151—152°; *carbomethoxymethyl* (III), m.p. 180—181°; *carbo-n-butoxymethyl*, m.p. 116—117°; *α-carbomethoxyethyl*, m.p. 165—166°; *α-carbomethoxyethyl*, m.p. 159—160°; *α-carbomethoxypropyl*, m.p. 116—117°; *α-carbomethoxy-n-butyl*, m.p. 113—114°; *α-carbomethoxy-n-amyl*, m.p. 122—123°; *β-acetoxyethyl*, m.p. 168—169°; *β-hydroxyethyl*, m.p. 208—209°; *β-phenoxyethyl*, m.p. 155—156°; *γ-hydroxypropyl*, m.p. 165—166°; *γ-bromopropyl*, m.p. 164—165°; *γ-cyanopropyl*, m.p. 194—195°; *phenacyl*, m.p. 258—259°; *β-benzoylethyl*, m.p. 205—206°. $CBr(CO_2Me)_3$ and $CHBr(CO_2Et)_2$ give (II) and (III), respectively; *Ph γ-chloropropyl ketone* (2:4-dinitrophenylhydrazones, m.p. 167°) is converted into benzoylcyclopropane.

H. B.

Determination of dihydrocholesterol in presence of coprosterol.—See this vol., 929.

Sensitive and specific reaction for ergosterol. J. BRUCKNER (Biochem. Z., 1934, 270, 346—348).—Ergosterol (I) is dissolved in 2 c.c. of C_6H_6 or $CHCl_3$ and 1 c.c. of Ac_2O , 0.5 c.c. of $COMe_2$, a crystal of $Cu(OAc)_2$, and then 0.5—1 g. of anhyd. $ZnCl_2$ are added. A bluish-violet solution with strong red fluorescence and a characteristic absorption band at 612 $m\mu$ is obtained, the reaction being still positive when 1 c.c. of C_6H_6 contains 0.0006 mg. of (I). Vitamin-D (II) under the same conditions gives a reddish-brown solution also showing characteristic absorption. (II) can be detected in irradiated (I) this reaction.

P. W.

Truhaut's colour reaction for uric acid. P. K. BOSE (Current Sci., 1934, 2, 427).—*o*- $C_6H_4(NO_2)_2$ (I), but not pure *m*- $C_6H_4(NO_2)_2$ (II), produces a violet colour with NaOH and small amounts of uric acid (III).

(II) used by Truhaut (A., 1933, 1314) in testing for (III) probably contained (I), which gave the colour.

L. S. T.

Detection of smallest quantities of nicotine. A. WENUSCH (Z. Unters. Lebensm., 1934, 67, 601—605).—A procedure is described for the isolation of nicotine and its identification by means of tests for the presence of the C_5H_5N nucleus; the absence of the C_4H_4N nucleus (I) before, and its presence after, dehydration; and the presence of a NMe group on (I).

E. C. S.

Green coloration of solutions of quinine salts. II. M. BACHSTEEZ and G. CAVALLINI (Annali Chim. Appl., 1934, 24, 266—270; cf. this vol., 88).—The Cu content of quinine salt solutions, which under certain conditions makes them green, may be determined photometrically by means of diphenylthiocarbazone, without previous incineration. Usually $4-5 \times 10^{-6}$ g.

of Cu per g. is present. The occasional yellow colour of the solutions containing Cu is due to incomplete oxidation caused by lack of O_2 .

T. H. P.

Gravimetric and volumetric determination of brucine and strychnine as dichromate. I. M. KOLTHOFF and J. J. LINGANE (J. Amer. Pharm. Assoc., 1934, 23, 404—408).—Brucine (I) and strychnine (II) salts yield ppts. with $K_2Cr_2O_7$, which after drying over deliquescent NaBr have the respective compositions $(C_{23}H_{26}O_4N_2)_2 \cdot H_2Cr_2O_7 \cdot 5H_2O$ and $(C_{21}H_{22}O_2N_2)_2 \cdot H_2Cr_2O_7 \cdot H_2O$. (I) and (II) may be detected in concns. $> 0.02\%$ by this method, which is suitable for their gravimetric determination. A volumetric method is also described, the EtOH-washed ppt. being dissolved in excess of $0.1N\text{-}Fe^{++}$ solution, and back-titrated with $0.1N\text{-}K_2Cr_2O_7$. Results for (I) are slightly low, owing to slight oxidation of (I) by $K_2Cr_2O_7$ even in presence of Fe^{++} .

A. E. O.

Biochemistry.

Oxygen saturation curves of blood. W. HEROLD (Z. physikal. Chem., 1934, 168, 227—231).—Assuming that the degree of aggregation of the haemoglobin, α , is uniform in the blood of animals of a particular species, but varies from species to species, and that the heat of binding of an O_2 mol. is const. and independent of the no. of mols. already bound by the complex, an equation is obtained which agrees satisfactorily with many existing data for O_2 and CO absorption curves below about 37° at CO_2 pressures below about 40 mm. The logarithm of the half-saturation pressure is a linear function of $1/\text{temp.}$ α represents the adjustment of the O_2 absorption to the needs of the particular organism.

R. C.

Gas and electrolyte equilibria in blood. XVIII. Solubility and physical state of atmospheric nitrogen in blood-cells and -plasma. D. D. VAN SLYKE, R. T. DILLON, and R. MARGARIA. XIX. Solubility and physical state of uncombined oxygen in blood. J. SENDROY, jun., R. T. DILLON, and D. D. VAN SLYKE (J. Biol. Chem., 1934, 105, 571—596, 597—632).—XVIII. The solubility coeffs. (I) of N_2 at 38° in plasma and cells are 0.0117 and 0.0146, whereas the val. for whole blood depends on the haemoglobin (II) content and in normal cases is $1-2\% >$ in H_2O . Dissolved (II) takes up approx. 1.3 times as much N_2 as H_2O , and the lipins also dissolve measurable amounts which, in non-lipæmic blood, is $1-2\%$. There is no evidence of adsorption

(II), as the N_2 taken up follows Henry's law.

XIX. (I) of O_2 at 38° are: H_2O 0.02323, plasma 0.0209, cells 0.0260, whole blood 0.0230. (II) takes up approx. 1.2 times as much O_2 as does H_2O , and in the whole blood this balances the depressing effect due to dissolved salts and inert protein. When formation of oxyhaemoglobin is prevented, dissolution follows Henry's law.

H. G. R.

Biochemistry of respiratory pigments. J. Roche (Bull. Soc. Chim. biol., 1934, 16, 793—821).—A lecture.

Oxygen to iron ratio in oxychlorocruorin and the total quantity of oxygen carried by the pigment in Spirographis. H. M. FOX (Proc. Roy. Soc., 1934, B, 115, 368—373).—One mol. of labile O_2 corresponds with one atom of Fe. Large variations were noted in the vals. for chlorocruorin-Fe per g. of worm.

H. G. R.

Blood-serum as a haemoglobin-destroying agent. L. DOLJANSKI and O. KOCH (Virchow's Arch., 1933, 291, 401—409).—Blood-serum of man, rabbit, and fowl can convert haemoglobin into methaemoglobin and also split off the haem part of the mol.

NUTR. ABS. (b)

Elimination of iron from blood-pigment and haematin by means of sulphurous acid and action of light. R. ZEYNEK and S. KITTEL (Z. physiol. Chem., 1934, 224, 233—243).—Haematin and haemochromogen are not affected by SO_2 in the dark, but in the light lose Fe and yield substances resembling haematoporphyrin (I), but differing from Nencki's (I) in S content and solubility. Nencki's (I) is similarly affected, so that (I) may be the first product. Blood-pigments similarly lose Fe, but give porphyrin-proteoses of varying protein content (40—60%). The sensitisation of white mice by these light- SO_2 products differs little from that obtained with Nencki's (I).

J. H. B.

Oxidation and phosphorylation in haemolysed horse blood-corpuscles. J. RUNNSTRÖM, A. LENNERSTRAND, and H. BOREI (Biochem. Z., 1934, 271, 15—21; cf. Warburg and Christian, A., 1932, 74).—Cozymase (I) from yeast greatly accelerates the oxidation of hexose-mono- and -di-phosphoric acid in haemolysed horse-blood corpuscles in presence of PO_4^{+++} buffer and methylene-blue (II), the degree of acceleration depending on the activity of (I) and the condition of the blood. When there is weakening or insufficiency of respiratory co-enzyme (I) acts as substitute. Adenylpyrophosphoric acid (III) sometimes acts like (I), but less effectively. During the

accelerated oxidation inorg. P enters into org. combination, but this does not occur if (II) is absent, and dephosphorylation, retarded by (I), takes place. The phosphorylation is inhibited by $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$, but not by NaF . The decomp. of added (III) is also retarded by (I). Ascorbic acid does not act like (I).

W. McC.

Physico-chemical correlations in the blood and criteria for application to clinical study. M. SIGON (Arch. Ist. Biochim. Ital., 1934, 6, 195—242).—Theoretical.

R. N. C.

Mechanism of methylene-blue action on blood. M. M. BROOKS (Science, 1934, 80, 15—16).—A discussion.

L. S. T.

Physical properties of blood-serum. M. DOLADILHE (Compt. rend., 1934, 198, 1884—1886).—The pptn. of globulin (I) in serum occurs over a zone of p_H with a max. of total pptn. at a definite p_H (II) depending on the degree of dilution. (II) increases with increasing dilution. Heating, by increasing the dispersive power of the albumin, restricts the pptn. zone of (I).

C. G. A.

Mol. wt. of the globulins of blood-serum. A. ROCHE and J. BRACCO (Compt. rend., 1934, 199, 98—99).—The mol. wts. (cf. A., 1925, ii, 965) of the serum-globulins of the horse and man are 150,000 and 130,000, respectively. Incubation of horse serum at 0° and 37° during 1—2 months changes the mol. wt. to 136,000 and 226,000, respectively (cf. this vol., 93). The val. for antidiphtheria serum is 213,000.

J. L. D.

Nephelometric determination of the protein fractions of blood-plasma with the step photometer. A. KORANYI and E. B. HATZ (Z. anal. Chem., 1934, 97, 266—270).—Total proteins in 1 c.c. of plasma (8 c.c. of blood + 2 c.c. of isotonic Na citrate) are coagulated by 50 c.c. of acid $(\text{NH}_4)_2\text{SO}_4$ (I) [1 vol. saturated aq. (I) + 1 vol. 0.2N-HCl]. Globulin + fibrinogen are pptd. from 1 c.c. by 25 c.c. of half-saturated (I), fibrinogen alone by a solution of 27 vols. of saturated (I) + 73 vols. H_2O . The turbidities produced are determined nephelometrically.

J. S. A.

Solubility of serum-proteins in concentrated solutions of neutral salts. A. BONOT (J. Chim. phys., 1934, 31, 301—325).—The solubilities of albumin and pseudo-globulin of ox-serum in aq. $(\text{NH}_4)_2\text{SO}_4$ have been determined by Sorensen's proportionality method. The limiting solubilities of the different fractions of serum-albumin obtained by pptn. indicate that the protein is a heterogeneous system of which the components are homeomeric. The solubility of a heterogeneous protein may be represented by a modification of Cohn's formula. The structure of the protein micelle is discussed.

M. S. B.

Absolute colorimetry. X. Determination of bilirubin in serum. A. THIEL and O. PETER (Biochem. Z., 1934, 271, 1—8; cf. A., 1933, 1134).—Bilirubin (< 1 unit upwards) is directly determined as azo-derivative by the abs. colorimetric method.

W. McC.

Changes in the calcium and magnesium of the serum and in the inorganic phosphorus of the

blood of cows at calving and of the calf during early life. W. M. ALLCROFT and W. GODDEN (Biochem. J., 1934, 28, 1004—1007; cf. A., 1932, 1272).—Serum-Mg (I) tends to increase just before, at, or within 24 hr. of calving, and in general varies inversely with serum-Ca (II). Calves at birth and for the first 8 weeks of life show higher levels of (II) and blood-inorg. P than the normals for the dam. (I) is < normal at birth, but has attained this normal after 3 weeks.

A. E. O.

Changes in the p_H of the blood of the Japanese beetle (*Popillia japonica*, Newman) during metamorphosis. D. LUDWIG (Anat. Rec., 1933, 57, No. 4, Suppl., 55—56).—During metamorphosis the p_H of the blood changes from an average of 7.07 in the third instar to 6.79 in the late prepupa, whilst pupation is marked by a return to p_H 6.94. The increase of acidity during the prepupal stage probably depends on the autolysis of larval tissues.

NUTR. ABS. (b).

Determination of p_H of plasma using the hydrogen electrode. J. LOISELEUR (Bull. Soc. Chim. biol., 1934, 15, 612—617).—Some modifications of the apparatus of du Noüy (A., 1932, 135) permit the p_H determination to be made in 20 min. with an accuracy of 0.01.

A. L.

Blood-sugar and -lactic acid during perfusion of the spleen. N. FIESSINGER, H. BENARD, R. CATTAN, and M. HERBAIN (Compt. rend. Soc. Biol., 1933, 114, 479—481).—Perfusion of the spleen with oxalated or defibrinated blood caused a fall in blood-sugar (I), accompanied by a rise in -lactic acid (II). No proportionality existed, however, between the decrease in (I) and the (II) formed. The living cells, supplied by partly oxygenated blood, probably accelerate one or other of two reactions, anaerobic [producing (II)] and aerobic [destroying (II)].

NUTR. ABS. (b)

Effect of iodoacetic acid and other substances on the disappearance of glucose from shed blood. D. M. MOWAT and C. P. STEWART (Biochem. J., 1934, 28, 774—778).— $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ (I) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ prevent glycolysis in shed human blood, the requisite concn. in each case being much > that required for (I) to prevent lactic acid formation in cardiac muscle. $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, $\text{CHMeI}\cdot\text{CO}_2\text{H}$, and $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{OH}$ (II) have similar though weaker actions, but $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is inactive. The action of (I) but not of (II) is inhibited by glutathione (III), and (II) does not react with (III) to produce HI. It thus appears that the action of (II) on glycolysis is different from that of (I). Both (I) and (II) inhibit the action of blood-phosphatase.

W. O.

Antiricin. R. GRUTZNER (Biochem. Z., 1934, 244, 32—53; cf. A., 1931, 507).—Dried sterile sera containing antiricin slowly lose their activity on O_2 keeping, but activity is completely restored by CO_2 treatment for 20 hr. with 0.05—0.01N-NaOH in physiological aq. NaCl and subsequent neutralisation. This process also increases the activity of other sera. Fractional pptn. with COMe_2 or followed by the treatment causes preferential accumulation of active material (I) in the first fraction. The activity of (I) is reduced but

destroyed by dil. H_2O_2 and HNO_3 , and unaffected by dil. CH_2O , MeCHO , PhCHO , salicylaldehyde, and furfuraldehyde. H_2SO_3 has no effect, but H_2S , cysteine, and KCN irreversibly reduce the activity. Possibly the sera contain a precursor of antiricin.

W. McC.

Swelling of the lens of the eye. F. P. FISCHER (Kolloid-Z., 1934, 67, 317—321).—The degree and velocity of swelling have been determined in acids, alkalis, and salts of different concn. Non-electrolytes diminish the swelling. The capacity of the lens for binding H_2O is < that of the cornea or corium, but the intensity of binding is greater. There is no direct relation between swelling and transparency or permeability of the lens.

E. S. H.

Sedimentation constants of muscle-proteins. H. J. DEUTICKE (Z. physiol. Chem., 1934, 224, 216—228).—By means of the ultra-centrifuge, from extracts of fresh frog's muscle a protein component with sedimentation const. (I) 7.57×10^{-13} was separated from a residue, from which sometimes there was obtained a component with (I) 1.06×10^{-13} . After muscular activity the first (I) is unchanged, indicating the absence of new protein of different mol. size. In extracts from rabbit's muscle, protein components having (I) vals. of 7.70 and 5.39×10^{-13} were obtained, the residue being negligible. The stability region of these proteins is between 5.1 and 5.5. J. H. B.

Nucleoprotein-purines in muscle. B. UMSCHWEIF (Bull. Soc. Chim. biol., 1934, 16, 543—549).—Guanine and adenine are the only purine bases found in the deproteinisation ppt. of muscle obtained by boiling in slightly acid aq. solution, and the ratio of the quantities present is similar to that in nucleic acid. Hypoxanthine is found only in the aq. extract. In muscular metabolism therefore only the adenine of the nucleotides is concerned, and not that of nucleic acid or nucleoprotein.

A. L.

Nucleoproteins of fish-testes. H. VON EULER and G. SCHMIDT (Z. physiol. Chem., 1934, 225, 92—102).—Fish-testes (I) contain only traces of phosphoproteins. Substances rich in P are obtained by pptn. at p_H 7 from the nucleoproteins (II) extracted with aq. NH_3 from (I); these are probably nucleoprotamines, and are more viscous than the (II) pptd. at acid reaction. The mol. ratio purine-N/P was 5/2, as for thymus-nucleic acid, for all (II) examined. The N distribution indicates that the changes on ripening occur principally in the protein constituents of (II).

J. H. B.

Carotenoids and the vitamin-A cycle in vision. G. WALD (Nature, 1934, 134, 65).—The combined pigment and choroid layers of *R. esculenta* and *R. pipiens* (dry wt. approx. 2.2 mg.) contain approx. 4×10^{-6} g. per eye of vitamin-A (I) and approx. 10^{-6} g. of another carotenoid possessing the properties of xanthophyll (II). These amounts are not appreciably altered by light or dark adaptation. The retinas of dark-adapted animals contain no (II) and only a trace of (I), but CHCl_3 extracts a third carotenoid, retinene (III), which shows a small absorption max. at approx. 410 m μ and larger ones at 310 and 280 m μ . (III) gives a strong blue colour with SbCl_3 due to a sharp band at 655 m μ . In light-adapted retinas, (III)

disappears and is replaced by (I). The mechanism of this change is described. C_6H_6 and CS_2 extract no (III). (I) is bound in visual purple (IV) and yellow to a colourless mol. insol. in fat solvents, and CHCl_3 breaks this complex to yield (III). Visual pigment appears to be a carotenoid protein; (IV) is probably a conjugated protein in which (I) is the prosthetic group.

L. S. T.

Yellow feather-pigment of the canary [*Serinus canaria canaria* (L.)] and the occurrence of carotenoids in birds. H. BROCKMANN and O. VOLKER (Z. physiol. Chem., 1934, 224, 193—215).—On a carotenoid-free diet the plumage of canaries becomes white (after moulting). Addition of lutein (I) or zeaxanthin (II) to the diet restores the yellow colour. Violaxanthin (III), β -carotene (IV), and lycopene (V) have no effect. In many birds the yellow plumage-colour is due to (I), often accompanied by its two degradation products, "canary-xanthophyll" and the "picofulvin" of the woodpecker. Indefinite degradation products of (I) or other carotenoids [(II)] may be present. Similar observations on the yolk of hen's eggs show that only (I) and (II) restore the colour, not (III), (IV), or (V). Thus only the xanthophylls with two OH groups appear to produce pigments. The pigment of the red papillae around the eye of the pheasant (*Phasianus colchicus*) is probably astacene.

J. H. B.

Body-fats of the hen. T. P. HILDITCH, E. C. JONES, and A. J. RHEAD (Biochem. J., 1934, 28, 786—795).—The body-fats belong to the group containing 30—35% of saturated acids. About 65% of the fats belong to the C_{18} series (oleic 35—38%, linoleic 20—22%). Small quantities of C_{20-22} unsaturated acids and 7—8% of palmitoleic acid suggest a relationship of these fats to marine-animal fats. Palmitic acid 25—30%, stearic acid 5—7%, and only traces of myristic acid are present. The fats from abdomen, gizzard, and neck were approx. identical, whilst the composition of the diet, which in no case contained > 4% of fat, had little effect.

W. O. K.

Fatty acids of pig liver. I. Octadecenoic acids and the desaturation theory. H. J. CHANNON, E. IRVING, and J. A. B. SMITH (Biochem. J., 1934, 28, 840—852).—The unsaturated fatty acids of pig's liver were oxidised by KOH-KMnO_4 (A., 1925, i, 1129, 1234) and the $(\text{OH})_2$ -acids separated. Fractionation by $\text{EtOH-Et}_2\text{O}$ (1:1) indicated the presence of \leq two octadecenoic acids, of which \leq 80% was oleic acid and the residue mainly an acid, m.p. 117—120°, probably the Δ^9 acid. The Δ^9 acid was not evident (cf. A., 1909, ii, 597). The results, together with the inability of the animal to synthesise certain unsaturated acids (A., 1932, 961), appear to invalidate the theory of desaturation of fatty acids by the liver.

F. O. H.

Protein-linking of physiologically important substances. Condition of glycogen in liver, muscle, and leucocytes. R. WILLSTATTER and M. ROHDEWALD (Z. physiol. Chem., 1934, 225, 103—124).—The solubility of glycogen (I) of liver, muscle, and leucocytes and the composition of the (I)-protein ppts. obtained from the extracts was examined. Dissolution was attained by heating with H_2O for

15—30 min. and by the action of 2% $\text{CCl}_3\cdot\text{CO}_2\text{H}$. Goose-liver contains very variable amounts of (I), the (I)-rich liver (II) contains most of the (I) in sol. form, in the (I)-poor liver (III) the greater part is firmly bound. The (I)-protein ppts. from (II) show high (I), from (III) low (I), content. Typical (I)-proteins yield 66—75% of glucose. Muscle and leucocytes show similar relations in respect of sol. and insol. (I) content. The respective terms lyo-(I), desmo-(I), and "symplex" are employed for sol. and insol. (I), and any complex such as (I)-protein, formed by the action of residual affinities. J. H. B.

Liver-glycogen. D. J. BELL and F. G. YOUNG (Biochem. J., 1934, 28, 882—889).—Examination of the reducing power, $[\alpha]$, ash content, coloration with I, and polarimetric behaviour on hydrolysis with aq. acids fails to reveal any significant difference between the glycogen (I) from the livers of fasted or fed rabbits, rats, or fish (cod, haddock, whiting). Pptn. from aq. solution by AcOH to 80% concn. affords a highly purified ash-free (I). Treatment with 30% KOH at 100° for 2—3 hr. does not influence the properties of (I) (cf. A., 1932, 1022). F. O. H.

Distribution of glycogen in the organs of *Sepia*. M. CHAIGNE (Compt. rend. Soc. Biol., 1933, 114, 1103—1105).—Glycogen (I) was found not only in the liver and muscles, but in practically all organs, the amount varying with the time of year. This may be related to the sexual cycle. The (white) nidamental organs of the female in spring contain 10 times as much (I) per g. of tissue as in October. NUTR. ABS. (b)

Galactogen. V. F. MAY (Z. Biol., 1934, 95, 277—297).—Galactogen [from snails or their eggs (A., 1932, 415)], decomp. $245\text{--}250^\circ$, gives no colour with I, is not hydrolysed by saliva or yeast, and does not reduce alkaline Cu solutions, but is pptd. as a Cu complex. Oxidation by HNO_3 gives mucic acid. The ash (2.85%) is mainly P and Fe, which are probably intrinsic parts of the mol. Hydrolysis by dil. acids yields galactose, $[\alpha]_D +53^\circ$, which exhibits no mutarotation and is probably a modification of β -galactose (A., 1897, i, 391), into which it is converted by treatment with EtOH etc. The differentiation of galactogen from glycogen by staining methods etc. and the quant. separation of the two polysaccharides are discussed. F. O. H.

Variations in copper content of organs of the edible snail. R. GUILLEMET and A. SIGOT (Compt. rend. Soc. Biol., 1933, 114, 1041—1043).—The Cu content is about 0.003% of the total wt. whether fasted or fed. About half of this Cu is in the blood and most of the residue is in the muscle and teguments. The liver and pancreas do not appear to act as storage organs for Cu. NUTR. ABS. (b)

Iodine survey of New Zealand live-stock. II. Sheep of the Wairarapa district. P. H. SYKES (Trans. Roy. Soc. New Zealand, 1934, 64, 17—34).—The I content of thyroids of sheep grazing on different soil types attained different mean vals. Sex differences in this respect were not observed. A decrease in the relative and abs. amounts of I in the gland is associated with an increase in fresh and dry wts.

Use of iodised licks for lambs during 2 months prior to killing increased the I of the glands, but no other effects were apparent. A. G. P.

Improved fixing solution for methylene-blue preparations. E. C. COLE (Stain Tech., 1934, 9, 89—90).—A mixture of 50 c.c. of distilled H_2O , 50 c.c. of glycerol, and 15 drops of conc. HCl is saturated with NH_4 molybdate. H. W. D.

Variations in the reaction of spiders' venom. J. VELLARD (Compt. rend., 1934, 198, 2123—2124).—The venom secretion (after initial emptying of the glands) of *Ctenus*, *Nephila*, and *Lycosa*, kept at 15° , is always acid, whereas that of spiders kept at 33° (other conditions const.) is alkaline, the latter being the more toxic. Species, age, sex, and other physiological factors are without effect. J. W. B.

Colloidal phosphate of milk. G. T. PYNE (Biochem. J., 1934, 28, 940—948).—Ca caseinogenate (I) and the colloidal Ca phosphate (II) in milk are considered to be in chemical combination. The effect of oxalate on the titratable acidity of milk and caseinogen-Ca phosphate complexes indicates that the inorg. colloid constituent is mainly a double salt of (I) and $\text{Ca}_3(\text{PO}_4)_2$. C. G. A.

Colloidal behaviour of sericin.—See this vol., 842.

Spectrography of ox-bile. C. GAUTIER and R. RICARD (Compt. rend., 1934, 198, 2026—2028).—The ash of ox-bile gives in the C arc lines of Na, K, Ca, Mg, P, Fe, Mn, Cu, and Al, the first five elements being relatively abundant. R. S. C.

Excretion of dyes by the liver. Y. TADA (Japan. J. Gastroenterol., 1933, 5, 191—200).—Dyes are removed from the blood into the bile by the parenchymatous cells of the liver. CH. ABS.

Excretion of dyes after experimental liver injury. E. WAKABAYASHI (Japan. J. Gastroenterol., 1933, 5, 201—235).—Excretion is influenced similarly by chemical or parasitic degeneration of the parenchymatous cells. CH. ABS.

Relation between chemical constitution and excretion of dyes by the liver and kidneys. Y. TADA and K. HISHIKAWA (Japan. J. Gastroenterol., 1933, 5, 187—190).—Monoazo-dyes with one sulphone group are excreted chiefly through the kidneys; with two such groups more is found in the urine, and with three, 41.9% was excreted in the urine and 6.4% in the bile. CH. ABS.

Urinary excretion of total fixed mineral bases and ammonia. M. CHATRON (Compt. rend. Soc. Biol., 1933, 114, 1100—1102).—Urinary excretion of fixed base is independent of excretion of acid radicals. Excretion of NH_3 maintains an approx. const. p_H in spite of variations in excretion of fixed base or acid. High NH_3 excretion may indicate a high abs. acid or low fixed base excretion. NUTR. ABS. (b)

Determination of ammonia in urine, and of triple phosphate in calculi, gasometrically. U. D'ESTE (Boll. Chim. Farm., 1934, 73, 401—412). NH_3 in urine is determined by pptn. in alkaline solution as MgNH_4PO_4 (I), the N then being determined gasometrically with NaOBr . A small correction is applied

for solubility losses. Urea and NH_2 -acids do not interfere. (I) in calculi can be determined directly, also total PO_4''' by pptn. with MgO mixture.

R. N. C.

Renal elimination of injected urea and creatinine. W. W. KAY and H. L. SHEEHAN (J. Physiol., 1933, 79, 359—415).—In rabbits increase in the concn. of urea or creatinine (I) in the blood causes reduction of the extraction ratio (amount of the substance retained by the kidney expressed as % of the total quantity carried to it by the blood), although the abs. amount removed per unit of blood increases. When the concn. of (I) is increased, the quantity of urea excreted is considerably decreased. Increase in the urea concn. does not affect the excretion of (I). The results confirm neither the secretion nor reabsorption theory of renal activity, but show that under certain conditions a return of urea from the tubules to the blood occurs.

NUTR. ABS. (m)

Presence of *d*-allantoin in animals. P. E. THOMAS and P. DE GRAEVE (Compt. rend., 1934, 198, 2205—2207).—*d*-Allantoin, $[\alpha]_D^{25} +93^\circ$ in H_2O , was isolated from calves' urine. (I) is fermented by allantoinase at 40° to allantoic acid more rapidly than the *l*-isomeride, which explains the "production" of the latter during fermentation of *dl*-allantoin.

R. S. C.

Renal excretion of carbohydrates in man. E. J. BIGWOOD (Ann. Physiol. Physico-chim. biol., 1932, 8, 401—409).—If all the reduction is due to sugar, urine of fasting normal subjects contains 0.2—2 g. per litre (average 0.8—0.9 g.) of non-fermenting carbohydrates (I). (I) appear to be a mixture, and the reducing power is increased by hydrolysis, the total reduction then corresponding with a physiological excretion of carbohydrate equiv. to 0.1—1.2 g. of C per litre.

NUTR. ABS. (m)

Excretion of urine in the dog. VII. Inorganic phosphate in relation to plasma-phosphate level. R. F. PITTS (Amer. J. Physiol., 1933, 106, 1—8).—In normal dogs in which inorg. PO_4''' has been injected intravenously the PO_4''' clearance (I) is a curvilinear function of the plasma concn. (II). At low (II) (1.1—1.5 m.-mol.) the urine is PO_4''' -free, but as (II) is raised the (I) rises and approaches the xylose or sucrose (glomerular) (I) without ever exceeding it. The relationship does not hold in phloridzinised dogs.

NUTR. ABS. (b)

Excretion of urinary products by the gastrointestinal tract in nephrectomised dogs. I. Vicarious secretion. G. HESSEL. II. Gastric secretion in nephrectomised dogs. III. Bile secretion in nephrectomised dogs. IV. Withdrawal of gastric and duodenal juice by jejunal fistula. V. Presence in digestive juices of waste products normally excreted in urine and the symptomatology and course of uræmia. G. HESSEL, E. PEKELIS, and H. MELTZER (Z. ges. exp. med., 1933, 91, 267—273, 274—306, 307—324, 325—330, 331—339).—In nephrectomised dogs (I) with gastric fistula the % of HCl and total Cl show no significant increase in the uræmic state, but waste substances (urea, creatinine, indican, phenols) reach

high vals., which, however, are < the concns. in the blood at the same time. Hence this is not a true vicarious secretion of urinary waste products. The total amount of urea excreted by the stomach is 12—40 mg. per hr. In (I) with gall-bladder fistula the total vol. of bile and its concns. of total N, non-protein-N, urea, NH_3 , and indican all rise in the uræmic state. The % of urea, non-protein-N, and occasionally indican are slightly greater in the bile than in the blood, possibly due to active secretion or to simple concn. of the bile. The total N in the bile is 19—56 mg. per hr. In (I) with high jejunal fistula the concns. of total N etc. are increased, the % of non-protein-N and urea being > those in the blood. (I) with fistulæ live about 60% longer than those without, and the blood-urea and indican rise much more slowly.

NUTR. ABS. (m)

Reduction of the iodo-mercuric reagent of Baudouin by a coloured sulphur compound of normal urine. B. GWOŹDŹ (Bull. internat. Acad. Polonaise, Classe Med., 1933, No. 2—5, 267—277).—From normal human urine, from which SO_4'' and PO_4''' have been removed, a S compound can be pptd. by the addition of $\text{Cu}(\text{OAc})_2$. The yellow ppt. contains neutral S and reduces the alkaline HgI_2 solution of Baudouin, Penau, and Tanret. 17—25% of the reducing power of this ppt., which changes with the diet of the subject, corresponds with the neutral S contained: 1 mg. of S corresponds with 8 mg. of Hg reduced.

NUTR. ABS. (b)

Isolation of crystalline stercobilin. C. J. WATSON (J. Biol. Chem., 1934, 105, 469—472).—Human faeces are ground with abs. AcOH and exhaustively extracted with Et_2O with additions of further AcOH. The Et_2O is removed in vac. and the residue poured into 6—8 vols. of 1% HCl, kept over-night, and filtered from pptd. fatty acids, coprosterol, copronigrin, and chlorin-e. The filtrate is neutralised with NaOAc and extracted first with Et_2O to remove copromesobiliviolin, and then with CHCl_3 . The CHCl_3 extract is repeatedly extracted with H_2O , the extract is acidified with HCl, and the stercobilin re-extracted as hydrochloride (I) with CHCl_3 . The extract is dried (Na_2SO_4) and (I) pptd. by light petroleum and purified by crystallisation from CHCl_3 . The free base is liberated by 0.1N-NaOH in presence of CHCl_3 .

H. A. P.

Effect of the proportions of fat and carbohydrate in the diet on excretion of metabolic nitrogen in the faeces. H. H. MITCHELL (J. Biol. Chem., 1934, 105, 537—546).—Excretion of metabolic N (I) in faeces is not affected by substitution of fat for starch, although the total dry wt. is increased. At low levels of food intake on a low-fat diet, the ratio of (I) to dry matter consumed is increased, due to the prominence of a fraction of (I), which is const. for each organism. At higher levels this fraction is negligible compared with that due to residues of digestive secretions.

H. G. R.

Dependence of the quantity of faecal nitrogen on volume of faeces. W. HEURKE (Arch. Hyg., 1933, 111, 188—195).—The total amount of N excreted daily in the faeces is directly related to their daily dry

wt., 1 g. of N and 1—2 g. of Et_2O extract being found for every 20 g. of dry matter. NUTR. ABS. (m)

Loss of nitrogen and sulphur on drying faeces. D. P. CUTHBERTSON and A. K. TURNBULL (Biochem. J., 1934, 28, 837—839).—The drying of faeces at 100° for 10—14 days produces a marked loss of N (mainly as NH_3) and of S (mainly as H_2S). The latter is prevented by addition of Cu acetate, whilst drying in a current of NH_3 -free air allows liberated NH_3 to be trapped by acid and subsequently determined.

F. O. H.

Merino fleece. I. Suint. M. F. FRENEY (J.S.C.I., 1934, 53, 131—134r).—Suint samples vary greatly in composition, but lower fatty acids and hippuric, lactic, and succinic acids were identified in those examined. Bacterial decomp. in the fleece probably accounts for the small amounts of urea and NH_3 found, and for the N bases detected. Suint differs from dry human sweat in containing considerably more K and much less Na and Cl.

Case of alcaptonuria. A. P. U. CINTRA (Rev. Med.-Cirur. Brazil, 1933, 41, 219).—There were no signs of ochronosis. Homogentisic acid was excreted in the urine at the rate of 7.14 g. in 24 hr. Urinary NH_3 was 1.32%. The alkali reserve of the blood-serum was normal. The patient had been alcaptonuric from birth. NUTR. ABS. (m)

Treatment of severe iron deficiency-anæmia and hæmorrhagic anæmia. V. Preparation of caseinate of iron and copper. G. FONTES and L. THIVOLLE (Le Sang, 1933, 7, 803—806).—Compounds prepared by the treatment of milk with CuSO_4 and $\text{Fe}(\text{ClO}_4)_3$ are recommended in the treatment of Fe deficiency and hæmorrhagic anæmia.

NUTR. ABS. (b)

Significance of iron in anæmia. III. Iron in urine. IV. Effect of food-iron on iron balance in untreated secondary and pernicious anæmia. V. Iron balance in secondary anæmia under the influence of liver-iron therapy. A. H. MULLER (Z. ges. exp. Med., 1933, 91, 463—470, 579—584, 585—592).—III. In health the Fe excreted in the urine over 24 hr. was ≥ 2 mg., being about 2.5% of that present in the faeces. In febrile illnesses (e.g., pneumonia) there was not, but in secondary, and more especially pernicious anæmia, there was, a slightly greater urinary excretion of Fe which did not appear to bear any relationship to the blood-Fe. The Fe of the food or liver or small doses of Fe *per os* had no effect on urinary Fe, but ingestion of > 1 g. of ferrum reductum led to a rapid increase of Fe in the urine.

IV. A positive retention of Fe was noted in untreated cases of both pernicious and secondary anæmia. The amount of Fe retained had no relation to the clinical condition or blood picture, but was greater with a greater Fe content of the food. In circulatory insufficiency with signs of congestion in the alimentary tract the absorption of Fe seemed to be impaired.

V. Administration of liver and min. doses of Fe in cases of secondary anæmia led to a decrease in Fe retention: with large doses (≤ 3 g. daily) there was a marked negative balance, although there was great

improvement in the blood picture. In hypochromic anæmia there is probably in the liver, spleen, and elsewhere a large store of Fe which is not capable of being utilised for the synthesis of hæmoglobin and is mobilised by medicinal Fe and finally excreted by the gut. NUTR. ABS. (b)

Relation of vitamin-A and -D to urinary calculus formation. A. R. BLISS, jun., G. R. LIVERMORE, and E. O. PRATHER, jun. (J. Urol., 1933, 30, 639—652).—Calculi were formed in 61.8% of the rats maintained on diets deficient in vitamin-A and -D and in 57.1% of those deficient in -A only. The calculi consisted chiefly of Ca and Mg phosphates.

Ch. Abs.

Relation between kidney- and bladder-stone formation and nutrition. A. POLAK (Arch. Neerl. Physiol., 1934, 19, 176—190).—Addition of 3% of CaCO_3 to the complete diet resulted in kidney- and bladder-stone formation in rats. KH_2PO_4 had a slight effect in vitamin-A deficiency. R. N. C.

Chemical analysis of new growths correlated with their pathological examination. W. R. MANKIN and A. M. WELSH (Med. J. Austral., 1933, [ii], 718—729).—The K content of tumours was approx. \propto their cellularity. The N content of tumours was $>$ that of normal tissues. NUTR. ABS. (b)

Cancer problem. VII. Potassium and calcium in the tumour and in the patient's serum. H. GUTHMANN, H. WINKLER, and N. GRZIMEK (Arch. Gynakol., 1933, 155, 185—196).—In tumour patients K was $<$ normal, K:Ca being 1.93 against 2.03. After X-rays or irradiation serum-K rose towards normal. The K content of tumours increased with malignancy.

NUTR. ABS. (b)

p_{H} of blood in cancer. G. BENETATO and M. BENETATO-MODVAL (Compt. rend. Soc. Biol., 1933, 114, 329—331).—The range of p_{H} of oxalated plasma in normal people is 7.32—7.38 and in cancer 7.21—7.52. The early cases are more alkaline.

NUTR. ABS. (b)

Cholesterol metabolism in cancer patients. O. KIRGREEN (Arch. klin. Chirurg., 1933, 177, 383—386).—Cancer patients, except in very advanced stages, show normal or, more often, raised serum-cholesterol (I) vals., which fall on complete removal of the tumour. After X-ray irradiation of the tumour or, after removal, of its former site, the (I) rises when the tumour has been apparently completely removed, falls when the cancer is inoperable or the primary tumour has been removed but gland metastases are present, and rises when the disease is in the very advanced stage showing abnormal low (I) vals. These results indicate a storage of cholesterol in the tumour, in such a condition that it is readily decomposed by irradiation. The removal of the tumour or the destruction of the tumour-cholesterol by irradiation involves a readjustment of the blood-cholesterol. NUTR. ABS. ()

Reducing activity of the tissues of normal and tumour-bearing rats and mice. A. F. WEAVER and M. MITOLO (Biochem. J., 1934, 28, 1—10).—Transplantable rat and mouse tumours contain substances which reduce $(\text{NH}_4)_2\text{MoO}_4$ in acid solution.

whilst $\text{CCl}_3\cdot\text{CO}_2\text{H}$ extracts reduce 2 : 6-dichlorophenol-indophenol. The reducing powers vary for different strains of tumours, but are relatively const. for the same strain, as shown by tumours of the same and different ages, multiple transplantable tumours in the same animal, and progressing and spontaneously regressing tumours. W. O. K.

Action of silver nitrate on normal and cancerous tissue of rats and mice. E. HARDE (Bull. Soc. Chim. biol., 1934, 16, 465—466).—Whilst the pituitary and suprarenal glands, the ovaries, and the spleens of adult cancerous mice reduce aq. AgNO_3 , the tumours are inactive in this respect. A. L.

Excretion of chlorides in eczema. P. POP-CHRISTOFF and R. ZORN (Compt. rend. Soc. Biol., 1933, 114, 8—10).—Ten cases of acute eczema were placed on a diet containing 5 g. of NaCl daily and the urinary Cl' excretion was determined. Two cases were in equilibrium. In three cases Cl' retention preceded recurrence of cutaneous eruptions; Cl' balance was again established as cure took place. Cl' retention may form the basis of skin oedema in this condition. NUTR. ABS. (b)

Iodine content of Polish drinking-water, in connexion with goitre. A. SZNOLIS and H. MARCINKOWSKA-ŁOPIEŃSKA (Arch. Chem. Farm., 1934, 1, 52—63).—The I content of the drinking- H_2O of various localities varies from 0.005 to 15.5×10^{-6} g. per 100 c.c., being on the whole lower for river- than for well- H_2O , and diminishing with height above sea-level. $0.85\text{—}3.5 \times 10^{-6}$ g. of I was found in Warsaw sewage- H_2O , as compared with 0.28×10^{-6} g. per 100 c.c. for tap- H_2O . R. T.

Is the high basal metabolic rate in "hyperthyroidism" due to thyroxine? J. W. CAVETT, C. O. RICE, and J. F. McCLENDON (Science, 1934, 80, 19—20). L. S. T.

Liver disease and metabolism. III. Amino-acids. K. TSUSHIMA (J. Chosen Med. Assoc., 1933, 23, 110—111).—There is an increase in the $\text{NH}_2\text{-N}$ of the blood and urine in cancer and cirrhosis of the liver and in coma hepaticum, but not in icterus. The rise in the $\text{NH}_2\text{-N}$ of blood and urine which normally follows the ingestion of large amounts of peptone or gelatin is prolonged in cases of liver disease. When the bile ducts of animals are ligatured, the $\text{NH}_2\text{-N}$ in the blood and urine is increased, and the further rise following over-feeding with peptone is still present after 6 hr. Eck fistula dogs show the normal rise after peptone over-feeding, and if, in addition, the hepatic artery is tied, the $\text{NH}_2\text{-N}$ of the blood rises markedly further. NUTR. ABS. (m)

Metabolism in liver disease. IV. Uric acid. H. INOUE (J. Chosen Med. Assoc., 1933, 23, 117).—In severe cancer of the liver and leucæmia the uric acid content of blood and urine increases. The similar increase which follows over-feeding with peptone is abnormally protracted in liver disease, because a lowered power of protein absorption in the alimentary canal. NUTR. ABS. (m)

Peptide content of the blood and of pathological fluids. P. VALDIGUIE (Bull. Soc. Chim. biol., 1934,

16, 498—526).—A study of the N distribution in 14 pathological fluids (I) such as occur in cases of cirrhosis indicates that the polypeptide content (II) is not related to the urea nor to the albumin content. (II) of (I), although a little >, is in most cases comparable with, that of the blood (III). Whilst renal impermeability and hepatic insufficiency both increase (II) of (I) and (III), in the former the increase is not proportional to the extent of the failure to eliminate phenolsulphonephthalein. A. L.

Creatine-creatinine metabolism. Treatment of muscle-diseases with glycine. A. MADER, E. SELTER, and R. SCHELLENBERG (Z. ges. exp. Med., 1933, 92, 151—164).—In infancy and childhood creatinuria normally occurs. The output of creatinine (I) increases with increasing age in children with healthy muscles. In progressive muscular dystrophy the (I) coeff. was reduced and the creatine coeff. raised. Administration of glycine tended to restore (I) and creatine metabolism to normal.

NUTR. ABS. (m)

Fate of intravenous saline in healthy and nephrotic subjects. A. GANDELLINI (Z. ges. exp. Med., 1933, 92, 361—366).—Intravenous injection of saline produces both in healthy and nephrotic subjects (I) an immediate slight rise of blood-Cl and a reduction in protein, red cell-count, and hæmoglobin content. After 24 hr. there is still a slight increase of blood-Cl in (I). Very little of the injected Cl appears in the urine of (I) within 24 hr., whereas in normal subjects 100% or more is excreted when the diet is NaCl-rich and 34—75% with NaCl-poor diet. The NaCl concn. of the urine of (I) reaches high levels in some cases. In all cases the Cl rapidly leaves the blood-stream, but in (I) is held by the tissues, whereas in health it rapidly passes back to the blood to be excreted.

NUTR. ABS. (b)

Mineral metabolism in renal disease. IV. Mineral excretion in normal subjects during prolonged administration of equivalent amounts of sodium and potassium chlorides. V. Mineral excretion in renal disease during prolonged administration of equivalent amounts of sodium and potassium chlorides. H. GLATZEL and W. MECKE (Z. ges. exp. Med., 1933, 91, 504—522, 523—538).—IV. A healthy subject, while on an acid diet, was given KCl or NaCl each for 8 days. Gradually the excretion of the administered alkali reached the level of the intake. There was a greatly increased excretion of the one not given, the Na loss during the KCl period being > the K loss in the NaCl period. During the NaCl period the urinary vol. was increased out of proportion to the output or retention of Na. During the KCl period there was a decrease of the alkali reserve and an increased urinary acidity and output of acid substances.

V. In a patient with nephrosclerosis, long-continued administration of KCl led to a loss of K, Ca, and Mg as well as Na. The ingestion of NaCl led to greater urinary vol. and to retention of K, Ca, and Mg, whilst the excretion of Na was four times that of K during the same period in the healthy subject. The height of the alkali reserve of the blood appeared to depend on the retention of K. NUTR. ABS. (b)

Edema and the serum-lipin ratio. H. KURTEN (Z. ges. exp. Med., 1933, 91, 178—192).—In nephritic and pregnancy oedema the increase in plasma-cholesterol is not accompanied by an equal increase (often a decrease) in phosphatide, so that the cholesterol-lecithin quotient is greatly increased. Hypercholesterolaemia seems to be associated with defective thyroid function. NUTR. ABS. (b)

Biology of the placenta. Blood-picture in the intervillous spaces and metabolism of the placenta. FRANKEN and KREBS (Arch. Gynakol., 1933, 156, 188—191).—Determination of the iso-haemagglutination titre (Saecker) in heterospecific pregnancy revealed that the blood in the intervillous spaces (I) equals the maternal blood (II) in titre, whilst the retroplacental blood has a lower titre because of contamination by amniotic fluid which is rich in foetal isoagglutinogens. There is less sugar and more non-protein-N in (I) than in venous (II) or foetal blood (III), whilst the NH_2 -acids of (I) are in concn. between those of (II) and (III). Urea is equally distributed throughout. No evidence of fat or protein oxidation by the placenta was obtained: carbohydrate appears to be the only material metabolised by the placenta, which explains the low sugar vals. in (I). NUTR. ABS. (b)

Pellagra in Sudanese millet-eaters. N. L. CORKILL (Lancet, 1934, 226, 1387—1390).—The fundamental condition appears to be lack of cholesterol and vitamin-A and -D in the food, lack of -C being a contributory factor. Pellagra is largely allergic. Vitamin-D, and not H_2O -sol. -B₂, is the anti-dermatitis vitamin. L. S. T.

Blood sedimentation rate and the plasma-proteins. G. R. P. ALDRED-BROWN and J. M. H. MUNRO (Lancet, 1934, 226, 1333—1336).—In rheumatic disease sedimentation rate does not run parallel to the fibrinogen (I) or globulin (II) % of the plasma-proteins; it has no connexion with the globulin-albumin ratio, the fibrinogen-globulin ratio, or the ratios of (I)+(II) to albumin and to total proteins. L. S. T.

Inorganic and organic acid-soluble phosphorus in spontaneous and experimental rickets. V. ANGELINI (Riv. Clin. Pædiat., 1933, 31, 1153—1171).—Both in rachitic infants and in rats made rachitic by a diet low in P, the total acid-sol. P of blood-serum is diminished. The fall is due to reduction in inorg. P and is closely correlated with the degree of rickets. Org. acid-sol. P shows no significant change, but tends to increase both in infants and in rachitic rats. NUTR. ABS. (b)

Metabolism of healing in celiac rickets. F. J. FORD (Arch. Dis. Childhood, 1933, 8, 355—359).—During antirachitic treatment Ca and P metabolism is similar to that of infantile rickets. CH. ABS.

Effect of the metal on the antirachitic activity of orthophosphates. R. LECOQ and H. VILLETTE (Compt. rend. Soc. Biol., 1933, 114, 1096—1098).—The phosphates of Na, K, Mg, and Sr have antirachitic potency \propto the $\text{PO}_4^{'''}$ present. The $\text{Ca}^{''}$ slightly reduced the potency of the $\text{PO}_4^{'''}$ in $\text{Ca}_3(\text{PO}_4)_2$,

whilst the phosphates of Fe, Mn, and Bi showed no antirachitic potency. NUTR. ABS. (b)

Chlorine distribution between the plasma and erythrocytes after injection of sodium chloride in the post-operative period. M. LEVY (Bull. Soc. Chim. biol., 1934, 16, 618—624).—Whilst usually in post-operative hypochloraemia injections of considerable amounts of NaCl increase the erythrocyte-Cl' (I), plasma-Cl' (II), and the ratio (I)/(II), in some cases the increases in (II) are such that the ratio (I)/(II) is lowered. A. L.

Amine production in the intestine of infants: significance of amines in the etiology of toxicosis in infants. D. BRANDES (Jahrb. Kinderheilk., 1933, 141, 128—134).—The faeces of bottle-fed infants are richer in amines (I) than those of breast-fed. Since (I) are found in the urine of infants with pyuria but no toxicosis (II), (I) are produced in the urinary tract and (II) does not necessarily result from poisoning with (I). NUTR. ABS. (m)

Action of urea on tissue respiration. B. KISCH (Biochem. Z., 1934, 271, 58—60).—At p_{H} 7.4 tissue (heart, liver, kidney, diaphragm of rat, guinea-pig, sheep, ox, pig) respiration (I) is slightly increased by low concn. of urea, whilst high concn. (0.5M) inhibits (I) in some cases (rat heart, ox retina) only. The stimulating effect is most pronounced with rat and guinea-pig kidney. The optimum concn. varies with the organ concerned. W. McC.

Effect of hypertonic solutions on tissue respiration. I. Effect of chlorides of univalent cations. B. KISCH (Biochem. Z., 1934, 271, 131—141).—The degree of restriction of respiration of tissues (heart, diaphragm, kidney, liver, retina of rat, guinea-pig, ox, sheep) at p_{H} 7.4 by 0.2M solutions of LiCl, NaCl, KCl, CsCl, or NH_4Cl is different for different animals and for different tissues of the same animal, sp. effects being observed in some cases. Variations in the effects occur according to the nutrient material (NH_2 -acids, lactate, pyruvate) provided for the tissue. The effects are due to the action of the ions on oxidation catalysis. W. McC.

Effect of oxidation-reduction potential of the medium on growth of tissue cultures. R. E. HAVARD and L. P. KENDAL (Biochem. J., 1934, 28, 1121—1130).—By passing N_2 and traces of O_2 through a culture medium, the E_h can be adjusted to various levels between +300 mv. and -100 mv. Growth of chick heart-tissue decreases with E_h , mitosis ceasing between +20 mv. and -30 mv. L. D. G.

Metabolic activity of the pancreas. E. U. STILL, A. L. BENNETT, and V. B. SCOTT (Amer. Physiol., 1933, 106, 509—523).—Activity due to injection of a very active secretin prep. is accompanied and followed by a marked O_2 consumption. The CO_2 which appears in the juice comes at partly from the blood, but later exclusively from the gland itself. NUTR. ABS. (b)

Effect of life at high altitude on blood-lactic acid. H. HARTMANN and A. VON MURALT (Biochem. Z., 1934, 271, 74—88).—At low altitudes the lactic acid content (I) of human blood remains const.

moving to high altitudes (3460 m.) (I) first falls and then rises, the deviation from normal being increased after administration of NH_4Cl and much more by that of NaHCO_3 , which in all circumstances increases (I) > does NH_4Cl . The large increase in (I) produced by vigorous bodily exercise is greater at high than at low altitudes, whilst the subsequent fall (after 15 min.) is also greater at high altitudes, the level reached being with NH_4Cl < with NaHCO_3 administration. Possibly (I) takes over part of the role of the CO_2 of blood at high altitudes. W. McC.

Metabolism in oxygen deficiency. VI. Alteration in protein metabolism at low tension due to administration of glucose. H. ELIAS and J. KAUNITZ. **VII.** Water metabolism at low oxygen tensions. **VIII.** Protein content of the liver at low oxygen tension and effect of glucose administration. **IX.** Non-protein-nitrogen and its fractions in the liver in oxygen deficiency. Effect of glucose administration. **X.** Prevention of characteristic changes in protein metabolism at low atmospheric pressures by administration of glucose. **XI.** Mechanism of effect of carbohydrate at low oxygen tensions (glucose effect). H. ELIAS, J. KAUNITZ, and R. LAUB (Z. ges. exp. Med., 1933, 92, 397—408, 409—429, 430—435, 436—449, 450—468, 469—479).—VI. The increase in serum-albumin and globulin produced in rabbits given only H_2O during exposure to diminished O_2 pressure is caused by H_2O loss. Administration of glucose (I) lessens these changes as well as the increase in non-protein-N of the serum, increased electrical excitability, and changes in the blood.

VII. There is an increase in urinary output of H_2O and a decrease in insensible perspiration during exposure of fasting rabbits to lowered O_2 pressure: the reverse is the case when (I) is given. Liver and brain of exposed animals contain slightly more, spleen slightly less, H_2O ; (I) administration has little effect.

VIII. The N content (on dry wt.) and the total wt. of the liver are about 25% greater when rabbits, exposed to low O_2 pressure, are given (I).

IX. Complete starvation, except for H_2O , causes a reduction in the abs. and relative wt. of liver. Administration of (I) maintains the relative but not the abs. wt. The % of non-protein-N in the liver is greatly reduced in all except the animals given (I) during exposure to low O_2 pressure where the reduction is slight. The contents of urea and NH_2 -acid are increased in all, but least when (I) is given; the polypeptide-N shows no significant change except in the (I) animals, where there is a marked diminution.

X. Exposure to low O_2 pressure causes a reduction in the H_2O content of the blood in the hepatic vein. Administration of (I) prevents any difference in the H_2O content of hepatic and portal blood, and also lessens the breakdown of proteins in the liver and tends to promote anabolism.

XI. Administration of sorbitol or galactose during exposure to low O_2 pressure has practically no protective action on the proteins, whereas both fructose and (I) have a marked effect. The reduction

of H_2O content of the liver is largely prevented by (I) or fructose, but only slightly by sorbitol and galactose. NUTR. ABS. (m)

Nutritive effect of ethyl alcohol. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1933, 9, 1035—1044).—Excess of fat in the diet had a bad effect on the nutrition of rats. Normal growth was obtained when EtOH (optimum 5%) was added. The liver- and body-fat increased considerably on addition of 5% of EtOH. The liver-glycogen was unaffected. CH. ABS.

Physiological behaviour of trioses and related compounds. V. Behaviour of liver- and muscle-glycogen after feeding glyceraldehyde with simultaneous dosage of insulin. R. STORR (Z. physiol. Chem., 1934, 224, 229—232; cf. A., 1933, 88).—Administration of glyceraldehyde to fasting rats causes marked deposition of glycogen (I) in the liver, but only slightly in muscle. When insulin is also given the effect is reversed, muscle- but not liver-(I) increasing. J. H. B.

Fructose and galactose tolerance in premature infants. W. FABISCH and F. ETZOLD (Z. Kinderheilk., 1933, 55, 702—707).—The average galactose tolerance is 1.6 g. per kg. body-wt. for premature and 2.2 for full-time infants, and the corresponding average fructose tolerances are 1.5 and 2.6. NUTR. ABS. (m)

Peculiarities of carbohydrate metabolism in infants and children. II. Keto-antiketogenic ratio of the food of infants and children. Effect of alkaline salts and hormones on ketone metabolism in children. W. HEYMANN and E. MAIER (Z. Kinderheilk., 1933, 55, 502—511).—Taking the ketogenic portion (I) of the food as 90% of the fat cal. and 60% of the protein cal. and the antiketogenic (II) as 10% of the fat cal., 40% of the protein cal., and 100% of the carbohydrate cal., a (I)/(II) ratio of 2.5 was found to produce ketosis equally in infants and children; 10—15 g. of NaHCO_3 or citrate per day, which raised the p_{H} of the urine to 8.4, did not increase the ketonic substances in the blood or the urine. Prolan, adrenaline, and thyroxine had no action on the formation and excretion of ketones. NUTR. ABS. (b)

Ketonæmia in rabbits. L. KALLÓS-DEFFNER (Z. ges. exp. Med., 1933, 92, 389—393).—Hunger leads to the appearance of considerable amounts of ketones in the blood of rabbits. Exposure to reduced atm. pressure (I) produces the same effect, which may be due to poor intake of food, since administration of glucose prevents ketosis. After removal to ordinary (I) the disappearance of ketones runs parallel with increase of wt. NUTR. ABS. (b)

Simultaneous occurrence of sugar and acetone in the urine of non-diabetic children (glyco-ketonuria). F. ALTMANN (Z. Kinderheilk., 1933, 55, 639—668).—After the administration of 100 g. of glucose (I) a simultaneous appearance of (I) and COMe_2 in the urine was observed in six non-diabetic patients with ketosis due to various causes and in twelve children who had previously been given a carbohydrate-poor, high-fat diet; the blood-sugar

curve was diabetic in type except for the low fasting level. No relationship was noted between the blood- or urinary COMe_2 and the presence of COMe_2 in the breath. In glycosuria and ketonuria large amounts of sugar must be given. There was a tendency to lose wt. on a high-fat diet with high calorific val.

NUTR. ABS. (b)

Role of the liver in the metabolism of carbohydrate and fat. C. H. BEST (Lancet, 1934, 226, 1155—1160, 1216—1221, 1274—1277).—Lectures.

L. S. T.

Digestion of food. III. Synthetic fats. S. SUZUKI (J. Agric. Chem. Soc. Japan, 1933, 9, 1007—1018).—Tristearin (I) and triolein (II) were given to dogs instead of fat. (II) is more digestible than (I). (I), but not (II), retarded the digestion of other components, especially protein.

CH. ABS.

Fat metabolism in the fowl. I. Composition of the egg-fat of the fowl as affected by the ingestion of large amounts of different fats. E. M. CRUICKSHANK (Biochem. J., 1934, 28, 965—977).—On normal cereal rations containing protein supplements the mixed fatty acids of the egg-fat (I) contained approx. 31% of solid acids, 47—51% of oleic, 15—19% of linoleic, and 2—3% of linolenic acid. The superficial and internal fat deposits (II) are more uniform in composition in the fowl than in pigs and cattle. The degree of saturation and proportion of components in (I) were modified by ingestion of unsaturated fatty acids (III), but very little by saturated fatty acids (IV). Ingestion of (III) causes a marked and rapid increase of unsaturation in (II); ingestion of (IV) increased saturation.

C. G. A.

Fat deposition in the lung. T. OLIARO (Z. ges. exp. Med., 1933, 91, 366—369).—Simultaneous determinations of the fat content (I) of the blood of rabbits from the left and right heart, peripheral veins, and vena cava reveal a reduction of 11.1—25.5% in the blood from the left heart, indicating that fat is stored in the lungs. (I) of the lungs is greater (7.3 as against 6.1%) when the animals are given olive oil 3 hr. before being killed.

NUTR. ABS. (m)

Effect of cholesterol and phloridzin on fat metabolism. Fat content of liver of cats and rabbits after intraportal or subcutaneous injection of these substances. H. TSENG (Z. ges. exp. Med., 1933, 92, 108—128).—Intraportal injection of cholesterol into cats and rabbits had no significant effect on the fat of the liver, in disagreement with Remesow's finding of fat-impoverishment and glycogen synthesis in rabbits. Phloridzin caused a great increase of liver-fat.

NUTR. ABS. (b)

Rôle of the liver in cholesterol and phosphatide metabolism. H. HEINLEIN (Z. ges. exp. Med., 1933, 91, 638—682).—In both full-grown and young dogs on normal diet only 50—70% of the cholesterol (I) and 3—6% of the phosphatide (II) of the food was excreted. Analysis of the organs indicated that (I) is synthesised in the growing animal but not in the adult, (II) in neither. Absorption of (I) took place even in the absence of bile, whilst (II), although hydrolysed, was not absorbed in the absence of bile.

The excretion of (I) and (II) takes place chiefly through the intestinal wall, since it was but little affected by the exclusion of bile from the gut by means of a fistula.

NUTR. ABS. (b)

Cerebroside storage. H. BEUMER and H. FASOLD (Z. ges. exp. Med., 1933, 90, 661—664).—Cerebrosides are contained in the nervous system and suprarenals, probably due to the medullary portion of the latter being rich in nerve-substance. Cerebroside (I) ingested by a breast-fed infant appeared *in toto* unchanged in the faeces (II): in a boy of twelve only 20% of 0.5 g. appeared in the (II) probably on account of bacterial action. Sphingosine did not appear in the urine after ingestion or subcutaneous or intravenous injection. Large amounts of (I) are stored unchanged in the liver and other organs after injection into dogs or rabbits.

NUTR. ABS. (b)

Significance of the liver in the metabolism of lipins. Change in the amounts of blood- and bile-lipin in parenteral administration of lecithin to normal rabbits. Metabolism of lipins in hepatic disturbance in rabbits. Y. OSODA (Japan. J. Gastroenterol., 1933, 5, 115—123, 124—131).—After injection of lecithin into rabbits the blood- and bile-lecithin, -cholesterol, and -total fatty acids increase. On intravenous injection of lecithin after hepatic injury the blood-lipin is high if the parenchymatous cells are blocked and normal if only the hepatic stellate cells are blocked.

CH. ABS.

Production of ketones and ammonia in different species of animals. H. TRIMBACH (Compt. rend. Acad. Sci., 1933, 197, 708—710).—In man, calves, pigs, dogs, rabbits, cats, and rats, on diets of cow's milk or carbohydrates alone, ketone and NH_3 excretion were very variable, per unit of wt., in the different species on the same diet, and did not vary together in the different species.

NUTR. ABS. (b)

Deamination of alanine in the liver. E. AUBEL (Ann. Physiol. Physico-chim. biol., 1933, 9, 929 933).— AcCO_2H was obtained from alanine but not from Na lactate. The medium must be well aerated. The reaction appears to be due to diastase.

NUTR. ABS. (b)

Intermediary metabolism of histidine. IV. S. EDLBACHER and M. NEBER (Z. physiol. Chem., 1934, 224, 261—272; cf. A., 1931, 513).—The probable course of the action of histidase is as follows. The glyoxaline ring is opened, with entry of $2\text{H}_2\text{O}$ and loss of NH_3 , yielding the enol or keto-form ω -formylglutamine (I). With NaOH , (I) affords NH_3 , HCO_2H , and glutamic acid (II), shown to be identical with the protein degradation product obtained by oxidative deamination (III) with kidney slices (Krebs), as both yield α -ketoglutaric acid (2:4-dinitrophenylhydrazone, m.p. 220°). With H_2O_2 the enzymic fission mixture, probably containing (I), gives succinic acid semi-aldehyde (2:4-dinitrophenylhydrazone, m.p. 201—202°) [also obtained with H_2O_2 from (II)]. α -Aminobutyric acid (IV) by (III) \rightarrow α -ketobutyric acid (2:4-dinitrophenylhydrazone, 196°; *p*-nitrophenylhydrazone, m.p. 203°). H_2O_2 , alanine and (IV) give MeCHO and E respectively.

Oxidation of sulphur of homocystine, methionine, and S-methylcysteine in the animal body. V. DU VIGNEAUD, H. S. LORING, and H. A. CRAFT (J. Biol. Chem., 1934, 105, 481—488; cf. this vol., 322).—Homocystine (I), S-methylcysteine (II), decomp. 248°, $[\alpha]_D^{25}$ —32° in H_2O [formyl derivative, m.p. 118—119° (corr.)], $[\alpha]_D^{25}$ —13.5° in H_2O , and dl-methionine (III) were fed to rats, and the total S, $SO_4^{''}$, and unoxidised S in the urine determined. The % of the extra total S excreted appearing as $SO_4^{''}$ is practically the same for both (I) and (III). (II) is also readily oxidised. H. D.

Proteins of the liver of frogs after fasting. C. GAUTIER (Bull. Soc. Chim. biol., 1934, 16, 414—418).—The right lobes of the livers of frogs were removed and compared with the remaining portions (I) of the livers of the same animals after fasting for some weeks. (I) decreased little in wt., and their protein content remained almost const. A. L.

Nitrogenous extractives of muscle in protein inanition. A. ROCHE (Compt. rend. Soc. Biol., 1933, 114, 1185—1187).—In rats, death from protein (I) starvation leads to extensive changes in muscle. (I), the H_2O -sol. N increasing by about 21%. In complete starvation the increase is 39%. Thus the H_2O -sol. N is intermediary in the equilibrium, circulatory N \rightleftharpoons extractable muscle-N \rightleftharpoons muscle-(I)-N, comparable with Voit's "circulatory (I)." NUTR. ABS. (m)

Nitrogen reserves in animals. A. ROCHE (Ann. Physiol. Physico-chim. biol., 1933, 9, 933—938).—In the absence of food protein, N requirement is met by partial mobilisation of muscle- and not of reserve-protein. Hence muscle-protein does not consist of mols. of fixed constitution, but is of vary variable composition. NUTR. ABS. (m)

Morphology of protein metabolism of animal cells. B. V. KEDROVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 312—316).—Observations have been made of the distribution of stained granules in various stages of development of tadpoles grown in dil. neutral-red, and the rôle of the chromophilic protein material is discussed. R. K. C.

Nutritive value of proteins of lucerne and clover hay when fed alone and with maize proteins. K. L. TURK, F. B. MORRISON, and L. A. MAYNARD (J. Agric. Res., 1934, 48, 555—570).—With growing lambs, the apparent digestibilities of the proteins of clover hay (I), lucerne hay (II), (I)+maize, and (II)+maize are 50, 56, 55, and 63%, respectively; the true vals. show the same relative differences. The efficiency of utilisation is indicated by the biological vals. of 81, 79, 80, and 77, respectively; with (II) alone the val. is 50, whilst addition of starch and sugar increases it to 72. When fed in a balanced diet, (II) is probably not deficient in the quality of its proteins. F. O. H.

Increase of food value of proteins in wheat and rye bread by the admixture of pea meal. Z. MARKUZE (Zdrowie, 1933, Nos. 19—20).—The biological val. of the food proteins is increased from about 1 for wheat bread, 1.1 for rye bread, and 1.21—1.38 for peas, to 1.6—1.9 with 80% wheat+20%

peas, or 60% rye+40% peas, and to 2 for 60% wheat +40% peas.

NUTR. ABS. (m)

Comparative digestive utilisation of protein by different animals. P. LELU (Compt. rend., 1934, 198, 2022—2024).—N utilisation (determined by a modified formula) by pigs, dogs, and rats is for milk 96.7, 95.4, and 96.4, and for meal of peas 95.9, 79.4, and 77.1, of barley 94.2, 71.9, and 65.6, and of soya-beans 89.6, 80.6, and 68.6%, respectively. R. S. C.

Effects on metabolism of a diet consisting chiefly of protein, egg-white, ox or fish muscle, or milk protein. A. GALAMINI (Problema alimentare, 1933, 3, 41—79).—A high-protein diet (I), in which the protein is in the form of egg-white or dried codfish, fed to rats, causes the appearance in the urine, after 25—30 days, of a green pigment (II) which does not appear on an exclusive meat diet. (II) appears earlier if EtOH is given with the egg-white or if the rats have previously been for some time on (I). During exclusive protein feeding urinary N excretion increases to 10—20 times the normal. When part of the egg-white is replaced by starch or butter in the proportion 1:6, the loss is greatly reduced and (II) disappears from the urine. On an exclusive meat diet little or no growth occurs in rats, and dried cod will not maintain body-wt. Milk-protein permits maintenance of wt. and health for a long time.

NUTR. ABS. (m)

Value of protein degradation products in silage for the nitrogen metabolism of milch cows and wethers. W. KIRSCH and H. JANTZON (Futterkonservierung, 1933, 4, 79—92).—In silage, true protein is broken down to amides. In clover silage (I), made by the cold process with addition of sugar, decomp. of 34.4% of true protein occurs. In milch cows and wethers fed on (I) containing amides sufficient for N requirement, the amides are utilised. The N balance is always positive. NUTR. ABS. (m)

Production of purines in exogenous protein metabolism. C. DEGAN (Ann. Physiol. Physico-chim. biol., 1933, 9, 481—493).—In rapidly growing pigs (wt. 14—20 kg.) addition of considerable quantities of starch to a diet of skim milk causes a marked increase in N retention and a simultaneous decrease in excretion of purines and of allantoin+purine derivatives. This indicates synthetic production of purines from dietary proteins. NUTR. ABS. (m)

Constancy of the level of endogenous purine excretion in the individual. C. DEGAN (Ann. Physiol. Physico-chim. biol., 1933, 9, 451—468).—The total urinary excretion (I) of purines is const., per unit wt., in animals of the same species, and of approx. the same size (pigs, rabbits, dogs), on a diet of carbohydrates only, this level representing the min. level of sp. endogenous N metabolism. On a diet free from purines but containing protein, (I) varies from individual to individual and is always > on a carbohydrate diet, indicating purine synthesis. The ratio of allantoin-N+total purine-N:total N, which is const. in adult rabbits from one individual to another, varies in growing pigs. NUTR. ABS. (m)

Dependence of the excretion of endogenous purines on the quantity and energy value of the

diet. C. DEGAN (Ann. Physiol. Physico-chim. biol., 1933, 9, 469—480).—With young pigs (wt. 15—20 kg.) on a diet without protein and consisting almost entirely of carbohydrates, fed in varying amounts, increases up to four times the lowest level cause no increase in the excretion of endogenous purines (I). Purine excretion parallels total N excretion and falls when the supply of carbohydrate and fat is insufficient to ensure the min. level of (I) metabolism. It is unlikely that processes connected with the work of the digestive tract and the associated glands play any important role in the production of (I). NUTR. ABS. (m)

Effect of amino-acids on purine metabolism. C. DEGAN (Ann. Physiol. Physico-chim. biol., 1933, 9, 494—507).—In pigs addition to the diet of glycine, glutamic acid, or asparagine in large quantities causes no increase in purine excretion. NUTR. ABS. (m)

Purine metabolism in hypophysectomised dogs. B. BRAIER (Compt. rend. Soc. Biol., 1933, 114, 1209—1212).—In normal and hypophysectomised dogs fed (a) for 6—10 days on lean beef free from bone, (b) for 10 days on a progressively decreasing N intake, and (c) on a N-free diet for 5 days, the N output is least from the operated dogs during protein starvation (I). Whilst normal and operated dogs have comparable outputs of total purine, the latter eliminate less uric acid and purine bases but more allantoin. The ratio allantoin-N : total N is higher in these dogs in all three periods than in controls. The ratio total purine-N : total N is similar in both groups. The coeffs. of purine oxidation during (I) is 72% for normal and 88% for operated dogs. NUTR. ABS. (m)

Nuclein metabolism. XXXIII. Adeninedeoxyriboside. W. KLEIN. XXXIV. Ribodeoxyadenylic acid from thymus-nucleic acid. W. KLEIN and S. J. THANNHAUSER (Z. physiol. Chem., 1934, 224, 244—251, 252—260; cf. A., 1933, 981).—XXXIII. Ag⁺ selectively inhibits the action of deaminase in the intestinal enzyme system and permits the isolation of cryst. adeninedeoxyriboside (+H₂O), m.p. 181°, [α]_D²⁰ -26° in H₂O (picrate), from the enzymic hydrolysis products of thymus-nucleic acid.

XXXIV. The EtOH-sol. fraction from the enzymic hydrolysis of thymus-nucleic acid in presence of arsenate was fractionated by means of brucine. It gave ribodeoxyadenylic acid [cryst. Ca salt (I) (+H₂O), decomp. without melting, [α]_D²⁰ -38° in H₂O]. Intestinal phosphatase hydrolyses (I), yielding adenine- and hypoxanthine-deoxyriboside.

J. H. B.

Muscle contraction. K. LOHMANN (Naturwiss., 1934, 22, 409—411).—The energy changes in muscle contraction are discussed with particular reference to the creatinephosphoric acid cleavage.

H. D.

Utilisation of yeast in man. F. M. KUEN and K. PURINGER (Biochem. Z., 1934, 271, 152—167).—Utilisation of the N and energy (calories) provided by fresh press yeast (dead) amounts to 52.5 and 37.1%. With dried yeast the vals. are 90.4 and 89.05%. The difference is due to the alteration in the walls of the yeast cells and consequent increased capability for diffusion caused by the drying.

W. MCC.

Hippuric acid. IV. Synthesis in the animal body. I. KANZAKI (Sei-i-kwai Med. J., 1933, 52, No. 1, 85—96).—In rabbits the kidneys are not the only organs concerned. Experimental P or CHCl₃ poisoning shows that the liver participates in the synthesis.

CH. ABS.

Origin of phenols in the organism. A. D. MARENZI (Compt. rend. Soc. Biol., 1933, 114, 800—801).—After complete excision of the intestinal tract in two dogs, the phenol content of the urine decreased from 490 to 189 mg. per litre. After bilateral nephrectomy (I) the total phenol content of the blood increased from 1.8 to 5.6 mg. per 100 c.c. in 3 days. After (I) and excision of the gastro-intestinal tract, the blood-phenol increased less rapidly, from 1.5 to 3.3 mg. per 100 c.c. in 34 hr. Part of the blood-phenol is of endogenous origin.

NUTR. ABS. (m)

Metabolism of naphthalene in rabbits. M. C. BOURNE and L. YOUNG (Biochem. J., 1934, 28, 803—808).—The urine of rabbits to which C₁₀H₈ has been fed contained (a) a sol. compound of unknown constitution which yields C₁₀H₈ when warmed with dil. HCl, and (b) 1- α -naphthylmercapturic acid, m.p. 170—171°, [α]_D²⁰ -25° in EtOH (cf. this vol., 888). When heated with acid it yields β -1-naphthylthiolpropionic acid, decomp. 160—165°, and AcOH, whilst with dil. NaOH, NH₃ is evolved and α -C₁₀H₇SH is formed.

W. O. K.

Effect of apple diet on nitrogen and mineral metabolism. H. HUTKER (Arch. Kinderheilk., 1933, 100, 2—15).—During a raw apple-diet period the N balance became negative and the non-protein-N of the serum reduced; serum-Cl was reduced and alkali reserve increased. S and P retentions were diminished due to reduced intake. The Ca balance was also reduced due to increased excretion through the gut. The good effect of the diet in renal disease is probably the result of increased excretion of nitrogenous waste substances.

NUTR. ABS. (b)

Nutritive value of the mountain apple, *Eugenia malaccensis* or *Jambosa malaccensis*. C. D. MILLER, R. C. ROBBINS, and K. HAIDA (Philippine J. Sci., 1934, 53, 211—221).—In comparison with ordinary apples mountain apples have approx. the same proportion of Ca, P, and Fe, higher H₂O contents, lower (50%) sugar, and somewhat lower vitamin-A, -B₁, -B₂, and -C contents.

A. G. P.

Effect of acidified silage on digestibility, nitrogen, calcium, and phosphorus balances in cattle, sheep, and dogs. F. GRAMATZKI (Z. Tierzuchtungsbiol., 1933, 28, 433—450).—In ruminants utilisation of N was reduced by addition of acids, and the P- and, to a smaller extent, the Ca-balance reduced. In pigs the results were similar, the P and Ca balances being most affected when free mineral acid was present in the silage.

NUTR. ABS. (b)

Effect of hot-fermentation silage from containing *Equisetum* on composition of milk and butter-fat. J. KESELING (Milch. Forsch., 1934, 16, 148—154).—Feeding silage containing *Equisetum* causes a fall in total protein, caseinogen, and albumin and a rise in the n of the milk, whereas feeding *Equisetum* changes these vals. in the opposite direction.

other vals. show changes in the same direction, but of different orders, with the two types of feeding, except the P_2O_5 content, which is unaltered. The acidity of the butter-fat and its I val. are raised and the Reichert-Meissl, Polenske, and sap. vals. are lowered by feeding either the silage or the hay. NUTR. ABS. (b)

Iodine metabolism in man. W. ELMER (Polska Gaz. lekarska, 1932, No. 49; 1933, Nos. 4 and 11).—In normal persons an increase in blood-I was observed up to 6 hr. after intravenous injection of KI containing 1.3 mg. of I; the increase lasted longer in hypothyroid persons (I). In hyperthyroidism (II) the original level was reached in 24 hr. Elimination of the injected I was greatest during the first 6 hr. and amounted in 24 hr. to 20–30% of the amount injected. In (I) the amount excreted was much > in (II), much < in normal subjects. There was no increase in the I of bile. It appears that hyperthyroid tissues absorb I with more avidity than normal. NUTR. ABS. (b)

Iodine excretion in the bile during fasting and after food. A. W. ELMER and Z. LUCZYNSKI (Compt. rend. Soc. Biol., 1933, 114, 1340–1342).—The I content of the bile in fasting rabbits was $4-14 \times 10^{-6}$ g., in rabbits after feeds of beetroot and oats, $27-69 \times 10^{-6}$ g. per 100 c.c. The liver probably plays an important part in the metabolism of I, excreting it in the bile after meals. NUTR. ABS. (b)

Chlorine impoverishment and regulation of osmotic pressure. E. KERPEL-FRONIUS (Z. ges. exp. Med., 1933, 90, 676–683).—In young puppies a carbohydrate-rich, NaCl-free diet led to great reduction of the Cl contents of blood and tissues, but no increase in non-protein-N or alkali reserve. There was an increased H_2O content of brain sufficient to cause cerebral disturbances. Addition of 3% of protein to the diet delayed the onset of osmotic disturbances (I) and hydraemia (II), whilst addition of NaCl prevented (I), but had no effect on (II). NUTR. ABS. (b)

Changes in calcium content of the embryo and egg of the hen during incubation. P. SACCARDI and P. LATINI (Arch. Sci. biol., 1933, 19, 55–61).—The Ca content of the egg (white+yolk) increases more during incubation than in the unincubated egg. The Ca is derived from the shell for the growth of the embryo. The increase becomes marked about the twelfth day of incubation and thereafter increases rapidly. NUTR. ABS. (b)

Calcium tolerance in cats. J. L. D SILVA (J. Physiol., 1933, 80, 6p).—Intravenous injection of $CaCl_2$ in Ringer solution (18 mg. of Ca per c.c.) into chloralosed cats caused a rise in serum-Ca (I) in some animals > in others, apparently due to a difference in capacity of the tissues to assimilate Ca. In cases where very high (I) vals. are obtained, the Ca may be in an inactive form, since Ca rigor of the heart would otherwise result. NUTR. ABS. (o)

Mineral metabolism. XXVII. Effect of two different calcium-phosphorus ratios on the growth of calves. P. J. DU TOIT, A. I. MALAN, and W. GROENEWALD (Onderstepoort J. Vet. Sci., 1933, 1, 421–424).—No difference in growth rate was

observed when the calves received 10 lb. of whole milk per day, whether the $CaO : P_2O_5$ ratio of the diet was kept at 1:1.4 (as in milk) or at 1:0.3 (by feeding $CaCO_3$). NUTR. ABS. (b)

Retention of calcium and phosphorus in rations with a wide $CaO : P_2O_5$ ratio. J. H. W. T. REIMERS (South African J. Sci., 1933, 30, 447–451).—No harmful results were observed with young pigs on a ration with a $CaO : P_2O_5$ ratio of 1:2 or 1:3. Extra P_2O_5 , supplied as Na_2HPO_4 , did not affect the Ca but increased the P balance. The excess P was almost all voided in the urine. NUTR. ABS. (b)

Influence of some acids on the calcium, phosphorus, and nitrogen metabolism and acid-base equilibrium in fowls. H. BURCKHARDT (Rept., Versuchsanst. Liebefeld-Bern).—The retention of Ca and P by two cockerels was increased by the addition of skim-milk to a basal ration, but was unaffected by the further addition of 1.2% of lactic acid (I). Addition of 0.5% of HCl had no effect on one cockerel, but in the other resulted in increased NH_3 -N content of the urine, a negative Ca balance, and decreased P and N retention. This addition is probably about the crit. level. With young chicks, (I) and AcOH were without harmful effect. The same amount of HCl was detrimental. NUTR. ABS. (b)

Water exchange in the body of the fish. G. VON HEVESY and E. HOFER (Z. physiol. Chem., 1934, 225, 28–34).—The H_2O in the body of fish immersed in H_2O containing 0.45% of H_2O takes up H_2O until equilibrium (i.e., equal H_2O content) is reached with the external H_2O (about 1 hr. for goldfish, longer for larger fish). If the fish is then transferred to H_2O , an exchange again occurs. With dead fish the exchange is slower. H^1 attached to C is not exchanged for H^2 . J. H. B.

Iron in the diets of pre-school children. H. MCKAY (Ohio Agric. Exp. Sta. Bimo. Bull., 1934, 19, 73–77).—Data showing the daily intake of Fe by children are recorded and discussed. A. G. P.

Intermediary iron metabolism in children. F. THOENES (Klin. Woch., 1933, 12, 1686–1688).—Barkan's "easily eliminated Fe" of whole blood (action of 0.4% HCl) is about 5% hæmoglobin-Fe (I). In serum or plasma very small quantities occur, about 0.4% of (I). Serum-Fe of children is highest at birth, 1.72×10^{-3} mg. per c.c. To the end of the second month the average is 1.29; later 0.80. For older children it is 1.21. It therefore approx. parallels (I). Under-nutrition and starvation increase and post-hæmorrhagic or nutritional anæmia reduces it. Scarlet fever, diphtheria, measles, and septic infections greatly reduce it. Whooping cough and tuberculosis have no effect. Medicinal Fe does not increase it regularly or definitely. Blocking the reticulo-endothelial system or diphtheria toxin reduces it. Hence serum-Fe is a measure of blood destruction which the reticulo-endothelial system controls. NUTR. ABS. (b)

Ethyl alcohol. IV. Distribution of alcohol in tissues. M. NICLOUX. V. Diffusion of ethyl alcohol. M. NICLOUX and G. GOSSELIN (Bull. Soc. Chim. biol., 1934, 16, 330–337, 338–354).—IV. The

penetration of EtOH into tissue may be analogous to that of CHCl_3 , but the H_2O , instead of the lipin content, will be the determining factor.

V. EtOH penetrates into biological fluids placed in collodion dialysing vessels surrounded by dil. aq. EtOH until the [EtOH] outside is equal to the concn. in the H_2O inside. When live fish, however, are placed in dil. aq. EtOH the ratio of [EtOH] in the H_2O of the tissue to that in the external medium is 0.86 for the whole gudgeon, 0.94 for the tadpole, 0.83 for the liver, 0.86 for muscle, and 0.92 for the blood of the carp.

A. L.

Occupational poisoning by the vapours of some esters employed as solvents. P. DUQUENOIS and P. REVEL (J. Pharm. Chim., 1934, [viii], 19, 590—601).— HCO_2Me , HCO_2Et , MeOAc , and EtOAc are toxic to man. The symptoms induced in frogs and guinea-pigs are described.

H. N. R.

Chemical and pharmacological studies on mixtures of sodium halides with quinine salts. G. MARTIGNETTI (Arch. Farm. sperim., 1934, 58, 14—33).—The min. concn. of quinine mono- (I) or di-hydrochloride (II) solution required to form a ppt. with solutions of NaCl varies approx. inversely as the min. [NaCl]. The ppt. is shown to consist of (I) or (II), the solubility of which is lowered by the Cl' of the NaCl. Rabbits injected intravenously with NaCl are not killed by the min. lethal dose of (I), and only after some considerable time by that of (II), unless NaCl is so conc. as to be itself toxic.

R. N. C.

Destruction of *l*-, *d*-, and *dl*-hyoscyne by egg-white and rabbit serum. W. F. VON OERTINGEN and I. H. MARSHALL (Proc. Soc. Exp. Biol. Med., 1933, 31, 224—225).—*l*-Hyoscyne, *dl*-hyoscyamine, and their isomerides are destroyed at the same rate on incubation with egg-white, but with rabbit serum the relative amount of destruction differs according to the period. The differences reside in the tropic acid radical.

CH. ABS.

Reaction given by urine after ingestion of novalgin or melubrin. S. DEZANI and A. M. B. SEMERIA (L'Ind. Chimica, 1934, 9, 764—767).—Following ingestion of novalgin (Na 4-sulphonylmethylamino-1-phenyl-2:3-dimethylpyrazolone) or melubrin (the sulphonylamino-compound), the urine gives a ruby-red colour with I, probably owing to hydrolysis of the two compounds in the organism to 4-amino-1-phenyl-2:3-dimethylpyrazolone (amino-antipyrin) or a related compound.

T. H. P.

Comparative pharmacological studies on calcium gluconate and camphorsulphonate. I. L. DONATELLI (Arch. Farm. sperim., 1934, 58, 34—48).—The actions of Ca gluconate (I) and camphorsulphonate (II) on the isolated frog's heart are similar. The effect of (II) on the isolated mammalian heart persists longer than that of (I) after washing out. (II) augments blood-pressure (III) and respiration (IV) steadily; (I) has no effect on (III), and causes unsteadiness in (IV). Cryoscopic measurements show that (II) is almost completely dissociable, but (I) only partly, their solutions isotonic with blood being, respectively, 4.75% and 9%.

R. N. C.

Extraction of the active principle of *Acocanthera Abyssinica*. C. BRAGA (Arch. Farm. sperim., 1934, 58, 1—13).—The active principle (I) has been obtained by extraction of the powdered leaves with H_2O , neutralisation with aq. NH_3 , pptn. as tannate, decomp. of this with ZnO , extraction with EtOH, and successive dissolution in H_2O and EtOH and filtration. (I) is difficult to separate from resins, and has not been obtained quite pure; it is apparently a glucoside, is dialysable, and arrests the heart in systole.

R. N. C.

Blood-sugar regulation as affected by psychic secretion of the glands of the digestive system. G. SANPAOLESI (Riv. Clin. Pediat., 1933, 31, 1076—1080).—In infants, after a fast of 7—8 hr., the sight of food, sucking an empty bottle, or sham feeding with an empty spoon in presence of food causes a 20% increase in blood-sugar.

NUTR. ABS. (m)

Carbohydrate metabolism and the effect of decapitation and decerebration under nitrous oxide anaesthesia. J. S. L. BROWNE and C. L. EVANS (J. Physiol., 1933, 80, 1—20).—Anaesthesia with N_2O containing 5—12% of O_2 results in a rise of blood-sugar and -lactate in cats. Decapitation or decerebration under N_2O results in a fall of liver-glycogen followed by a rise, the fall being less in animals with inactivated adrenal glands. In the decapitated cat glycconeogenesis usually proceeds at the rate of at least 0.6 g. per hr.

NUTR. ABS. (m)

Liver-glycogen during decerebration hyperglycaemia: influence of atropine and ergotamine on this condition. M. L. LONG (J. Physiol., 1933, 80, 296—304).—Intravenous injection of atropine (1—11 mg. per kg.) into rabbits with a high liver-glycogen (I) 0—4 hr. after pontine puncture, only slightly retards, whilst ergotamine (0.4—0.9 mg. per kg.) under the same conditions, and also when (I) is low, almost entirely prevents, decerebration hyperglycaemia. Atropine does not influence the breakdown of (I), whilst in most experiments with ergotamine (I) and blood-lactic acid remain practically unchanged. No correlation could be found between decrease in (I) and increase in blood-sugar following decerebration.

NUTR. ABS. (m)

Effect of splanchnicotomy and phloridzin on decerebration hyperglycaemia. M. G. FORSTER (J. Physiol., 1933, 80, 323—328).—Pontine decerebration of fasted rabbits is not followed by the usual rise of blood-sugar if the splanchnic nerves are tied several days before, or if phloridzin is administered during, the experiment, provided the renal vessels are not ligated.

NUTR. ABS. (m)

Autonomic cell regulation after administration of phloridzin. A. PARTOS and A. HERZOG (Z. ges. exp. Med., 1933, 91, 602—607).—After subcutaneous injections of phloridzin into rabbits and dogs there are increase and decrease of the sugar of the whole blood, plasma, and corpuscles. The corpuscular sugar varies inversely with the cholesterol concn., which appears therefore to be an important regulator of the cellular content of sugar.

NUTR. ABS. (m)

Action of phloridzin on sugar absorption. E. WERTHEIMER (Pflüger's Archiv, 1933, 233, 314—

528).—Subcutaneous or oral administration of phloridzin (I) to rabbits reduces the absorption (II) of sugars from the alimentary tract. The reduction runs parallel with the rapidity of (II) demonstrated by Cori for the various sugars, being greatest with galactose and glucose and least with the pentoses. The rate of (II) of glucose with (I) is the same as that of arabinose alone. The (II) of sugars from the peritoneal cavity is not affected by (I), nor is (II) of NH_2 -acids from the intestine. (I) has an elective action, preventing the active (II) by, but not diffusion of sugar through, the bowel wall and renal tubules. The prevention of active (II) is possibly due to inhibition of hexose phosphate production by (I). NUTR. ABS. (m)

Determination of phloridzin in the liver and kidneys after intravenous injection into the dog. A. LAMBRECHTS (Compt. rend., 1934, 198, 2029—2030).—The amount of phloridzin in the liver and kidneys of the dog 25—80 min. after intravenous injection is found by ultra-violet spectrography to be small.

R. S. C.

Influence of the autonomic nerves on alimentary hyperglycæmia and the absorption of glucose. E. A. HORNE, E. J. McDOUGALL, and H. E. MAGEE (J. Physiol., 1933, 80, 48—64).—Ergotoxine (I) and atropine (II) suppress hyperglycæmia (III) in normal rabbits after oral administration of glucose partly by delaying absorption (IV), whilst in amygalised animals splanchnicotomy, vagotomy, or injection of atropine increases the rate of (IV) of glucose and the degree of (III); (I), or (I) + (III), stimulate (IV), but temporarily suppress (III). The promotion of (IV) by (I) and (II) is due to inhibition of impulses passing down the autonomic nerves. The results favour the view that alimentary (III) is due to an overflow of absorbed glucose through the liver. NUTR. ABS. (m)

Experimental tolerance to some poisons. J. LÉVY (Bull. Soc. Chim. biol., 1934, 16, 631—709).—A lecture.

Protective action of various antidotes on poisoning by α -aminopropionitrile. C. SANNIE (Bull. Soc. Chim. biol., 1934, 16, 562—580).—Cysteine and glutathione have a preventive but no curative effect, glucose and methylene-blue are without action, NaNO_2 , NaH_2PO_2 , and sulphates of NH_4OH and N_2H_4 have curative but not preventive effect when used as antidotes for poisoning in guinea-pigs injected with lethal doses of $\text{NH}_2\text{-CHMe-CN}$. A. L.

Neuro-muscular action of amides and cyanides. R. BONNET (Compt. rend., 1934, 198, 1880—1881).— $\Delta\text{H}_2\text{Ac}$ and urea (I) at a concn. of 0.093 g. N per 100 c.c. are not toxic to nerve (II) or muscle (III). At a concn. of 0.7 g. per 100 c.c. they poison (III) only. At much lower concn. ($\frac{1}{12}$ and $\frac{1}{8}$, respectively) HCN and KCN poison both (II) and (III). (I) thus behaves as an amide and not as a cyanide. C. G. A.

Clinical significance of traces of fluorides in water. N. J. AINSWORTH (Analyst, 1934, 59, 380)

— H_2O in areas associated with the clinical condition of "mottled teeth" contained 4.5—5.5 p.p.m. of F. E. C. S.

Effect of sulphide, sulphite, and sulphate compounds on metabolism. M. KOJIMA (Z. ges. exp.

Med., 1933, 91, 257—266).—Administration of $\text{S}^{''}$ to rats increased the C/N ratio in the urine and lowered the vacat-O/N and vacat-O/C ratios, i.e., decreased the oxidation of C, but increased that of N compounds. The effect of $\text{SO}_3^{''}$ and $\text{SO}_4^{''}$ was much less. A transient hyperglycæmia was produced in rabbits, greatest with $\text{S}^{''}$ and least with $\text{SO}_4^{''}$. NUTR. ABS. (b)

Glutathione and ascorbic acid content of the liver of rats poisoned with phosphorus. S. LANG and A. SCHÉDA (Biochem. Z., 1934, 271, 180—184).—Starvation has no effect on the (very variable) glutathione (I) content of the rat liver, on the ratio oxidised (I) : reduced (I), or on the ascorbic acid (II) content. The (I) content of the liver is much < that of the adrenals (III). Administration of P is also without effect on these vals. and on the (II) content of (III). There is no relation between the carbohydrate and the (I) contents of the liver. W. McC.

Pharmacology of lead. IX. Distribution of lead by the autohistoradiographic method. X. Relationship of lead deposition to calcium metabolism. B. BEHRENS and A. BAUMANN (Z. ges. exp. Med., 1933, 92, 241—250, 251—264).—Injection of radioactive Pb (Th-B) was followed by deposition of the metal in various organs and tissues, especially the bones. Large amounts were found in liver and spleen, and Pb was demonstrated in the bile a few min. after the injection. Pb was deposited in those areas of the bones where Ca was being deposited. When pathological calcification was produced (arterial degeneration, hypervitaminosis-D) Pb was always deposited in the calcified zones. Administration of acid reduced the deposition of Pb in all organs except the kidneys. Previous administration of Ca gluconate also decreased the retention of Pb. The parallelism between Ca and Pb is attributed to their affinity for $\text{PO}_4^{'''}$, that of Pb being the greater. NUTR. ABS. (b)

Copper balance in normal rats after ingestion of different amounts of copper. R. GUILLEMET (Compt. rend. Soc. Biol., 1933, 114, 1038—1040).—Practically all the Cu ingested as a sol. salt by a rat over a period of 34 days was excreted in the fæces, and there was no indication of storage of Cu when the animal was killed after a post-period of 20 days. The very small amount of Cu excreted in the urine was independent of the amount ingested.

NUTR. ABS. (b)

Extent of the retention of ingested aluminium. E. W. SCHWARTZ, G. J. COX, R. B. UNANGST, F. J. MURPHY, and H. B. WIGMAN (J. Amer. Med. Assoc., 1933, 101, 1722—1725).—Fresh tissues of guinea-pigs, receiving no added Al, contained about 0.4 p.p.m. Al, the carcasses of growing animals containing > those of the adult animal. Feeding large amounts of sol. Al salts (lactate or chloride) produced a scarcely detectable deposition of Al in the soft tissues and somewhat larger amounts in bone. Al does not appear to be cumulative in the tissues and no systemic pharmacological effect can be ascribed directly to absorbed Al. No harmful effects can be expected from sol. Al occurring in foods or introduced by utensils into a diet of normal P content. NUTR. ABS. (b)

Biological separation of heavy water. W. W. STEWART and R. HOLCOMB (J. Amer. Chem. Soc., 1934, 56, 1422—1423).—The d of H_2O obtained (repeated distillation with $KMnO_4$) from cow's milk and urine and tap- H_2O is the same in each case. H. B.

Relation of materials of the cell nucleus to the lethal action of ultra-violet radiation. J. R. LOOFBOUROW and F. F. HEYROTH (Nature, 1934, 133, 909).— λ 2950 Å. is approx. the longest effective in destroying thymus-nucleic acid, adenine, uracil, etc. Materials of the cell-nucleus appear to play an important part in the lethal action of ultra-violet radiation for many kinds of micro-organisms. When rays $<$ approx. 2900 Å. are filtered out, irradiation of nuclear compounds brings about absorption changes indicative of the formation of isomerides or more complex compounds. L. S. T.

Geochemistry of living matter. B. P. UVAROV (Nature, 1934, 134, 11—12). L. S. T.

Dehydrases. A. BERTHO (Angew. Chem., 1934, 47, 497—501).—A review.

Action of inhibitors on potato pyrocatechol-oxidase. D. RICHTER (Biochem. J., 1934, 28, 901—908).—Pyrocatechol-oxidase preps. (I) from different sources (potato, lilac, elder, mushroom, *Polyporus hispidus*, mealworm) show marked sp. differences in their behaviour towards the inhibitory effect of varying concns. of resorcinol. The conditions under which (I) effect the secondary oxidation of o - $C_6H_4(NH_2)_2$ and of $AcSH$ were determined. The rate of oxidation of p -cresol by potato (I) is markedly accelerated by substances which produce o -quinones (e.g., adrenaline, glycine, dihydroxyphenylalanine) and inhibited by substances which combine with o -quinones (e.g., $NaHSO_3$, KI , NH_2Ph); hence o -quinones play an essential part in the oxidation of monohydric phenols. F. O. H.

Flavin respiration. T. WAGNER-JAUREGG, H. RAUEN, and E. F. MÖLLER (Z. physiol. Chem., 1934, 225, 145—146; cf. this vol., 807).—Since cryst. lactoflavin shows a lower redox potential than the succinate-fumarate-succinodihydrogenase system, the actual H donor is probably formed from succinic acid during the experiment. O_2 is concerned in its production, which explains the inhibition of the reaction by HCN and CO . J. H. B.

Thermostability of fumarase. J. P. JACOBSON and F. B. PEIREIRA (Bull. Soc. Chim. biol., 1934, 16, 550—561).—Determinations of the const. of inactivation of fumarase for varying temp. indicate that the rate of inactivation (I) does not correspond with that of a unimol. reaction. (I) in more conc. is $>$ in dil. solutions of the enzyme, and increases with p_H of the solution and with age of the enzyme material. The presence of malate retards (I). A. L.

Inactivation of catalases from certain marine animals by oxygen. G. W. MARKS (J. Biol. Chem., 1934, 105, 489—500; cf. this vol., 109).—For catalases from various sources the inactivation in air is $>$ in N_2 . Assuming the quantity of H_2O_2 decomposed is directly \propto the enzyme concn. a unimol. equation expresses the inactivation. H. D.

Oxidation of thiosulphate to sulphate by tissue slices *in vitro*. N. W. PIRIE (Biochem. J., 1934, 28, 1063—1075).— $Na_2S_2O_3$ is oxidised to SO_4^{2-} by rat-liver, -kidney, and -chorion and goose-kidney without increase in O_2 consumption. This will not take place anaerobically, and the tissue is irreversibly inactivated by anaerobic incubation. $Na_2S_4O_6$ is also oxidised, but there is no evidence that it is an intermediate in the above reaction. H. G. R.

Interferometric method [applied to Abderhalden's reaction]. A. DURUPT (Bull. Soc. Chim. biol., 1934, 16, 461—464).—A reply to Guillaumin (this vol., 428). A. L.

Propepsin and prorennin. S. P. L. SØRENSEN, H. HOLTER, and B. ANDERSON (Biochem. Z., 1934, 271, 199—205).—Recent papers (A., 1932, 881; 1933, 1081, 1203; this vol., 450) contain many contradictions because insufficient care is taken to distinguish between the substances concerned and to take into account the peculiarities of coagulation. W. McC.

Determination of pepsin. L. UTKIN (Biochem. Z., 1934, 271, 127—130).—As in Robertson's method of trypsin determination (A., 1912, ii, 819) caseinogen (I) (about 2%) in 0.25*N*-HCl is treated with pepsin at 30°. After pptn. of (I) with aq. 0.133*N*- $NaOAc$ n is determined. A second determination is made after 30 min. (p_H 1.6—1.7). The amount of pepsin which changes n by 0.0005 is a pepsin unit. The error is $\pm 2.5\%$. W. McC.

Plant proteases. XVII. Aminopolypeptidase of yeast. W. GRASSMANN, L. EMDEN, and H. SCHNELLER (Biochem. Z., 1934, 271, 216—228; cf. A., 1931, 393; 1933, 1081).—Increased purity and yield are attained by liberating the enzyme from yeast with papain, pptg. with $AcOH$ (avoiding excess), dissolving the ppt. in aq. NH_3 , removing impurities (including most of the nucleic acid) by adding $NaOAc$ and $(NH_4)_2SO_4$ to saturation, and dialysing. The yield obtained by grinding yeast with liquid air is almost as high; hence the enzyme is probably present as such in the cells. The purest samples contain about 1% of P, exhibit protein reactions, and have activity equiv. to > 400 units. W. McC.

Nucleotidase and its relationship to the deamination of nucleotides in the heart and in muscle. J. REIS (Bull. Soc. Chim. biol., 1934, 16, 385—399).—A study of the phosphatase content of various tissues of the frog, rat, dog, man, pig, rabbit, calf, hen, goose, and pigeon using adenylic (I) and inosic (II) acids and adenine nucleotide as substrate, indicates that there exists a nucleotidase (III) sp. for purineriboside 5-monophosphates which is distributed in varying amounts throughout the tissues, but is not found in the skeletal muscle (IV). Whilst in (I) of the frog no nucleotidase is present, with that of the rat only (I) and (II) yield H_3PO_4 . The influence of Mg^{++} and substrate concn. on (III) is the same as that on bone-phosphatase. A parallel study of deamination (V) and dephosphorylation (VI) using (I) as substrate indicates that in the skeletal muscle of the frog and rabbit and in the heart-muscle of the pigeon, where the nucleotidase content is small or nil, (V) can take place independently of (VI). PO_4^{3-} inhibits ()

only in the heart-muscle of the pigeon. (V) may therefore take place directly without previous (VI). A. L.

Glycolysis. E. LUNDGAARD (Angew. Chem., 1934, 47, 495—497).—A review.

Influence of the hydrogen-ion concentration of the medium on the hydrolysis of α - and β -glycerophosphoric acids by maltase. J. COURTOIS (Compt. rend., 1934, 199, 95—97).—The optimum p_H for the hydrolysis of α -glycerophosphoric acid (I) of concns. 0.01, 0.1, and 0.333*N* is 4.7, 4.5, and 5.2, respectively, and 3.9, 4.0, and 5.2 for the β -form (II). The rate of hydrolysis of both isomerides is higher for lower concns. of substrate and smaller p_H than for higher concns. and greater p_H . The rate of hydrolysis of (II) is $>$ that of (I) because (II) has (a) a larger affinity for maltase (cf. A., 1913, i, 540) than (I), and (b) because of the greater speed of hydrolysis of its maltase-substrate complex. The p_H influences (a) and (b) in opposite senses. J. L. D.

Specificity of β -glucosidase and enzymic equilibrium. C. N. IONESCU and A. KIZYK (Ber., 1934, 67, [B], 990—996).—Repetition of the work of Bourquelot (J. Pharm. Chim., 1914, [vii], 10, 361) on the hydrolysis/synthesis of β -methylglucoside (I) by emulsin in MeOH-H₂O confirms his results, and is supported by a similar series of experiments in OEt·CH₂·CH₂·OH-H₂O. The discrepancy between the const. calc. from the ratio of the velocities and from the concns. is not due, as supposed by von Euler and Josephson (A., 1924, i, 1266), to the greater affinity of β -glucosidase for glucose than for (I), but to their failure to take into account the different concn. of MeOH and H₂O. The general laws of chemistry are applicable to these reactions, which do not form exceptions to the law of mass action. H. W.

Specificity of glucosidases in moulds and bacteria. E. HOFMANN (Naturwiss., 1934, 22, 406—409).—EtOH-Et₂O-treated *B. Delbrücki* and *B. coli* decomposed 60% in 48 hr. and 97% in 24 hr., respectively, of solutions of β -phenylgalactoside (I), whilst β -phenylglucoside (II) was unattacked under the same conditions. Enzyme preps. from *A. niger* hydrolysed both (I) and (II) in proportions varying with the substrates on which they were reared. Preps. from *Mucor javanicus* hydrolysed (I) only. D

Function of phosphates in the fermentations of sugars. W. J. YOUNG (J. Proc. Roy. Soc. N.S.W., 67, 1—17m).—A lecture. C. M. B.

Equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid [in biological fluids]. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1934, 271, 89—110; cf. this vol., 560).—Dialysed muscle extract (rabbit) or yeast extract contains a H₂O-sol. enzyme, zymohexase (I), which is not readily adsorbed and is relatively thermostable (destroyed in 30 min. at 60°, in 10 min. at 70°). (I) is unaffected by CH₂I·CO₂H, NaF, and Na₂C₂O₄, is most active at p_H 6—10, and rapidly (a few min. at room temp.) converts hexose diphosphate or dihydroxyacetonephosphoric acid into an equilibrium mixture of the two. K varies from 22×10^{-3} at 70° to 0.18×10^{-3} at -7°. W. McC.

Conversion of diphosphoglyceric acid into pyruvic acid. C. NEUBERG, W. SCHUCHARDT, and A. VERCELLONE (Biochem. Z., 1934, 271, 229—232).—At p_H about 6.7 fresh top yeast or maceration juice from bottom yeast converts diphosphoglyceric acid into AcCO₂H. W. McC.

Decomposition of lactic acid by yeast enzymes. III. A. HAHN and M. DURR (Z. Biol., 1934, 95, 298—306; cf. this vol., 110).—Formation of lactic acid (I) in yeast suspensions in PO₄''' buffer digested for 3 hr. at p_H 7 occurs in vac. but not in O₂. In presence of CH₂Br·CO₂H, formation of (I) in vac. is inhibited, whilst a decrease in the content of (I) occurs in O₂, a process inhibited by KCN. In presence of washed muscle, 0.008% of CH₂Br·CO₂H suppresses the increase of (I) in vac., no oxidation of (I) occurring in O₂. This absence of O₂ carrier is due to inactivation by EtOAc used in the prep. of the yeast. Addition of the cell-residues of the extract produces a marked oxidation of (I), which is also shown by suspensions of dried yeast and, to a smaller extent, by yeast macerates. F. O. H.

Cozymase. I. Mol. wt. K. MYRBACK. II. Isolation. K. MYRBACK and H. LARSSON (Z. physiol. Chem., 1934, 225, 125—130, 131—140).—I. The mol. wt. of purified cozymase (I) by the free diffusion method is probably about 500, certainly 450. The (I) in the various layers was determined by fermentation. Ionic dissociation is repressed by NaCl, which, however, inhibits the fermentation and tends to give high vals. for mol. wt.

II. (I) solutions were purified by pptn. of impurities with Pb(OAc)₂, pptn. of (I) with Hg(NO₃)₂, and liberation by H₂S. Pb(OAc)₂+Ba(OH)₂ may also be used in place of Hg(NO₃)₂, Pb being removed by H₂SO₄. Other precipitants used consecutively for further purification are phosphotungstic acid, picric acid (to remove impurities), and AgNO₃. The best fraction, $[\alpha] -70^\circ$, had an activity of 180,000 units. Various colour reactions are given. (I) contains 15% of N, of which 80—85% is purine (adenine)-N, the remainder a different form. J. H. B.

Cozymase as co-enzyme in enzymic dehydrogenations. B. ANDERSSON (Z. physiol. Chem., 1934, 225, 57—68).—In addition to the enzymic dehydrogenation of malic, lactic, citric, and glutamic acids and EtOH, that of HCO₂H and glucose is also activated by cozymase (I), but not by succinic dehydrogenase. The enzymic oxidation of EtOH and lactic acid by O₂ and washed, dried top yeast or washed heart-muscle is activated by (I). The co-enzyme of lactic acid- and probably of glucose-dehydrogenase is identical with cozymase. J. H. B.

Resistance of micro-organisms, particularly yeasts, to ultra-violet light. J. BEAUVERIE (Compt. rend., 1934, 198, 2017—2019).—Individuals of *Saccharomyces cerevisiae* have varying resistance to ultra-violet light, some being killed, some unable to reproduce, and some unaffected after the same exposure. R. S. C.

Biochemistry of micro-organisms. XXXVIII. Metabolic products of *Penicillium minioluteum*, Dierckx. Minioluteic acid. J. H. BR-

KINSHAW and H. RAISTRICK (Biochem. J., 1934, 28, 828—836).—*P. minio-luteum* grown on Czapek-Dox medium with glucose as the sole source of C yields spiculisporic acid (γ -hydroxy- $\beta\delta$ -dicarboxypentadecoyl-lactone (cf. Clutterbuck *et al.*, A., 1931, 1094), and *minioluteic acid* (I), $C_{14}H_{24}O_3(CO_2H)_2$, m.p. 171° , $+108.1^\circ$, $[\alpha]_{D}^{20} +94.5^\circ$ (in $COMe_2$), $[\alpha]_{D}^{19} +62.4^\circ$, $[\alpha]_{D}^{20} +54.6^\circ$ (Na_2 salt in H_2O) (Me_2 ester, m.p. 86.5° ; trihydrazide, sinters 157 – 160° , m.p. 201°). When fused with KOH (I) yields $H_2C_2O_4$, *n*-dodecoic acid (hydrazide, m.p. 104 – 105°), and *decylsuccinic acid* (II), m.p. 90 – 91° [*anhydride* (III), m.p. 66 – 67°], the constitution of which is proved by condensing Et α -bromo-*n*-dodecoate with Et sodiomalonate to give Et $\alpha\beta$ -dicarbethoxytridecoate, b.p. $172^\circ/1$ mm., hydrolysed to $\alpha\beta$ -dicarboxytridecoic acid, m.p. 148° , vac. distillation of which yields (III), hydrolysed to (II). (I) with Na-Hg gives the γ -lactone of α -hydroxy- γ -carboxy-*n*-tetradecoic acid (IV), m.p. 119° , also obtained by condensing Et_2 decylsuccinate, b.p. 155 – $159^\circ/2$ mm., with $Et_2C_2O_4$ in NaOEt to impure α -keto- γ -carboxy-*n*-tetradecoic acid (2:4-dinitrophenylhydrazone, m.p. 180°), reduced (Na-Hg) to (IV). (I) is therefore the γ -lactone of $\alpha\beta$ -dihydroxy- $\beta\gamma$ -dicarboxy-*n*-tetradecoic acid. W. O. K.

Formation of urease by *Aspergillus niger*. T. MIWA and S. YOSHII (Sci. Rep. Tokyo Bunrika Daigaku, 1934, 1, 243—270).—*A. niger* and *Penicillium glaucum* produce both urea and urease when grown in media containing NH_4NO_3 or protein fission products (hydrolysates of silk, fibrin, or ovalbumin). The production of urease is accelerated by addition of glucose or fat to peptone cultures and, except when NO_3^- is used as a source of N, by increase of $[H^+]$, whilst it is less marked with old cultures. F. O. H.

Hydrocyanic acid as a nitrogen source for the growth of *Aspergillus niger*. N. N. IVANOV and L. K. OSNIZKAJA (Biochem. Z., 1934, 271, 22—31).—In a N-free medium containing sugar, N, in a form which cannot be utilised by the mould, is given up to the medium, despite the N-insufficiency, by *A. niger*. When KCN is added its N is assimilated, the N content of the mycelium increasing almost five-fold. W. McC.

Fermentation of sugar by the root nodule bacteria. A. I. VIRTANEN, M. NORDLUND, and E. HOLLO (Biochem. J., 1934, 28, 796—802).—Fermentation of glucose by heavy suspensions of *Rhizobium trifolii* (I) gives rise to $PrCO_2H$, considerable quantities of lactic acid being found as intermediate. CO_2 , H_2 , and small amounts of AcOH and EtOH are also produced, the mol. ratio of $PrCO_2H$ to CO_2 and H_2 being 1:2:2. Similar fermentation of glucose is also caused by crushed nodules from plants grown in sterile quartz sand cultures. An aq. extract of *Aspergillus niger* mycelium stimulates the growth of (I). The catalase content of (I) is comparatively low. W. O. K.

Isoelectric point of bacteria. G. YAMAHARA and S. ABE (Sci. Rep. Tokyo Bunrika Daigaku, 1934, 1, 221—229; cf. A., 1933, 1334).—Flocculation and micro-cataphoresis in 0.9% NaCl-HCl or 0.02M- PO_4''' buffer give, respectively, the p_H vals.: *B. pseudodiphtheriae* (?), 1.6 and 4.3, 1.8; *B. subtilis*, 2.2, 3.6; *B. pertussis*, 1.9, 2.5; *B. proteus*, 2.4, 2.1; *B. anthracis*,

2.5, 3.1; *Sarcina lutea*, 2.7, 2.6; *Diplococcus gonorrhoeae*, 3.3, 2.5; *Staphylococcus aureus*, 3.5, 3.4; *B. pyocyaneus*, 3.8, 3.1. As with caseinogen, the isoelectric point depends on the suspension medium. F. O. H.

Effect of hypertonic sugar solutions on the thermal resistance of bacteria. A. C. FAY (J. Agric. Res., 1934, 48, 453—468).—The increased resistance to heat shown by bacteria in the presence of sugar solutions is influenced by the permeability of the cells. The protective action increases with the osmotic pressure of the sugar solution, but is not the same for equimol. solutions of different sugars. Maltose and lactose have small activity in this respect. The protective effect is paralleled by the ability of the sugar solutions to retard the coagulation of ovalbumin and the inactivation of rennin by heat. The mechanism of these changes is discussed. A. G. P.

Influence of flavins on the respiration of lactic acid bacteria (*Thermobacterium helveticum*). E. ADLER and H. VON EULER (Z. physiol. Chem., 1934, 225, 41—45).—Lactoflavin, ovoflavin, and a prep. of "lumiflavin" from liver increase the respiration of lactic acid bacteria in glucose solution and are not inhibited by 0.001M-KCN. J. H. B.

Preparation of *l*-sorbose. K. MAURER and B. SCHIEDT (Biochem. Z., 1934, 271, 61—63).—Sorbitol in aq. yeast extract is treated at 28 – 30° in shallow glass vessels with *B. xylinum*. When max. reducing power has been attained (about 6 weeks) the liquid is treated with Pb acetate, filtered, freed from Pb with H_2S , and evaporated to a thin syrup. Cryst. *l*-sorbose is deposited and is recryst. from MeOH. Yield 50—70%. W. McC.

Respiration and fermentation of pathogenic bacteria. II. *B. diphtheriae*. A. FUJITA and T. KODAMA (Biochem. Z., 1934, 271, 185—198; cf. this vol., 698).—The effect of $[H^+]$, temp., time, salt concn. (PO_4'''), kind of substrate (glucose, maltose, mannose, fructose, galactose, lactose, sucrose, rhamnose, arabinose, NH_2 -acids, AcOH, $AcCO_2H$, glycerophosphoric, succinic, malic, propionic acids, glycerol), methylene-blue, and CH_2I-CO_2H on the respiration (I) and fermentation (II) is described. The p_H optimum is 7.1—7.7 for (I) and 7.47 for (II). (I) increases with rise of temp., but the % increase per 1° is the greater the lower is the temp. (I) and (II) decrease rapidly with time except when the temp. is low (0°), the decrease then being slow. PO_4''' has no effect on (II). Of the substrates glucose is the most easily fermented and the best supporter of (I). Lactose, sucrose, and the pentoses scarcely support (I) at all. Asparagine and glutamic acid support (I) well, some of the other NH_2 -acids (e.g., leucine, glycine) not at all. Lactic acid and AcOH are completely, $AcCO_2H$ and glycerol incompletely, oxidised. In a growth-supporting medium (I) of the bacteria increases 100—200% (I) of asparagine is greatly increased, (I) of glucose and AcOH is not affected, by addition of cystine. (I) and (II) are equally restricted by CH_2I-CO_2H , but degree of restriction varies with the substrate. Anaerobic (II) of 1 mol. of glucose produces 2.2 eq. of acids, chiefly HCO_2H and lactic acid with much AcOH and succinic acid. V.

Autolysis of *B. pneumococcus*. B. BORGH (Z. physiol. Chem., 1934, 225, 69—78).—On autolysis of the cultures for periods up to 80 days, the total N decreased slightly, the residual N (after $\text{CCl}_3\cdot\text{CO}_2\text{H}$ pptn.) and the acidity by CH_2O titration increased. The autolysed material was dialysed. The dialysate from "young" autolysates caused fever and leucocytosis when injected into rabbits. From older autolysates the pyrogenic, dialysable substances had disappeared and the dialysate now acted on the leucocytes and reticulo-endothelial system. The non-dialysable products were always strongly pyrogenic and toxic. J. H. B.

Toxic and immunising substance isolated from *Bacillus artrycke*. A. BOIVIN, L. MESROBEANU, and I. MESROBEANU (Compt. rend., 1934, 198, 2124—2126).—The toxic substance isolated from this bacillus by $\text{CCl}_3\cdot\text{CO}_2\text{H}$ is capable of immunising mice against injections of the living bacillus. J. W. B.

Toxic and immunising substance isolated from *Bacillus artrycke*. A. BOIVIN and L. MESROBEANU (Compt. rend., 1934, 198, 2211—2212).—Evaporation in vac. of an aq. solution from the bacillus gives a yellow substance (I), sol. in H_2O ; insol. in org. solvents, which with hot 0.2*N*-AcOH gives a less toxic, white ppt. On acid hydrolysis it becomes non-toxic and yields a polysaccharide (about 40%) and fatty acids (about 22%). (I) contains a little N, P, S, and Ca, and is probably the Ca salt of a phosphatide-polysaccharide complex. R. S. C.

Formation of coprosterol in the intestine. I. Possible role of dihydrocholesterol, and a method of determining dihydrocholesterol in presence of coprosterol. II. Action of intestinal bacteria on cholesterol. H. DAM (Biochem. J., 1934, 28, 815—819, 820—825).—I. A method for the determination of dihydrocholesterol (I) in presence of coprosterol (II) depends on the difference of solubility of the digitonides in dry MeOH. (I) administered to man is recovered in the faeces, and is therefore not converted in the intestine into (II).

II. During the putrefaction of faeces, the total sterol content remains const., but the degree of saturation rises unless it is initially very high. The product of reduction is (II) and not (I). The reaction is not accelerated by the presence of formates. Putrefaction of the contents of the small intestine does not result in reduction of the unsaturated sterols. Cholesterol added before putrefaction in the form of egg-yolk, sol. esters, or colloidal suspensions is not significantly reduced. W. O. K.

Tubercle bacillus. I. Extraction and separation of lipin substances. M. MACHEBŒUF, G. N. FETHKE, J. DIERYCK, and A. BONNEFOI (Bull. Soc. Chim. biol., 1934, 16, 355—384).—Tubercle bacilli (1 kg.) sterilised by heating to 120° and washed free from glycerol with H_2O were extracted consecutively with COMe , (I), cold EtOH (II), hot EtOH (III), Et_2O (IV), and CHCl_3 (V). Extract (I) (11 g.) contained no P or haptene and had no acid-resistant power. Extract (II) (7.1 g.) contained much P and a high haptene content; phosphatides and glycerols were present. Extract (III) (5.4 g.) contained

little P and had a high acid-resistant power. Extracts (IV) (5.2 g.) and (V) (1.8 g.) contained P and gave on hydrolysis reducing sugars, including a pentose in (IV). The total glycerol content of the lipins, mainly present in extract (I), was < 12%. A. L.

Inhibiting action of phloridzin on the fermentation of sugar by *B. coli*. L. CALIFANO (Biochem. Z., 1934, 271, 123—126).—The fermentation of glucose, fructose, and mannose by *B. coli* is restricted by phloridzin (I) presumably because it inhibits phosphorylation. Fermentation of glucose is restricted 25% and 80% when the concn. of (I) is 0.0067*M* and 0.0133*M*, respectively. W. McC.

Reversible dehydrogenase systems. I. Reversibility of the hydrogenase system of *B. coli*. D. E. GREEN and L. H. STICKLAND (Biochem. J., 1934, 28, 898—900).—The equilibrium between H_2 and H^+ [as measured colorimetrically with methylviologen (A., 1933, 958) or electrometrically] is attained in the presence of *B. coli* exactly as in the presence of Pt-black (A., 1931, 525). The catalysis by *B. coli* is completely reversible, the hydrogenase system being the most negative reversible oxidation-reduction system as yet described in living cells. F. O. H.

Influence of heavy water on the biological processes of bacteria. G. LOCKEMANN and H. LEUNIG (Ber., 1934, 67, [B], 1299—1302).—Increase in the concn. of H_2O between 0.02% and 0.54% has a favourable influence on the life of *B. coli* and *B. pyocyaneus*, since more AgNO_3 is required for their destruction as the concn. increases. H. W.

Decomposition of sodium formate by *B. coli* in the presence of heavy water. A. FARKAS, L. FARKAS, and J. YUDKIN (Proc. Roy. Soc., 1934, B, 115, 373—379).—Decomp. of HCO_2Na by hydrogenolysis of *B. coli* and by Pd-black occurs through at. reactions and the primary formed H^1 and H^2 exchange with those of H_2O and H_2O before formation of H^1 and H^2 . H. G. R.

Action at a distance of staphylococcal bacteriophage on staphylococcus. I. LOMINSKI (Compt. rend., 1934, 199, 168—170).—The bacteriophage has a mitogenetic effect on the bacteria. Induction is probably due to chemical reactions, as evidenced by the progressive disappearance of a catalase from the filtrates on exposure to air. J. L. D.

Increase in the resistance of protozoa to X-radiation caused by lecithin in colloidal solution. B. S. LEVIN and C. PIFFAULT (Compt. rend., 1934, 198, 2024—2026).—Lecithin (I) in colloidal solution increases the resistance of *Paramecium aurelia* to X-rays, the effect increasing if contact with (I) occurred 3—8 days before exposure, and thereafter decreasing. R. S. C.

Effect of hormones on creatine-creatinine metabolism: total nitrogen, uric acid, and allantoin. S. BUADZE (Z. ges. exp. Med., 1933, 90, 762—804).—In a bitch fed on a completely creatine (I)-free diet, injection of thyroxine (2 mg. daily) caused an increase in total creatinine (II) (especially pre-formed), uric acid (III), and allantoin (IV) and a slight rise in total N (V). During oestrus thyroxine (1 mg.) produced a greater increase of (II) with very slight rise

of (V) and insignificant change in (IV). Injection of *l*-adrenaline (3 mg. daily for 2 days) led to definite rise of (I), (II), (IV), and occasionally (III), but little change in (V). Smaller doses had practically no effect. Injection of phloridzin caused an increased output of (V) but no other significant change. Injection of 1 c.c. of menformone (40 units of folliculin) caused an increased output of (II) but no other change. Anterior pituitary hormone occasionally produced slight rise in (II) output, whilst after posterior lobe hormone no change was noted. Injection of insulin (20 units) caused a reduction of (II), (IV), and (V). 30 units of insulin produced an increased output of (II), (III), and (IV), but not of (V). Injection of parathormone led to an increased output of (II) and (V), but variations in (III) and (IV). Injection of guanidine carbonate (0.4 g. previously neutralised) caused a marked reduction in output of (II), (IV), and (V). When parathormone was given with guanidine there was no change from the normal, indicating some relationship between these two substances. NUTR. ABS. (m)

Effect of thyreotropic hormone and of desiccated thyroid on creatine and creatinine excretion. L. I. PUGSLEY, E. M. ANDERSON, and J. B. COLLIP (Biochem. J., 1934, 28, 1135—1140).—Feeding of thyreotropic hormone (I) and desiccated thyroid to normal rats produces increased creatine excretion (II). Extracts of adrenotropic and growth hormones, and of boiled thyreotropic extract, have no effect. (I) causes a greater rise in (II) with hypophysectomised than with normal rats, and also causes increased (II) in the dog. Increased (II) is not prevented by addition of antithyreotropic substance. L. D. G.

Influence of thyroid preparations on the plumage of birds. R. PRAWOCHEŃSKI and B. ŚLIZYŃSKI (Nature, 1934, 133, 950: cf. A., 1933, 1199). L. S. T.

Effect of splenic hormone, prosplen, on chlorine metabolism. H. PROBST (Z. ges. exp. Med., 1933, 92, 311—323).—Injection of splenic hormone into healthy fasting subjects changes the [Cl] of the urine in one of three ways: steady reduction, reduction with temporary increases before the min. val. is reached in about 3 hr., or increase for 30—45 min., then reduction. The Cl content of the blood moves in an opposite direction to that of the urine. Injection of hormone prior to administration of saline causes a fall in blood-Cl, whilst previous administration of saline produces a rise. NUTR. ABS. (b)

Spleen and carbohydrate metabolism. F. RATHERY and R. COSMULESCO (Ann. Physiol. Physicochim. biol., 1933, 9, 939—942).—The effect of splenectomy (I) on blood-sugar and alimentary hyperglycaemia in the normal and depancreatized dog and of (I) followed by pancreatectomy (II) is variable. Most often (I) causes or increases hyperglycaemia, causes loss or prevents production of liver-glycogen, and aggravates the effect of (II). NUTR. ABS. (m)

Specific dietary factor for lactation. W. NAKAHARA, F. INUKAI, and S. KATO (Proc. Imp. Acad. Tokyo, 1934, 10, 268—270).—Extracts (I) prepared from ox liver by acidified 60% EtOH have a lactation-promoting action (II) in rats when added to diets

adequate for growth, pregnancy, and parturition, but inadequate for lactation. Treatment of (I) with acid clay yields an adsorbed fraction which is poor in (II), whilst the non-adsorbed material has a marked (II). Hence the (II) of (I) is apparently not related to the content of vitamin-B complex. The factor to which (II) is due is designated "lactation factor" or "factor L" (cf. A., 1932, 1174). F. O. H.

Lactation. II. Lactation-promoting substance in liver extract. W. NAKAHARA and F. INUKAI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 33—38).—Female albino rats maintained on a certain diet (this vol., 317) failed to suckle their young. The young were often suckled after feeding with liver extract (prep. described), their growth was above the average, and in every case there was evidence of milk secretion. J. L. D.

Effect of vagotonin on adrenaline hyperglycaemia. D. SANTENOISE, G. FUCHS, L. MERKLEN, and M. VIDACOVITCH (Compt. rend. Soc. Biol., 1933, 114, 1021—1023).—Adrenaline, injected into dogs in physiological amounts after administration of vagotonin, exerts no hyperglycaemic action. The parasympathetic system appears to be involved. NUTR. ABS. (m)

Adrenalectomised, depancreatized cats. C. N. H. LONG and F. D. W. LUKENS (Science, 1934, 79, 569—571).—Details of sugar metabolism in cats in which both adrenals and the pancreas have been removed in stages are given. Unilateral adrenalectomy does not appear consistently to prevent or alleviate the course of pancreatic diabetes, but complete adrenalectomy markedly ameliorates the usual results of complete pancreatectomy whether or not the diabetes has already developed. L. S. T.

Mode of action of the contra-insular hormone of the anterior pituitary. IV. Effect of the hormone when active extracts are introduced into cerebrospinal fluid. V. Effect of sympathetic poisons and narcosis on the blood-sugar reaction following administration of the hormone. VI. Possibility of biological demonstration of the hormone in cerebrospinal fluid. H. LUCKE and H. HAHNDEL (Z. ges. exp. Med., 1933, 91, 689—695, 696—703, 704—709).—IV. Suboccipital injection of active contra-insular hormone of the anterior pituitary produces immediately a marked and lasting rise of blood-sugar (I). Injection of normal saline has no effect, and boiling of the active pituitary extract lessens the intensity and duration of the hyperglycaemic action.

V. Injection of ergotamine during the hyperglycaemic effect of the hormone quickly nullifies it, (I) falling to normal: as the ergotamine effect on the sympathetic passes there is a very slight rise in (I). The action of somnifen on the central nervous system inhibits or prevents the action of the hormone even when injected directly into the cerebrospinal fluid (I).

VI. (II), whilst normally having no contra-insular effect, contains large amounts of the hormone after intramuscular administration, the highest concentration found in the second half hr. after injection.

The hormone is produced in the anterior pituitary.

passes into (II), acts on the sugar centre, and thence through the sympathetic and adrenals on the (I).

NUTR. ABS. (m)

Anterior pituitary extract and hyperglycæmia due to adrenaline or morphine. B. A. HOUSSAY and E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 114, 82—83).—After several days of treatment with large doses of anterior pituitary extract, prepared by the method of Evans and Simpson (Amer. J. Physiol., 1931, 98, 511), dogs exhibit an enhanced hyperglycæmic response to injections of morphine or adrenaline.

NUTR. ABS. (m)

Nervous system in the production of posterior pituitary hyperglycæmia. B. A. HOUSSAY and E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 114, 795—797).—The hypoglycæmic action of posterior pituitary extracts is lacking in the absence of the liver and adrenal glands, but pancreatectomy does not enhance it. It is slightly less after section of the splanchnic nerves, but is unaffected by vagotomy and may be due, in part, to a hypersecretion of adrenaline as well as to a direct action of the extract.

NUTR. ABS. (m)

Relation of the anterior pituitary to carbohydrate metabolism. B. O. BARNES and J. F. REGAN (Endocrinol., 1933, 17, 522—528).—A dog deprived of both pancreas and hypophysis showed glycosuria (I) only when injected with anterior pituitary extracts (II); it was very sensitive to insulin. Of 11 normal dogs, 7 exhibited (I), reduced glucose tolerance, and raised fasting blood-sugar when injected with (II), but thyroidectomised dogs did not respond in this way. The injection of female sex hormone into dogs increased their sensitivity to insulin.

NUTR. ABS. (m)

Pituitary and nitrogen excretion in the toad. BRAIER (Compt. rend. Soc. Biol., 1933, 114, 80—82).—Hypophysectomised toads on a N-free diet excrete less N in the urine than do normal toads. Grafting of the glands on to such animals increases the output to normal.

NUTR. ABS. (m)

Hyperglycæmic action of posterior pituitary extract. B. A. HOUSSAY and E. DI BENEDETTO (Compt. rend. Soc. Biol., 1933, 114, 793—795).—Following intravenous injections, spread over 1 hr., of different amounts of a neutralised AcOH extract of a standard posterior pituitary powder, the curve connecting rise of blood-sugar and amount of extract injected is S-shaped.

NUTR. ABS. (m)

Preparation of the homogeneous hormone from the corpus luteum. K. H. SLOTTA, H. RUSCHIG, and E. FELS (Ber., 1934, 67, [B], 1270—1273).—With the aid of suitable ketonic reagents, the following ketones have been isolated from the purified oils of the corpus luteum of the swine or from the active, cryst. products derived therefrom: *luteosterone-A*, m.p. 185—186° (crystallographical data), physiologically inactive; *luteosterone-B*, also inactive, and, like *A*, does not show a max. between 200 and 300 m μ characteristic of the absorption spectrum of the follicle hormone; *luteosterone-C*, C₂₀H₂₈O₂ or ²¹H₃₀O₂, m.p. 127—128° (corr.), and *luteosterone-D*, m.p. 118—119° (corr.), which are physiologically active and very similar to one another.

H. W.

Effect of sex hormones on the metabolism of the sex organs. S. ASCHHEIM and H. GESENIUS (Arch. Gynakol., 1933, 153, 434—446).—The O₂-quotient (I) of immature mouse-uterus was raised by previous injection into the animal of the urine of pregnant women. This is due to its content of oestrin, not to prolactin. The response is not sp., being elicited by aolan, cantharidin, yohimbine, and male hormones. The injection of male hormone preps. into immature male mice increased the (I) of the testes. This effect is sp. The increases in tissue respiration occur very rapidly after the injections.

NUTR. ABS. (b)

Carotene. VIII. Separation of carotenes by adsorption. H. H. STRAIN (J. Biol. Chem., 1934, 105, 523—535).— α - and β -Carotenes may be isolated from natural products by adsorption on MgO without previous crystallisation. They occur as such in plants.

H. G. R.

Substance A', intermediate between vitamin-A and β -ionone. A. CHEVALIER, Y. CHORON, and J. GUILLOT (Compt. rend., 1934, 198, 2207—2208).—When vitamin-A is irradiated in 95% EtOH, the absorption max. at 3280—3250 Å. remains unchanged until a late stage in the decomp., but changes occur between 3000 and 2700 Å. There is formed a *substance*, sparingly sol. in EtOH, provisionally named A', having an absorption max. in hexane at 3125 Å., and giving β -ionone when further irradiated.

R. S. C.

Substance inhibiting the Carr-Price reaction. O. RYGH (Bull. Soc. Chim. biol., 1934, 16, 609—611).—Cod-liver oil contains a substance, saponified with difficulty, which inhibits the Carr-Price reaction for vitamin-A.

A. L.

Relation of growth response to dosage of vitamin-A. K. H. COWARD (Biochem. J., 1934, 28, 865—869).—The validity of the previously established curve (I) relating response to dosage of vitamin-A (II) (A., 1931, 269) was confirmed by testing (II) in doses of known ratio. (I) is applicable to various sources of (II) (butter, fish-meal, cod-liver oil, dried milk, wheat germ, etc.) in doses from that just sufficient to maintain wt. in rats to that 50 times as great. Comparison with (I) from other laboratories indicates differences, probably due to the basal diet used.

F. O. H.

Simplification of vitamin tests. [Vitamin-A and -D.] K. H. COWARD and K. M. KEY (Biochem. J., 1934, 28, 870—874).—With vitamin-A tests on rats, the increase in wt. is approx. the same for either daily or half-weekly doses, whilst the accuracy of the test is not significantly decreased. Similarly with vitamin-D (cod-liver oil or international standard) the whole dose can be administered at the beginning of the 10 days' curative period instead of in ten daily doses.

F. O. H.

Influence of solvent on the vitamin-A activity of carotene and cod-liver oil. F. J. DYER, K. M. KEY, and K. H. COWARD (Biochem. J., 1934, 28, 875—881).—The biological activity of the provisional international vitamin-A standard (I) (a carotene prep.) depends on the nature of the solvent used. Thus solutions in arachis or coconut oil have a potency 5—6 times that of equal (wt./vol.) solutions in hardened

cotton-seed oil or Et laurate. Similarly the activity of cod-liver oil depends on the diluent used. No correlation appears to exist between the yellow colour of different solutions and their activity. β -Carotene has a potency 175% of that of (I). F. O. H.

Relation of the colour and vitamin-A content of butter to the nature of the ration fed. I. Influence of the ration on the yellow colour of the butter. S. J. WATSON, G. BISHOP, and J. C. DRUMMOND. II. Carotenoid and vitamin-A contents of the butter. A. E. GILLAM and I. M. HELLBRON (Biochem. J., 1934, 28, 1076—1085).—The yellow colour (I) of cow-butter (II) is increased by the addition of 50% of artificially dried grass to winter rations. Although there is considerable difference in the "ceiling" val. of (I) for Shorthorn and Ayrshire (II) when equiv. amounts of carotene (III) are fed, there is very little difference in vitamin-A content (IV). (IV) in goat-butter is similar to that of (II), although (III) was <5% of that in (II). H. G. R.

Long-duration experiments on the fat-soluble vitamins. L. RANDOIN and R. NETTER (Bull. Soc. Chim. biol., 1934, 16, 595—608).—Small amounts of maize-gum oil administered to young rats, fed on a diet complete in all respects except that it kept the animals sterile, permitted reproduction, but not the survival of the young. Wheat-germ oil (I), however, which contained only traces of vitamin-A (II), whilst unable to promote reproduction, permitted the survival of the young of older rats when administered before weaning. (I) administered to rats fed on a diet which contained no (II) promoted better growth over long periods than that obtained with supplements of comparable amounts of carotene or cod-liver oil. Hence (I) probably contains a growth factor different from the known forms of (II). A. L.

Comparative antirachitic efficiency of irradiated ergosterol and cod-liver oil for the chicken. Determination of rachitic leg-weakness. M. J. L. DOLS (Arch. Néerland. Physiol., 1934, 19, 290—294).—The observations of Steenbock and others, that irradiated ergosterol in peanut oil is less effective against rachitic leg-weakness (I) in chickens than the rat equiv. of cod-liver oil, are confirmed. The radiographic examination of the ribs is recommended as a shorter and more trustworthy method for the determination of (I). R. N. C.

Calcifying properties of green, artificially dried, and sun-cured pasture herbage. R. E. HODGSON and J. C. KNOTT (J. Agric. Res., 1934, 48, 439—446).—The degree of calcification (I) in rats was practically the same whether herbage was fed fresh, hayed, or artificially dried. Optimum (I) was attained by inclusion of 3% of herbage (dry wt.) in the ration. A. G. P.

Vitamin-D international standard. Determination of the biological activity. L. RANDOIN (Bull. Soc. Chim. biol., 1934, 16, 428—439).—The curing of young rats (30—32 g. wt.) made rachitic by the feeding of a vitamin-D-free diet requires a daily dose of 0.0005 mg. of the 1932 standard solution of irradiated ergosterol, i.e., 5 international units of vitamin-D. A. L.

Antisterility vitamin and the fat-soluble growth vitamins. L. RANDOIN and R. NETTER (Bull. Soc. Chim. biol., 1934, 16, 581—594).—The relationship in occurrence and properties between the carotenoid substances (auxematols) possessing vitamin-A and -E activity is pointed out. A. L.

Realisation of alimentary equilibrium permitting growth in rats in the absence of all known fat-soluble vitamins. L. RANDOIN and R. NETTER (Compt. rend., 1934, 198, 2120—2122).—A diet consisting of caseinogen 15%, brewer's yeast 5%, lard 20%, dextrin 56%, salts 4%, cellulose (filter paper), and distilled H₂O, but free from vitamin-A, -D, and -E, maintains normal life and growth in rats, and acts as a curative diet for avitaminosis-A.

J. W. B.
Vitamin-B₁ international standard. Determination of the biological activity. L. RANDOIN (Bull. Soc. Chim. biol., 1934, 16, 440—447).—Adult pigeons fed on a diet containing no vitamin-B require a min. daily dose of 75 mg. of the international standard prep. (I) of vitamin-B₁, i.e., 7.5 international units, to prevent the appearance of symptoms of polyneuritis. (I) also contains vitamin-B₂ and -B₃. A. L.

Comparative determinations of the antineuritic vitamin content of rice, made by experiments on the rice-bird, and by the rat tests. J. P. SPRUYT (Arch. Néerland. Physiol., 1934, 19, 295—300).—Determinations of the vitamin-B₁ contents of six samples of rice gave identical results with rice-birds and rats. R. N. C.

Antineuritic vitamin. V. Preparation of vitamin concentrate suitable for parenteral use. E. H. STUART, R. J. BLOCK, and G. R. COWELL (J. Biol. Chem., 1934, 105, 463—466).—Rice polishings are extracted with CHCl₃-H₂O and Lloyd's reagent (I) is added at *p*_H 4.5. Vitamin-B₁ is eluted from (I) with warm EtOH-HCl. Further purification is obtained by repeating the adsorption on (I). H. D.

Action of crystalline vitamin-B₁ on the respiration of polyneuritic tissues *in vitro*. R. H. S. THOMPSON (Biochem. J., 1934, 28, 909—915).—Addition of vitamin-B₁ to minced muscle, heart, and liver tissue from polyneuritic pigeons has no effect on their O₂ uptake, but with kidney it causes a large increase, restoring the val. almost to normal. C. G. A.

Pyruvic acid as an intermediary metabolite in the brain tissue of avitaminous and normal pigeons. R. A. PETERS and R. H. S. THOMPSON (Biochem. J., 1934, 28, 916—925).—Disappearance of AcCO₂H (I) accompanies the increased O₂ uptake induced by cryst. in pigeon-brain tissue (II) *in vitro*, 2 O₂ corresponding approx. to 1 (I). It is thought that (I) is a normal intermediate in the metabolism of (II). (I) accumulates in norm (II) in presence of CH₃I-CO₂Na, but not

Reduction-oxidation potential of lactoflavin and its derivatives. R. KUHN and G. MOR (Ber., 1934, 67, [B], 1220—1223).—The norm potentials of lactoflavin (I) and its tetra-a lumilactoflavin and its *N*-Me and *NN*-Me₂

atives, and of the degradation acid (II), $C_{12}H_{12}O_3N_2$, have been measured against the normal H_2 electrode at p_H 5.9 and p_H 7.0. The redox behaviour is very little affected by acetylation, methylation, or removal of the sugar-like side-chain. Since the behaviour of (II) is also closely similar to that of the flavins, it follows that the unexplored fundamental unit of the flavin mol. with 2 N is entirely responsible for the oxidation-reduction behaviour. Addition of the alkali-labile ring system and, further, of the sugar-like side-chain is practically without influence. The ring system containing $\cdot N \cdot CO \cdot NH \cdot CO \cdot$ determines the colour and absorption spectrum of the flavins, which is not influenced by addition of the sugar-like side-chain and only slightly affected by subsequent union with protein. The sugar-like side-chain is causative of the vitamin nature of (I), which is retained on further addition of protein. The presence of the latter imparts enzymic character to the pigment. H. W.

Alkali-labile ring of lactoflavin; monomethyl and dimethyl compounds. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 1125—1130).—Treatment of the Ag salt of lumilactoflavin (I) with MeI at room or slightly elevated temp. yields *N*-methyl-lumilactoflavin (II), m.p. 326° (decomp.), which contains one active H (Zerevitinov). The absorption spectra of (I) and (II) are identical. The brilliant green fluorescence of (II) is reversibly destroyed by dil. alkali. Treatment of (I) with NaOH and Me_2SO_4 yields *NN'*-dimethyl-lumilactoflavin (III), $C_{15}H_{16}O_2N_4$, m.p. 286° (corr.), which does not contain active H. Its fluorescence is irreversibly destroyed by NaOH owing to hydrolysis. When heated with NaOH (III) loses 2NMe and yields the carboxylic acid, $C_{12}H_{12}O_3N_2$, m.p. 215° , identical with that obtained from (I). (I) is therefore $C_{11}H_{10}N_2 \left\{ \begin{array}{l} \cdot NH \cdot CO \\ \cdot CO \cdot NH \end{array} \right.$. H. W.

Constitution of lumilactoflavin. R. KUHN and H. RUDY (Ber., 1934, 67, [B], 1298—1299).—Lumilactoflavin yields about 0.5 mol. of alkyl iodide, and therefore consists of about equal parts of an alkyl-imide-free (α) and alkylimide-containing (β) pigment. The Na_2CO_3 -sol. portion obtained by alkaline hydrolysis is free from Nalk and therefore derived from α -lumilactoflavin. The carboxylic acid (I) $C_{12}H_{12}O_3N_2$, the product $C_{11}H_{12}ON$, of its decarboxylation, and the 0-free base obtained from (I) by energetic alkaline degradation contain Nalk. H. W.

Constitution of photoflavin. Experiments in the alloxazine series. K. G. STERN and E. R. HOLIDAY (Ber., 1934, 67, [B], 1104—1106).—When melted with $KMeSO_4$ or $KEtSO_4$ benzalloxazine, $CH=CH-C \begin{array}{c} \parallel \\ \text{7} \quad \text{8} \end{array} N=C \begin{array}{c} \parallel \\ \text{9} \quad \text{10} \end{array} NH-CO$, its 7- and 1-Me, $CH=CH-C \begin{array}{c} \parallel \\ \text{6} \quad \text{5} \end{array} N=C \begin{array}{c} \parallel \\ \text{4} \quad \text{3} \end{array} CO-NH$ 1:3-, 6:7-, 7:8-, and 6:8-Me₂ derivatives, with exception of those substituted in the alloxan ring, give compounds closely similar to but not identical with photoflavin. H. W.

Vitamin- B_3 . J. R. O'BRIEN (Biochem. J., 1934, 926—932).—Supplements of 20—30 doses of vitamin- B_1 (I) failed to restore the wt. of pigeons (II) a diet of polished rice (III) or autoclaved whole

wheat. Extracts (IV) obtained by hydrolysis of wheat germ with boiling $N-H_2SO_4$ restore the wt. of (II) on (III)+(I). (IV) is inactivated by oxidation. (II) on (III)+6 to 12 doses of (I) do not regain wt. when given 2 g. of caseinogen daily. Vitamin- B_3 is regarded as a wt.-restoring factor. C. G. A.

Maintenance nutrition in the pigeon and its relation to heart block. C. W. CARTER (Biochem. J., 1934, 28, 933—938).—The failure of restoration of wt. of pigeons on a polished rice diet supplemented by a yeast concentrate is partly due to inadequate protein allowance which can be made good by addition of caseinogen. Such regain in wt. may, however, be accompanied by cardiac arrhythmia, which can be eliminated by wheat-germ extract (see preceding abstract). C. G. A.

Vitamin-C in the human pituitary. J. GOUGH (Lancet, 1934, 226, 1279—1281).—The Szent-Györgyi test shows that the reaction for ascorbic acid is less intense in old than in young individuals (I), that it is intense in the anterior lobe of young or middle-aged (I) in whom general body nourishment had been normal, and that it is slight or negative in (I) who had died of prolonged illness with severe emaciation. L. S. T.

Ascorbic acid content of certain citrus fruits and manufactured citrus products. A. L. BACHARACH, P. M. COOK, and E. L. SMITH (Biochem. J., 1934, 28, 1038—1047).—Titration of ascorbic acid (I) in fruit juice with 2:6-dichlorophenol-indophenol gives slightly but appreciably more reproducible results than titration with I, the two methods giving results usually in good agreement. Extreme and mean vals. of (I) per ml. of juice were: for oranges (II), 0.22, 0.89, 0.51 mg.; for tangerines, 0.10, 0.78, 0.37 mg.; lemons (III), 0.47, 0.73, 0.64 mg. Variations were often found even between fruits from the same consignment. Storage for 1 month caused, on the average, nearly 20% loss of (I) in (II), but only 6% in (III). Concn. and subsequent storage of (II) juice leads to no appreciable loss of (I). Marmalades containing most peel are richest in (I) (up to 0.14 mg. per g.). In all types of citrus fruits, the flavedo is richest and the albedo next richest in reducing power; the juice was poorer in (I) than the peel, whilst the pips contained no demonstrable amount. A. E. O.

Nature of the precursor of vitamin-C in the vegetable kingdom. I. Vitamin-C in the growing pea seedling. S. N. RAY (Biochem. J., 1934, 28, 996—1003).—Pea seedlings were grown on nutrient gelatin containing a possible precursor of ascorbic acid (I). The rate of production of (I) bore no direct relation to the rate of growth. Hexoses (II), especially mannose (a growth inhibitor), favoured greatly increased production of (I) (up to 0.5 mg. per g. wet tissue) over the control (0.05 mg. per g.); disaccharides were less effective; arabinose and xylose (good growth-promoters), starch and dextrin, sugar alcohols, glycerol, $AcCHO$, and $AcCO_2Na$, Na glutamate, lactate, and glycerophosphate were all ineffective. The (I) content fell steadily during prolonged cultivation. (II) may serve as precursors of (I) in germinating seeds. A. E. O.

Synthesis of vitamin-C.—See this vol., 869.

Influence of vitamin-C on plant and animal amylases. A. PURR (Biochem. J., 1934, 28, 1141—1148).—Vitamin-C (ascorbic acid) (I) is a sp. activator for β -amylase (II) of animal origin. With barley-amylase, (I) has an inhibiting effect on (II), but no effect on α -amylase (III); the oxidised form of (I) has no effect on (II), but inhibits (III). L. D. G.

Effect of ascorbic acid on fatty acid oxidations in the liver. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1934, 28, 1014—1027).—In presence of liver slices (I), ascorbic acid (II) is only partly oxidised at 37° at p_H 7.4 in presence of O_2 . Presence of (II) results in increase in Q_{10} , and in the production of $CH_3Ac \cdot CO_2H$ (III) when rat (I) or scorbutic guinea-pig (I) [but not normal guinea-pig (I)] are placed in a glycerophosphate-Locke medium containing Na butyrate or crotonate. (II) also prolongs the steady rate of O_2 uptake by (I). It is suggested that the effects of (II) on production of (III) are due to the oxidation of fatty acids, being inherently connected with the general respiratory metabolism of (I). (II) appears not to affect the oxidation of $dl\text{-OH} \cdot CHMe \cdot CH_2 \cdot CO_2H$ in presence of rat (I). The large inhibitory effect of 0.0002N- $CH_2I \cdot CO_2H$ on the production of (III) is reduced by presence of (II), the reduction not being due to a chemical reaction between these compounds. There is no distinct correlation between production of (III) and the glycogen content of the liver (cf. this vol., 210). A. E. O.

Physiological action of ascorbic acid and some related compounds. V. DEMOLE (Biochem. J., 1934, 28, 770—773).—Large doses of ascorbic acid (I) (up to 5 g. per kg. in one dose or up to 12 g. per kg. over a no. of days) administered to various warm- and cold-blooded animals produced no toxic effect. Of 0.1 g. of (I) per kg. administered subcutaneously to a dog 75% was excreted in the urine. Synthetic *l*-(I) (A., 1933, 1035) behaved biologically identically with *l*-(I) from paprika, but synthetic *d*-(I) as well as *l*-erythro-3-ketohexonic acid, *d*-lyxo-3-ketohexonic acid, *l*-xylo-3-ketohexonic acid, and *d*-arabo-3-ketohexonic acid were without biological activity. *d*-Erythro-3-ketohexonic acid had an activity about 1/20 of that of *l*-(I). W. O. K.

Hæmorrhages in chicks reared on artificial diets; a new deficiency disease. H. DAM (Nature, 1934, 133, 909—910).—Extensive subcutaneous or intramuscular hæmorrhages (I) occur in chicks fed on a diet of vitamin-A-free caseinogen, marmite, salt mixture, starch, and cod-liver oil concentrates. Vitamin-C (II) as lemon juice or as ascorbic acid has no effect on the symptoms, but with a diet of cereals or seeds+salts (I) do not occur. The disease is due to an anti-hæmorrhagic factor different from (II) and present in cereals or seeds. L. S. T.

Chemical aspects of carbon assimilation. N. R. DHAR (J. Indian Chem. Soc., 1934, 11, 145—178).—A lecture, mainly historical. F. R. S.

Relationship between nitrogen and chlorophyll content in the natural and morbid yellowing of leaves. R. S. HILPERT and K. HEIDRICH (Ber., 1934, 67, [B], 1077—1081).—Data are given for

the % of N and chlorophyll (I) determined by the authors' method and according to Willstatter for the strong, green leaves, the lower leaves from incipient to complete fading, the stalks and pale green, lower portions of leaves, and the ears including the grains of wheat. It appears that (I) is united with a certain portion of the protein ("mobile protein") in contrast to the fixed portion which remains after fading. The relationship is quant. when taken over the complete period of vegetation. Acute poisoning (SO_2 or Cl_2) causes little alteration in the % of N, whilst different vals. for (I) are given by the two methods of determination, indicating that much (I) exists in a colourless or slightly coloured form which yields a coloured Cu compound. Necrosis and rust cause diminution of % N to 1.09% and 1.94%, respectively, the latter val. corresponding with the presence of (I) in considerable amount. H. W.

Adsorption of sunflower oil by the hulls. J. KOLPAKOV (Masloboino Zhir. Delo, 1933, No. 4, 19—22).—16.6—18.5% of the oil may be adsorbed. CH. ABS.

Absorption by plants. VI. Urea and its comparison with ammonium salts. F. DIAZ AGUIRRECHE and A. CASTILLO (Anal. Fís. Quím., 1933, 31, 669—671; cf. B., 1932, 653).—Urea shows a pronounced toxic effect, causing loss in wt. comparable with that caused by NH_4Cl , but more intense with small concns. The effects of urea, NH_4Cl , and NH_4NO_3 (in which the toxicity of NH_4^+ is partly neutralised by NO_3^-) are directly compared.

Variations of the apparent r_H of soil during growth of plants. L. MEYER (Compt. rend., 1934, 198, 2199—2201).—Beans (I) and *Lolium* growing in soil, or (I) in Knop's liquid, induce an r_H in the soil or liquid independent of the initial r_H , but dependent on the plant and nature of the soil. R. S. C.

Effect of yeast extract on the growth of plants. B. V. NATH and M. SURYANARAYANA (Nature, 1934, 134, 27).—A claim for priority (cf. this vol., 463). L. S. T.

Effect of folliculin on plant growth. H. VON EULER and B. ZONDEK (Biochem. Z., 1934, 271, 64—73; cf. A., 1931, 1337; 1932, 1068).—Although folliculin (I) added to nutrient media of growing hyacinths (II) disappears and cannot be recovered from plant or medium, no acceleration of growth or development of (II) can be observed. Living or pulped roots of (II) rapidly inactivate (I) which cannot then be re-activated by boiling with HCl. No inactivation of (I) is caused by fresh or dried yeast or by boiled root pulp from (II). W. McC.

Influence of hormones on foliage and development of vegetables. D. V. HYKES (Compt. rend. Soc. Biol., 1933, 113, 629—632).—Adrenaline (I), thyroxine (II), and hypophysis have either a stimulatory or inhibitory action on plant growth, according to the concn. in which they are applied. The action of (II) is mainly on the leaves, and of (I) and (III) on root development. Insulin and tricrosol favour affected growth at all concns. examined. A. G.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1934.

General, Physical, and Inorganic Chemistry.

Comparison of the Paschen and the Balmer series of hydrogen lines in stellar spectra. P. W. MERRILL and O. C. WILSON, jun. (*Astrophys. J.*, 1934, 80, 19—50).
L. S. T.

Arcs in inert gases. II. G. E. DOAN and A. M. THORNE (*Physical Rev.*, 1934, [ii], 46, 49—52; cf. A., 1932, 551).—Arcs between Fe electrodes in A, He, and Ne, and between Ag and Zn in A, the gases and electrodes being highly purified, are inherently unstable. The boundary conditions within which stable arcing may occur are limiting vals. of the parameters: open circuit voltage, electrode separation, and pressure of arc atm. Higher purity of electrodes and inert atm. move the voltage-current curve towards higher voltage.
N. M. B.

Perturbations in the $(9,8)^2\Sigma$ — $^2\Sigma N_2^+$ band. H. H. BRONS (*Physica*, 1934, 1, 739—744).—A new perturbation in this band has been measured.
H. J. E.

Nitrogen molecular spectra in the vacuum ultra-violet. W. W. WATSON and P. G. KOONTZ (*Physical Rev.*, 1934, [ii], 46, 32—37).—Data and analyses for spectra in the region 900—2300 Å. are given. From bands in the $\rightarrow ^1\Sigma g^+$ system the consts. are $B_0' = 1.632 \pm 0.002$, $B_0'' = 1.998 \pm 0.002$, $\alpha' = 0.021$, $\alpha'' = 0.018$. New bands, due to N_2^+ , in a system with an origin at 1847 Å., and several new N_2 ground state progressions among the bands in the 900—1300 Å. interval, are reported.
N. M. B.

Discharge through compressed gas in inhomogeneous electric fields. J. M. GOLDMAN and B. M. VUL (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 2, 542—547).—The potentials necessary to produce a discharge in N_2 at pressures varying from 1 to 18 kg. per sq. cm., between a point and a plate placed at various distances from it, have been measured for direct, alternating, and condensed discharges. In certain cases the potential-pressure curves show a max.
H. S. P.

Afterglow of active nitrogen. G. CARIO (*Z. Physik*, 1934, 89, 523—536).—The metastable 6.2-volt N_2 level is used to give an explanation of the complete afterglow spectrum. Active N is at.
C

Nitrogen afterglow. H. A. JONES and A. C. GRUBB (*Nature*, 1934, 134, 140).—The afterglow formed by passing $N_2 + 0.25\%$ O_2 through an uncondensed discharge produced by a 25,000-volt transformer is greenish-yellow at the crit. voltage

and under certain conditions shows many of the auroral colours. The glow disappears at 30° and is intensified at -20°. The visible spectrum consists of first positive, second positive, first negative, and NO bands. A line appears at 5577 Å. and a first negative band at 4780 Å.; the band 4059 Å. is intense. When the N_2 is bubbled through conc. H_2SO_4 before passing the discharge the yellow afterglow is replaced by a blue glow.
L. S. T.

Wave-lengths and terms of the fluorine spectrum F v. B. EDLEN (*Z. Physik*, 1934, 89, 597—600).
A. B. D. C.

Effect of an electric field on the absorption series of sodium. E. SEGRE (*Atti R. Accad. Lincei*, 1934, [vi], 19, 595—599).—The absorption spectra of Na and K in an electric field are compared. Na vapour shows dichroism and anomalous double refraction.
O. J. W.

Band spectrum of ionised aluminium hydride. G. M. ALMY and M. C. WATSON (*Physical Rev.*, 1934, [ii], 45, 871—876).—Data and analyses are given for the band spectrum of AlH excited by a Schüler hollow Al cathode lamp containing He and H_2 . A new system with principal head at 3632 Å. consists of the (0,0) and (1,1) bands of a $^2\Pi$ (regular) $\rightarrow ^2\Sigma^+$ system due to AlH^+ .
N. M. B.

New band system of aluminium hydride. W. HOLST (*Nature*, 1934, 134, 63).—The new band system at 3380 Å. (this vol., 124) belongs to a $^1\Pi^* \rightarrow ^1\Pi$ transition.
L. S. T.

Effect of an electric field on the limit of the potassium series. E. AMALDI (*Atti R. Accad. Lincei*, 1934, [vi], 19, 588—594).—In the absorption spectrum of K subjected to fields up to 2700 volts per cm. the series $4S-nS$ and $4S-nD$ have been observed with polarisation parallel to the electric field. Only the latter series is observed when the polarisation is perpendicular to the field. The existence of dichroism and of anomalous double refraction is shown.
O. J. W.

Continuous emission spectrum of arsenic. G. BALASSE (*Bull. Acad. roy. Belg.*, 1934, [v], 20, 563—568).—Using the electrodeless discharge, data for 48 lines between 8600 and 5000 Å. are tabulated. Results confirm the mechanism of emission: $As^+ + \text{electron} = As$ (neutral).
N. M. B.

Spectrum of selenium. III. Extension of Se III. IV. Se I and Se VII. K. R. RAO and S. G. K. MURTI (*Proc. Roy. Soc.*, 1934, A, 145,

681—694, 694—698).—III. About 15 new levels assignable to Se III have been revealed. An investigation of the infra-red region of the spectrum has confirmed the 5s and 4d terms previously identified (A., 1933, 655).

IV. About 50 lines have been assigned to Se I, and about 40 in the region 860—560 Å. to Se VII.

L. L. B.

Spectrum of trebly-ionised bromine, Br IV. A. S. RAO and S. G. KRISHNAMURTY (Proc. Physical Soc., 1934, 46, 531—536).—Data and analyses for the vac. spark and discharge tube spectra of Br are tabulated. Classifications due to Deb (cf. A., 1930, 651) are corr. The ionisation potential of Br IV is approx. 50 volts.

N. M. B.

First spark spectrum of bromine. L. BLOCH, E. BLOCH, and P. LACROUTE (Compt. rend., 1934, 199, 41—43; cf. A., 1931, 992).—Forty-five terms (classifying 170 lines) of the A and B groups of the Br II spark spectrum are tabulated.

B. W. B.

Spectra of niobium V and molybdenum VI. M. W. TRAWICK (Physical Rev., 1934, [ii], 46, 63—65).—Data, classifications, and term vals. are reported for the Rb r-like spectra of Nb and Mo.

N. M. B.

Mercury high-pressure discharge. W. ELENBAAS (Physica, 1934, 1, 673—688; cf. this vol., 232).—Discharge characteristics can be calc. by assuming a temp. equilibrium between Hg atoms, Hg ions, and electrons.

H. J. E.

Mean life of the 7^3S_1 state of mercury from polarisation measurements on the visible triplet. A. C. G. MITCHELL and E. J. MURPHY (Physical Rev., 1934, [ii], 46, 53—58; cf. Randall, A., 1930, 970).—Measurements of polarisation of Hg fluorescence lines $\lambda\lambda$ 4047, 4358, 5461 in zero field and as a function of applied magnetic field give, from 4047 and 4358, the val. $(0.8 \pm 0.1) \times 10^{-8}$ sec., and from λ 5461, $(0.6 \pm 0.1) \times 10^{-8}$ sec. at about 3 mm. N_2 pressure. The collision cross-section for the 7^3S_1 state against N is 1.3×10^{-16} sq. cm.

N. M. B.

Spontaneous light transmission variation of thin silver foils. II. A. JAGERSBERGER and F. SCHMID. III. Relation to spontaneous resistance change and structure of thin metal films. A. JAGERSBERGER (Z. Physik, 1934, 89, 557—563, 564—581; cf. this vol., 588).—II. Quant. vals. are given; a lower thickness limit applies to structural, but not to gas, effects.

III. Observed spontaneous light transmission changes can be deduced from resistance changes if the no. of free electrons converge with time to zero for films < a crit. thickness. Optical measurements are used to calculate the amount of gas taken up by the film.

A. B. D. C.

Optical examination of thin films. I. Optical constants of mercury. L. TRONSTAD and C. G. P. FEACHEM (Proc. Roy. Soc., 1934, A, 145, 115—126).—The vals. of the optical consts. of Hg have been measured for 4350, 5460, and 5780 Å. They are discussed in relation to previously published vals. for wave-lengths in the visible region of the spectrum.

L. L. B.

Spectrograms of A_0 and F_0 stars. Total breadth of the three rays H_γ , H_δ , and $H_\epsilon + H$ in width of composite H_ϵ and H line. Relative breadths of the hydrogen and calcium rays. P. ROSSIER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 11—13, 18—19, 19—20).

J. W. S.

Ultra-violet extremity of night sky spectrum. J. GAUZIT (Compt. rend., 1934, 199, 29—31).— λ and intensity measurements are tabulated for the interval 4175—2963 Å. Most of the lines appear in the auroral spectrum and are identified with known emitters (cf. Cabannes and Dufay, this vol., 232).

B. W. B.

Continuous spectra of comets. E. BALDET (Compt. rend., 1934, 199, 31—34).

B. W. B.

A II in the spectrum of γ Sagittarii. W. W. MORGAN (Astrophys. J., 1934, 79, 513—515).—Seventeen lines in this spectrum agree in position with the strongest laboratory lines of A II.

L. S. T.

Discharge rays. G. REBOUL (J. Phys. Radium, 1934, [vii], 5, 287—288).—Polemical against Dauvillier (cf. this vol., 712).

N. M. B.

Secondary interference fringes. W. F. C. FERGUSON (J. Opt. Soc. Amer., 1934, 24, 157—158).

N. M. B.

Weak lines of the K series of the elements from chromium to copper. Fluorescence lines of some compounds of these elements. PRIVAULT (Compt. rend., 1934, 199, 280—281).—Using a Cauchois spectroscope (A., 1932, 902), three new lines (designated a, b, and c) of very low intensity have been observed in the K series of Fe, and corresponding a lines for Cr, Mn, Co (doubtful), and Cu (doubtful), b lines for Co, Ni, and Cu (all doubtful), c lines for Cr, Co, and Ni. The X-ray fluorescence of Fe_2O_3 (hæmatite), MnO_2 , and $K_2Cr_2O_7$ shows in general a doubling of the β_5 , β' , β'' , and β''' lines.

J. W. S.

L absorption spectra in the very soft X-ray region. V. H. SANNER (Nature, 1934, 134, 100).—The L_{III} absorption edges of Al and Mg have been measured.

L. S. T.

Mass scattering coefficients. L. M. HEIL (Physical Rev., 1934, [ii], 46, 58—62).—By graphical integration the mass scattering coeffs. of C, Al, Fe, Sn, and Au are calc. over the wave-length range 0.4—1.1 Å. Results agree with available experimental data, and can be expressed by $0.0230Z^{1.16}\lambda$ over the wave-length range, and upwards from at. no. 12.

N. M. B.

Fluorescent yield of X-ray emission. G. VON HEVESY and H. LAY (Nature, 1934, 134, 98—99).—The fluorescent yield of the L-radiation increases from 6 to 45% from Zr to U.

L. S. T.

Positive and negative thermionic emission from niobium. H. B. WAHLIN and L. O. SORDAHL (Physical Rev., 1934, [ii], 45, 886—889).—The positive ion and electron work functions for well outgassed Nb were 5.52 and 3.96 volts, respectively. The effect of impurities on the former was investigated.

N. M. B.

Emission of electrons under the influence of chemical action. III. Action of chlorine, bromine, iodine, nitrosyl chloride, hydrogen chloride, nitrous oxide, and carbonyl sulphide on NaK_2 . A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1934, A, 145, 18—51).—Characteristic energy distribution curves and other data are given for the electrons emitted when NaK_2 is acted on by Cl_2 , NOCl , COCl_2 , Br , I , and COS at low pressures. Current—pressure curves are given for Cl_2 , NOCl , and COS , and current—time curves for Cl_2 . The data are consistent with the theory of the electron emission mechanism previously developed (this vol., 468). L. L. B.

New transition produced by electron impact in helium. R. WHIDDINGTON and H. PRIESTLEY (Proc. Roy. Soc., 1934, A, 145, 462—464).—Electrons of energy 100—600 volts, passing through He at low pressure, produce a new excitation transition with associated energy 59.25 ± 0.12 volts, which may be due to a double excitation of the He atom involving the transition of both s electrons to p states. L. L. B.

Small-angle inelastic electron scattering in helium, neon, and argon. R. WHIDDINGTON and J. E. TAYLOR (Proc. Roy. Soc., 1934, A, 145, 465—474).—The probabilities of the most probable excitations in He, A, and Ne are compared over the range of incident electron energies 50—350 volts, and for the particular case where the electron is apparently undeviated by the collision. Only one excitation ($1^1S_0-2^1P_1$) is involved in He; two at least in A, ($3^1S_0-4^1P_1$) and ($3^1S_0-4^3P_1$); two at least in Ne, ($2^1S_0-3^1P_1$) and ($2^1S_0-3^3P_1$). L. L. B.

Polarisation of electrons by scattering. II. E. G. DYMOND (Proc. Roy. Soc., 1934, A, 145, 657—668).—Previous experiments have been extended to higher electron velocities with an improved apparatus (A., 1932, 789). Up to 160 kv., no asymmetry in the scattering which could be ascribed to a polarisation effect $> 1\%$ was observed, whereas Mott predicts a max. asymmetry of 15%. In view of the divergence of theory from experiment, it is suggested that the Dirac wave equation needs modifying to account for the absence of polarisation. L. L. B.

Probability of inner shell ionisation of atoms by electron impact. E. H. S. BURHOP (Proc. Roy. Soc., 1934, A, 145, 612—628).—The probability of ionisation of Ag atoms in the L_{III} shell by electron impact has been measured as a function of the energy of the incident electrons for the energy range $9V_{Kc}-18V_{Kc}$, V_{Kc} being the ionisation potential of the shell. A method of investigating the relative probability of ionisation by electron impact of an atom in the K and L shells is described. This enables a comparison to be made of the relative intensities of the lines of the K and L series spectra. L. L. B.

Behaviour of gases and vapours, especially organic, towards slow alkali ions. O. SCHMIDT (Z. Elektrochem., 1934, 40, 498—499).—The mass-spectrographic distribution curve for collision of K^+ in various gases and vapours is discussed. E. S. H.

Theory of the combination coefficients for large ions and for uncharged particles at any pressure. W. R. HARPER (Phil. Mag., 1934, [vii], 18, 97—113).—Theoretical. H. J. E.

At. wt. of niobium and tantalum. O. HONIGSCHMID (Naturwiss., 1934, 22, 463—464).—The at. wt. of Nb determined from NbCl_5 is 92.91 ± 0.01 ; that of Ta, determined from TaBr_5 , is 180.89. These vals. agree with those of Aston. A. J. M.

At. wt. and mechanical nuclear moment of protoactinium. H. SCHULER and H. GOLLNOW (Naturwiss., 1934, 22, 511).—The hyperfine structure of the Pa spectrum has been investigated in the range 6500—4300 Å. From the hyperfine structure splitting, it must have an odd at. wt. Pa is converted into Pb by six α -ray changes, and since only one Pb of odd at. wt. is known (Pb^{207}), this must be the end-product of the Ac series, and Pa must have at. wt. 231. Pa has a nuclear moment of $3/2$. A. J. M.

Constitution of carbon, nickel, and cadmium. F. W. ASTON (Nature, 1934, 134, 178).—The most probable ratio of abundance of C^{12} and C^{13} appears to be 140 ± 14 . Allowing for the packing fraction of C^{12} and the change of scale, the at. wt. of C is 12.0080 ± 0.0005 . More intense mass spectra of $\text{Ni}(\text{CO})_4$ reveal two new isotopes 62 and 61; lines at 56 and 64 present to $< 1\%$ are probably also due to isotopes. Mass nos. 114, 112, 110, 111, 113, and 116 in Cd are confirmed, and faint new ones at 106, 108, and 115 are revealed. Svensson's results (A., 1933, 108) are criticised. L. S. T.

Frequency of the number of isotopes of chemical elements. W. YEH (Compt. rend., 1934, 199, 62—63).—A discussion of existing data. The nos. of isotopes of elements of even at. no. differ systematically from those of odd at. no. B. W. B.

Isotopes. J. MATTAUCH (Physikal. Z., 1934, 35, 567—621).—A comprehensive review of methods of investigation and results.

Isobaric isotopes. H. J. BRENNEN (J. Amer. Chem. Soc., 1934, 56, 1642).—Speculative. E. S. H.

Radioactivity of rare earths. G. VON HEVESY and M. PAHL (Z. physikal. Chem., 1934, 169, 147—151).—The radioactivity exhibited by many rare-earth preps. is usually due to contamination with radioactive elements. No rare earth has an activity even approx. as strong as that of Sm (cf. A., 1933, 762). R. C.

Energies of α -, β -, and γ -rays. H. A. WILSON (Proc. Roy. Soc., 1934, A, 145, 447—461).—Low-energy β - and γ -rays are emitted by the electronic system after it has been excited by previous γ -rays from the nucleus. Evidence is adduced in support of the theory that the nuclei of all radioactive atoms emit γ -rays of which the energies are multiples of 3.85×10^5 ev. (this vol., 579). L. L. B.

Experiments with natural H-rays. C. WEISS (Physikal. Z., 1934, 35, 508—516).—The determination of the range of protons emitted from paraffin

by the action of α -rays from various sources is described. The semi-empirical theory of Blackett gives accurate vals. up to a range of 40 cm. The efficiency vals. for emission angles between 0° and 8.7° are considerably $>$ those of Chadwick and Bieler.

A. J. M.

Anomalous scattering of α -particle. K. K. MUKHERJEE (Current Sci., 1934, 2, 470—471).—Theoretical.

L. S. T.

Stopping powers of certain gases. J. BREHAIN and J. STORMS (Bull. Soc. chim. Belg., 1934, 43, 331—334).—The stopping power for α -particles was determined by measuring the equiv. pressures for air and other gases by the method of scintillations. The following are ratios to air: CH_4 0.861, C_2H_6 1.442, C_2H_4 1.255, C_2H_2 1.107, CO_2 1.501, SO_2 1.895, Cl_2 1.818.

A. G.

Fine structure of the α -particle groups from thorium-C and of the long-range groups from thorium-C'. W. B. LEWIS and B. V. BOWDEN (Proc. Roy. Soc., 1934, A, 145, 235—249).—Precise measurements of the fine structure of the α -particle groups from Th-C have been made, confirming previously established agreement with γ -ray energies required by Gamow's theory. The energy difference between the two most prominent groups of α -particles from Th-C has been accurately determined by a direct electrostatic measurement. Good agreement is found with the energy of a strong γ -ray deduced from the β -ray spectrum measurements of Ellis (A., 1932, 556). The two long-range groups from Th-C' have been re-examined in detail.

L. L. B.

Wave-length and intensity of secondary radiation from hard γ -rays. W. GENTNER (Naturwiss., 1934, 22, 435).—Results of experiments reported by various workers on the absorption of hard γ -rays, particularly by heavy elements, vary a great deal. Experiments with Mg, Cu, Sn, Au, and Pb as scattering material show that very intensive electrons are given off, some of them having velocities approaching those of the γ -rays producing them.

A. J. M.

Delivery of heat by γ -radiation from radium. I. ZLOTOWSKI (Compt. rend., 1934, 199, 284—286).—Using the Swientoslawski adiabatic micro-calorimeter (A., 1932, 137) for measuring the rise of temp. of a Pb block containing Ra prep. of known age, and thence calculating corrections to be deducted for radiations due to the disintegration products of Ra and for α - and β -radiations, the heating effect due to the γ -radiation has been determined as 8.9 ± 0.3 g.-cal. per g. Ra per hr.

J. W. S.

γ -Radiating artificially radioactive element. R. FLEISCHMANN (Naturwiss., 1934, 22, 434—435).—Fe, Al, and SiO_2 were bombarded with neutrons from Rn and Be. γ -Rays were obtained from all, and the half-life of the element producing them was determined. From Fe and Al, β -rays were also obtained, and provided another method of calculating the half-life. The absorption of the γ -rays obtained by bombarding Fe with neutrons was investigated. The intensity was reduced to 34% on passing through 1 cm. Pb, giving $\mu = 0.96$ cm. $^{-1}$, and quantum energy of about 800 kv.

A. J. M.

Visible glow of pure liquids under the action of γ -rays. P. A. TSCHERENKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 451—457).—Twenty pure liquids on irradiation with filtered γ -rays gave a feeble blue luminescence. This was not a true fluorescence, for it was not extinguished by added substances such as KI or AgNO_3 , and was unaltered by heating to 100° . The emitted light was always polarised.

H. J. E.

Possible causes of the blue γ -glow of liquids. S. I. VAVILOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 457—461; cf. preceding abstract).—The luminescence is attributed to electrons produced by Compton scattering in the liquids.

H. J. E.

Radioactivity of light elements. H. J. WALKER (Phil. Mag., 1934, [vii], 18, 156—164; cf. this vol., 940).—It is suggested that induced radioactivity in the light elements is due to formation within the nucleus of a proton with excess energy. The theory developed accounts for spontaneous disintegration, the varying periods of decay being due to differences between the nuclear potential fields.

H. J. E.

Energy distribution between the products of the transmutation of boron atoms. A. D. FOKKER, H. D. KLOOSTERMAN, and F. J. BELINFANTE (Physica, 1934, 1, 705—714).—Theoretical.

H. J. E.

Penetrating radiation obtained on artificial disintegration of lithium. A. ECKARDT, R. GEBAUER, and H. R. VON TRAUBENBERG (Z. Physik, 1934, 89, 582—591).—This radiation can be detected through 180 mm. of Pb, and has $1/10$ the α -ray scintillation intensity.

A. B. D. C.

Validity of the principle of the conservation of spin angular momentum in the process of the artificial disintegration of lithium atoms. B. ARAKATSU (Mem. Fac. Sci. Agric. Taihoku, 1934, 10, 81—84).—In the disintegrations expressed by ${}_3\text{Li}^{7+}_1\text{H}^1 = {}_2\text{He}^4$ and ${}_3\text{Li}^{6+}_1\text{H}^2 = {}_2\text{He}^4$ consideration of the nuclear moments indicates that the total angular momentum can be conserved only if a photon is emitted in each case.

H. S. P.

Transformation of boron into the isotope of beryllium of mass 8. F. KIRCHNER (Naturwiss., 1934, 22, 480).—In the bombardment of B with protons, particles with a continuous distribution of ranges between 5 and 48 mm. are produced, and superimposed on them there is a group of particles with uniform range. The continuous distribution is explained by the change ${}_5\text{B}^{11}_1\text{H}^1 = {}_4\text{Be}^8 + \Delta m$. A homogeneous group, however, can be obtained only in cases where, as a result of the nuclear disintegration, only two particles are formed. The only reaction which can satisfy this condition is ${}_5\text{B}^{11}_1\text{H}^1 = {}_4\text{Be}^8 + {}_2\text{He}^4 + \Delta m$. The mass of Be^8 , obtained in the above change, calc. on the basis of Aston's val. for Be^{11} , is 8.0074 ± 0.0015 . Hence the mass of Be is $> 2\text{He}^4$. It is possible that the particle obtained in this change is excited, and changes into the unstable Be^8 nucleus, with emission of γ -rays.

A. J. M.

Transmutation of fluorine by proton bombardment and the mass of fluorine 19. M. C. HEN-

DERSON, M. S. LIVINGSTON, and E. O. LAWRENCE (Physical Rev., 1934, [ii], 46, 38—42).—By bombardment with protons, the transmutation of F into O₂ and He has been effected. The no. of transmutations for the proton energy range (0.675—1.63) × 10⁶ ev. has been followed. The range of the emitted α-particles is > 6 cm., increasing with proton energy in accordance with theory. Calc. and experimental variation of transmutation probability with proton energy are in agreement. The mass of the F atom, calc. from the reaction, is 19.0031.

N. M. B.

Induced radioactivity and transmutation. F. H. NEWMAN and H. J. WATKES (Nature, 1934, 134, 64).—It is suggested that in the bombardment of elements with neutrons (this vol., 714), unstable and missing isotopes containing α-particles, a dipion, and neutrons are produced. The missing isotopes are unstable, emitting either an electron or a positron. Thus with Al the transmutations would be $_{13}\text{Al}^{27} [6\alpha + \text{D} + n] \text{ (stable)} + n \rightarrow _{13}\text{Al}^{28}$; $_{13}\text{Al}^{28} [6\alpha + \text{D} + 2n] \text{ (unstable)} \rightarrow _{14}\text{Si}^{28} [7\alpha] + \beta$.

L. S. T.

Induced radioactivity of potassium. M. ZYW (Nature, 1934, 134, 64—65).—When bombarded with 55-mm. α-rays of Ra-C', KCl, but not NaCl, acquires a greater radioactivity. The induced activity decays exponentially with a half-period of 3 hr., and the radiation consists of positrons when the α-ray range is > 45 mm. The probable reactions are $_{19}\text{K}^{41} + _2\text{He}^4 = _{21}\text{Sc}^{44} + \text{neutron}$ and $_{21}\text{Sc}^{44} = _{20}\text{Ca}^{44} + \text{positron}$.

L. S. T.

Radioactivity induced by bombardment with neutrons of different energies. T. BJERGE and C. H. WESTCOTT (Nature, 1934, 134, 177).—Fermi's results (this vol., 714) have, in general, been confirmed using Rn+Be as the neutron source. The relative rates of production of active atoms from F, Si, P, and Ag by bombardment with neutrons from different sources, viz., Be+Rn, Li+dipions, Be+dipions, and dipions+dipions, have been determined and are discussed.

L. S. T.

Wave-statistical theory of artificial disintegration. K. C. KAR and A. GANGULI (Current Sci., 1934, 2, 471—472).—The artificial disintegration of protons by the lighter elements can be regarded as a double process of capturing of the α-particle by the core followed by spontaneous emission of the protons (cf. this vol., 5).

L. S. T.

Energy spectrum of positive electrons ejected by radioactive nitrogen. A. J. ALICHANOV, A. J. ALICHANIAN, and B. S. DZELEPOV (Nature, 1934, 133, 950—951).—The energy distribution curve of positive electrons emitted by B when bombarded by α-particles of Ra-C' with a range reduced to 6.3 cm. is similar in shape to that of the β-spectrum of Ra-E, with a limit corresponding with approx. 1.3×10^6 ev.

L. S. T.

Analysis of the cosmic-ray absorption curve. C. ECKART (Physical Rev., 1934, [ii], 45, 851—859).

N. M. B.

Relativistic basis of the quantum theory. II. H. T. FLINT (Proc. Roy. Soc., 1934, A, 145, 645—666).—Mathematical.

L. L. B.

Energy, temperature, and at. wt.: rapid interconversion scale. C. H. D. CLARK (Phil. Mag., 1934, [vii], 18, 80—90; cf. A., 1932, 896).—Arithmetical relations for converting one energy scale into another are tabulated.

H. J. E.

Hydrogen isotopes and the wave nature of matter. C. E. H. BAWN (Chem. and Ind., 1934, 606—610).—A review of applications made of the wave-mechanical conception of zero-point energy in explaining the differences in chemical reactivity of the H isotopes.

H. J. E.

Properties of radiation at very high energy densities. M. P. BRONSCHEIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 462—465).—Theoretical.

H. J. E.

Tensorial fields which accompany the Dirac electron: theory of neutrino and antineutrino. B. KWAL (Compt. rend., 1934, 199, 23—24; cf. *ibid.*, 198, 1582).—Generalisation of de Broglie's photon field (this vol., 236) by introduction of anti-symmetrical current and spin vectors provides a mathematical basis for the neutrino and antineutrino, and meets Pauli's objections (Z. Physik, 1933, 80, 573).

B. W. B.

Energy of binding, mass of neutron, and grouping of atomic nuclei. G. MONOD-HERZEN (Compt. rend., 1934, 199, 45—46).—A discussion of the mass of the neutron and the mass defects of isotopic nuclei.

B. W. B.

Energies of binding in the radioactive U-Ra and Th series. W. M. ELSASSER (Compt. rend., 1934, 199, 46—48).—Radioactive disintegration energies, tabulated against the nos. of protons and of neutrons in the corresponding nuclei, show discontinuities which are attributed to a nuclear structure consisting of successive shells of protons and neutrons.

B. W. B.

Empirical stability limits of atomic nuclei. G. GAMOW (Z. Physik, 1934, 89, 592—596).

A. B. D. C.

Structure of atomic nuclei. I. K. GUGGENHEIMER (J. Phys. Radium, 1934, [vii], 5, 253—256).—The limits of stability of various classes of atoms and the probable existence, in the nuclei, of independent layers of neutrons and protons are discussed.

N. M. B.

Energetic relations in the periodic system of simple chemical compounds. H. G. GRIMM (Z. Elektrochem., 1934, 40, 522—523).—Theoretical (cf. this vol., 234).

E. S. H.

Atomic constants deduced from secondary cathode-ray measurements. H. R. ROBINSON (Nature, 1934, 134, 179).—A correction (this vol., 125).

L. S. T.

Energy and stability related to composition of atomic nuclei. E. D. EASTMAN (Physical Rev., 1934, [ii], 46, 1—16).—Theoretical. Heisenberg's postulates are examined and extended. The evaluation and application of the consts. are discussed and illustrated. The energy of formation of nuclei and energies in nuclear collision processes are calc. The α-disintegration is considered to be possible in elements down to Sb. The possibility of β-changes or their

reverse in certain isobaric pairs among the non-radioactive elements, the end of the periodic system, and the limiting spread in mass nos. of isotopes as influenced by the various types of nuclear instability are discussed. N. M. B.

Representation of nuclear moments of atoms by vectors. O. STERN (Z. Physik, 1934, 89, 665). H. SCHÜLER (*ibid.*, 666).—Polemical (cf. this vol., 580). A. B. D. C.

Structure of atomic nuclei. H. J. WATKINS (Phil. Mag., 1934, [vii], 18, 129—155; cf. this vol., 827).—Theoretical. It is shown that no free protons exist within nuclei, but that they are bound as α -particles or diplons. The neutrons are less firmly bound and form a shell system in the heavier elements surrounding the nuclear core. Proton emission is attributed to the formation of these particles within the nucleus due to interaction between the bombarding α -particle and the nucleus. Nuclear structures for various elements are discussed. H. J. E.

Atomic radius of fluorine. C. H. D. CLARK (Nature, 1934, 134, 99—100).—The equilibrium nuclear distance of F_2 , calc. by means of a modified Morse formula, is 1.331 Å.; at. radius 0.67 Å.

Nuclear moment of Tl. L. A. WILLS (Physical Rev., 1934, [ii], 45, 883—885).—Mathematical. Using a method due to Breit (cf. A., 1931, 1104) the calc. magnetic moment of the Tl nucleus is $1840g \pm 2.7$.

Nuclear moments of antimony isotopes: discussion of Landé's theory. M. E. CRAWFORD and S. BATESON (Canad. J. Res., 1934, 10, 693—702).—Investigation of the hyperfine structure of Sb IV showed I vals. of Sb^{121} and Sb^{123} $\frac{5}{2}$ and $\frac{7}{2}$, respectively, and magnetic moments 4.0 and 3.2 proton magnetons. The ratio of the $g(I)$ factors is $g(I)_{121}/g(I)_{123} = 1.82 \pm 0.02$, and applying Landé's $g(I)$ formula the magnetic factor of the proton spin $g_s = 4$ instead of 3 as found by Landé. This gives better agreement between calc. and experimental $g(I)$ vals., but the theory is considered to be incomplete.

Ratio of the magnetic moments of proton and diplon. F. KALCKAR and E. TELLER (Nature, 1934, 134, 180).—The tentative val. calc. for this ratio is 4.

Spectrophotometry of rapidly changing systems. E. R. HOLIDAY and F. C. SMITH (Nature, 1934, 134, 102).—A continuous representation of the absorption curve of a changing system has been obtained by an application of the cathode-ray oscillograph, the time response being < 0.02 sec.

Ultra-violet sources and their radiation. W. E. FORSYTHE, B. T. BARNES, and M. A. EASLEY (J. Opt. Soc. Amer., 1934, 24, 178—182).—The intensities, distribution, and output of ultra-violet radiation from the quartz-Hg arc and several types of "sunlamp" were investigated.

Absorption of ultra-violet and visible light by water. L. H. DAWSON and E. O. HULBURT (J.

Opt. Soc. Amer., 1934, 24, 175—177).—The absorption coeffs., measured in tubes of pure H_2O up to 272 cm. long, were $(0.8—80) \times 10^{-3}$ in the range 4000—2000 Å., or > 10 times those calc. from mol. scattering. For wave-lengths 5400—6900 Å. the coeffs. were 0.0004—0.0039, and for 4000—5400 Å. < 0.0004 . N. M. B.

Photo-dissociation of the NO_3' ion and its dependence on the polarisation of the exciting light quantum. K. S. KRISHNAN and A. C. GUHA (Current Sci., 1934, 2, 476—477).—The absorption band of aq. solutions of nitrates from 350 to 270 $m\mu$ probably corresponds with photo-dissociation of NO_3' into NO_2' and O in the ground state (3P_2). The band beginning at approx. 230 $m\mu$ probably corresponds with the dissociation of NO_3' into NO_2' and an excited O atom.

Absorption spectra of some higher sulphides. P. K. SEN-GUPTA (Bull. Acad. Sci. Agra and Oudh, 1933, 3, 65—68).—In the absorption spectra of TeS_3 and P_2S_5 there are three regions of continuous absorption, from which the vals. of $3P-^3D_2$ and 1D_2 —for S are obtained. The results agree with those obtained for other sulphides.

Line absorption spectrum of crystalline chrome alum. F. H. SPEDDING and G. C. NUTTING (J. Chem. Physics, 1934, 2, 421—431).—Photographs of the line absorption spectrum of $KCr(SO_4)_2 \cdot 12H_2O$ have been made for the temp. range 85—14° abs. The intensities of some of the lines vary with temp. and, at 14° abs., there is a new group of faint sharp lines near 4500 Å. Possible energy states giving rise to the lines are considered and the nature of energy levels in solids is discussed.

Band spectrum of CS. F. H. CRAWFORD and W. A. SHURCLIFF (Physical Rev., 1934, [ii], 45, 860—870).—From high-dispersion photographs data are extended for the main $A^1\Pi \rightarrow x^1\Sigma$ system, and a new system $C^1\Sigma \rightarrow B^1\Sigma$ is revealed. The anomalies of bands with extra heads or displaced origins (cf. Jevons, A., 1928, 105) are due to rotational perturbations.

Photo-dissociation of the vapours of organo-metallic compounds. A. TEREIN (J. Chem. Physics, 1934, 2, 441—442).—The ultra-violet absorption spectra of $HgMe_2$ (I), $ZnMe_2$ (II), and $PbEt_4$ (III) have been studied. (I) has diffuse bands in the region 2100—1970 Å. and continuous absorption to 2800 Å. By comparison with the behaviour of $HgMeI$ or $HgMeBr$ which, when illuminated by short ultra-violet light, give spectra belonging to excited HgX ($X=I$ or Br) mols., the photo-dissociation process for (I) is probably $h\nu + HgMe_2 \rightarrow Me + HgMe$. From these experiments the strength of the linking $Hg-C$ is of the order of 60 kg.-cal. per mol. (II) and (III) give only a continuous absorption spectrum. Their vapours are readily decomposed by ultra-violet light with the formation of metallic dust in the path of the light beam.

Absorption spectra of ethyl nitrate, ethyl nitrite, and nitroethane. (MISS) J. W. GOODEVE (Trans. Faraday Soc., 1934, 30, 504—508).—Measure-

ments of the ultra-violet absorption of the vapours have been made and the extinction coeffs. determined. Absorption in each case consists of two broad, continuous, overlapping bands; extinction coeff. curves for Et nitrate and nitrite are similar, but different from that of EtNO₂. The absorbing group in all cases is probably N·O. M. S. B.

Chromophoric groups. I. Ultra-violet absorption spectra of indene and certain of its derivatives. II. Absorption spectra of naphthalene, hydronaphthalenes, and related compounds. R. A. MORTON and A. J. A. DE GOUVEIA (J.C.S., 1934, 911—916, 916—930).—I. The absorption spectra of hydrindene (I) (λ_{max} , 273·6, 267, 260, 254, [?] 291 m μ ; log ϵ_{max} , 3·25, 3·16, 3·00, 2·75, and 1·00, respectively), indene (II) (249, 279·5, 286·5, 290·8 m μ ; 4·06, 2·65, 2·50, 2·37) and of benzylidene- (III) (340·0, 280·0, 238·0 m μ ; 4·34, 4·33, 4·22) and cinnamylidene-indene (IV) (388·0, 371·0, 358·5, 308·5, 297·0, 290·0, 245·0 m μ ; 4·66, 4·77, 4·72, 4·26, 4·30, 4·24, 4·26) in C₆H₁₄ and in EtOH are plotted. Absorption due to the simple chromophore C=C is influenced by vibrational frequencies and modified by its inclusion in a complex chromophore. Thus the extinction curve of (I) is benzenoid, similar to that of xylene, Ph[CH₂]_n·CH:CH₂, etc.; that of (II) is similar to that of CHPh:CH₂ and CHPh:CH[CH₂]_n·Me and is due to the complex chromophore CPh:C; the band 292—262 m μ is probably produced by an absorbing electron of the C₆H₆ ring influenced by the conjugated ethylene linking, to which the unresolved intense 249 m μ band is due. The vibrational frequencies 460 and 920 cm.⁻¹ appear in (II), and 940 cm.⁻¹ in (I). In (III), (IV), and crotonylideneindene, three regions of absorption, separated by 6000—7000 cm.⁻¹ (as in carotene etc.), are exhibited, the spectra being compared with those of [CHPh]₂ and [CHPh:CH]₂. The theory of correspondence between different absorption regions and different chromophores is discussed.

II. The absorption spectra of various carefully purified hydronaphthalenes are plotted. That of C₁₀H₈ (I) confirms the results of Henri *et al.* (A., 1922, i, 928) and de Laszlo (A., 1925, ii, 179), but the ϵ vals. of Kimura (A., 1932, 211) are, in all cases, 10 times too high. The vals. of λ_{max} and log ϵ , respectively, are Δ^1 (262, 296 m μ ; 4, 2·68) and Δ^2 -dihydro- (benzenoid bands at 274, 267, 262 m μ ; 2·93, 2·90, 2·7; and a series of sharp max. in the region 293—330 m μ , possibly due to an isomeric dihydronaphthalene), 1:2:3:4-tetrahydro-naphthalene (purified by fractional crystallisation of the Ba and Na sulphonates) (274, 267, 261 m μ ; ϵ =approx. 760, 740, 600): *ar*-tetrahydro- α - (281, 269 m μ) and - β - (286, 267 m μ), and *ac*-tetrahydro- β - (273, 266·5 m μ ; 3·15, 3·14)-naphthols. Hexahydronaphthalenes are only weakly absorbing. Cadinene shows a broad unresolved band (246 m μ ; ϵ =480), and *isocadinene* exhibits max. at 279·5 and 262·5 m μ ; ϵ , 440, 580. Conclusions for 1:2:3:4:9:10-hexahydronaphthalene are rendered difficult by its oxidation-reduction during purification, but its absorption appears to be non-selective over the range 290—245 m μ . Pure octahydro- and decahydro-naphthalene and decahydro- β -naphthol show no appreciable absorption

at > 210 m μ . The absorption spectra of 1- and 2-methyl-, 2:6- and 2:7-dimethyl-, 1-methyl-5-, -6-, and -7-ethyl-, 1:3:5-, 1:3:8-, and 2:3:5-trimethyl-, and 1:6-dimethyl-4-*isopropyl*- (cadalene)-naphthalene are tabulated, the introduction of alkyl groups in (I) causing relatively slight changes in the absorption spectrum. The (I) skeleton gives rise to three separate regions of absorption (a) 295—325 m μ , low ϵ vals., good resolution (Δ cm.⁻¹ 1000), (b) 250—290 m μ , higher ϵ vals., moderate resolution (Δ cm.⁻¹ 1000), and (c) *ca.* 220 m μ , high ϵ vals., moderate resolution (Δ cm.⁻¹ *ca.* 1200), which are assumed to be due to three complex chromophores, capable of some degree of independent variation, since the same regions, but with different relative intensities, are shown by quinoline and *isoquinoline*, and the above spectra are discussed on this basis. Abietic acid (249·7, 242·5, 234 m μ ; 4·10, 4·16, 4·16 in C₆H₁₂), α -camphorene (inflexion at 230—250 m μ ; 2·82), *isotricyclocamphorene* (246·5 m μ ; 3·72: inflexion at 285 m μ), and ergosterol and its derivatives exhibit selective absorption of a type which cannot be explained in terms of existing ideas of chromophoric groups. J. W. B.

Absorption spectra of coloured organic salts of violentin and alloxantin. K. N. GAIND and S. DUTT (Bull. Acad. Sci. Agra and Oudh, 1933, 3, 79—82).—The positions of the absorption max. for a no. of salts of these compounds are tabulated.

A. J. M.

Weak secondary valency forces having a definite direction as the real chromophores. R. REINCKE (Z. physikal. Chem., 1934, B, 26, 159—186; cf. A., 1933, 450, 552).—Assuming the activity domains of C, O, and N atoms to be tetrahedral, both principal and secondary valencies having definite directions, it is shown that the appearance of colour is due to the secondary valencies, and the presence of chromophores and auxochromes is of subsidiary importance. From the C atom there extend eight valency forces; four principal valencies directed towards the corners of the tetrahedron and four secondary valencies directed towards the centres of the faces. The structure of a layer of the graphite lattice may be represented by an assemblage of tetrahedra. The cause of colour is the peculiar at. linking of the C₆H₆ ring, with its analogy to the graphite structure. The larger is the section of a graphite layer a mol. represents the deeper is its colour. The extremes are graphite on the one hand and C₆H₆, with its ultra-violet absorption bands, on the other. R. C.

Ultra-violet absorption of certain aromatic hydrocarbons. AUBERT and T. GHEORGHIU (Ann. Office nat. Combust. liq., 1933, 8, 451—478; Chem. Zentr., 1934, i, 510).—Absorptions of C₆H₆, PhMe, PhEt, PhPr, and PhBu are discontinuous, and of C₆H₄Et₂, C₅H₁₁Ph, C₆H₃Me₃, ψ -cumene, and C₆H₂Et₃ are continuous. A. A. E.

Infra-red spectrum of heavy water vapour. E. BARTHOLOME and K. CLUSIUS (Z. Elektrochem., 1934, 40, 529—531).—The spectrum of H₂O vapour containing varying amounts of H² has been determined in the region 2—10 μ . E. S. H.

Pure rotation spectrum of the HCl flame. J. STRONG (Physical Rev., 1934, [ii], 45, 877—882).—Data are tabulated for pure rotation lines for $j=17-33$ of the emission spectrum of the HCl flame measured with a KBr prism. Empirical formulae for two series of lines corresponding with pure rotation in the two lowest oscillation states are deduced, and linear coeffs. agree with those calc. from the oscillation-rotation formula. N. M. B.

High rotational levels of the water molecule. M. ELJASCHEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 539—541).—Lines corresponding with rotational quantum nos. 5 and 6 in the H_2O vapour spectrum have been calc., and observed in the telluric lines of the solar spectrum. H. S. P.

Electric moments and infra-red spectra, and the structure of CO. R. S. MULLIKEN (J. Chem. Physics, 1934, 2, 400—402).—The val. of infra-red intensities in the determination of electric moments as functions of inter-at. distances is indicated by reference to the data for HCl, HI, CO, and H_2O .

M. S. B.

Spectroscopic structure determinations of simple hydrocarbons and their derivatives. R. MECKE [with P. GANSWEIN and O. VIERLING] (Z. Elektrochem., 1934, 40, 474—475).—A preliminary note on observations in the infra-red region.

E. S. H.

Constitution of water in different states. I. R. RAO (Proc. Roy. Soc., 1934, A, 145, 489—509).—The intensity distribution with respect to wave-length of the Raman bands for ice and water at 0° , 4° , 38° , and 98° is determined. The intensity curves indicate that each is due to a superposition of three components, attributed to the single vapour mols., double water mols., and triple ice mols., respectively.

L. L. B.

Effect of electric field on the polarisation of Raman lines. S. C. SIKKAR (Indian J. Physics, 1934, 8, 377—385).—Photographs and photomicrographic records are given showing the effect of an alternating electric field of the order 15,000—25,000 volts per cm. on the polarisation of the Raman scattering by cyclohexane, PhCl, and C_6H_6 . Results are also discussed for PhMe, CCl_4 , and $CHCl_3$. Some lines show an increase, some a decrease, in polarisation, whilst others are unchanged. N. M. B.

Raman effect in fused inorganic nitrates. V. N. THATTE and A. S. GANESAN (Indian J. Physics, 1934, 8, 341—344).—Data for the nitrates of Li, Na, K, Ag, Mg, Zn, Cd, Al, and Tl show that the characteristic frequency of the NO_3 group at 1050 cm^{-1} persists, but with sufficient variation to indicate differences in the dimensions of the NO_3 group for different nitrates. N. M. B.

Raman spectra of metallo-chloroforms in relation to their structure. H. VOLKRINGER, A. TCHAKIRIAN, and (MME.) M. FREYMAN (Compt. rend., 1934, 199, 292—294).—The Raman spectra of $GeHCl_3$ (I) and $SnHCl_3 \cdot 3H_2O$ (II) have been studied in aq. and HCl solution. Raman frequencies of (I) are 131, 162, 251, and 315 cm^{-1} , all broad diffuse lines, of (II) 112 (very broad and diffuse), 218 and

265 (diffuse), and 312 cm^{-1} (narrow and weak). The results are like those for $CHCl_3$ and $SiHCl_3$, indicating similarity of structure. Neither (I) nor (II) shows a frequency corresponding with the 3018 and 2258 cm^{-1} of $CHCl_3$ and $SiHCl_3$, respectively, and attributed to the linking of the H atom to the rest of the mol. This is explained by supposing that ionisation occurs with the Ge and Sn compounds (cf. A., 1932, 901). It is suggested that the structure $Cl_3C \cdot Cl \cdot H$ (A., 1933, 1138), which is in agreement with the Raman spectrum data, should be extended to $SiHCl_3$. J. W. S.

Raman spectrum and organic chemistry. K. W. F. KOHLRAUSCH (Z. Elektrochem., 1934, 40, 419—434).—A lecture. E. S. H.

Raman spectrum of carbon disulphide. A. LANGSETH, J. U. SORESENSEN, and J. R. NIELSEN (J. Chem. Physics, 1934, 2, 402—409).—The Raman spectrum of liquid CS_2 with high dispersion shows five very faint additional lines. The intensities of the stronger lines have been measured and the degrees of depolarisation of the two principal bands determined. The results are considered to be in agreement with the views of Fermi (A., 1931, 1111) and others as to the origin of the two principal bands of CO_2 and CS_2 . M. S. B.

Raman effect. XXXII. Raman spectra of paraffins. K. W. F. KOHLRAUSCH and F. KOPPL (Z. physikal. Chem., 1934, B, 26, 209—237; cf. this vol., 346).—The Raman spectra of straight-chain paraffins from C_3H_8 to $C_{12}H_{26}$ and of cyclopropane (I), isobutane, CMe_4 , and *n*-heptyl chloride and bromide have been determined. The central force system model fails to describe the results, and the valency force system (cf. A., 1933, 209) is adequate only when there is no branching. The frequencies of the C-C chain are $> 1100\text{ cm}^{-1}$; higher frequencies in the paraffins are CH deformation frequencies, but in (I) the chain frequency reaches 1187 cm^{-1} . With increasing branching the valency bending force falls. The spectra of the unbranched paraffins from C_5H_{12} to $C_{12}H_{26}$ are very regular and simple, corresponding with the chain spectra in singly substituted paraffins. They exhibit a deformation frequency which falls systematically with increasing length of the chain and a valency frequency which oscillates on passing from one homologue to the next. R. C.

Measurement of Raman effect at low temperatures. H. EPSTEIN and W. STEINER (Z. physikal. Chem., 1934, B, 26, 131—157).—An improved apparatus is described permitting investigation of the effect of temp. and state of aggregation on Raman spectra at 50° to -150° . A decrease in wave-no. of 0—0.2% is exhibited by various Raman lines of C_6H_6 on freezing. The wave-no. of the max. of the Raman vibration band of liquid HI is 2165 cm^{-1} ; there is a fall of about 0.25% on freezing, which agrees with Cremer and Polanyi's calculations (A., 1931, 1358). R. C.

Influence of various radicals on the characteristic frequency of the ethylenic linking in derivatives of cyclopentene. L. PIAUX (Compt. rend.,

1934, 199, 66—68; cf. this vol., 583).—Raman spectra of Δ^1 -cyclopentene-1-aldehyde (A., 1930, 1039), Me cyclopentene-1-carboxylate, 1-phenyl-, 1-methyl-, and 1-ethyl-cyclopentene (cf. this vol., 10) are measured. The lines 889, 1032, 1205, and 1290 cm^{-1} of cyclopentane are reproduced in these derivatives. Conjugation in the mol. has a variable effect on the lines produced by the C:C and C:O linkings. J. L. D.

[Raman spectra of] acetylenic ethers. (MLLE.) B. GREDY (Compt. rend., 1934, 198, 2254—2256; cf. this vol., 239).—Methylation of $\text{CR}\cdot\text{C}\cdot\text{CH}_2\cdot\text{OH}$ ($\text{R}=\text{C}_5\text{H}_{11}$, C_6H_{13} , or cyclohexyl) changes the line 2228 cm^{-1} into lines 2217 and 2234 cm^{-1} . Methylation of $\text{CR}\cdot\text{CHMe}\cdot\text{OH}$ ($\text{R}=\text{C}_5\text{H}_{11}$ or cyclohexyl) reduces the characteristic frequency (2250 cm^{-1}) of the alcohol by 10 cm^{-1} . Ph adjacent to the triple linking completely alters the spectrum in the region 2100—2300 cm^{-1} . The following ethers, prepared by the usual methods, are described: α -methoxy- Δ^8 -octinene, b.p. 77°/19 mm., $-\Delta^8$ -noninene, b.p. 97—98°/17 mm., $-\gamma$ -phenyl- Δ^8 -propinene, b.p. 112·5°/16 mm., and $-\delta$ -cyclohexyl- Δ^8 -butinene, b.p. 117—118°/19 mm.; β -methoxy- Δ^7 -noninene, b.p. 81°/17 mm., $-\epsilon$ -cyclohexyl- Δ^7 -pentinene, b.p. 119—119·5°/20 mm., and $-\delta$ -phenyl- Δ^7 -butinene, b.p. 114—114·5°/20 mm. J. L. D.

[Raman] spectra of some acetylenic compounds of the cyclic series. (MLLE.) B. GREDY (Compt. rend., 1934, 199, 294—296; cf. this vol., 239, and preceding abstract).—The Raman spectra of $\text{CH}\cdot\text{C}\cdot\text{C}_5\text{H}_9$, $\text{CH}\cdot\text{C}\cdot\text{C}_6\text{H}_{11}$, $\text{CMe}\cdot\text{C}\cdot\text{C}_5\text{H}_9$, $\text{CMe}\cdot\text{C}\cdot\text{C}_6\text{H}_{11}$, $\text{CMe}\cdot\text{C}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_{11}$, and $\text{OH}\cdot\text{CHMe}\cdot\text{C}\cdot\text{C}_6\text{H}_{11}$ have been determined. Cyclic groups in the immediate neighbourhood of the triple linking do not greatly affect the spectrum of a true acetylene, but in compounds $\text{CR}\cdot\text{CMe}$ the 2235 cm^{-1} frequency changes to 2239, the 2303 line disappears and is replaced by two weak lines on either side of this, and the strong frequency 376 does not appear clearly; the 1380 line remains. With a CH_2 group between the cyclic group and the triple linking the results are normal. With the alcohol the weak lines of the acetylenic region do not appear on account of fluorescence, but the strong line occurs at 2237 cm^{-1} . The spectrum of this alcohol resembles that of an acetylenic hydrocarbon rather than a sec.-alcohol. J. W. S.

Luminosity of shock waves. A. MICHEL-LÉVY and H. MURAOUR (Compt. rend., 1934, 198, 1760—1762; cf. this vol., 605).—The luminosity (I) produced around solid objects by impact of shock waves (II) from detonated PbN_6 is photographed. The spectrum of (I) consists of a continuous background (III) crossed by reversed Pb and Na lines, (III) being attributed to heated air in the track of (II) (cf. Anderson, A., 1926, 605). B. W. B.

Micropyrotechny. Luminous effects accompanying detonation are not independent of the nature of the gas surrounding the explosive. A. MICHEL-LÉVY and H. MURAOUR (Compt. rend., 1934, 198, 2091—2093; cf. preceding abstract).—The luminosities (I) produced during the transmission of detonation around a ring of separated PbN_6 grains in atm. of A , N_2 , H_2 , CO_2 , and C_4H_{10} decreased in that order. It is concluded that the shock waves were

responsible for (I). C_2H_2 at 1 atm. pressure was not decomposed during detonation. B. W. B.

Influence of viscosity on the decrease of fluorescence of dye solutions with concentration. J. BOUCHARD (Compt. rend., 1934, 199, 43—45).—The coeffs. of fluorescent power of uranine in 0·1N-NaOH decreased only slightly on addition of glycerol, when corr. for changes in dielectric const. (cf. Perrin, A., 1924, ii, 514, 713). Intensity of fluorescence is a function of mol. velocity of diffusion. B. W. B.

Heat flow during surface colour formation [on metals]. F. H. CONSTABLE (Nature, 1934, 134, 100).—A discussion. L. S. T.

Ionisation potentials and energies of formation of non-polar molecules. III. J. SAVARD (J. Phys. Radium, 1934, [vii], 5, 283—286; cf. this vol., 347, 584).—Causes of apparent anomalies to the relation previously deduced are examined from a consideration of the mols. O_2 , HBr , Br , HI , I , H_2O , NO , NO_2 , N_2O , NH_3 , and ZnCl_2 . N. M. B.

Photo-electric measurements of the absorption of fused and crystalline quartz between 1633 and 1463 Å. W. M. POWELL, jun. (Physical Rev., 1934, [ii], 46, 43—46).—The coeff. of absorption of a no. of sections of three specimens of quartz showed very wide variations. N. M. B.

Photo-electric secondary current. W. LEHFELDT (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 263—270; Chem. Zentr., 1933, ii, 3538).— ZnS and AgCl crystals have been studied between -180° and 200° . A. A. E.

Photo-chemistry of silver chloride crystals. F. LOHLE (Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl., 1933, 271—277; Chem. Zentr., 1934, i, 13—14).—An investigation of the absorption bands. L. S. T.

Determination of dipole moments by the method of dilute solutions. I, II. M. A. G. RAU and B. N. NARAYANASWAMY (Z. physikal. Chem., 1934, B, 26, 23—44).—The divergent results obtained for the same substance by different workers are attributed to unsatisfactory methods of calculating the mol. polarisation of the solute at infinite dilution. Hedestrand's method (A., 1929, 647) is the best, and may conveniently be combined with the method depending on determination of the temp. coeff. of the polarisation to give accurate dipole moment vals. independent of any assumptions concerning at. polarisation. Dipole moment measurements with $\text{C}_5\text{H}_5\text{N}$ and derivatives support Kekule's theory of dynamic isosterism. At. polarisation shows no signs of additivity, and is probably vectorial rather than scalar. Propylidene-ethylamine, b.p. 74·2°, has been obtained by condensation of EtCHO with NH_4Et . R. C.

Dependence of the dielectric coefficient of air on pressure and frequency. A. R. JORDAN, J. W. BROXON, and F. C. WALZ (Physical Rev., 1934, [ii], 46, 66—72).—Using an improved modification to a.-c. measurements of an apparatus previously employed (cf. A., 1931, 890), the dielectric const. of air, measured up to 170 atm. pressure and frequencies up to 70,000 cycles per sec., increased linearly with pressure.

N. M. B.

Polarity of chemical compounds. VI. K. HIGASHI (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 703—715).—The following electric moments (μ), in Debye units, have been determined in C_6H_{14} solution: $(CH_2Cl)_2$ -50° 1.13, -25° 1.21, 0° 1.30, 25° 1.36, 50° 1.42; $CH_2Cl \cdot CH_2Br$ -50° 0.85, -25° 0.95, 0° 1.04, 25° 1.14, 50° 1.21; $(CH_2Br)_2$ -50° 0.57, -25° 0.67, 0° 0.79, 25° 0.91, 50° 0.92; $(CH_2I)_2$ 25° 0.44, 50° 0.55. The dependence of μ on temp. is discussed. R. S. B.

Dipole moments of vapours. I. L. G. GROVES and S. SUGDEN (J.C.S., 1934, 1094—1098).—The moments of C_6H_6 , $PhCl$, $PhNO_2$, and $PhCN$ in the vapour state have been measured by a resonance method, with pressures from 50 to 200 mm.; gas law corrections were < 1 in 500. The method uses the steep slope or resonance curve. The current change of the galvanometer when vapour is introduced is so large that the pointer instrument is adequate. All results are $>$ those obtained from measurements in solution and are of importance in connexion with interpretation of the latter. Results indicate that P_A is unimportant. The following dipole moments (μ) in Debye units, and mol. electron+atom (P_{E+A}) and atom (P_A) polarisations, have been determined: C_6H_6 0, 26.2, 1.1; $PhCl$ 1.69 ± 0.01 , 34.9, 3.9; $PhNO_2$ 4.23 ± 0.01 , 36.2, 4.2; $PhCN$ 4.39 ± 0.02 , 31.4, negligible. L. G. G.

Dielectric properties of cellulose. W. N. STROOS (J. Amer. Chem. Soc., 1934, **56**, 1480—1483).—The dielectric const. and power factor of dry, glycerol-free Cellophane have been determined at intervals of 20° from -50° to 110° over a wide range of frequencies. The dielectric const. is nearly twice that of cellulose acetate. Anomalous dispersion and absorption have been found; the phenomena are discussed in relation to structure. E. S. H.

Uniformity in the dispersion of liquid and gaseous hydrocarbons. S. FRIBERG (Z. physikal. Chem., 1934, **B**, **26**, 195—202).—Available data show that within the paraffin and olefine series, taking the mol. refraction (Lorentz-Lorentz), R , as 1000 for each homologue at $546 m\mu$, the dispersion curves of the various homologues are almost coincident up to $230 m\mu$, irrespective of whether they are gaseous or liquid. In both series R is an additive magnitude over the whole spectral range, except for the first member of the series. The consts. of the usual dispersion formulæ can be determined only approx. R. C.

Optical rotatory power. T. M. LOWRY (J. Phys. Radium, 1934, [vii], **5**, 225—229).—A lecture.

N. M. B.

Occurrence of optical rotation and anomalous rotation dispersion in aldehydes and ketones. T. M. LOWRY (Z. Elektrochem., 1934, **40**, 475—478).—A lecture. E. S. H.

Optical activity and solubility of some cobalt-ammines. J. P. MATHIEU (Compt. rend., 1934, **199**, 278—280).—The optical rotatory power, circular dichroism, and solubilities have been studied for the forms of $[Co(en)_2Cl_2]Cl \cdot H_2O$; $[Co(en)_2Cl(SCN)]Cl$; $[Co(en)_2Cl(NO_2)]Cl$; $[Co(en)_2(SCN)(NO_2)]Cl$; $[Co(en)_2(NO_2)_2]Cl$; $[Co(en)_2(CO_3)]Cl$; and

$[Co(en)_2(C_2O_4)]Cl$ which either give the less sol. compound with *d*-bromocamphorsulphonic acid or are derived from this form of another cobaltamine. Study of the optical activity over a wide range of wave-length shows that the long wave-length band possesses a positive anisotropy for all these cobalt-ammines. J. W. S.

Optical rotation and atomic dimension.—See this vol., 866.

Fused organic substances. I. Method and apparatus for determining refractive indices. II. The invariant of magnetic rotation. III. Determination of magnetic rotatory power. IV. Calculation of Verdet's constant, Λ , from atomic refractivities. V. Verification of the law of magnetic rotatory dispersion. C. SAL-GEANU (Bull. Acad. Sci. Roumaine, 1933, **16**, 8—12, 13—15, 16—19, 20—23, 24—26).—I. The min. deviation method is applied to the liquid in a hollow glass prism maintained at $>$ room temp. by the enclosure described.

II. In the range 34 — 188° , the relation $\Lambda nd/(n^2-1)^2$, where Λ is Verdet's const., is const. for $C_{10}H_8$, $CHPh_3$, and phenanthrene and increases $< 5\%$ for $2-C_{10}H_7Me$, showing that in these substances association and mol. deformation, which are not included in the theory (A., 1927, 8), do not play an important part.

III. The data refer to 19 — 217° . The magnetic rotatory dispersion, M , of $1-C_{10}H_7Me$ decreases slightly with rise of temp. For phenanthrene at 104° , $[\omega]_{436}/[\omega]_{546}$ is 1.97, whilst the magnetic anisotropy of benzil is very large. It is inferred that magnetic birefringence is a mol. phenomenon, whilst magnetic rotation is of at. origin.

IV. Calc. vals. of Λ for $CHPh_3$, $C_{10}H_8$, and phenanthrene (cf. *loc. cit.*) accord with observed vals. for the liquids.

V. The M (obs.) of fused $2-C_{10}H_7Me$ and phenanthrene deviate progressively from the calc. vals. towards the ultra-violet and the inclusion in the theory of terms for absorption bands is indicated (cf. *loc. cit.*). J. G. A. G.

Paramagnetic rotation of tysonite. J. H. VAN VLECK and M. H. HEBB (Physical Rev., 1934, [ii], **46**, 17—32).—Mathematical. In rare-earth compounds the Verdet const. and magnetic susceptibility χ should vary similarly with temp. From available data thereon information concerning the χ vals. for crystallographic axes in tysonite are obtained. The assumption of rhombic symmetry for the local field, with three possible orientations, differing by 120° , for the rhombic axes, gives better agreement with experiment than Kramer's proposed triclinic field.

N. M. B.

Thermal variation of the magnetic birefringence of mixtures. Mixture with a critical point. A. GOLDET and A. PIEKARA (Compt. rend., 1934, **199**, 271—273).—The magnetic birefringences of mixtures of $PhNO_2$ with CCl_4 and C_6H_{14} are $<$ the vals. expected from a linear variation with concn. The temp. coeffs. for solutions of $PhNO_2$ in CCl_4 and dil. solutions of $PhNO_2$ in C_6H_{14} diminish with increasing dilution, but are $>$ the vals. calc. from the Langevin

theory. Near the crit. solution point, the temp. coeff. for the latter solution becomes abnormally high. These results are explained by supposing that dilution or rise of temp. dissociates the mol. aggregates, and that either these aggregates orient better than the mols. or the aggregates are more anisotropic than the single mols. J. W. S.

Dispersion and thermal variation of the electric birefringence of some optically active liquids. M. SCHÖB (Compt. rend., 1934, 198, 2232—2235).—Vals. of Kerr const., dielectric const., n , and d are tabulated for *d*-Et₂ tartrate (0—80°) and *d*-Bu₂ tartrate (4—24°) at several λ . Abnormal temp. variations of electric birefringence and of birefringent dispersion occurred over certain temp. ranges, attributed to polymorphism. B. W. B.

Kerr effect and molecular structure. H. A. STUART (Z. Elektrochem., 1934, 40, 478—483).—A lecture. E. S. H.

Molecule planning. (SIR) W. H. BRAGG (Trans. Faraday Soc., 1934, 30, 665—673).—Spiers Memorial Lecture.

Stereochemistry of four-covalent palladium, platinum, and nickel compounds. F. P. DWYER and D. P. MELLOR (J. Amer. Chem. Soc., 1934, 56, 1551—1552).—Recent published work is discussed. To test the possibility of a pyramidal configuration for Pd^{IV}, *cis*- and *trans*-forms of *Pd bis*-anti-benzyl-methylidioxime (m.p. 175° and 207°) have been isolated. E. S. H.

Diamagnetism of ions. L. ABONNENC (Compt. rend., 1934, 198, 2237—2239).—Magnetic susceptibilities of aq. KF and Na, K, Li, Rb, Cs, Mg, Ca, Sr, Be, and La chloride solutions were measured by the drop method (A., 1930, 992). χ vals. of the salts, of the dissolved and free cations, and of F⁻ are tabulated. B. W. B.

Diamagnetism and molecular association in organic liquids. S. R. RAO and P. S. VARADACHARI (Current Sci., 1934, 2, 475—476).—The sp. susceptibility (I)—concn. curves measured between 15° and 75° by the Quincke method for mixtures of COMe₂ and CHCl₃ and of COMe₂ and PhNO₂ are linear. The diamagnetic susceptibility of PhNO₂ does not vary with temp. Mol. association has no effect on the (I) of org. liquids. L. S. T.

Diamagnetism of nitrobenzene at different temperatures. S. R. RAO and S. SRIRAMAN (Indian J. Physics, 1934, 8, 315—322).—Using a modified Quincke's capillary method, the diamagnetic susceptibility of PhNO₂ was determined in the range 30—110°. As the temp. rises, the sp. susceptibility decreases to a flat min. at 75° and then increases. Optical anisotropy shows a similar variation, probably due to association. N. M. B.

α - and β -Ferrous tetrapyridine dithiocyanate. I. Magnetic properties. R. W. ASMUSSEN (Z. anorg. Chem., 1934, 218, 425—428).—The magnetic susceptibilities of these compounds, prepared by different methods, have been determined. The results are comparable, and indicate that the compounds are

well defined. Vals. calc. for the magnetic moment are in agreement with the val. for magnetically normal Fe^{II} compounds. M. S. B.

Magnetic anisotropy of the naphthalene molecule. C. SALCEANU (Bull. Acad. Sci. Roumaine, 1933, 16, 5—7).—The calc. val. for the liquid is 204.0×10^{-14} . J. G. A. G.

Magnetic properties of benzene vapour. R. JAANUS and J. SEUR (Nature, 1934, 134, 101).—The mol. susceptibility of C₆H₆ vapour is $(59 \pm 3) \times 10^{-6}$, practically the same as that of the liquid. L. S. T.

Application of the paramagnetic para-hydrogen transformation to the determination of the magnetic moment and the reaction cross-section. H. SACHSSE (Z. Elektrochem., 1934, 40, 531—535).—The transformation effected in solution by paramagnetic ions is independent of the nature of the anion, of the concn. of the salt, and of the solvent (H₂O or EtOH). From the measured reaction velocities the radii of the ions Cr^{III}, Fe^{III}, Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Er^{III}, and Yb^{III} have been calc. E. S. H.

Ferromagnetism and structure of ferroferric oxide. A. KRAUSE (Z. physikal. Chem., 1934, B, 26, 58—62).—A constitutional formula for Fe₃O₄ is advanced and discussed, particularly in relation to the magnetic properties. R. C.

Elementary discussion of ferromagnetism. F. BITLER (Proc. Roy. Soc., 1934, A, 145, 629—644).—Mathematical. The origins of some of the undesired results of the Weiss equation are discussed, and the type of solution which a correct theory would give for perfect crystals is deduced. L. L. B.

Quantum numbers and valency. L. W. O. MARTIN (J. Proc. Roy. Soc. New South Wales, 1934, 67, 244—250).—Theoretical. The linking strength in series of H and C halides depends on the degree of electronic excitation necessary to form an electron pair, and the reactivity in a series of compounds increases with the no. of promoted electrons belonging to the central atom. R. S.

Linking of CO₂ and CO. H. LESSHEIM and R. SAMUEL (Proc. Physical Soc., 1934, 46, 523—530).—From calculations due to Adel (cf. A., 1933, 885) it is shown that the ground level of CO₂ arises adiabatically from C (*p*⁴ ³P) + O (³P) + O (³P), i.e., the C-O linkings are identical and are due to a pronounced *p*²=*p*⁴ linking (O:C:O). Excitation, in the ground level of the CO mol., of those two electrons which in the adiabatic dissociation become the *s*² group of C in such a way that in the dissociation they become two additional *p* electrons, brings about the carbonyl term of CO. Adiabatic dissociation of CO₂ into CO and O leads to the :C:O term and an unexcited O. The linking in CO is double. N. M. B.

General equation for induced polarity. W. A. WATERS (Nature, 1934, 134, 178—179).—Theoretical. L. S. T.

Energies of the atomic linkings in the normal paraffin hydrocarbons. F. D. ROSSINI (Proc. Nat. Acad. Sci., 1934, 20, 323—327).—The energy of dissociation (I) of the normal gaseous mol. C_nH_{2n+2}

into C and H is a linear function of n when $n > 6$. The deviation in (I) when $n < 6$ is due to the influence of the end groups. Three types of C·H and C·C linkings are postulated. R. S.

Chlorine-chlorine distance in carbon tetrachloride. V. E. COSSLETT and H. G. DE LASZLO (*Nature*, 1934, 134, 63).—The mean val. for the Cl-Cl separation in CCl_4 is 2.86 ± 0.03 Å. L. S. T.

Significance of the activation energy of collision. H. B. HUNTINGTON (*J. Chem. Physics*, 1934, 2, 441).—A more precise expression for the activation energy of collision has been deduced theoretically and found to agree with experimental vals. for CO_2 , CS_2 , etc. M. S. B.

Degeneracy, selection rules, and other properties of the normal vibrations of certain polyatomic molecules. E. B. WILSON, jun. (*J. Chem. Physics*, 1934, 2, 432—439).—The properties of the normal modes of vibration are tabulated for mols. of 3—9 atoms in which several atoms are bound to a central atom. Data for Raman and infra-red spectra are included. M. S. B.

Molecular symmetry and the reduction of the secular equation. II. A. E. STEARN, C. H. LINDSLEY, and H. EYRING (*J. Chem. Physics*, 1934, 2, 410—416).—The method previously given (this vol., 133) for the reduction of secular equations is applied to the case of 9 univalent atoms forming a body-centred cube. The results are used to calculate approx. the energy of the isolated unit cell of Na. Van Vleck's vector method may be employed as a check on such calculations. M. S. B.

Valency-theoretical calculation of energy of aromatic compounds. H. TAMAKI (*Proc. Phys.-Math. Soc. Japan*, 1934, 16, 52—66).—Vals. are calc. by means of the Heitler-Weyl theory. The energy level of a hexagonal ring of tervalent radicals is approx. equal to that of three pairs. CH. ABS.

Equation of state and parachor. A. EUCKEN (*Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl.*, 1933, 340—349; *Chem. Zentr.*, 1934, i, 352).—A modified equation of state for a condensed isotropic substance is derived, agreeing with experimental vals. for CS_2 at 273—353° abs. up to pressures of 10,000 kg. per sq. cm. London's theory of mol. attraction gives the same vol. function for the cohesion pressure. A relation between cohesion pressure and surface tension is derived. The equation of state and parachor are related. H. J. E.

Mechanism of equilibrium of small crystals. I. I. N. STRANSKI and R. KAISCHEV. II. R. KAISCHEV and I. N. STRANSKI (*Z. physikal. Chem.*, 1934, B, 26, 100—113, 114—116).—I. Following Volmer's theory that the growth and resolution of crystals occur by way of the formation of two-dimensional nuclei (A., 1931, 1133) the equilibrium of a finite crystal is reduced to the equilibrium three-dimensional nucleus—two-dimensional nucleus—vapour. The condition of equilibrium is that the mean work of separation per structural unit for a complete surface lattice plane of the three-dimensional nucleus shall be equal to the work of separation taken over a

complete edge-row of the two-dimensional nucleus. At equilibrium the probabilities of formation of a two-dimensional nucleus by condensation of vapour and dissipation of the outer lattice planes of the three-dimensional nucleus must be equal, and similarly for the probabilities of formation and dispersion of rows along the two-dimensional nucleus.

II. The significance of the mean work of separation is considered. R. C.

Separation of small quantities of foreign substances from crystallised salts. O. HAHN, H. KADING, and R. MUMBRAUER (*Z. Krist.*, 1934, 87, 387—416).—The separation is followed using radioactive atoms as the foreign substance, with photographic registration; A being the impurity in B , classification is made into uniform (A/B const.), non-uniform (A/B varies through crystal), and anomalous (A and B not isomorphous) mixed crystals; inner absorption systems (A deposited preferentially on certain planes of B); and irregular cases.

B. W. R.

Experimental production of vicinal faces by touching a crystal during growth. G. G. LEMMLEIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 2, 554—555).—When an octahedral crystal of K alum is slightly scratched with a needle and then immersed in a supersaturated solution of the alum, a no. of small vicinal faces (I) are formed in 2 or 3 sec. at the position of the scratch. After 2 or 3 min. the whole face which has been scratched is covered with a few large (I), due to the spreading of some of the faces.

H. S. P.

Deformations of cubic crystalline lattices. J. WEIGLE (*Arch. Sci. Phys. Nat.*, 1934, [v], 16, Suppl., 15—18).—Slight distortion of a cubic lattice causes the X-ray pattern to split up and exhibit a fine structure. The no. of components to be expected from each plane is calc. The effect is greatest for large angles of reflexion and the accuracy of the cubic structure can be tested to 0.05%.

J. W. S.

Mechanical twinning in bismuth crystals. W. F. BERG (*Nature*, 1934, 134, 143). L. S. T.

Growth of metal crystals in metal vapour. III. M. STRAUMANIS (*Z. physikal. Chem.*, 1934, B, 26, 246—254).—Mg crystals grown slowly in H_2 at 0.001—360 mm. are bounded by the faces (0001), (1010), and (1011). This result agrees with Stranski's theory of homopolar crystal growth (A., 1931, 1115) if it is assumed that the forces emanating from a lattice point die away with increasing distance so rapidly that their effect on all but the immediately adjoining neighbours does not materially influence the equilibrium form of the crystal. Laminated crystals of Mg could not be obtained. Mg crystals are very readily deformed, the slip occurring in the same way as with Zn. R. C.

Fracture of fibred iron-silicon sheets. F. BITTER (*Proc. Roy. Soc.*, 1934, A, 145, 668—675). Fe-Si sheets were prepared having a fibre structure in which diagonal axes of the crystal grains were disposed symmetrically about two mutually perpendicular directions in the plane of the sheet. Experiments on strips cut from such sheets in various

directions indicate that a relationship exists between grain orientation and fracture in this material.

L. L. B.

X-Ray photographic fine structure investigations of copper. F. LIHL (Z. Physik, 1934, 89, 537—545).—Cu and Fe undergo similar crystallographic changes on stretching, bending, and under variable stresses.

A. B. D. C.

X-Ray diffraction studies of the crystallisation of amorphous silica. F. P. DWYER and D. P. MELLOR (J. Proc. Roy. Soc. New South Wales, 1934, 67, 420—428).—Heat-treatment of vitreous SiO_2 with a KCl flux gave a mixture of α - and β -cristobalite (I), whilst SiO_2 gel and opal gave β only. A Na_2WO_4 flux gave α -tridymite (II). The nature of the product depends on the growth of (I) crystals and also on the inversion of (I) to (II).

R. S.

Crystalline B_2O_3 . N. W. TAYLOR and S. S. COLE (J. Amer. Chem. Soc., 1934, 56, 1648—1649).—Cryst. B_2O_3 , prepared by dehydration of H_3BO_3 in vac. at $< 225^\circ$, has m.p. $294 \pm 1^\circ$, $n \ 1.458 \pm 0.002$, $d^{25} \ 1.805$.

E. S. H.

Crystal structure of FeP_2 . K. MEISEL (Z. anorg. Chem., 1934, 218, 360—364; cf. this vol., 964).— FeP_2 is in the rhombic system of the marcasite type with axial ratios similar to those of FeSb_2 : $a \ 2.725$, $b \ 4.975$, $c \ 5.657$, Å. The unit cell contains 2FeP_2 ; $d \ 5.07$. The X-ray data for Fe_3P and Fe_2P confirm other investigations. The structure of FeP could not be determined.

M. S. B.

Crystal structure of the high-temperature modifications of Ag_2HgI_4 and Cu_2HgI_4 . J. A. A. KETELAAR (Z. Krist., 1934, 87, 436—445; cf. A., 1931, 1359).— α -Modifications of Ag_2HgI_4 (above 60°) and Cu_2HgI_4 (above 90°), examined by powder method, are isomorphous and cubic; $a=6.383$, 6.103 Å., respectively, space-groups T_h and T_h . Three $[\text{Hg} + 2\text{Ag}(\text{or Cu})]$ atoms occupy on average the four positions of face-centred lattice of Zn-blende type. Transition β (tetragonal, pseudo-cubic) $\rightarrow \alpha$ (cubic) is discussed in terms of at. positions.

B. W. R.

Crystal hydrates. II. Structure of chromium chloride and aluminium chloride hexahydrates. K. R. ANDRESS and C. CARPENTER (Z. Krist., 1934, 87, 446—463; cf. this vol., 479).—Structures of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are hexagonal and almost identical, being referred to a rhombohedral cell with $a \ 7.85$ or 7.95 Å., $\alpha \ 97^\circ$. Space-group D_{3d}^6 . The metal ion is surrounded by $6 \text{H}_2\text{O}$ mols. to form a complex cation octahedral in shape. Detailed intermol. distances are given.

B. W. R.

Ammonium and potassium molybdatellurates, two homeomorphous orthorhombic substances. J. D. H. DONNAY and J. MELON (Proc. Nat. Acad. Sci., 1934, 20, 327—335).—

$3(\text{NH}_4)_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 7\text{H}_2\text{O}$ (I) is dipyramidal orthorhombic; $a : b : c = 0.9523 : 1 : 0.9777$; $d \ 2.78 \pm 0.02$; hardness $2\frac{1}{2}$ (Mohs' scale). $3\text{K}_2\text{O} \cdot \text{TeO}_3 \cdot 6\text{MoO}_3 \cdot 8\text{H}_2\text{O}$ (II) is dipyramidal orthorhombic and exhibits pseudo-tetragonal symmetry; $a : b : c = 1 : 1 : 1.0519$; $d \ 3.25 \pm 0.05$, hardness $2\frac{1}{2}$. Crystal habit and optical properties have been studied. The homeomorphism of (I) and (II) is shown by stereographic projections and

a table of corresponding interfacial angles. The crystal lattice is face-centred orthorhombic in each case.

R. S.

Crystal structure and magnetic susceptibility of caesium argentous auric chloride, $\text{Cs}_2\text{AgAuCl}_6$, and caesium aurous auric chloride, $\text{Cs}_3\text{Au}^{\text{III}}\text{Cl}_6$. N. ELLIOTT (J. Chem. Physics, 1934, 2, 419—421).—Magnetic susceptibility measurements and X-ray powder photographs show that both compounds are diamagnetic and have cubic structure with $a_0 \ 5.33$ Å. Intensity vals. show general agreement with the perovskite structure, but indicate slight differences in the at. arrangement. The valency type of the compounds is discussed.

M. S. B.

X-Ray spectra of manganous sulphate and its hydrates. F. HAMMEL (Compt. rend., 1934, 199, 282—283).—The X-ray spectra of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (I) prepared by five different methods differ only in the sharpness of the lines, and not in relative intensities. $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ (II), $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (III), and the hydrate $\text{MnSO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ (IV) have X-ray spectra differing only in the relative intensities of the lines, indicating a similarity in structure. The spectra of MnSO_4 and of (I) differ from one another and from those of the other hydrates. (IV) crystallises spontaneously at about 40° from a solution supersaturated with respect to (III) as long prismatic crystals. Unlike (II) and (III), it does not effloresce at 25° in air saturated with H_2O vapour.

J. W. S.

X-Ray investigation of the feldspars. W. H. TAYLOR, J. A. DARBYSHIRE, and H. STRUNZ (Z. Krist., 1934, 87, 464—498).—The K-Ba series of feldspars (KAlSi_3O_8 — $\text{BaAl}_2\text{Si}_2\text{O}_8$) is structurally monoclinic; typical is sanidine, the structure of which is based on a continuous chain of tetrahedron rings of SiO_4 and AlO_4 . In albite Na replaces K and the chain persists with only slight alterations, but the higher members of the plagioclase series ($\text{NaAlSi}_3\text{O}_8 \rightarrow \text{CaAl}_2\text{Si}_2\text{O}_8$) show a doubling of the unit cell with increasing Ca content.

B. W. R.

Crystal form and molecular unit of rinkite. B. GOSSNER and O. KRAUS (Centr. Min., 1933, 369—374; Chem. Zentr., 1934, i, 24—25).—Rinkite probably belongs to the rhombic system: $a \ 18.47$, $b \ 5.67$, $c \ 7.46$ Å. The formula is $[\text{SiO}_4]_2[(\text{Ti}, \text{Ce})\text{F}]\text{Ca}_2\text{Na}$, where $\text{Ti} : \text{Ce} \sim 1 : 1$ and to some extent 2Ca is replaceable by $\text{TiNa} + \text{F}$. The unit cell contains four formula wts.

L. S. T.

Properties of aluminosilicate framework structures. W. H. TAYLOR (Proc. Roy. Soc., 1934, A, 145, 80—103).—The structures of feldspars and zeolites are based on strong frameworks of linked tetrahedral (SiO_4) and (AlO_4) groups, with cations and H_2O mols. in the interstices. Three-dimensionally infinite frameworks of various types have been described, but it is suggested that the frameworks of the zeolites heulandite and stilbite may be of finite thickness, and infinite in only two dimensions. Two types of isomorphous replacement of cations are observed in framework structures: (1) the no. of cations remains unaltered, (2) one bivalent cation is replaced by (or replaces) two univalent cations. Base-exchange experiments with zeolites are discussed. The binding of the

H₂O mols. in zeolites is such as will satisfy the tetrahedral positive and negative linkings which Bernal and Fowler have ascribed to the mol. in liquid H₂O (A., 1933, 1106). Twinning and intergrowths are frequent in both feldspars and zeolites because the frameworks often possess a high structural symmetry to which the dimensional symmetry approximates.

L. L. B.

Crystallographic investigation of fagarine. J. OLSACHER (Invest. Labor. Quim. biol. Univ. Cordoba, 1933, 1, 100—105; Chem. Zentr., 1934, i, 67).—Data for α -, β -, and γ -fagarine are given. L. S. T.

Structure of the carboxyl group. II. Crystal structure of basic beryllium acetate. L. PAULING and J. SHERMAN (Proc. Nat. Acad. Sci., 1934, 20, 340—345).—The space-group is T_h^1 (cf. Morgan and Astbury, A., 1926, 995). Comparison of observed with calc. X-ray intensities indicates that the mol. consists of four BeO₄ tetrahedra with one common corner, each having three edges of 2.55 Å., and three of 2.80 Å. extending from the central O. The distance Be—O is 1.65 Å. and the angle α between the C—O linking of the OAc group is $124^\circ \pm 3^\circ$, as in HCO₂H, whence it is concluded that α is a const. for all aliphatic acids. The arrangement of mols. in the crystal corresponds with the diamond structure. A table of interat. distances is given. R. S.

Structure of the azide group. (SIR) W. H. BRAGG (Nature, 1934, 134, 138).—X-Ray analysis of cyanuric triazide (I) [by MISS KNAGGS] confirms the linearity of the arrangement of the N atoms in the azide group. Details of the structure of (I) are given. L. S. T.

X-Ray analysis of the crystal structure of dibenzyl. J. DHAR (Current Sci., 1934, 2, 480—481).—The C atoms of each C₆ ring form a regular hexagon; one aliphatic C lies on the prolongation of the line joining 4 and 1 and the other on that joining 4' and 1'. The line joining these two C is at 109.5° to these prolongations. The two C₆ rings lie in parallel planes slightly separated from each other. L. S. T.

Orientation of molecules in the *p*-benzoquinone crystal by X-ray analysis. J. M. ROBERTSON (Nature, 1934, 134, 138).—X-Ray analysis confirms and extends the results obtained by magnetic measurements (A., 1933, 557). The crystal is monoclinic with a 7.03, b 6.79, c 5.77 Å., β 101.0° ; space-group $P2_1/a$, with two centrosymmetric mols. per unit cell. L. S. T.

Structure of unstretched rubber studied by means of electron rays. G. BRUNI and G. NATTA (Atti R. Accad. Lincei, 1934, [vi], 19, 536—540).—Electron diffraction measurements reveal a regular structure in thin films (about 10^{-4} mm.) of unstretched rubber, with unit length of 8.1—8.4 Å. O. J. W.

X-Ray diffraction in cork. J. A. PRINS (Physica, 1934, 1, 752).—A diffuse ring corresponding with a spacing of 4.1 Å. was observed, corresponding approx. with the 4.4 Å. spacing of liquid long-chain aliphatic compounds, and differing radically from cellulose and wood structures. Cork is probably a polymerised aliphatic compound. H. J. E.

Swarm theory of liquid crystals. L. S. ORNSTEIN (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 318—322).—This theory ascribes the macroscopic properties of liquid crystals to the formation of regions in which the mols. have spontaneously taken up certain directions. H. S. P.

Orientation of molecules in thin films of anisotropic liquids and measurement of two constants characteristic of their elastic properties. V. FREDERIKS and V. TZVETKOI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 548—552).—The orientation of the mols. at different depths in a thin film of *p*-azoxyanisole contained between an object and cover glass has been investigated by means of the total reflexion of the extraordinary ray. The vals. of the elastic constns. with magnetic fields parallel and perpendicular to the glass walls decrease with rise of temp. H. S. P.

The Beilby layer. G. I. FINCH, A. G. QUARRELL, and J. S. ROEBUCK (Proc. Roy. Soc., 1934, A, 145, 676—681).—Metal vapours have been condensed on polished and etched metal surfaces, under observation in an electron diffraction camera. Polished surfaces give rise to random electronic scattering, whilst on etched surfaces cryst. structure is exhibited. On a polished substrate the diffraction pattern given by a deposit disappears more or less rapidly, but is permanent on an etched surface. If several layers are formed on a polished surface, the diffraction patterns vanish at rates decreasing with each successive deposit. These facts give a direct experimental proof of the existence of the Beilby layer and its formation by polishing. L. L. B.

Catalytic properties and structure of metal films. II. Electrical condition of platinum films. G. I. FINCH and (MISS) A. W. IKIN (Proc. Roy. Soc., 1934, A, 145, 551—563).—Surface potentials and rates of charging-up of cathodically sputtered Pt films in contact with electrolytic gas at room temp. have been determined, and the structures examined by electron diffraction. Electrically active films were catalytically active whilst electrically neutral films were inert, and the rates at which the active films catalysed the combination of H₂ and O₂ were directly \propto the rates of charging-up. In the case of the more active films, the crystals exhibit random orientation, whilst with the inactive films a considerable proportion of the crystals possess a common direction of orientation. The diffuse background in electron diffraction patterns obtained from active films increased in intensity with increased activity. Heating rapidly destroyed the latent activity of a film and, if prolonged sufficiently, destroyed the crystal structure. It is deduced that catalytic action is determined by a prior interaction between the surface and one or both of the constituents of the combining mixture, during which the catalyst becomes electrically charged, and that activity is not determined by either crystal size or orientation. L. L. B.

Determination of structure of free molecules of *s*-tetrabromo- and *s*-tetraiodo-neopentane by electron diffraction. H. DE LASZLO (Compt. rend., 1934, 198, 2235—2237).—The vapours [C(CH₃)Br]₄

(a) at 145° , $C(CH_2I)_4$ (b) at 200°] give $\sin(\theta/2)/\lambda$ max. indicating that the halogen atoms are arranged at the corners of a square of diagonal 6.0 Å. (a) or 6.3 Å. (b), the min. interat. distances being: C-C 1.54, C-Br 1.94, and C-I 2.10 Å. B. W. B.

Effect of temperature on diffraction of slow electrons and its application. V. E. LASCHKAREV and G. A. KUZMIN (Nature, 1934, 134, 62).—The effect of temp. on the intensity max. due to diffraction of slow electrons from a cleavage plane of Ceylon graphite has been investigated. L. S. T.

Theory of heat-conductivity in crystals. A. PAPAPETRU (Physikal. Z., 1934, 35, 527–528).—The theory of Peierls (A., 1929, 283) is extended, the effect of temp. on the heat-conductivity of crystals being obtained, by kinetic considerations, over the complete temp. range. A. J. M.

Action of an external electric field on hydrogenated metals. T. FRANZINI (Atti R. Accad. Lincei, 1934, [vi], 19, 584–588).—By applying a negative potential of 15,000 volts to a Ni cylindrical plate surrounding a hydrogenated Pd wire in vac. the H is rapidly removed from the Pd. O. J. W.

Electrical conductivity of compressed mercuric sulphate. W. SCISŁOWSKI (Acta phys. polon., 1932, 1, 457–463; Chem. Zentr., 1934, i, 515).—A current passed through compressed $HgSO_4$ between Zn and Pt in the direction $Zn \rightarrow HgSO_4$ is < in the reverse direction. A. A. E.

Polymorphic transition of calcium. A. SCHULZE and H. S. OVERBERG (Metallwirt., 1933, 12, 633–635; Chem. Zentr., 1934, i, 333).—From measurements of thermal expansion and electrical resistance and from the heat effect, Ca has been shown to have a transition temp. at $430\text{--}450^\circ$. The temp. coeff. of resistance in the β -phase (that above the transition temp.) is >, and the sp. heat is <, for the α -phase. The heat of transformation is 2.3 ± 0.3 g.-cal. per g. The coeff. of expansion of Ca between 0° and 100° is 27.1×10^{-6} . H. J. E.

Influence of illumination on dielectric losses in X-irradiated rock-salt. A. KRASIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 356–358).—A 2-mm. plate of NaCl, intensely coloured with X-rays, was illuminated by strong light. Illumination increased the angle of dielectric loss by > 12%, in agreement with theory. W. R. A.

Influence of pressure on the electrical resistance of a rod of impure zirconia in air. J. BASSET (Compt. rend., 1934, 199, 38–41; cf. A., 1933, 248).—The resistances of conductors of the second class vary markedly with the pressure of the surrounding atm. The resistance of a $1.4 \times 1.4 \times 15$ mm. rod (ZrO_2 80%, ThO_2 10%, Y_2O_3 10%) in air was 4500 ohms at 1 atm. and $> 10^6$ ohms at 4000 kg. per sq. cm. B. W. B.

Theory of electrolytic conduction and diffusion crystals. II. W. JOST (Z. physikal. Chem., 1934, 169, 129–134; cf. this vol., 11).—The fact that the factor independent of the temp. in the empirical conductivity and diffusion formulæ is in many cases > the theoretical max. val. (A., 1932, 446) is explained

if certain assumptions are made relative to the dependence of the threshold energy for the motion of an ion on the lattice const. Similarly conclusions are reached concerning the effect of pressure on the conductivity of crystals. R. C.

Superconductivity and the Hall effect. B. LASAREW (Nature, 1934, 134, 139).—Zn appears to belong to the group of superconductors only in one crystallographic direction. L. S. T.

Principal magnetic susceptibilities of graphite. B. C. GUHA and B. P. ROY (Indian J. Physics, 1934, 8, 345–352; cf. Goetz, A., 1933, 1236).—Susceptibilities along the hexagonal axis and along perpendicular directions are -22.8×10^{-6} and -0.4×10^{-6} c.g.s. e.m.u. per g., respectively, for Ceylon graphite. N. M. B.

Magnetic susceptibilities of dilute solid solutions of nickel in copper at various temperatures. W. H. ROSS (Physical Rev., 1934, [ii], 46, 46–48).—For 0–10% Ni alloys at low temp. there is approx. the usual Curie-Weiss decrease in χ with rise of temp., and above room temp. there is an abnormal paramagnetism increasing with rise of temp. Variations are continuous with respect to temp. and concn. The calc. magnetic moment per Ni atom in the lattice is 0.3–0.4 Bohr magneton. N. M. B.

Statistical method for calculating magnetochemical phenomena. N. A. KULOV and E. KONDORSKI (J. Exp. Theor. Phys., U.S.S.R., 1933, 109–114).—The distribution function of the axis of spin in elastically deformed monocrystals has been related to the external field and the tension, whence magnetostriction can be calc. for any direction of tension and field. Hooke's law is not strictly valid for ferromagnetic substances. CH. ABS.

Hot compression of highly disperse metal powders. III. W. TRZEBIATOWSKI (Z. physikal. Chem., 1934, 169, 91–102; cf. this vol., 245).—Au and Cu powders have been subjected to a pressure of 15,000 atm. at $20\text{--}600^\circ$ in an O_2 -free atm. The resistivity and its temp. coeff. for the masses formed at the higher temp. differed little from those of the normal massive metals. Up to 200° the d and hardness, H , increased with rise in the temp. of compression. From 200° to 400° d increased further, but H fell, due to recovery effects. The d of the massive metals were reached in this way. From 450° to 600° H fell further, presumably owing to onset of recrystallisation. R. C.

Strength of metal single crystals. R. ROSCÖE (Nature, 1934, 133, 912).—Crystals of Cd, containing 0–15% of Pb and of Zn, show increased resistance to shear when grown in presence of O_2 , but not N_2 , CO_2 , or H_2O vapour. L. S. T.

Crystal plasticity. I. Low-temperature plasticity and Becker's formula. II. Dynamic interpretation of crystal plasticity. III. Mechanism of slip. E. OROWAN (Z. Physik. 1934, 89, 605–613, 614–633, 634, 659).—I. An observed temp. variation of elastic limit agrees with Becker's flow velocity of crystals. Crystal plasticity is principally due to material flaws and thermal stress variations.

II. The dynamic theory which considers the slip velocity, rather than the amount of slip, as a function of applied stress, agrees with empirical observations on crystal plasticity.

III. Slip is supposed due to an avalanche effect of spontaneously formed nuclei, in a way similar to the effect of nuclei in phase change. A. B. D. C.

Form of lattice distortion that may render a crystal plastic. M. POLANYI (Z. Physik, 1934, 89, 660—664).—If at a flow plane a lattice displacement exists such that n atoms of one interface are superimposed on $(n+1)$ of the other, the tension is reduced to $1/n$ of its normal val. A. B. D. C.

Mechanism of plastic deformation of crystals. I. Theoretical. II. Comparison with observations. G. I. TAYLOR (Proc. Roy. Soc., 1934, A, 145, 362—387, 387—404).—I. The deformation of a single crystal in tension or compression consists of a shear strain s in which sheets of the crystal parallel to a crystal plane slip over one another, the direction of motion being some simple crystallographic axis. It is supposed that slipping occurs over limited lengths L of the slip plane, and a theory is developed which leads to the parabolic relationship $S/\mu\sqrt{s} = K\sqrt{(\lambda/L)}$ between stress and plastic strain (S =resistance to shear).

II. The above expression is in good agreement with the results of experiments with metals which crystallise in the cubic system. At room temp. the calc. vals. of L are of the same order as the observed spacings of faults in metals and rock-salt. L. L. B.

Strength of rock-salt. G. I. TAYLOR (Proc. Roy. Soc., 1934, A, 145, 405—415).—A new theory of the strength of metals (cf. preceding abstract) is applied to rock-salt and leads to a parabolic relationship between tensile stress and plastic strain. The val. of L , the mean free path of centres of dislocation, is of the order 10^{-4} cm. This corresponds with the observed spacing of faults in rock-salt. The theory assigns a definite function to the faults in determining the strength of crystals, irrespective of their crystallographic or at. nature. L. L. B.

Supposed allotropy of aluminium. A. SCHULZE (Metallwirt., 1933, 12, 667—669; Chem. Zentr., 1934, i, 333).—Al shows no allotropy. H. J. E.

Has aluminium a transition point? O. TIEDEMANN (Metallwirt., 1933, 12, 669—671; Chem. Zentr., 1934, i, 333—334).—Polemical. The existence of allotropy in Al is asserted. H. J. E.

Cessation period of rotation heat of hydrogen. H. O. KNESER and M. WALLMANN (Naturwiss., 1934, 22, 510).—There is no increase in the velocity of sound in pure H_2 at frequencies below 1481 k.Hz. The cessation period of rotation heat of H_2 at room temp must be $< 10^{-8}$ sec. A. J. M.

Longitudinal thermoelectric effect. I. Copper. P. C. FENG and W. BAND (Proc. Physical Soc., 1934, 46, 515—522).—The e.m.f. produced by asymmetrical temp. distributions in a Cu wire was investigated. A vector formula connecting potential gradient and temp. gradient is deduced, and the

dependence of the consts. on tension in the wire is evaluated. N. M. B.

Electrical resistance of thin films of nickel prepared by electrodeposition. R. C. L. BOSWORTH (Trans. Faraday Soc., 1934, 30, 549—560).—Films $< 0.08 \mu$ were prepared electrolytically. The electrical resistance is approx. twice the normal val. and the temp. coeff. two thirds. On heating the 0.08μ film, its resistance shows a big jump at 50° . This disappears when the film is heated at 100° for several hr., but returns on keeping at room temp. for a few days. M. S. B.

Work in the Charlottenburg cryoscopic laboratory on superconductivity and on the hydrogen isotope. W. MEISSNER (Helv. phys. Acta, 1933, 6, 414—418; Chem. Zentr., 1934, i, 349).—V and Mo become superconducting at 4.3° and 1.1° abs., respectively. As—Pb alloys become superconducting at the transition point of Pb. H_2 containing 3% of H^3 has at the crit. point a v.p. difference from H^1 of < 0.1 mm. H^2 has nuclear moment 1. H. J. E.

Thermal conductivity of air by a parallel plate method. E. O. HERCUS and D. M. SUTHERLAND (Proc. Roy. Soc., 1934, A, 145, 599—611).—Using an improvement of Hercus and Laby's parallel plate method (*ibid.*, 1918, A, 95, 190), the thermal conductivity k of dry air at 20° and atm. pressure is found to be 6.063×10^{-5} . Using a temp. coeff. of 0.00298 per $^\circ C$, $k = 5.72 \times 10^{-5}$, in good agreement with hot-wire determinations. L. L. B.

Heat of dissociation of the nitrogen molecule. G. HERZBERG and H. SPONER (Z. physikal. Chem., 1934, B, 26, 1—7).—From the triplet level of N_2 , deduced from the intercombination system discovered by Vegard (A., 1932, 557) and Kaplan (Physical Rev., 1933, [ii], 44, 947), and from the predissociation points in the N_2 triplet bands the heat of dissociation of N_2 is calc. to be 169.3 kg.-cal. The term scheme of the N_2 mol. is discussed. R. C.

Heat of decomposition of chlorine. M. TRAUTZ and H. ADER (Z. anorg. Chem., 1934, 218, 104—110).—The heat of decomp., calc. from fresh data, is 57.1 ± 2.1 kg.-cal., in agreement with spectroscopic theory. F. L. U.

Melting curve of nitrogen to 110 kg. per sq. cm. W. H. KEESOM and J. H. C. LISMAN (Physica, 1934, 1, 735—738).—Measurements are recorded from the triple point to 111.1 kg. per sq. cm. and 65.50° abs. 1

Relation between the b.p. of hydrocarbons and their structure. R. L. WAKEMAN (Rec. trav. chim., 1934, 53, 832—834).—The methods for calculating the b.p. of acyclic hydrocarbons are reviewed. Whilst van Arkel's general conclusions (cf. this vol., 240) are sound, many of his quoted data are inaccurate, more recent determinations having been ignored. D. R. D.

Physical properties of methoxymethyl ethyl ketone. N. E. RIGLER, W. A. FELSING, and H. R. HENZE (J. Amer. Chem. Soc., 1934, 56, 1499). The following data are recorded: b.p. 132.9 , v.p. $\log p = -1429.5/(t+205) + 7.11187$, latent heat of

vaporisation at b.p. 9364 g.-cal., d_4^{20} 0.9509—0.001018t, surface tension 30.10 dynes/cm., n_D^{20} 1.40454.

E. S. H.

Heats of rotation of the molecules H^1H^2 and H_2 and nuclear spin of H^2 atom. K. CLUSIUS and E. BARTHOLOMÉ (Z. Elektrochem., 1934, 40, 524—529; cf. this vol., 722).—The nuclear spin of H^2 is 1.

E. S. H.

Relationships between constitution and magnitude of the molar latent heat of fusion of organic compounds. Influence of ring strain. J. PIRSCH (Ber., 1934, 67, [B], 1303—1307).—The vals. of the mol. depression of the f.p. of 2 : 5-endoethylene- (I) and 2 : 5-endoethylene-cyclohexanone are so closely similar that ring strain does not appear to affect the magnitude of the const. The ratio E/M of (I) is identical with that of a series of solvents of the camphor type. The peculiar structure of the dicyclo-[1 : 2 : 2]-heptane and dicyclo-[2 : 2 : 2]-octane systems is therefore solely responsible for the very high mol. depression. The mol. latent heat of fusion (calc. from van 't Hoff's equation) is approx. the same for (I), camphor, 2 : 6-dichloro- and 2 : 6-dibromocamphane, and bornylamine. Ring strain has no influence, but constancy of the val. is conditioned by approx. identity of m.p. of the compounds under comparison.

H. W.

Thermal data on organic compounds. XIII. Heat capacities and entropies of n -tetradecane and the hydroxybenzoic acids. Relative free energies of some benzenoid position isomerides. G. S. PARKS and D. W. LIGHT. **XIV. Heat capacity, entropy, and free energy data for cyclic substances.** C. J. JACOBS and G. S. PARKS (J. Amer. Chem. Soc., 1934, 56, 1511—1513, 1513—1517; cf. A., 1925, ii, 491).—XIII. The sp. heats of n -tetradecane and o -, m -, and p -OH- C_6H_4 -CO $_2$ H have been determined over the approx. range 93—280° abs., and the corresponding entropies calc. The calc. free energies of formation of o -, m -, and p -OH- C_6H_4 -CO $_2$ H are -101,810, -101,570, and -102,370, respectively.

XIV. The sp. heats of cyclopentane (I), thiophen (II), 1 : 4-dioxan (III), pyrene, and graphite have been measured from liquid-air temp. to room temp. The heats of fusion are (I) 2.06, (II) 14.11, (III) 34.85, and the heats of transition (I) 16.17, 1.22, (II) 3.44, (III) 6.38 g.-cal. per g., respectively. The entropies and free energies of formation have been calc.

E. S. H.

Heat-capacity data for nitrobenzene. No indication of allotropy. G. S. PARKS and S. S. TODD (J. Chem. Physics, 1934, 2, 440—441).—Sp. heats of PhNO $_2$ have been measured over the temp. range 0—26° and no discontinuity has been observed at 9.6°. Thus there is no transition point between two allotropic forms at this temp.

M. S. B.

Heat-capacity curves of the simpler gases. VI. Rotational heat-capacity curves of molecular deuterium and of deuterium hydride. The equilibrium between the ortho- and para-forms of deuterium. Free energy, total energy, entropy, heat capacity, and dissociation of H^1H^2 and of H^1H^2 to 3000° abs. H. L. JOHNSTON and

E. A. LONG (J. Chem. Physics, 1934, 2, 389—395).—The thermodynamic properties of H^1H^2 and H_2 have been calc. and tabulated. The ortho-para equilibrium for both gaseous and solid H_2 is discussed. Rotational heat-capacity curves are compared with that for H_2 and with the hypothetical curve for N_2 . Calculations of the dissociation up to 3000° abs. indicate that both H^1H^2 and H_2 dissociate to the extent of about 4% at this temp. (dissociation of H_2 approx. 8%). The contributions of mol. stretching and anharmonic vibration to the high-temp. heat capacities are given for H_2 , H^1H^2 , and H_2^+ , and also the distributions of the mols. among the vibrational levels as a function of temp.

M. S. B.

Exact measurement of the specific heats of solid substances at higher temperatures. XVI. Specific heats of metallic thorium and of thorium dioxide between 20° and 1400°. F. M. JAEGER and W. A. VEENSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 327—332).—The mean sp. heats of Th and ThO $_2$ have been measured between room temp. and 1200° for Th and to 1400° for ThO $_2$. The at. heat of Th increases continuously from 8.235 at 300° to 11.785 at 1200°, whilst the mol. heat of ThO $_2$ changes from 18.904 at 300° to 20.756 at 1400°, with min. about 17.8 at 720°.

H. S. P.

Specific heat of iron nitrides. S. SATOH (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 716—719).—The sp. heat of Fe nitride has been determined for a range of N content from 0° to 100°. From the sp. heat-N content curve, which rises to a max., the sp. heats of Fe $_4$ N and Fe $_2$ N have been calc. as 0.1242 and 0.1343, respectively.

R. S. B.

Specific heat of nickel and of some nickel-copper alloys. K. E. GREW (Proc. Roy. Soc., 1934, A, 135, 509—522).—The sp. heats of Ni and of three Cu-Ni alloys (94.0, 87.2, 78.8% Ni, respectively) have been measured from -180° to 450° by an electrical method. In the alloys, as in pure Ni, the change in sp. heat at the Curie point can be explained quantitatively by the disappearance of the magnetic term.

L. L. B.

Transition point of ammonium nitrate. J. STRAUB and R. N. M. A. MALOTAUX (Chem. Weekblad, 1934, 31, 455—456; cf. A., 1933, 465).—The transition point of NH $_4$ NO $_3$ has been determined as 34.2° (warming) and 31.8° (cooling), the heat of transition being 5 g.-cal. per g. Addition of Na, Li, Ag, or Tl nitrate has no effect, but K, Rb, and Cs nitrates, which form mixed crystals with NH $_4$ NO $_3$, alter the transition point.

S. C.

Vapour pressure of small liquid drops. I. KRITSCHEVSKI (Kolloid-Z., 1934, 68, 15—16).—Theoretical.

E. S. H.

Surfaces of state of cyclohexane. L. ROTINJANZ and N. NAGORNOV (Z. physikal. Chem., 1934, 169, 20—30).—The v.-p. curve and orthobaric vols. up to the crit. point, the fusion curve, the change in vol. on fusion, the latent heat of fusion, the triple point solid-liquid-vapour, and isotherms from 2° to 300° have been determined. The isochores are rectilinear. The reduced gas-liquid surfaces for

cyclohexane (I) and C_6H_6 coincide, but the liquid-crystal surfaces do not. For (I) there seems to be a crit. point liquid-crystal at about 100° under about 2000 atm. R. C.

Physical properties of vinyl bromide. W. MEHL (Z. physikal. Chem., 1934, 169, 312—313).—The v.p. from -66° to 11.9° is given by $\log p = 7.4985 - 1368.1/T + 0.0004211T$. The mol. heat at 15° is 25.8 g.-cal. $\pm 2\%$, and the latent heat of evaporation 6200 g.-cal. per mol. R. C.

Vapour pressure of water. L. B. SMITH, F. G. KEYES, and H. T. GERRY (Proc. Amer. Acad. Arts Sci., 1934, 69, 137—168).—Experiments between 150° and 374° lead to the equation $\log p_c/p = (x/T)(a + bx + cx^2 + ex^3)/(1 + dx)$, where $x = T_c - T$, $p_c = 218.167$ atm., $T_c = 647.27^\circ$ abs., $a = 3.3463130$, $b = 4.14113 \times 10^{-2}$, $c = 7.515484 \times 10^{-9}$, $d = 1.3794481 \times 10^{-2}$, and $e = 6.56444 \times 10^{-11}$. CH. ABS.

Vapour pressures of ethyl nitrate, ethyl nitrite, and nitroethane. (MISS) J. W. GOODEVE (Trans. Faraday Soc., 1934, 30, 501—503).—For the temp. range -80° to 20° $\log_{10} P$ (mm.) is: $EtNO_3$, $-2010/T + 8.57$; $EtO \cdot NO$ $-1453/T + 7.88$; $EtNO_2$, $-1985/T + 8.01$. The calc. latent heats of evaporation are 9200, 6650, and 9075 g.-cal. and the entropy changes at b.p. 26, 23.1, and 23.4 g.-cal. per degree, respectively, indicating some association in each case. M. S. B.

Fundamental equation of gases. VI. K. JABECZYNSKI (Rocz. Chem., 1934, 14, 285—294).—Theoretical. The $f_2(w)$ function is given by $A + B(w - b)/w^2$, where A and B are consts. for a given gas, and the gas equation then takes the form $RT/[p + a/w^2 - \{AT + BT(w - b)/w^2\}/w](w - b)$; the calc. results differ from experimental for CO over the range 25—800 atm. and -50° to 200° by $> 1\%$, but deviate more widely at lower temp. and higher pressures. R. T.

Theory of moderate deviations from van 't Hoff's law. J. J. COLEMAN and F. E. E. GERMAN (J. Chem. Physics, 1934, 2, 396—399).—An extension of van 't Hoff's analogy between dil. solutions and gases, on the lines originally suggested by Noyes, is developed in accordance with modern views. M. S. B.

Van der Waals forces in liquid mercury and in the Hg_2 molecule. H. EKSTEIN and M. MAGAT (Compt. rend., 1934, 199, 264—266).—The theory of Born and Mayer (A., 1932, 564) is extended to the calculation of the van der Waals forces and energy of dissociation of Hg_2 . J. W. S.

Lattice constant and expansion coefficient of solid carbon dioxide. W. H. KEESOM and J. W. L. KOHLER (Physica, 1934, 1, 655—658).—Measurements have been made between 20° and 114° abs. The lattice const. (a_0) in Å. in this range is given by $a_0 = 5.540 + 4.68 \times 10^{-6}T^2$ (cf. this vol., 244). H. J. E.

Thermal expansion of calcite measured by X-rays. J. WEIGLE (Arch. Sci. phys. nat., Suppl., 1934, [v], 16, 14).—The coeffs. of expansion of calcite between 18° and 300° parallel and perpendicular to the axis, as measured by X-ray

methods, are 2.10 and -0.38 , each $\times 10^{-5}$, respectively, compared with 2.572 and -0.5509×10^{-5} as determined by macroscopic methods. J. W. S.

Highly-polymerised compounds. XCVI. Viscosity investigations on high-term ring systems. XCVII. Viscosity investigations of Karrer and Ferri. H. STAUDINGER and R. C. BAUER (Helv. Chim. Acta, 1934, 17, 863—865, 866—868).—Viscosity measurements with cyclopentadecane, methylcyclopentadecane, cyclotriacontane, cyclotriacontanone, cyclotriacontane-1:16-dione, 1:16-dimethylcyclotriacontane, cyclotetatriacontane, and cyclotetatriacontanone in dil. CCl_4 solution at 20° and 60° show that the ring increment of the sp. viscosity increases with increasing no. of C atoms in the ring. The variation with temp. is $>$ in n -paraffins.

XCVII. A criticism (cf. this vol., 481). E. S. H.

Highly-polymerised compounds. XCVIII. Viscosity law. H. STAUDINGER (Z. Elektrochem., 1934, 40, 434—446; cf. this vol., 760).—A lecture in which published work on the relation between viscosity and form of the mol. is discussed. E. S. H.

Relation between temperature and viscosity of sulphuric acid and its chlorides. G. P. LUTSCHINSKY (Z. physikal. Chem., 1934, 169, 269—274).—Batschinsky's formula, $\eta = c/(v - \omega)$, where η is the viscosity and v the sp. vol., and c and ω are consts. for the given liquid, has been confirmed for H_2SO_4 , $ClSO_3H$, and SO_2Cl_2 , the viscosities and d of which have been measured at various temp. R. C.

Viscosity, heat conductivity, and diffusion in gas mixtures. XXIX. New methods of determining critical volume and a relation between gaseous viscosity and the vapour-pressure curve, which is continued beyond T_K , p_K . M. TRAUTZ (Ann. Physik, 1934, [v], 20, 313—327; cf. A., 1933, 561).—Theoretical. H. S. P.

X-Ray diffraction in liquid mixtures. I. S. PARTHASARATHY (Phil. Mag., 1934, [vii], 18, 90—97).—In mixtures of Et_2 phthalate with C_6H_6 , C_5H_5N , or m -xylene, of C_5H_5N with $PhEt$, and of $AcOH$ with m -xylene and $PhEt$, a broad diffraction ring, attributed to a complex mol., has been observed, its position and intensity varying with the composition.

Ultra-violet absorption of binary organic liquid mixtures. IV. M. PESTEMER (Z. Elektrochem., 1934, 40, 493—498; cf. this vol., 237).—Ultra-violet absorption measurements can be used to indicate mol. combination or changes in mol. association on mixing org. liquids. Data are given for several binary mixtures. E. S. H.

Dielectric constants of liquid mixtures of phenol-water, phenol- m -cresol, phenol-aniline, and phenol- p -toluidine. O. R. HOWELL and W. JACKSON (Proc. Roy. Soc., 1934, A, 145, 539—551).—The dielectric const. of the system $PhOH-H_2O$ has been measured at 70° , and that of $PhOH-m$ -cresol, $PhOH-NH_2Ph$, and $PhOH-p-C_6H_4Me-NH_2$ at 50° . No parallelism exists between the change of conductivity and dielectric const. with composition.

Mixture rule and the Faraday rotation of cerium nitrate. B. N. CHUCKERBUTTI (Indian J. Physics, 1934, 8, 387—395).—For solutions of $\text{Ce}(\text{NO}_3)_3$ more dil. than those of Pillai (cf. A., 1932, 794) the Schonrock mixture rule (cf. A., 1928, 221) does not apply. N. M. B.

Viscosity on mixing or dilution. E. L. LEDERER (Proc. World Petroleum Congr., 1933, 2, 526—528).—Arrhenius' formula for the viscosity of ideal binary mixtures may be utilised to calculate viscosity if the mol. wts. of the components are known and a factor taking account of solvation or association is introduced. H. S. P.

Viscosities of aqueous solutions of electrolytes. I. Sodium sulphate solutions over the temperature range 25—40°. H. M. GLASS and W. M. MADGIN (J.C.S., 1934, 1124—1128).—The results give no evidence of change at the transition point of the solid hydrate, but there is probably a progressive increase in total hydration of solute as the temp. falls. The effect of hydration of solute and depolymerisation of solvent on the form of the η -temp. curves is discussed. Hydration effects predominate as concn. increases, but become less pronounced for any one concn. as temp. rises. $\eta = 1 + A\sqrt{C} \pm BC$ is applicable to dil. solutions at 25° for $A = 0.0155$ and $B = 0.357$. M. S. B.

Exchange of material and heat in mixtures of two components. E. KIRSCHBAUM (Ann. Physik, 1934, [v], 20, 261—278).—Mathematical. Owing to convection, the equations for the exchange of material are similar to those for heat exchange. The results are applied to the reflux condensers of a rectification apparatus. H. S. P.

Theory of concentrated solutions. X. Application of the Duhem-Margules equation to the study of partial pressures. N. I. JOUKOVSKY (Bull. Soc. chim. Belg., 1934, 43, 299—319).—A simplified method is described for the derivation of the partial pressures of the constituents of a two-component mixture from the total pressure and the v.p. of the pure components by means of the Duhem-Margules equation. The accuracy of the method is illustrated by its application to the mixtures CS_2 - C_6H_6 (slightly abnormal), CS_2 - MeOH (highly abnormal), and Et_2O - MeNO_2 (liquids of very different v.p.). A. G.

Ternary liquid systems: their classification from the point of view of ebullition. M. LECAT (Ann. Soc. Sci. Bruxelles, 1934, 54, 120—125).—Sixty-four ternary azeotropic mixtures are listed. C. W. G.

X-Ray examination of certain copper-zinc alloys at elevated temperatures. E. A. OWEN and L. PICKUP (Proc. Roy. Soc., 1934, A, 145, 58—267).—The thermal expansions of the β -constituent in the $\alpha + \beta$, β , and $\beta + \gamma$ regions of the Cu-Zn alloys have been determined up to 600° (in vac.) by an X-ray method. The β -phase in each region expands at the same rate up to the transformation temp., but is slower above this temp. The change points observed are 450°, 470°, and 485° in the $\alpha - \beta$, and $\beta + \gamma$ regions, respectively, in agree-

ment with previous workers. All the conditions prevailing at the moment of quenching are not retained, but this process prevents atoms from passing into or out of the lattice; the abrupt changes in the expansion curves must be explained by the behaviour of the atoms in the lattice. L. L. B.

Transformation of the β - and γ -phases of copper-zinc alloys. B. PETRENKO (Ukrain. Chem. J., 1934, 9, 17—24).—The results of Bauer and Hansen and of Ruer and Kremers (B., 1927, 939; A., 1930, 161) are confirmed. A new transformation has been observed in 1:1 alloys at 345°. R. T.

Cu_2Mg phase in the copper-magnesium system. V. G. SEDERMAN (Phil. Mag., 1934, [vii], 18, 343—352).—The existence of this phase has been confirmed by X-ray methods. J. W. S.

Structure of tin bronzes. J. VERO (Z. anorg. Chem., 1934, 218, 402—424).—Thermal and microscopic data are recorded for alloys containing 13—38 wt.-% Sn, and the phase diagram is constructed. The solubility of Sn in Cu is 13.3% at 795°, 16% at 520—586°, and 14% at 200°. The melting interval of Cu_3Sn is at the most 2—3°, and not 15—20° as previously recorded. The irregularities in the electrical resistance of alloys of 26—30% Sn at 600° cannot be ascribed to a transition, but are probably due to mechanical separation of different phases. M. S. B.

Equilibrium diagram of the cobalt-silicon system. R. VOGEL and K. ROSENTHAL (Arch. Eisenhüttenw., 1933—1934, 7, 689—691).—Thermal analysis and micrographic examination have failed to confirm Co_3Si_2 , but have established Co_3Si , which separates from the melt at 1210° and decomposes at 1160° into Co_2Si and Si-Co solid solution. Co_2Si melts at 1332° and undergoes transformation at 1320°. Co and Co_2Si form a eutectic at 12.5% Si and 1200°, and Co_2Si and CoSi (m.p. 1440°) a second eutectic at 23% Si and 1270°. Both α - and β - Co_2Si dissolve Si, the saturated β -solid solution with 20.8% Si decomposing at 1208° into saturated α with 19.8% Si and CoSi. A. R. P.

X-Ray investigation of the arsenic-tin system of alloys. W. H. WILLOTT and E. J. EVANS (Phil. Mag., 1934, [vii], 18, 114—128).—Alloys containing 0—29.5% As have a simple tetragonal structure and consist of solid solutions of As in Sn. No Sn_3As_2 is formed (cf. Mansuri, J.C.S., 1923, 123, 214). SnAs (NaCl structure) persists from 34.5 to 49.0% As, the change in lattice const. indicating dissolution of Sn and As. Two regions of mixed phases exist (29.5—34.5 and 49.0—68.0% As). Above 68.0% As solid solutions of Sn in As exist. Variations of lattice const. in the solid solutions are recorded. H. J. E.

X-Ray study of the transformations of chromium-nickel steel. J. ŠPLÍČAL and F. CABICAR (Coll. Czech. Chem. Comm., 1934, 6, 251—268).—X-Ray diagrams of a Cr-Ni steel (0.46% C) show that the martensite II which forms the γ -phase when the rate of cooling is $> 100^\circ$ per hr. is tetragonal ($c/a = 1.018$); austenite is also found, but the amount of martensite I is too small for the corresponding

lines to be observed. With 0.30% C more martensite ϵ is present, and this has a cubic structure. A. G.

Solubility of copper in zinc. M. HANSEN and W. STENZEL (*Metallwirt.*, 1933, 12, 539—542; *Chem. Zentr.*, 1934, i, 278).—The Zn-rich region of η -mixed crystals has been studied by X-rays and metallographically, the solubility relations being correlated with changes in the lattice const. The peritectic point is at 424° (2.73 at.-% Cu). H. J. E.

Physical properties of iron-aluminium alloys. C. SYKES and H. EVANS (*Proc. Roy. Soc.*, 1934, A, 145, 529—539).—The resistivity at room temp. of Fe-Al alloys containing 11—16 wt.-% Al depends on the rate of cooling from about 600°. Alloys in this range consist of a single solid solution at all temp. concerned. The max. effect corresponds with Fe₃Al. The results indicate that rearrangement of atoms takes place in the alloys under slow cooling conditions, the more regular arrangement so produced leading to a decrease in resistance. L. L. B.

Electrochemical investigation of solid thallium-bismuth alloys. A. ÖLANDER (*Z. physikal. Chem.*, 1934, 169, 260—268).—From measurements of the e.m.f. and its temp. coeff. of $Tl_{solid}|(Na,K,Tl)OAc|(Tl,Bi)_{solid}$ for twelve alloy electrodes at 245—295° and similar measurements with $Tl_{solid}|TlOAc|(Tl,Bi)_{solid}$ for thirty-two alloy electrodes at 120—165° the equilibrium diagram has been revised and ranges of existence of the two intermediate phases have been determined. The distribution of the atoms in these phases seems to be a random one. It is possible that the ϵ phase has an ordered structure at the composition Bi₂Tl, but it is only incompletely ordered, and it is estimated that one third of the unit cells contain randomly placed atoms. The decrease in free energy, rise in entropy, and heat effect accompanying alloy formation have been calc. R. C.

System lithium-cadmium. A. BARONI (*Atti R. Accad. Lincei*, 1934, [vi], 19, 507—509).—Polemical against Zintl and Schneider (this vol., 356).

H. F. G.

Iron corner of the iron-manganese-chromium system. W. KOSTER (*Arch. Eisenhüttenw.*, 1933—1934, 7, 687—688).—In Fe alloys with $\geq 40\%$ Mn and $\geq 30\%$ Cr the only solid phases are the α - and γ -solid solutions. Up to 12% Cr has no effect on the structure or behaviour of Mn-Fe alloys; with 12—28% Cr the alloys lie in the $\alpha+\gamma$ field, which extends parallel to the Fe-Mn side of the ternary diagram. With 12—20% Cr the alloys solidify as $\alpha+\gamma$, and with 20—28% Cr as homogeneous α which decomposes into $\alpha+\gamma$ on cooling from 1200° to 800°. Equilibrium diagrams for const. Cr contents of 5, 10, 15, and 20%, and for const. Mn contents of 3, 8, 20, and 30% Mn are given. A. R. P.

Equilibrium diagram of the system aluminium-copper-manganese. H. SAWAMOTO (*Suiyokwai-shi*, 1933, 8, 239—244).—In Al-Cu ($\geq 40\%$)-Mn ($\geq 30\%$) alloys a peritectic-eutectic reaction liquid + Al₃Mn \rightleftharpoons Al₃Mn + (Al) occurs at 630° (Cu 8.3, Mn 1.75, Al 89.95%), and a ternary eutectic reaction liquid \rightleftharpoons CuAl₃ + Al₃Mn + (Al) at 544° (Cu 30.5, Mn 0.65, Al 68.85%). CH. ABS.

Effect of thermal agitation on atomic arrangement in alloys. W. L. BRAGG and E. J. WILLIAMS (*Proc. Roy. Soc.*, 1934, A, 145, 699—730).—The effect of thermal treatment on the arrangement of the atoms in an alloy is considered. The equilibrium states of the alloy are dealt with, and the degree of order of the structure as a function of temp. is calc. It is shown that the ordered structure has a lower potential energy than the disordered structure, but thermal agitation promotes disorder. A general law connecting the rate of relaxation towards equilibrium with temp. is deduced, which renders possible the prediction of the effects of annealing and quenching.

L. L. B.

Disperse structure of mixed crystals. D. BALAREV (*Kolloid-Z.*, 1934, 68, 33—36).—The theory of mosaic structure is applied to mixed crystals.

E. S. H.

Solubility of potassium chloride in aqueous potassium iodide solutions. S. E. HARRIS and W. G. CHRISTIANSEN (*J. Amer. Pharm. Assoc.*, 1934, 23, 563—565).—The solubility of KI in H₂O at 20°, 30°, and 40° is depressed by addition of increasing amounts of KCl.

J. W. B.

Effect of one salt on the solubility of another.

V. Solutions in allyl and benzyl alcohols. J. R. PARTINGTON and R. J. WINTERTON (*Trans. Faraday Soc.*, 1934, 30, 619—626).—The following solubilities have been determined at 25°: KI in presence of NaI in allyl alcohol (I) and CH₂Ph·OH (II); NaCNS in presence of NaI in (I). Up to a concn. of 8×10^{-4} mol. of NaI per ml. the solubility (S) of KI in (I) in presence of NaI of concn. C is approx. given by $\log S/S_0 - KC$, where $S \rightarrow S_0$ when $C \rightarrow 0$, and K is a const. The results cannot be given a quant. explanation in terms of the Debye-Hückel equation and its simple extensions.

R. S. B.

Solubility of aniline in water and in aqueous salt solutions. V. G. GULINOV and E. I. KOBTEVA (*Ukrain. Chem. J.*, 1934, 9, 105—110).—The solubility of NH₂Ph in H₂O is not significantly depressed by various salts.

R. T.

Influence of salts of fatty acids on solubility in the system phenol-water. S. JENCIC (*Arch. Hemiju*, 1934, 8, 62—66).—The solubility of PhOH in H₂O in presence of R·CO₂Na increases in the series Me < Et < Pr < C₆H₁₃ < C₁₁H₂₃.

R. T.

"Induced" solubility of ferric hydroxide and other hydroxides in alkali hydroxides in presence of chromic hydroxide. III. H. KNOCHE (*Kolloid-Z.*, 1934, 68, 37—41; cf. this vol., 726).—In presence of Cr(OH)₃ the hydroxides of Co^{II}, Ni^{II}, and Mg are peptised by NaOH or KOH, giving turbid solutions, whilst hydroxides of Fe^{III}, Ti^{III}, Cu, and Cd dissolve at first, but react after a time to form chromates. The induced solubility effect is greater the less is the solubility product of the hydroxide. The solubility of Al(OH)₃ and Zn(OH)₂ is not increased under these conditions.

E. S. H.

Calculation of the composition of an aqueous solution saturated with an arbitrary number of highly soluble strong electrolytes. G. AKERLOF (*J. Amer. Chem. Soc.*, 1934, 56, 1439—1443).—The

method described for ternary systems (this vol., 490) is extended so as to be applicable to more complex systems.

E. S. H.

Monobasic, polybasic, and polymonobasic acids. II. Solubility of alkali and ammonium salts in aqueous acetone. E. WEITZ and E. GROHROCK. III. Formation of mixed crystals of salts of monobasic acids with those of polymonobasic acids. E. WEITZ and E. MOSTER (Ber., 1934, 67, [B], 1085—1091, 1092—1094; cf. A., 1928, 722).—II. The alkali and NH_4 salts of polybasic inorg. acids (I) are practically insol. in anhyd. COMe_2 , certain salts of monobasic acids (II) (HMnO_4 , HClO_4 , HI , HCNS) are moderately sol. (the Na and NH_4 salts generally > the K salts), whereas others are sparingly sol. or almost insol. COMe_2 therefore diminishes the solubility of the alkali and NH_4 salts of all (I) and many (II), the diminution with (I) being invariably > with (II). The differentiation is more marked when the abs. solubility is replaced by the ratio of the solubility in H_2O (g. salt in 100 g. H_2O) in presence of COMe_2 to the solubility in H_2O alone. The graphs for salts of (I), including HF and HIO_3 , fall most steeply and form a class by themselves. $\text{H}_2\text{S}_2\text{O}_8$ and $\text{H}_2\text{S}_4\text{O}_6$ (including the higher polythionic acids) behave like (I). The acids are arranged in order of increasing depression, MnO_4' , ClO_4' , SCN' , I' , Br' , ClO_3' , $\text{S}_2\text{O}_8''$, NO_3' , Cl' , $\text{S}_4\text{O}_6''$, $\text{S}_2\text{O}_6''$, IO_3' .

III. Examples are cited of the formation of mixed crystals of salts of polymonobasic and monobasic acids. $\text{K}_2\text{S}_2\text{O}_8$ and KMnO_4 give mixed crystals from a saturated solution of either component. K_2SO_4 , KCl , KBr , and H_3BO_3 do not form mixed crystals with KMnO_4 , but the cryst. form of the last is changed; indications of such crystals are obtained with KClO_3 . Crystals of KClO_4 take up $\text{K}_2\text{S}_2\text{O}_8$, but the reverse phenomenon is not observed. The lattice of KClO_4 may take up small amounts of $\text{K}_2\text{S}_4\text{O}_6$. H. W.

Crystallisation of sodium bromide from supersaturated solutions. II. Z. C. MUTAVTSCHIEV (Z. physikal. Chem., 1934, 169, 186—188; cf. A., 1930, 1362).—The separation of NaBr and NaI from supersaturated aq. solutions on various specimens of galena has been examined. The temp. at which crystallisation occurs does not depend on the fineness of the crystals of the galena, but is raised by the presence in it of impurities, such as FeS and ZnS , which create new boundary lines or singular points. The transition point $\text{NaI}, 2\text{H}_2\text{O}$ — NaI lies above 65.5° .

R. C.

Mineral precipitation in glass. M. BILLY and M. A. FOEX (Compt. rend., 1934, 199, 57—59).—Cu, Au, and Ag have been obtained as cryst. deposits in a bead of alkaline glass slowly cooled in N_2 . The solubilities and conditions of pptn. of Cr_2O_3 , CoO , Fe_2O_3 , and NiO in alkaline SiO_2 , B_2O_3 , and P_2O_5 glasses have also been studied. The NiO — B_2O_3 — Na_2O solubility diagram indicates the formation of $\text{B}_2\text{O}_3, 2\text{NiO}$ and $\text{B}_2\text{O}_3, 3\text{NiO}$.

B. W. B.

Precipitation. P. JOLIBOIS (Bull. Soc. chim., 1934, [v], 1, 597—612).—A lecture.

Liesegang phenomenon. I. Tentative theory J. A. Christiansen. J. A. CHRISTIANSEN and

I. WULFF (Z. physikal. Chem., 1934, B, 26, 187—194).—Following the same lines as Michalev (this vol., 363), and assuming that the de Broglie and the corresponding Schrödinger equation can be applied to the average motion of diffusing particles, the Liesegang phenomenon is treated as a consequence of the wave concept of mechanical processes. It is deduced that the no. of rings must be finite, and that the difference between the logarithms of the abscissæ of two successive points of pptn. must be const. These deductions are confirmed by experiment.

R. C.

Periodic precipitation phenomena. Influence of concentration changes of the reaction components on the precipitate formation. B. TEŽAK (Kolloid-Z., 1934, 68, 60—69).—The turbidity curve representing addition of dil. AgNO_3 to dil. $\text{K}_2\text{Cr}_2\text{O}_7$ in presence of gelatin passes through one small and two large max., corresponding, respectively, with the formation of AgCl , Ag_2CrO_4 , and $\text{Ag}_2\text{Cr}_2\text{O}_7$. Similar phenomena have been observed in the pptn. of AgI and PbCrO_4 . A theory of the formation of periodic structures is advanced.

E. S. H.

Absorption of chemical fog in gas-washing bottles. H. REMY [with E. VICK] (Kolloid-Z., 1934, 68, 22—29).—Fogs of SO_3 and NH_4Cl behave similarly in spite of their dissimilarity. Absorption in 1% gelatin solutions is < in H_2O . Washing-bottles consisting of sintered glass plates are the most efficient.

E. S. H.

Absorption of acetone by cellulose nitrates. J. DESMAROUX (Compt. rend., 1934, 199, 148—150).—Nitrates containing 11.6 and 13.52% N absorb COMe_2 vapour at 40° to form perfect solutions. J. L. D.

Partition of (A) succinic acid between two liquid phases, (B) hydrogen peroxide between water and esters. (C) Effect of electrolytes on the partition of saturated fatty acids between water and toluene. N. A. DE KOLOSOVSKI (Ukrain. Chem. J., 1934, 9, 34—36, 37—40, 41—45).—(A) [with A. BEKTUROV and M. RASULEV.] The partition coeff. (r) of $[\text{CH}_2\text{CO}_2\text{H}]_2$ has been determined at 25° for 1 : 1 H_2O —*iso*- $\text{C}_5\text{H}_{11}\text{OH}$ and EtOH —glycerol.

(B) [with F. S. KULIKOV.] For H_2O — EtOAc , $-\text{C}_5\text{H}_{11}\text{OAc}$, and $-\text{CH}_2(\text{CO}_2\text{Et})_2$ r diminishes with increasing concn. of H_2O_2 .

(C) [with I. S. MESHENIN.] For HCO_2H , AcOH , and EtCO_2H at 25° r may be calc. from the formula $r = K - N(a + b)$, where $K - r$ in the absence of electrolyte, a and b are consts. characteristic of the anion and cation, and N is the concn. of the electrolyte in the aq. layer.

R. T.

Extraction of indium chloride by ether. S. ATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 162—164).—Approx. 1% of InCl_3 in HCl solution is extracted by Et_2O . Washing with 4*N*- HCl removes almost the whole of this extracted InCl_3 from the Et_2O .

R. S. B.

Distribution of radioactive elements between a liquid phase and a crystalline solid phase. Distribution of radium between the solution and crystals of $\text{BaCl}_2, 2\text{H}_2\text{O}$ in presence of HCl . A. POLESITSKI (Compt. rend. Acad. Sci. U.R.S.S.,

1934, 2, 483—489).—The distribution is independent of the relative amounts of the two phases, but is influenced by the HCl concn. (cf. Marques, A., 1933, 562).
H. J. E.

Behaviour of hydrogen dissolved in palladium. K. F. HERZFELD and M. GOEPPERT-MAYER (Z. physikal. Chem., 1934, B, 26, 203—208; cf. A., 1931, 1112).—Theoretical. Energy and conductivity are calc. by Debye and Huckel's method on the assumption that the Fermi statistics are applicable to the electron.
R. C.

Production of copper powder with a high-vacuum milling apparatus, and the adsorption of gases by these powders. F. DURAU and H. FRANSSEN (Z. Physik, 1934, 89, 757—773).—N₂ is removed from Cu powder at room temp. by evacuation; H₂, C₂H₆, C₂H₄, and CO can be similarly removed, but O₂ and CO₂ show chemical adsorption.
A. B. D. C.

Adsorption. A. KEMPER (Z. physikal. Chem., 1934, 169, 275—286).—After being heated, Ni and Ag wires have lost a large proportion of their adsorbent power for dissolved Me-violet and methylene-blue. The decrease in adsorptive power after heating is greater the higher is the temp. of heating. The decline is initially more marked with Ag than with Ni. After protracted heating at a high temp. the amount adsorbed at saturation is than corresponds with a unimol. film. The adsorptive power of an adsorbent which has been heated is increased by etching with dil. HNO₃, but falls again on heating. All these observations are satisfactorily explained by the active centre hypothesis, points and imperfections in the crystals being assumed to have a particularly high adsorptive power. After drawing, the mol. roughness of the wires is great, but after heating is largely smoothed out.
R. C.

Absorptive power of solid cobalt for hydrogen and nitrogen. A. SIEVERTS and H. HAGEN (Z. physikal. Chem., 1934, 169, 237—240).—The solubility of H₂ in Co under pressures up to 1 atm. has been measured at 600—1200°. The solubility is proportional to the square root of the H₂ pressure. The absorptive power of technical Co containing 2.5% Fe does not differ appreciably from that of pure Co. N₂ is practically insol. in Co up to 1200°.
R. C.

Adsorption of hydrogen chloride on potassium chloride. R. S. BRADLEY (Trans. Faraday Soc., 1934, 30, 587—596).—The rate of adsorption of HCl on a mass of KCl crystals for a range of pressures 0.35—286.5 mm. at 20.4° and 28.9° has been measured by means of a SiO₂ torsion microbalance. Results agree with the equation for activated diffusion into cracks of finite depth. The diffusion energy of activation is 7090 g.-cal., and corresponds with the calc. adsorption energy of a HCl mol. in the surface field of KCl.
R. S. B.

Chlorinated charcoal as adsorbent and catalyst. R. KLAR and A. MÜLLER (Z. physikal. Chem., 1934, 169, 297—304).—Measurements of the adsorption of Cl₂ on chlorinated C, and of CO₂ on chlorinated C and re-reduced C, have shown that

the adsorption of chlorinated C for Cl₂ is sp. and that Henry's law is valid for the sorption of CO₂. Chlorinated C exhibits a sp. catalytic activity in chlorination reactions, e.g., the H₂-Cl₂ reaction. Reduction of chlorinated C increases the surface area.
R. C.

Dissociation of sulphuryl chloride and its adsorption by active charcoal. K. ARII (Sci. Rep. Tôhoku, 1934, 23, 193—207).—The dissociation of saturated and unsaturated vapour has been examined between 30° and 50°, and the adsorption of the vapour by active animal charcoal measured between 20° and 40° and pressures of 23.5 and 142.0 mm.
H. S. P.

Vapour-binding power of active charcoals. V. Dependence of the amount of bound vapour on the temperature. F. KRCZIL and H. WEJROCH (Kolloid-Z., 1934, 68, 29—32; cf. this vol., 358).—The vapour-binding power at 100° is < at 20°.
E. S. H.

Adsorption from solutions. I. Adsorption of picric acid by charcoal. L. S. TSAI and H. A. YÜ (J. Chinese Chem. Soc., 1934, 2, 99—107).—The adsorption of picric acid by purified animal charcoal is irregular. The adsorption isotherm for activated sugar charcoal over the concn. range 0.002—0.17 consists of six distinct curves, each of which follows a Langmuir equation. The transition from one equation to another occurs at regular concn. intervals, this being in accord with the concentric row hypothesis, but the charcoal does not offer a plane crystal surface to the solution, as required by this hypothesis.
J. W. S.

X-Ray study of the fixation of acetone by cellulose nitrate. M. MATHIEU (Compt. rend., 1934, 199, 55—57).—Nitro-ramie (11.6 or 13.52% N) fibres exposed to COMe₂ (I) vapour inside an X-ray camera give no indication of compound formation during absorption, but the displacement of glucose radicals (II) attains a max. at the mol. ratio (I)/(II)=1. A structureless gel is formed when the no. of mols. of (I) absorbed becomes equal to the no. of NO₂ groups in the fibre.
B. W. B.

Adsorption of hydrogen chloride by hide powder. L. S. TSAI and C. J. HSIAO (J. Chinese Chem. Soc., 1934, 2, 87—98).—Hide proteins form a definite chemical compound with HCl, the v.p. of which is 1.41 mm. at 35°. The compound adsorbs HCl, and if low pressures are excepted the isotherm follows the Freundlich equation. Hide powder containing adsorbed HCl is pink, and on exposure to air absorbs moisture and changes to a glue-like substance. The equiv. wt. of collagen, calc. from the composition of the HCl compound, is 1380.
J. W. S.

Adsorption of polysaccharides on fats and lipins. S. J. VON PRZYLECKI and R. MAJMN (Biochem. Z., 1934, 271, 174—179).—The adsorption of polysaccharides (glycogen, dextrin) on olive oil in Ringer solution is very slight, but is increased by addition of lecithin, and still more (up to 80%) by moderate amounts of lecithin with globulin. In the presence of suspended cholesterol, paraffin, or stearic acid adsorption scarcely occurs. The adsorbed substances form separate layers enclosing the

oil. The non-ionised polar groups of the oil, lipins, and polysaccharides form the linkings which bind the substances together. W. McC.

Hysteresis in silica gel sorption systems. L. M. PIDGEON (Canad. J. Res., 1934, 10, 713—729).—Using a sorption balance, the sorption of H_2O , C_6H_6 , and EtOH has been examined. A hysteresis loop appears for H_2O only, and cannot be eliminated by evacuation. The loop is evident only when the v.p. are reasonably const. during sorption, and if the pressure changes are very large the loop may disappear. H. S. P.

Determination of the tenacity of adsorbed molecules at the boundary surface solid/liquid. G. LINDAU and G. SALOMON (Ber., 1934, 67, [B], 1296—1298).—In an attempt to determine the frequency with which a mol. passes from the adsorption layer into the solution and *vice versa*, use is made of the equal adsorbability of optical antipodes. The adsorption isotherm of a pure, optically active substance is determined with each component separately. The adsorbate is removed from such a system containing one optical component and transferred to the equilibrium system of the other component. After thorough agitation the optical activity of the solution is measured after definite intervals. In the system C—tartaric acid the equilibrium is reached within 20 sec. With diisopropyl alcohol 70—80% of the final val. is reached after 20 sec. H. W.

Validity of Langmuir's adsorption isotherm in presence of forces between the adsorbed particles. G. DAMKOHLER (Z. physikal. Chem., 1934, 169, 120—128).—Taking into account the forces between the adsorbed particles in an incomplete unimol. film on a homogeneous surface, there is derived an adsorption isotherm differing from Langmuir's isotherm in having prefixed to the concn. of the gas phase in the denominator a factor β , which depends on the temp. and the strength of the intermol. forces in the adsorbed film. If β is positive, the isotherm follows the normal course of Langmuir's isotherm with a saturation val. at infinite d of the gas phase. The saturation val. falls with rising temp. if the forces are attractive, and rises if they are repulsive. If β is negative, which is possible only if the forces are attractive and only below a crit. temp., the course of the isotherm diverges from that of Langmuir's isotherm, and at a still finite d of the gas phase there is practically spontaneous saturation of the adsorbent. This is largely equiv. to the formation of a two-dimensional liquid film on the adsorbent. C.

Fundamental facts on base exchange. G. AUSTERWEIL (J.S.C.I., 1934, 53, 185—189r; cf. Marshall and Gupta, this vol., 251).—Theoretical. The base-exchange reaction is an extraction phenomenon, the solid base-exchanger acting as a non-miscible solvent for the cation in aq. solution. The extraction is accompanied and limited by an equilibrium of the two cations in solution, which is governed by the laws of mass action and the phase rule. Minor side reactions also occur. The time factor and effect of viscosity are discussed. E. S. H.

Negative adsorption in soil, clay, and humus. G. BARBIER (Compt. rend., 1934, 199, 226—228).—Negative adsorption by soils is the greater the less conc. is the solution; it varies with the nature of the fixed ion in the soil. From the nature of the salts expressible under different conditions it is inferred that the capacity of humate for absorbing H_2O is due to mechanical retention of H_2O between its particles, whilst osmotic swelling occurs in the case of clay. Addition of small quantities of humic acid to clays does not greatly affect their absorption of non-free H_2O , although it increases considerably their total capacity for retaining H_2O . J. W. S.

Base exchange reactions of bentonite and salts of organic bases. C. R. SMITH (J. Amer. Chem. Soc., 1934, 56, 1561—1563).—When bentonite (I) (5 g.) is shaken (30 min.) with nicotine (II) (0.25 g.) in dil. aq. solution (200 c.c.), 49% of (II) is removed; with half-neutralised (H_2SO_4) and completely neutralised (H_2SO_4 , HCl , H_3AsO_4 , or $\text{H}_2\text{C}_2\text{O}_4$) solutions the corresponding vals. are 80 and about 92%, respectively. With varying amounts of (II) (in an excess of dil. HCl), it is found that the amount of (II) removed in combination with 5 g. of (I) reaches a max. of 31 c.c. of 0.1N-base; similar results are found using piperidine, strychnine, amylamine, and diamylamine, but NH_3 and N_2H_4 are not removed to the same extent. Flocculation accompanies max. removal of base. Washing of (I) saturated with (II) with H_2O removes a little (II); 1% NaCl (after H_2O) removes considerably more owing to Na^+ tending to reverse the (exchange) reaction. H. B.

Thermodynamic study of surface tension. Affinity and rate of absorption. R. DEFAY (Bull. Acad. roy. Belg., 1934, [v], 20, 559—562).—Mathematical. Consideration is given to the influence of radius of curvature on the solubility of emulsion globules at const. temp. and pressure, and on the solubility of small crystals. N. M. B.

Thin films of mercury on glass. H. E. BENT (J. Amer. Chem. Soc., 1934, 56, 1549—1550).—The adherence of Hg to clean glass in vac. is reported. E. S. H.

Surface activity measurements and the range of validity of Traube's rule. L. I. WEBER and P. STERNGLANZ (Z. physikal. Chem., 1934, 169, 241—259).—The surface tension, γ , of aq. solutions of the saturated alcohols and fatty acids has been measured over wide concn. ranges at 20°. The capillary rise method can be used from C_7 onwards only with special precautions, and is useless from C_{10} onwards. There is good agreement between the results of the max. bubble pressure, stalagmometric, and stagonometric methods up to C_8 , but for C_9 , C_{10} , and C_{11} the bubble pressure method gives lower vals. of γ than the other two methods. The alcohols are still active at C_{16} . The ratio, Q , of the concn. of a solution of an alcohol or acid to the concn. of a solution of equal γ of the next higher homologue is not const. for a given pair of homologues, but is the larger the smaller is the γ for which the comparison is made. Traube's rule seems to be a special case of a more general rule, according to which the surface activities of chemically related surface active substances are related to each other. The

surface activity, measured by Q , of straight-chain compounds is $>$ that of the corresponding *iso*-compounds. Of branched-chain isomerides Q is greatest for those with the side chain most remote from the OH group. In deriving Q , the comparison must be made between substances not merely homologous, but exactly similar in constitution, *e.g.*, with the chain branched at the same point in the mol. Traube's rule is valid up to very high concns., which is accounted for by the adhesion pressure theory. R. C.

Surface resistivity of adsorbed moisture films on glazed porcelain. F. W. JOHNSON (Phil. Mag., 1934, [vii], 18, 63—80).—The resistivity has been measured as a function of time and the % humidity of the atm. The leakage film, if continuous, probably consists of two components, one adsorbed (I) and the other a surface solution (II), the relative proportions of (I) and (II) being const. for a fixed humidity.

H. J. E.

Spreading of a tripeptide. E. GORTER, T. M. MEYER, and G. T. PHILIPPI (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 355—357; cf. A., 1929, 1141).—The effect of length of chain and of the no. of chains linked together has been studied for α -NH₂-acids and the corresponding peptides. The capillary activity of α -aminopalmitic acid is $>$ that of α -amino-octioic acid (I). The tetrapeptide from alanine does not spread, and that of leucine spreads poorly compared with tributyrin, but the tripeptide of (I) spreads well. The influence of p_H in the spreading of (I) has also been studied. H. S. P.

Theory of flotation. III. WO. OSTWALD (Kolloid-Z., 1934, 68, 103—109; cf. A., 1932, 335, 1085).—Criticisms of the theory of linear flotation and the effect of mean wettability are discussed. E. S. H.

Optical examination of thin films. II. Behaviour of thin films of fatty acids on mercury. C. G. P. FEACHEM and L. TRONSTAD (Proc. Roy. Soc., 1934, A, 145, 127—135; cf. this vol., 936).—The behaviour of a no. of fatty acid films on Hg has been studied by an optical method. The acids spread with difficulty, which increases with the length of the chain. The films can exist in three phases, the solid and expanded being ultimately stable; the characteristic areas are solid, up to 22 Å.²; liquid, up to 45 Å.²; expanded, from 45 Å.². Homogeneous films of expanded phase can be compressed through the liquid phase, sometimes up to 22 Å.² per mol. L. L. B.

Polymorphism in unimolecular layers of fatty acids on the surface of water. D. G. DERVICHIAN (Compt. rend., 1934, 199, 347—349).—Examination of solid films on the surface of H₂O shows three forms of structure for which the dimensions correspond with those found by X-ray diffraction. The mol. surfaces found for stearic acid on different supports (0.002*N*-acid, 0.01*N*-acid, 0.01*N*-alkali) are grouped around the vals. 20, 21, and 24 Å.², the transition from one form to the other being discontinuous. A. J. M.

Behaviour of secondary alkali sulphates in diffusion through a difficultly permeable membrane. H. BRINTZINGER and J. WALLACH (Kolloid-Z., 1934, 68, 36—37).—Acid is formed when a salt, the cation of which diffuses much more rapidly

than the anion, is dialysed through a slightly permeable membrane. The effect is observed with alkali sulphates, especially K₂SO₄. E. S. H.

Membrane equilibria and the phase rule. O. GATTY (Phil. Mag., 1934, [vii], 18, 273—288).—The phase rule is applied and the equations for the Donnan equilibrium are deduced for simple cases. A simple three-phase Donnan equilibrium is discussed, and it is suggested that polyphase membrane equilibria may play a role in vital processes. J. W. S.

Flow potential at a porcelain diaphragm in barium chloride solutions. J. BABOROVSKY and B. BURGL (Arh. Hemiju, 1934, 8, 1—7).—The flow potential diminishes asymptotically with increasing concn. of BaCl₂ from —53.2 mv. to $<$ 0.01 mv. in 0.005*N*-BaCl₂. The effects obtained are in agreement with the Helmholtz-Smoluchowski theory. R. T.

Osmotic pressure of polymerised substances. (MME.) A. DOBRY (Compt. rend., 1934, 199, 289—290).—The osmotic pressure (P) of solutions of various concns. (c) of cellulose nitrate in COMe., MeOH, AcOH, PhNO₂, *o*-OH-C₆H₄-CO₂Me, EtOBz, and cyclohexanone has been measured. The P/c - c curves are either straight lines or curves of sufficiently large radius to be extrapolated to $c=0$. The vals. of P/c for zero concn. are independent of the solvent, and the mol. wt. calc. therefrom (110,000) is considered to be the true val. for the colloid. It seems that solutions of colloids obey perfect gas type laws only at mol. concns. of $<$ about 10⁻⁵, whereas ordinary compounds still follow the laws to about 10⁻² to 10⁻¹*M*. J. W. S.

Precision determinations of viscosity of solutions of higher hydrocarbons. K. H. MEYER and A. VAN DER WYK (Z. Elektrochem., 1934, 40, 446—448).—By careful control of all the factors (experimental details to be published elsewhere) the sp. viscosity can be determined with an error of $<$ 1.5%. Results are given for several higher *n*-paraffins in CCl₄ solution at 20°. E. S. H.

Accurate determinations of the viscosity of polystyrene solutions. I. V. Z. DANEŠ (Kolloid-Z., 1934, 68, 110—115).—The viscosity of three fractions of polystyrene (low, medium, and high mol. wt.) has been determined in C₆H₆ solution. The variation with concn. is not in accordance with the equations of Staudinger or of Arrhenius and Duclaux. E. S. H.

Theory of electrolytic solution. I. K. SHIBA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 664—683).—Formulae have been deduced for the mean electrostatic potential and osmotic coeff. of an ionic solution. R. S. B.

Individual behaviour of organic ions in very dilute aqueous solutions. J. LANGE (Z. Elektrochem., 1934, 40, 507—510).—Anomalies in the *f*-*p*. lowering and conductivity of NR₄X solutions (R = alkyl, X = halogen) are discussed. E. S. H.

General characteristics of volume changes accompanying reactions in aqueous solutions. J. J. SASLAVSKI (Z. physikal. Chem., 1934, 169, 305—311).—When equal vols. of electrolytic solutions of

different concn. are mixed there is usually a contraction. This is a min., or even becomes an expansion, for a definite, and generally simple, ratio of the concns. of the solutions being mixed. Expansion on mixing is certain evidence of complex formation. From the presence or absence of expansion it is possible to decide whether or not an acid or basic salt is formed on adding to a solution of a salt the corresponding acid or base. R. C.

Variation with concentration of the apparent molecular volume and of the apparent molecular refraction in dilute solution. W. GEFFCKEN and D. PRICE (*Z. physikal. Chem.*, 1934, **B**, 26, 81—99; cf. this vol., 24).— d and n have been measured for 0.01—1.5*N* aq. solutions of NaBr, KCl, NH_4NO_3 , Na_2SO_4 , and Na_2CO_3 . For NaCl, KCl, and NaBr the apparent mol. refraction passes through a max. between 0.5 and 1*N*. For these halides the graphs of apparent mol. vol., Φ , against \sqrt{C} , where C is the concn., coalesce at high dilution into a single limiting straight line, the slope of which is determined solely by the valency of the solute and properties of the solvent, as foreseen by Redlich and Rosenfeld (A., 1931, 905). The mode of variation of Φ with C for moderately strong electrolytes, e.g., H_2SO_4 or H_3PO_4 , depends principally on the variation of the degree of dissociation, and may be deduced quantitatively from the vals. of the true degree of dissociation. When the vals. of Φ for Na_2CO_3 are corr. for hydrolysis, the variation of Φ with \sqrt{C} becomes normal. R. C.

Viscosity of strong electrolytes measured by a differential method. W. M. COX and J. H. WOLFENDEN (*Proc. Roy. Soc.*, 1934, **A**, 145, 475—488).—The viscosities of aq. solutions of MgSO_4 and LaCl_3 , of NET_4 picrate in H_2O and in PhNO_2 , and of NaI in EtOH have been measured at concns. from 0.0002*M* to 0.01*M*, and the results compared with the Falkenhagen equation (A., 1932, 461). The B coeff. in the Jones-Dole equation (A., 1929, 1385) has been evaluated for several uni-univalent electrolytes in aq. solution. It is made up additively of two quantities characteristic of anion and cation. It is shown that Stokes' law must lead to erroneous results for many ions. L. L. B.

Concept of colloidal systems based on probability. M. MATTIKOW (*Science*, 1934, 79, 589—590). L. S. T.

The double layer theory of colloids. E. J. W. VERWEY (*Rec. trav. chim.*, 1934, 53, 933—940).—The potential distribution across the interface solution-colloidal AgI is derived from the data of Verwey and Kruyt (this vol., 143). D. R. D.

Form of thread-like molecules in solutions. W. KUHN (*Kolloid-Z.*, 1934, 68, 2—15).—A theoretical discussion on a statistical basis. E. S. H.

Stability and charging of aerosols. N. FUCHS (*Z. Physik*, 1934, 89, 736—743).—Smoluchowski's coagulation theory shows that unipolar charging greatly hinders coagulation, whilst bipolar charging tends in a much less degree to accelerate it. Taking decrease in velocity of particle concn. as criterion for stability, the unipolar effect outweighs the bipolar effect. A. B. D. C.

Foams. A. V. DUMANSKI, T. A. GRANSKAYA, and N. V. NOVIKOV (*Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm.*, U.S.S.R., 1933, 3, 361—391).—Foaming power in hydrophilic colloids diminishes in the order: saponin, molasses, peptone, gelatin, albumin (I), pectin, casein. For (I) the max. occurs just below the coagulation temp.; max. foam stability occurs at p_{H} 4.7. Replacement of air by CO_2 or SO_2 decreases the stability, but not the amount, of the foam. CH. ABS.

Physico-chemical nature of emulsions. G. R. VISHNEVSKAYA and A. G. KNIGA (*Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm.*, U.S.S.R., 1933, 3, 392—405).—Emulsifying powers for C_6H_6 in H_2O of agar, saponin, albumin, pectin, gelatin, lecithin (I), and casein (II) have been compared. Large concns. of sugar favour emulsification. Double emulsions with (I) are described. The use of two emulsifying agents, e.g., (I) and (II), may lessen the stability of the emulsion. CH. ABS.

Mechanism of the emulsification process. L. KREMNEV (*Kolloid-Z.*, 1934, 68, 16—22).—A discussion in which the conditions for emulsification are differentiated from those for stability. E. S. H.

Phase volume theory and the homogenisation of concentrated emulsions. II. J. B. PARKE (*J.C.S.*, 1934, 1112—1115).— $\text{H}_2\text{O}-\text{C}_6\text{H}_6$ emulsions, in which a mixture of Na and Mg oleates was used as stabiliser, have been examined by a modification of Clayton's electrical conductivity method. Na oleate stabilises a H_2O -continuous and Mg oleate an oil-continuous emulsion. The concns. of C_6H_6 and H_2O at which a change of type of emulsion occurs has been determined. The results indicate that, under the action of a dual emulsifier, a complicated multiple emulsion in which the globules of disperse phase also contain emulsion is generally formed. M. S. B.

Structure viscosity. III. Structure viscosity of pure and salt-containing dye sols. W. OSTWALD and V. TRAKAS (*Kolloid-Z.*, 1934, 68, 42—55; cf. this vol., 729).—Structure viscosity has been observed in sols of cotton-yellow (I), geranin (II), Congo-red (III), and benzopurpurin 4B (IV) in absence of Cl^- and SO_4^{2-} , especially at low pressures and velocities. The general features resemble those observed in suspensoid colloids. In presence of 40—50% Na_2SO_4 the abs. viscosity of the sols is markedly increased, whilst the sol resembles lyophilic systems in that the concn. of the dye has a large influence. Addition of Na_2SO_4 extends the region of structure viscosity of (I) and (II) in the direction of higher velocities of flow, but narrows the region with (III) and (IV). Structure turbulence is observed in the sols containing Na_2SO_4 . E. S. H.

Changes in the charge on colloidal particles during dialysis of sols. B. N. DESAI (*Current Sci.*, 1934, 2, 473).—Prussian-blue sol, peptised by $\text{H}_2\text{C}_2\text{O}_4$ solution, resembles colloidal Au, $\text{Fe}(\text{OH})_3$, $\text{Th}(\text{OH})_4$, and $\text{Cu}_2\text{Fe}(\text{CN})_6$ in that the cataphoretic speed (I) increases and then decreases as dialysis progresses. With As_2S_3 , however, (I) decreases to a min., increases to a max., and finally decreases. The amount of H_3AsO_3 in the sol increases as (I) initially

decreases, and after the min. speed is reached, the amount of H_3AsO_3 begins to decrease. L. S. T.

Theory of the coagulation of colloids and of smokes. W. R. HARPER (Trans. Faraday Soc., 1934, 30, 636—643).—Smoluchowski's formula (I) for the rapid coagulation rate of colloids is criticised on the grounds of artificial assumptions. The author's alternative derivation gives a result differing from (I) by a factor of 4. The observed agreement of experiment with (I) does not imply confirmation of (I), since heterogeneity and departure from spherical shape of the particles, and electrical attraction, must be allowed for. The influence of these factors is discussed. R. S. B.

Coagulation of hydrophobic sols by congelation in relation to mechanical coagulation. W. HELLER (Compt. rend., 1934, 199, 354—356).—The p_H limit below which strong agitation will not produce quant. mechanical coagulation is 6.5. For congelation it is 6.1, or a little lower when the congelation proceeds over a considerable period. Coagulation at the surface of a sol, although important, is not the only cause of mechanical coagulation. Particles can coagulate in the interior of a sol when they come into contact at high speeds. Increase of coagulation by congelation with time is probably due to growth of the particles in the aggregates, accompanied by a corresponding decrease in their no., followed by spontaneous coagulation. A. J. M.

Determination of colloids in aqueous solutions. A. V. DUMANSKI and A. P. DUMANSKAYA (Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm., U.S.S.R., 1933, 3, 406—422).—The breaking of aq. emulsions with Et_2O - EtOH mixtures can be utilised for determining colloids in hydrosols to ± 0.5 —2%. Optimum conditions must be ascertained for each hydrosol. For albumin the optimum p_H is approx. 6. Sugars do not affect accuracy in albumin, gelatin, starch, dextrin, etc. sols. CH. ABS.

Suspension effect. G. WIEGNER, H. PALLMANN, A. MUSIEROWICZ, and J. ALBAREDA (Polish Agric. Forestal Ann., 1932, 28, 323—356).—Addition of the dispersed phase to a saturated dispersion medium causes a rise in H^+ activity. The effect is a normal characteristic of medium or highly dispersed systems. The activity of the saturated dispersion medium is const. and independent of the abs. amount of the suspended phase. The effect is caused by H^+ adsorbed by the dispersed phase, micelles of which are composed of (1) the ultramicrone, (2) the compact inner layer, and (3) the loosely attached outer layer of ions. The part played by these components is discussed. CH. ABS.

Theory of lyosorption phenomena. Wo. OSTWALD (Z. physikal. Chem., 1934, 169, 173—176).—Cohen and Addink's theory (this vol., 625) is rejected. R. C.

Spontaneous change in aqueous solutions of stannic chloride. I. Analytical and ionometric data. II. Flocculation by sodium sulphate. J. GUÉRON (Bull. Soc. chim., 1934, [v], 1, 561—572, 573—575; cf. A., 1933, 910; this vol., 254).—I. Details of earlier work are given. The induction period

(I) decreases with rise of temp. and the conductivity rises during (I) and attains a const. val. at the onset of opalescence. The Cl of the first hydrolysis product, an oxychloride or mixture of oxychlorides richer in Cl in more conc. solutions, rapidly dissolves, whilst the particles are sufficiently small to pass the ultra-filter.

II. As the age, t , of 0.3N- SnCl_4 increases, the time, θ , elapsing between the addition of Na_2SO_4 and the development of a given opacity rises rapidly to a max., and then decreases slowly. Sn is not separable by ultra-filtration from solutions with high vals. of θ , and after adding Na_2SO_4 to such solutions (I) precedes the appearance of opalescence. The final opacity is independent of t , but increases with $[\text{Na}_2\text{SO}_4]$. J. G. A. G.

Variations of light-diffusing power and viscosity of stannic chloride solutions during hydrolysis. J. GUÉRON (Compt. rend., 1934, 199, 136—138; cf. this vol., 254).—The Tyndall effect was measured photometrically, and the viscosity by a capillary-tube method. Deviations from Poiseuille's law are observed, a thixotropic system being formed during the initial period of homogeneous turbidity. The autocatalysis of flocculation indicated by previous results is confirmed. The Raman spectrum of freshly prepared aq. 2N- SnCl_4 solution approximates more closely to that of chlorostannic acid (Redlich *et al.*, A., 1933, 113) than to that of anhyd. SnCl_4 . B. W. B.

Blue-coloured water solutions of the alkali metals. H. J. WOLTHORN and W. C. FERNELIUS (J. Amer. Chem. Soc., 1934, 56, 1551).—When alkali metals react with H_2O in a confined space, transient blue-coloured patches are observed at intervals near the metal. E. S. H.

Solvation of cellulose nitrate in acetone-water mixtures. G. L. WILSON and F. D. MILES (Phil. Trans., 1934, A, 233, 247—277).—Measurements are recorded of the apparent solvation of cellulose nitrate (I) with COMe_2 in COMe_2 - H_2O mixtures; the fall in total v.p. of the mixed solvent due to addition of (I) is observed and solvation with H_2O assumed to be zero. Solvation decreases with increasing COMe_2 concn., with increasing (I) concn., with decreasing % N in (I), with decreasing viscosity of (I), and with rise of temp. There is apparently a discontinuity in the solvation at the COMe_2 concn. at which dissolution becomes complete. Data are given for the v.p. of COMe_2 - H_2O mixtures. A. G.

Sodium benzoate gels. H. HENSTOCK (Trans. Faraday Soc., 1934, 30, 560—566).— NaOBz forms gels similar to those given by $\text{Ca}(\text{OAc})_2$, but the former contain a larger concn. of the salt. Gels have been prepared from H_2O solutions by pptn. with alcohols and from MeOH solutions by pptn. with a no. of different org. solvents. The effect of temp., electrical conductivity at 25°, penetration by dyes, possibility of bubble formation, optical properties, and the radii of the capillaries have been determined for the MeOH gels. p_H is a little > 7 . The concn. of NaOBz in the gels is 1.37—4.11%. The possibility of gel formation in EtOH and, to some extent, in PrOH has also been observed, but not in Bu^nOH . M. S. B.

Optical properties of permutite. J. H. HELLMERS (Z. Pflanz. Düng., 1934, A, 34, 285—295).—Measurements of the n of permutites favour the view that these substances are essentially intimate mixtures of SiO_2 and Al_2O_3 gels. The mixed gel exhibits base-exchanging properties. Differences between permutite and zeolites are established. A. G. P.

Diffusion of some electrolytes in gelatin. (Mlle.) S. VEIL (J. Chim. phys., 1934, 31, 407—410; cf. A., 1933, 1244).—Previous results are summarised and discussed. The use of the characteristic diffusion figures (I) in qual. analysis is envisaged. The alteration of (I) in weak electric fields is not in agreement with classical electrochemistry. R. S.

Anodic depression in the electrolysis of gelatin. J. SWYNGEDAUF (Compt. rend., 1934, 199, 193—195; cf. this vol., 842).—When a current is passed through a thin film of gelatin (I) on a microscope slide between electrodes of Sn-foil, a narrow (1 μ) zone is formed next to the positive electrode, in which (I) is swollen. This region neither enlarges nor diminishes during the electrolysis. Next to this is a zone of shrinkage, which creeps down towards the negative electrode as electrolysis proceeds, at approx. const. velocity, provided the current is const. The of the swollen anode region is about 2, whilst that of the shrinkage region is 4.7 throughout its area. This is the isoelectric point of (I). With an acid (I) of p_H 3—4, the phenomenon is reversed, the region of shrinkage developing from the cathode. The increase in the resistance of (I) during electrolysis is due entirely to the increased resistance of this isoelectric zone. J. W. S.

Relation between molecular electric moment and gelatinising power for cellulose nitrates. L. MÉDARD (Mém. Poudres, 1934, 25, 449—454).—Cellulose nitrates are not gelatinised by liquids with dipole moments $< 1.5 (\times 10^{-18})$. Liquids with high gelatinising powers have moments ≤ 3 , but the vals. for the simple aliphatic acid esters are about 1.8. The feeble activity of alcohols and of H_2O ($\mu=1.7$ —1.8) is due to association. A. G.

Solubility of serum-proteins in concentrated solutions of neutral salts.—See this vol., 912.

Titration curve of wool keratin. J. B. SPEAKMAN and E. STOTT (Trans. Faraday Soc., 1934, 30, 539—548).—A study of the swelling of wool fibres in acid and alkaline solutions indicates that the isoelectric range is 5—7. The form of the acid and alkali titration curves of wool indicates the presence of salt linkings within the fibre. Unlike gelatin, wool contains no excess of acid side-chains. M. S. B.

Diffusion of fatty acid suspensions containing lecithin and the formation of lecithin-fatty acid-bile acid complex compounds. O. FÜRTH, J. BREYER, and H. HERRMANN (Biochem. Z., 1934, 271, 233—245).—Aq. solutions of alkali bile salts (I) are destabilised by oleic acid (II) suspensions and stabilised by lecithin (III). Et_2O extraction of an acidified (II)-(I) solution removes only a small amount of (II), and it is found that iodobehenic acid (IV) is more suitable for studying the diffusion of these complex compounds. Using suspensions of (IV) with gelatin gels or parchment membranes, the

diffusion process is inhibited considerably by (III), whilst with agar gels the diffusion is accelerated or inhibited by (III), according to the presence or absence of 0.9% NaCl. P. W. C.

Polysaccharoproteins. II. Compounds with denatured proteins. S. J. VON PRZYŁECKI and R. MAJMIN (Biochem. Z., 1934, 271, 168—173; cf. A., 1933, 226, 903).—Large variations in the adsorption of starch and dextrin by proteins (ovalbumin, serum-albumin, serum-globulin, ovoglobulin, and mixtures of ovoglobulin and albumin) have been observed. The degree of adsorption is affected by salts, p_H , coagulating power, and other factors. W. McC.

Lyotrope series in swelling and its extension to organic and non-ionising substances. XII. Effect of double and triple carbon linkings and of branching of aliphatic carbon chains on the swelling of potato starch. J. R. KATZ and A. WEIDINGER (Biochem. Z., 1934, 271, 54—57; cf. A., 1933, 1012).—At p_H 6.7—6.8 swelling is increased by substances containing one or more double linkings ($\text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$, $\text{CHMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$, $\text{CH}_2 \cdot \text{CH} \cdot \text{CO}_2\text{Na}$, $\text{CHMe} \cdot \text{CH} \cdot \text{CO}_2\text{Na}$, $\text{CHPh} \cdot \text{CH} \cdot \text{CO}_2\text{Na}$, $\text{CHMe} \cdot \text{CH} \cdot \text{CH} \cdot \text{CO}_2\text{Na}$, Na fumarate and maleate) and still more by substances containing a triple linking ($\text{CH} \cdot \text{C} \cdot \text{CO}_2\text{Na}$, $\text{CPh} \cdot \text{C} \cdot \text{CO}_2\text{Na}$). The greater is the extent of branching in an aliphatic chain the weaker is the swelling action. W. McC.

Polymorphism of starch preparations showing so-called "paste-spectrum" [Verkleisterungs- or V-spektrum]. J. R. KATZ and A. WEIDINGER (Rec. trav. chim., 1934, 53, 949—951; cf. this vol., 145).—Starch pptd. from aq. solution by EtOH may give X-ray patterns differing in sharpness and relative intensities of the rings. It is uncertain whether they are hazy cryst. patterns or cryst. patterns superposed on an amorphous diagram. D. R. D.

Physical chemistry of starch and bread-making. XVIII. Further attempts at rendering the organised structure of the starch granule microscopically visible. (Use of other methods to check the results obtained in lintnerisation of wheat starch.) E. A. HANSON and J. R. KATZ. XIX. Adsorption of Congo-red from very dilute solution as a means of characterising various native starches. J. R. KATZ and A. WEIDINGER (Z. physikal. Chem., 1934, 169, 135—142, 143—146).—XVIII. Previous conclusions relative to the structure of the starch granule on the basis of observations on maceration with HCl (this vol., 843) are supported by examination of granules at the commencement of peptisation by heating and by grinding in the moist state and of swelling in 2*M*- $\text{Ca}(\text{NO}_3)_2$ solution of granules previously coloured with fuchsin.

XIX. Various native starches show great differences in their power of adsorbing Congo-red from 0.008% solution. There is no simple parallelism between adsorbent power and the X-ray diagram or acidity of the amylopectin, but adsorbent power seems largely to run parallel with the amount of α -amylose. R. C.

Swelling of the lens of the eye.—See this vol., 913.

One-sided reaction equilibrium. W. BADER (Helv. Chim. Acta, 1934, 17, 747—753).—Catalysts for the reaction $2\text{AcOH} \rightarrow \text{COMe}_2 + \text{CO}_2 + \text{H}_2\text{O}$ are ineffective for the reverse reaction. E. S. H.

Exchange reaction of hydrogen and deuterium oxide. R. H. CRIST and G. A. DALIN (J. Chem. Physics, 1934, 2, 442—443).—The equilibrium consts. for the reaction $\text{H}^1\text{H}_2\text{O} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H}^2\text{H}_2$ at 300—600° abs. have been calc. from recent spectroscopic data and compared with experimental vals. determined at approx. 500° and found to be in agreement within the limits of experimental error. Analyses were made by the interferometer. Measurements of the rate of replacement of H^2 by H^1 in $\text{H}^1\text{H}_2\text{O}$ have a qual. val. only. M. S. B.

Theory of solutions of molecules containing widely separated charges with special application to zwitterions. J. G. KIRKWOOD (J. Chem. Physics, 1934, 2, 351—361).—Theoretical. The influence of salts and of the dielectric const. of the solvent on the activity of a spherical ion with a complex charge distribution, e.g., a zwitterion, has been investigated. Those solutions only are considered in which the concn. of the complex ions is so low that their mutual electrostatic forces are negligible. The theory accounts approx. for the solubility relations of glycine at low concns. in $\text{EtOH}-\text{H}_2\text{O}$ mixtures, in presence and in absence of salts. A val. of 15×10^{-18} e.s.u. has been calc. for the glycine dipole moment and 2.6 Å. for the radius of the zwitterion. The theory also explains qualitatively the solubility relations of the other aliphatic NH_2 -acids. M. S. B.

Hydration of ions. J. BABOROVSKÝ (Coll. Czech. Chem. Comm., 1934, 6, 283—284).—No trustworthy method exists for determining the no. of solvent mols. bound by co-ordinate linkings to an ion.

A. G.

Theory of acids and bases and protolytic solvents. J. N. BRONSTED (Z. physikal. Chem., 1934, 169, 52—74).—Every protolytic reaction is a special case of acid 1 + base 2 acid 2 + base 1, and the protolysis const. can be expressed in terms of the potential strength consts. of the acids and bases. Electrolytic dissociation of a pure solvent is to be regarded as autoprotolysis, and the electrolytic dissociation of dissolved acids and bases is caused by the protolytic properties of the medium. It is impossible to compare the strengths of acids and bases in different media by means of protolytic reactions, such as indicator reactions. R. C.

Acidity of strong acids and methods for its determination. A. HANTZSCH (Z. physikal. Chem., 1934, 169, 189—192).—Polemical against Blaser (this vol., 371). H_3PO_2 is not suitable as a substrate for measuring the strength of strong acids, for it gives different results from other methods and its constitution is unknown. R. C.

State of iodine in solution. M. CHATELET (Ann. Chim., 1934, [xi], 2, 5—57).—The evaporation at 18° of solutions of I in $\text{C}_5\text{H}_5\text{N}$ containing 450 g. per litre gives yellow needles which decompose to black

crystals of I (complete in about 10 min.). From arrests in the wt.-time curves for an evaporating solution it is inferred that the unstable compound $(\text{I}, \text{C}_5\text{H}_5\text{N})_m$ is formed, where m is probably 2. The addition of H_2O to the I solution produces a yellowish-orange ppt. By plotting results on a triangular diagram the existence of the compounds (not isolated) $\text{I}_2(\text{C}_5\text{H}_5\text{N})_4$, approx. $29\text{H}_2\text{O}$ and $\text{I}_2\text{C}_5\text{H}_5\text{N} \cdot 6\text{H}_2\text{O}$ is inferred. Solubilities of I in various solvents have been determined at 18°, and the relation between solvent and solubility is discussed. Measurements of the absorption coeff. (μ) show that all solutions (except CCl_4) deviate from Beer's law. The plot of μ against λ gives a max. for the violet and red, but not for the brown, solutions. It is inferred that the whole of the I in the brown solutions is combined, but that in the violet or red solutions it exists in two forms, probably free and combined, the former of which disappears in very dil. solution.

R. S. B.

Dissociation of the selenates of zinc and cadmium in water. W. H. BANKS (J.C.S., 1934, 1010—1012).— $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$ have been prepared and the electrical conductivities of aq. solutions of the two salts measured. They behave as weak electrolytes of the same order of strength as the corresponding sulphates. The vals. for Λ_0 are 128.8 and 130.0, and for the dissociation const. K , 0.0065 and 0.0054, respectively.

M. S. B.

Equilibrium constant of the bromine hydrolysis and its variation with temperature. H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1934, 56, 1500—1505).—The conductivity of aq. Br has been measured at 0—35° and the equilibrium const., K_1 , for the hydrolysis calc. The variation of with temp. is anomalous near 0°. The existence of Br_5^- is highly probable; the vals. 0.025 at 0° and 0.050 at 25° for $[\text{Br}']/[\text{Br}_2]^2/[\text{Br}_5^-]$ are confirmed. E. S. H.

Equilibria in aqueous solutions of bromine and potassium bromide. G. JONES and S. BAERCKSTROM (J. Amer. Chem. Soc., 1934, 56, 1517—1523).—Conductance measurements at 25° show that the hydrolysis const. of Br in H_2O is 5.8×10^{-9} , whilst the calc. equiv. conductances of Br_3^- and Br_5^- are 43 and 30 reciprocal ohms per cm., respectively. Activity coeffs. of Br in aq. KNO_3 (0.1—1.0*N*) have been measured. The total solubility of Br in H_2O at 25° is 0.2141 mol. per litre, of which 0.2098 is present as Br_2 . The solubility of Br in KBr (0.01—1.0*N*) has been determined. The equilibrium consts. of the reactions $\text{Br}_2 + \text{Br}'$ Br_3' and $2\text{Br}_2 + \text{Br}'$ Br_5' are 16.0 and 40, respectively. E. S. H.

Influence of ionic forces on the dissociation of organic acids of medium strength. H. VON HALBAN and G. KORTUM (Z. Elektrochem., 1934, 40, 502—507).—A photo-electric method has been used for determining the concn. dissociation const. K_a of 2:4-dinitrophenol in aq. solution with and without neutral inorg. salts. The mean activity coeff. of the dinitrophenyl ion in < 0.01*M* solutions and the true thermodynamic dissociation const. K_a have been calc. Uni-univalent electrolytes increase K_a equally up to the ionic concn. 0.01*N*; at higher concns. individual

differences appear among the salts; about 0.5*N* salt solutions produce a max. val. of K_c , after which a rapid fall occurs.

E. S. H.

Activity of hydrogen chloride in glacial acetic acid and other solvents. B. O. HESTON and N. F. HALL (J. Amer. Chem. Soc., 1934, 56, 1462—1466).—Calculations of the activity of HCl from e.m.f. measurements of cells of the type Pt|chloranil (satd.), hydrochloranil (satd.), HCl (*m*), AgCl (satd.)|Ag are in agreement with the v.-p. measurements of Rodebush and Ewart (A., 1932, 339) and with the theory of Gronwall, La Mer, and Sandved (A., 1928, 841).

E. S. H.

Activity coefficients of sulphuric acid in aqueous solutions of ammonium sulphate at 25°. H. D. CROCKFORD and N. L. SIMMONS, jun. (J. Amer. Chem. Soc., 1934, 56, 1437—1438).—Activity coeffs. of H_2SO_4 have been calc. from e.m.f. measurements of the cells $H_2|(NH_4)_2SO_4(m), H_2SO_4(m=0.1 \text{ and } 0.01)|Hg_2SO_4|Hg$.

E. S. H.

Dissociation constants of organic acids. IX. Some amic acids. G. H. JEFFERY and A. I. VOGEL (J.C.S., 1934, 1101—1105).—In order to determine the primary dissociation const. of certain dibasic org. acids, the conductivity of the Na salt of the corresponding amic acid has been measured. Since the mol. vols. of the CO·NH₂ and CO₂H groups are approx. equal, a close approximation to the mobility of the acid ion may be obtained. Data for Na malonate, succinate, glutamate, and adipate show that the mobilities of the anions are 34.7, 30.3, 28.4, and 27.1, respectively. By determining also the conductivity of the corresponding acids the classical dissociation consts. of the latter have been obtained, viz., $K \times 10^5 = 2.482, 3.052, 2.641, \text{ and } 2.477$, respectively.

M. S. B.

Thermodynamic dissociation constant of benzoic acid from conductance measurements. F. G. BROCKMAN and M. KILPATRICK (J. Amer. Chem. Soc., 1934, 56, 1483—1486).—The equiv. conductivities of aq. BzOH and KOBz have been determined at 25°. The calc. thermodynamic dissociation const. for BzOH is 6.312×10^{-5} . The results confirm the limiting law of Debye and Hückel.

E. S. H.

Ionisation constants of certain sulphur derivatives of phenylacetic acid at 0° and 25°. H. D. CROCKFORD and T. B. DOUGLAS (J. Amer. Chem. Soc., 1934, 56, 1472—1473).—Ionisation consts. of PhS·CH₂·CO₂H, Ph·SO·CH₂·CO₂H, and Ph·SO₂·CH₂·CO₂H have been determined conductometrically, and the corresponding free energies and heats of ionisation calc.

E. S. H.

Dissociation constants of aminium and silver-diamine ions, and a relation between them. E. LARSSON (Z. physikal. Chem., 1934, 169, 207—223).—The dissociation exponents, pK , of various Ag-diamino-ions in aq. EtOH (50 mol.-%) have been obtained from determinations of $[Ag^+]$ in solutions of AgNO₃ and amine. For such an ion pK is about 0.7 times pK for the corresponding aminium ion in H₂O. The weaker is the base the less stable is the corresponding complex ion. For these complex ions pK varies little with the ratio of EtOH to H₂O in the sol-

vent. Existing data show that the difference in pK for an aminium ion in H₂O and aq. EtOH is practically independent of the constitution of the solute, and the same is true for many carboxylic acids.

R. C.

Hydrolysis of chrome alum solutions. W. R. ATKIN and E. CHOLLET (J. Soc. Leather Trades Chem., 1934, 18, 356—375).—Titration curves for boiled and unboiled aq. Cr alum (I) show that free H₂SO₄ is formed on boiling, but that this is not in equilibrium with the basic Cr salt. The ppt. formed on adding NaOH to boiled (I) is a basic sulphate containing one SO₄ per 4Cr. The SO₄ groups outside the complex are equally divided between the Cr complex and the H⁺ of the free acid. The 24 co-ordination positions corresponding with the 4 Cr atoms are occupied in 1% (I) by 3OH, 3SO₄, and 12H₂O, and in 15% (I), by 2OH, 4SO₄, and 12H₂O.

D. W.

F.p. of aqueous solutions. VII. Ethyl alcohol, glycine, and their mixtures. G. SCATCHARD and S. S. PRENTISS (J. Amer. Chem. Soc., 1934, 56, 1486—1492; cf. this vol., 596).—A method for expressing the thermodynamic functions of dil. solutions of several non-electrolyte components is developed, reducing to a min. the no. of measurements necessary to determine the chemical potential of any component. The method is applied to f.-p. determinations with glycine, EtOH, and their mixtures.

E. S. H.

Relative strengths of certain monohydric phenols in aqueous-alcoholic solution. L. J. SUMMERBELL (J.C.S., 1934, 996—998).—The reactivities of the 0.25*N*-K salts of seventeen monohydric phenols towards 0.5*N*-EtOAc, -EtCO₂Et, and -PrCO₂Et have been determined at 60° in EtOH with 5% H₂O. The velocity coeffs. obtained are the product of the dissociation const. K of the phenoxide and the velocity coeff. of hydrolysis k of the ester, which is the same for a given ester independently of the phenoxide employed. The relative acidities of the phenols examined and also, by comparison with K for *o*-C₆H₄Me·OK (hydrolysis 4.9%; cf. this vol., 970), the approx. % hydrolysis of the 0.25*N*-K salts have been calc. The MeO group increases the acidity, whilst alkyl groups reduce it in the order Pr^o > Me > Et. The steric effect of Me groups in reducing acidity is $o > p > m$.

M. S. B.

Complex formation involving weak acids. VIII. Optical rotation of solutions of tartaric acid, tartaric acid during neutralisation, and of neutral tartrates, with a note on the effect of sodium chloride. IX. Complex formation between boric and tartaric acids. X. Complex formation between tartaric acid and (a) arsenic acid, (b) arsenious acid, (c) antimonious hydroxide, in acid and alkaline solutions. The dissociation constants of arsenious and arsenic acids. XI. Complex formation between tartaric acid and (a) molybdic acid, (b) tungstic acid. H. T. S. BRITTON and (MISS) P. JACKSON (J.C.S., 1934, 998—1002, 1002—1010, 1048—1055, 1055—1062).—VIII. The rotatory power of solutions of (a) tartaric acid (I) alone and during neutralisation with NaOH, (b) Na₂, K₂, and (NH₄)₂ tartrates, and (c) (I) and Na₂ tartrate in presence of NaCl, has been

measured at 25° with the Na-D and Hg 5461 Å. lines. The mol. rotations of (I), HT', and T'' have thus been calc., and show that variations in optical activity of solutions of (I) on dilution can be explained by the extent of ionisation (calc. on the basis of the classical theory) to $H^+ + HT'$. The progressive increase in optical activity during neutralisation can be accounted for by the mol. rotations of (I), HT', and T''.

IX. Rotatory powers, p_H , and electrical conductivities of five series of solutions, containing (I) and HBO_2 in various stages of neutralisation, have been determined at 25°. The variations observed are in accordance with the view that a complex borotartaric acid is formed, probably $2H_2T.HBO_2$, that the salt formed in acid solution is $NaHT.Na_2T.HBO_2$, and that in alkaline solution a levorotatory complex salt, involving also the alcoholic groups, is obtained.

X. K_1 , K_2 , and K_3 for H_3AsO_4 , determined by the glass electrode, are, respectively, 5.6×10^{-3} , 1.7×10^{-7} , and 3.0×10^{-12} , and K_1 for H_3AsO_3 is 5.7×10^{-10} . Optical and electrometric titration measurements indicate that complex formation occurs in acid solutions of (I) and H_3AsO_3 until sufficient NaOH is added to form $NaHT.xH_3AsO_3$. Further addition of NaOH causes decomp., which is complete when sufficient is present to give Na_2T and NaH_2AsO_3 . In (I)- $Sb(OH)_3$ solutions the max. effect is given by $NaHT.Sb(OH)_3$. Further addition of alkali results in another type of complex formation. The solutions become strongly levorotatory to an extent depending on the ratio of $Sb(OH)_3$ to (I). No complex formation appears to occur in (I)- H_3AsO_4 solutions.

XI. In the neutralisation of solutions containing 0.1M-(I) + $xM.XO_3$ ($X=Mo$ or W) polarimetric and electrometric measurements indicate the formation of a complex salt $Na_2(XO_3)_xT$ until NaOH equiv. to (I) has been added. Further addition of NaOH results in the formation of Na_2T and Na_xXO_4 .

M. S. B.

Activity of sodium in concentrated liquid amalgams. E. S. GILFILLAN, jun., and H. E. BENT (J. Amer. Chem. Soc., 1934, 56, 1505—1509).—The activity of Na in conc. Na-Hg is approx. that of pure Na. The v.p. of Hg in the conc. amalgam is probably $< 10^{-10}$ mm.

E. S. H.

Thermodynamic functions of aluminium, α -aluminium oxide, β -graphite, oxygen, and carbon monoxide. L. TEREBESI (Helv. Chim. Acta, 1934, 17, 804—819).—A discussion of published work.

E. S. H.

Zero entropy of β -graphite. L. TEREBESI (Helv. Chim. Acta, 1934, 17, 819—837).—A review of the available evidence does not favour the view that β -graphite is associated with zero entropy.

E. S. H.

Determination of activity coefficients by adsorption. P. P. KOZAKEVITCH and K. F. MICHALKOV (Bull. Soc. chim., 1934, [v], 1, 644—653).—Assuming that only non-ionised mols. of weak electrolytes are adsorbed, activity coeffs. of undissociated AcOH in salt solutions are calc. from adsorption data (A. 1931, 1121). The vals. for NaCl solutions agree with those from distribution data (A., 1926, 1094), but with other salts there are discrepancies, especially

nitrites which have an abnormal influence on adsorption. Activity coeffs. of picric acid (I) at 30° have been calc. from the distribution between aq. NaCl and C_6H_6 . The solubility and activity coeff. of undissociated (I) pass through maxima with increasing [NaCl]. NaCl, at all concns., diminishes the adsorption of (I) on C owing to adsorption of Na picrate, and hence the activity coeff. of (I) cannot be calc. from these data.

J. G. A. G.

Foundation of the second law of thermodynamics on cyclic processes. H. HAUSEN (Physikal. Z., 1934, 35, 517—524).—Theoretical.

A. J. M.

Systematic studies in combination. LX. Combination of phosphorus with iron. W. FRANKE, K. MEISEL, and R. JUZA (Z. anorg. Chem., 1934, 218, 346—359).—By means of v.p. and X-ray measurements the existence of Fe_3P , Fe_2P , and FeP has been confirmed, and that of the compound FeP_2 established; $d_4^{25} = 7.11, 6.77, 6.07$, and 4.95 , respectively. The heats of formation of the compounds diminish markedly per atom of P with increasing P content.

M. S. B.

System $SiO_2-Al_2O_3$. O. REBUFFAT (Giorn. Chim. Ind. Appl., 1934, 16, 213—215).—Composition-m.p. diagrams for the systems SiO_2 (tridymite)- Al_2O_3 (I), SiO_2 -sillimanite (II), and SiO_2 -dehydrated kaolinite (III) have been determined. For (I), addition of Al_2O_3 causes a continuous fall of the m.p. to a eutectic at 1650° and 40% Al_2O_3 . For (II) and (III) the eutectic is at 1630—1640° and 20% Al_2O_3 . No evidence could be obtained for the existence of a eutectic at 1545° and 5.5% Al_2O_3 , as reported by Bowen and Greig. Mullite does not resist attack by HF; all fused mixtures of SiO_2 and Al_2O_3 , of whatever type, lose SiO_2 when treated repeatedly with HF, the residue being mainly AlF_3 .

H. F. G.

Thermal analysis of the system sulphuric acid-water and the low-temperature densities of crystallised sulphuric acid hydrates. O. HULSMANN (Z. anorg. Chem., 1934, 218, 369—378).—Thermal analysis indicates two new hydrates, $H_2SO_4.6H_2O$ and $H_2SO_4.8H_2O$; peritectic decomp. temp. -54° and -62° , and $d^{-273} 1.44_5$ and 1.45_5 , respectively. M.p. and d^{-273} for the other hydrates are: H_2O , 8.5° , 2.02; $2H_2O$, -39° , 1.76_5 ; $4H_2O$, -28.5° , 1.59_5 . The nature of the combined H_2O is discussed on the basis of differences of mol. vol. at -273° .

M. S. B.

Binary system $Ni(NO_3)_2-H_2O$ and the 25° isotherm of the ternary system $Ni(NO_3)_2-HNO_3-H_2O$. A. SIEVERTS and L. SCHREINER (Z. anorg. Chem., 1934, 219, 105—112).—The solid phases in the binary system between -35° and 120° are ice and the hydrates $Ni(NO_3)_2.9, 6, 4$, and $2H_2O$. No $Ni(NO_3)_2.3H_2O$ formation was observed. The solid phases in the ternary system at 25° are $Ni(NO_3)_2.6, 4$, and $2H_2O$.

M. S. B.

F.p. and v.p. of the system potassium fluoride-hydrogen fluoride. G. H. CADY (J. Amer. Chem. Soc., 1934, 56, 1431—1434).—Besides the three recognised acid salts, $KF.4HF$ and $2KF.5HF$ have been

identified. Two solid forms of $\text{KF} \cdot \text{HF}$ exist, having a transition point at 195° . E. S. H.

Equilibrium diagram of the system Na_2TiO_3 - K_2TiO_3 . U. NISHIOKA (Sci. Rep. Tohoku, 1934, 23, 261—264).—A eutectic point has been found at 773° with 18 mol.-% Na_2TiO_3 and a monotectic at $893^\circ \pm 3^\circ$ with 50—80 mol.-% Na_2TiO_3 . H. S. P.

Fusion curves of systems Br_2 - CHCl_3 , Br_2 - CCl_4 , CHCl_3 - CCl_4 . J. SAMESHIMA and T. HIRAMATSU (Bull. Chem. Soc. Japan, 1934, 9, 260—262).— CHCl_3 - Br_2 and CCl_4 - Br_2 are simple eutectic systems, but CCl_4 - CHCl_3 forms a compound $\text{CHCl}_3 \cdot 4\text{CCl}_4$, m.p. -55° . R. S. B.

Equilibrium in the system camphor-sulphur dioxide. F. ISHIKAWA, S. MITSUI, and T. MUROOKA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 684—696).—Equilibrium pressures for the system $\text{C}_{10}\text{H}_{16}\text{O}$ - SO_2 have been measured from 30° to -38° . The affinity and heat of reaction have been calc. R. S. B.

Fusion diagrams of organic substances which form mixed crystals. W. BRULL (Naturwiss., 1934, 22, 436).—The investigation of pairs of org. substances forming continuous ranges of mixed crystals by thermal analysis shows that crystal layers are formed on freezing, and not, as is usually supposed, homogeneous mixed crystals. Complete homogenisation takes place only after a considerable time. In the outer cryst. layer there is an increase in the proportion of the compound of lower mol. wt.; hence the initial m.p. is lower than that of homogeneous mixed crystals. Dilatometric experiments show that the homogeneity of the crystals deposited on freezing varies with the rate of cooling. A. J. M.

Temperature of the transformation interval of binary glasses of B_2O_3 with Na_2O and BaO . E. JENCKEL (Z. Elektrochem., 1934, 40, 541).—When the transformation temp., determined from viscosity-temp. measurements, is plotted against composition, the curve consists of three parts: (a) from B_2O_3 to $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ (or $\text{BaO} \cdot 4\text{B}_2\text{O}_3$), (b) from $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ to $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$, (c) from $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ to higher alkali contents. E. S. H.

Decomposition pressures, especially of hydrated oxides, as equilibrium magnitudes. R. FRICKE and P. ACKERMANN (Z. physikal. Chem., 1934, 169, 152—155; cf. this vol., 133).—The decomp. pressure observed with a hydrated oxide at a given temp. often rises slowly for weeks. Measurements of heat of dissolution show that the decomp. product, particularly the oxide, has initially an abnormally high energy content, which approaches the normal val. the more nearly as the time allowed for the establishment of a "const." pressure increases. The high energy content is primarily due to the very imperfect oxide lattice formed at relatively low temp. R. C.

Thermal dissociation of sodium hydrogen sulphate. F. ISHIKAWA, K. MASUDA, and H. HAGISAWA (Sci. Rep. Tohoku, 1934, 23, 164—181).—The rate of decomp. of NaHSO_4 , m.p. 182° , at various temp. has been studied. At 240 — 250° pure $\text{Na}_2\text{S}_2\text{O}_7$ is formed. The v.p. of the system $2\text{NaHSO}_4 \rightleftharpoons \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$

has been measured from 130° to 180° and the solubility of $\text{Na}_2\text{S}_2\text{O}_7$ in NaHSO_4 determined. H. S. P.

Crystallisation diagrams of the system copper-lead-sulphur. W. GUERTLER and G. LANDAU (Z. anorg. Chem., 1934, 218, 321—345).—Space diagrams of the systems Pb - Cu_2S - PbS and Pb - Cu_2S - Cu have been constructed on the basis of thermal data previously obtained. M. S. B.

System CaO - SiO_2 - H_2O at 30° and the reaction of water on the anhydrous calcium silicates. E. P. FLINT and L. S. WELLS (Bur. Stand. J. Res., 1934, 12, 751—783).—The solubility of SiO_2 in solutions of $\text{Ca}(\text{OH})_2$ combined with electrometric measurements for saturated and supersaturated solutions indicate the existence of $\text{Ca}(\text{H}_2\text{SiO}_4)_2$, CaH_2SiO_4 , $\text{Ca}_3(\text{HSiO}_4)_2$, and Ca_2SiO_4 . The hydrolysis consts. of these compounds have been determined, and ionisation consts. for the successive stages in the dissociation of H_4SiO_4 are given as 2.2×10^{-10} , 2.0×10^{-12} , 1×10^{-12} , and 1×10^{-12} , respectively. On keeping with H_2O , $3\text{CaO} \cdot 2\text{SiO}_2$, γ - $2\text{CaO} \cdot \text{SiO}_2$, β - $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{SiO}_2$ all pass into hydrated forms corresponding with the equilibrium relation of the CaO - SiO_2 - H_2O system, but $\text{CaO} \cdot \text{SiO}_2$ is unaffected. The probable products of the action of H_2O on Portland cement are $\text{Ca}_2\text{SiO}_4 \cdot n\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2$. The presence of traces of CaSO_4 has practically no effect on the rate of reaction between H_2O and the silicates. The reactions between diatomaceous SiO_2 and aq. $\text{Ca}(\text{OH})_2$ and between SiO_2 gel and $\text{Ca}(\text{OH})_2$ have also been investigated. J. W. S.

System cadmium sulphate-cobalt sulphate-water. H. BASSETT and (Miss) I. SANDERSON (J.C.S., 1934, 1116—1120).—The system has been studied at 25° and 80° . The results show definitely the existence of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, which at 80° forms red solid solutions with the corresponding Co compounds, indicating that Cd is not so exceptional in forming a fractional hydrate as previously supposed. Solid solutions are formed by $\text{CdSO}_4 \cdot 7\text{H}_2\text{O}$ and $4\text{H}_2\text{O}$ and α - and β - $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ with the corresponding Co compounds. Simple structures are suggested for $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ and $\text{CdSO}_4 \cdot \text{H}_2\text{O}$. M. S. B.

System zinc oxalate, potassium oxalate, water. II. At 35° . V. METLER (J. Amer. Chem. Soc., 1934, 35, 1509—1510; cf. A., 1933, 906).—The solubility of ZnC_2O_4 (I) and $\text{K}_2\text{Zn}(\text{C}_2\text{O}_4)_2$ (II) in $\text{K}_2\text{C}_2\text{O}_4$ solutions has been determined at 35° . The stable compound in equilibrium with dil. solutions is (I), and with conc. solutions (II). $\text{K}_2\text{Zn}_2(\text{C}_2\text{O}_4)_3 \cdot 12\text{H}_2\text{O}$ exists in metastable equilibrium with dil. aq. $\text{K}_2\text{C}_2\text{O}_4$. E. S. H.

Thermodynamic studies of sodium iodide and potassium iodide. F. ISHIKAWA, K. TACHIKI, and T. MUROOKA (Sci. Rep. Tohoku, 1934, 23, 147—163).—E.m.f. data for the cells $\text{K}(\text{Hg})|\text{KI}(\text{s})$, EtOH solution, $\text{AgI}|\text{Ag}$, $\text{K}(\text{Hg})|\text{KI}(\text{s})$, EtOH solution, $\text{CuI}|\text{Cu}$ or $\text{Cu}(\text{Hg})$, $\text{Na}(\text{Hg})|\text{NaI}(\text{s})$, isoamyl alcoholic solution, $\text{CuI}|\text{Cu}(\text{Hg})$ at 25° lead to the following: $\text{K} + 0.5\text{I}_2 = \text{KI}(\text{s})$, $\Delta F_{298}^\circ = -77,524$ g.-cal., $\Delta H_{298}^\circ = -79,670$ g.-cal., $\text{Na} + 0.5\text{I}_2 = \text{NaI}(\text{s})$, $\Delta F_{298}^\circ = -68,465$ g.-cal., $\Delta H_{298}^\circ = -69,700$ g.-cal. A complex $\text{AgI} \cdot 2\text{KI}$ is formed in EtOH solution at 25° . The solubilities of

NaI and CuI in isoamyl alcohol at 25° are 16.32 g. and 2.496 g. per 100 g., respectively, and the formation of the complex $(\text{CuI}_2)_2\text{Na}$ has been established.

H. S. P.

Heat of formation of nitrides. V. **Heat of combustion of some metals and metallic nitrides.** B. NEUMANN, C. KROGER, and H. KUNZ (Z. anorg. Chem., 1934, 218, 379—401).—The heats of combustion of Zr, Ti, Mo, Be, and Ta and their nitrides, and also that of Th_3N_4 , have been determined and the heats of formation of the nitrides calc. The relation between the at. no. of an element and the heat of formation of its nitride is considered and the properties of the nitrides are discussed in reference to the above relation.

M. S. B.

Heats of formation of iron nitrides. S. SATOH (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 720—724).—The heats of formation of Fe_4N and Fe_2N have been calc. by means of Nernst's heat theorem from sp. heats, and equilibrium data for the systems $\text{Fe}-\text{Fe}_4\text{N}-\text{NH}_3-\text{H}_2$ and $\text{Fe}_4\text{N}-\text{Fe}_2\text{N}-\text{NH}_3-\text{H}_2$ calc. Vals. agree with those determined calorimetrically.

R. S. B.

Free energy of sulphur monoxide and the dissociation constants of S_2 . C. W. MONTGOMERY and L. S. KASSEL (J. Chem. Physics, 1934, 2, 417—418).—Free energies of S_2 , SO, and S have been calc. from spectroscopic data and equilibrium consts. have been obtained for the reactions: $2\text{SO} \rightarrow \text{S}_2 + \text{O}_2$; $2\text{SO} \rightarrow 0.5\text{S}_2 + \text{SO}_2$; $\text{S}_2 \rightarrow 2\text{S}$. SO is stable with respect to the first mode of decomp., and also with respect to the second at flame temp., but with respect to the latter it is very unstable below 1000° abs.

M. S. B.

Dissociation of ammonium phosphate. A. DE PASSILLÉ (Compt. rend., 1934, 199, 356—358).—In the Nernst equation, $\log p = (-Q_0/4.57T) + 1.75 \log T + 3.3$, Q_0 is 16,600 g.-cal. for $(\text{NH}_4)_2\text{HPO}_4$, and 11,540 g.-cal. for $(\text{NH}_4)_3\text{PO}_4$. A compound $(\text{NH}_4)_5\text{H}(\text{PO}_4)_2$ is probably formed in the dissociation of $(\text{NH}_4)_3\text{PO}_4$, and breaks down as follows: $(\text{NH}_4)_5\text{H}(\text{PO}_4)_2 \rightarrow (\text{NH}_4)_4\text{H}_2(\text{PO}_4)_2 + \text{NH}_3$. For this dissociation, Q_0 is 13,650 g.-cal.

A. J. M.

Thermochemistry of the ammonium phosphates. A. DE PASSILLÉ and M. SÉON (Compt. rend., 1934, 199, 417—419).—The heats of neutralisation of the successive H atoms of H_3PO_4 with aq. NH_3 have been measured calorimetrically, and the heats of dissolution and heats of formation of $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_3\text{PO}_4$, and $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ are calc.

J. W. S.

Heat of crystallisation of hydrated salts in slightly supersaturated solutions. J. PERREU (Compt. rend., 1934, 199, 48—51).—"Intermediate heat of crystallisation," K_c^i , is defined as the mol. heat evolved during the crystallisation of a slightly supersaturated solution through the concn. range C_1 —Measurements of K_c^i for a no. of hydrated salts give vals. $-q_c$, the limiting heats of dissolution, as required by theory.

B. W. B.

Heats of dilution of ammonium chloride and mono-, di-, tri-, and tetra-methylammonium chlorides in water up to high dilution, (a) at

25°. H. STREECK (Z. physikal. Chem., 1934, 169, 103—112).—Integral and differential heats of dilution are recorded from 0.0002 to 0.5 molal.

R. C.

Apparent paradox in the theory of the heats of dilution of completely dissociated electrolytes. O. GATTY (Phil. Mag., 1934, [vii], 18, 46—63).—Theoretical.

H. J. E.

Heats of combustion and combination of organic compounds in relation to their composition. E. JANECKE (Z. Elektrochem., 1934, 40, 462—468).—Published data for (a) hydrocarbons, (b) amines and nitriles, and (c) compounds containing O are recorded graphically.

E. S. H.

Calorimetric determination of the heats of combustion of ethane, propane, normal butane, and normal pentane. F. D. ROSSINI (Bur. Stand. J. Res., 1934, 12, 735—750; cf. A., 1931, 433, 1011, 1236; 1932, 341).—Using the calorimetric method described previously, the following results have been obtained: C_2H_6 372.18 ± 0.11 ; C_3H_8 530.57 ± 0.12 ; $n\text{-C}_4\text{H}_{10}$ 687.94 ± 0.15 ; and $n\text{-C}_5\text{H}_{12}$ 845.27 ± 0.21 kg.-cal. per mol.

J. W. S.

Determination of heat of combustion of organic sulphur compounds. G. BECKER and W. A. ROTH (Z. physikal. Chem., 1934, 169, 287—296).—In the combustion of S compounds in the bomb under suitable conditions all the S is converted into H_2SO_4 . The results for heat of combustion must therefore be recalcd. to a definite concn. of H_2SO_4 , which is conveniently $\text{H}_2\text{SO}_4, 10,000\text{H}_2\text{O}$. Heats of dilution to this concn. are tabulated, and determinations of the heat of combustion of cystine, cysteine, and $\text{CS}(\text{NH}_2)_2$ are reproduced as examples.

R. C.

Theory of molecular compounds of organic nitro-compounds. G. BRIEGLEB (Z. physikal. Chem., 1934, B, 26, 63—70).—Heats of dissociation of mol. compounds of C_{10}H_8 and anthracene with NO_2 -compounds calc. on the assumption that the mutual saturation of residual affinity depends on an induction effect are of the same order of magnitude as the observed vals. The calculation is only approx., since the initially localised perturbation spreads over the whole mol. and this effect cannot be precisely evaluated.

R. C.

Application of the ice calorimeter to determination of the heat evolved by pitchblende. W. ŚWIĘTOSTAWSKI, I. ŻŁOTOWSKI, J. SALCEWICZ, J. USAKIEWICZ, and A. ZMACZYŃSKI (Roczn. Chem., 1934, 14, 301—303).—The results obtained for pitchblende are > those obtained by other authors using different calorimeters; the discrepancy is ascribed to the comparatively high experimental error (> 10% for heat effects of the order of 7×10 g.-cal. per hr.)

R. T.

Molar Peltier heats of pure metallic two-phase systems. J. MONHEIM (Z. Elektrochem., 1934, 40, 375—378).—Theoretical.

E. S. H.

New method for determination of transport numbers. I. Theory of the method. G. HARTLEY. II. Exploratory. E. DREW and G. HARTLEY. III. Balanced boundary apparatus. B. COLLIE and G. S. HARTLEY (Trans. Faraday

Soc., 1934, 30, 648—653, 653—657, 657—662).—I. The theory of a new application of the moving-boundary method for the determination of transport nos. (T) is described, using Kohlrausch's relation between the concns. of the leading and indicator solutions. Measurements show that T for radicals of very low mobility can be determined. The influence of vol. changes and of impurities is discussed.

II. An apparatus is described for determining the concn. of the Kohlrausch solution by conductrimetric (a) and external (b) analysis. (a) is unsatisfactory for 0.01*N* solutions owing to cyclic electrolysis, whilst (b) gives erratic results owing to mixing of the leading and indicator solutions during displacement.

III. An improved method of external analysis, in which the sample of Kohlrausch solution is displaced by a piston without interrupting the current, is described. Results agree satisfactorily with calc. vals. for electrolytes of known T . R. S. B.

Conductivity of concentrated mixtures of alkali chlorides. P. VAN RYSELBERGHE and L. NUTTING (J. Amer. Chem. Soc., 1934, 56, 1435—1437).—A formula is derived for the equiv. conductivity of a mixture of alkali chlorides in terms of the conductivities and transport nos. of the pure components at the same concn. as the total concn. of the mixture. With KCl and NaCl the calc. and determined vals. agree up to a total concn. of 4*N*. E. S. H.

Conductivity of some chlorides, iodides, and nitrates of alkalis and alkaline earths in water and methyl, ethyl, and *n*-propyl alcohols. H. N. DESAI, D. B. NAIK, and B. N. DESAI (Indian J. Physics, 1934, 8, 323—340).—Data tabulated and plotted for an extended range of concns. show wide departures from the Debye-Huckel-Onsager theory, particularly at high concns. The data show, on the other hand, that the relation between λ_c and c can be expressed by $\lambda_c = Kc^n$. N. M. B.

Electrical conductivity of salts in anhydrous hydrogen cyanide. J. E. COATES and E. G. TAYLOR (Nature, 1934, 134, 141).—Over a concn. range 0.0001—0.005*N* most of the salts obey the relation $\Lambda_c = \Lambda_0 - x\sqrt{c}$, and the vals. of x agree with those calc. by means of the Debye-Huckel-Onsager equation. There appears to be an increasing tendency to ionic association in the order $K < Na < Li$. The vals. of Λ_0 , obtained by extrapolation of the linear portions of the $\Lambda_c - \sqrt{c}$ plots, are approx. 3 times those in H_2O , and support the view that the dissociation is practically complete at the dilutions used. The order of increasing ionic mobility is $Na^+ < Li^+ < NEt_4^+ < K^+ < NMe_4^+$, NH_4^+ and picrate $< NO_3^- < ClO_4^- < CNS^- < Cl^- < Br^- < I^-$. L. S. T.

Electrolytes in media of low dielectric constant. R. M. FUOSS and C. A. KRAUS (J. Chem. Physics, 1934, 2, 386—389).—Halpern and Gross' conductivity relation for electrolytes in media of low dielectric const. (this vol., 599) is compared with the conductivity data for tetraisoamylammonium picrate in C_6H_6 and shown to be unsatisfactory, whilst the authors' formula (cf. *ibid.*, 25) reproduces

experimental data over a wide range of conditions. It is also shown that the Bjerrum radius is not of decisive importance in the interpretation of conductivity data. M. S. B.

Electrolytic potential of nickel. L. COLOMBIER (Compt. rend., 1934, 199, 273—275).—Previous measurements of the electrode potential of Ni have probably been vitiated by using specimens which have been exposed to the air or have been prepared in a superactivated state by electro-deposition with a high c.d. Using samples of metal cut out of commercial sheet, electrolytic Ni, and reduced Ni, pre-treating these by heating at 500° in vac. for 1 hr., and making contact with the electrolyte in the absence of air, the potential of Ni against *N*- $NiSO_4$ solution at 20° is -0.227 ± 0.002 volt. J. W. S.

Variation of the electrolytic potential of nickel with acidity. L. COLOMBIER (Compt. rend., 1934, 199, 408—409; see preceding abstract).—Above p_H 4, the potential of pure Ni (heated in vac. at 500° for 1 hr.) against *N*- $NiSO_4$ remains const. Below this p_H the potential rises and runs parallel with that of the H_2 electrode. With unheated Ni the results are similar, but the potential is less negative. J. W. S.

Standard potential of the bromine electrode. G. JONES and S. BAECKSTROM (J. Amer. Chem. Soc., 1934, 56, 1524—1528).—E.m.f. of cells of the type $Pt|KBr+Br_2, KBr, AgBr|Ag$ have been measured at 25°: $E_{298} = -0.9940$ volt; free energy of formation of $AgBr = -22,935$ g.-cal. The $Ag, AgBr$ electrode has been compared with the Hg, Hg_2Cl_2 and $Ag, AgCl$ electrodes and the vals. -1.0652 and -1.0852 volts have been deduced for the standard electrode potentials of liquid Br and of Br at unit activity, respectively. E. S. H.

Measurements with the hydrogen and quinhydrone electrodes in concentrated salt solutions. A. VON KISS and A. URMANCZY (Z. physikal. Chem., 1934, 169, 31—40).—The salt error, E , of the quinhydrone electrode in solutions of various neutral salts has been determined at 25°. With $CaCl_2$ at concns. $> 4N$ and with the other salts above *N*, E increases linearly with the ionic strength, being positive with sulphates and negative with chlorides and nitrates. E is determined primarily by the anion, but is not additively constituted of effects due to anion and cation. For $CaCl_2$ and $MgCl_2$ from 4*N* upwards and for the other salts from *N* upwards the logarithm of the H^+ activity coeff. changes linearly with the salt concn. R. C.

Electrometric titrations of unsaturated dicarboxylic acids. H. W. ASHTON and J. R. PARTINGTON (Trans. Faraday Soc., 1934, 30, 598—614).—Electrometric data and vals. of the first and second dissociation consts. (K_1 and K_2) at 25° are given for succinic, maleic, fumaric, citraconic, mesaconic, itaconic, chloro- and bromo-maleic and -fumaric, and acetylenedicarboxylic acids. The effect of substitution on for the *trans*- is much $>$ for the *cis*-acids, whereas the reverse is the case for K_2 . The distance (r) between the centres of the CO_2H groups has been calc. using (a) Bjerrum's and (b)

Gane and Ingold's formula, the latter giving better agreement with vals. calc. from geometrical considerations for maleic and fumaric acids. r for a substituted maleic acid is always $> r$ for the unsubstituted acid. The charge on the CO_2H group required to account for the divergence between the vals. of K_1/K_2 calc. using (b) and those determined experimentally has been calc. R. S. B.

Oxidation-reduction potentials. I. System phenylhydrazinesulphonate-diazobenzenesulphonate. G. HOLST (Z. physikal. Chem., 1934, 169, 1—19).—The system $\text{PhN:N}\cdot\text{SO}_3' + \text{H}_2 \rightleftharpoons \text{NHPh}\cdot\text{NHSO}_3'$ has been studied over a range of p_{H} at 18° and 37°. Polarisation experiments with bright Pt electrodes have shown that in both 2*N*- H_2SO_4 and *N*-NaOH the cathodic reduction process over a fairly wide range of c.d. agrees with Haber's theory (A., 1904, ii, 309). The potential of a solution containing equal concns. of $\text{PhN:N}\cdot\text{SO}_3\text{K}$ and $\text{NHPh}\cdot\text{NH}\cdot\text{SO}_3\text{K}$, referred to a H electrode under 1 atm. in the same electrolyte solution, is 0.443 at 18° and 0.429 volt at 37°. The change in free energy at 18° is 20.43 and the heat effect 30.3 kg.-cal. Rise in temp. and total concn. facilitates the attainment of a const. and reproducible potential. Various dyes have also been used to catalyse equilibration.

R. C.

Determination of the affinity of formation of silver sulphide (selenide, telluride) by electrometric measurements with solid cells. H. REINHOLD (Z. Elektrochem., 1934, 40, 361—364).—Data for Ag_2S , Ag_2Se , and Ag_2Te have been obtained by measuring the e.m.f. of the cells $\text{Ag}|\alpha\text{-AgI}|\alpha\text{-Ag}_2\text{X}|X$ (where $X=\text{S}$, Se , or Te) at 200°. The e.m.f. of the cell $\text{Ag}|\alpha\text{-AgI}|I$ has been determined at 150°, 200°, and 300°. The thermo-e.m.f. of the cell (S_1) graphite| $\alpha\text{-Ag}_2\text{S}$ |graphite (S_1) at 180—330° is 1.5×10^{-4} volt per degree.

E. S. H.

Electromotive force of the cell $\text{Ag}|\text{AgI}|\text{Ag}_2\text{S}|\text{Pt}(+\text{S})$. C. WAGNER (Z. Elektrochem., 1934, 40, 364—365).—Theoretical. Thermodynamic data for Ag_2S are derived.

E. S. H.

Combination and Daniell cells in melts. G. GRUBE and E. A. RAU (Z. Elektrochem., 1934, 40, 352—360).—The e.m.f. and temp. coeff. of the cells $\text{Pb}|\text{PbCl}_2|\text{Cl}_2$ and $\text{Ag}|\text{AgCl}|\text{Cl}_2$ are altered slightly by inserting a glass diaphragm, whilst in the cell $\text{Pb}|\text{PbCl}_2|\text{glass}|\text{AgCl}|\text{Ag}$ the e.m.f. at 628° (0.158 volt) differs widely from that (0.311 volt) of the same cell without the glass diaphragm. The temp. coeff. of the cells with glass is negative, except the cell $\text{Cl}_2|\text{PbCl}_2|\text{glass}|\text{AgCl}|\text{Ag}$. The difference rule of Lorenz holds. Observations with cells of the type $\text{Pb}|\text{PbCl}_2, \text{KCl}|\text{glass}|\text{AgCl}|\text{Ag}$ show that the temp. coeff. is linear only at high temp., indicating the existence of complexes in the melt.

E. S. H.

Electrochemical behaviour of iron in relation to mechanical or thermal pre-treatment. H. DOMSCHKE (Korros. u. Metallschutz, 1933, 9, 261—268; Chem. Zentr., 1934, i, 115).—The anodic over-voltage and the limiting potential of pure Fe powder compressed in the cold and heated are independent of the pressure employed when measured in 0.1*N*- FeSO_4

against a *N*-KCl, $\text{Hg}_2\text{Cl}_2|\text{Hg}$ electrode. The relation between the thermal and mechanical after-treatments of samples of electrolytic Fe and the corrodibility is a function of the active centres present in the surface.

L. S. T.

Investigation of the surface of iron by the electrogram method. P. D. DANKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 556—561).—Electrograms have been taken of Fe surfaces which have been treated in various ways and conclusions reached relative to the nature of the surface.

H. S. P.

Cathodic and anodic polarisation in aqueous alkali solutions and the influence of the time factor. C. F. HOLMBOE (Z. Elektrochem., 1934, 40, 366—370).—Mainly theoretical. The p.d.-c.d. curve for Fe as anode and cathode in aq. KOH is discussed, with special reference to the influence of time.

E. S. H.

Polarographic investigations of passivity. I. The activation- and passivation-potential of iron. O. M. MÜLLER (Coll. Czech. Chem. Comm., 1934, 6, 269—282).—When the e.m.f. applied to a cell composed of Fe and platinised Pt electrodes in *N*- H_2SO_4 is gradually increased the current at first increases, but falls rapidly at 0.30 volt and again abruptly at 0.56 volt (passivation potential) almost to zero, at which it remains until O_2 is evolved at 1.8 volts. Reducing the e.m.f. causes a sudden increase in current at 0.54 volt (activation e.m.f.). Similar relations are observed at other concns. Three changes in current are observed with H_3PO_4 and one with HNO_3 ; these correspond with the no. of different anions formed. The interval between the passivation and activation e.m.f. depends on the resistance of the cell and disappears when this is zero. If the e.m.f. is maintained at about this val. periodic phenomena are obtained.

A. G.

Surface layer polarisation with chemical passivity. W. I. MÜLLER (Naturwiss., 1934, 22, 479).—According to the electronic theory of passivity, this can occur over the whole surface only if there is very high c.d., whereas it actually occurs with quite small c.d. It is suggested that it is only the c.d. in the pores of the material that should be considered, and if this is so, the val. of the polarisation potential should be about 1 volt. The reversible potential for a metal going into solution in its highest state of oxidation can be calc. by Luther's rule, and can be determined experimentally. The difference between calc. and observed vals. is about 1 volt, thus agreeing with theory.

A. J. M.

Limiting currents in electrolysis with the dropping mercury cathode. J. HEYROVSKY (Arh. Hemiju, 1934, 8, 11—17).—In the reduction of cations the ratio $i_a/i_l = v/(u+v)$, and of anions $= (2v+u)/(u+v)$, where i_a is the diffusion current, and i_l is the limiting current. The i_l of cations is diminished, and that of anions increased largely, by addition of indifferent electrolytes (I); in the reduction of non-electrolytes (I) have no effect. Quant. polarographic determinations should be performed in presence of excess of (I) if diffusion currents are to be measured.

Special cases of the heat effect of electric current in electrolytes and gases. G. J. SMISCH-LIAEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 474—477).—The distribution of potential between the electrodes in electrolytes depends chiefly on the c.d., and is non-uniform. With high c.d. the drop near the anode may be 80—90% of the average drop. The thermal centre is close to the anode. In gases this centre is near the cathode. The distribution of the electric field may be deduced from the location of the thermal centres.

H. J. E.

Dependence on pressure of the electrolytic electrode resistance, particularly in sodium chloride solutions. R. A. J. BOSSCHART (Physica, 1934, 1, 715—724).—The current-voltage relation in aq. NaCl with C or Pt electrodes, measured at pressures to 3 atm. and with c.d. 0.1—8 amp. per sq. cm., is linear (cf. A., 1925, ii, 43). The dependence of over-voltage on pressure is due to a change of resistance with pressure.

H. J. E.

Theoretical treatment of chemical reactions in streaming systems. T. FORSTER and K. H. GEIB (Ann. Physik, 1934, [v], 20, 250—260).—Mathematical. Formulæ have been deduced to represent chemical reactions of the first order in systems in which diffusion as well as streaming occurs.

H. S. P.

Method for measuring the rate of high-velocity gas reactions. L. FROMMER and M. POLANYI (Trans. Faraday Soc., 1934, 30, 519—529).—A modification of the "diffusion method" for measuring the velocity of high-speed gas reactions is described. n particles per sec. of a gas A are introduced into a reaction chamber containing an excess of the other reacting gas of concn. c , and the no. N of A particles in the stationary reaction zone, i.e., the flame, is measured. $k = n/N \times c$. The method enables the fastest gas reaction velocities to be measured and is applied to the measurement of the reaction of Na vapour with MeBr. The vals. obtained are much > those deduced from earlier methods, but are in agreement with those from a revised form of the diffusion method. The velocity of the reaction increases slightly with rise of temp. and is about twenty-five times as great for MeBr as for MeCl. The quantity N of Na vapour in the flame is measured by absorption of light.

M. S. B.

Rate of recombination of atomic hydrogen. II. H. M. SMALLWOOD (J. Amer. Chem. Soc., 1934, 56, 1542—1549; cf. A., 1929, 1016).—Measurements in a static system show that, after eliminating the wall reaction, the rate of recombination of at. H \propto [at. H]². The temp. coeff. is small. A lower limit has been obtained for the ratio efficiency of atom: efficiency of mol. in causing combination of a pair of atoms. Some properties of the afterglow are described. The results are discussed in relation to the triple impact mechanism.

E. S. H.

Limits of detonation of some gaseous mixtures. P. LAFFITTE and J. BRETON (Compt. rend., 1934, 199, 146—148).—The upper and lower limits and corresponding velocities of detonation of H₂-O₂, H₂-air, moist CO-O₂, H₂-CO-O₂, and H₂-CO-air mixtures were determined by the photographic shadow method.

Striated records, indicating helicoidal flame propagation, were chiefly observed with mixtures in the neighbourhood of the limits, and in general with mixtures difficult to detonate.

B. W. B.

Homogeneous reaction C₃O₂ + CO₂ + C₂ in the gaseous phase at 200°. Properties of di-carbon gas. A. KLEMENC [with R. WECHSBERG and G. WAGNER] (Z. Elektrochem., 1934, 40, 488—489).—The initial product of the reaction, C₂, is a carmine-red gas, which rapidly polymerises to purplish-red, solid C, showing selective absorption at 4600 Å. Solutions in dil. alkali show absorption beginning at about 4700 Å. C₂ is very reactive towards O₂. At 300—650° C₃O₂ polymerises rapidly, yielding CO₂ and CO; the proportion of CO increases at higher temp.

E. S. H.

Influence of temperature on the limits of inflammability of some combustible vapours, pure or mixed. M. BRIAND, P. DUMANOIS, and LAFFITTE (Compt. rend., 1934, 199, 286—288; cf. A., 1933, 909).—The upper and lower concn. limits for the inflammation of isopentene, COMe₂, MeOH, EtOH, and BuOH, mixed with air, have been determined over the temp. range 100—275°. The concn. vals. obtained vary linearly with temp. The lower limits of concn. for the inflammation of mixtures of C₆H₆ and EtOH, cyclohexane and EtOH, cyclohexane and C₆H₆, EtOH, C₆H₆, and cyclohexane, and of MeOH, EtOH, and C₆H₆, with air are in good agreement with the vals. calc. from the additivity formula of Le Chatelier (Ann. Mines, 1891, 19, 388).

J. W. S.

Homogeneous decomposition of diethyl ether at low pressures; theory of unimolecular reactions. O. K. RICE and D. V. SICKMAN (J. Amer. Chem. Soc., 1934, 56, 1444—1455).—The rate of decomp. of Et₂O has been measured at 525°, 478°, and 462° at approx. 0.1—500 mm. When the rate coeff. is plotted as ordinate against log. pressure, the curve is concave upward, contrary to the usual case with unimol. reactions. Two alternative theories are advanced in explanation.

E. S. H.

Influence of hydrogen on the decomposition of acetaldehyde. C. J. M. FLETCHER and C. N. HINSHELWOOD (Trans. Faraday Soc., 1934, 30, 614—619).—The thermal decomp. at 556° of MeCHO at initial pressures (p_0) 50—200 mm. has been studied in the presence of H₂ at the same initial pressures. The shape of the curve connecting p_0 with t^{-1} (t =time of half-change) is not fundamentally altered by the presence of the H₂. It is inferred that no one activated state of the MeCHO is favoured rather than another when energy is communicated by collision with H₂. From experiments at p_0 =200 mm. and over a range 564—500° it is inferred that the energy of activation is not influenced by the presence of the H₂.

R. S. B.

Reactions with heavy water. A. H. HUGHES, J. YUDKIN, I. KEMP, and E. K. RIDEAL (J.C.S., 1934, 1105—1112).—By means of the micro-methods described it is found that heavy H₂O (< 90% H₂O) does not appreciably affect (i) the rate of hydrolysis of palmityl chloride on H₂O, (ii) the rate of enzymic hydrolysis of films of triolein by pancreatin, (iii) the rate of O₂ absorption by the xanthine oxidase and

cytochrome-indophenol oxidase systems, and (iv) the rate of swelling of gelatin. The rate of fermentation of glucose by yeast is retarded by 30% H_2O in buffered solutions, and the respiration rate is similarly affected, possibly by an inhibition of the dehydrogenases, as with narcotics. From the hydrolysis reactions (i) and (ii), any effects due to higher viscosity are seen to be negligible, and if the reaction proceeds in stages, then the slow stage does not involve H_2O or its ions, or, alternatively, H_2O and OH^- react at the same speed as H_2O and OH^- . The bearing of the results on the mechanism of oxidation-reduction processes is considered. J. G. A. G.

Reactions of hypophosphorous acid with bromine and with chlorine. R. O. GRIFFITH and A. MCKEOWN (Trans. Faraday Soc., 1934, 30, 530—539).—The rate of oxidation of H_3PO_2 by Br at 0.25° and 10°, and by Cl_2 at 0.20°, has been studied in slightly acid and neutral solutions, and for varying concns. of the reactants. The oxidation of H_3PO_2 is due to reaction with free halogen, X_2 , and not to X_3 or HOX. The oxidation of non-ionised H_3PO_2 depends on the intermediate formation of an active tautomeric form through the catalytic action of H^+ . Halogen reacts with the active form as X_3 and probably also as X_2 , but not as HOX. The velocity coeffs. of the individual processes are discussed, and it is suggested that energy of activation is required only for the tautomeric process, and not for the reaction of the tautomeric form with halogen. M. S. B.

Effect of neutral salts on interionic reactions in concentrated salt solutions. I. Reaction between chloroacetate and xanthate ions. A. VON KRIS and I. BOSSANYI (Rec. trav. chim., 1934, 53, 903—916).—With $NaCl$, $NaNO_3$, Na_2SO_4 , KNO_3 , and $MgSO_4$ the velocity coeff. k of the reaction increases linearly with the concn. of added salt in the range 1—6*N*; with $CaCl_2$, $Mg(NO_3)_2$, and $Ca(NO_3)_2$ k increases less rapidly at higher concns., and with $MgCl_2$, k passes through a max. In all cases, for a fixed salt concn. (including 0), $\log k \propto 1/T$, but the salts have sp. effects on the temp. coeff. Without added salts, the temp. coeff. is independent of concn. and gives a heat of activation of 17,370 g.-cal.

D. R. D.

Effect of solvent on reaction velocity. V. Interaction of *N*-chloroacetanilide and hydrobromic acid in dilute aqueous solution. I. JONES and F. G. SOPER (Proc. Roy. Soc., 1934, A, 144, 643—655).—The influence of neutral salts on the rate of reaction of HBr and $NClAcPh$ (I) has been studied over the range of ionic strength 0.001—0.025 μ . The slopes of the $\log k - \sqrt{\mu}$ curves vary from -0.64 to -0.89 with the nature of the added electrolyte, and the order of the effects is approx. that of the activity coeffs. of the acid and of the internal pressures of the solutions. The difference in the velocities of reaction of (I) with HCl and HBr is due chiefly to the difference in the energy of activation of the two reactions. L. L. B.

Rate of transformation in aqueous solution of methylammonium cyanate into methylcarbamide. (Miss) C. C. MILLER (Proc. Roy. Soc., 1934, A, 145, 288—306).—The rate of formation of

$NHMe \cdot CO \cdot NH_2$ from $NH_3Me \cdot CNO$ was determined in aq. solution ($< 0.1 M$) at 40° and 50°. The vals. of μ for the solutions were determined to see if the degree of dissociation entered into the reaction rate equation, but the rate conforms rather to an equation of the Bronsted type, involving thermodynamic activities. The velocity coeff. calc. for an infinitely dil. solution at 40° with the aid of Christiansen's equation (A., 1925, ii, 47) is in good agreement with the experimental results. Extension of the theory to the rates of transformation of other alkylammonium cyanates in H_2O and of NH_4CNO in H_2O and $EtOH$ indicates that the ions are the determining factor in the reaction. L. L. B.

Kinetics of the conversion of the *aci*-form into the nitro-form of nitroethane. R. JUNELL (Svensk Kem. Tidskr., 1934, 46, 125—136; cf. A., 1929, 516).—The reaction has been studied in a series of buffer solutions. When $[H^+] < \pi$, the dissociation const. of $CHMe \cdot NO_2H$, the velocity is independent of $[H^+]$ and \propto free acid concn., but when $[H^+] > \pi$, the rate $\propto 1/[H^+]$. The average of pairs of experiments gives $\pi = 7 \times 10^{-5}$. Vals. of k_A for the buffer acids H_3O^+ , $CH_2Cl \cdot CO_2H$, $CH_2Cl \cdot CH_2 \cdot CO_2H$, $AcOH$, succinate, $AsMe_2O_2H$, $H_2PO_4^-$, and H_2O , are 150, 3.8, 1.63, 0.67, 0.42, 0.99, 0.18, and 5×10^{-5} , respectively. The relation between k_A and K_A^0 is given by $1/p \cdot k_A = 35(q/p \cdot K_A^0)^{0.37}$. R. S.

Mechanism of aromatic side-chain reactions with special reference to the polar effects of substituents. II. Kinetics of the interaction of benzyl bromides with (1) pyridine, (2) aqueous alcohol, and (3) silver nitrate. J. W. BAKER (J.C.S., 1934, 987—992).—The effects of concn. and added benzylpyridinium nitrate show that the reaction (A) between $p\text{-}R \cdot C_6H_4 \cdot CH_2Br$ (I) ($R=H$), and C_5H_5N in 90 wt.-% aq. $EtOH$ (II) and in dry $COMe_2$ is bimol., the correction for solvent reaction being small in the latter. The reaction (B) of (I) with (II) is probably ψ -unimol., and the unimol. coeffs. for the reaction (C) of (I) with $AgNO_3$ in 90% $EtOH$ are increased owing to catalysis by the pptd. $AgBr$. When $R=Me$ (electron-repelling), the velocity coeff. of (A) is increased three-fold, that of (B) four-fold, and that of (C) > sixty-fold, whilst when $R=NO_2$ (electron-attracting) the corresponding velocity coeffs. are depressed to 0.25, 0.1, and 0.02, respectively. The bimol. character of (A) confirms that the formation of the final product involves the completion of two processes of opposite polar requirements, one of these including the anionisation of Br from (I), and the results are further discussed (cf. A., 1933, 1151).

J. G. A. G.

Reaction between potassium *o*-tolylloxide and aliphatic esters in aqueous-alcoholic solutions. L. J. SUMMERBELL (J.C.S., 1934, 992—996).— H_2O is essential for the reaction which proceeds by the hydrolysis of the *K o*-tolylloxide (I) and the subsequent saponification of the ester by the liberated KOH . The equations developed lead to a composite velocity coeff., k , consisting of the product of an equilibrium const., K , and a velocity coeff., and vals. of k have been calc. from data at 50—70° for eight aliphatic esters. HCO_2Et affords very high vals., possibly

owing to the presence of HCO_2H , whilst PhOAc with KOPh yields low vals. owing to retardation of the hydrolysis of KOPh by liberated PhOH . The rate of reaction is greatly accelerated by increase of $[\text{H}_2\text{O}]$, but k decreases, probably owing to variations of K induced by the change of medium, and whilst partial replacement of EtOH by PrOH and BuOH leads to increased velocities, possibly owing to alcohol-cresol association, MeOH produces irregular results. The hydrolysis of (I) in 90% and 95% aq. EtOH has been determined.

J. G. A. G.

Factors determining the velocity of reactions in solution. Molecular statistics of the benzoylation of amines. E. G. WILLIAMS and C. N. HINSHELWOOD (J.C.S., 1934, 1079—1084).—The anomalies previously observed (A., 1933, 1251) almost disappear when C_6H_6 solutions are used, and velocity coeffs., k , for the interaction of several substituted anilines and benzoyl chlorides have been determined in the range 5—100°. The no. of mols. reacting in a bimol. reaction in solution is $Pze^{-E/RT}$, where z is the no. of collisions and P is of the order 10^{-7} for the benzoylation of NH_2Ph in C_6H_6 . The effect of the substituents on k depends principally on changes in E , and only to a much smaller extent on changes in P when the medium is unchanged. A functional relationship exists between E and the polarity of the substituent groups in benzoylation reactions, as well as in cases where P approaches 1. Experiments in mixed solvents show that P cannot be interpreted as a purely kinetic factor depending on ternary collisions with solvent mols., although such collisions appear to play an essential part in the reaction mechanism.

J. G. A. G.

Benzoylation of nitroanilines in benzene solution. W. B. S. NEWLING, L. A. K. STAVELEY, and C. N. HINSHELWOOD (Trans. Faraday Soc., 1934, 30, 597—598).—The bimol. velocity coeffs. (k) for the reactions between o -, m -, and p - $\text{NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$ and BzCl in C_6H_6 solution have been measured for a temp. range 25—111°. $k_m > k_p > k_o$ (e.g., at 70° $k_m = 44.3 \times 10^{-4}$, $k_p = 5.99 \times 10^{-4}$, $k_o = 0.45 \times 10^{-4}$; units, g.-mol., litre, sec.). The activation energies (E) for the m -, p -, and o -compounds are, respectively, 10,500, 11,800, and 13,800 g.-cal. The presence of the NO_2 reduces the velocity of benzoylation considerably, and increases E . The relation between k and E is discussed.

R. S. B.

Kinetics of the saponification of acetylated hydroxy-acids. V. K. LA MER and J. GREENSPAN (J. Amer. Chem. Soc., 1934, 56, 1492—1499).—Kinetic measurements have been made with acetylmandelic, acetylsalicylic, and α - and β -acetoxy- β -phenylpropionic acids. The reactions with aq. NaOH are bimol. and free from side reactions. The end products have been isolated. The β -acetoxy- β -phenylpropionic ion reacts more than twice as rapidly as the corresponding α ion. The saponification of Na acetylbenzilate follows a unimol. and bimol. course simultaneously. The dependence of reaction rate on concn. has been studied over the range 0.005—0.025*M*. The theoretical significance of these results is discussed.

E. S. H.

Mechanism of Cannizzaro reaction, particularly of furfuraldehyde. K. H. GEIB (Z. physikal. Chem., 1934, 169, 41—51).—The reaction of furfuraldehyde (I) at 0—40° is of the fourth order, being bimol. in respect of both $[\text{OH}']$ and (I) (cf. A., 1900, i, 552). The velocity is practically the same with either NaOH or KOH . The temp. coeff. is about 1.9. EtOH retards the reaction, and in 60% EtOH solution the velocity is 0.2 of that in H_2O . Attempts to influence the velocity by catalysts failed. It is suggested that an essential step in the reaction is collision between two mols. of a complex formed by addition of OH' to (I).

R. C.

Kinetics of mutarotation of glucose in heavy water. E. A. MOELWYN-HUGHES, R. KLAR, and K. F. BONHOEFFER (Z. physikal. Chem., 1934, 169, 113—119; cf. this vol., 494).—The velocity coeff. of the mutarotation of α -glucose in various mixtures of light and heavy H_2O has been determined at several temp. At a given temp. the velocity coeff. ratio $k_{\text{H}_2\text{O}} : k_{\text{H}_2\text{O}}$ falls from 1.00 to 0.316 as the mol. fraction of H_2O in the solvent rises from 0 to 1.00, but is independent of the temp. The observed energy of activation is 17.53 kg.-cal., but corr. for viscosity the val. becomes 21.55 for the reaction in ordinary H_2O and 22.06 kg.-cal. for H_2O (0.97). The results agree with $k_{\text{H}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.64(\eta_{\text{H}_2\text{O}}/\eta_{\text{H}_2\text{O}})e^{510/RT}$.

C.

Influence of the constitution of esters on their sensitivity to hydroxyl and hydrogen ions during hydrolysis. S. C. J. OLIVIER and A. P. WEBER (Rec. trav. chim., 1934, 53, 899—902).—Published data for k_b (velocity coeff. when $[\text{OH}'] = 1$) and k_a (velocity coeff. when $[\text{H}'] = 1$) for a no. of esters are quoted. For esters from the same alcohol and different acids, the stronger is the acid, the greater is the val. of k_b/k_a . The introduction of positive groups (e.g., Me) into either the alkyl or the acyl radical of the ester causes a decrease in k_b/k_a , negative groups (e.g., Ph) having the reverse effect.

D. R. D.

Relations between the constitution of the substance hydrolysed and its sensitivity to the hydroxyl ion during hydrolysis. S. C. J. OLIVIER and A. P. WEBER (Rec. trav. chim., 1934, 53, 869—890).—The velocity of hydrolysis of CH_2PhCl , CHPhCl_2 , CPhCl_3 , and numerous substitution products of these compounds by aq. COMe_2 solutions of KOH and H_2SO_4 and by aq. COMe_2 has been measured. The reactions are pseudo-unimol. and are in no case catalysed by H' . The hydrolysis of CH_2PhCl is catalysed by OH' , whereas that of CHPhCl_2 and CPhCl_3 is not. Hence, in the prep. of PhCHO from CHPhCl_2 , simple hydrolysis with H_2O is better than alkaline saponification. The influence of the orientation and polarity of substituents on the rate of hydrolysis and sensitivity to OH' is traced in detail. The more negative the Cl is rendered by the influence of the substituents, the less pronounced is the effect of OH' .

D. R. D.

Influence of the nature of the solvent on the catalytic power of hydroxyl ions in hydrolysis. S. C. J. OLIVIER (Rec. trav. chim., 1934, 53, 891—894).—When CH_2PhCl is hydrolysed by H_2O , in

which its solubility is only 0.0465 g. per 100 c.c. at 30°, the reaction is of zero order and proceeds in the aq. layer. The velocity coeff. is $>$ in aq. COMe_2 (preceding abstract), and is raised to a much smaller extent by KOH . The difference is attributed to the higher dielectric const. of the H_2O , as a result of which the Cl is more negative, although it is possible that the solvation of the Cl by COMe_2 may be a contributory cause. D. R. D.

Investigation of reaction velocity by means of the hydrogen electrode. I. Alkaline saponification of esters. G. J. R. KRIGE and K. HOLLOW (Trans. Faraday Soc., 1934, 30, 644—648).—The hydrolysis of $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ by NaOH has been studied by means of a H_2 electrode (new method). The velocity coeffs. at 15°, 25.3°, and 34.9° are 40.76, 75.24, and 132.5, respectively (units g.-mol., litre, min.). The temp. coeff. agrees with Dean's val. determined by the titrimetric method. The heat of activation is 10,500 g.-cal. R. S. B.

Velocity of decomposition of diazo-compounds in water. XIV. E. YAMAMOTO, R. GOSHIMA, and J. HASHIMA (J. Soc. Chem. Ind. Japan, 1934, 37, 400—404B; cf. this vol., 369).—Velocity coeffs. at various temp. are recorded for decomp. of 2:5-, 2:6-, and 2:8- $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\text{Cl}$. G. H. C.

Kinetic study of the oxidation of cystine by iodine. K. SHINOHARA and M. KILPATRICK (J. Amer. Chem. Soc., 1934, 56, 1466—1472).—The rate-determining step in the reaction $\text{RS}\cdot\text{SR} + 5\text{I}_2 + 6\text{H}_2\text{O} = 2\text{RSO}_3\text{H} + 10\text{HI}$ is the reaction between 1 mol. of cystine and 1 mol. of I . The velocity coeff. is almost invariable over the range p_{H} 1—5, but increases with increasing $[\text{I}']$ over the range 0.01—0.06N- I' . The reactant is probably I_3' . When $[\text{H}][\text{I}'] > 0.003$ the velocity coeff. increases with time. E. S. H.

Decomposition of hydrogen peroxide by hydrogen atoms. K. H. GEIB (Z. physikal. Chem., 1934, 169, 161—172).—The reaction $\text{H} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{OH}$ proceeds with a collision efficiency of $10^{-4.4}$ at room temp. In the reaction of O_2 with activated H some H_2O is formed directly, $\text{H} + \text{O}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{OH}$, without H_2O_2 being an intermediate product. The formation of very conc. H_2O_2 by reaction of H_2 with O_3 (A., 1933, 236) apparently depends on $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$, $\text{HO}_2 + \text{H} + \text{M} = \text{H}_2\text{O}_2 + \text{M}$ or $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$. R. C.

Kinetic study of the action of nitric oxide on alkali sulphite, alkali hydrogen sulphite, and sulphurous acid in aqueous solution. E. TERRES and H. LICHTI (Z. angew. Chem., 1934, 47, 411—412).—Rate of absorption of pure NO in (1) K_2SO_3 solution, (2) KHSO_3 solution, and (3) H_2SO_3 was determined and expressed as pressure-time curves. In all cases the reaction velocity shows that the reaction is of the first order, and may be expressed as follows: (a) $\text{H}_2\text{SO}_3 + \text{NO} = \text{H}_2\text{SO}_3\cdot\text{NO}$, (b) $2\text{H}_2\text{SO}_3\cdot\text{NO} = \text{H}_2\text{SO}_3(\text{NO})_2 + \text{H}_2\text{SO}_3$, (c) $\text{H}_2\text{SO}_3(\text{NO})_2 = \text{H}_2\text{SO}_4 + \text{N}_2\text{O}$. Reaction (a) controls the velocity of the absorption, that of (b) and (c) being very high. C I

Action of magnesium on solutions of nickel chloride. G. GIRE and A. M. DE NARBONNE (Compt. rend., 1934, 198, 2250—2252).— Mg powder dissolves 2—3 times as rapidly in aq. NiCl_2 (I) as in NiSO_4 (this vol., 159); H_2 is liberated and green, cryst. $\text{NiCl}_2\cdot 8\text{NiO}\cdot n\text{H}_2\text{O}$ slowly pptd. $\text{Ni}(\text{OH})_2$ is slightly sol. in (I). B. W. B.

Oxidation of arsenic in nitrous oxide and in oxygen. A. G. H. DAMERELL and H. J. EMELEUS (J.C.S., 1934, 974—979).—Although the rate of thermal decomp. of N_2O alone in a Pyrex vessel is very small at 460° and is negligible at lower temp., the gas converts As into As_2O_3 with increasing velocity in the range 190—370°, a rapid increase occurring between 265° and 290°. Ignition occurs at 410—450° and the product contains some As_2O_5 . No chemiluminescence and no upper crit. oxidation pressure were observed with 500—10 mm. of N_2O at 260—400°. The reaction occurs at the As surface, and the mechanism is discussed. The chemiluminescent reaction between As and O_2 takes place in the vapour phase, and between 266° and 306° there is a crit. total pressure (4—10 mm.) decreasing with rise of temp., below which the chemiluminescent oxidation of saturated As vapour ceases, whilst the slower surface reaction continues to < 0.001 mm. (cf. A., 1927, 497). J. G. A. G.

Magnesium light. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1934, 53, 839—846).—The emission of light by burning Mg has been studied quantitatively. The total quantity of light evolved \propto wt. of Mg burned, viz., 700 lm.-sec. per mg. of Mg , the efficiency of light production being 28 lm./w. Mg wire burns more quickly than Mg ribbon of the same thickness, the velocity increasing with the fineness of the wire. Spectroscopic data are given and the action on photographic plates of different types is investigated. The rate of combustion in N_2O is $<$ in NO , which is about half that in O_2 , the quantity of light liberated being the same. Mg does not burn well in SO_2 , CO , CO_2 , or NO_2 . D. R. D.

Zirconium light. J. A. M. VAN LIEMPT and J. A. DE VRIEND (Rec. trav. chim., 1934, 53, 895—898).—The results are closely similar to those obtained with Mg (preceding abstract), except that the rate of combustion is slower and the quantity of light liberated is only 441 lm.-sec. per mg. of Zr , although the efficiency is 36 lm./w. D. R. D.

Propagation of explosive decomposition in a high vacuum. H. MURAOUR and W. SCHUMACHER (Compt. rend., 1934, 199, 140—142; cf. A., 1932, 233).—The explosives were evacuated by a Hg -vapour pump, and ignited by a hot Ni-Cr wire. N iodide exploded equally well in air and in vac. $(\text{CH}_2)_6\text{N}_4$ peroxide exploded in vac. only when initially compressed. Hexogen [nitrated $(\text{CH}_2)_6\text{N}_4$] did not explode in vac. in any circumstances. It is concluded that self-propagation of decomp. in vac. occurs only with primers. B. W. B.

Detonation of explosives.—See B., 1934, 702.

Internal corrosion of zinc. E. ARENDT (Compt. rend., 1934, 199, 142—143).—Passive Zn in aq. HCl

or H_2SO_4 is slowly corroded beneath the superficial passive film.

B. W. B.

Velocity of reaction between camphor and sulphur dioxide. F. ISHIKAWA and N. HASHIMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 697—702).—The velocity of formation of $\text{C}_{10}\text{H}_{18}\text{O}_2\text{SO}_2$ from $\text{C}_{10}\text{H}_{16}\text{O}$ and SO_2 at 20° and at const. pressures 760, 700, and 500 mm., is represented by $v=at^n$ for the first part of the reaction, followed by $v=b+k \log t$, where v =vol. of SO_2 reacted at time t , and a , n , b , and k are consts.

R. S. B.

Reaction of methane and oxygen sensitised by nitrogen peroxide. I. Thermal ignition. R. G. W. NORRISH and J. WALLACE (Proc. Roy. Soc., 1934, A, 145, 307—321).—Ignition temp. of equimol. const. concns. of CH_4 and O_2 with varying concns. of NO_2 have been determined by a static method. Three const. concns. of the gases were employed. The induction period passes through a max. with increasing NO_2 pressure. The mechanism proposed involves the initiation of chains by the O atoms arising from the NO_2 in which CH_2 radicals and O atoms take part. When a limiting velocity due to self-heating of the mixture is reached, explosion occurs. The effect of surface on the reaction is also studied.

L. L. B.

Autoxidation of ammonium persulphate in the presence of silver salts and the tervalency of silver. P. C. CARMAN (Trans. Faraday Soc., 1934, 30, 566—577).—The rate of autoxidation of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in presence of Ag^+ has been determined and measurements have been made of the final acidity of the solutions. The results confirm the view that Ag^{+++} is formed, and subsequently oxidises NH_4^+ to NO_3^- . More direct proof is obtained by the analysis of the black ppt. formed. Its composition varies, according to conditions, between Ag_2O_3 and $\text{Ag}_2\text{O}_3 \cdot 2\text{AgO}$. E.m.f. measurements also confirm the existence of Ag_2O_3 .

M. S. B.

o-Quinones as enzyme models. XIII. Anaerobic activations. B. KISCH and U. HECHT (Biochem. Z., 1934, 271, 424—426). CdCl_2 and CaCl_2 , which activate considerably the deamination of NH_2 -acids by benzoquinone in presence of O_2 , are inactive when O_2 is replaced by a H_2 acceptor, although deamination of glycine proceeds under these conditions. Phenylglycine under these conditions gives PhCHO .

P. W. C.

Quinones as enzyme models. XIV. Comparison of borate and phosphate buffering in the oxidative deamination of amino-acids. K. SCHUWIRTH (Biochem. Z., 1934, 271, 427—434).—Under aerobic conditions the yield of NH_3 from NH_2 -acids is greater with borate than with phosphate buffer, the difference not being explicable in terms of different displacement. In experiments under anaerobic conditions using $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ or nitro-anthraquinone as H_2 acceptor it appeared probable that borate, besides buffering, also activates the quinone enzyme model.

P. W. C.

Rate of hydrolysis of the trimeric aldehydes. A. SKRABAL, W. STOCKMAIR, and H. SCHREINER (Z. physikal. Chem., 1934, 169, 177—185).—The rate of

acid-catalysed hydrolysis of $(\text{MeCHO})_3$ has been measured at $15\text{--}35^\circ$ and that of $(\text{CH}_2\text{O})_3$ at $35\text{--}55^\circ$. Both reactions follow the unimol. law, and there is no evidence of any reversal of the first hydrolysis. The temp. coeffs. of both reactions and the ratio of the temp. coeff. for $(\text{MeCHO})_3$ to that for $(\text{CH}_2\text{O})_3$ at the same temp. fall continually, and similarly with rise of temp. Collected data for the hydrolysis coeffs. of compounds with etheric O show that the trimeric aldehydes come into the same group as the cyclic acetals, which agrees with their ring structure. The hydrolysis velocities of the cyclic acetals of MeCHO afford a kinetic measure of the strain of the ring.

R. C.

Retardation of Eder's reaction by foreign substances. K. WEBER (Z. physikal. Chem., 1934, 169, 224—236).—Mono- and di-hydric phenols cause marked retardation of the unsensitised reaction in absence of O_2 , apparently by deactivating activated mols. or ions. If the solution is kept saturated with O_2 the retardation is much less marked; the phenol now acts only by internal filter action. The photochemically active component in the unsensitised reaction is a complex compound of HgCl_2 and $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and the primary act is the direct decomp. of this by light absorption. When O_2 is absent, but not when it is present, the products of reaction apparently have a retarding action. The reaction sensitised by eosin is retarded by phenols, which also have a marked quenching action on the fluorescence of the sensitiser. Apparently the photoactive component is a complex compound of the sensitiser with Eder's solution.

R. C.

Increase of the velocity of dissolution of iron by oxidising and reducing substances. F. TODT (Z. Elektrochem., 1934, 40, 536—541).—Examples showing the enhanced dissolution velocity of Fe in certain buffer solutions by adding $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , KNO_3 , Na_2SO_3 , or NH_2OH are given. The presence of KCN counteracts the effect of Na_2SO_3 .

E. S. H.

Catalytic replacement of hydrogen by diplogen in benzene. J. HORIUTI, G. OGDEN, and M. POLANYI (Trans. Faraday Soc., 1934, 30, 663—665).—Experiments are described in which H_2 at 331—136 mm. containing H_2^1 (1.14—20.9%) is shaken with C_6H_6 in presence of Pt-black and Ni. A partial replacement of H_2 by H_2^1 occurs in the gaseous phase, owing to an interchange between the H^2 atoms of the gas and the H^1 atoms of C_6H_6 . Very little hydrogenation occurs. The mechanism of the reaction is discussed.

R. S. B.

High-temperature catalysts for carbon monoxide oxidation. W. H. LOCKWOOD and J. C. W. FRAZER (J. Physical Chem., 1934, 38, 735—745).—Methods of prep. and efficiency for CO oxidation have been determined at $50\text{--}350^\circ$ for the following catalysts: unsupported—Co, Cu, Ni, Zn chromites, Cu, Ni, Fe, Zn cobaltites, Co, Cu, Ni, Mn ferrites, Cu, Co manganites, Co, Mn, Ni, Zn, Fe aluminates; supported on Al_2O_3 —Co aluminate and CuO . From experiments using N_2O instead of O_2 it is inferred that catalysis with chromites, cobaltites, ferrites, and manganites proceeds by alternate oxidation and

reduction. The adsorption isotherms of O_2 and CO on the CuO catalysts have been determined at -79° , 0° , and 27° , and a mechanism is proposed for the action of these catalysts. R. S. B.

Preparation of pure metallic hydroxides. V. W. MELOCHE and S. WEINER (J. Amer. Chem. Soc., 1934, 56, 1645—1646).—A very active catalyst for oxidising CO is obtained by passing O_3 through neutral aq. $Mn(OAc)_2$ or $MnCl_2$, washing the ppt. with conc. HNO_3 , and drying in vac. at 100° , or by electrolysis $Mn(NO_3)_2$ with a cathode surrounded by a porous cup containing aq. NH_4NO_3 . E. S. H.

Inflammation of mixtures of hydrogen, carbon monoxide, and air in contact with a heated surface. PRETTE (Mem. Poudres, 1934, 25, 531—546).—The temp. of inflammation (I) of H_2 -CO-air mixtures in Pyrex glass vessels is raised if the wall is coated with KCl or NaCl by condensation of the vapours. The effect is most marked when the % of air is small. Thus for mixtures in which $CO:H_2=3-15$ (I) rises 100° when the % of air is decreased from 20% to 7% in a clean vessel, but when the wall is coated with KCl the rise is 200° starting from the same initial temp. A. G.

Catalyst for production of hydrogen by means of the water-gas reaction. XV.—See B., 1934, 716.

Catalysts for production of hydrogen by the water-gas reaction. XVI. Promoter action of Cr_2O_3 in Fe_2O_3 - Cr_2O_3 catalysts. R. YOSHIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 350B; cf. A., 1933, 234).—The previously published results are explained by assuming that Cr inhibits the movement of active atoms to inactive positions. G. H. C.

Oxidation of ammonia by non-platinic catalysts. J. I. TSCHERNIAEVA (Ukrain. Chem. J., 1934, 9, 92—204).—Adadurov and Veinschenker's $CaO-SnO_2-SiO_2$ catalysts (A., 1930, 1132), as well as a no. of other catalysts, oxidise NH_3 to NO and NO_2 , but not directly to HNO_3 , as claimed by these authors. R. T.

Catalytic oxidation of ammonia. C. TONIOLO and G. GIAMMARCO (Atti Congr. naz. Chim., 1933, 4, 843—859; Chem. Zentr., 1934, i, 1442).—An Al preheater is used to produce higher temp. and increased yields. Several catalytic gauzes in succession are also used. The addition of O_2 and the use of higher pressures favour the subsequent conversion of the oxidation products into HNO_3 . The yields with Pt catalyst are such that a search for other catalysts is not profitable. L. S. T.

Reaction power of crystals. K. FISCHBECK, L. NEUNDEUBEL, and F. SALZER (Z. Elektrochem., 1934, 40, 517—522).—In the catalytic decomp. of NH_3 by wires of electrolytic Fe, and in the oxidation of the wires by CO_2 , H_2O vapour, and NO, a discontinuity occurs at the temp. of the α - γ transformation. The rate of reaction is not controlled, therefore, mainly by the rate of diffusion through the oxide film. A similar discontinuity at the transformation temp. occurs in the oxidation of Mn by O_2 . E. S. H.

Limiting dimensions of catalyst particles. P. D. DANKOV and A. A. KOTSCHETKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 359—364).—Pt-black primary crystals prepared between 0° and 5° have linear dimensions of about 40 Å., whilst particles prepared below 5° have dimensions of about 25—30 Å. The activity, tested in the reactions H_2+O_2 and $C_2H_4+H_2$, depends on temp. of recrystallisation and on particle size. By extrapolation zero activity is exhibited by particles <20 Å.

W. R. A.

Catalytic decomposition of formic acid vapour by copper-gold alloys. G. RIENACKER (Z. Elektrochem., 1934, 40, 487—488).—The reaction is of zero order, yielding H_2 and CO_2 . The energies of activation are Cu 25,500, Au 29,000, Cu-Au (3:1, 1:1, 1:3) 24,000—24,500 g.-cal. E. S. H.

[Catalytic] synthesis of formaldehyde from water-gas.—See B., 1934, 709.

Manufacture of cyclohexanone and its derivatives by the contact process.—See B., 1934, 709.

Kinetics of catalysed hydrogenation of ethylene. H. ZUR STRASSEN (Z. physikal. Chem., 1934, 169, 81—90).—The reaction has been studied at -10° to 130° under low pressures over Ni ribbon as catalyst. The velocity is approx. a linear function of the C_2H_4 pressure at the higher temp. and independent of it at the lower temp.; over the whole temp. range it \propto the H_2 pressure. The temp. of max. velocity falls with the pressure. In explanation it is suggested that both C_2H_4 and H_2 undergo adsorption, in part activated, equilibrium with the gas phase being continually maintained, and that the actual hydrogenation is the lowest part of the whole process. Above 130° the catalyst showed signs of fatigue due to poisoning by C_2H_4 . R. C.

Heterogeneous catalysis of stereoisomeric change in oximes. T. W. J. TAYLOR and E. M. W. LAVINGTON [with (MISS) G. M. PRICE] (J.C.S., 1934, 980—987).—Of the many adsorbents investigated, charcoals alone were found to catalyse the transformation of alcoholic α -(I) into β -benzilmonoxime(II), and this catalysis does not extend to the isomeric change of α -O-methylbenzilmonoxime, although this is adsorbed as strongly as (II). The rate of the change (I) \rightarrow (II) \propto wt. of C used, and increases with decrease of particle size, increased rate of stirring, and rise of temp. The reaction is of zero order with respect to (I), and whereas the catalytic activities, c , of sugar, coconut, and palm-nut C \propto their adsorbing powers, A , measured in terms of the adsorption of (II), c of blood and animal C (III) are \geq the vals. $\propto A$. c for the first three samples of C is not affected by KCN, but vals. for (III) are diminished to vals. $\propto A$. The enhanced c of (III) are related to their Fe content and there is a very close parallelism between the heterogeneous catalysis of stereoisomeric change and that of the oxidation of org. compounds on C surfaces by O_2 . c for Bismarck-brown C is increased equally by specially incorporated Fe and Cr, to a smaller extent by Co and Mn, and not at all by Ni and Cu, parallel with the decreasing stability of one of the valency states of these meta s.

Further, c for all of the samples of C is diminished to small vals. proportional to A when the contained O_2 is removed by heating in an atm. of H_2O_2 and is, in general, restored by warming with H_2O_2 . It is concluded that the actual catalyst for the change (I)— is the O_2 on the C, the configurational inversion proceeding by an active O atom from the C entering the oxime group and an O atom from that group being retained by the C (cf. this vol., 36).

J. G. A. G.

Concentration of the hydrogen isotope H^2 by the electrolysis of water. I. Y. OTA (Mem. Fac. Sci. Agric. Taihoku, 1934, 10, 71—79).—The efficacy of various methods of concentrating the H^2 electrolytically has been investigated by measuring the relative intensities of the spectral lines H_β and $H\gamma$ in the H_2O as the electrolysis proceeds.

H. S. P.

Separation of the oxygen isotopes. C. H. GREENE and R. J. VOSKUYL (J. Amer. Chem. Soc., 1934, 56, 1649).— H_2O produced by combustion of O_2 obtained by electrolyzing 5% NaOH with Ni electrodes is lighter than that produced by combustion of atm. O_2 .

E. S. H.

Theory of chromium plating. E. MÜLLER (Z. Elektrochem., 1934, 40, 326—337, 344—352).—A re-statement of Muller's theory (A., 1932, 473), which is further developed and supported by additional observations. The influence of foreign acids, effect of temp., throwing power, and conditions for bright plating are discussed in the light of the theory.

E. S. H.

Chemistry of the lead accumulator.—See B., 1934, 681.

Electrolysis in a magnetic field. A. GLAZUNOV and O. RADA (Chim. et Ind., 1934, 31, Spec. No., 579—582).—Deposits of Ag on the cathode and of Ag_2O_2 on the anode from $AgNO_3$ solutions in a strong magnetic field occur in such a way that the dendritic crystals are disposed in the direction of the magnetic lines of force.

A. R. P.

Theory of electrolysis of melts. P. DROSSBACH (Z. Elektrochem., 1934, 40, 370—375).—Theoretical.

E. S. H.

Chemical reactions in different parts of a low-pressure gas discharge. P. JOLIBOIS (Compt. rend., 1934, 199, 53—55).— CO_2 was circulated through a d.c. discharge tube permitting separate examination of the anode- and cathode-zone and positive-column reactions. The following % decomp. were observed: (i) in the anode zone at 5 mm. pressure, 0.55% (at 17.3 watts energy dissipation), (ii) in the cathode zone at 0.11 mm., 8.25—46.5% (3.14—69.4 watts), (iii) in the positive column at 0.11 mm., 8.79—47.2% (3.78—48.6 watts). Equilibrium was attained in 0.01 sec.; dissociation efficiencies decreased with increasing current.

B. W. B.

Initiation of gas reactions by ions. P. GÜNTHER and G. COHN (Z. physikal. Chem., 1934, B, 26, 8—22).—In the formation of HCl on admixture with H_2 of a stream of Cl_2 previously charged with Cl ions by a point discharge, positive and negative ions are equally effective in inducing reaction and

the p.d. between the electrodes does not affect the yield per ion. The recombination of positive and negative ions does not influence the reaction. These results agree qualitatively with Mund's form of Linde's cluster theory (A., 1931, 1139). R. C.

Inhibition of photolysis of carbon dioxide by extreme desiccation. A. COEHN and B. W. MAY (Z. physikal. Chem., 1934, B, 26, 117—130).—Earlier results have been confirmed. CO_2 passed through H_2SO_4 is decomposed to the extent of < 1% on irradiation with unresolved ultra-violet light, whilst with CO_2 passed very slowly over P_2O_5 under 1 atm. the decomp. amounts to 18%. In ultra-violet light a Ag plate which has been heated in H_2 reacts with highly dried O_2 in such a way that an image can be produced on it by a physical developer. By utilising this phenomenon it has been shown that extremely dry CO_2 prepared by reaction between fractionally distilled CO and O_2 without chemical drying agents undergoes no decomp. in ultra-violet light. It seems doubtful if Bodenstein's theory of intensive drying (cf. A., 1933, 788) affords a comprehensive explanation of all the observed phenomena. The mechanism of the action of H_2O probably varies from case to case, so that no single explanation can be adequate.

R. C.

Validity of the mass-action law for the photochemical gaseous equilibrium $2SO_2 + O_2 = 2SO_3$. M. TRAUTZ and F. HELFRICH (Z. wiss. Phot., 1934, 33, 72—80).—The work of Coehn and Becker (B., 1910, 269) has been repeated with greater accuracy and varied procedure. Using various mixtures exposed to a Hg-vapour lamp, and various exposure times, the mass-action law is found to hold within experimental error. The equilibrium const. varies linearly with the square of the current strength.

J. L.

Chemical reactivity and light absorption. N. R. DHAR and A. K. BHATTACHARYA (J. Indian Chem. Soc., 1934, 11, 311—324; cf. this vol., 496).—Further examples—chiefly oxidation reactions—are cited of the absorption of light of longer λ by reacting systems than by the reactants. The effect is more marked with systems of higher reaction velocity.

J. S. A.

Heat as an agent for the production of the latent photographic image. J. M. BLAIR and P. A. LEIGHTON (J. Opt. Soc. Amer., 1934, 24, 185—187).—Developable densities produced at various temp. are plotted against time of exposure to heat, and were high and uniform except at low temp., when variations over the plate surface were found. The general effect is similar to that due to exposure to light. $Cr_2(SO_4)_3$ acted as a sensitiser to heat, but not to light.

N. M. B.

Mode of action of infra-red sensitizers. R. MECKE [with G. SEMERANO] (Z. Elektrochem., 1934, 40, 511).—The mechanism is discussed.

E. S. H.

Blair-Leighton equation applied to the production of the latent photographic image by hydrogen peroxide. M. W. JONES and J. M. BLAIR (J. Franklin Inst., 1934, 218, 29—34; cf. A., 1932, 1006).—The data of Sheppard and Wightman (B.,

1923, 426A) are interpretable by the Blair-Leighton equation. New emulsions have also been tested. No correlation between the behaviour of emulsions to light and to H_2O_2 has been found, but the evidence shows that the processes of the production of the latent image by heat, light, or by H_2O_2 are fundamentally identical. J. L.

Law of the geometric mean as a sensitometric function. C. C. LIENAU (J. Franklin Inst., 1934, 218, 35—39).—Theoretical. The generalised law is shown to be a useful empirical formula for the behaviour of photographic emulsions. For medium densities the formula reduces to the usual linear equation. L. J.

Photolysis of silver halides. P. FELDMAN and A. STERN (Z. physikal. Chem., 1934, B, 26, 45—57; cf. A., 1931, 920).—The quantum yield, ϕ , for pptd. AgCl at 313 $m\mu$ in presence of NaNO_2 as halogen acceptor is about 1.0, whilst for the photolysis in either presence or absence of NaNO_2 of AgCl crystallised from aq. NH_3 is 0.13—0.20. For pptd. AgBr at 365 and 436 $m\mu$ in presence of NaNO_2 ϕ is about 1.0, whilst at 365 $m\mu$ for pptd. AgBr without NaNO_2 or cryst. AgBr in presence of NaNO_2 ϕ is about 0.4. In some cases the decomp. of the AgBr was $>$ that of the AgBr of a highly sensitive photographic plate caused by an exposure lying on the rising part of the blackening curve; it is deduced that in the production of the latent image ϕ is probably ~ 1 . R. C.

Shape of the photographic density curve in relation to the colour of the acting light. A. VAN KREVELD (Phot. J., 1934, 74, 377—380).—The variations of contrast with λ of the acting light have been measured for seventeen makes of plates, all but one being undyed. The thickness of the developed image was controlled so as to be $> 2\mu$. The factors of absorption and turbidity and of dye-sensitisation are here eliminated, and the variations still found are ascribed to the inherent colour-sensitiveness of the AgBr grains. The effect of mixed colours is treated by the author's formulæ (cf. this vol., 264). J. L.

Temperature coefficient of photographic sensitivity. I. Low temperatures and the natural and optical sensitivities of dyed silver halides. S. E. SHEPPARD, E. P. WIGHTMAN, and R. F. QUIRK (J. Physical Chem., 1934, 38, 817—831).—Sensitometric data have been determined for panchromatic plates exposed to red and blue-violet light, and for process plates exposed to yellow and blue-violet light, at 20°, -70°, and -180°. From 20° to -70° the drop in natural and optical sensitivities is relatively small, from -70° to -180° the drop is large, but even at -180° 5% of the original sensitivity at 20° persists. For the most sensitive grains the diminution in sensitivity at very low temp. is less for the natural (blue-violet) sensitivity than for the optical (dye) sensitivity; for grains of lower sensitivity the changes are of the same order. The interpretation of these results is discussed. R. S. B.

Photographic intermittency effect and the discrete structure of light. L. SILBERSTEIN and J. H. WEBB (Phil. Mag., 1934, [vii], 18, 1—24; cf. A., 1933, 682, 1127).—A theory of the intermittency effect

has been developed. In agreement with this theory, the frequency at which the effects of intermittent and continuous exposures become experimentally indistinguishable \propto the radiation intensity and the grain size, and increases in a more complex way with the sector ratio. H. J. E.

Optimum of detail reproduction by photographic layers. E. LAU and J. JOHANNESSON (Physikal. Z., 1934, 35, 505—507).—The blackening produced on photographic plates of various types on exposure to a logarithmic distribution of brightness was measured photometrically. A blackening corresponding with 50—70% shows a min. of irregularities due to oscillation of the nuclei. The min. of oscillation of nuclei is the optimum condition for reproduction of detail. A. J. M.

Photochemical polymerisation of acetylene. S. C. LIND and R. LIVINGSTON (J. Amer. Chem. Soc., 1934, 56, 1550—1551).—A discussion of mechanisms. The formation of C_6H_6 is explained by side reactions. E. S. H.

Photochemical decomposition of keten. R. G. W. NORRISH, H. G. CRONE, and O. D. SALT-MARSH (J. Amer. Chem. Soc., 1934, 56, 1644—1645).—A reply to criticism (cf. this vol., 740). E. S. H.

Oxidation of ferrous sulphate by benzoquinone and the inverse reaction. D. PORRET (Helv. Chim. Acta, 1934, 17, 703—716).—In the dark the reaction velocity approx. \propto the concn. of benzoquinone and $[\text{Fe}^{++}]^{1.5}$, but is almost independent of $[\text{H}^+]$. The inverse reaction \propto the concn. of quinol, $[\text{Fe}^{+++}]^{1.5}$, and $1/[\text{H}^+]$. Only the direct reaction is sensitive to light. Using $\lambda\lambda$ 405, 408, and 436 $m\mu$ the quantum efficiency is 1, independently of the concns. of the reagents, and temp. E. S. H.

Photochemical oxidation of ethyl and isopropyl alcohols by benzoquinone. A. BERTHOUD and D. PORRET (Helv. Chim. Acta, 1934, 17, 694—701).—Reaction does not occur in the dark. The photochemical efficiency for $\lambda\lambda$ 405, 408, and 436 $m\mu$ is nearly 1, and is independent of the concn. of benzoquinone, the intensity of illumination, and temp., but decreases with decreasing concn. of alcohol. E. S. H.

Chain photolysis of gaseous acetaldehyde. J. A. LEERMAKERS (J. Amer. Chem. Soc., 1934, 56, 1537—1541).—The photolysis of MeCHO (I) at $> 80^\circ$ is a chain reaction. The rate at λ 3130 Å. is given by $-d(\text{I})/dt = 1 \times 10^6 e^{-10,000/RT} \sqrt{(I_{\text{abs}}) \cdot [\text{I}]}$, where the units are mols. per c.c. and einsteins per c.c. per sec. The quantum yield varies from 0.03 at room temp. to 300 at 309.5°. The mechanism is discussed. E. S. H.

Photochemical gas phase reaction between chlorine and trichlorobromomethane. H. G. VESPER and G. K. ROLLEFSON (J. Amer. Chem. Soc., 1934, 56, 1455—1461).—The reaction is expressed by $\text{Cl}_2 + \text{CBrCl}_3 = \text{BrCl} + \text{CCl}_4$ (1) and $\text{Cl}_2 + 2\text{CBrCl}_3 = \text{Br}_2 + 2\text{CCl}_4$ (2), the latter being almost negligible. A kinetic study has been made, using the λ 0.366 μ . The photochemical reaction goes to completion; the rate \propto the absorbed intensity raised to a power slightly > 0.5 . The rate is retarded markedly by

BrCl, is not affected by increase of total pressure, but is doubled by raising the temp. from 28° to 50°. The quantum yield decreases from about 30 at the beginning of the reaction to < 10 as [BrCl] increases, and decreases with decreasing [Cl₂] or [CBrCl₃]. No reaction occurs in the dark at temp. < 50°. A mechanism for the photochemical reaction is proposed and a rate law derived.

E. S. H.

Photochlorination and chlorine-sensitised photo-oxidation of gaseous tetrachloroethylene. R. G. DICKINSON and J. L. CARRICO (J. Amer. Chem. Soc., 1934, 56, 1473—1480).—The Cl₂-sensitised photo-oxidation of C₂Cl₄ under the influence of light (4358 Å.) yields mainly CCl₃·COCl with some COCl₂. Quantum yields of about 300 mols. C₂Cl₄ oxidised per quantum absorbed have been obtained; no marked dependence on concn. or light intensity has been observed. Chlorination to C₂Cl₆ in absence of O₂ also proceeds as a chain reaction at rates fairly well represented by $-d[Cl_2]/dt = k(I_{abs})^{1/2}[Cl_2]$. The mechanism is discussed.

E. S. H.

Mechanism of the decomposition of complex oxalates in light. M. V. BHAGWAT (Z. anorg. Chem., 1934, 218, 365—368).—The photochemical decomp. of complex K oxalates K_nX(C₂O₄)_n is known to take place with a quantum output 0—2. K₂Cu(C₂O₄)₂ is decomposed by ultra-violet light only and requires a sensitiser. The CuC₂O₄ first formed is subsequently decomposed with the production of Cu, Cu₂O, and CuO, contrary to the behaviour of freshly pptd. CuC₂O₄ in sunlight, and in presence of a sensitiser; a min. of 3 light quanta must be required for the decomp. of 2K₂Cu(C₂O₄)₂. Thus the quantum yield is > 0.66.

M. S. B.

Photochemistry of simple organic compounds. K. F. BONHOEFFER (Z. Elektrochem., 1934, 40, 425—428).—A lecture, with special reference to aldehydes and ketones.

E. S. H.

Photo-oxidation of rubrene. E. J. BOWEN and F. STEADMAN (J.C.S., 1934, 1098—1101).—The quantum efficiency, γ , of the oxidation of rubrene (I) in C₆H₆ rises to unity at concn. > 0.01M and is independent of λ between 3660 and 5460 Å. The reaction depends on a termol. collision between an activated and a normal mol. of (I) and an O₂ mol. γ is diminished by many substances, some of which are very powerful inhibitors, and it appears that the deactivation is of the nature of a prototropic change of the excited mol.

J. G. A. G.

Influence of sensitisers in chemical reactions produced by X- and γ -radiation. G. HARKER (J. Cancer Res. Comm. Sydney, 1934, 5, 189—196).—An extended account of work already noted (this vol., 375).

X-Irradiation of fused silica. F. TWYMAN and F. BRECH (Nature, 1934, 134, 180).—Fused SiO₂ is discoloured by exposure to X-rays, and ultra-violet reflexion from the irradiated part is increased. Cryst. quartz is only slightly discoloured.

L. S. T.

Formation of ammonia by positive ion bombardment. I. MOTCHAN, S. ROGINSKI, F. FEDOROV, and A. SCHECHTER (Compt. rend. Acad. Sci.

U.R.S.S., 1934, 2, 365—369).—The amount synthesised increases with the at. wt. of the ion. Results are given for Li⁺, Na⁺, K⁺, and Cs⁺, and for each there is a crit. potential varying from about 26 volts for Li⁺ to 127 volts for Cs⁺. The maximal energies given by ionic bombardment to mols. of N₂ and H₂ are calc.

W. R. A.

Heavy hydrogen as a research tool. E. K. RIDEAL (Chem. and Ind., 1934, 610—611).—A review.

H. J. E.

Reactions with heavy hydrogen. K. F. BONHOEFFER (Z. Elektrochem., 1934, 40, 469—474).—A summary of published work.

E. S. H.

Hydrogen isotopes. Fractionation by diffusion through palladium. V. LOMBARD and C. EICHNER (J. Chim. phys., 1934, 31, 396—406; cf. A., 1932, 906).—The rate of diffusion (I) varied in dynamic experiments, with the rate of flow. (I) of H₂ after diffusion through Pd was > that of the residual gas. The effect was attributed (in 1930) to a partial separation of the isotopes (cf. A. and L. Farkas, this vol., 156). Later experiments failed to reproduce this result, probably owing to smaller H₂ content of the H₂ used.

R. S.

Experiments with heavy water. R. SCHNURMANN (Z. Elektrochem., 1934, 40, 365—366).—Comments on the work of Gunther-Schulze and Keller (this vol., 612).

E. S. H.

Decomposition of sodium formate by *B. coli* in presence of heavy H₂O.—See this vol., 929.

Concentration of heavy water by spontaneous evaporation. E. D. HUGHES, C. K. INGOLD, and C. L. WILSON (Nature, 1934, 134, 142).—A criticism (this vol., 853).

L. S. T.

Fluoride as an impurity in sodium phosphate. A. HARDEN (Nature, 1934, 134, 101).—A sample of "recryst. Na phosphate," owing to its F⁻ content, inhibited alcoholic fermentation by dried yeast. One recrystallisation from H₂O gave a product which reacted normally with sugar and yeast.

L. S. T.

Reactions of soda decompositions. A. ROMWALTER (Mitt. berg-hüttenm. Abt. Hochschule Berg-Forstwes., Sopron, 1933, 5, 38; Chem. Zentr., 1934, i, 1526).—A micro-volumetric method for investigating the reaction mechanism between oxides and a melt of Na₂CO₃ at 1000° with exclusion of air is described. Parallel investigations with melts in an open crucible show marked differences in the end products. In gas-heated, Pt-covered, small Pt tubes an equilibrium almost invariably results. BeO and ZnO scarcely react with the Na₂CO₃ melt, B₂O₃ yields more CO₂ than corresponds with the formation of metaborate, Al₂O₃ gives rise to an equilibrium between NaAlO₂ and Na₃AlO₃, Fe₂O₃ yields only NaFeO₂, TiO₂ is not completely converted into Na₂TiO₃, SiO₂ yields meta- and ortho-silicate, and SnO₂ behaves similarly. PbO acts slowly on the fused mass, and an equilibrium is established after the formation of some Na₂PbO₂.

L. S. T.

Preparation of iodine-free potassium hydroxide. C. O. HARVEY (Analyst, 1934, 59, 479—480).—The saturated aq. KOH is extracted ten times with I-free COMe₂.

E. C. S.

Binding and interchange of water molecules in a salt hydrate. A. W. C. MENZIES and F. T. MILES (J. Amer. Chem. Soc., 1934, 56, 1647—1648).—When $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ is rehydrated by exposing to the vapour of H_2O , complete interchange of H_2O and H_2O occurs. E. S. H.

Preparation and explosion temperatures of cupric chlorate-primary amine complexes. J. AMIEL (Compt. rend., 1934, 199, 51—53).— $\text{Cu}(\text{ClO}_3)_2 \cdot 4\text{NH}_3$ (I) and the compounds $\text{Cu}(\text{ClO}_3)_2 \cdot 4\text{X}$, where $\text{X} = \text{NH}_2\text{Me}$, NH_2Et , NH_2Pr^n , or $\text{NH}_2 \cdot \text{CH}_2\text{Ph}$, were prepared by Ephraïm and Jahnson's method (A., 1915, ii, 166). In all cases the blue, cryst. compounds were hydrolysed in aq. solution to $\text{Cu}(\text{OH})_2$, and decomposed slowly at room temp., losing NH_3 . Maquenne-block and sealed-tube explosion temp. were determined. (I) was the most stable and exploded at a max. temp. of 200° . B. W. B.

Optical properties of calcium aluminates and ferrites. K. AKIYAMA and G. SAWAYAMA (Bull. Waseda Appl. Chem. Soc., 1933, 21, 17—26).— $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ has n 1.710. A new (β) form of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (I) was produced by heating the raw mixture at 1450 — 1470° for 2 hr. and cooling slowly; n 1.6152 $< n_1 < n_2 < 1.6175$; d 2.70. Methods of prep. and optical properties of α - and α' -(I), $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ are given. CH. ABS.

Non-existence of cadmous compounds. (Miss) W. R. A. HOLLENS and J. F. SPENCER (J.C.S., 1934, 1062—1063).—The cadmous oxide and hydroxide described in the lit. are shown by magnetic susceptibility measurements to be equimol. mixtures of Cd and the corresponding Cd^{II} compound. The "subchloride," Cd_4Cl_7 , is a mixture and the observed mass susceptibility equals that calc. for the mixture $\text{Cd} + 7\text{CdCl}_2$ from the vals. for Cd, -0.167×10^{-6} , and CdCl_2 , -0.375×10^{-6} . The "suboxide," Cd_4O , contains free Cd. J. G. A. G.

Reaction mechanism of the formation and dissolution of aluminium and beryllium hydroxides. W. D. TREADWELL and J. E. BONER (Helv. Chim. Acta, 1934, 17, 774—787).—The titration of aq. AlCl_3 and BeCl_2 with NaOH and the back-titration of the alkaline solution with HCl have been examined with regard to (a) p_{H} , (b) turbidity, and (c) viscosity. The production and spontaneous flocculation of the ppt. can be differential. In the titration with alkali a pronounced viscosity max. is observed in the turbid liquid just before the neutral point. E. S. H.

Structure of kaolin. III. Sodium anhydrokaolins. M. DOMINKIEWICZ (Arch. Chem. Farm., 1934, 1, 142—151).— $\text{Na}_{12}\text{Al}_6\text{Si}_6\text{O}_{27}$, on treatment with boiling SOCl_2 in absence of H_2O yields the substance, $\text{Na}_4\text{Al}_2\text{Si}_2\text{O}_{25}$ (I), which with dry HCl at 150 — 160° gives $\text{Na}_4\text{Al}_2\text{Si}_2\text{O}_{23}$ (II), and on hydrolysis with H_2O at 180 — 190° affords $4\text{Na}_4\text{H}_4\text{Al}_2\text{Si}_2\text{O}_{27} \cdot 3\text{H}_2\text{O}$. (II) is not acted on by aq. AgNO_3 , with which (I) yields the corresponding Ag_4 salt; this affords $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_{27}$ on boiling with aq. NH_4Cl , and $\text{Ag}_2\text{Na}_4\text{H}_4\text{Al}_2\text{Si}_2\text{O}_{27}$, in which the Ag is present as $\cdot\text{SiO}_2\text{Ag}$, on boiling with aq. NaCl . R. T.

Primary processes in the oxidation of graphite. V. SIHVONEN (Z. Elektrochem., 1934, 40, 456—460).—A lecture summarising published work. E. S. H.

Graphite-sulphuric acid compound (graphite disulphate). A. FRENZEL and U. HOFMANN (Z. Elektrochem., 1934, 40, 511—516).—The "blue graphite" (cf. A., 1932, 217), formed by treating a suspension of graphite in conc. H_2SO_4 with small amounts of HNO_3 , is shown (X-ray) to consist of a compound of C and H_2SO_4 . The composition is approx. 80% C and 20% SO_4H . The compound is stable in conc. H_2SO_4 , but is decomposed by H_2O . E. S. H.

Fluorination of trichlorosilane. H. S. BOOTH and W. D. STILLWELL (J. Amer. Chem. Soc., 1934, 56, 1531—1535).—The reaction of SiHCl_3 with SbF_3 in presence of SbCl_5 gives SiHF_3 , SiHCl_2F , and small amounts of SiHClF_2 . SiHF_3 is unstable even at the temp. of liquid N. The following data are recorded: SiHF_3 , m.p. $-131.2 \pm 0.1^\circ$, b.p. $-97.5 \pm 0.1^\circ$, v.p. $\log p = -1561.87^\circ/T - 9.4206 \log T + 32.834$; SiHClF_2 , m.p. $> -144^\circ$, b.p. approx. -50° ; SiHCl_2F , m.p. $-149.5 \pm 0.1^\circ$, b.p. $-18.4 \pm 0.1^\circ$, v.p. $\log p = -912.871/T - 1.30853 \log T + 3.3170$. E. S. H.

Trichlorosilane. H. S. BOOTH and W. D. STILLWELL (J. Amer. Chem. Soc., 1934, 56, 1529—1530).—The best yields of SiHCl_3 are obtained by acting on Si with HCl at 380° . SiHCl_3 has m.p. $-128.2 \pm 0.1^\circ$ and b.p. $31.5 \pm 0.1^\circ$. E. S. H.

Structure of ultramarine. II. Action of silver nitrate on ultramarines of high silica content. M. DOMINKIEWICZ (Arch. Chem. Farm., 1934, 1, 170—192).—The entire Na content of ultramarines (I) is replaced by Ag on boiling with aq. AgNO_3 , pointing to the absence of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}$ and $\text{Na}_4\text{Al}_6\text{Si}_6\text{O}_{23}$. The composition of the Na salts of various (I) indicates that commercial (I) contains 70—87% of pure (I), 14—27% of $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{25}$, and 0.5—4% of kaolin. Pure (I) is $\text{Na}_6\text{Al}_4\text{Si}_6\text{O}_{20}\text{S}_4$. R. T.

Complexes of germanous bromide with caesium bromide and with bromides of organic bases. T. KARANTASSIS and L. CAPATOS (Compt. rend., 1934, 199, 64—66; cf. A., 1925, ii, 1182).—The following compounds have been prepared by pptn. from a solution of GeBr_2 (X) in HBr : $\text{X} \cdot \text{CsBr}$; $2\text{X} \cdot \text{CsBr}$; $2\text{X} \cdot 3\text{NMe}_4\text{Br}$; $3\text{X} \cdot 2\text{AsMe}_4\text{Br}$; $\text{X} \cdot \text{As}(\text{Me}_3\text{Et})\text{Br}$. All were cryst. and hydrolysed to $\text{Ge}(\text{OH})_4$ by H_2O . RbBr gave no ppt. under the same conditions. B. W. B.

Preparation and constitution of thiostannates. II. Tetra- and octa-sodium dioxypentathio-stannates. E. E. JELLEY (J.C.S., 1934, 1076—1078).—The solution obtained by refluxing excess of Sn and S with conc. Na_2S for 50 hr. deposits crystals of Na_4 dioxypentathio-stannate (I), $\text{Na}_4\text{Sn}_2\text{S}_{10}\text{O}_2 \cdot 18\text{H}_2\text{O}$, at 37° and $\text{Na}_4\text{Sn}_5\text{S}_{10}\text{O}_2 \cdot 20\text{H}_2\text{O}$ at room temp. Other preps. are described. The salts lose all but $2\text{H}_2\text{O}$ at 150 — 180° . Na_8 dioxypentathio-stannate (II), $\text{Na}_8\text{Sn}_5\text{S}_{12}\text{O}_2 \cdot 32\text{H}_2\text{O}$, is obtained by crystallising two eqvs. of Na_2S with one of (I). The optical properties of the crystals are recorded. The marked stability of (I) and (II) towards reagents (cf. Na_4SnS_4 and Na_2SnS_3)

indicates a nuclear, rather than a chain, structure and formulæ on the basis of hexavalent Sn are proposed.

J. G. A. G.

Mechanism of hydrolysis. Alkaline saponification of amyl acetate. M. POLANYI and A. L. SZABO (Trans. Faraday Soc., 1934, 30, 508—512).—When amyl acetate is hydrolysed using H_2O containing excess of O^{18} , the isotopic ratio of O in the $C_5H_{11}OH$ obtained is normal, proving that it is the acid O linking of the ester mol. which is broken in hydrolysis. The results also show that $C_5H_{11}OH$ does not exchange its OH with that of H_2O after prolonged treatment with conc. aq. NaOH at 70° .

M. S. B.

Action of water on selenium and tellurium. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 501—508).—Whilst grey Se does not react with H_2O at 100° and only very slightly at 160° , red Se reacts at 50° . Te affords TeO_2 with H_2O at 160° and 100° . Freshly pptd. Te reacts at 50° .

J. G. A. G.

Reactions of chromous chloride. M. CHATELET (Compt. rend., 1934, 199, 290—291).—Anhyd. $CrCl_2$ (prepared by reduction of $CrCl_3$ with H_2 at about 700°) dissolves in C_5H_5N yielding a green solution and green crystals of the compound $CrCl_2 \cdot 2C_5H_5N$. This compound shows traces of oxidation after some hr. in the air. 1 mol. of $CrCl_2$ absorbs 5.48 mols. of dry NH_3 at atm. pressure and at room temp. The higher absorption found by Ephraim and Zapata (this vol., 499) is attributed to their lower reduction temp. The composition varies with NH_3 pressure and at zero pressure corresponds with $CrCl_2 \cdot 3NH_3$, confirming the existence of this compound, but no evidence could be obtained of the existence of $CrCl_2 \cdot 5NH_3$ by studying the pressure-composition curve. When, however, the $CrCl_2$ is kept saturated with NH_3 at 22° and 76 cm., the colour changes from pale green to violet-rose, and in 20 hr. the product corresponds with the composition $CrCl_2 \cdot 5NH_3$ and its composition does not vary over changes of NH_3 pressure from 11 to 83 cm.

J. W. S.

Existence of oxyacids of fluorine. G. H. CADY (J. Amer. Chem. Soc., 1934, 56, 1647).—The observations of Dennis and Rochow (A., 1932, 485) are criticised.

E. S. H.

Recovery of iodine from residues from iodometric analysis. L. N. SLOTINTSEV (Zavod. Lab., 1934, 3, 461—462).—I and IO_3' in the residues are converted into I' by Na_2SO_3 , and I' is pptd. as CuI by adding $CuSO_4$ to the feebly acid or neutral solution in presence of a small excess of $Na_2S_2O_3$. The supernatant fluid is siphoned off, and the residue of CuI is heated with $Na_2Cr_2O_7$, Fe alum, or MnO_2 , when I distils off.

R. T.

Periodic acid and periodates. I. Analytical determination of periodic acid. II. Dehydration of paraperiodic acid. III. Sodium and silver periodates. J. R. PARTINGTON and R. K. BAHL (J.C.S., 1934, 1086—1088, 1088—1091, 1091—1094).—I. The prep. and properties of H_5IO_6 are described. The acid was analysed (1) by heating with aq. KI and HCl at 60° for 15 min. and determining the I liberated, (2) by reducing with SO_2

and determining the I' as AgI , (3) by boiling with conc. HCl, the Cl liberated showing that only three O atoms are active and ICl is probably formed during the reaction, (4) by titration with NaOH, the acid being monobasic to Me-orange and dibasic to phenolphthalein, and (5) by heating in an atm. of CO_2 , the whole of the O being evolved and collected in a Schiff's nitrometer.

II. H_5IO_6 at 100° in vac. loses $2H_2O$ (v.p. 10 mm.) forming HIO_4 , which sublimes with slight decomp. At 125° , HIO_3 is formed. At 80° , in vac., dimesoperiodic acid, $H_4I_2O_9$, is formed. The v.p. at 85° are: H_5IO_6 7.5 mm., $H_4I_2O_9$ 5 mm., and HIO_4 3 mm. H_3IO_5 and I_2O_7 were not obtained.

III. $Na_2H_3IO_6$, when strongly heated, decomposes: $4Na_2H_3IO_6 = 4Na_2O + 2I_2 + 6H_2O + 7O_2$, but does not lose H_2O in vac. at 100° , whence it is inferred that the constitution differs from $Na_4I_2O_9 \cdot 3H_2O$. $Ag_2H_3IO_6$ (I) loses all of its H_2O at 90° in vac., in accord with the constitution $Ag_4I_2O_9 \cdot 3H_2O$. Attempts to dehydrate (I) in air at atm. pressure lead to decomp. Intermediate hydrates were not obtained by dehydration in vac.

J. G. A. G.

Volatility product. [Interaction of vapours.] E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 505—506).—The reaction of I vapour with the vapour of Hg, aq. NH_3 , $(NH_4)_2CO_3$, and camphor (II) is demonstrated. The reactants are placed, unmixed, in closed right-angled tubes. Liquefaction occurs in the systems (II)-chloral (III), (II)-PhOH, (II)-thymol (IV), (III)-menthol (V), (III)-PhOH, (V)-PhOH, but not in (II)-(V), (IV)-(III), (IV)-(V), or (III)-PhOH.

J. G. A. G.

Rhenium trichloride. W. BILTZ, W. GEHMANN, and F. W. WRIGGE (Annalen, 1934, 511, 301—303).—Contrary to Manchot *et al.* (this vol., 616), the analytical data, Re $63.58 \pm 0.03\%$, Cl $36.40 \pm 0.07\%$, and chemical reactions show that $ReCl_3$ is O-free.

J. W. B.

Composition of Prussian and Turnbull's blue. A. K. BHATTACHARYA (J. Indian Chem. Soc., 1934, 11, 325—330; cf. A., 1933, 920).—Addition of excess of $K_4Fe(CN)_6$ to $FeCl_3$ gives $K_3Fe(CN)_6$; similarly, $FeSO_4$ with excess of $K_3Fe(CN)_6$ forms $K_4Fe(CN)_6$. With equiv. amounts of $FeSO_4$ and $K_4Fe(CN)_6$, both Fe^{++} and Fe^{+++} are present in the filtrate. $H_2C_2O_4$ is also formed.

J. S. A.

Complex compounds of the olefines with metallic salts. I. Zeise's salt.—See this vol., 994.

Isomerides of quadricovalent palladium and platinum.—See this vol., 994.

Principle of a quantitative X-ray analysis of the concentration of metal phases in an alloy or mixture. R. GLOCKER (Metallwirt., 1933, 12, 599—602; Chem. Zentr., 1934, i, 251).—A review.

H. J. E.

Use of Röntgen spectroscopy in chemical analysis. W. NODDACK (Ergeb. tech. Röntgenkunde, 1933, 3, 67—72; Chem. Zentr., 1934, i, 86—87).—Possible applications, their sensitivity, and limits are discussed. An example is described.

L. S. T.

Microchemical analysis of plane polished surfaces by means of monochromatic X-ray images. L. VON HAMOS (*Nature*, 1934, **134**, 181—182).—A method for the examination of surfaces which show local variations in chemical composition is described. It can be applied to metals and ores, and to reactions occurring in the solid state.

L. S. T.

Determination of hydrogen-ion concentration. A. KUFFERATH (*Papier-Fabr.*, 1934, **32**, 317—318).—A standard solution (I) is coupled with the test solution (II) by an inverted KCl-agar-agar U-tube and titrated with alkali until equivalence of p_H is shown by a modified Lippmann electrometer. (I) is of lower p_H than (II), and may be HCO_2H , $AcOH$, KH_2PO_4 , or H_3BO_3 , covering p_H 2.8—8.8. A graph is drawn for each standard connecting p_H with vol. of alkali used.

D. A. C.

Importance of the method of application of the potassium chloride bridge in the determination of the p_H of suspensions. C. DU RIETZ (*Svensk Kem. Tidskr.*, 1934, **46**, 136—139; cf. *A.*, 1933, 1113).—Abnormally high, varying e.m.f. are obtained when the KCl tube dips directly into a suspension of acid-treated cellulose. This can be avoided if the arrangement, $Hg_2Cl_2|KCl|filtrate$ or $centrifugate|suspension|quinhydrone$, is employed.

R. S.

Potentiometric titration. L. GUZELJ (*Arh. Hemiju*, 1934, **8**, 67—72).—A review of known methods.

R. T.

Furoic acid as an acidimetric standard. H. B. KELLOG and A. M. KELLOG (*Ind. Eng. Chem. [Anal.]*, 1934, **6**, 251—252).—Advantages are indicated.

E. S. H.

Indicators. XXIII. Indirect method for measurement of half-change points and limiting curves. A THIEL and D. GREIG (*Z. physikal. Chem.*, 1934, **169**, 193—206; cf. this vol., 618).—The method is for use where one limiting state of the indicator is attainable only in solutions having a high electrolyte concn., so that the limiting colour and half-change point are subject to marked salt errors. It involves measurement of at least two isobaths in a range in which there is no appreciable salt error. From these and the other limiting curve the inaccessible limiting curve and half-change point can be calc. The procedure is also useful where the direct measurement of the limiting colours is prevented by the overlapping of several ranges. A mixed-colour colorimeter is employed in conjunction with monochromatic illumination. The results of the application of the above method to various indicators are reported.

R. C.

Determination of moisture in unstable products. E. B. HOLLAND and C. P. JONES (*Science*, 1934, **79**, 526).—The vac. oven gives more trustworthy results than the electrically heated and controlled drying oven for the determination of H_2O in unstable products, e.g., tobacco.

L. S. T.

Separation of chloride from bromide by means of ammonia. T. B. SMITH (*J.C.S.*, 1934, 783—790).
For the detection of Cl' in presence of Br' , dil. **HNO₃** is added to the solution containing 40 mg. Br' ,

and then a small excess of $AgNO_3$. The ppt. is washed and shaken with 50 c.c. of 6*N*-aq. NH_3 , 5 c.c. of 0.1*N*- $AgNO_3$ are added, the solution is boiled for 3 min., and made up to 50 c.c. with 3*N*- NH_3 , without interrupting heating. The liquid is diluted to 50 c.c. at intervals of 1 min. four times, boiling is continued for 1 min., the solution is cooled, filtered, and 1/5 of its vol. of $4 \times 10^{-3} M$ - $HgNO_3$ in 6*N*- HNO_3 is added to the filtrate. A turbidity indicates Cl' . For traces of Cl' , the solution of the Ag halides in 40 c.c. of conc. aq. NH_3 is evaporated to half its vol. on the steam bath, the clear liquid is decanted and made up to 20 c.c. with 3*N*- NH_3 . The solution is boiled and the vol. made up at intervals of 1 min. four times, boiling is continued for 1 min., and after cooling to 50° 4 c.c. of nicotine buffer (3 c.c. of conc. $H_2SO_4 + 30$ c.c. $H_2O + 40$ c.c. of nicotine, diluted to 80 c.c.), and 0.5 c.c. 0.1*N*- $AgNO_3$ are added to 8 c.c. of the solution, which is then left in a dark place for at least ½ hr. The solution is filtered and 1/5 of its vol. of 8—12*N*- H_2SO_4 is added to the filtrate. Cl' gives a turbidity in 5—10 min. The theory is discussed.

R. S. B.

Determination of small quantities of hydrofluoric acid. B. VISINTIN (*Annali Chim. Appl.*, 1934, **24**, 315—326).—< 0.5 mg. of HF may be determined with satisfactory accuracy by Greeff's volumetric method (B., 1913, 992), if bromophenol-blue is used as an indicator of neutrality. Sol. silicates and phosphates, which exert a buffering action, may be eliminated by means of ammoniacal $Zn(OH)_2$.

T. H. P.

Determination of hydrogen sulphide in waters. A. HEMMELER (*L'Ind. Chimica*, 1934, **9**, 894—898).—Total S'' in natural H_2O is determined by pptg. S with $CdCl_2$, and treating the CdS with excess of 0.1—0.5*N*-I solution. The reaction is quant. and $CdCO_3$ does not interfere. Excess of I is titrated with $Na_2S_2O_3$.

R. N. C.

Colorimetric determination of sulphur chloride. A. CASTIGLIONI (*Annali Chim. Appl.*, 1934, **24**, 273—277).—Addition of a solution of S_2Cl_2 in CCl_4 , C_6H_6 , or CS_2 to 95% EtOH containing a little conc. aq. NH_3 gives a violet colour which detects 0.0005 g. of S_2Cl_2 in 100 ml. and serves for its determination. A colorimetric arrangement, including two Se cells and a galvanometer, is described.

T. H. P.

Volumetric determination of soluble sulphates by the sodium carbonate method. S. K. TSCHIRKOV and E. GONIBESOVA (*Zavod. Lab.*, 1934, **2**, 420—424).—Monhaupt's method, consisting in addition of standard $BaCl_2$, and titration of excess of $BaCl_2$ with standard Na_2CO_3 in presence of EtOH, gives trustworthy results for $[SO_4''] < 0.05\%$, in absence of NH_4 and of considerable excess of $BaCl_2$.

R. T.

Determination of selenium in pyrites etc.—See B., 1934, 670.

Dilution method for micro-Kjeldahl determinations. O. HARTLEY (*Ind. Eng. Chem. [Anal.]*, 1934, **6**, 249).— H_2SO_4 is used as a dilution medium for H_2O -insol. substances, such as wool and silk.

E. S. H.

Rapid determination of ammonia. Z. V. OGUR (*Zavod. Lab.*, 1934, **3**, 418—420).—2*N*- $NaOCl$ is

preferred to NaOBr in the nitrometric determination of NH_3 according to Knop. R. T.

Comparison of the methods of determining nitrites and rapid determination of small amounts of nitrite. K. M. PANDALAI and G. GOPALARAO (J. pr. Chem., 1934, [ii], 140, 240—246).—The errors associated with the customary methods of determining NO_2' by KMnO_4 or iodometrically are investigated. The following process is recommended. NaHCO_3 (4 g.) is added to 20 c.c. of the nitrite solution followed by 5 c.c. of 10% KI and a little sol. starch. A brisk current of CO_2 is passed through the solution for 10 min. to remove O_2 , after which 10 c.c. of 5N- H_2SO_4 are added. The liberated I is titrated with 0.0002N- $\text{Na}_2\text{S}_2\text{O}_3$. The error is 0.25% when small amounts of NO_2' are present. The colorimetric method is inaccurate, but is the only one which permits determination of minute amounts of NO_2' . H. W.

Rapid electrolytic determination of nitrate-nitrogen. N. J. UGNJATSCHEV and I. I. MISCHNAEVSKI (Zavod. Lab., 1934, 3, 409—413).—The nitrate, dissolved in standard H_2SO_4 , is reduced to NH_3 (determined by titration of residual acid) in a Cu cathode chamber with a corrugated inner surface, which is activated by treatment with 1—2% H_2O_2 after every five determinations. The duration of reduction of 0.1 g. of nitrate is 10—20 min. R. T.

Separation of phosphate from calcium, and of phosphate, calcium, and magnesium. H. BRINTZINGER and E. JAHN (Z. anal. Chem., 1934, 97, 312—314).—Addition of $(\text{NH}_4)_2\text{MoO}_4$ + conc. HNO_3 ppts. PO_4''' as NH_4 phosphomolybdate. Excess of aq. NH_3 added to the filtrate ppts. CaMoO_4 , leaving Mg in solution. J. S. A.

Detection of arsenic. R. INTONTI (Atti Congr. naz. Chim., 1933, 4, 732—737; Chem. Zentr., 1934, i, 1527).—The HCl solution of As is heated with a Cu spiral in a reflux condenser and the grey ppt. dissolved by heating with H_2O_2 and 10% HNO_3 . After evaporation to dryness and addition of $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 , the As is identified by Bougault's reaction (I). 0.2 mg. of As in 200 c.c. can be detected, but the separation of > 0.4 mg. of As is not quant. Sn, Pb, and Zn do not interfere with (I), and Sn and sulphite do not affect the separation of As on Cu. L. S. T.

Rapid determination of small amounts of arsenic. C. E. LACHELE (Ind. Eng. Chem. [Anal.], 1934, 6, 256—258).—In a modified Gutzeit procedure the AsH_3 impinges on a diaphragm impregnated with HgBr_2 , which is then developed in aq. KI and compared with a colour standard. The method is applicable in presence of Fe, Sn, Sb, or reducible S or P compounds and can detect 0.001—0.040 mg. As_2O_3 . E. S. H.

Determination of arsenic in sulphuric acid.—See B., 1934, 670.

Drop reaction for boron. N. A. TANANAEV and O. A. KULSKA (Ukrain. Chem. J., 1934, 9, 1—5).—A drop of solution is placed on curcumin paper (I), when a rose coloration indicates ≤ 0.01 mg. B, or ≤ 0.005 mg. B if the paper is first moistened with 1 : 2 glycerol-EtOH, saturated aq. mannitol, or 5% aq.

tartaric acid, and ≤ 0.001 mg. with 5% aq. $\text{H}_2\text{C}_2\text{O}_4$. B is detected in glass by fusion with Na_2CO_3 , dissolving the melt in HCl, adding MeOH, boiling, and placing wet (I) in the vapour. R. T.

Spectral analysis by sensitive lines within the range of the glass spectrograph: measurements in the spark spectrum of high-percentage boron- and phosphorus-iron alloys. W. KRAEMER (Z. anal. Chem., 1934, 97, 401—404).—Measurements for alloys containing 20% B and 25% P are given, using the apparatus described previously (A., 1933, 1110). J. S. A.

Determination of free silica in coal-measure rocks. A. SHAW (Analyst, 1934, 59, 446—461).—No satisfactory method for the direct determination could be found. Selvig's method (I) of rational analysis gives trustworthy results, that of Lunge and Millberg (B., 1897, 762) does not. The sources of error in (I), and their magnitude, are discussed. The analyses of twelve samples of rock by four analysts agreed to within 1%. Calculation of the % of free SiO_2 from ultimate analysis gives erroneous results unless the minerals present are identified. E. C. S.

Possible sources of error in determination of calcium and magnesium. N. I. BELIAEV (Zavod. Lab., 1934, 3, 462—463).—Ca and Mg are often present in alleged ash-free filter paper, which should be washed with 1% HCl before use. R. T.

Determination of calcium and magnesium in natural and purified water. R. DUROUDIER (Ann. Falsif., 1934, 27, 273—277).—MgO and CaO are determined together by titrating the H_2O with standard palmitic acid in aq. PrOH. MgO is determined separately after removal of Ca as oxalate. E. C. S.

Volumetric determination of beryllium in presence of fluorine. V. M. ZVENIGORODSKAJA and A. A. GAIGEROVA (Z. anal. Chem., 1934, 97, 327—331).—F⁺ is pptd. as CaF_2 by addition of excess of neutralised 20% aq. CaCl_2 . Be may then be determined by direct titration with alkali against phenolphthalein (A., 1912, ii, 491). J. S. A.

Nephelometric micro-determination of magnesium. E. V. VASILIEV (Ukrain. Chem. J., 1934, 9, 6—9).—0.3 g. of dolomite or 0.7 g. of limestone is dissolved in HCl, NH_4Cl and a mixture of aq. $\text{K}_3\text{Fe}(\text{CN})_6$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ are added to complete pptn. of Ca, when 0.1 vol. of conc. aq. NH_3 , and H_2O to 50 c.c. are added, and the solution is filtered. 1 c.c. of the filtrate is added to a mixture of 1 c.c. of aq. NH_3 , 39 c.c. of H_2O , and 10 c.c. of 0.2N- Na_2HPO_4 , the solution is diluted to 80 c.c., and Mg is determined nephelometrically. The experimental error is 0—10%. R. T.

Detection of small amounts of zinc with diethizone. H. FISCHER and G. LEOPOLDI (Z. anal. Chem., 1934, 97, 385—394).—The use of acid, NaOAc-buffered solution in testing for Zn is preferable to testing in alkaline solution (cf. this vol., 48). Zn may then be detected directly in presence of Ni, Co, and Cd by the discharge of red colour on shaking the CCl_4 layer with 5% AcOH. Sn^{++} should be oxidised

with FeCl_3 , and Cu, Hg, Ag, Au, and Pd removed by H_3PO_2 . J. S. A.

Rapid determination of zinc in ores.—See B., 1934, 722.

Detection of cadmium and lead. F. I. TRISCHIN (Ukrain. Chem. J., 1934, 9, 29—33).—Excess of 25% aq. NH_3 and 1 c.c. of $N\text{-KI}$ are added to 1 c.c. of solution (I) (containing all the common cations), conc. aq. KCN is added to complete decolorisation of the filtrate, and aq. Na_2S is added, when a yellow ppt. is indicative of 0.28 mg. Cd. Pb (≤ 0.52 mg.) is detected by adding dil. HCl to 1 c.c. of (I), dissolving the ppt. in aq. NaOAc , and adding aq. K_2CrO_4 to the solution, when a yellow ppt. of PbCrO_4 is obtained. R. T.

Dimercaptothiodiazole as an analytical reagent. J. GUPTA (J. Indian Chem. Soc., 1934, 11, 403; cf. this vol., 502).—Dimercaptothiodiazole (I) may be used for the separation of Cu from Zn, Mn, Ni, Co, Mo, W, and Fe^{2+} in dil. acid solution; from As and Sn^{IV} in tartaric acid (II) solution, and from Sn and Sb in presence of NaF . Pb may be pptd. by (I) in presence of As, Sb, and Sn from solutions containing (II) + NaF . J. S. A.

Determination of traces of mercury. V. MAJER (Chem. Listy, 1934, 28, 169—173).—Hg ($\leq 0.01 \times 10^{-6}$ g.) is determined in 5 c.c. of solution by pptn. on Fe wire (I) in presence of Cu salts; the Hg is distilled from the (I) in such a way as to receive a single drop of distillate (II), the diameter of which is measured micrometrically. Should it not be possible to obtain (II) in one drop, the individual drops are measured in a Jorgensen counter. A similar procedure serves for the detection of $\leq 0.001 \times 10^{-6}$ g. of Hg. The electrolytic method gives trustworthy results with $\leq 10^{-6}$ g. of Hg. The colorimetric method, using diphenylcarbazone, is applicable only in absence of other substances, when $\leq 0.2 \times 10^{-6}$ g. of Hg can be determined. A no. of other methods intended for $\leq 10^{-6}$ g. of Hg have an experimental error of $> 10\%$. R. T.

Volumetric determination of cerium using the induced oxidation of cerous salts by chromic acid+arsenious acid. R. LANG (Z. anal. Chem., 1934, 97, 395—401).— Ce^{III} in acid solution in presence of HPO_3 is oxidised inductively during the oxidation of As^{III} by $\text{K}_2\text{Cr}_2\text{O}_7$. Standard $\text{K}_2\text{Cr}_2\text{O}_7$ and As_2O_3 are added to the Ce solution, with NHPh_2 as indicator, and excess of $\text{K}_2\text{Cr}_2\text{O}_7$ is titrated back with $0.1N\text{-FeSO}_4$. J. S. A.

Determination of alumina in steel.—See B., 1934, 676.

Rapid analysis of mixtures of alum, calcium oxide, and calcium carbonate.—See B., 1934, 716.

Separation of aluminium and iron from beryllium with hydroxyquinoline. V. M. ZVENIGORODSKAJA and T. N. SMIRNOVA (Z. anal. Chem., 1934, 97, 323—326).—The addition of $\text{H}_2\text{C}_2\text{O}_4$ in the pptn. of $\text{Fe} + \text{Al}$ with 8-hydroxyquinoline may lead to error. The method of Kolthoff (A., 1928, 981) is preferable. J. S. A.

Determination of the sum of aluminium and ferric oxides in presence of silicic acid by hydro-

lytic precipitation according to A. Stock. G. S. BRIZGALOV (Zavod. Lab., 1934, 3, 508—510).—Stock's method is not applicable to solutions containing $> 0.03\%$ SiO_2 . R. T.

Micro-reactions. I. M. KORENMAN (Z. anal. Chem., 1934, 97, 418—421).—A 0.15% solution of methylene-blue in 3% NaOAc gives with MnO_4^- ($\leq 0.003N$) fine blue needles of the insol. permanganate. The Emich "fibre tests" with litmus (for H^+) and with ZnS for heavy metals may be performed on paper without serious loss of sensitivity. Photographic paper, after removal of Ag salts, is suitable for the ZnS test. J. S. A.

Determination of manganese and chromium in organic matter after nitro-sulpho-perchloric destruction. E. KAHANE and D. BRARD (Bull. Soc. Chim. biol., 1934, 16, 710—719).—Mn and Cr in org. material may be determined volumetrically or colorimetrically in the liquid (I) obtained after destruction with HNO_3 , H_2SO_4 , and HClO_4 . In the distillate from (I), however, there are present small quantities of Mn, and to a smaller extent Cr (determined using formaldoxime and diphenylcarbazide, respectively) which cannot be accounted for by the volatility of inorg. salts or mechanical separation. A. L.

Mixed perchloric and sulphuric acids. II. Potassium ferro- and ferri-cyanides as reference standards in the evaluation of titanous solutions. G. F. SMITH and C. A. GETZ (Ind. Eng. Chem. [Anal.], 1934, 6, 252—254; cf. this vol., 743).— $\text{K}_2\text{Fe}(\text{CN})_6$ can be used as a reference standard for Fe^{III} after treatment with HClO_4 or $\text{HClO}_4 + \text{H}_2\text{SO}_4$. $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, dried at 140° , can be used as a standard. By this method TiCl_3 solutions can be standardised with an accuracy of 0.1%. E. S. H.

Potassium permanganate as microchemical reagent for metals. N. S. POLUEKTOV and V. A. NASARENKO (Pharm. Zentr., 1934, 75, 424—426).— KMnO_4 ppts. from aq. NH_3 solution characteristically cryst. complex salts of Ni, Zn, and Cd. Cu and Ag give ppts. in presence of $\text{C}_5\text{H}_5\text{N}$, and Ag also with $\text{KMnO}_4 + (\text{CH}_2)_6\text{N}_4$. J. S. A.

Application of mercuri-ammonium derivatives to quantitative analysis. Gravimetric determination of Cr^{III} , and its separation from Mn^{II} . B. ŠOLAJA (Arh. Hemiju, 1934, 8, 35—41).— Cr^{III} is quantitatively pptd. by adding a suspension of Millon's base to the solution, together with 1.5% NH_4I to p_H 5.0—5.5; under these conditions Mn^{II} is not pptd. Satisfactory results are not obtained at other p_H , or in presence of F^- , Cl^- , Br^- , SO_4^{2-} , OAc^- , $\text{C}_2\text{O}_4^{2-}$, or other ions forming complex anions with Cr. R. T.

Iodometric determination of chromate. A. FRIEDRICH and E. BAUER (Z. anal. Chem., 1934, 97, 305—311).—The $\text{Na}_2\text{S}_2\text{O}_3$ titre of CrO_4^{2-} solutions is high by an amount const. under given conditions, independent of the vol. of CrO_4^{2-} titrated (cf. A., 1926, 1221). The effect is attributed to an induced reduction of CrO_4^{2-} to CrCl_2 , and is considerable with 0.01N solutions. With solutions containing $\leq 1\%$ of $\text{HI} + 20\text{—}25\%$ of AcOH , titrated after ≤ 15 min., the magni-

tude of the error may be found by comparing the titre of three different vols. of $\text{CrO}_4^{''}$. J. S. A.

Determination of chromates in air. J. D. GOLDENBERG (Zavod. Lab., 1934, 3, 506—507).—The colorimetric is preferred to the volumetric method for determination of traces of $\text{CrO}_4^{''}$. R. T.

Potentiometric separation of chromium and tungsten and their determination in steel.—See B., 1934, 722.

Determination of tungsten and molybdenum in ferro-alloys containing both.—See B., 1934, 721.

Use of solid carbon dioxide in determination of tin. H. I. WHITE (Ind. Eng. Chem. [Anal.], 1934, 6, 234).—About 0.5 cu. in. of solid CO_2 is added to the reaction vessel to replace the usual current of gaseous CO_2 . E. S. H.

Determination of tin in organic material.—See B., 1934, 699.

Determination of small quantities of germanium in presence of arsenic. I. S. A. COASE (Analyst, 1934, 59, 462—465).—The method is based on that of Grant (A., 1929, 165) for the determination of Sb as SbH_3 . The Ge salt is electrolysed in alkaline solution. The GeH_4 so formed is decomposed by heat, and the mirror of Ge is compared with mirrors of known Ge content (0.0189—0.1 mg.). E. C. S.

Use of antipyrine iodide reagent in spot analysis. G. GUTZEIT and R. WEIBEL (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 33—38).—The reaction between a mixture of antipyrine and KI and the HCl solutions of the metals of the H_2S group has been investigated. It can be utilised to detect Sb as follows. The sulphides sol. in alkali polysulphides are dissolved in aqua regia, evaporated to dryness, and redissolved in HCl. A drop is placed on filter-paper, 5 drops of 35% CH_2O are added, and after 2—3 min. a drop of KI-antipyrine reagent. A yellowish-brown stain indicates Sb. J. W. S.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXVI. Interference of tungsten in earth-acid determinations. W. R. SCHOELLER and C. JAHN (Analyst, 1934, 59, 465—468; cf. A., 1927, 1047).—When the earth acids are pptd. by tartaric hydrolysis, the co-pptn. of subordinate amounts of W is incomplete. Neither tannin nor cupferron ppts. W by itself from tartrate or oxalate solutions, but preponderating quantities of earth acid induce partial pptn. of W. A definite position cannot yet be assigned to W in the proposed analytical scheme. E. C. S.

Thermal expansion measurements with iron by means of X-rays. W. SCHMIDT (Ergebn. techn. Röntgenkunde, 1933, 3, 194—201; Chem. Zentr., 1934, i, 184).—A vac. camera for measurements to 1435° is described, measurements for the α , β , γ , and δ phases of Fe being recorded. The vol. contraction in the transition $\beta \rightarrow \gamma$ was 1%; the vol. increase for $\gamma \rightarrow \delta$ was approx. 0.4%. Expansion coeffs. have been calc. H. J. E.

Calorimeter for determination of the specific heat of liquids. W. MEHL (Chem. Fabr., 1934, 7, 240—241).—The temp. rise of a vol. of PhMe in which

a vessel containing a known wt. of the liquid may be placed, on passage of a known current for a known time, is determined. The apparatus is almost wholly of glass. The total error is $\pm 1.5\%$. The sp. heats, in kg.-cal. per kg., of $(\text{CHCl}_2)_2$ (16°), oleic acid (17°), and $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ (17°) are 0.266 ± 0.004 , 0.493 ± 0.007 , and 0.597 ± 0.01 , respectively.

H. F. G.

Prospective standard substances for bomb calorimetry. VI. Succinic acid. L. J. P. KEFFLER (J. Physical Chem., 1934, 38, 717—733).—It is proposed to adopt succinic acid as a secondary standard for bomb calorimetry, and to accept for the heat of combustion at 20° , per g. weighed in vac., 3025 ± 1 g.-cal. (15°). R. S. B.

Realisation of the international temperature scale between 0° and 600° . C. M. FOCKEN (New Zealand J. Sci. Tech., 1934, 15, 423—425).—A Pt resistance thermometer gives sufficient accuracy.

C. W. G.

Control of regularity of graduation [calibration] of a thermometer. P. VERNOTTE (Compt. rend., 1934, 198, 2230—2232).—Scale intervals may be checked over a narrow temp. range without abs. calibration. B. W. B.

Obtaining constant low temperatures. J. V. SULTZOV (Zavod. Lab., 1934, 3, 557).—58% CaCl_2 is frozen by means of liquid air; the temp. of the melting product remains at -40° until all is liquefied.

R. T.

Release of supercooling in cryoscopic determinations. D. E. KENYON and G. A. HULETT (J. Amer. Chem. Soc., 1934, 56, 1649).—Supercooling may be released at a convenient stage by dropping into the system a small glass bead, which has been wetted in the solvent and stored in contact with solid CO_2 .

E. S. H.

M.p. determination. II. Evaluation of stem correction and the principle of simultaneous determination of m.p. by the capillary tube method. C. L. TSENG (Sci. Quart. Nat. Univ. Peking, 1934, 4, 283—324).—Increased trustworthiness in comparison is obtained by carrying out the m.p. simultaneously. C. W. G.

Preparation of specimens for the measurement of thermal conductivity. J. M. ADAMS (Rev. Sci. Instr., 1934, [ii], 5, 250—252).—An exactly reproducible method of applying metallic coatings to the surfaces of solid specimens and of imbedding thermocouples at any given depth in the coatings is described. The variable discontinuity in temp. between the specimen and metallic surface in contact in thermal conductivity measurements is thus eliminated.

N. M. B.

Determination of the thermal resistance of metal single crystals at low temperatures. W. J. DE HAAS and W. H. CAPEL (Physica, 1934, 1, 725—734).—The temp. difference between the two ends of the crystal is measured with two vapour-tension thermometers when electrical energy is supplied at a steady rate. Measurements with Bi at 81.4° and 20 — 16.5° abs. are recorded, the resistance decreasing with falling temp. in this range. H. J. E.

Exact measurements of specific heats of solid substances at high temperatures. VII. Calorimetric behaviour of zirconium. F. M. JAEGER and W. A. VEENSTRA (Rec. trav. Chim., 1934, 53, 917—932).—Reproducible results are not attainable owing to internal changes in the region 400—630°, resulting in prolonged slow evolution of heat after initial cooling within the calorimeter. D. R. D.

Laboratory electric resistance furnaces. C. RIGOLLET (J. Phys. Radium, 1934, [vii], 5, 262—266).—Mathematical. Heat losses and the equation of heating are examined. A method of obtaining a linear rise of temp. with time is described. N. M. B.

Apparatus for distilling mercury under reduced pressure. H. VOGELS (Bull. Soc. chim. Belg., 1934, 43, 327—330).—The apparatus described is easily constructed, prevents mechanical entrainment of impurities, and switches off the heating when the Hg is exhausted or the pressure too high. A. G.

Use of the prism for the determination of the principal refractive indices of crystals. A. CAVINATO (Atti R. Accad. Lincei, 1934, [vi], 19, 640—645).—A mathematical treatment is given for the use of single prisms for determination of n of all rhombic and, especially, monoclinic crystals. H. F. G.

Interference method of determining indices of refraction in the infra-red. H. J. FROST (J. Proc. Roy. Soc. New South Wales, 1933, 67, 223—230).—Vals. of n can be calc. with an accuracy of 0.3% from measurements of the interference max. obtained when a beam of infra-red light falls on thin sheets of the material. R. S.

Photo-electric apparatus for turbidity and light penetration measurement. M. M. ELLIS (Science, 1934, 80, 37). L. S. T.

Photo-electric colorimeter. A. WEIL (Science, 1934, 79, 593). L. S. T.

Optical determination of photochemical reaction products. E. MIESCHER (Nachr. Ges. Wiss. Gottingen, 1933, 329—334; Chem. Zentr., 1934, i, 13).—The determination from the height and width of the absorption bands of the no. of colour centres in natural NaCl crystals in their at. distribution and after flocculation to colloids of different sizes shows that the method of optical determination of the no. of centres is applicable to colloiddally flocculated centres. L. S. T.

Filtration at low temperature. Chromatographic analysis of colourless substances (ultra-chromatogram). P. KARRER and K. SCHOPP (Helv. Chim. Acta, 1934, 17, 693).—A filter of solid CO₂ is described. The atm. of CO₂ prevents oxidation of the product, which is obtained pure by evaporation of the CO₂ filter. Colourless substances may be separated by the chromatographic method, using a quartz tube and ultra-violet light. E. S. H.

Polarimeter tube. Shaking table. J. STRAUB (Chem. Weekblad, 1934, 31, 465—466).—An ebonite polarimeter tube (10 cm.), especially suited for starch or sugar solutions in aq. or conc. HCl, is described.

A shaking table is made by mounting a board horizontally on two synchronised, vertical cranks, which can be given a small, rapid circular movement. Vessels fixed on the table with plasticine are given a rotatory movement similar to that resulting from hand shaking. S. C.

Reflectometer for all types of surfaces. F. BENFORD (J. Opt. Soc. Amer., 1934, 24, 165—174).—The theoretical basis, construction, and calibration of an "abs." part-sphere instrument are described. N. M. B.

Improved wire grating spectrometer for the far infra-red. R. B. BARNES (Rev. Sci. Instr., 1934, [ii], 5, 237—243).—An instrument for use with solids, liquids, or gases, and giving high resolution in the range 30—180 μ , is described. N. M. B.

Ratiometer for intensity analyses of microphotometer records. G. O. LANGSTROTH (Rev. Sci. Instr., 1934, [ii], 5, 255—256).—An instrument to eliminate direct distance measurements and ratio calculations, and interpreting the photometer record directly in terms of relative intensities, is described. N. M. B.

Focal isolation versus the monochromator for photochemical work in the ultra-violet. G. S. FORBES, L. J. HEIDT, and L. W. SPOONER (Rev. Sci. Instr., 1934, [ii], 5, 253—255).—For the group of Al lines at λ 194 m μ focal isolation is preferable, spectral purity being 0.98, and intensity seven times that obtainable from the monochromator. For the group of Zn lines λ 203—214 m μ focal isolation is preferable for intensity if spectral purity need not exceed 0.8. For other lines the monochromator was superior. N. M. B.

Determination of transmission values by means of the Hilger rotating sector photometer. A. DINGWALL, R. G. CROSEN, and H. T. BEANS (Rev. Sci. Instr., 1934, [ii], 5, 248—250).—Details of work previously reported are described (cf. Amer. J. Cancer, 1932, 16). N. M. B.

Kinetic measurements with the Pulfrich step photometer. A. WASSERMANN (Nature, 1934, 134, 101—102).—The method described has been used to investigate the kinetics of a diene synthesis. L. S. T.

Photo-electric photometer for reaction velocity measurements. G. BRAUER (Z. physikal. Chem., 1934, B, 26, 71—80).—An apparatus utilising two photo-electric cells, intermittent illumination, and an amplifying arrangement and permitting the determination of I_0/I with a precision of 0.05% is described. The properties of cells by various makers are reported. C.

Ultra-violet photo-electric spectrophotometer. D. H. FOLLETT (Proc. Physical Soc., 1934, 46, 499—509).—A high-precision instrument is described. The transmission of the sample is found by comparison with an improved cylindrical type rotating sector, adjustable when running, and by which light intensity is varied. Two photo-cells are used and fluctuations in the intensity of the source are compensated for. N. M. B.

Röntgen spectrograph and a spectrum experiment tube. O. BERG and W. ERNST (Ergeb. tech. Röntgenkunde, 1933, 3, 111—117; Chem. Zentr., 1934, i, 87). L. S. T.

Preparation of spectrographic scales. B. N. PETROVSKI (Zavod. Lab., 1934, 3, 455—456).—Directions for prep. of spectrometer scales are given. R. T.

X-Ray diffraction by crystals, and X-ray spectrum analysis. Reversed polar lattice in the determination of crystal structure by means of X-rays. V. LINITZKI (Ukrain. Chem. J., 1934, 9, 46—60, 61—72).—An exposition of the theory of X-ray spectral analysis is given. R. T.

Convenient X-ray vacuum camera for any low temperature. E. POHLAND (Z. physikal. Chem., 1934, B, 26, 238—245).—The camera is entirely of metal and permits the substance for examination to be condensed in a form suitable for Debye photographs on a metal wire adjusted to any desired low temp. The film is separated from the main chamber of the camera to avoid disturbances due to H₂O. R. C.

Portable ultra-violet meters. A. H. TAYLOR (J. Opt. Soc. Amer., 1934, 24, 183—184).—A small portable form of an instrument previously reported (cf. *ibid.*, 1933, 23, 60), with improved d.c. amplifier, is described. N. M. B.

Photography of flame in gaseous explosions. R. P. FRASER (Phot. J., 1934, 74, 388—405).—The various high-speed cameras for the photography of explosions employing the high-speed rotating drum, rotating mirror, or rotating shutter methods are described. In typical photographs the phenomena of flame arrest, compression waves, the production of detonation, the helical spin of the highly luminous detonation head, and the banded appearance of the flame behind the detonation head are demonstrated. The results are discussed. A high-speed shock wave may itself be spinning. The speed of a detonation wave is reduced by an electric field. Photographs of explosions in internal-combustion engine cylinder heads are also given. J. L.

Determination of the electrical resistance of water. Audiotohmmeter actuated by rectified alternating current. C. CUAU (Ann. Falsif., 1934, 27, 280—282).—A.c. from the main, rectified by a Cu-Cu₂O rectifier, is used for conductivity measurements. E. C. S.

Conductometric titrations and conductometric measurements and visual methods for carrying them out. G. JANDER and O. PFUNDT (Chem.-Ztg., 1934, 58, 611—613).—The principle and details of the method are discussed, and a visual method which avoids the use of the telephone as a null-point instrument is described. Examples are: titration in 3 min. of SO₄" (e.g., in drinking-H₂O) with Ba(OAc)₂ in the presence of AcOH and EtOH, titration of Ca(HSO₃)₂ with Ba(OH)₂ after oxidation with H₂O₂; strong and weak acids and bases and alkalimetric replacement reactions; determination CO by oxidation with I₂O₅ and titration with Ba(OH)₂; titration of halogens with AgNO₃. J. G.

Effect of inner discharges on the functioning of the Geiger-Müller counter. R. BRUNETTI and Z. OLLANO (Nuovo Cim., 1933, 10, 189—197; Chem. Zentr., 1934, i, 14).—The increased inner discharge observed after irradiation with X-rays also occurs when the polarity of the counter is reversed (partition positive) and then again when the normal state is restored (partition negative). The increase in the no. of impacts quickly falls, the rate being influenced by the nature of the partition material. The effect occurs with partitions of Al, Pb, Cu, Zn, or Mg, but not with brass. The process is assumed to be due to a soft radiation emitted by the activated metal. L. S. T.

Determination of the magnetic susceptibility of gases and vapours. R. I. JANUS and J. S. SCHUR (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 465—469).— χ is deduced from measurements of the velocity of circulation of a gas or vapour in a closed circuit, due to the influence of a magnetic field. The method is suitable for high temp. (cf. Lehrer, A., 1926, 1086). H. J. E.

Constant-head gas scrubber for small pressure drops. A. S. SMITH (Ind. Eng. Chem. [Anal.], 1934, 6, 279). E. S. H.

Gas-washing bottle. A. H. MCKINNEY (Ind. Eng. Chem. [Anal.], 1934, 6, 258). E. S. H.

Stationary wash-bottle equipment for the washing of analytical precipitates. A. HABERLAND (Chem. Fabr., 1934, 7, 251).—A series of wash-bottles is connected to a low-pressure compressed-air line, each outlet being fitted with a rubber tube ending in a glass jet and containing a glass sphere which serves as a valve. The system is hygienic, economises time, and obviates confusion between the various liquids used for washing. H. F. G.

Surface-tension measurements by the ripple method. H. E. BECKETT and H. SHEARD (J. Sci. Instr., 1934, 11, 214—216).—A stationary wave pattern formed between two vibrating styles is projected on a screen. C. W. G.

Purity required for surface tension measurements. T. C. SUTTON and H. L. HARDEN (Proc. Physical Soc., 1934, 46, 510—511).—Relative vals. of the surface tension found by dynamic and static methods, on which the effect of impurities differs, are used as an indication that the purity of the substance is adequate and that the val. obtained is that of the pure material. N. M. B.

Immersion method. II. Use of antimony bromide, with selenium. L. H. BORGSTRÖM (Bull. Comm. géol. Finlande, 1933, No. 101, 28—29; Chem. Zentr., 1934, i, 86).—Solutions of SbBr₃ in CH₂I₂ are stable, non-poisonous, and transparent and n can be raised by addition of SnI₄. n_D is 1.7656—1.8229 with from 16 to 44.5% of SbBr₃ and a mixture of 30% SbBr₃ and 27% SnI₄ with CH₂I₂ has n_D 1.8598. The following mixtures are also stable and transparent: 85% AsBr₃+10% As₂S₃+5% Se, n_D 1.884; 77% AsBr₃+9% As₂S₃+14% Se, n_D 1.929; 74% AsBr₃+13% As₂S₃+13% Se, n_D 1.974. L. S. T.

Vacuum indicator for low pressures. G. HERZOG and P. SCHERRER (*Helv. phys. Acta*, 1933, 6, 277—278; *Chem. Zentr.*, 1934, i, 86). L. S. T.

Direct-reading volumenometer for the determination of the real volume and specific gravity of porous bodies. C. H. SPIERS (*J. Sci. Instr.*, 1934, 11, 216—218).—The vol. of air displaced by the porous body is measured by the alteration in the vol. of Hg necessary to maintain equality of total vol.

Micro-method of measuring osmotic pressure. E. J. BALDES (*J. Sci. Instr.*, 1934, 11, 223—225).—Drops of solutions evaporate from looped junctions of a differential thermocouple. C. W. G.

Metal-to-silica joints and vacuum seals. S. D. D. MORRIS (*J. Sci. Instr.*, 1934, 11, 232—233).—(1) The SiO_2 surface is roughened and coated successively with Pt (from PtCl_4), Cu (by electrolysis), and soft solder. (2) A tapered hole in the metal, coated inside with soft solder, is pressed while hot over the outside of the tapered SiO_2 tube. C. W. G.

Simple seal for vacuum stirrers. W. RUD-BACH (*Chem.-Ztg.*, 1934, 58, 552).—The axis of the stirrer carries a rubber stopper, the lower end of which makes a vac.-tight joint with the rounded end of a coaxial glass tube, which forms a bearing lubricated with vaseline. H. J. E.

Accurate universal viscosimeter with a measuring range of 0.01 to above 500,000 centipoises. F. HOPPLER (*Proc. World Petroleum Congr.*, 1933, 2, 503—507).—The principle of eccentric ball drop through a cylindrical tube has been utilised to design a highly accurate viscosimeter, which is described in detail. By using balls of different diameters the instrument may be utilised to determine viscosity over a range extending from gases to liquids as dense as tar with an average error of about $\pm 0.2\%$. H. S. P.

Unified French method of measuring viscosity. H. WEISS (*Proc. World Petroleum Congr.*, 1933, 2, 490—495).—Conditions for exact measurement are specified. C. W. G.

Absolute viscosimeter. G. DUFFING (*Proc. World Petroleum Congr.*, 1933, 2, 499—502).—A ball attached to a pivoted arm is drawn upwards through the liquid contained in a cylindrical thermostat. C. W. G.

Soya-bean curd skin as dialysis membrane. T. Y. CHANG (*Sci. Rep. Nat. Tsing Hua Univ.*, 1934, 2, 257—261).—Soya-bean curd skin is a more efficient dialysis membrane for Fe_2O_3 and As_2S_3 sols than is pig's bladder. H. N. R.

Device for constant flow of liquids. J. H. WALES (*Science*, 1934, 79, 545—546). L. S. T.

Practical laboratory hints. L. GISIGER (*Z. anal. Chem.*, 1934, 97, 317—320).—Minor accessories and points of analytical technique are discussed. J. S. A.

Highly-polymerised compounds. XCV. Ultra-centrifugal polydispersity determinations on highly-polymerised substances. R. SIGNER and H. GROSS (*Helv. Chim. Acta*, 1934, 17, 726—737).—The determination of the distribution of particle size

in a polydisperse system by means of sedimentation analysis is described. Results are given for polystyrene. E. S. H.

[Preventing bumping in] micro-Kjeldahl digestion process. H. PETERSILIE (*J. Lab. Clin. Med.*, 1934, 19, 672—673).—A Pyrex tube, 7 mm. \times 3 mm. (internal), sealed to the end of a Pyrex rod 20 cm. \times external diameter of the tube, is inserted. CH. ABS.

New types of linear bolometers. R. C. L. BOWORTH (*Trans. Faraday Soc.*, 1934, 30, 554—560).—Self-supporting Ni strips have been prepared electrolytically (cf. this vol., 950) and used in the construction of both straight and differential types of bolometers of high sensitivity. Their behaviour has been examined. A simple and effective type of bolometric relay is described. Two devices for increasing further the sensitivity of the bolometer are also described; one is a regenerating device which increases the damping of the galvanometer, whilst the other, a compensated valve bridge amplifier, reduces it. M. S. B.

Modification of the gas circulating pump. FAZAL-UD-DIN and S. S. MANGAT (*Nature*, 1934, 134, 104—105). L. S. T.

Possibility of sedimentation measurements in intense centrifugal fields. T. SVEDBERG, G. BOESTAD, and I. B. ERIKSSON-QUENSEL (*Nature*, 1934, 134, 98).—Accurate measurements can be carried out in centrifugal fields of the order of 10^6g . L. S. T.

Simple sublimation apparatus. C. L. TSENG and M. HU (*Sci. Quart. Nat. Univ. Peking*, 1934, 4, 327—332).—The sublimate is collected on a filter-paper resting under a funnel on a cold surface. C. W. G.

Simple glass-blowing lamps. C. L. TSENG and M. HU (*Sci. Quart. Nat. Univ. Peking*, 1934, 4, 325—326).—Simple adaptations of ordinary burners are described. C. W. G.

Laboratory film-type evaporator. S. Y. CHEN (*J. Chinese Chem. Soc.*, 1934, 2, 126—128).—A jacketed condenser is fitted at the bottom to a flask and at the top to a dropping funnel and to a bent tube passing to another condenser. The first condenser is heated with a vapour of b.p. $>$ that of the liquid to be distilled. The latter drops in at the top and is distributed over the heated surface by a cotton-wool plug. The vapour is condensed in the second condenser. J. W. S.

Micro-burette. G. W. STANDEN and M. L. FULLER (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 299—300). E. S. H.

Constant-feed burette and apparatus for catalytic dehydration of alcohols. B. B. CORSON (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 297—298).—The apparatus described operates on the principle of opposing a const. liquid head to a const. resistance, and is especially suitable when a vaporised liquid is to be passed over a solid catalyst at approx. atm. pressure. S. H.

Distillation trap. O. S. RASK, E. KAPLAN, and H. C. WATERMAN (*Ind. Eng. Chem. [Anal.]*, 1934, 299). E. S. H.

Large-size modified Soxhlet for hot extractions. L. S. GRANT, jun., and W. M. BILLING (Ind. Eng. Chem. [Anal.], 1934, 6, 285). E. S. H.

Automatic all-glass extractors for the laboratory. W. A. LA LANDE, jun., and E. C. WAGNER (Ind. Eng. Chem. [Anal.], 1934, 6, 300).—The apparatus is designed for use with immiscible solvents lighter than H_2O . E. S. H.

Modified hydrogen-evolution method for [determining] metallic magnesium, aluminium, and zinc. R. H. KRAY (Ind. Eng. Chem. [Anal.], 1934, 6, 250—251).—Apparatus and technique are described. E. S. H.

Contamination of platinum by graphite. L. J. COLLIER, T. H. HARRISON, and W. G. A. TAYLOR (Trans. Faraday Soc., 1934, 30, 581—587).—The f.p. of Pt heated in vac. in a graphite crucible falls by approx. 40° to $2007 \pm 3^\circ$ abs. in 0.5 hr. and then remains const. It is inferred from spectroscopic, microscopic, and X-ray analysis, and from cooling curves, that the sample of above f.p. consists of a eutectic mixture of (a) a solid solution of 0.25% of graphite in Pt and (b) graphite (approx. 1.2% of the whole). R. S. B.

Determination of mol. wt., especially of highly-polymerised substances. M. ULMANN (Z. Elektrochem., 1934, 40, 451—455).—Apparatus and technique for determining osmotic pressure and hence mol. wt. by isothermal distillation are described. The application of the method to following changes in the degree of polymerisation is illustrated. E. S. H.

Use of rubber balloons in place of glass aspirators. P. A. PUZAKOV (Zavod. Lab., 1934, 3, 554—555).—The use of rubber balloons for taking gas samples is advocated. R. T.

Reagents for macro-etching. P. I. ORLETZ (Zavod. Lab., 1934, 3, 534—541).—The application of various known reagents is discussed. R. T.

Sorel cement in the preparation of micro-sections of soil. H. BJØRLYKKE (Chem. Erde, 1934, 9, 50—51).—The mineral grains are added to a thick paste made on a slide by adding MgO powder to conc. aq. $MgCl_2$. This sets to a hard cement and the section can then be prepared in the usual way. An examination of the weathering of different grains is thus possible. L. J. S.

Geochemistry.

Sulphur in the sun. C. E. MOORE and H. D. BABCOCK (Astrophys. J., 1934, 79, 492—497).—The spectroscopic evidence of the presence of S in the sun is discussed. 17 S lines have been identified in the solar spectrum with certainty and 6 with some uncertainty. L. S. T.

Determinations of the equivalent thickness of atmospheric ozone made at the Kutchino astrophysical observatory. V. G. FESENKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 448—451).—Data are recorded. H. J. E.

Distribution of atmospheric ozone as a function of altitude. D. BARBIER (J. Phys. Radium, 1934, [vii], 5, 243—252; cf. this vol., 626).—Mathematical. N. M. B.

Relative proportions of deuterium in natural hydrogen compounds. C. H. GREENE and R. J. VOSKUYL (J. Amer. Chem. Soc., 1934, 56, 1649—1650).— H_2O produced from the combustion of maize oil or natural gas is richer in H^2 than is ordinary H_2O . E. S. H.

Heavy water in water from deep oil wells. A. F. SCOTT (Science, 1934, 79, 565).—The d of H_2O associated with petroleum from wells > 5000 ft. deep does not differ from that of ordinary surface H_2O by > 2 in 10^6 . L. S. T.

Salt content and motion of water in the Suez Canal. G. WÜST (Naturwiss., 1934, 22, 447—450).—The connexion between meteorological factors (air temp., wind direction, rainfall) and the salt content and height of H_2O at three stations in the Suez Canal is discussed.

Lake Elton. N. A. SCHLESINGER and I. B. FEIGELSON (Sci. Mem. Univ. Saratov, 1933, 10, No.

2, 35—60).—L. Elton (Lower Volga) contains 7×10^6 tons of $MgCl_2$ and 40,000 tons of Br; the latter enters the lake with R. Tscherniavka H_2O , which contains 1—4 mg.-% of Br, the yearly increment from this source being approx. 35 tons. R. T.

Destructive action of soil-water on Volga district Portland cement, and the protective action of Saratov sandstone. R. G. MALKINA-OKUN (Sci. Mém. Univ. Saratov, 1933, 10, No. 2, 95—109).—Ground- H_2O containing sulphates has a destructive action on ordinary Portland cement (I), but not on (I) containing 30% of Saratov sandstone. R. T.

Neglected factors in the development of thermal springs. E. T. ALLEN (Proc. Nat. Acad. Sci., 1934, 20, 345—349).—The influence of geological and topographical features is discussed. R. S.

Thermal springs of Acqua Cotta (Villasor). E. PUXEDDU, A. RATTU, and E. MOSS (Annali Chim. Appl., 1934, 24, 289—300).—Analytical and physico-chemical data are given for this Sardinian water. T. H. P.

Occurrence of alkali metals in natural waters. R. BOSSUET (Compt. rend., 1934, 199, 131—133; cf. A., 1933, 692).—A max. vol. of 1 litre of the H_2O was conc., the alkali metal fraction separated, and either further fractionated by successive treatment with conc. HCl and $EtOH$, or pptd. as cobaltinitrites. The final residues or ppts. were analysed spectrographically. H_2O from primary geological sources (Pyrenees, Alps, Vosges, and Normandy) contained Li, Na, K, Rb, and Cs; Cs was absent from surface and river H_2O . B. W. B.

Composition of water from melted snow. G. BATTÀ and E. LECLERC (Bull. Soc. chim. Belg., 1934, 43, 320—326).—Analyses of melted snow show that the impurities arise from sources close to the fall. A. G.

Activation of sphalerite. A. B. BECK (Chem. & Ind., 1934, 104).—Since covellite can be floated only with difficulty and Cu⁺ salts are less effective than Cu²⁺ in the activation of Zn blende, it is suggested that the film formed on ZnS minerals by treatment with aq. CuSO₄ consists of a mixture of CuS, Cu₂S, and S and that the free S is the real activator. A. R. P.

Thermal expansion of aragonite and its atomic displacements by transformation into calcite between 450° and 490° in air. II. S. KÔZU and K. KANI (Proc. Imp. Acad. Tokyo, 1934, 10, 271—273; cf. this vol., 837).—The displacements of Ca and CO₃ are calc. C. W. G.

Identification of synthetic hornblende by layer line photographs. W. LÜDKE (Naturwiss., 1934, 22, 452).—The identity period of a synthetic hornblende in the direction of the needle axis was 5.28 Å., the val. agreeing well with that for the natural substance. A. J. M.

Sodalite from Bolivia. W. BRENDLER (Amer. Min., 1934, 19, 28—31).—The mineral has d^{145} 2.295, n 1.4837. Weathered sodalite is lower in alkalis and Cl and has a higher H₂O content. CH. ABS.

Occurrence of selenium in pyrites. K. T. WILLIAMS and H. G. BYERS (Ind. Eng. Chem. [Anal.], 1934, 6, 296—297).—The Se content of numerous soils has been determined. The results indicate a wider distribution of Se than has hitherto been suspected. The effect on vegetation is discussed. E. S. H.

Pyrite-marcasite relation. M. J. BÜRGER (Amer. Min., 1934, 19, 37—61).—Pyrite corresponds closely with FeS₂, whilst marcasite is low in S, the excess of Fe being present as proxy solid solution. CH. ABS.

Egorevsk phosphorites. N. L. KHERUVIMOVA (Inst. Mech. Treat. Ores, Russia; Rep. Concn. Non-metallic Ores, 1930, No. 1, 95—97).—A mineralogical description and analysis. CH. ABS.

Khiba apatite-nephelite deposit. N. L. KHERUVIMOVA (Inst. Mech. Treat. Ores, Russia; Rep. Concn. Non-metallic Ores, 1930, No. 1, 237—253).—A mineralogical and petrographical report. CH. ABS.

Analysis of Bedford cyrtolite for lead and uranium. O. B. MUENCH (J. Amer. Chem. Soc., 1934, 56, 1536).—The Pb : U ratio confirms that previously recorded (cf. A., 1932, 492). E. S. H.

Fluorescence of scapolites. H. HABERLANDT and A. KÖHLER (Chem. Erde, 1934, 9, 139—144).—Scapolite from many localities was tested for fluorescence in ultra-violet light, before and after ignition and in liquid air. Variable results were obtained. The strongly fluorescent scapolite from Grenville, Quebec, contains 7.72×10^{-12} g. Ra per g. of material. L. J. S.

Luminescence of apatite, pyromorphite, and some other phosphates. A. KÖHLER and H.

HABERLANDT (Chem. Erde, 1934, 9, 88—99).—Several minerals from various localities were tested for fluorescence in ultra-violet light with variable results. Apatite shows a yellow or pale violet fluorescence, or none. L. J. S.

Lead content of North German salt deposits and its relation to radioactivity. H. J. BORN (Chem. Erde, 1934, 9, 66—87).—As suggested by the crystal structure, small amounts of Pb can be taken up by NaCl and KCl, but not by carnallite and kainite. This is found also to be the case with the natural salts. The amount of Pb in rock-salt ranges from < 0.01 to 0.49 mg. per kg. of salt. He is also present (up to 14×10^{-6} c.c. per g.) in sylvine. It is suggested that the Pb and He have been derived from the Ra of neighbouring thermal springs. L. J. S.

Asbestos from Klettigshammer near Wurzbach, Thuringia. H. JUNG (Chem. Erde, 1934, 9, 52—54).—A new analysis of the asbestos from this locality shows it to be an amphibole-asbestos, and not a serpentine-asbestos as previously supposed. L. J. S.

Chromium and nickel in tectites. E. PREUSS (Naturwiss., 1934, 22, 480).—The amounts of Cr and Ni in moldavite, australite, billitonite, and borneoite were determined by spectral analysis. There is a comparatively low Ni content. The results do not agree with the theory that tectites are formed by the fusion of terrestrial rocks as a result of collision with large meteorites. Comparison is made with the results of other workers. A. J. M.

Bentonite and its occurrence in New Zealand. H. E. FYFE (New Zealand J. Sci. Tech., 1934, 15, 386—394).—Analyses are given. C. W. G.

Extraction of rubidium and caesium from lepidolite. T. G. KENNARD and A. I. RAMBO (Amer. J. Sci., 1934, [v], 28, 102—109).—0.67% Rb₂O and 0.16% Cs₂O were found by an improved method. C. W. G.

Unusual series of varved clays from Northern Ontario. G. RITTENHOUSE (Amer. J. Sci., 1934, [v], 28, 110—120).—Chemical and mechanical analyses are given. C. W. G.

Correlations by radioactive minerals in the metamorphic rocks of Southern New England. W. G. FOYE and A. C. LANE (Amer. J. Sci., 1934, [v], 28, 127—138).—Analyses are given, and the age of the Strickland pegmatite dikes of Portland, Connecticut, are calc. to be about $2.8\text{--}2.9 \times 10^8$ years. C. W. G.

Variability in artificial ferromagnetic iron oxides. L. A. WELO and O. BAUDISCH (Amer. J. Sci., 1934, [v], 28, 139—149).—The effect of impurities is minor. A high temp. during formation causes magnetic hardness. C. W. G.

Structural formula of enargite. J. SZÉKI and A. ROMWALTER (Mitt. berg-huttenm. Abt. Hochschule Berg-Forstw., Sopron, 1933, 5, 57—60; Chem. Zentr., 1934, i, 1469).—Decomp. with conc. KOH shows that enargite is to be regarded as cuprous thio-orthoarsenate, Cu₂AsS₄, and not 4CuS.Cu₂S₂As₂S₂. L. S. T.

Analysis of the gases obtained from monazite and ilmenite. P. DE CORI (Atti Congr. naz. Chim., 1933, 4, 714—720; Chem. Zentr., 1934, i, 1446).—When heated in vac. at 1100°, 100 g. of ilmenite gave 52.04 c.c. of gas (86.10% CO₂, 5.43% CO, 8.47% N₂, H₂, and inert gases). Evolution of gas commenced at 450°. 100 g. of monazite gave in all 50.23 c.c. of He, increasing in amount from 250° to 850°, reaching a max. between 650° and 850°, and then decreasing to 1100°. The radioactivity as compared with U₃O₈ is approx. 5 times < corresponds with the He content.

L. S. T.

Meteoric stone of Lanzenkirchen, Lower Austria. E. DITTLER (Chem. Erde, 1934, 9, 126—132).—A previously published paper (A., 1927, 642) with some additional details of the method of analysis.

L. J. S.

Buried soils of Alsace. V. AGAFONOFF (Compt. rend., 1934, 198, 2266—2268).—The stratigraphy and analyses of the buried soils of Aachenheim (Alsace) are compared with those of other localities, and indicate formation by the action of subterranean H₂O rather than forest bed origin.

B. W. B.

Rock weathering and soil formation in the "terra roxa" region of Sao Paulo, Brazil. F. W. FREIS (Chem. Erde, 1934, 9, 100—125).—Analyses are given of the red earths formed by the weathering of basalt.

L. J. S.

Relation between the original structure and the dispersed phase of soils and the crystalline

and metasomatic transformation of sediments. J. P. AREND (Compt. rend., 1934, 199, 155—157).—A comparative study of the states of flocculation and chemical composition of a soil of the Briey basin at distances of 100, 250, and 400 m. from its source.

B. W. B.

Oil deposits in southern Baichunas, Ural-Emba district. K. V. BUSKIN (Nef. Choz., 1934, 26, No. 1, 12—19).—Crude oils and waters are described.

CH. ABS.

Gas deposits in the Melnikov gas fields, lower Volga river. V. A. SOKOLOV and Y. K. YUREV (Nef. Choz., 1934, 26, No. 1, 20—22).—At > 100 m. the gas contained CO₂ 1.5—3, O₂ 16.8—20.2, hydrocarbons 0.04%.

CH. ABS.

Gas evolved from well No. 11 at Krynica. S. JURKOWSKI (Arch. Chem. Farm., 1934, 1, 152—169).—The gas, evolved in large quantities, contained CO₂ 91.51, CH₄ 1.52, C_nH_{2n+2} 0.03, O₂ 0.07, N₂ 6.87 vol.-%.

R. T.

Waikato coal. W. PENSELER (Fuel, 1934, 13, 176—185, 198—208).—The microstructure is described. The seam is uniform in constitution and consists of (a) ulmins, derived in the main from the cellulosic portions of the original vegetation, (b) resistant plant entities, and (c) resins. From the types of structure found it is concluded that the coal-forming vegetation grew and accumulated in a fresh-H₂O swamp of the wooded or forested type.

A. B. M.

Organic Chemistry.

Electromeric theories in organic chemistry. (1) W. A. NOYES. (2) R. ROBINSON (Chem. and Ind., 1934, 716—717, 717).—A further discussion (see this vol., 863).

Unitary conception of aliphatic and aromatic compounds. M. REBEK (Arh. Hemiju, 1934, 8, 53—62).—Differences in the behaviour of aromatic and aliphatic compounds are discussed from the viewpoint of the octet theory.

R. T.

Magneto-optical properties of hydrocarbons and their mixtures.—See this vol., 832.

Preparation of ethane. A. J. BERRY (Chem. and Ind., 1934, 534).—Attention is directed to the work of Brodie (Phil. Trans., 1863, 153, 407) on the reaction between Ac₂O and BaO₃ and the explosive nature of the product. No C₂H₆ is obtained.

A. R. P.

Influence of various radicals on the characteristic frequency of the ethylenic linking in derivatives of cyclopentene.—See this vol., 942.

Peroxide effect in addition of reagents to unsaturated compounds. M. S. KHARASCH, J. A. HINCKLEY, jun., and M. M. GLADSTONE (J. Amer. Chem. Soc., 1934, 56, 1642—1644).—Addition of HBr to Δ^α-pentene alone, in AcOH, or in presence of anti-oxidants gives < 84% of β-bromopentane (I) (the normal product). *n*-Amyl bromide (II) (the abnormal product) is formed in presence of ascaridole and no

solvent or pentane; in AcOH, however, (I) is the sole product, whilst in EtCO₂H a mixture of (I) and (II) (40%) results. Contrary to Sherrill *et al.* (this vol., 630), solvents play little part in governing the direction of addition.

H. B.

Addition of hydrogen bromide to Δ^α-pentene and Δ^α-heptene. M. L. SHERRILL (J. Amer. Chem. Soc., 1934, 56, 1645).—A reply to Kharasch *et al.* (this vol., 864).

H. B.

Preparation of acyclic unsaturated hydrocarbons. A. L. WARD and W. H. FULWEILER (J. Amer. Chem. Soc., 1934, 56, 1641—1642).—Chlorination of β_γ-dimethyloctane gives Cl₁- (I), b.p. 81—83°/3 mm., and Cl₂- (II), b.p. 121—125°/12 mm., -derivatives. Addition of (I) to C₆H₅Me·OK at > 180° affords a good yield of (probably) β_γ-dimethyl-Δ^β-octene, b.p. 159.6—162.8°, f.p. —79.5°. (II) and 25% EtOH-KOH (1.5 mols.) give a chloro-β_γ-dimethyl-octene, converted [as (I)] into decadiene, b.p. 161—166°/764.4 mm., f.p. —92.6°.

H. B.

Action of the iodo-silver benzoate complex on butadienes. C. PRÉVOST and R. LUTZ (Compt. rend., 1934, 198, 2264—2266; cf. A., 1933, 711).—Δ^{α,γ}-Butadiene in boiling C₆H₆ containing an excess of the I-AgOBz complex (I) and AgOBz gives meso-erythritol tetrabenzoate, m.p. 187°. If a limited amount of (I) is used and the product is distilled and hydrolysed, Δ^α-butene-γδ-diol is obtained in 80% yield.

J. L. D.

Relations between isosterism and chemical character of acetylene, hydrogen cyanide, and derivatives.—See this vol., 833.

Deuteriumacetylene. A. KLEMENC and O. B. VON FRUGNONI (Naturwiss., 1934, 22, 465).—The v.p. between -110° and -85° of acetylene from 50% $\text{H}_2\text{O} + \text{CaC}_2$ is $<$ that of C_2H_2 . R. K. C.

Polymerisation of acetylene by heat. Yellow gaseous hydrocarbon, **chlone**. G. MIGNONAC and E. DITZ (Compt. rend., 1934, 199, 367—369).— C_2H_2 is rapidly circulated through a narrow SiO_2 tube at 750° and the products are immediately cooled to -70° . Much C_6H_6 and a polymeride C_4H_4 (I), b.p. 7° , condensable to a stable, colourless liquid, are obtained. If (I) is very carefully fractionated very shortly after its formation, a yellowish-green polymeride (C_4H_4) $_n$, designated **chlone** (II), is obtained which gives the typical acetylenic reactions and can be condensed to a greenish liquid. When preserved, (II) appears to pass into (I). H. W.

Acetylene polymerides and their derivatives. XXI. **Polymerisation of vinylacetylene.** H. B. DYKSTRA (J. Amer. Chem. Soc., 1934, 56, 1625—1628; cf. A., 1932, 40).—Reduction (H_2 , PtO_2 , EtOAc) of the EtOH -sol. fraction of the polymeride (A) obtained when $\text{CH}_2\text{:CH:C:CH}$ (I) is heated at 105° in steel bombs, and fractionation gives hydrocarbons, $\text{C}_{12}\text{H}_{22}$ (3% of original material), b.p. $36^{\circ}/0.5$ mm., $\text{C}_{16}\text{H}_{28}$ (11%), b.p. $83\text{--}86^{\circ}/0.5$ mm., $\text{C}_{16}\text{H}_{28}$ (5%), b.p. $97\text{--}98^{\circ}/0.5$ mm., and $\text{C}_{20}\text{H}_{34}$ (8%), b.p. $140\text{--}160^{\circ}/0.5$ mm., which are considered to be cyclobutane derivatives. (A) heated at $110^{\circ}/1$ mm. gives about 1% of (probably) 1:2-di(acetylenyl)cyclobutane, b.p. $50\text{--}53^{\circ}/30$ mm., reduced to (probably) 1:2-diethylcyclobutane, b.p. about $120^{\circ}/760$ mm. When (I) is heated at 105° in presence of 1—10% of AcOH , $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$, BzOH , $\text{CH}_2(\text{CO}_2\text{H})_2$, abietic acid, HCl , Ac_2O , $o\text{-C}_6\text{H}_4(\text{CO})_2\text{O}$, pyrogallol, or MeOH , styrene is obtained in 20—50% yield [on (I) used]; resinous material (resembling A) is also formed, but polystyrene could not be isolated. H. B.

Alkyl fluorides. V. DESREUX (Bull. Acad. roy. Belg., 1934, [v], 20, 457—476).—The following are prepared by the method of Swarts (A., 1922, i, 101): α -, b.p. $31.95\text{--}31.98^{\circ}/745.8$ mm., and β -fluorobutane, b.p. $25.25\text{--}25.27^{\circ}/765$ mm.; α -, b.p. $93.15^{\circ}/755$ mm., and β -fluorohexane, b.p. $86.1\text{--}86.2^{\circ}/758$ mm. d , n , R_L , η , and ϕ are recorded for these compounds; none of them reacts with cold $\text{KOH}\cdot\text{EtOH}$, the *sec.*- but not the *n*-compounds react with P_2O_5 , and all give HF readily with cold conc. H_2SO_4 . In every case the F-compound is accompanied by an olefine, and in the prep. of the *n*-compounds isomerisation occurs with production of the *sec.*-compound. In the case of *n*-heptyl iodide fluorination results in an inseparable mixture. A mechanism is suggested for the isomerisation. H. N. R.

Haloform reaction. XIV. **Improved iodoform test.** R. C. FUSON and C. W. TULLOCK (J. Amer. Chem. Soc., 1934, 56, 1638—1640).—The CHI_3 test, carried out in dioxan (details given), is positive for compounds containing $\cdot\text{COMe}$, $\cdot\text{CO}\cdot\text{CH}_2\text{I}$, and $\cdot\text{CO}\cdot\text{CHI}_2$ groups joined to H or C which does not carry

highly activated H atoms or groups causing excessive steric hindrance; the above groups may be formed in the reaction. If the above groups are destroyed by the hydrolytic action of the reagent before iodination is complete, the test is negative. A positive test is given by 63 substances examined; 28 substances which do not give the test are mentioned. H. B.

Detection of di- and tri-chloroethylene in presence of other chlorinated paraffins. Determination of trichloroethylene. H. SCHMALFUSS and H. WERNER (Z. anal. Chem., 1934, 97, 314—316).—The liquid is shaken with a solution of 50 g. of $\text{Hg}(\text{CN})_2 + 23$ g. of KOH in 200 c.c. of H_2O . $[\text{CHCl}]_2$ causes pptn. of $\text{Hg}(\text{C}_2\text{Cl}_2)_2$, decomp. 195° , and the non-aq. layer yields $\text{Hg}(\text{CCl}_2\text{CCl}_2)_2$ (I), m.p. 83° , formed from $\text{CHCl}\cdot\text{CCl}_2$ (II), on evaporation. Quant. formation of (I) is slow, but comparison of the amount of (I) formed in 16—24 hr. with that formed by solutions of known (II) content affords a measure of (II). J. S. A.

Preparation of acetylenic alcohols and their transformation into diethylenic alcohols. R. LESPIEAU and R. LOMBARD (Compt. rend., 1934, 198, 2179—2180).— $[\text{C}\cdot\text{MgBr}]_2$ (from 50 g. of Mg) and acetaldehyde (25 g.) give 11 g. of $\text{CH}_3\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{CH}_2$, b.p. $128.5\text{--}129.5^{\circ}$. Crotonaldehyde (30 g.) gives similarly 10 g. of γ -hydroxy- Δ^6 -hexen- α -inene (probably *trans*-), b.p. $58\text{--}59^{\circ}/13$ mm., $153^{\circ}/769$ mm. (slight decomp.) [*Cu* and *Ag* salts; Br_4 - and (less easily formed) Br_6 -derivatives]. Hydrogenation (*Pt*-starch) then affords γ -hydroxy- Δ^6 -pentadiene, b.p. $114.5\text{--}116^{\circ}$, and -hexadiene (I), b.p. $52^{\circ}/13$ mm., $140^{\circ}/762$ mm. (slight decomp.). Further hydrogenation of (I) gives $\text{CH}_2\text{EtPr}\cdot\text{OH}$. R. S. C.

Iodometric micro-determination of glycerol. F. VON BRUCHHAUSEN (Z. Unters. Lebensm., 1934, 68, 32—33).— Pr^{I} formed by distillation of glycerol with HI is determined by a method similar to that of Viebock and Brecher for OMe groups (A., 1931, 246). E. C. S.

Existence of carbon monoxide acetals. I. F. ADICKES, W. SIMSON, and P. P. PECKELHOFF (Ber., 1934, 67, [B], 1436—1440).—Pure NaOEt , free from EtOH , does not react appreciably with pure CO at room temp. and 120—150 atm. within 27—86 hr. Subsequently, the surface of the NaOEt becomes brown and there is a great increase in the HCO_2H content. The initial reaction is therefore due to a small amount of surface impurity. If EtOH of crystallisation is present, the equiv. amount of CO is absorbed with formation of $\text{ONa}\cdot\text{CH}(\text{OEt})_2$, which decomposes more or less rapidly. $\text{ONa}\cdot\text{C}\cdot\text{OEt}$ is not formed in this manner; Scheibler's observations (this vol., 390) are invalidated by the presence of CO_2 in technical CO . H. W.

Glycol monoalkyl ethers of high mol. wt. L. PALFRAY and M. ROTBART (Compt. rend., 1934, 198, 2183—2185).—The appropriate alkoxy-acetal with MgEtI gives 60% yields of β -hydroxy- α -(α -methylheptyloxy)-, b.p. $125\text{--}126^{\circ}/20$ mm. (*Ac* derivative, b.p. $129\text{--}131^{\circ}/20$ mm.), α -benzyloxy-, b.p. $141\text{--}144^{\circ}/15$ mm. (*Ac* derivative, b.p. $157\text{--}159^{\circ}/20$ mm.), and α -cyclohexyloxy-butane, b.p. $116\text{--}118^{\circ}/22$ mm. (*Ac* derivative, b.p. $123\text{--}124^{\circ}/22$ mm.). R. S. C.

Mechanism of reaction of methyl sulphate with magnesium aryl halides. A. C. COPE (J. Amer. Chem. Soc., 1934, 56, 1578—1581).—The reactions between Me_2SO_4 and MgBr_2 , MgI_2 , MgPhBr , MgPhI , $s\text{-C}_6\text{H}_4\text{Me}_3\text{MgBr}$, and $\text{Mg } m\text{-4-xylyl bromide}$ and iodide are investigated. The results indicate that the Grignard reagent exists as $2\text{MgRX} \rightleftharpoons \text{MgR}_2 + \text{MgX}_2$; each component reacts simultaneously, but at different rates. The possible reactions are formulated. The original must be consulted for details. H. B.

Migration of the phosphoric radical during the hydrolysis of methyl α -glycerophosphate. Transformation of α - into β -glycerophosphates. O. BAILLY and J. GAUME (Compt. rend., 1934, 198, 2258—2260; cf. this vol., 754).—Na α -glycerophosphate (A., 1932, 251) with Me_2SO_4 (1 mol.) in H_2O at room temp. affords Me α -glycerophosphate (65%). Heating the neutral reaction liquid at 100° during 3 hr. with the amount of NaOH required for conversion of di- into mono-ester results in the migration of 40% of α -glyceryl to the β -position. J. L. D.

Ether enolates and keten acetals. XVIII. Course of ester condensations. H. SCHEIBLER (Ber., 1934, 67, [B], 1341—1343).—In reply to Tschelincev (this vol., 868) it is pointed out that the formation of an additive product from 1 mol. of ester enolate and 1 mol. of keto-ester is a necessary precursor to keten acetal formation. Esters, $\text{CHR}_2\text{-CO}_2\text{Et}$, are capable of yielding additive products and thence keten acetals. The non-occurrence of these reactions with NaOEt (I) and $\text{CHMe}_2\text{-CO}_2\text{Et}$ (II) is due to the slight additive capacity of (I) to (II). The enolate can be obtained by other methods. With $(\text{OEt})_2\text{CH-CO}_2\text{Et}$ and $(\text{OPh})_2\text{CH-CO}_2\text{Et}$ reaction occurs readily and the keten acetals have been obtained. H. W.

Mechanism of aldehyde, ketone, and ester condensations. K. BODENDORF (Ber., 1934, 67, [B], 1338—1341).—Tschelincev's explanation (this vol., 868) of the course of ester condensations does not cover the initial formation of enolate. The difficulty is overcome by assuming a preliminary production of a labile additive product through which the actual initial product results. The readiness for reaction is conditioned by the magnitude of the dipole moment, the polarisation of the reactive groups, and constitutional factors. The following scheme is typical:



$\longrightarrow \text{ONa}\cdot\text{CMe}(\text{OEt})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \longrightarrow \text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et} + \text{NaOEt}$. Failure of condensation in the case of dialkylated esters is explained by the sheltering action of the accumulated alkyl groups. Many analogous processes can thus be explained generally. The first phase is conditioned by the presence of a polarisable double linking. With enolisable CO compounds, the condensing agent catalyses the occurrence of the ketonic-enolic equilibrium. The *cyclosemi*acetal may then pass into the hydroxy-ketone or the ring may be opened by the action of a third substance, e.g., an amine. H. W.

Synthesis of unsaturated fatty acids. Synthesis of oleic and elaidic acids. C. R. NOLLER

and R. A. BANNEROT (J. Amer. Chem. Soc., 1934, 56, 1563—1565).—Ozonolysis (method: Noller and Adams, A., 1926, 712) of Δ^9 -octadecenyl chloride, b.p. $165.5\text{--}168.5^\circ/3$ mm. (from oleyl alcohol, SOCl_2 , C_6H_6 , and a trace of $\text{C}_5\text{H}_5\text{N}$), gives θ -chlorononanaldehyde, b.p. $100^\circ/3$ mm., which when treated successively with Br in CCl_4 , MeOH, and dry HBr affords θ -dibromo-*n*-methoxynonyl chloride. This and Mg *n*-octyl bromide give θ -bromo-*n*-methoxyheptadecyl chloride, converted by Zn dust in boiling BuOH into Δ^9 -heptadecenyl chloride, b.p. $143\text{--}149^\circ/2$ mm. Hydrolysis (aq. EtOH-NaOH) of the nitrile from this and EtOH-NaCN affords oleic (about 37%) and elaidic acids (about 63%). H. B.

Degradation of lactic and pyruvic acids and of carbohydrates of high mol. wt. by light from quartz mercury-vapour lamp. F. LIEBEN, L. LOWE, and B. BAUMINGER (Biochem. Z., 1934, 271, 209—212).—Aq. solutions of starch, inulin, glycogen, dextrin, amylose (I), and amylopectin (II) in presence of 0.1N-NaOH and 0.1% Na anthraquinonesulphonate (III) are degraded by the light, glucose, other reducing substances, and lactic acid (IV) being produced. (I) and (II) are less affected than is starch itself. (IV) and AcCO_2H in alkaline solution are also decomposed, (IV) producing no AcCO_2H , which is more rapidly attacked, giving 3.9% of the possible MeCHO. AcCO_2H also very probably yields AcOH. Alkaline Li lactate is 73% decomposed by diffused daylight in presence of (III). W. McC.

Ricinic acid and μ -ketostearic acid. R. PEROTTE (Compt. rend., 1934, 199, 358—360).—The acid, m.p. 51° (Me ester, b.p. $178\text{--}180^\circ/0.8$ mm., m.p. $44.5\text{--}45^\circ$), obtained with Me hexyl ketone by heating Ba ricinoleate at $250\text{--}270^\circ/11$ mm., is identified as μ -ketostearic acid, since it is also obtained by hydrolysis of Et μ -ketostearate, m.p. $34\text{--}35^\circ$, prep. by oxidising Et μ -hydroxystearate, m.p. $50\text{--}51^\circ$, produced by hydrogenation of Et ricinoleate (Pt-black- Et_2O). H. W.

Preparation of Et malonate. C. H. KAO and K. H. CHEN (J. Chinese Chem. Soc., 1934, 2, 173—174).— $\text{CH}_2(\text{CO}_2)_2\text{Ca}$ is decomposed with $\text{H}_2\text{C}_2\text{O}_4$ and the resulting $\text{CH}_2(\text{CO}_2\text{H})_2$ esterified with 95% EtOH and HCl, the H_2O formed being removed as the ternary mixture with C_6H_6 and EtOH. The yield is 70%. H. N. R.

Microchemistry of stereoisomerides. II. L. ROSENTHALER (Z. anal. Chem., 1934, 97, 405—411; cf. A., 1931, 1319).—The differing characteristic cryst. ppts. given by *r*- and *d*-tartaric acid with Pb, Ca, Hg^{++} , Ba, Tl, and Sr acetates and with HgNO_3 , AgNO_3 , and KBr are described and illustrated. J. S. A.

Walden inversion. III. Transformation of mesotartaric acid into an optically active form under asymmetric conditions. V. A. RAO and P. C. GUHA (Ber., 1934, 67, [B], 1358—1362).—*l*-Menthyl mesotartrate is transformed by PCl_5 in CHCl_3 into *l*-menthyl *l*- β -chloromalate (I), hydrolysed by KOH-EtOH or Ag_2O to a product containing a slight excess of *l*-tartaric acid. (I) is reduced by Al-Hg to slightly laevorotatory malic acid. *d*-Bornyl mesotartrate, m.p. $84\text{--}85^\circ$, $[\alpha]_D^{25} + 31.50^\circ$ in abs. EtOH, gives an inactive tartaric acid. H. W.

Determination of citrate. W. F. BRUCE (Ind. Eng. Chem. [Anal.], 1934, 6, 283—285).—The KMnO_4 - HgSO_4 method is modified to determine 0.1—10 mg. of citrate ion in 1—5 c.c. of solution in 3—4 hr.

R. S. C.

Colour reaction of ascorbic acid. A. SZENT-GYORGYI (Z. physiol. Chem., 1934, 225, 168).—With FeSO_4 , ascorbic acid (I) gives in air a dark violet coloration, stable at p_{H} 7.2—8.5, due to an oxidation of the primary Fe^{++} -(I) complex. It is bleached by $\text{Na}_2\text{S}_2\text{O}_4$, but reoxidised by atm. O_2 .

J. H. B.

Metabolic products of *Penicillium minioluteum*, Dierckx. Minioluteic acid.—See this vol., 927.

Emetic of saccharic acid. H. PARISELLE and F. CHIRVANI (Compt. rend., 1934, 199, 203—205).—Determination of the val. of α for solutions of K H saccharate and SbCl_3 to which KOH is gradually added and of solutions containing K_2 saccharate and $\text{Sb}(\text{OH})_3$ in varying amount indicates the existence of two saccharates of Sb or SbO of low $[\alpha]$ and of an emetic the very high $[\alpha]$ of which is attributed to the presence of two heterocyclic rings.

H. W.

δ -Keto-*l*-galactonic (*d*-tagaturonic) acid. F. EHRLICH and R. GUTTMANN (Ber., 1934, 67, [B], 1345—1347).—The acid obtained by the action of $\text{Ca}(\text{OH})_2$ - H_2O on *d*-galacturonic acid is shown to be δ -keto-*l*-galactonic acid, since it is oxidised by dil. HNO_3 at 50° to *d*-trihydroxyglutaric acid, characterised as the Ca and K salts.

H. W.

Influence of free acid on the determination of aldehydes and ketones by hydroxylamine hydrochloride. L. PALFRAY and S. TALLARD (Compt. rend., 1934, 199, 296—298).—With few exceptions, the determination of aldehydes and ketones by $\text{NH}_2\text{OH}\cdot\text{HCl}$ and subsequent titration with 0.5*N*-KOH is inaccurate in presence of org. acids, but less so when bromophenol-blue (I) is used as indicator than when Me-orange is employed. Acids liable to be present in essential oils and artificial perfumes have little effect if (I) is used, but a blank experiment is desirable.

H. W.

Reaction of zinc diethyl with acetoxime. D. F. MENARD and J. G. ASTON (J. Amer. Chem. Soc., 1934, 56, 1601—1602).— ZnEt_2 (1 mol.) and $\text{CMe}_3\text{N}\cdot\text{OH}$ (I) (2 mols.) in Et_2O give C_2H_6 (2 mols.) and *Zn diacetoximate*, $(\text{CMe}_3\text{N}\cdot\text{O})_2\text{Zn}$, hydrolysed (dil. HCl) to (I). Equimol. quantities afford C_2H_6 (1 mol.) and the compound, $\text{CMe}_3\text{N}\cdot\text{O}\cdot\text{ZnEt}$, decomp. 190° (sealed tube), which hydrolyses readily in moist air, and with dil. HCl gives C_2H_6 and (I).

H. B.

Micro-determination of aldoses. C. DUMAZERT (Bull. Soc. Chim. biol., 1934, 16, 932—940).—By oxidation with I in aq. Na_2HPO_4 -NaOH, 0.1—0.3 mg. and 0.5—3 mg. may be determined with an accuracy of 5 and 5%, respectively.

A. L.

Preparation of *d*-arabinose from calcium gluconate. R. C. HOCKETT and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 1632—1633).—Ruff's method (A., 1899, i, 324; 1902, i, 590) is improved.

H. B.

Preparation of xylose from maize cobs. C. ANTONIANI (Atti R. Accad. Lincei, 1934, [vi], 19, 599—601).—An increased yield of xylose is obtained by treatment with 0.1% HNO_3 for 2 hr. at 2 atm., the solution obtained being almost free from humic substances; most of the HNO_3 is removed by subsequent concn. in vac.

T. H. P.

Oxygen valency angle and structure of glucose and related compounds.—See this vol., 831.

Determination of small amounts of glucose, fructose, and invert sugar in absence and presence of sucrose. R. B. WHITMOYER (Ind. Eng. Chem. [Anal.], 1934, 6, 268—271).—0.5—2 mg. of reducing sugar is rapidly and accurately determined by oxidation with $\text{K}_3\text{Fe}(\text{CN})_6$ (I) in Na_2CO_3 at 80° and back-titration of the excess of (I) in acid solution with $\text{Ce}(\text{SO}_4)_2$ using alphazurine G as indicator. Chlorides and tartrates do not interfere; acetates and citrates have a slight influence.

R. S. C.

Preparation of β -*d*-(α -galaheptose). R. M. HANN, A. T. MERRILL, and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 1644).— β -*d*-(α -Galaheptose) monohydrate, m.p. 77 — 78° (corr.), $[\alpha]_D^{20}$ (in H_2O) -22.5° (3 min.) — -14.1° (180 min.), is obtained by reduction (Na - Hg , acid) of α -galaheptonolactone and subsequent removal of Na α -galaheptonate by repeated extraction with MeOH. The H_2O is not lost in a vac. over CaCl_2 or conc. H_2SO_4 at room temp.

H. B.

Isomerism of sucrose and isosucrose. (Sir) J. C. IRVINE and D. ROUTLEDGE (Nature, 1934, 134, 143).—Evidence that isosucrose is a stereoisomeride of sucrose, in the sense that it is a glucofructose containing a normal glucose residue coupled with a γ -fructose residue, is given.

L. S. T.

Cleavage of glycosides by catalytic hydrogenation. N. K. RICHMYER (J. Amer. Chem. Soc., 1934, 56, 1633—1637).—Of the aryl- and aralkyl-glycosides investigated, only β -benzyl-*d*-glucoside (I) undergoes fission [to glucose and PhMe (and thence to methylcyclohexane)] on reduction with H_2 and Pd-black in AcOH (or H_2O); saturation of the C_6H_5 rings occurs in the other cases. With Pt catalysts in various solvents, (I), β -phenyl-*d*-glucoside, salicin (II), arbutin (III), aesculin, phloridzin, phenyltrimethylglucoside, and (IV) undergo varying amounts of fission (usually a max. in very dil. HCl); cyclohexanol is produced from (III). (II) is reduced (H_2 , Pd-black alone or + Pt-black, dil. HCl) to *o*-tolylglucoside. Acetobromoglucose, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$, and Ag_2O in Et_2O give β -(β -phenylethyl)-*d*-glucoside tetra-acetate, m.p. 72 — 73° , $[\alpha]_D^{20}$ -19.2° in CHCl_3 , de-acetylated (NaOMe or EtOH - NH_3) to β -(β -phenylethyl)-*d*-glucoside, m.p. 119 — 120° , $[\alpha]_D^{20}$ -30.5° in H_2O . β -(γ -Phenylpropyl)-*d*-glucoside, m.p. 100 — 101° , $[\alpha]_D^{20}$ -27.3° in H_2O (tetra-acetate, m.p. 79 — 80° , $[\alpha]_D^{20}$ -13.1° in CHCl_3), and β -cyclohexylmethyl-*d*-glucoside, m.p. 122 — 124° , $[\alpha]_D^{20}$ -37° in H_2O (tetra-acetate, m.p. 94 — 95° , $[\alpha]_D^{20}$ -22.2° in CHCl_3), are similarly prepared. The tetra-acetate, m.p. 151 — 152° , $[\alpha]_D^{20}$ -13.2° in CHCl_3 , of β -*p*-diphenyl-*d*-glucoside (IV), m.p. 200° , re-solidifying with m.p. 214 — 215° , $[\alpha]_D^{20}$ -43.3° in $\text{C}_5\text{H}_5\text{N}$, is prepared by the method of Helferich *et al.* (A., 1933, 379).

H. B.

Organic polymerides of high mol. wt. G. NATTA (Giorn. Chim. Ind. Appl., 1934, 16, 285—295).—The author's investigations of the structure of highly polymerised compounds by the electron diffraction method are reviewed. D. R. D.

Plant colloids. XXXVI—XXXVIII.—See this vol., 843.

Structure and reactions of cellulose. G. CHAMPELIER (Bull. Soc. chim., 1934, [v], 1, 613—635).—A lecture.

Nitration and nitric esterification of alcohols. G. DARZENS (Mem. Poudres, 1934, 25, 437—439).—Nitration may be effected without risk of other reactions by the use of equimol. amounts of HNO_3 and Ac_2O in CHCl_3 , preferably at -5° to -15° . Thus cellulose may be nitrated to the trinitrate (13.7% N) sol. in COMe_2 and insol. in EtOH – Et_2O and in EtOAc . A. G.

Preparation and explosion temperatures of cupric chlorate-primary amine complexes.—See this vol., 978.

Complexes of ferrous salts with ethylenediamine or trimethylenediamine. R. E. BREUIL (Compt. rend., 1934, 199, 298—300).—The salts FeCl_2tn_3 , FeBr_2tn_3 , and FeI_2tn_3 (tn=trimethylenediamine) are described. FeSO_4en_2 is obtained from FeSO_4 and $\text{C}_2\text{H}_4(\text{NH}_2)_2$ in MeOH or from $\text{FeSO}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$ and $\text{C}_2\text{H}_4(\text{NH}_2)_2$ in EtOH . The following salts are prepared by the second method: $\text{FeC}_2\text{O}_4\text{en}_3$; FeSO_4tn_3 ; $\text{FeC}_2\text{O}_4\text{tn}$; $\text{FeC}_2\text{O}_4\text{tn}_2$. H. W.

Compounds of triethanolamine [$\beta\beta'\beta''$ -trihydroxytriethylamine] with salts of bivalent metals. A. TETTAMANZI and B. CARLI (Gazzetta, 1934, 64, 315—321; cf. A., 1933, 1280).—Complex salts $[\text{B}=\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3]$ are described: $\text{CoSO}_4 \cdot 2\text{B}$; $\text{Co}(\text{OAc})_2 \cdot 2\text{B} \cdot 3\text{H}_2\text{O}$; $\text{CoI}_2 \cdot 2\text{B}$; $\text{NiSO}_4 \cdot 2\text{B} \cdot 5\text{H}_2\text{O}$; $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{B}$; $\text{NiBr}_2 \cdot 2\text{B}$; $\text{CuSO}_4 \cdot 2\text{B}$; $\text{Pb}(\text{OAc})_2 \cdot 2\text{B} \cdot 3\text{H}_2\text{O}$. R. K. C.

Diurethanes as local anæsthetics. S. Y. MA and R. L. SHRINER (J. Amer. Chem. Soc., 1934, 56, 1630).—*Et*, m.p. 108—109°, and *isoamyl*, m.p. 99—101°, ethylenedicarbamates are prepared from $\text{C}_2\text{H}_4(\text{NH}_2)_2$ and ClCO_2Et and *isoamyl* chloroformate, respectively, at 0°. They have a low toxicity and produce surface anæsthesia (cf. A., 1933, 1044). H. B.

Methylation of arginine. K. DIRK and A. LANG (Z. physiol. Chem., 1934, 225, 79—91).—Methylation of arginine with $\text{Me}_2\text{SO}_4 + \text{NaOH}$ at p_H 9—10 afforded as picrates: arginine- α -betaine, inactive (*picrate*, decomp. 237°; *dihydrochloride*, decomp. 212°, then 250°; *hydrochloride*, decomp. 240°; *dipicrate*, decomp. 180°; *disflavianate*, decomp. 260°; *flavianate*, decomp. 222°; *hydrochloride* of Bz derivative, decomp. 205°), active (*picrate*, decomp. 225°; *dihydrochloride*, decomp. 205°; $[\alpha]_D +6.25^\circ$ in H_2O ; *dipicrate*, m.p. about 140°, decomp. 165°; *disflavianate*, decomp. 245°); methylarginine- α -betaine (Me attached to guanidine) (*dipicrate*, decomp. 165°); arginine ester (with 2 Me at the α -N and probably 2 Me attached to guanidine) (*dipicrate*, decomp. 161°). Esterification of these picrates gave only arginine- α -betaine (*diaurichloride*, decomp. 170°). Thus 1 or 2 Me groups of the guanidine

group must be eliminated. Also in the ester the *O*-Me group must wander to the α -N. All the hydrochlorides on fission with $\text{Ba}(\text{OH})_2$ yield ornithine- (*dipicrate Ba picrate*, decomp. 222°; *hydrochloride*, decomp. 255°; *dipicrate*, decomp. 130°) and citrulline- α -betaine (*picrate*, decomp. 206°; *hydrochloride*, decomp. 185°; *flavianate*, decomp. 218°). With Me_2SO_4 , arginic acid yields the *Me*, derivative (*flavianate*, m.p. 238°); nitro-arginine affords methyleitrullinebetaine (*aurichloride*, m.p. 290°). J. H. B.

Separation of arginine and histidine by Hopkins' reagent. J. BUSSIT (Bull. Soc. Chim. biol., 1934, 16, 727—735).—Arginine, although not itself pptd. by Hopkins' reagent (HgSO_4 in H_2SO_4) for histidine (I), is taken up by the (I) complex, from which it cannot be completely separated either by repeated washing or by double pptn. A. L.

Canavanine. IV. Constitution of cananiline, a product of enzymic hydrolysis of canavanine. M. KITAGAWA and S. MONONOBE (J. Agric. Chem. Soc. Japan, 1933, 9, 845—858).—Cananiline (I) is reduced (H_2 –Pt in AcOH or MeOH) to α -amino- γ -hydroxybutyric acid, m.p. 201—202° (decomp.); canavanine and dibenzoylcananiline (II) were not catalytically reduced. Acetylation of (II) in acid or neutral solution gave dibenzoylcananiline anhydride, m.p. 163—164°. (I) is considered to be $\text{ONH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$. Canavanine is not toxic to mice. CH. ABS.

Alkaline hydrolysis of glycine and alanine anhydrides.—See this vol., 848.

Absorption and reactivity of some classes of amides. (MME.) RAMART, NAIK, and TRIVEDI (Bull. Soc. chim., 1934, [v], 1, 525—538).—The ultra-violet absorption and rates of hydrolysis of a no. of *N*-substituted malondiamides, acetoacetamides, and carbethoxyacetamides have been measured. The absorption of fully *N*-substituted amides differs markedly from that of compounds containing NHR or NH_2 , thus supporting the chemical evidence in favour of the tautomerism of the latter compounds. R. S. C.

Preparation of succinimide. T. S. MA and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 241—243).—50 g. of $[\text{CH}_2\text{CO}_2\text{H}]_2$ heated with 14 g. of $\text{CO}(\text{NH}_2)_2$ at 175° and distilled give 30 g. of recryst. succinimide. H. N. R.

NN'-Dichloroazodicarbonamidine (azochloroamide), a *N*-chloro-derivative of the oxidant in an oxidation-reduction system. F. C. SCHMELKES and H. C. MARKS (J. Amer. Chem. Soc., 1934, 56, 1610—1612).—Azo- (I) and hydrazo-dicarbonamidine (II) (as sulphates) are converted by aq. NaOCl at 10—15° into NN'-dichloroazodicarbonamidine (III), $[\text{N}\cdot\text{C}(\text{NH}_2)\cdot\text{NCl}]_2$, dimorphous, decomp. 155.5°, which with an excess of Cl_2 in cold H_2O gives an amorphous product, decomp. 80—85°. (III) and ammoniacal Ag_2O give a brick-red ppt. which is sol. in an excess of aq. NH_3 . (III) is reduced by SO_2 in COMe_2 or $\text{OEt}\cdot\text{CH}_2\text{CH}_2\cdot\text{OH}$ at < 25 —30° to (I). Reduction (H_2S or SO_2 in cold H_2O) and subsequent evaporation to dryness gives (II); in the latter case, addition of EtOH to the aq. solution gives the compound, $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{N}(\text{SO}_3\text{H})\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}\cdot 0.5\text{H}_2\text{SO}_4$. Treatment of this with an excess of cold aq. BaCl_2 ,

removal of BaSO_4 , and heating the filtrate results in a further pptn. of BaSO_4 . Hydrolysis (method: Soper, A., 1925, i, 381) of (III) occurs only slightly. The solubility of (III) in numerous org. solvents is determined. (III) resembles the *N*-chloroquinoneimines (IV) more closely than any other *N*-Cl-compound studied. (III) is much more stable than (I) [the oxidant in the system (I)–(II) (the E° of which is unusually high)]. Similarly, (IV) are more stable than the quinoneimines. The properties of (III) are better represented by the structure $[\text{N}-\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{Cl}]_2$.

H. B.

ϕ-Halogens. XXV. Determination of fulminic acid. L. BIRCKENBACH and K. SENNEWALD (Annalen, 1934, 512, 38–45).—Philip's method is trustworthy for fulminates (I) and for fulminic acid (II). In the presence of polymerides of (II) the results are uncertain to the extent of 0.3–0.5%. The process cannot be used in presence of substances which react with $\text{Na}_2\text{S}_2\text{O}_3$ or I. (I) can be determined by titration with AgNO_3 until a permanent turbidity is obtained; addition of KI (which cannot be replaced by KCl or KBr) is essential. Accurate results can be obtained in presence of NH_3 if the final addition of AgNO_3 is made slowly and without agitation. (II) is similarly determined without indicator.

H. W.

Rate of polymerisation of fulminic acid. L. BIRCKENBACH and K. SENNEWALD (Annalen, 1934, 512, 45–54).—The rate of polymerisation of fulminic acid in 0–0.15*N*-mineral acid diminishes rapidly with increasing acidity to a limit which remains almost const. until the acidity attains 2*N*. Similar behaviour is shown by HNO_3 and H_2SO_4 . In > 0.15*N*- H_2SO_4 reaction is approx. of the second order. With diminishing acidity, the consts. show markedly progressive character, and in solutions with 0.025*N*- H^+ give the impression of a unimol. change. The absence of isocyanilic acid from the products of polymerisation indicates a discrepancy between the order of reaction and its products in more strongly acidic medium which is explained by the primary formation of dicarbonyldioxime $[\text{C}:\text{N}:\text{OH}]_2$. The rate of polymerisation increases 3.2-fold for 10° rise in temp. The rate of polymerisation in Et_2O is much > in H_2O when the limiting val. of mineral acid content is exceeded.

H. W.

Reduction of cyanides. L. A. WALTER and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 1614–1616).—The nos. quoted after the following RCN (I) denote the extent (%) of the reactions (i) $\text{RCN} \rightarrow \text{RH} + \text{NaCN}$ (determined by Volhard titration of CN^- in the H_2O -sol. products) and (ii) $\text{RCN} \rightarrow \text{CH}_2\text{R}\cdot\text{NH}_2$ (determined by isolation), respectively, during reduction with Na [1.5 atoms per 0.25 mol. of (I)] and EtOH : Bu^nCN , 16, 76; Pr^nCN , 24, 63; Bu^iCN , 33, 60; δ -cyano-octane (II), b.p. 72–73°/9 mm. [from BuCN , Bu_3Br , and NaNH_2 ; method, Ziegler and Ohlinger (A., 1932, 727)], 6, 64; ϵ -cyano- ϵ -*n*-propylnonane, b.p. 115–116°/9 mm. [from (II), BuBr , and NaNH_2], 10, 54; PhCN , 84, 7; $\text{CH}_3\text{Ph}\cdot\text{CN}$, 88, 10; $\text{OPh}[\text{CH}_2]_3\text{CHPh}\cdot\text{CN}$, 91, 5; α -piperidinoisobutyronitrile, 61, 23 (21% of piperidine and 11% of NH_4Bu^n are also formed). The following are new: ϵ -*n*-propyl-

nonane, b.p. 195–196°/740 mm.; β -*n*-propylhexylamine, b.p. 183–184°/740 mm.; β -*n*-propyl- β -*n*-butylhexylamine, b.p. 113–114°/10 mm. (hydrochloride, m.p. 139–141°); β -piperidinoisobutylamine, b.p. 215–216°/740 mm. [dihydrochloride, m.p. 260–265° (decomp.)]; *Ph* δ -phenylethyl ether, b.p. 144–146°/1 mm.

H. B.

Organometallic compounds of group II. F. SCHULZE (Iowa State Coll. J. Sci., 1933, 8, 225–228).— BeMe_2 , sublimes 200°; BeEt_2 , m.p. -13° to -11° , b.p. 180–240°; and BeBu_2 , b.p. 170°/28 mm., are best prepared from BeCl_2 and the appropriate Grignard reagent. Be and HgMe_2 in presence of a trace of HgMeI yield BeMe_2 ; BePh_2 and Be di-*p*-tolyl from Be , Hg aryls, and a trace of HgCl_2 in a sealed tube at 225° (6 hr.). EtI , BuI , $\text{C}_8\text{H}_{17}\text{I}$, and PhI with Ca produce organometallic compounds.

CH. ABS.

Organo-lead compounds. E. B. TOWNE (Iowa State Coll. J. Sci., 1933, 8, 229–230).—The introduction of functional groups into organo-Pb compounds was attempted by coupling organo-Pb halides with substituted halogen compounds, and by rearrangement of diazonium complexes of Pb^{II} and Pb^{IV} chlorides. Diazonium complexes of PbCl_2 were prepared, but no substituted organo-Pb compounds were formed. PbEt_3Br reacts with Mg affording MgEtBr and PbEt_4 , indicating the formation of unstable $\text{PbEt}_3\cdot\text{MgBr}$. Pb Ph_3 *p*-anisyl has been prepared.

CH. ABS.

Complex compounds of the olefines with metallic salts. I. Zeise's salt. J. S. ANDERSON (J.C.S., 1934, 971–974).—Ethyleneplatinous chloride

(I) $\text{C}_2\text{H}_4 \begin{smallmatrix} \text{Pt} < \text{Cl} \\ \text{Cl} < \text{Pt} \end{smallmatrix} \begin{smallmatrix} \text{Cl} \\ \text{C}_2\text{H}_4 \end{smallmatrix}$ is isolated from the

products of the reduction of Na_2PtCl_6 by evaporation with EtOH < 50°/high vac. The structure assigned, contrary to that of Drew *et al.* (A., 1932, 562), is proved by the following reactions. (I) is reduced quantitatively by H_2 at room temp.: $(\text{I}) + 2\text{H}_2 = \text{Pt} + 2\text{HCl} + \text{C}_2\text{H}_6$. Zeise's salt $\text{K}[\text{PtCl}_3\cdot\text{C}_2\text{H}_4]\cdot\text{H}_2\text{O}$ (II) (prepared by Jorgensen's method, A., 1900, i, 542) is analogous to $\text{K}[\text{PtCl}_3\cdot\text{CO}]\cdot\text{H}_2\text{O}$. Addition of excess of quinoline to solutions of (II) ppts. *quinolinium ethylenetrichloroplatinite* $\text{C}_9\text{H}_7\text{NH}[\text{PtCl}_3\cdot\text{C}_2\text{H}_4]$, m.p. > 130° (decomp.) (III), whereas aq. quinoline affords *quinolinoethyleneplatinous chloride* $[\text{C}_9\text{H}_7\text{N}\cdot\text{PtCl}_2\cdot\text{C}_2\text{H}_4]$, reconverted into (III) by hot 2*N*-HCl. Aq. KCN causes quant. liberation of C_2H_4 from (II): $(\text{II}) + 4\text{KCN} = \text{K}_2\text{Pt}(\text{CN})_4 + 3\text{KCl} + \text{C}_2\text{H}_4$, similar decomp. with KNO_2 affording 75% of the C_2H_4 (10% at room temp.), and the reaction with KSCN is intermediate. Heated with H_2O in a sealed tube (II) gives Pt and a 60% recovery of C_2H_4 , indicating that the initial hydrolytic product has reducing properties, and at 100° in N_2 an aq. solution of (II) decomposes thus, $(\text{II}) + \text{H}_2\text{O} = \text{KCl} + 2\text{HCl} + \text{Pt} + \text{MeCHO}$ (as its dimedon compound). With $\text{C}_5\text{H}_5\text{N}$ (II) gives C_2H_4 and $\text{PtCl}_2(\text{C}_5\text{H}_5\text{N})_2$, which with aq. $\text{C}_5\text{H}_5\text{N}$ affords $\text{Pt}(\text{C}_5\text{H}_5\text{N})_4\text{Cl}_2$.

W. B.

Isomerides of quadricovalent palladium and platinum. F. W. PINKARD, E. SHARRATT, W. WARDLAW, and (in part) E. G. COX (J.C.S., 1934, 1012–1016).—The *cis-trans* isomerism of *cis*- (I) (prisms) and *trans*- (II) (plates) -diglycineplatinum

postulated by Grünberg *et al.* (A., 1933, 381), and the structures there assigned, are confirmed by their direct interaction with warm, aq. $[-CH_2 \cdot NH_2]_2$; (I) thus affords, after addition of K_2PtCl_4 , *ethylenediaminoglycineplatinum platinochloride monohydrate* $[Pt en(NH_2 \cdot CH_2 \cdot CO_2H)_2][PtCl_4]$, whereas (II) gives $[Pt en_2](NH_2 \cdot CH_2 \cdot CO_2)_2$, converted by HCl and K_2PtCl_4 into $[Pt en_2][PtCl_4]$. By similar methods using NH_3 (I) gives *diamminodiglycine platinochloride*, and (II), the corresponding salt. With C_5H_5N (I) affords the *cis-plato-salt* $[Pt(C_5H_5N)_2(NH_2 \cdot CH_2 \cdot CO_2H)_2][PtCl_4] \cdot H_2O$, but (I) gives no ppt. With hot $5N-HCl$ (II) gives *trans-dichlorodiglycineplatinum* (Grünberg, *loc. cit.*) and a mixture from which with tetra-amminoplatinous chloride, $[Pt(NH_3)_4][PtCl_4]$ is obtained, and with NH_3 , the *plato-salt* $[Pt(NH_3)_3(NH_2 \cdot CO \cdot CO_2H)][PtCl_4]$. Similar interaction of K_2PdCl_4 and $NH_2 \cdot CH_2 \cdot CO_2H$ at room temp. affords *cis-* (prisms), $+3H_2O$ and anhyd., and *trans-* (plates) *-diglycinepalladium*, also differentiated by X-ray diagrams and by the observation that with cold saturated aq. $CS(NH_2)_2$ the *trans*-form ppts. a yellow substance $\{Pd[(NH_2)_2CS]_2(NH_2 \cdot CH_2 \cdot CO_2)_2\}$, whereas the *cis*- gives a red solution and a black ppt. of mixed decomp. products. J. W. B.

Complexes of germanous bromide with caesium bromide and with bromides of organic bases.—See this vol., 978.

Dimethylthallium methoxide. R. C. MENZIES and A. R. P. WALKER (J.C.S., 1934, 1131).—Interaction of $TlOMe$ and $TlMe_2Br$ affords *dimethylthallium methoxide*, m.p. $177-181^\circ$, completely hydrolysed by H_2O . J. W. B.

Trimethylrhenium. J. G. F. DRUCE (J.C.S., 1934, 1129).—Interaction of $ReCl_3$ with $MgMeI$ in Et_2O affords *Re trimethyl*, m.p. approx. 60° , oxidised by aq. H_2O_2 to per-rhenic acid and other products. J. W. B.

cyclopentadiene. I. Peroxide effect [in addition of bromine to *cyclo-* and *dicyclo-pentadiene*]. G. R. SCHULTZE (J. Amer. Chem. Soc., 1934, 56, 1552—1556).—Atm. O_2 is absorbed rapidly by *cyclo-* (I) and *dicyclo-* (II) -pentadiene; the resulting peroxide prevents quant. addition of Br (which is assumed to be a chain mechanism). Quant. addition is effected by titration with $Br'-BrO_3'$ (when H_2SO_4 of $\approx 0.4N$ must be used owing to the polymerising action) or, better, $Br-H_2O$ in a vac. Titration can be carried out in presence of air provided an excess of Br is present throughout. Details are given. Mixtures of (I) and (II) are analysed by the $Br-H_2O$ (vac.) method. Polymerisation of (I) to (II) is practically independent of the presence of O_2 or peroxide.

ψ-Halogens. XXVII. Reaction of metallic salts with iodine in presence of cyclohexene. Relationship between nature of linking and reactivity. L. BIRCKENBACH and J. GOUBEAU (Ber., 1934, 67, [B], 1420—1431).—Passage of C_6H_4 through a suspension of $Hg(NO_3)_2$ and I in Et_2O leads to the formation of β -iodoethyl nitrate (I), b.p. $80^\circ/22$ mm., and $C_6H_4(O \cdot NO_2)_2$. Since $Hg(NO_3)_2$ and react in presence of Et_2O , reaction was investigated

in CCl_4 with similar results. $Hg(NO_3)_2$, I, and *cyclohexene* in Et_2O similarly afford *1-iodocyclohexyl nitrate* (II), b.p. $125^\circ/16$ mm., and *cyclohexene dinitrate*. (II) is also obtained by use of $AgNO_3$ if the latter is very finely divided, the apparent inactivity of coarser samples being attributed to the enclosing action of AgI. (I) and $C_2H_4(O \cdot NO_2)_2$ are also obtained from $C_2H_4I_2$ and $Hg(NO_3)_2$ in Et_2O . $C_2H_4I_2$ and $Pr \cdot CO_2Ag$ yield β -iodoethyl n-butyrate, b.p. $96-98^\circ/20$ mm. I, CuCl or AuCl, and *cyclohexene* in Et_2O afford *1-chloro-2-iodocyclohexane*, b.p. $105^\circ/8$ mm., which, mixed with much 1:2-di-iodocyclohexane (III), is slowly derived from $PbCl_2$. Almost homogeneous (III) is obtained with $PbBr_2$. $Pb(OAc)_2$ containing a little basic salt affords mainly (III) with a little 1-iodocyclohexyl acetate. $Pb(OBz)_2$ slowly yields ill-defined products, whereas $TlBr$ scarcely reacts. Reaction of $CdCl_2$ or $CdBr_2$ with I and *cyclohexene* is slow and ill-defined. EtI in Et_2O reacts much more rapidly with $Hg(NO_3)_2$ than with $AgNO_3$.

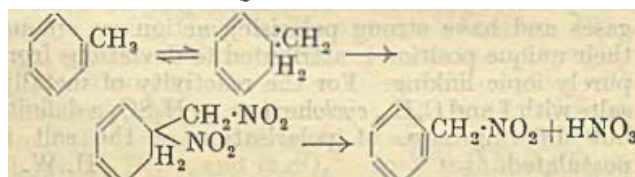
In the I-cyclohexene reaction the same differences of reactivity between salts of Ag, Hg, Au, and Cu and those of Pb, Tl, Cd, and the other metals is exhibited as with reactions with C_6H_6 and H_2SO_4 . The former salts give the I-mixed halogen additive products (IV) in 70—80% yield within a few hr., whereas the latter, after months, give mainly (III) mixed with small amounts of (IV). Since the reactive salts contain heavy-metal cations without similitude to the rare gases and have strong polarising action on anions, their unique position is attributed to deviations from purely ionic linking. For the reactivity of metallic salts with I and C_6H_6 , *cyclohexene*, or H_2SO_4 a definite but differing min. of polarisation of the salt is postulated. H. W.

Reactions catalysed by aluminium chloride. X. Hydrogenating action of the system, aluminium chloride-saturated hydrocarbon, towards inorganic halides. C. D. NENITZESCU and D. A. ISACESCU (Ber., 1934, 67, [B], 1391—1393).—In absence of an acceptor (I) the main reaction between $AlCl_3$ and *cyclohexane* (II) is isomerisation to methylcyclopentane. In presence of (I), a dehydrogenating condensation occurs: $2C_6H_{12} \rightarrow C_{12}H_{22}$ (III) + $2H$; $3C_6H_{12} \rightarrow C_{18}H_{32} + 4H$; $4C_6H_{12} \rightarrow C_{24}H_{42} + 6H$. Thus $AlCl_3$, $AsCl_3$, and (II) at $65-70^\circ$ afford (III), m.p. 46° , and As. PCl_3 yields P as Schenk's pale-red modification. $SbCl_3$ reacts very slowly, whilst S chlorides yield S and HCl without apparent formation of org. chlorides or S compounds. $SiCl_4$ and $SnCl_4$ slowly afford (III), but Si or Sn could not be isolated. $HgCl_2$ and $AgCl$ do not react. $AsPhCl_2$ yields much As, but metal is not obtained from $PbPh_4$. SO_2Cl_2 smoothly gives SO_2 and HCl, whilst $SOCl_2$ violently yields SO_2 , HCl, and S. CrO_2Cl_2 and $POCl_3$ do not react. H. W.

Preparation of some acetylenic compounds of the cyclanic series. (MLLE.) B. GRÉDY (Compt. rend., 1934, 199, 153—154).—*cyclopentyl Me ketone* with PCl_5 gives a mixture of Cl-compounds which with $NaNH_2$ affords some *cyclopentylacetylene* (I), b.p. $107-109^\circ$. *cyclohexylacetylene* (II) (cf. A., 1909, i, 899) is prepared similarly. (I) and (II) with $NaNH_2$ and Me_2SO_4 afford α -*cyclopentyl-*, b.p. $142-$

143°, and α -cyclohexyl- Δ^{α} -propinene, b.p. 162—164°, respectively. The Mg derivative of (II) with MeCHO gives α -cyclohexyl- Δ^{α} -buten- γ -ol, b.p. 110—114°/14 mm. Raman spectra measurements confirm the structure of these compounds. J. L. D.

Nitration of hydrocarbons by nitrogen dioxide in the gas phase with or without irradiation with ultra-violet light. P. SCHORIGIN and A. TOPTSCHIEV (Ber., 1934, 67, [B], 1362—1368).—Nitration of PhMe by NO₂ in presence of CO₂ proceeds best at 14—15° with irradiation, giving CH₂Ph·NO₂ (I), a mixture of isomeric mononitrotoluenes (II), and unchanged PhMe. The formation of C₆H₅Me(NO₂)₂ or BzOH is not observed. Without irradiation less PhMe enters into action, but the relative amounts of (I) and (II) are little affected. Irradiation has little influence on the nitration of C₆H₆. With cyclohexane and *n*-hexane reaction proceeds with much greater difficulty, leading to nitrocyclohexane and β -nitrohexane; irradiation is very little helpful. Thiophen (without irradiation) reacts somewhat violently, giving resin, C₄H₃S·NO₂, m.p. 44°, and C₄H₂S(NO₂)₂, m.p. 51—52°. In general, irradiation is helpful only when the completely symmetrical structure of the C₆H₆ mol. is disturbed by the presence of a side-chain which can give rise to tautomerisation and formation of a different system of conjugated double linkings. With PhMe the changes are formulated:



H. W.

Hydrolysis of substituted benzenesulphonanilides. III. Acid hydrolysis. R. S. SCHREIBER and R. L. SHRINER (J. Amer. Chem. Soc., 1934, 56, 1618—1619; cf. this vol., 288, 642).—The respective % yields of amine, sulphonic acid (I), and hydrocarbon [from (I)] obtained from the following anilides and boiling 25% HCl are given in parentheses: PhSO₂·NPh (91, 82, 0); PhSO₂·NPhMe (94, 78, 0); *p*-C₆H₄Me·SO₂·NPh (90, 76, 0); *p*-C₆H₄Me·SO₂·NPhMe (93, 80, 0); *m*-4-xylenesulphonanilide, m.p. 109—110° (90, 56, 9.4); *m*-4-xylenesulphonmethylanilide, m.p. 55° (91, 70, 11.3); *s*-C₆H₅Me₃·SO₂·NPh (92, 0, 89); *s*-C₆H₅Me₃·SO₂·NPhMe (95, 0, 92); *o*-NO₂·C₆H₄·SO₂·NPhMe (17, 6, 0; 71% unhydrolysed during 36 hr.); *m*-NO₂·C₆H₄·SO₂·NPhMe (87, 65, 0; 6% unchanged); *p*-NO₂·C₆H₄·SO₂·NPhMe (31, 20, 0; 61% unhydrolysed). Hydrolysis of *o*-, *m*-, and *p*-NO₂·C₆H₄·SO₂·NPh does not occur to any appreciable extent during 36 hr.; *m*-4-xylenesulphonic acid (chloride, b.p. 163—165°/15 mm., m.p. 34°) similarly gives 39% of *m*-xylene. H. B.

Halogenation. IX. Bromination of ψ -cumene. P. S. VARMA and D. N. SEN-GUPTA (J. Indian Chem. Soc., 1934, 11, 351—352; cf. this vol., 762).— ψ -Cumene (I) and Br in light give ω -Br-, -Br₂, or -Br₃-derivatives, or mixtures according to the temp. and amount of Br used. 5-Bromo- ψ -cumene in light

gives nuclear Br₂- or Br₃-compounds. (I) and Br in H₂SO₄, HNO₃, or mixtures thereof give good yields of 5-Br-, 5:6-Br₂-, and 3:5:6-Br₃-derivatives.

R. S. C.

Mutual influence of chromophoric groups. Stilbene and similar systems. H. LEY and H. DIRKING (Ber., 1934, 67, [B], 1331—1338).—The absorption spectra of CHPh:CHPh (I), CH₂Ph:CH₂Ph (II), CHPh:CH₂Ph (III), CHPh:CH·CO₂H (IV), [CH·CH₂Ph]₂ (V), [CH₂·CH₂Ph]₂, and CH₂Ph:CH:CH·CH₂·CO₂H (VI), have been measured. It appears improbable that the bands of longest λ of (I) and (IV) are attributable to the ethylenic linking, since a similar band is not shown by (V), which closely resembles (II). The influence of solvent is slight. The band is therefore attributed to the conjugated system Ph·C:C·Ph. If the ethylenic linking is conjugated with a single C₆ nucleus as in (III), the corresponding band appears at considerably shorter λ , so that certain C₆H₆ bands of longer λ can appear. Analogously, the broad bands of (IV) can scarcely be attributed to electrons of the ethylenic linking, since they are not represented in the spectrum of (VI).

H. W.

Preparation of isostilbene. T. W. J. TAYLOR and C. E. J. CRAWFORD (J.C.S., 1934, 1130).—A 60—65% yield of *iso(cis)*stilbene is obtained by heating CHPh:CPh·CO₂H in quinoline with a little Cu chromite at 210—220°.

J. W. B.

Diphenyl series. V. 2:4'-Dihalogenodiphenyls. C. FINZI and V. BELLAVITA (Gazzetta, 1934, 64, 335—345; cf. A., 1933, 388).—2:4'-Dichloro-4-aminodiphenyl (I), m.p. 83° (*Ac* derivative, m.p. 182°), is obtained by reduction of the 4-NO₂-compound (Sn+HCl), and diazotisation and treatment with either H₃PO₂ or Hg(NO₃)₂ (Schwechter, A., 1932, 1244); it yields 2:4'-dichlorodiphenyl, m.p. 46° (cf. DeCrauw, A., 1931, 1283). Similarly, 2:4'-dibromo-4-aminodiphenyl, m.p. 105° (*Ac* derivative, m.p. 195°), yields 2:4'-dibromodiphenyl, m.p. 56° (Gugliemelli and Franco, A., 1932, 1240, give m.p. 109°). 2:4'-Di-iodo-4-aminodiphenyl, m.p. 129° (*Ac* derivative, m.p. 231°), yields insol. salts and cannot be diazotised. 2-Nitro-4'-aminodiphenyl, m.p. 99° (improved prep.), is converted by diazotisation and treatment with KI into 4'-iodo-2-nitrodiphenyl, m.p. 94.5, which is reduced to 4'-iodo-2-aminodiphenyl (II), m.p. 67.5° (*Ac* derivative, m.p. 156°). 2:4'-Di-iodo-5:3-diaminodiphenyl (III), m.p. 148° (*Ac derivative, m.p. 129°), is prepared from the corresponding NO₂-derivative. 4'-Nitro-2-aminodiphenyl (improved prep.) is converted into 2-iodo-4'-nitrodiphenyl, m.p. 103°, which yields 2-iodo-4'-aminodiphenyl (IV), an oil (*Ac* derivative, m.p. 163°). 2:4'-Di-iododiphenyl, m.p. 42°, is prepared from (II), (III), or, preferably, (IV). R. K. C.*

Action of sodium on 1:3-diphenyl-1-benzylindene. C. F. KOELSCH (J. Amer. Chem. Soc., 1934, 56, 1605—1606).—1:3-Diphenyl-1-benzylindene, m.p. 100—102° [from 1-sodio-1:3-diphenylindene (I) and CH₂PhCl in Et₂O], is cleaved by 40% Na-Hg in Et₂O to (I) and PhMe (from NaCH₂Ph and Et₂O). *o*yl-, m.p. 150—152°, 1-*p*-chlorobenzoyl-, (II), m.p. 133—135° (+AcOH, m.p. 88—90°), and 1-methyl- (III),

m.p. 59—60°, 1 : 3-*diphenylindenes* are prepared from (I) and BzCl , $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COCl}$. and MeI , respectively. (II) is oxidised (CrO_3 , AcOH at 80—85°) to $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CO}_2\text{H}$ and $o\text{-C}_6\text{H}_4\text{Bz}_2$ (IV); (III) is similarly oxidised (at 23—27°) to *o*-benzoyl- α -*diphenylpropionic acid*, m.p. 139—140°, and at 80° to (IV). 9-Phenyl-9-benzylfluorene is cleaved slowly by 40% Na-Hg to 9-sodio-9-phenylfluorene. H. B.

Naphthalene di-derivatives. W. P. WYNNE (Chem. and Ind., 1934, 686—688).—A résumé of the orientation of heteronuclear di-derivatives of C_{10}H_8 . H. W.

High-pressure hydrogenation of naphthalene in presence of nickel on kieselguhr. H. I. WATERMAN, J. F. CLAUSEN, and A. J. TULLENERS (Rec. trav. chim., 1934, 53, 821—831).—Hydrogenation of C_{10}H_8 in presence of Ni-kieselguhr (I) proceeds to completion only if (I) is changed after absorption of 4H; it is faster with pure than with commercial C_{10}H_8 . The product is a mixture of *cis*- and *trans*-isomerides, the former changing to the latter in presence of (I) at 260—280°. A saturated, dicyclic product of very low *d* and a saturated product containing > 3 rings are also produced. R. S. C.

Sulphonation of naphthalene. V. N. UFMIZEV and A. F. KRIVOSCHLÛKOVA (J. pr. Chem., 1934, [ii], 140, 172—184).—($2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3$) $_2\text{Ba}$, + H_2O , and oleum at < 40° give 1 : 6- (II) (*C* α salt, + $4\text{H}_2\text{O}$; dichloride, m.p. 126.7—128°) and 1 : 7- $\text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2$ (dichloride, m.p. 122.2—122.8°). 1 : 3 : 6- $\text{C}_{10}\text{H}_5(\text{SO}_3\text{H})_3$ (III) (5—6%) is obtained from the technical sulphonate; it is converted quantitatively into the NO_2 - and NH_2 -derivative and can be determined in this way. Complete sulphonation of (I) at high temp. gives 78% of (III) and 20% of 1 : 3 : 5 : 7- $\text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_4$. (III) is also obtained from (I) and (II). R. S. C.

Hydrogenation in the sterol group by the action of selenium. C. DORÉE and V. A. PETROW (J.C.S., 1934, 1129—1130).—When heated with Se at 230—250°, cholesterolene, $\text{C}_{27}\text{H}_{44}$, affords a 25% yield of cholestane. No ψ -cholestane could be isolated. J. W. B.

Hydrocarbon, $\text{C}_{42}\text{H}_{30}$, a dimeride of diphenylphenylethynylmethyl; its conversion into tetraphenylrubene, $\text{C}_{42}\text{H}_{28}$. C. DUFRAISSE and A. WILLEMART (Bull. Soc. chim., 1934, [v], 1, 576—580).—The hydrocarbon (I), $\text{C}_{42}\text{H}_{30}$, m.p. 179°, of Moureu *et al.* (A., 1927, 355) with various oxidising agents, best (34%) with PbO_2 in hot xylene, gives tetraphenylrubene, for which a colorimetric method of determination is described. The poor yields obtained prevent deductions regarding the structure of (I). R. S. C.

Di-radical formula of rubene and constitution of its dissociable peroxide. II. A. SCHÖNBERG (Ber., 1934, 67, [B], 1404—1407).—A reply to Dufraisse (this vol., 882). H. W.

***m*-Nitrophenylthiocarbimide as reagent for the identification of amines.** P. P. T. SAH and H. H. LEI (J. Chinese Chem. Soc., 1934, 2, 153—158).—*m*-Nitrophenylthiocarbimide is recommended for the characterisation of primary amines, with which it condenses in EtOH solution to form substituted thio-

carbamides. The following are described: phenyl-, m.p. 156—157°; 2-, m.p. 150—151°; 3-, m.p. 166—167°, and 4-nitro-, m.p. 183—184°, 4-chloro-, m.p. 169—170°, and 4-bromo-phenyl-, m.p. 172—173°; *o*-, m.p. 165—166°, *m*-, m.p. 164—165°, and *p*-tolyl-, m.p. 172—173°, α -, m.p. 161—162°, and β -naphthyl-, m.p. 167—168°; 3-bromo-*p*-tolyl-, m.p. 142—143°; 2-hydroxy-, m.p. 167—168°, and 4-hydroxy-phenyl-, m.p. 154—155°, 3'-nitrophenylthiocarbamides. H. N. R.

Azides. I. 3 : 5-Dinitrobenzazide as reagent for the identification of primary and secondary amines. P. P. T. SAH and T. S. MA (J. Chinese Chem. Soc., 1934, 2, 159—166).—3 : 5-Dinitrobenzazide (I) is recommended as a reagent for amines in place of phenylcarbimide. With primary and *sec.* amines in PhMe solution, (I) gives the corresponding substituted 3 : 5-dinitrophenylcarbamide and N_2 . The following are described: phenyl-, m.p. 226—227°; 2-, m.p. 253—254°, 3-, m.p. 240—241°, and 4-nitro-, m.p. 280—281°, 4-chloro-, m.p. 270—271°, and 4-bromo-phenyl-, m.p. 277—278°, *N*-methyl-, m.p. 215—216°, and *N*-ethyl-phenyl-, m.p. 161—162°, *o*-, m.p. 241—242°, *m*-, m.p. 220—221°, and *p*-tolyl-, m.p. 233—234°, 3-nitro-, m.p. 232—233°, and 3-bromo-*p*-tolyl-, m.p. 244—245°, α -, m.p. 261—262°, and β -naphthyl-, m.p. 262—263°, *N*-acetyl-phenyl-, m.p. 191—192°, and *o*-tolyl-, m.p. 212—213°, 3' : 5'-*di*-nitrophenylcarbamides. H. N. R.

Reaction of nitrocarbamide with aromatic amines. P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 227—233).—The reaction between nitrocarbamide and the corresponding aromatic amine is the most convenient method for the prep. of *o*- and *p*-tolyl- and α - and β -naphthyl-carbamides. The reaction is recommended for the characterisation of primary amines (except those with negative substituents), the m.p. of a no. of substituted carbamides being tabulated. H. N. R.

Absorption spectra of the nitrotoluidines and related substances. R. A. MORTON and A. MCGOOKIN (J.C.S., 1934, 901—911).—The electronic mechanism of absorption in C_6H_6 , PhMe, and CH_2Ph_2 , etc. is essentially the same, any small differences in spectra being due to vibrational effects (λ_{max} about 260 μ). The main absorption band in PhNO_2 , the nitrotoluenes (I), and the chloronitrobenzenes is due to the same electronic transition. New electronic levels emerge when NH_2 or CO_2H is introduced into the C_6H_5 ring; quanta corresponding with about 230 and 280 μ recur in the toluic acids, in NH_2Ph , and in the toluidines. The nitroanilines show new levels at 375 and 405 μ approx. The determining factor in the absorption of the nitrotoluidines (II) is the relative position of NH_2 and NO_2 ; for instance, isomerides with these groups in the *o*-position give spectra resembling that of *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ etc. The 375 μ max. is about 10 times as intense in *p*- as in *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$. This ratio also applies to (II), in which NH_2 and NO_2 are *p* and *m*, respectively, with regard to one another. The spectra of (II) in acid solution resemble those of the (I), the relative position of Me and NO_2 now exercising the determinative role. In the absorption spectra of (II) in EtOH

and H_2O the maxima vary irregularly, although the general shape of the curves is always the same in the two solvents. The broad bands shown in solution are considerably influenced by vibrational effects, and the actual λ of max. absorption afford only very approx. estimates of the electronic levels. The displacements due to change of solvent appear to correspond with vibrational sub-levels. Theories involving possible integral multiple relationships between λ_{max} vals. are not supported. The following data are recorded for the nitrotoluidines, $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)\cdot\text{NH}_2$: 1:3:2-, m.p. 97°; 1:4:2-, m.p. 107°; 1:5:2-, m.p. 129°; 1:6:2-, m.p. 92°; 1:2:3-, m.p. 108°; 1:4:3-, m.p. 110°; 1:5:3-, m.p. 98°; 1:6:3-, m.p. 134°; 1:2:4-, m.p. 78°; 1:3:4-, m.p. 117°. H. W.

Derivatives of β -phenylethylamines and β -phenylethylmethylanilines. J. S. BUCK (J. Amer. Chem. Soc., 1934, 56, 1607—1608).—The following are prepared from the appropriate amine and KNCO in dil. H_2SO_4 : β -phenylethyl-, m.p. 115° (all m.p. are corr.), β -o-, m.p. 98°, -m-, m.p. 104°, and -p-, m.p. 133°, -anisylethyl-, and β -2:3-, m.p. 135°, -2:4-, m.p. 169°, -2:5-, m.p. 131°, and -3:4-, m.p. 162°, -dimethoxyphenylethyl-carbamides; N- β -phenylethyl-, m.p. 143°, N- β -o-, m.p. 82°, -m-, m.p. 102°, and -p-, m.p. 158°, -anisylethyl-, and N- β -2:3-, m.p. 69°, -2:4-, m.p. 94°, -2:5-, m.p. 91°, and -3:4-, m.p. 129°, -dimethoxyphenylethyl-N-methylcarbamides. 1- β -Phenylethyl-, m.p. 147°, 1- β -o-, m.p. 60°, -m-, m.p. 96°, and -p-, m.p. 173°, -anisylethyl-, and 1- β -2:3-, m.p. 122°, -2:4-, m.p. 92°, -2:5-, m.p. 92°, and -3:4-, m.p. 87°, -dimethoxyphenylethyl-5:5-diethylbarbituric acids are prepared from $\text{CH}_2\text{Ar}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, $\text{CEt}_2(\text{CO}_2\text{Et})_2$, and $\text{EtOH}\cdot\text{NaOEt}$. H. B.

Action of nitrous acid on dimethylaniline. II. J. C. EARL and A. W. MACKNEY (J. Proc. Roy. Soc. New South Wales, 1933, 67, 419).—p-Nitroso-dimethylaniline nitrate is a by-product of the action of HNO_2 on NPhMe_2 , although repeated analyses for N give variable results (cf. this vol., 644).

C. M. B.

Action of halogens on arylazoacetylacetones. F. D. CHATTAWAY and R. D. ASHWORTH (J.C.S., 1934, 930—935).—Benzeneazoacetylacetone (I) and Br (1 mol.) in AcOH or CHCl_3 at room temp. afford mainly p-bromobenzeneazoacetylacetone (II), m.p. 142°, also obtained from $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{Cl}$ and CH_2Ac_2 . Under similar conditions (I) and Br (2 mols.) give an inseparable mixture of compounds, whilst with Br (3 mols.) in hot or cold AcOH $\alpha\gamma$ -dibromo- β -ketopropaldehyde-p-bromophenylhydrazine (III) $\text{CH}_2\text{Br}\cdot\text{CO}\cdot\text{CBr}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$, m.p. 175°, results, also obtained from Br (2 mols.) and (II) or β -ketopropaldehyde-p-bromophenylhydrazine in hot AcOH . Continued action of excess of Br on (III) in boiling AcOH produces first $\alpha\alpha\gamma$ -tribromo- β -ketopropaldehyde-p-bromophenylhydrazine, m.p. 164°, and then more slowly $\alpha\alpha\gamma$ -tribromo- β -ketopropaldehyde-2:4-dibromophenylhydrazine (IV). 2:4-Dibromobenzeneazoacetylacetone and Br (2 mols.) in boiling CHCl_3 give quantitatively 2:4-dibromobenzeneazo- $\gamma\gamma'$ -dibromoacetylacetone, m.p. 162°, transformed by Br (1 mol.) in boiling AcOH into 2:4-dibromobenzene-

azo- $\gamma\gamma\gamma'$ -tribromoacetylacetone, m.p. 165°, converted by prolonged action of excess of Br at 100° into (IV). Similarly 2:4:6-tribromobenzeneazoacetylacetone (V) affords 2:4:6-tribromobenzeneazo- $\gamma\gamma'$ -dibromoacetylacetone, m.p. 123°, and then $\alpha\gamma\gamma$ -tribromo- β -ketopropaldehyde-2:4:6-tribromophenylhydrazine. The action of Br on o-nitrobenzeneazoacetylacetone in CHCl_3 leads to o-nitrobenzeneazo- $\gamma\gamma$ -dibromoacetylacetone, m.p. 163°, transformed by 4Br in boiling AcOH into o-nitrobenzeneazo- $\gamma\gamma\gamma\gamma'$ -tetra-bromoacetylacetone, m.p. 132°. p-Nitrobenzeneazo- $\gamma\gamma'$ -dibromoacetylacetone has m.p. 150°. (V) is transformed by Cl_2 in AcOH into α -chloro- β -ketopropaldehyde-2:4:6-tribromophenylhydrazine, m.p. 136°; the corresponding -2:4-dibromophenylhydrazine, m.p. 141°, is obtained similarly. α -Chloro- β -ketopropaldehyde-2-chloro-4-nitrophenylhydrazine, m.p. 148°, and the corresponding -4-chloro-2-nitrophenylhydrazine, m.p. 155°, are described. α -Chloro- γ -bromo- β -ketopropaldehyde-2-chloro-4-nitrophenylhydrazine has m.p. 178°. p-Nitrobenzeneazoacetylacetone or β -ketopropaldehyde-p-nitrophenylhydrazine is transformed by Cl_2 in CHCl_3 into α -chloro- β -ketopropaldehyde-p-nitrophenylhydrazine, m.p. 224° (corresponding o-derivative, m.p. 173°), converted by $\text{NH}_3\cdot\text{EtOH}$ into α -amino- β -ketopropaldehyde-p-nitrophenylhydrazine (corresponding -2-chloro-4-nitrophenylhydrazine, m.p. 201°). β -Ketopropaldehyde-4-chloro-2-nitrophenylhydrazine, m.p. 170°, -2-chloro-4-nitrophenylhydrazine, m.p. 168°, and p-bromophenylhydrazine, m.p. 143°, have been obtained. H. W.

Influence of nuclear substituents on the photosensitivity of benzenediazonium chlorides. V. L. LJASCHENKO and N. A. KIRZNER (Anilinokras. Prom., 1934, 4, 272—276).—The photostability (I) of $p\text{-R}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}$ derivatives is $>$ that of PhN_2Cl (II) when $\text{R}=\text{CO}_2\text{H}$, Ac, and NO_2 , equal when $\text{R}=\text{OEt}$, and less when $\text{R}=\text{Cl}$, SO_3H , OMe, Me, OH, and NMe_2 . For o-derivatives (I) is $>$ for (II) when $\text{R}=\text{CO}_2\text{H}$, and less when $\text{R}=\text{Me}$, Cl, OMe, NO_2 , and for m-derivatives (I)=that of (II) when $\text{R}=\text{NO}_2$, CO_2H , SO_3H , and less when $\text{R}=\text{Me}$ or OH. For disubstituted compounds the effect is in some cases the mean of that due to each substituent separately, whilst in others it is greater. R. T.

Chloromethyl derivatives of phenols. M. SOMMELET and I. MARZAK (Compt. rend., 1934, 198, 2256—2258; cf. A., 1933, 1044).—Chloromethyl derivatives of the Et carbonates of m-cresol, m-xyleneol, b.p. 151—153°/3 mm., guaiacol, b.p. 180°/6 mm., and “guaiethol,” b.p. about 180°/3 mm., are formed by interaction of the compound with CH_2O and HCl . Anisole with CH_2O in $\text{C}_6\text{H}_6\text{--HCl}$ (gas) during 1 hr. affords p-chloromethylanisole, b.p. 95°/5 mm. Similarly, phenetole affords a chloromethyl derivative, b.p. 105—107°/3 mm., converted by $(\text{CH}_2)_6\text{N}_4$ into phenetaldehyde. PhOBu^a similarly affords chloromethylphenyl Bu^a ether, b.p. 115—135°/3 mm., and butoxybenzaldehyde, b.p. about 135°/3 mm. J. L. D.

Synthesis of α -chloroethyl derivatives of phenol ethers; application to some vinylanisoles. R. QUELET (Compt. rend., 1934, 199, 150—152; cf. this vol., 290).— PhOMe (1 mol.) with MeCHO (1 mol. in conc. HCl —light petroleum containing ZnCl_2 (1 hr.)

followed by C_5H_5N at 115° (10 hr.) affords *p*-methoxystyrene (cf. A., 1907, i, 404) and α -di-*p*-anisylethane. The following are prepared similarly: 4-methoxy-3-methyl-, b.p. $105^\circ/16$ mm., 4-methoxy-2-methyl-, b.p. $107^\circ/16$ mm., 2-methoxy-5-methyl-, b.p. $107^\circ/16$ mm., and 4-methoxy-2-methyl-5-isopropylstyrene, b.p. $122^\circ/12$ mm. J. L. D.

Synthesis of chloromethyl derivatives of *p*-bromoanisole and the nitroanisoles. R. QUELET (Bull. Soc. chim., 1934, [v], 1, 539—545).— CH_2O , HCl , $ZnCl_2$, and the substituted anisole afford about 80% yields of 4-bromo-, m.p. 27.5° , b.p. $153—154^\circ/15$ mm., 4-nitro-, m.p. 80° , b.p. $193—195^\circ/16$ mm., and 5-nitro-2-chloromethylanisole, m.p. $89.5—90^\circ$, b.p. $190^\circ/15$ mm. (decomp.), and 2-nitro-4-chloromethylanisole, m.p. 86° , b.p. $195—196^\circ/15$ mm., and small amounts of 5:5'-dibromo-2:2'-dimethoxy-, m.p. 109° (lit. 108°), and 3:3'-dinitro-4:4'-dimethoxy-diphenylmethane, m.p. 168° . R. S. C.

Preparation of 2:6-dichlorophenol-indophenol from *p*-nitrophenol. V. HOO, T. S. MA, and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 235—239).—Full details of the prep. of 2:6-dichlorophenol-indophenol from *p*- $NO_2 \cdot C_6H_4 \cdot OH$ through 2:6-dichloro-4-nitro- and -4-amino-phenol and 2:6-dichlorobenzoquinone chloroimide are given. H. N. R.

Isomeric nitrocresols. L. W. CLEMENCE and G. W. RAIZISS (J. Amer. Pharm. Assoc., 1934, 23, 536—541).—A crit. discussion of the lit. methods for the prep. of the ten isomeric nitrocresols. Improved methods for the prep. of nine (all but the 6- NO_2) are described. J. W. B.

Rearrangement of phenyl alkyl ethers at moderate temperatures. Synthesis of *tert*-amyl-, *tert*-butyl-, and diisobutyl-[$\alpha\gamma\gamma$ -tetramethylbutyl]-phenols. S. NATELSON (J. Amer. Chem. Soc., 1934, 56, 1583—1586).—Addition of $\alpha\gamma\gamma$ -tetramethylbutyl chloride (I) to $KOPh$, $o-C_6H_4Me \cdot OK$, and $o-OMe \cdot C_6H_4 \cdot OK$ at 75° and subsequent heating at 125° (3—4 hr.) and 180° (about 1 hr.) gives $\alpha\gamma\gamma$ -tetramethylbutyl-phenol (II), m.p. 84° , *o*-cresol, m.p. 54° , and -guaiacol, b.p. $295—298^\circ$, respectively. *p*-*tert*-Amylphenol and $C_6H_4Bu \cdot OH$ are similarly obtained. $Ph \alpha\gamma\gamma$ -tetramethylbutyl ether (III) [from (I) and $EtOH-NaOPh$] rearranges at 250° into (II). The above phenols are also prepared by addition of conc. H_2SO_4 (1 mol.) to a mixture of $PhOH$ (1 mol.) and the requisite olefine (1 mol.) at $<10^\circ$ and subsequent reaction at room temp. and 65° (cf. A., 1933, 819). Rearrangement of (III) in presence of Ph_2O gives (II) and no tetramethylbutyldiphenyl ether, indicating that reaction is not intermol. (cf. Smith, this vol., 521). The above (and related) rearrangement is considered to be analogous to benzenoid-quinonoid tautomerism; the effect of various conditions on the dynamic equilibrium is discussed. H. B.

Transformations of phenyl benzyl ethers at higher temperatures. O. BEHAGEL and H. FREIENSENER (Ber., 1934, 67, [B], 1368—1377).—When heated at 250° or under reflux, $CH_2Ph \cdot OPh$ is converted into $PhOH$, the *p*-, m.p. 83° (benzoate, m.p. 87°),

and *o*- α -naphthylurethane of benzylphenol, and 2:4-dibenzylphenol (I) (α -naphthylurethane, m.p. 143°). Reaction is more rapid and more complete in presence of a little Zn or Cu , but the high temp. is necessary. $Ph \ o$ -benzylphenyl ether at 240° passes into $o-OH \cdot C_6H_4 \cdot CH_2Ph$, (I), and probably 2:6-dibenzylphenol. $o-C_6H_4Me \cdot O \cdot CH_2Ph$ gives $o-C_6H_4Me \cdot OH$, *p*-benzyl- and dibenzyl-*o*-cresol. Guaiacyl benzyl ether affords guaiacol, *p*-benzylguaiacol, b.p. $187—196^\circ/15$ mm. (*p*-toluenesulphonate, m.p. $102.5—103^\circ$), and dibenzylguaiacol, b.p. $247^\circ/15$ mm., m.p. 107° . $\alpha-C_{10}H_7 \cdot O \cdot CH_2Ph$ at 240° gives $\alpha-C_{10}H_7 \cdot OH$ and 4-benzyl- α -naphthol (II), m.p. 120° , whilst $\beta-C_{10}H_7 \cdot O \cdot CH_2Ph$ at $240—250^\circ$ yields $\beta-C_{10}H_7 \cdot OH$ and 1-benzyl- β -naphthol (III), m.p. 110° . The possibility of using $CH_2Ph \cdot OPh$ as a nucleus-benzylating agent is established by the production of (III) from it and $\beta-C_{10}H_7 \cdot OH$ at the b.p., and the possibility that this is an effect of re-etherification is excluded by the formation of 4-benzyl-naphthyl *Me* ether, m.p. 83° , from $\beta-C_{10}H_7 \cdot OMe$ [the product is also obtained from $\alpha-C_{10}H_7 \cdot OMe$ and CH_2PhCl in presence of Zn and from (II) and Me_2SO_4]. $\beta-C_{10}H_7 \cdot OH$ and *p*- $C_6H_4Me \cdot O \cdot CH_2Ph$ give *p*- $C_6H_4Me \cdot OH$, $\beta-C_{10}H_7 \cdot OH$, and (III). 3-Nitro-4-methoxybenzyl chloride, m.p. 86° (prep. from *p*- $NO_2 \cdot C_6H_4 \cdot OMe$, CH_2O , and HCl), is converted into *Ph* 3-nitro-4-methoxybenzyl ether, m.p. 100° , and pyrocatechol di-3-nitro-4-methoxybenzyl ether, m.p. 159° , which could not be isomerised. H. W.

Mobility of halogen in 1-halogeno-2-naphthols. RINGEISSEN (Compt. rend., 1934, 198, 2180—2183).—1-Chloro- or -bromo- β -naphthol with $AgNO_2$ in dry Et_2O gives a poor yield of 1-nitro- β -naphthol. With aq. Na_2S at 85° in N_2 97.5% of di-2-hydroxy-1-naphthyl sulphide and a little of the corresponding disulphide are obtained. R. S. C.

Preparation and germicidal properties of some alkyl derivatives of hydroxydiphenyls. S. E. HARRIS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 530—536).—Various 2-hydroxy-3- and -5-alkyldiphenyl derivatives have been prepared (1) by condensation ($AlCl_3$) of the fatty acid chloride with 2-methoxydiphenyl, reduction (Clemmensen), and demethylation, or (2) by rearrangement ($AlCl_3$) of the ester of 2-hydroxydiphenyl (I), separation of the 3-(sol.) and 5-acyl compounds by ligroin, and reduction. The following have been prepared: 2-hydroxy- (*propionate*, b.p. $151—152^\circ/4$ mm., *n*-butyrate, b.p. $154^\circ/3.5$ mm., and *n*-valerate, b.p. $162—167^\circ/4$ mm.), 2-hydroxy-3-, b.p. $183—185^\circ/3.5$ mm., and -5-*propionyl*-, m.p. $151—152^\circ$, -3-, b.p. $185—190^\circ/3.5$ mm., and -5-*n*-butyryl-, m.p. $116—117^\circ$, -3-, b.p. $200—210^\circ/5$ mm., and -5-*n*-valeryl-, m.p. 104° , -5-ethyl-, b.p. $152^\circ/5$ mm., -3-, b.p. $155—160^\circ/8$ mm., and -5-*n*-propyl-, b.p. $171—172^\circ/9$ mm., -3-, b.p. $160—167^\circ/4$ mm., and -5-*n* butyl-, b.p. $173—175^\circ/6$ mm., -3-, b.p. $166—171^\circ/5$ mm., and -5-*n*-amyl-, b.p. $181—183^\circ/6$ mm., -diphenyl; 2-methoxy-5-acetyl-, m.p. $90—90.5^\circ$, -5-*propionyl*-, m.p. $93—94^\circ$, and -5-*n*-valeryl-, b.p. $202—204^\circ/4$ mm., -5-ethyl-, b.p. $163—166^\circ/7$ mm., -5-*n*-propyl-, b.p. $171—172^\circ/9$ mm., and -5-*n*-amyl-, b.p. $178—182^\circ/5$ mm., -diphenyl; 3-hydroxy- (*propionate*, b.p. $160—165^\circ/2$ mm.), 3-hydroxy-4-*prop*-

ionyl-, m.p. 109°, and -4-, b.p. 162—163°/3 mm., and -6-n-propyl-, m.p. 140—141°, -diphenyl; 3-methoxy-, b.p. 140°/5 mm., 3-methoxy-6-propionyl-, m.p. 72°, and -6-n-propyl-, b.p. 153—170°/3 mm., -diphenyl; 3:4-dimethoxy-, b.p. 153°/4 mm., m.p. 70°, 3:4-dimethoxy-5-propionyl-, b.p. 228—230°/3 mm., m.p. 113°, and -5-n-propyl-, b.p. 195—210°/7 mm.; 2:5-dimethoxy-, b.p. 147—149°/4 mm.; 2:5-dihydroxy-4-propionyl-, b.p. 220—230°/6 mm., m.p. 138—139°, and -4-n-propyl-, b.p. 195°/9 mm., -diphenyl. Alkylation of (I) in the 3-position decreases, and in the 5-position increases (max. with Pr⁺), its bactericidal action towards *Staph. aureus* (II), but in both positions decreased activity against *B. typhosus* (III) results. Propylation of the 3-OH- and of the 2:5- and 3:4-(OH)₂-compounds has little effect on the activity against (III), but, respectively, decreases and increases activity against (II). J. W. B.

Action of sodium hydrogen sulphite on resorcinol. W. M. LAUER and C. M. LANGKAMMERER (J. Amer. Chem. Soc., 1934, 56, 1628—1629).—Contrary to Fuchs and Elsner (A., 1920, i, 545) and Bucherer and Hoffmann (A., 1929, 554), prolonged interaction of *m*-C₆H₄(OH)₂ and aq. NaHSO₃ gives *Na phenol-m-sulphonate* (I). Diazotisation of *m*-NH₂-C₆H₄-SO₃H, decomp. of the resulting solution by heating, and successive treatment with NaCl and Br gives *Na 2:4:6-tribromophenol-3-sulphonate* (II), also prepared from (I). Methylation (Me₂SO₄, aq. NaOH) of (I) and (II) affords *Na anisole-m-sulphonate* (+H₂O) and *2:4:6-tribromoanisole-3-sulphonate*, respectively. *2:4:6-Tribromoanisole-3-sulphonyl chloride* and -sulphonamide have m.p. 57.2—58.2° and 176.6—178°, respectively. H. B.

Vanillylamides of normal fatty acids. A. H. FORD-MOORE and J. W. C. PHILLIPS (Rec. trav. chim., 1934, 53, 847—859).—Most acylvanillylamides exist in two forms, the m.p. being given in the order α, β: Ac, m.p. 109—109.5° (α); propionyl, m.p. 111.5° (α); butyryl, m.p. 75.5—76° (α); valeryl, m.p. 60—60.5° (β); hexoyl, m.p. 49—49.5° (β); heptoyl, m.p. 61° (α); octoyl, m.p. 44.5—45.5° (α); nonoyl, m.p. 59.5—60°, 51.5°; decoyl, m.p. 60.5—61°, 52—52.5°; undecoyl, m.p. 69.5°, 62—62.5°; dodecoyl, m.p. 72.5—73°, 67—67.5°; tridecoyl, m.p. 79.5—80°, 74—74.5°; tetradecoyl, m.p. 82°, 76.5—77°; pentadecoyl, m.p. 87.5°, 82—82.5°; heptadecoyl, m.p. 91.5—92°, 88°; palmityl, m.p. 89—89.5°, 84—84.5°; stearyl, m.p. 94.5—95°, 90—90.5°. Pungencies and solubilities in PhMe are given. The nonoyl compounds are the most pungent. R. S. C.

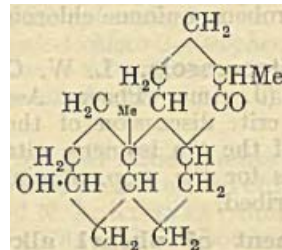
β-Hydroxycarotene. R. KUHN and H. BROCKMANN (Ber., 1934, 67, [B], 1408—1409).—Elementary analysis of β-hydroxycarotene (I) is complicated by the firmness with which it retains MeOH, but after allowance for this, the formula C₄₀H₅₆O₂ is assigned. Oxidation of (I) with CrO₃ (=5O) gives the aldehyde C₂₇H₃₆O₃ in the same yield as from β-carotene (II). It is therefore probable that 27 C of (II) remain unchanged in (I) and that the 2 O are located on the second ionone ring with 13 C. H. W.

Action of magnesium phenyl bromide on l-dibenzoylglyceraldehyde. Preparation of l-α-

phenylglycerol dibenzoate. M. TIFFENEAU and (MLLE.) I. NEUBERG (Compt. rend., 1934, 198, 2174—2176).—MgPhBr and OBz·CH₂·CH(OBz)·CHO (but not the Ac₂ derivative or free aldehyde) give l-α-phenylglycerol dibenzoate, α-form, an oil, giving the known Bz₃ derivative (α-form), m.p. 147°. R. S. C.

Hydration of α- and γ-phenyl-β-epoxypropyl alcohol to a mixture of stereoisomeric phenylglycerols. (MLLE.) M. DARMON (Compt. rend., 1934, 198, 2177—2179).— $\text{CHPh} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{array}$ and $\text{OH} \cdot \text{CHPh} \cdot \text{CH} \begin{array}{c} \diagup \text{CH}_2 \\ \diagdown \text{O} \end{array}$ with hot H₂O and a little HCl give mixtures of the α- (I) and β-forms of α-phenylglycerol, containing 80 and 50% of (I), respectively (cf. Hibbert *et al.*, A., 1933, 398). R. S. C.

Action of ozone on β-ergosterol acetate. T. ACHTERMANN (Z. physiol. Chem., 1934, 225, 141—144).—β-Ergosterol acetate in AcOH yields an ozonide which on treatment in AcOH with Zn dust and thermal decomp. of the neutral product affords an acetate, m.p. 142°, b.p. 120—130°/0.006 mm. [oxime, m.p. 145—150° (decomp.)], a keto-alcohol, C₁₈H₂₆O₂, m.p. 117—119° (dinitrobenzoate, m.p. 192—193°), the probable constitution of which is



J. H. B.

Conversion of coprostanone into coprosterol. H. GRASSHOF (Z. physiol. Chem., 1934, 225, 197—198).—Hydrogenation of coprostanone (Pt-sponge) in AcOH and isoamyl ether affords in 60—70% yield (as ester) coprosterol, [α]_D²⁵ +28° in CHCl₃ (benzoate, m.p. 124—125°, [α]_D +31° in CHCl₃). J. H. B.

M.p. as a test for coprosterol. H. DAM (Biochem. J., 1934, 28, 826—827).—The m.p. diagrams of mixtures of coprosterol (I) with dihydrocholesterol or cholesterol have been determined by the methods of Rheinboldt and Kircheisen (A., 1926, 1001) and of Lettré (A., 1932, 737) and are discussed in reference to the determination of the purity of samples of (I). W. O. K.

Law of periodicity. X. P. PETRENKO-KRITSCHENKO (Ber., 1934, 67, [B], 1349—1351).—A reply to Hantzsch *et al.* (this vol., 769). H. W.

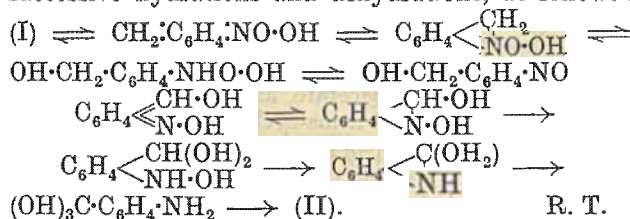
Constitution and absorption of light of triphenylmethane derivatives. I. LIFSCHITZ (Ber., 1934, 67, [B], 1413—1417).—A reply to Hantzsch *et al.* (this vol., 769). H. W.

Organic sulphur compounds. II. Action of ozone on thioamides and thioanilides. S. ISHII-KAWA and Y. KATOH (Sci. Rep. Tokyo Bunrika Daigaku, 1934, 2, 17—26).—PhCS·NH₂ in CCl₄, CHCl₃, C₆H₆, CS₂, Et₂O, or COMe₂ with O₃ during several hr. readily affords PhCN and dibenzazoylsulphim (cf. A., 1925, i, 1149) by way of benzimino-

isothiobenzamide. Reaction proceeds with difficulty in EtOH; in H₂O the product is NH₂Bz. Similarly, *p*-thiotoluamide affords *p*-C₆H₄Me·CN, di-*p*-toluenylazosulphim, and *p*-toluimino-*p*-isothiobenzamide. CSMe·NH₂ in C₆H₆ or H₂O with O₃ during 2 hr. gives AcOH, H₂SO₄, S, and NH₃. Thiobenz- and thioacet-anilide similarly afford benz- and acet-anilide.

J. L. D.

Rearrangement of *o*-nitrotoluene to yield anthranilic acid derivatives. A. E. PORAI-KOSCHITZ (Anilinokras. Prom., 1934, 4, 261—264).—The conversion of *o*-C₆H₄Me·NO₂ (I) into *o*-NH₂·C₆H₄·CO₂H (II) takes place by a series of successive hydrations and dehydrations, as follows:



R. T.

Rearrangement of 2-nitrotoluene-4-sulphonic acid to yield sulphanthranilic acid. E. N. SCHAGOVA (Anilinokras. Prom., 1934, 4, 264—267).—Max. yields (62%) of *o*-toluidine-4-sulphonic acid (I) are obtained by heating 2 : 1 : 4-NO₂·C₆H₃Me·SO₃H (II) with NaOH [2 c.c. of 10% NaOH per g. of (II)] at 94—96° during 6 hr.; substituting saturated Ba(OH)₂ for NaOH the reaction proceeds very slowly [6.2% yields of (I) after 2 hr. at 100°]. The Ba, Bi, Sn, Co, Fe, Al, and Hg salts of (I) are readily sol. in H₂O. Addition of 0.05 mol. of BaCl₂ per mol. of (I) in the reaction mixture (III) ppts. a coloured impurity, apart from which 4-sulphosalicylic acid is present in (III). (I) is best pptd. from (III) by adding HCl to give a distinctly acid reaction; further excess of HCl leads to incomplete pptn.

R. T.

Syntheses with the magnesium halide derivative of phenylacetic acid by oxidation or bromination. D. IVANOV and A. SPASSOV (Arh. Hemiju, 1934, 8, 8—11).—CHPh(MgBr)·CO₂Na (I) in Et₂O combines with O₂ at 0° to yield CHPh(OMgBr)·CO₂Na, which on boiling with H₂O gives mandelic acid (38%) and αβ-diphenylsuccinic acid (II) (8%). (I) in Et₂O reacts with Br in CCl₄ to yield a mixture of CHBrPh·CO₂H and (II).

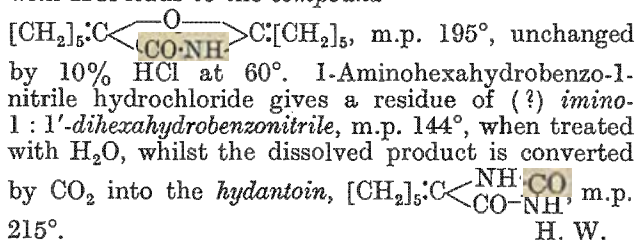
R. T.

α-Di- and tri-substituted amides. (MLLE.) AMAGAT (Compt. rend., 1934, 198, 2172—2174).—The ultra-violet absorption spectra of CHPhEt·CO·NH₂, CPhEt₂·CO·NH₂, CHPhEt·CO·NH₂Et, m.p. 69—70°, CHPhEt₂·CO·NH₂Et, (I), m.p. 37°, and CPhEt₂·CO·NH₂Et, b.p. 170—171°/17 mm. (?), are very similar. Slight differences are attributed to changes in the position of the amide-imino-alcohol equilibrium. The curve for CHPhEt·CO·NHPh is markedly different. (I) does not react with Grignard reagents.

R. S. C.

1-Hydroxyhexahydrobenzoic acid. H. T. BUCHERER and K. DAHLEM (J. pr. Chem., 1934, [ii], 140, 251—272).—The action of PBr₅ on hydroxyhexahydrobenzoic acid (I) in boiling C₆H₆ does not give org. acidic products, but mainly an oil contaminated by ketonic resin which slowly regenerates (I).

Similar results are obtained in CS₂ or CHCl₃. PBr₃ or POBr₃ offers no advantage. (I) and PBr₅ in CHCl₃ at -10° afford the acid [CH₂]₅C(CO₂H)·O·PO(OH)₂, m.p. 163° (decomp.), unchanged (I), neutral oil, and resin. (I) and HBr·H₂O (saturated at 0°) at 150° yield 4-bromohexahydrobenzoic acid, m.p. 171°, also obtained similarly from Et 1-hydroxyhexahydrobenzoate. H₃PO₄ (d 1.7) and (I) at 140° yield cyclohexanone, Δ^{1,2}-tetrahydrobenzoic acid (II), m.p. 44°, and, mainly, a dark, brittle resin. (II) and 2 Br in CHCl₃ give 1 : 2-dibromohexahydrobenzoic acid, m.p. 147°, accompanied by a Br₃-compound. Hydrogenation of (II) (colloidal Pt) gives hexahydrobenzoic acid. (II) and PBr₅ afford 2-bromohexahydrobenzoic acid, m.p. 112°. SOCl₂ and (I) in C₆H₆ at 40° give the lactidic acid [CH₂]₅C(OH)·CO·O·C(CO₂H)·[CH₂]₅, m.p. 163° (Na, m.p. 234°, and Ca, m.p. 209°, salts), hydrolysed by KOH to (I) and converted by Ac₂O·NaOAc at 160° into the lactide, [CH₂]₅C<O>C[CH₂]₅, m.p. 181°, hydrolysed by 10% NaOH at 60° to (I). cycloHexanone, (I), and 37% HCl at 100° give the substance [CH₂]₅C<O>C[CH₂]₅, b.p. 149—153°/24 mm., m.p. 39°, also formed from (I) and cyclohexanone at 175° without solvent. (I) and AcCl at 45° yield 1-acetoxyhexahydrobenzoic acid, m.p. 111°. Treatment of cyclohexanone cyanohydrin in dry Et₂O with HCl leads to the compound



H. W.

Rearrangement of *o*-nitrotoluoylbenzoic acid in presence of alkali. A. A. CHARCHAROV (Anilinokras. Prom., 1934, 4, 268—272).—56% yields of 3-aminobenzophenone-2' : 4-dicarboxylic acid (I) are obtained by heating 1 mol. of 3-nitro-4-methylbenzophenone-2'-carboxylic acid with 3.5 mols. of NaOH at 94—96° during 1.5—2 hr. On adding HCl to the reaction mixture tarry impurities at first separate, after filtration from which fairly pure (I) is pptd. on further addition of HCl. (I), on diazotisation and coupling with various β-naphtholsulphonic acids, yields a series of reddish-brown dyes for wool. On diazotization and boiling with H₂O (I) affords 4-terephthaloylsalicylic acid, m.p. 247°, which yields on dehydration a mixture of 2-hydroxyanthraquinone-3- and 1-hydroxyanthraquinone-2-carboxylic acids.

R. T.

Organic catalysts. IX. Structure specificity of esterase models.—See this vol., 849.

Synthesis of norpinic acid. P. C. GUHA and K. N. GAIND (Current Sci., 1934, 2, 479).—Norpinic acid is synthesised by condensing Et sodiomethylenedimalonate with CCl₂Me₂ or Et sodioisopropylidenedimalonate with CH₂I₂, followed by hydrolysis and decarboxylation of the resulting tetracarboxylic ester.

Improved methods of prep. of isopropylidene-malonic and -dimalonic esters have been devised. L. S. T.

Fused carbon rings. Introduction and I. Fusion of five-membered rings in the *cis*- and *trans*-positions. Synthesis of β -0:3:3-dicyclooctanones and related compounds. R. P. LINSTEAD and E. M. MEADE. **II. Synthesis of *cis*- α -0:3:3-dicyclooctanone and related compounds.** A. H. COOK and R. P. LINSTEAD. **III. Synthesis of *cis*- and *trans*-cyclopentane-1-carboxy-2-acetic acids and the stability of their anhydrides.** A. H. COOK and R. P. LINSTEAD (J.C.S., 1934, 935—946, 946—956, 956—961).—I. In accordance with the requirements of the tetrahedral theory, *cis*-0:3:3-dicyclooctane systems are more stable than the corresponding *trans*-compounds and there is at present no indication of the operation of other factors in determining the stability of these dicyclic mols.

Et cyclopentanone-2-carboxylate (improved prep. from Et adipate) is converted by $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ and mol. Na in boiling C_6H_6 and subsequent hydrolysis with boiling conc. HCl into cyclopentanone-2-acetic acid, m.p. 53° (yield 87%). The corresponding Et ester (I) condenses with $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ in presence of piperidine (yields 10—35%) or of KOEt (yield 35%) to Et cyclopentylidenecyanoacetate-2-acetate, b.p. 180—205°/5 mm., reduced (Al-Hg and moist Et_2O or H-PtO₂) to Et *cis*-cyclopentane-1-cyanoacetate-2-acetate, b.p. 170—173°/5 mm., hydrolysed by boiling conc. HCl to *cis*-cyclopentane-1:2-diacetic acid (II), m.p. 173°, containing a small proportion of the *trans*-acid and a little crude *cis*- β -dicyclooctanone. (I) and $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{Et}$ (or $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$) with Zn (or Mg) in presence of C_6H_6 , PhMe, or xylene afford Et cyclopentanol-1:2-diacetate, b.p. 143—144°/4 mm., dehydrated by P_2O_5 or, preferably, by Darzens' method to (?) the lactone of cyclopentanol-1-acetic ester 2-acetic acid, b.p. 166°/6 mm., and two unsaturated esters, one of which was hydrolysed to a mixture of unsaturated acids, m.p. 169—172°, whereas the other yielded cyclopentylidenecetic acid-2-acetic acid, m.p. 179°, hydrogenated (PtO₂) to (II). The lactone of cyclopentanol-2-acetic acid (III), b.p. 130°/20 mm., 98°/4 mm., is obtained in quantity from cyclopentanone through Et cyclopentanol-1-acetate, which is converted by $\text{C}_5\text{H}_5\text{N}$, anhyd. Et_2O , and SOCl_2 into Et Δ^1 -cyclopentenecetate and lactonised by 60% H_2SO_4 at 90°. Other processes examined are the treatment of Et cyclopentylidenecyanoacetate with boiling HCl or $\text{AcOH}\cdot\text{H}_2\text{SO}_4$, of Δ^2 -cyclopentenylacetic acid with 60% H_2SO_4 at 90°, and the reduction of cyclopentanone-2-acetic acid with Na-Hg in H_2O or catalytically. (III) is converted by PBr_5 and EtOH or by $\text{HBr}\cdot\text{EtOH}$ into Et (? *cis*+*trans*)-2-bromocyclopentaneacetate, b.p. 125°/15 mm., which condenses with $\text{CHNa}(\text{CO}_2\text{Et})_2$ best at 130° to Et₃ cyclopentane-1-malonate-2-acetate, b.p. 174°/5 mm.; this is not smoothly hydrolysed by acid or alkali, yielding *trans*-cyclopentane-1:2-diacetic acid (IV), m.p. 137°, in small and varying yield together with AcOH and parent lactone. *cis*- β -dicyclooctanone (V) b.p. 78°/10 mm. (semicarbazone, m.p. 197—198°), is obtained by heating (II) with a little BaO at 280—310°, or by con-

verting (II) into the Ag_2 salt, and thence into the Et₂ ester, b.p. 160°/17 mm., which is converted by mol. Na in C_6H_6 into Et *cis*-dicyclooctan-2-one-1-carboxylate, b.p. 136°/17 mm., which is hydrolysed by boiling conc. HCl. (IV) and BaO at about 340° afford *trans*- β -dicyclooctanone (VI) (semicarbazone, m.p. 251°). The difference in temp. required by the two acids gives a method of obtaining (V) and (VI) separately from the mixed acids. Selective ring closure of the mixed esters is also described. (V) is reduced by Zn-Hg, AcOH, and conc. HCl or its semicarbazone by a modified Wolff reaction to *cis*-0:3:3-dicyclooctane, b.p. 137—138°, and is oxidised by KMnO_4 in $\text{H}_2\text{O}\cdot\text{COMe}_2$ to *cis*-cyclopentane-1-carboxy-2-acetic acid (VII), m.p. 89°. (VI) when similarly oxidised affords (VII) in small amount. (VII) is obtained by hydrogenation and subsequent hydrolysis of Et 2-carbethoxy- Δ^1 -cyclopentenylcyanoacetate and is isomerised by conc. HCl at 180° to *trans*-cyclopentane-1-carboxy-2-acetic acid, m.p. 68° (Ag salt).

II. Cautious addition of conc. H_2SO_4 to indane gives indane-5-sulphonic acid (+3 H_2O , m.p. 92°) in 80% yield, converted by fusion with KOH in presence of Zn dust into 5-hydroxyindane, m.p. 54—55° (Bz derivative, m.p. 111—112°), catalytically reduced (Adams) to *cis*-5-hydrindanol (I), b.p. 113°/15 mm. (phenylurethane, m.p. 121°). Addition of (I) to conc. HNO_3 at about 40° affords *cis*-cyclopentane-1-carboxy-2-propionic acid (II), m.p. 101° (dianilide, m.p. 190°; Ag_2 salt; Et₂ ester (III), b.p. 160°/20 mm.). The *cis*-configuration of (II) is established by its isomerisation by conc. HCl at 180° into *trans*-cyclopentane-1-carboxy-2-propionic acid (IV), m.p. 101.5° (dianilide, m.p. 192°), and by the transformation of (III) by mol. K in anhyd. Et_2O into Et₂ *trans*-cyclopentane-1-carboxylate-2-propionate, b.p. 161°/19 mm. Treatment of Et cyclopentanone-2-carboxylate with mol. Na in C_6H_6 and subsequently with $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ affords Et₂ cyclopentanone-2-carboxylate-2- β -propionate, b.p. 189°/18 mm., which does not yield ketonic derivatives and is converted by boiling conc. HCl into cyclopentanone-2- β -propionic acid (V), b.p. 175°/10 mm., m.p. 37° [semicarbazone, m.p. 219° (slight decomp.)]. Et cyclopentanone-2- β -propionate (VI), b.p. 150°/18 mm. (semicarbazone, m.p. 153.5°; 2:4-dinitrophenylhydrazones, m.p. 92.5°), is converted by NaOEt in warm EtOH into Et₂ γ -carbethoxysuberate (VII), b.p. 186°/9 mm. [γ -carboxysuberic acid, m.p. 111°, is transformed by BaO at 300° into CO_2 , H_2O , and (V)]. (VII) is converted by mol. Na in C_6H_6 into Et₂ cyclopentanone-2-carboxylate-5-propionate, b.p. 186°/20 mm. (Cu derivative; dinitrophenylhydrazones). The cyano-hydrin of (VI), b.p. 154°/8 mm., 182°/18 mm., is dehydrated in $\text{Et}_2\text{O}\cdot\text{C}_5\text{H}_5\text{N}$ by slow addition of SOCl_2 to Et Δ^1 - (or Δ^5)-1-cyanocyclopentene-2- β -propionate, b.p. 173°/17 mm. (corresponding acid, m.p. 122°), hydrolysed and esterified to Et₂ cyclopentene-1-carboxylate-2-propionate, b.p. 171—172°/20 mm., which could not be reduced. (VI), $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, and piperidine afford Et₂ cyclopentylidene-1-cyanoacetate-2- β -propionate, b.p. 220°/17 mm., reduced (Al-Hg in moist Et_2O) to Et₂ *cis*-cyclopentane-1-cyanoacetate-2- β -propionate, b.p. 202°/12 mm., which is hydrolysed to *cis*-cyclopentane-1-acetic-2- β -propionic acid (VIII), m.p. 9°. Ketoneisation of (VIII) by BaO at 315—320° smoothly

affords *cis*-5-hydrindanone [5-keto-*cis*-0:3:4-dicyclononanone], b.p. 96.5°/11 mm. (semicarbazone, m.p. 203°; 2:4-dinitrophenylhydrazones, m.p. 163°), oxidised by conc. HNO₃ to (II). (II) is transformed by BaO at 280—290° into *cis*- α -dicyclooctanone (IX), b.p. 71°/15 mm. [semicarbazone (X), m.p. 180° (decomp.)]; 2:4-dinitrophenylhydrazones, m.p. 115—116°, obtained in approx. the same yield from (IV) at 310—315°. Cyclisation of the Et₂ ester of either acid by mol. Na in C₆H₆ yields the keto-ester, b.p. 140°/20 mm. (Cu derivative, m.p. 106°), hydrolysed by boiling HCl to (IX). When heated with solid KOH (X) yields *cis*-dicyclooctane, b.p. 138—138.5°/758 mm. Oxidation of (IX) with fuming HNO₃ in AcOH at room temp. gives *cis*-cyclopentane-1-carboxy-2-acetic acid, m.p. 87°.

III. *cyclopentanone* cyanohydrin, b.p. 114°/14 mm., 126°/26 mm., is obtained in 65% yield from the H sulphite and KCN and in 87% yield from *cyclopentanone* and HCN in presence of NaOH and then of H₂SO₄. It is converted by SOCl₂ in dry C₆H₆ into Δ^1 -cyclopentenonitrile (I), b.p. 69°/15 mm., which is not reduced by Al-Hg, but is hydrolysed by aq. KOH to Δ^1 -cyclopentenecarboxylic acid (II), m.p. 124°. (I) simulates aromatic properties in its resistance to additive reagents. Et Δ^1 -cyclopentenecarboxylate (III), b.p. 75°/10 mm., 92°/25 mm., is prepared in poor yield by the action of EtI on the Ag salt of (II), in good yield from the chloride of (II) and EtOH or by hydrolysis of (I) by H₂SO₄-EtOH; it is transformed by HBr at 0° into Et (? *trans*-)2-bromocyclopentane-1-carboxylate, b.p. 126—127°/24 mm., in which Br is very mobile. (III) is also obtained by treatment of Et 1-hydroxycyclopentane-1-carboxylate with PCl₅ and then with NPhEt₂ (Sircar's method), but better yields are obtained when use of the *tert.* base is omitted. (III), CN·CH₂·CO₂Et, and NaOEt yield Et₂ cyclopentane-1-carboxylate-2-cyanoacetate (IV), b.p. 182—184°/12 mm., whilst (III), CH₂(CO₂Et)₂, and NaOEt give Et₂ trans-cyclopentane-1-carboxylate-2-malonate (V), b.p. 181—182°/11 mm., which could not be condensed with CH₂Cl·CO₂Et. (V) is hydrolysed by short treatment with boiling conc. HCl to trans-cyclopentane-1-carboxy-2-malonic acid, m.p. 181.5°, or by extended treatment to the corresponding *-acetic acid* (VI), m.p. 66°, also obtained from (IV) and boiling conc. HCl. (VI) is converted by boiling Ac₂O into trans-cyclopentane-1-carboxy-2-acetic anhydride (VII), m.p. 43—44°, hydrolysed by cold dil. aq. NaOH or by H₂O to (VI). (VI) is transformed by PCl₅ followed by NH₂Ph into the *dianilide*, m.p. 214°, whilst (VII) and NH₂Ph in C₆H₆ afford the trans-*anilic acids*, C₆H₅(CO₂H)·CH₂·CO·NHPh and C₆H₅(CO·NHPh)CH₂·CO₂H, m.p. 130° and m.p. 108°, respectively. (VI), EtOH, and HCl or the Ag salt of (VI) and EtI yield Et₂ trans-cyclopentane-1-carboxylate-2-acetate, b.p. 148°/16 mm., which does not condense with Et₂C₂O₄ and Na. When (VII) is heated at 240° and the equilibrated mixture is distilled (b.p. 174—175°/17 mm.), and the distillate hydrolysed with just sufficient hot HCl to effect dissolution, *cis*-cyclopentane-1-carboxy-2-acetic acid (VIII), m.p. 89°, is obtained. (VIII) gives a liquid *anhydride* which with NH₂Ph yields a mixture of *anilic acids*, one of which has m.p. 115°. The *dianilide* of (VIII) has m.p. 234°.

The two forms of *cyclopentane*-1-carboxy-2-acetic acid are closely similar and cannot be quantitatively separated. The salts are very like one another (*Ag*, *Ca*, *Cu*, and *Pb* salts described). The composition of mixtures of the anhydrides is determined by hydration to the mixed acids and "thermal analysis."

H. W.

Formation and transformation of carbon-ring compounds. I. Selenium dehydrogenation of 1:2:3:4-tetrahydronaphthalene-3:3-spirocyclopentane. S. C. SEN-GUPTA (J. Indian Chem. Soc., 1934, 11, 389—394).—The anhydride of 1-carboxycyclopentane-1-acetic acid or Me cyclopentane-1-acetate-1-carboxyl chloride with AlCl₃ and C₆H₆ gives 1-benzoylcyclopentane-1-acetic acid, m.p. 165—166° [semicarbazone, m.p. 162° (decomp.)], reduced (Clemmensen) to 1-benzylcyclopentane-1-acetic acid, m.p. 99—100°, which with 85% H₂SO₄ at 100° gives a 60% yield of 1-keto-1:2:3:4-tetrahydronaphthalene-2:2-spirocyclopentane, b.p. 113—114°/4 mm. This with Se at 300—350° gives phenanthrene and a little anthracene. This rearrangement throws doubt on the validity of the evidence for the accepted formulae for the sterols, bile acids, and related hydrocarbons.

R. S. C.

Constitution and ultra-violet absorption of ethyl diphenylmuconates. A. A. POLICARD (Compt. rend., 1934, 199, 73—75).—The Et $\beta\beta'$ -diphenylmuconates are assigned the following stereochemical structures: isomeride, m.p. 72° (A., 1912, i, 889), is *cis-cis* (I), i.e., both Ph and CO₂Et are in *cis*-positions; isomeride, m.p. 136° (A., 1927, 448), is *trans-trans* (II), and the isomeride, m.p. 174°, is *cis-trans* (III). (I) gives no amide, but the *amide* of (II) has m.p. 220° (decomp.). (II) is hydrolysed to a dibasic acid; (I) gives a lactone. The absorption curve of (II) is displaced towards the ultra-violet relatively to that of (I).

J. L. D.

Synthesis of ψ -opianic acid, and a new general method of synthesising phthalonic acids. S. N. CHAKRAVARTI and M. SWAMINATHAN (Current Sci., 1934, 2, 472—473).—Boiling 5:6-dimethoxyhomophthalic acid (I) with an equimol. amount of SeO₂ in xylene yields the corresponding phthalonic acid (II), which is converted into ψ -opianic acid through its NaHSO₃ compound. Alternatively, (II) is obtained from (I) after treatment with PCl₅. Other homophthalic acids give good yields of the corresponding phthalonic acid with SeO₂.

L. S. T.

Lichen substances. XLIII. Identity of saxatilis acid with salazic acid. Y. ASAHINA and Y. TANASE (Ber., 1934, 67, [B], 1434—1435).—Extraction of the thalli of *Parmelia saxatilis*, Ach., from Japan with Et₂O and then with COMe₂ yields atranorin and saxatilis acid (I) (+H₂O), decomp. 270° after darkening at 240°. (I) is identified as salazic acid, since it yields red crystals, with alkali affords hexaacetylsalazic acid, m.p. 178°, and is reduced (Pd-C) to hyposalazic acid (Me₃ derivative, m.p. 165°).

H. W.

Synthesis of glucosidoferulic acid. R. M. HANN (J. Amer. Chem. Soc., 1934, 56, 1631; cf. A., 1931, 201).— β -Tetra-acetyl-*D*-glucosidovanillin (simplified prep. given; cf. Fischer and Raske, A., 1909, i,

365) and $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ and piperidine give β -tetra-acetyl- δ -glucosidoferulic (3-methoxy-4- β -tetra-acetylglucosidoxycinnamic) acid, m.p. 207° (corr.), $[\alpha]_D^{20}$ -33.9° in CHCl_3 , de-acetylated (N -MeOH-NaOMe in CHCl_3) to β - δ -glucosidoferulic acid ($+\text{H}_2\text{O}$), m.p. 198—199°, m.p. (anhyd.) 227° (corr.; decomp.), $[\alpha]_D^{20}$ -45.4° in $\text{C}_6\text{H}_5\text{N}$ (cf. *loc. cit.*). H. B.

2:6-Dimethylbenzaldehyde. G. LOCK and K. SCHMIDT (J. pr. Chem., 1934, [ii], 40, 229—232).—Acetylmesitylene is oxidised by Noyes' method to 2:6- $\text{C}_6\text{H}_3\text{Me}_2\text{CO}_2\text{H}$ (I), whereby the intermediate formation of 4-iodo-2:6-dimethylbenzoic acid, m.p. 199° (corr.), is observed. (I) and PCl_5 afford 2:6-dimethylbenzoyl chloride, b.p. 217°/752 mm. [2:6-dimethylbenzamide, m.p. 139° (corr.)], reduced (Rosenmund's catalyst and regulator) to 2:6-dimethylbenzaldehyde, b.p. 226—228° (corr.)/741.5 mm., m.p. 11° [semicarbazone, m.p. 158° (corr.)]. H. W.

Synthesis of α -aldehydocarboxylic acids. J. H. GARDNER (J. Indian Chem. Soc., 1934, 11, 401—402).— α - $\text{C}_{10}\text{H}_7\text{OMe}$ and alkaline KMnO_4 give a product which with NH_2Ph gives the NH_2Ph -derivative of phthalonic acid, decomposed in boiling, dry xylene to the NH_2Ph -derivative of phthalaldehydic acid. No OMe-acid is formed. R. S. C.

Colour and structure of [aromatic] oximes. (MME.) RAMART-LUCAS (Bull. Soc. chim., 1934, [v], 1, 719—730).—A more detailed account of work already noted (this vol., 296).

Preparation of the enolic forms of ketones. W. HUCKEL and B. RADZAT (J. pr. Chem., 1934, [ii], 140, 247—250).—Hydrolysis of cyclohexenyl acetate with $\text{H}_2\text{C}_2\text{O}_4$ gives almost exclusively cyclohexanone; the product may contain traces of enol which cannot be determined with certainty by titration with Br.

H. W.

Action of optically active alcohols on ketens. A. MCKENZIE and E. W. CHRISTIE (J.C.S., 1934, 1070—1075).— r -Phenyl- p -tolylacetyl chloride has been obtained cryst., m.p. 74—75°. (—)Menthyl (+)phenyl- p -tolylacetate has m.p. 52—53°, $[\alpha]_D^{20}$ -53.0°, $[\alpha]_{5461}^{20}$ -62.7° in COMe_2 , $[\alpha]_D^{20}$ -43.8°, $[\alpha]_{5461}^{20}$ -51.8° in CS_2 and $[\alpha]_{5461}^{20}$ -67.3°, -79.3° in EtOH . (—)Menthyl (—)phenyl- p -tolylacetate (I), m.p. 57.5—58°, $[\alpha]_D^{21}$ -58.0°, $[\alpha]_{5461}^{21}$ -68.8° in COMe_2 , $[\alpha]_D^{20}$ -51.4°, $[\alpha]_{5461}^{20}$ -60.8° in CS_2 , $[\alpha]_D^{20}$ -69.1°, $[\alpha]_{5461}^{20}$ -82.3° in EtOH , can be distilled, b.p. 210—212°/4 mm., without change in m.p. or $[\alpha]$. (—)Menthyl dl -phenyl- p -tolylacetate (II), obtained by mixing equal amounts of the diastereoisomerides or by esterifying the r -acid with (—)menthol and HCl at 100°, has m.p. 33—34°, $[\alpha]_D^{21}$ -55.5°, $[\alpha]_{5461}^{21}$ -65.8° in COMe_2 . (II) is resolved by repeated crystallisation from $\text{EtOH-H}_2\text{O}$ yielding (I) as the less freely sol. component, this material having been assumed previously to be (II). r -Phenyl- p -tolylglycollic acid, m.p. 133—134°, obtained by the action of p - $\text{C}_6\text{H}_4\text{Me-MgBr}$ on BzCO_2H in Et_2O , is converted by PCl_5 into dl - α -chlorophenyl- p -tolylacetyl chloride, transformed by Zn turnings into phenyl- p -tolylketen (III), which, contrary to Weiss, reacts with (—)menthol in Et_2O to give (II). Similarly, (III) and (—)bornol yield (—)bornyl dl -phenyl- p -tolylacetate, b.p. 235°/12 mm., $[\alpha]_D^{20}$ -25.9°, $[\alpha]_{5461}^{20}$ -30.2° in

COMe_2 . Analogously CMeEt:CO and (—)menthol afford (—)menthyl dl - α -methyl- n -butyrate, b.p. 131—132°/18 mm., $[\alpha]_D^{20}$ -64.4°, $[\alpha]_{5461}^{20}$ -75.6° in C_6H_6 . In every case, therefore, the action of a keten on an optically active alcohol leads to the ester of the dl -acid. dl - α -Bromo- α -methylbutyryl bromide, b.p. 70—71°/17 mm., 96—97°/50 mm., is incidentally described.

H. W.

Action of potassium cyanide on an α -chloro-ketone. G. RICHARD (Compt. rend., 1934, 199, 71—73).— $\text{CH}_2\text{Ph}\cdot\text{COMe}$ with SOCl_2 affords α -chloro- α -phenylacetone, b.p. 122.5—123°/15 mm., which with KCN in Et_2O gives β -cyano- α -phenyl- Δ^a -propylene oxide (cf. this vol., 655), converted by dry HCl in EtOH at 0° into Et β -chloro- α -hydroxy- β -phenyl- α -methylpropionate, m.p. 71—72°, which with KOEt affords β -carbethoxy- α -phenyl- Δ^a -propylene oxide (cf. A., 1906, i, 137).

J. L. D.

Reduction by magnesium + magnesium halide. XIII. Reaction between epoxy-ketones and Grignard reagents. W. E. BACHMANN and F. Y. WISELOGLE (J. Amer. Chem. Soc., 1934, 56, 1559—1560).— p -Diphenyl styryl ketone, prepared by Bergmann and Wolff's method (A., 1932, 616), has m.p. 155—156° (cf. *loc. cit.*); it is oxidised (30% H_2O_2 , 40% KOH , dioxan) to the oxide (I), m.p. 136—137° (cf. *loc. cit.*), which with MgPhBr (II) (1 equiv.) gives p -phenylbenzophenone. (I) and an excess of (II) afford p -phenyltriphenylcarbinol, but no 4:4'-diphenylbenzopinacol (III) (cf. *loc. cit.*). (III) is obtained from (I), (II), Mg powder, and MgBr_2 ; α -benzoyl- β -phenylethylene oxide similarly gives benzpinacol. (III) is not similarly produced from the oxide, m.p. 158—161° (decomp.; previous softening), of p -diphenyl p -methoxystyryl ketone, m.p. 146° (lit. 140°). H. B.

Resolution of benzoin. A. B. CRAWFORD and F. J. WILSON (J.C.S., 1934, 1122—1124).—Acetone- l - δ -menthylsemicarbazone crystallises in rhombic prisms, m.p. 179.5—180°, and prismatic needles, m.p. 128° (cf. A., 1925, i, 318). s - l -Dimethylcarbamyldiazine, m.p. 240°, $[\alpha]_D^{20}$ -83.4° in EtOH , is obtained from l -menthylcarbimide and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. r -Benzoin and l - δ -menthylsemicarbazide give l -benzoin- l - δ -menthylsemicarbazone, m.p. 194—195°, $[\alpha]_D^{15}$ -165.9° in CHCl_3 , hydrolysed to l -benzoin. F. R. S.

Absorption spectra in relation to the constitution of keto-enols. R. A. MORTON, A. HASSAN, and T. C. CALLOWAY (J.C.S., 1934, 883—901).—Benzoylacetone (I) in dil. solution in hydrocarbons exists almost entirely as $\text{COPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{OH}$ and in other solvents this is in equilibrium with appreciable quantities of diketone. The amount of the latter is small in all solvents except H_2O . Chelation through H of the mono-enol, if it occurs at all, must be different in kind from that which obtains with metallic derivatives. The absorption spectrum of the diketone is the same as that of diketonic CHMeBzAc and resembles closely that of CMe_2BzAc (and also COPhMe). Na (and K) benzoylacetone, at the dilutions necessary for spectrographic examination, differ in structure from enol-(I) and are probably $\text{ONa}\cdot\text{CPh}\cdot\text{CHAc}$. In the presence of excess of NaOEt , the chelated compound is formed with a small proportion of a dienolic derivative, probably $\text{ONa}\cdot\text{CPh}\cdot\text{C}\cdot\text{CMe}\cdot\text{ONa}$. The absorption spectra of

metallic derivatives differ appreciably from that of the mono-enol, and on account of the approx. const. character of the absorption of the chelated derivatives, Sugden's singlet linking is supported. Enolic methylbenzoylacetone consists entirely of $\text{OH}\cdot\text{CPh}\cdot\text{CMeAc}$ and is probably unchelated. In presence of NaOEt the chelated Na derivative is formed. Since the enol and enolic (I) possess different structures, but yield spectrographically similar chelated Na derivatives, there is strong evidence in favour of a singlet, rather than a duplet, linking for the residual valency, since this abolishes the distinction between enolisation on Ac and Bz. Dibenzoylmethane exists almost entirely as unchelated $\text{OH}\cdot\text{CPh}\cdot\text{CHBz}$, but in presence of excess of NaOEt the chelated Na derivative is stable. Et benzoylacetate exists as an equilibrium mixture of $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ and $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, the enol being unchelated. In presence of excess of NaOEt , the chelated derivative, $\text{CPh}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ is stable. In keto-enolic tauto-

merides, the same $\lambda\lambda$ of max. absorption reappear frequently, but bands at 280, 310, and 345 $\text{m}\mu$ are much more intense (order 100 times) in the enols than in the ketonic forms. The absorbing entities are chromophores which are complex, i.e., made up of two or more simple chromophores such as $\text{C}\equiv\text{C}$ and $\text{C}=\text{O}$. As the result of the operation of a complex chromophore it is often possible to distinguish 2 or 3 bands and to localise the acts of absorption in the simple constituent chromophores. For instance, of the bands associated with Bz, that near 310–320 $\text{m}\mu$ of low intensity is due to CO and may be written C^*O , whilst that at 280 $\text{m}\mu$ is due to CO influenced by Ph and may be written $\text{Ph}\cdot\text{CO}^*$, and that at 242 $\text{m}\mu$ is due to Ph influenced by CO, Ph^*CO . The electronic energy levels associated with CO and the ethenoid group are approx. the same. The exact specification of the energy levels is not possible from the data of org. compounds in solution.

H. W.

Action of zinc on $\alpha\delta$ -dibromo- $\alpha\delta$ -dibenzoylbutane. Intramolecular Reformatsky reaction. R. C. FUSON and M. W. FARLOW (J. Amer. Chem. Soc., 1934, 56, 1593–1595).— $\alpha\delta$ -Dibromo- $\alpha\delta$ -dibenzoylbutane, Zn dust, and NaI in COMe_2 give (mainly) 5-benzoyl-1-phenyl- Δ^1 -cyclopentene oxide (I), m.p. 169.5–170° (all m.p. are corr.), 5-benzoyl-1-phenyl- Δ^1 -cyclopentene (II), m.p. 99–100° (lit. 98°), $(\text{CH}_2\cdot\text{CH}_2\text{Bz})_2$, and a rearrangement product of (I). Ozonolysis of (I) gives a neutral compound, m.p. 123.5–124° [isomeric with (I)], and $\gamma\gamma$ -dibenzoylbutyric acid, m.p. 117.5–118° [also obtained by ozonolysis of (II) (Et ester, m.p. 95–95.5°, also prepared from $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, CH_2Bz_2 , and $\text{EtOH}\cdot\text{NaOEt}$), which is hydrolysed (15% KOH) to γ -benzoylbutyric acid and BzOH . (I) is also obtained from (II) and BzO_2H in CHCl_3 . A mechanism involving an intramol. Reformatsky reaction is suggested to explain the production of (I) and (II).

H. B.

Heterogeneous catalysis of stereoisomeric change in oximes.—See this vol., 974.

Alkyl ethers of α -hydroxy- $\alpha\beta$ -di-(2:4:6-trimethylbenzoyl)ethylene. R. E. LUTZ (J. Amer. Chem. Soc., 1934, 56, 1590–1593; cf. A., 1925, i, 681;

1927, 58).—*meso*- $\alpha\beta$ -Dibromo- $\alpha\beta$ -di-(2:4:6-trimethylbenzoyl)ethane (I) and boiling $\text{MeOH}\cdot\text{NaOMe}$ give about 30% of the yellow *trans*- (II), m.p. 105.5°, and 55% of the colourless *cis*- (III), m.p. 114–116°, -forms (*loc. cit.*) of α -methoxy- $\alpha\beta$ -di-(2:4:6-trimethylbenzoyl)ethylene; with more dil. $\text{MeOH}\cdot\text{NaOMe}$ at 4–5°, (III) is the main product. (III) is best obtained by exposure of (II) or mixtures of (II) and (III) in EtOH to sunlight. Ozonolysis of (III) affords $s\text{-C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$ and $s\text{-C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{CO}_2\text{Me}$. (II) and (III) are converted into similar equilibrium mixtures by $\text{MeOH}\cdot\text{NaOMe}$. Approx. equal amounts of *cis*- (IV), m.p. 106–107° (corr.), colourless, and *trans*- (V), m.p. 129° (corr.), yellow, - α -ethoxy- $\alpha\beta$ -di-(2:4:6-trimethylbenzoyl)ethylenes are similarly obtained from (I) and $\text{EtOH}\cdot\text{NaOEt}$ at 50°; at 4–5°, (IV) predominates. (IV) is also best obtained by exposure of (V)+(IV) in EtOH to sunlight. (IV) and (V) are equilibrated by $\text{EtOH}\cdot\text{NaOEt}$; with $\text{MeOH}\cdot\text{NaOMe}$ new products appear to be formed. (V) is also obtained from (II) (?) and NaOAc in EtOH . (I) and $\text{MeOH}\cdot\text{NH}_3$ give α -amino- $\alpha\beta$ -di-(2:4:6-trimethylbenzoyl)ethylene, m.p. 133° (corr.), also prepared similarly from (III); it is reduced (Zn dust, AcOH) to $\alpha\beta$ -di-(2:4:6-trimethylbenzoyl)ethane and is hydrolysed ($\text{EtOH}\cdot\text{NaOH}$) slowly to (VI) (below). (I) and NaOH in 80% MeOH afford α -hydroxy- $\alpha\beta$ -di-(2:4:6-trimethylbenzoyl)ethylene (VI) (cf. *loc. cit.*) [Na salt, m.p. 308–310°, also obtained by prolonged hydrolysis ($\text{EtOH}\cdot\text{NaOH}$) of (II)–(V)], which is methylated (CH_2N_2) and ethylated (CHMeN_2) to (II) and (V), respectively. (VI) is unaffected by sunlight or $\text{EtOH}\cdot\text{NH}_3$.

H. B.

Interaction of toluquinone and benzaldehyde under the influence of light. A. ANGELETTI (Gazzetta, 1934, 64, 346–350).—Insolation of toluquinone and PhCHO in C_6H_6 yields *toluquinol dibenzoate*, m.p. 119–120° (also synthesised), and phenolic products.

R. K. C.

Quinones. II. Preparation of thymoquinone by hydrolysis of nitrosothymol. C. L. TSENG, M. HU, and E. J. H. CHU (J. Chinese Chem. Soc., 1934, 2, 136–152; cf. this vol., 776).—Nitrosothymol (I) is hydrolysed by refluxing for 30 hr. with H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, or (best) 8% aq. HCl , the quinone being removed from the acid immediately after formation. This is claimed to be the first case of the hydrolysis of a nitrosophenol to a true quinone. Treatment of (I) by Lapworth's procedure (J.C.S., 1907, 91, 1134) led to a yellow substance, m.p. 98–100°.

H. N. R.

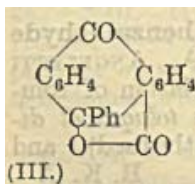
Tautomerism of aminonaphthaquinones. L. F. FIESER and M. FIESER (J. Amer. Chem. Soc., 1934, 56, 1565–1578).—Reduction (cold alkaline $\text{Na}_2\text{S}_2\text{O}_4$) of 2-amino-1:4-naphthaquinone-1-oxime gives 3:4-diamino- α -naphthol (I) [Ac_3 derivative, m.p. 270–275° (decomp.)], oxidised (FeCl_3) to 2-amino-1:4-naphthaquinone (II). 2-Amino-1:4-naphthaquinone-4-imine (III) [Ac_2 derivative (IV), m.p. 189°] is conveniently prepared by reduction ($\text{Na}_2\text{S}_2\text{O}_4$) of Martius yellow and subsequent oxidation (FeCl_3 , dil. HCl) of the intermediate 2:4-diamino- α -naphthol (V) [2:4- Ac_2 derivative (VI), m.p. 225° (decomp.)], prepared by acetylation (Ac_2O) of (V) in H_2O . Oxidation (FeCl_3 , dil. HCl , AcOH) of (VI) gives 2-acetamido-1:4-naphtha-

quinone, m.p. 204°, hydrolysed (conc. H_2SO_4) to (II). (IV) is hydrolysed (aq. EtOH-NaOH) to 4-amino-1:2-naphthaquinone (VII). (III) (as hydrochloride), $\text{NH}_2\text{OH}\cdot\text{HCl}$, and NaOAc afford 2-amino-1:4-naphthaquinone-4-oxime, reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to (V). 1:2:4-Triaminonaphthalene (VIII) (dihydrochloride) is prepared by reduction (SnCl_2 , conc. HCl) of 2:4-dinitro- α -naphthylamine.

The oxidation-reduction potentials of the systems from the following reductants are determined at 25° using the method previously described (A., 1931, 172): 1:4- and 1:2- $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, 1:2-aminonaphthol-4-sulphonic acid, 1:4- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$, (I), (VIII), β -naphthaquinol (cf. *ibid.*, 489), and 2-hydroxy-1:4-naphthaquinone (cf. *loc. cit.*). Measurements with (II), (VII), (V), and the system 1:4-diamino- β -naphthol-4-amino-1:2-naphthaquinone-1-imine indicate that when an aminoquinone can exist in two tautomeric forms the one with the lower potential predominates in the equilibrium mixture. (VII) exists as the aminoquinone at $p_{\text{H}} < 11$; the hydroxyquinoneimine is formed at $p_{\text{H}} 11-13$. The relationship between structure and potential is discussed.

H. B.

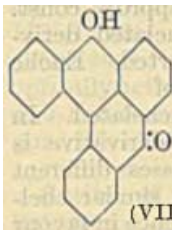
Tautomerism of anthraquinone-1-carboxyl chloride and synthesis of ring systems of the cœranthrene series. III. R. SCHOLL and J. DONAT [with W. MESSE, F. RENNER, and I. JULIUS]. IV. Tautomerism of 4-methyl- and 2-bromo-anthraquinone-1-carboxyl chloride. R. SCHOLL, A. KELLER, K. MEYER, and H. PENZ [with J. DONAT] (Annalen, 1934, 512, 1-29, 30-38).—III. Application of the Friedel-Crafts reaction to anthraquinone-



1-carboxyl chloride (I) and C_6H_5 gives Ph 1-anthraquinonyl ketone (II) and 9-hydroxy-9-phenyl-10-anthrone-1-carboxylolactone (III), m.p. 166-166.5°. In general, the ratio (II):(III) depends on the catalyst (AlCl_3 or FeCl_3), solvent, and temp. AlCl_3 at low temp. favours (III), whereas FeCl_3 at high temp. favours (II). For preparative purposes FeCl_3 at high temp. is generally preferable. (III) is reduced by SnCl_2 and HCl in boiling AcOH to 9-phenyl-10-anthrone-1-carboxylic acid (IV), m.p. 246-248°, oxidised by CrO_3 in AcOH to (III), and is converted by KOH-MeOH and subsequently by Zn dust into 9-phenylanthracene-1-carboxylic acid (V), m.p. 275-276° after darkening at 230° when rapidly heated (*Ag* salt, converted by *EtI* into the *Et* ester, m.p. 138-139°, hydrolysed with unusual difficulty). (I), PhMe , and AlCl_3 yield 9-p-tolyl-10-anthrone-1-carboxylic acid, m.p. 198°. 9-Hydroxy-9-p-chlorophenyl-10-anthrone-1-carboxylolactone (VI), m.p. 177°, is transformed by boiling KOH-EtOH into 9-hydroxy-9-p-chlorophenyl-10-anthrone-1-carboxylic acid, m.p. 199°, with re-formation of (VI). (I), PhBr , and AlCl_3 afford p-bromophenyl 1-anthraquinonyl ketone, m.p. 236°, with only traces of the lactone; 5'-bromo-9-p-bromophenyl-9:10-dihydrocœranthra-10:7'-dione, m.p. 280°, is isolated as coloured by-product. (I), PhOMe , and AlCl_3 in CS_2 yield p-anisyl 1-anthraquinonyl ketone and 9-hydroxy-9-p-anisyl-10-oxanthrone-1-carboxylolactone, m.p. 183-184°, hydrolysed and reduced to 9-p-anisylanthracene-1-carboxylic acid, m.p.

250° (decomp.) when rapidly heated. (IV) is transformed by conc. H_2SO_4 into cœranthr-7'-one-10-ol [1:9-benzoylene-anthr-10-ol] (VII) (*Ac* derivative, m.p. 232-233°). When treated similarly (V) gives cœranthr-7'-one, m.p. 178-179°, oxidised by CrO_3 in boiling AcOH to 9-hydroxy-9:10-dihydrocœranthra-10:7'-dione, m.p. 237-239°. (IV) and PCl_5 at 110-120° give 10-chlorocœranthr-7'-one [10-chloro-1:9-benzoyleneanthracene], m.p. 209-210°, also obtained by the successive action of POCl_3 in H_3PO_4 and PCl_5 on triphenylmethane-2:2'-dicarboxylic acid (VII), m.p. 217-219° [2-methylbenzophenone-2'-carboxylic acid is transformed by successive treatment with SOCl_2 and then with C_6H_6 and AlCl_3 into phenyl-o-tolylphthalide, m.p. 119-121°, converted by Na-Hg in EtOH into 2-methyltriphenylmethane-2'-carboxylic acid, m.p. 197-198.5°, whence (VII)]. (III) and PCl_5 at 110-120° give 9:10:10':7:7'-pentachloro-9:10-dihydrocœranthrone, m.p. 277-279° (decomp.), which with AcOH and H_2SO_4 affords 10:1'-dichlorocœranthrone, m.p. 278-280°. Benzophenone-2:2'-dicarboxylolactone is converted by MgPhBr into 2-benzoylbenzophenone-2'-carboxylic acid, m.p. 222-224°, transformed by $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ at 100° into 9-hydroxy-9-phenylanthr-10-one-2-carboxylolactone (VIII), m.p. 232-234°. Oxidation of (VII) with CrO_3 in AcOH leads to triphenylcarbinol-2:2'-dicarboxylolactone, m.p. 238-241°, converted by $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$ at 80-90° into (VIII). Anthraquinone-1-carboxylic acid is reduced by Zn dust and aq. NH_3 or NaOH to 9:10-dihydroanthracene-1-carboxylic acid, m.p. 205-206°, transformed by MgPhBr in $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$ into diphenyl-9:10-dihydro-1-anthrylcarbinol (IX), m.p. 163.5-165°, reduced by Zn dust and AcOH to diphenyl-9:10-dihydro-1-anthrylmethane, m.p. 131-132°, which is dehydrogenated by red-hot Cu to diphenyl-1-anthrylmethane (X). Oxidation of (IX) with CrO_3 in AcOH affords diphenyl-1-anthraquinonylcarbinol, m.p. 198-199°, reduced by short treatment with Zn dust and AcOH to diphenyl-1-anthraquinonylmethane (XI), m.p. 224-225°, also obtained by oxidation of (X). (XI) and conc. H_2SO_4 at 0° yield 10-phenylcœranthr-7'-one [10-phenyl-1:9-benzoylanthracene], m.p. 179-181°, transformed by CrO_3 in dil. AcOH into 9:10-dihydroxy-10-phenyl-9:10-dihydrocœranthr-7'-one.

IV. 1:4-Dimethylantraquinone in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ is oxidised by MnO_2 to 1-methylantraquinone-4-carboxylic acid, m.p. 230-231°, reduced by $\text{Zn-NH}_3\text{-H}_2\text{O}$ to 1-methylanthr-4-carboxylic acid (I), m.p. 209°. The chloride (II) of (I) is transformed by C_6H_6 and sublimed FeCl_3 into 10-hydroxy-10-phenyl-1-methylanthr-9-one-4-carboxylolactone (III), m.p. 177-178°, with very small amounts of 4-benzoyl-1-methylantraquinone. Treatment of (III) with KOH-MeOH followed by oxidation with KMnO_4 leads to 9-hydroxy-9-phenylanthr-10-one-1:4-dicarboxylic acid, m.p. 166-167°, which does not yield its lactone when treated with boiling AcOH . 4-m-Xyloyl-1-methylantraquinone, m.p. 149-150°, and 10-hydroxy-10-m-xylyl-1-methylanthr-9-one-4-carboxylic acid, m.p. 155.5-156°, are derived from (II), m-xylene, and FeCl_3 . Hydroxy-10-p-chlorophenyl-1-methylanthr-9-one-4-car-



oxylactone, m.p. 145—146°, and very little ketone are derived from PhCl and (II), which, with PhOMe and FeCl₃, affords mainly 10-hydroxy-10-p-anisyl-1-methylanthr-9-one-4-carboxylactone, m.p. 188.5—189.5°, with a small amount of 4-p-anisoyl-1-methylanthraquinone.

2-o-Toluoylbenzophenone-2'-carboxylic acid, m.p. 191—193°, is transformed by H₂SO₄-H₂O at 80—90° into 10-hydroxy-10-phenyl-1-methylanthr-9-one-2'-carboxylactone, m.p. 216—217°, hydrolysed and then oxidised to 10-hydroxy-10-phenylanthr-9-one-1:2'-dicarboxylactone, m.p. 236—237°, which is reduced by Zn dust and NaOH to 10-phenylanthracene-1:2-dicarboxylic acid, m.p. 264—266°. 2-Bromoanthraquinone-1-carboxyl chloride, m.p. 225—226°, C₆H₆, and FeCl₃ yield 2-bromo-1-benzoylanthraquinone, m.p. 268—269°, and 2-bromo-9-hydroxy-9-phenylanthr-10-one-1-carboxylactone, m.p. 210°. 2-Bromo-1-p-toluoylanthraquinone, m.p. 214—215°, 2-bromo-9-hydroxy-9-p-tolylanthr-10-one-1-carboxylactone, m.p. 189°, and 2-bromo-1-m-xyloylanthraquinone, m.p. 239°, are described.

H. W.

Chrysanthine and chrysanthene, crystalline neutral principles from *Chrysanthemum cinerariifolium*. Bocc. T. Q. CHOU and J. H. CHU (Chinese J. Physiol., 1934, 8, 167—170).—Extraction of Chinese pyrethrum flowers with C₆H₆ and treatment of the extract with Et₂O yields *chrysanthine*, C₁₀H₁₃O₃, m.p. 200°, [α]_D²⁰ -30° in CHCl₃, lethal to rabbits when injected in doses of approx. 50 mg. per kg., and *chrysanthene*, C₁₈H₃₅O, m.p. 80°, [α] 0°.

F. O. H.

Chemical and physiological properties of kojic acid. T. E. FRIEDEMANN (Science, 1934, 80, 34—35).—Kojic acid has a marked toxic action on dogs, rabbits, and rats. It forms a coloured Fe complex even at dilutions of 1—400,000, which cannot be reversibly oxidised or reduced. It is not oxidised by I in acid solution, but absorbs 4 equivs. of I at p_H 6—7.

L. S. T.

Saponins and sapogenins. II. Products of selenium dehydrogenation of echinocystic acid. C. R. NOLLER (J. Amer. Chem. Soc., 1934, 56, 1582—1583).—Dehydrogenation (Se at 310—345°) of echinocystic acid gives 1:2:3:4-C₆H₂Me₄, 2:7-C₁₀H₆Me₂, 1:2:7-C₁₀H₆Me₃, 1:2:7-C₁₀H₄Me₃-OH, 1:2:5:6-C₁₀H₄Me₄, a hydrocarbon C₂₅H₂₀ [all foregoing are similarly obtained from sumaresinolic acid (Ruzicka *et al.*, this vol., 530)], and a hydrocarbon, C₂₆H₂₈₍₃₀₎, m.p. 166—167° [picrate, m.p. 209—210° (decomp.)].

H. B.

Constituents of santonin-free wormseeds. II. H. NAKAMURA and T. OHTA (Proc. Imp. Acad. Tokyo, 1934, 10, 215—217).—*Dihydroisotemisin* (I), C₁₅H₂₂O₃·H₂O, m.p. 86° (anhyd., m.p. 70—73°), [α]_D¹⁸ -24.4° in CHCl₃ (acetate, m.p. 133°), has been obtained in a yield of approx. 0.02% from the mother-liquors from the isolation of temisin (cf. A., 1933, 651). (I) is hydrogenated by Pt-H₂ to *tetrahydroisotemisin*, C₁₅H₂₄O₃·H₂O, m.p. 90—91° (anhyd.), [α]_D¹⁸ -24.88° in CHCl₃ (acetate, m.p. 140°), which is dehydrogenated by Se to 1:7-C₁₀H₆MeEt, b.p. 120—130°/10 mm. (picrate, m.p. 95°).

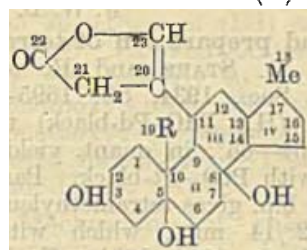
S. C.

Pterosantalin, a crystalline dye from red sandalwood. H. LEONHARDT and W. BUSCKE

(Ber., 1934, 67, [B], 1403—1404).—Coarsely powdered sandalwood is extracted with Et₂O, the extract is conc., and the crystals which separate are treated with cold COMe₂, whereby *pterosantalin*, decomp. about 318° after darkening, is obtained. The hydrochloride, picrate, Ac and Bz derivatives have been obtained.

H. W.

Constitution of strophanthidin. G. A. R. KON (Chem. and Ind., 1934, 593—595).—Jacob and Elderfield's formula (A) (A., 1933, 1165) for strophanthidin (I) and periplogenin (II) do not account for (i) the formation of the same methylcyclopentanophenanthrene from each, or (ii) the formation of undephanthiontriacid Me₂ ester.



The annexed formula [R=CHO in (I); R=Me in (II)] is logically developed; it has all the advantages of (A), explains reactions (i) and (ii), but fails to account for the formation of trianhydrostrophanthidin. Other possible positions of the substituents are shown to be less satisfactory.

R. S. C.

Action of sodium on bornyl chloride and on some halogenated derivatives of cineole. A. GANDINI (Gazzetta, 1934, 64, 302—314).—The product of interaction of Na and bornyl chloride yields dicamphane and a fraction, b.p. 150—160° (cf. A., 1880, 669; 1898, i, 443), containing camphane, camphene, and bornylene. 2-Chloro-, 3-chloro-, and 2:3-dichloro-cineole react with Na to give eucalyptene (Δ²-cineolene), α-terpineol, and cineole.

R. K. C.

Catalytic dehydration of borneol by thoria. G. BRUS and V. BRUSTIER (Bull. Inst. Pin, 1934, 99—100).—Passage of borneol in N₂ over ThO₂ at 350° gives camphene (70%), tricyclene (a little), dipentene (15%), terpinolene (5%), and cracking products, including cymene (10%).

R. S. C.

Transformation of *d*-camphor into *l*-camphor. Y. ASAHINA, M. ISHIDATE, and T. MOMOSE (Ber., 1934, 67, [B], 1432—1433).—Oxidation of *l*-epi-camphor with SeO₂ in Ac₂O at 140—150° affords 2:3-diketocamphane, m.p. 198°, [α]_D²⁵ -101.1° in EtOH. Similarly, *d*-epi-camphor (I) gives 5:6-diketocamphane (II), m.p. 198°, [α]_D²⁵ +100.1° in abs. EtOH [monosemicarbazone, m.p. 228—229° (decomp.)]. Reduction of (II) with Zn and AcOH followed by treatment of the product with MeOH-HCl leads to 5-keto-6-methoxycamphane, m.p. 150° [hydrolysed by conc. HCl to 5-keto-6-hydroxycamphane (III), m.p. 214°, [α]_D²⁵ -10.2° in abs. EtOH], and 6-keto-5-hydroxycamphane (IV), m.p. 192—195°, [α]_D²⁵ -13.8° in EtOH. Reduction of (IV) by Na-Hg leads to *l*-camphor, m.p. 176°, [α]_D²⁵ -41.4° in EtOH (semicarbazone, m.p. 237—238°), whilst reduction of (III) gives (I).

H. W.

Synthesis of myrtenol and myrtenal. G. DUPONT, W. ZACHAREWICZ, and R. DULOU (Bull. Inst. Pin, 1934, 101—102).—Pinene and SeO₂ in hot EtOH give *d*-myrtenol and *d*-myrtenal (cf. A., 1932, 1253).

R. S. C.

Preparation of terpene ketones. R. DULOU (Bull. Inst. Pin, 1934, 49—63, 95—98).—Methods described in the lit. are classified. R. S. C.

Derivatives of normeconin. R. ROBINSON and H. R. L. STREIGHT (J.C.S., 1934, 1130—1131).—Bromomeconin is converted (81% yield) by heating with HBr (*d* 1.5) and AcOH-Ac₂O, at 90°, into *bromonormeconin*, m.p. 203—209° (*Ac.*, m.p. 152°, and *Bz.*, m.p. 104—105°, derivatives), converted by CPh₃Cl₂-C₆H₅N into *6-bromo-O-3:4-diphenylmethylenenor-meconin*, m.p. 160°. J. W. B.

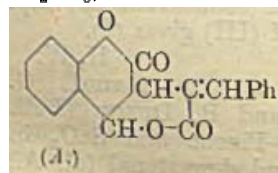
Reduction of furan and preparation of tetramethylene derivatives. D. STARR and R. M. HIXON (J. Amer. Chem. Soc., 1934, 56, 1595—1596).—Furan is reduced (H₂, PdO-Pd-black) to tetrahydrofuran (I), b.p. 64—66°, in quant. yield; reduction does not occur with PtO₂-Pt-black. Passage of HCl into (I) at the b.p. gives tetramethylene chlorohydrin, b.p. 81—82°/14 mm., which with PBr₃ (method: Cloke *et al.*, A., 1931, 1031) affords *tetramethylene chlorobromide*, b.p. 175—176°. This is converted (method: Allen, A., 1928, 624) into *δ-chlorovaleronitrile*, b.p. 101—102°/16—17 mm. H. B.

Production of furfuraldehyde from concentrated solutions of xylose. R. L. FOSTER (Iowa State Coll. J. Sci., 1933, 8, 191—196).—Furfuraldehyde was produced by the action of various acids and salts on conc. aq. xylose and removing it with C₆H₆, CCl₄, or PhMe. Yields (max. 37 g. from 100 g.) for various conditions were determined. CH. ABS.

New route from the sugar to the furan series. E. VOTOČEK and S. MALACHTA (Coll. Czech. Chem. Comm., 1934, 6, 241—250; cf. A., 1929, 1166).—*δ*-Ketogluconic acid in boiling MeOH containing 35% HCl affords *Me aldehydopyromucate*, m.p. 93°, hydrolysed rapidly by warm Ba(OH)₂ to the acid (cf. A., 1894, i, 442) (*K* and *Ba* salts), which with Ba(OH)₂ in boiling H₂O affords dehydromucic and hydroxymethylpyromucic acid. J. L. D.

Pyrone problem. L. LORENZ [with H. STERNITZKE] (Z. Elektrochem., 1934, 40, 501).—The constitutional formula is discussed. E. S. H.

Reactivity of the methylene group in coumarin-3-acetic acids. Condensation with aromatic aldehydes. B. B. DEY and Y. SANKARANARAYANAN (J. Indian Chem. Soc., 1934, 11, 381—387).—Coumarin-3-acetic acid (I) condenses with aldehydes by Perkin's, but not by Knoevenagel's, reaction. This degree of reactivity, < that of coumarin-4-acetic (II), and the non-reactivity of 4-methylcoumarin-3-acetic acid are explained by electronic considerations. The condensation products may exist as lactones, *e.g.*, A, since they are insol. in Na₂CO₃, but sol. in NaOH, and can be titrated with



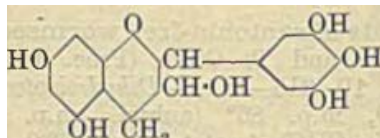
o-quinone formation. The following derivatives of

Ba(OH)₂, but could not be esterified; the salts may be formed by opening of either O-ring; colour changes with excess of alkali, similar to those of the products from (II), are explained by

(I) are prepared: *benzylidene*-, m.p. 262°; *p*-*acetoxy*-, m.p. 244° (decomp.), and thence *p*-*hydroxy*-, m.p. 272° (decomp.), *m*-*acetoxy*-, m.p. 188°, *m*-*hydroxy*-, m.p. 242°, *4*-*acetoxy-3-methoxy*-, m.p. 207°, *4*-*hydroxy-3-methoxy*-, m.p. 211°, *p*-*methoxy*-, m.p. 225°, and *3:4-methylenedioxy-benzylidene*-, m.p. 270°. As by-products are formed a little *p*-, m.p. 165°, and *m*-*acetoxyphenyl-3-coumarylethylene*, m.p. 140°, hydrolysed to the corresponding OH-compounds, m.p. 272° and 193°, respectively. Similar condensations yield *7*-*acetoxy-4-methyl-3-coumaryl-3'-coumarin*, m.p. 268°, *7:7'-diacetoxy-4-methyl-3:3'-dicoumarin*, m.p. 220°, *7*-*acetoxy-4-methyl-3-coumaryl-3'-β-α-1:2-naphthapyrone*, m.p. 272°, *β-α-naphtha-3-coumarylphenylacrylic acid*, m.p. 253°, and *3:3'-di-β-α-naphthapyrone*, m.p. 345°. R. S. C.

Action of alkali on 4-methyl-β-α-5:6-naphthapyrone and its 3-chloro- and -bromo-derivatives. Formation of *cis*- and *trans*-hydroxynaphthylcrotonic acids and a naphthylpropaldehyde derivative. B. B. DEY and A. K. LAKSHMINARAYANAN (J. Indian Chem. Soc., 1934, 11, 373—380).—4-Methyl-β-α-5:6-naphthapyrone (I) and red HgO in boiling aq. NaOH give (?) *trans-2-hydroxy-1-naphthylcrotonic acid* (II), which at the m.p. (112°) regenerates (I) as readily as the (?) *cis*-isomeride (III), m.p. 146° (J.C.S., 1915, 107, 1630). (II) in dry CHCl₃ in ultra-violet light, however, gives (I) under conditions which do not affect (III), the change probably occurring by way of an activated form of (III). The 3-Cl-derivative of (I) with hot 2*N*-NaOH gives the chlorocoumarinic acid, but with hot 20% KOH gives also much *4-methyl-β-α-2:3-naphthafuran-5-carboxylic acid* (IV), m.p. 240° (*Et* ester, m.p. 100°). The 3-Br-derivative, m.p. 145°, however, with hot 2*N*-NaOH gives a little (IV) and much *2-hydroxynaphthyl-1-α-propaldehyde*, m.p. 136° (*Ac* derivative, m.p. 117°; *oxime*, m.p. 182°; *phenylhydrazone*, m.p. 144°; *semicarbazone*, m.p. 186°), which with Ag₂O yields the corresponding *acid*, m.p. 156°, and with HCl-EtOH forms *4-methyl-β-α-naphthafuran*, m.p. 57°. R. S. C.

Isolation of a new catechin, tea catechin II or gallo-catechin, from green tea. M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 149—154).—*Tea catechin II* or *gallo-catechin* (annexed formula), m.p. 218°, [α]_D²⁰ -67.5° (*diacetate*, m.p. 189—190°, hydrolysed to phloroglucinol with KOH; *Me*₅ ether, m.p. 183°, oxidised by KMnO₄



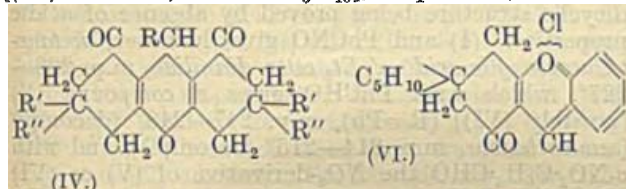
to trimethylgallic acid), has been isolated in a yield of 0.25% from Shizuoka green tea. It gives a violet colour with FeCl₃, whereas tea catechin I gives a green colour. S. C.

Caricaxanthin, a colouring matter in the fruit pulp of *Carica papaya* and *Citrus poonensis*. II. R. YAMAMOTO and Y. KATO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 41).—Caricaxanthin, C₄₀H₅₆O (this vol., 121), contains 1 MeOH, which is lost at

100°/0.01 mm. It has one active H, has $[\alpha]_D^{20}$ 0°, and shows max. absorption at 515, 483, 453 m μ . It has also been isolated from the peel of *Citrus poonensis* and fruit pulp of *C. tankan*. 20–30 $\times 10^{-6}$ g. per diem maintains the growth of albino rats.

S. C.

Dihydroresorcinols. III. Condensation of aldehydes with cyclohexanespirocyclohexane-3:5-dione. R. D. DESAI (J. Univ. Bombay, 1933, 2, No. 2, 62–67; cf. this vol., 530).—So far as the condensation of PhCHO and salicylaldehyde is concerned, *cyclohexanespirocyclohexane-3:5-dione* (I) behaves similarly to dimethyldihydroresorcinol. Condensation of the corresponding aldehyde with (I) in presence of piperidine gives *benzylidene-*, m.p. 132–133° (II), and *salicylidene-biscyclohexanespirocyclohexane-3:5-dione*, m.p. 185° (III), [Ac derivative, m.p. 190°, from *o*-OAc-C₆H₄·CHO; converted by Ac₂O or AcOH into (V) below]. On dehydration with Ac₂O or AcOH methylenebiscyclohexanespirocyclohexane-3:5-dione, (II), and (III) yield, respectively, 1:8-diketo-3:6-bispirocyclohexanooctahydroxanthene [(IV): R=H, R'R''=C₅H₁₀], m.p. 215°, and its



9-Ph [(IV) R=Ph], m.p. 188–189°, and 9-salicyl derivative, m.p. 193–194° [Ac derivative (V), m.p. 183–184°]. Condensation of *o*-OH·C₆H₄·CHO with (I) in presence of HCl, however, yields scarlet 4-keto-2-spirocyclohexanetetrahydrobenzopyrylium chloride (VI), m.p. >300°, which resists hydrolysis by KOH·EtOH, giving only the corresponding base, m.p. >300°.

H. N. R.

Dimorphism of rotenone. R. S. CAHN (J.C.S., 1934, 1129).—The high-melting form (I), m.p. 183°, of rotenone is obtained when the form (II), m.p. 164°, is pressed on porous tile, is kept for a few min. at 170–175°, or when the solvate (from CCl₄) is heated at 100°/H₂O-pump. vac. Reconversion of (I) into (II) occurs slowly on keeping or on recrystallisation.

Rotenone. XXIX. Isomerism of the rotenolones. F B LA FORGE and H. L. HALLER (J. Amer. Chem. Soc., 1934, 56, 1620–1625).—Deguelin is oxidised (30% H₂O₂ in 5% MeOH-KOH) to *hydroxydeguelin-C* (I), m.p. 203°, which, unlike the isomeric tephrosin, is not dehydrated by EtOH-H₂SO₄ or Ac₂O-NaOAc. *iso*Rotenone (II) is similarly oxidised to *isorotenolone-C* (III), m.p. 212° (Ac derivative, m.p. 145–146°; Me ether, m.p. 160–161°), and a little *isorotenolone-D* (IV), m.p. 188–189 (Me ether, m.p. 190–191°). (III) and (IV) are stable to mineral acids. (II) and I in EtOH-KOAc give *isorotenolone-I* (V), m.p. 203–204° [Me ether (VI), m.p. 153], whilst atm. oxidation of (II) in EtOH-KOH affords *isorotenolone-II* (VII), m.p. 193–194° [Me ether (VIII), m.p. 133–134°]. (V) and (VII) are dehydrated (EtOH-H₂SO₄) to *isodehydrorotenone* (IX). (III), (IV), (V), and (VII) (and their Me ethers) are all

reduced (Zn dust, aq. EtOH-KOH) to *isoderritol* and *isorotenol*. Short treatment of (VI) or (VIII) with MeOH-H₂SO₄ gives (IX) and (VI); more prolonged treatment affords (IX). *Methylrotenolone-I* (X), m.p. 174–175°, and *methylrotenolone-II* (XI), m.p. 148–149°, are prepared by methylation (MeI, Ag₂O) of rotenolone-I and -II (Takei et al., A., 1933, 512), respectively; use of MeOH-HCl leads to (X) in both cases. Short treatment of (X) and (XI) with MeOH-H₂SO₄ gives (X) and dehydrorotenone (the sole product on more prolonged treatment); the Me ethers of (III) and (IV) are similarly unaffected. (X) and (XI) are both reduced (Zn dust, aq. EtOH-KOH) to *derritol* and *rotenol*; 2:2'-dimethoxybenzoin Me ether similarly gives 2:2'-dimethoxydeoxybenzoin. Possible structures are suggested for rotenolone-I and -II and *isorotenolone-I* and -II.

H. B.

Mechanism of sulphur oxidation. J. C. ANDREWS and K. C. ANDREWS (Amer. J. Med. Sci., 1934, 187, 146).—Cysteic acid hydantoin and phenylhydantoin are very unstable, neutralisation with dil. alkali at room temp. affording inorg. sulphate (10% and 15% of the S, respectively). Other evidence points to two simultaneous methods of decomp., one involving loss of H₂SO₄ and the other fission of the hydantoin ring, the S remaining stable as a sulphonic acid.

CH. ABS.

Compounds of pyridine with tervalent iodine. O. J. MAGIDSON and J. B. LOSSIK (Ber., 1934, 67, [B], 1329–1331).—2-Chloropyridine-5-iododichloride, m.p. 107° (decomp.), obtained by the action of Cl₂ on 2-chloro-5-iodopyridine in CHCl₃, is transformed by cold Na₂CO₃ into 2-chloro-5-iodosopyridine, m.p. >200° (decomp.). 2-Aminopyridine-5-iododichloride, m.p. 133° (decomp.), is converted by 10% Na₂CO₃ into a dark resin. *p*-C₆H₄I·NH₂ does not yield a dichloride. 2-Acetamidopyridine-5-iododichloride, decomp. 220° after altering at 170°, is relatively very stable. 5-Iodoso-2-acetamidopyridine has m.p. 155°. 2-Methoxypyridine-5-iododichloride, m.p. 119° (decomp.), readily loses Cl.

H. W.

3-Aminopyridine. I. Bromination, sulphonation, and methylation. E. PLÁZEK and A. MARCINKÓW (Rocz. Chem., 1934, 14, 326–334).—3-Aminopyridine (I) affords 2:6-di-, m.p. 142°, and 2:4:6-tri-bromo-3-aminopyridine, m.p. 115°, with respectively 2 and 3 parts of Br in MeOH; the Br₁- and Br₂-derivatives are not obtained by direct bromination. 3-Aminopyridine-2(6?)-sulphonic acid (II), m.p. 283–285°, is obtained from ClSO₃H and (I), but not by direct sulphonation with H₂SO₄. (II) yields the internal *diazonium* salt, exploding on heating, on diazotisation with C₅H₁₁·O·NO, and the salt is converted into *pyridine-2-sulphonic acid*, m.p. 240°, by heating with HCO₂H and Cu. 3-Dimethylaminopyridine, b.p. 105–106°/12 mm. (picrate, m.p. 178–180°; picrolonate, m.p. 225–226°; methiodide, m.p. 161–162°), is prepared by passing MeOH and (I) vapours over Al₂O₃ at 380–420°.

R. T.

γ -Dimethylamino- α -3-pyridylpropyl benzoate. J. M. SNELL and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 1612–1614).—3-Acetylpyridine,

NHMe₂, HCl, and paraformaldehyde in EtOH give the unstable 3-pyridyl β-dimethylaminoethyl ketone (*dihydrochloride*, m.p. 178.5—180°); the *hydrochloride*, m.p. 163.5—164°, is reduced (H₂, Pt-black, H₂O) to γ-dimethylamino-α-3-pyridylpropyl alcohol, b.p. 140—143°/3 mm. [*dihydrochloride*, m.p. 148—149°; *benzoate hydrochloride* (I), dimorphous, m.p. 151.5—152.5° and 162.5—163° (stable)]. (I) is an effective local anæsthetic.

H. B.

Substituted amides of pyridinecarboxylic acids. E. GRYSZKIEWICZ-TRUCHIMOWSKI (Rocz. Chem., 1934, 14, 335—338).—The 2'-pyridyl-, m.p. 138—139°, α-2'-camphoryl-, m.p. 144—145°, and α-2'-bornylethyl-, m.p. 89—90°, -amide of nicotinic acid, and the *bisdiethylamide*, m.p. 122—123°, of *isocinchomeronic acid*, are prepared from the appropriate acid chloride and amine in Et₂O solution in presence of C₆H₅N.

R. T.

Nicotinylthiocarbimide and its derivatives. I. B. DOUGLASS and L. E. FORMAN (J. Amer. Chem. Soc., 1934, 56, 1609).—Nicotinyl chloride and NH₄NCS in PhMe give *nicotinylthiocarbimide*, b.p. 121°/12 mm., which with the appropriate amine in COMe₂ affords *N-phenyl-*, m.p. 154—155°, *N-o-*, m.p. 160—161°, *-m-*, m.p. 149—150°, and *-p-*, m.p. 174—175°, *-tolyl-*, *N-α-*, m.p. 171—172°, and *-β-*, m.p. 193—194°, *-naphthyl-*, *N-phenyl-N-methyl-*, m.p. 156—157°, *N-phenyl-N-ethyl-*, m.p. 123—124°, *NN-diphenyl-*, m.p. 162—163°, and *N-phenyl-N-benzyl-*, m.p. 150—151°, *-N'-nicotinylthiocarbimide*. *Nicotinylthiocarbamide* has m.p. 209—210°.

H. B.

Complex additive compounds of copper nitrate and sulphate with quinoline. J. V. DUBSKY and J. TRTILEK (J. pr. Chem., 1934, [ii], 140, 185—192).—The following compounds are prepared [A = Cu(NO₃)₂; B = CuSO₄; Q = quinoline]: 2A, 3Q, H₂O, decomp. 245—250°; 2A, 3Q, 5H₂O, decomp. 250°; A, 2Q, m.p. 254°; A, 2Q, 2H₂O, decomp. 220°; A, 3Q, m.p. 180°; A, 3Q, H₂O, m.p. 175—177°; A, 4Q, m.p. 170°; A, 4Q, H₂O, m.p. 168°; B, 4Q, H₂O, m.p. 70°; B, 2Q, 4H₂O, m.p. 124—127°; B, 2Q, 5H₂O, m.p. 88°. Other conditions give A₃Cu(OH)₂ (obtained from all the A-compounds by hot H₂O) and B₃Cu(OH)₂·4H₂O, m.p. >300°.

R. S. C.

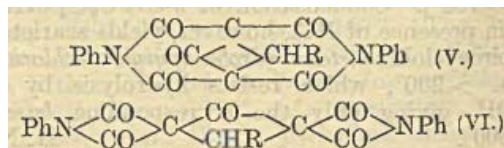
Sulphonic acids of quinophthalone and 6-ethyl-quinophthalone.—See B., 1934, 711.

Acridones. VI. Constitution of the so-called *N*-hydroxyacridones and acridols. I. TANASESCU and E. RAMONTIANU (Bull. Soc. chim., 1934, [v], 1, 547—561; cf. this vol., 195).—The properties of the so-called *N*-hydroxyacridone (I) (modified prep.), m.p. > 300° [obtained from *o*-NO₂-C₆H₄-CHO, C₆H₆, and H₂SO₄ (A., 1914, i, 867)], and the "acridol", m.p. 169°, derived therefrom by Na-Hg, are best in accord with formulation of these compounds as 9-hydroxyacridine *N*-oxide and acridine *N*-oxide, respectively. (I) or its Me ether, m.p. 153°, with Zn dust and a trace of CaCl₂ in hot aq. EtOH gives acridone. The Bz derivative, m.p. 157°, of (I) is hydrolysed by NaOH-EtOH to (I), but with HCl-EtOH gives a substance with properties of an acridone. Similar condensations afford 2-chloro- (*Me ether*, m.p. 179°; *Bz derivative*, m.p. 158°) and 3-nitro-9-hydroxyacridone *N*-oxide (II), m.p. >

360° [*Me ether* (III), m.p. 197°; *Bz derivative*, m.p. 179°]. These have properties similar to those of (I) and yield 2-chloro-acridone, -acridine, m.p. 170° (0.5HgCl₂-compound, m.p. 245—247°), and -acridone *N*-oxide, m.p. 204° (0.5HgCl₂-compound, m.p. 238°), and 3-nitroacridone. Reduction of (II) or (III) with Zn dust gives 3-aminoacridone, m.p. 292° (*Bz*, m.p. > 300°, and *Ac* derivatives).

R. S. C.

Extension of Michael's reaction. IV. T. N. GHOSH and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 353—361; cf. this vol., 400).—The Na₂ salt of CO(CH₂·CO₂Et)₂ (I) with PhNCS or its analogues in Et₂O gives *Et* 2-phenyl-, (II), m.p. 128—129° (decomp.), *-o-* (III), m.p. 150° (decomp.), and *-p-tolyl-imino-4:6-diketothiopyran-3-carboxylate* (IV), m.p. 145° (decomp.), (III) and (IV) give with hot KOH-EtOH 2-*o-*, m.p. 210° (decomp.), and *-p-tolylimino-4:6-diketothiopyran*, m.p. 214—215° (decomp.), respectively. The ring structures are proved by absence of mercaptan properties and stability to HgO. (II) and (IV) give 3:5-benzylidene derivatives, m.p. 274—275° (*semicarbazone*, m.p. > 290°) and > 280°, respectively, the dicyclic structure being proved by absence of acidic properties. (I) and PhCNO give, however, *acetone-tetracarboxylic acid αα'-Et₂ ester dianilide*, m.p. 226—227°, which with PhCHO gives a compound (V) [possibly (VI)] (R = Ph), m.p. 247—248° (decomp.) [*semicarbazone*, m.p. 214—215° (decomp.)], and with *o*-NO₂-C₆H₄-CHO the NO₂-derivative of (V) or (VI) (R = *o*-NO₂-C₆H₄), m.p. 199—200° (decomp.). Et₄ propane-ααγγ-tetracarboxylate and PhCNO afford *α-carbanilido-αα'-tricarboxy-N-phenylglutarimide*,



m.p. 123—124°, giving with *N*-NaOH *α-carbanilido-N-phenylglutarimide-αα'-dicarboxylic acid*, m.p. 180° (decomp.). PhCNO gives an oil with the Na₂ salt of ketipinic acid and does not react with Et₂ 2:6-diketothio-4:4-dimethylcyclohexane-3:5-dicarboxylate or Et cinnamylideneacrylate.

R. S. C.

Pyrazole group. III. Derivatives of 3:5-dimethylpyrazole. Q. MINGOIA and F. INGRAFFIA (Gazzetta, 1934, 64, 279—289).—The following have been prepared by the action of acyl chlorides in Et₂O on the Mg derivative of 3:5-dimethylpyrazole: 1-acetyl-, b.p. 88—90°/40 mm.; 1-propionyl-, b.p. 99—99.5°/24 mm. (*hydrochloride*, m.p. 240°; *perchlorate*, m.p. 51°); 1-butyryl-, b.p. 126—128°/40 mm. [*iodate*, m.p. 157—158° (decomp.)]; 1-benzoyl-, b.p. 200—202°/50 mm. (*picrate*, m.p. 160°); 1-chloroacetyl-, (I), m.p. 67.5—68°, and 1-carbethoxy-3:5-dimethylpyrazole, m.p. 35—36°, b.p. 131—132°/40 mm. [*iodate*, m.p. 152 (decomp.)], which with cold KOH yields the 1-carboxylic acid, m.p. 90° (decomp.). (I) with NH₃ in EtOH at 100° gives the 1-aminoacetyl derivative, m.p. 101—102° (*dihydrochloride*, m.p. 134—135°), and NH₂Me yields the 1-methylaminoacetyl derivative, m.p. 95°, b.p. 148—151° (*picrate*, m.p. 151°). The simple acyl derivatives are very weak bases.

R. K.

N-Monoarylated piperazines. V. PRELOG and Z. BLAZEK (Arh. Hemiju, 1934, 8, 86—89).—The following *N*-arylpiperazines are obtained from arylamines and $(\text{CH}_2\text{Br})_2\text{NH}\cdot\text{HBr}$: *N*-*o*- (*dihydrobromide*, m.p. 278°) and *N*-*p*-tolylpiperazine, m.p. 32—33° (*hydrobromide*, m.p. 242°); *N*- α - (*HBr* and *HCl* salts, m.p. > 290°) and *N*- β -naphthylpiperazine, m.p. 78° (*hydrobromide*, m.p. 280°); *N*-*o*-, m.p. 242.5°, and *N*-*p*-anisylpiperazine *hydrobromide*, m.p. 219°; *N*-*p*-bromophenylpiperazine, m.p. 98.5° (*hydrobromide*, m.p. 239°); *Et p*-*N*-piperazylbenzoate *hydrobromide*, m.p. 188.5°, yielding on hydrolysis the corresponding acid, m.p. > 300°; the *hydrobromide*, m.p. 290°, of *N*-*o*-, and the *dihydrobromide*, m.p. 275°, of *N*-*p*-hydroxyphenylpiperazine. The following bis- β -arylaminoethylamines are obtained as by-products of certain of the above reactions: the *hydrobromides* of bis- β -*o*-, m.p. 188—189°, of bis- β -*p*-tolylamino-, m.p. 245°, and of bis- β -2-naphthylaminoethylamine, m.p. 216—217°.

R. T.

2:3'-Dipyridyl derivatives. W. BRYDOWNA (Rocz. Chem., 1934, 14, 304—325).—The *distrychnine* salt, m.p. 245—247° (decomp.), of 2:3'-dipyridyl-2':3'-dicarboxylic acid (I) [Me_2 , m.p. 77—78°, *Et*, m.p. 150—151°, and *Et*₂ ester (II), b.p. 220/8 mm. (decomp.)] was resolved into two fractions, $[\alpha]_D -24^\circ$ and -101.2° , respectively; the *diquinine* salt, m.p. 150—152°, similarly gave fractions of $[\alpha]_D +63.6^\circ$ and -63.96° . (I) liberated from these fractions was always optically inactive. The *diamide*, m.p. 224—225°,



of (I), prepared by heating (II) with $\text{NH}_3\text{-EtOH}$ at 140—150° during 16 hr., yields 2':3'-diamino-2:3'-dipyridyl (III), m.p. 117—118° (*dihydrochloride*, m.p. 276—280°; *dimethiodide*, m.p. 245—246°), by the Hofmann reaction, together with the by-products, 2':3'-carbamido-2:3'-dipyridyl, m.p. 368—369° (N''-Me_2 derivative, m.p. 118—118.5°) [also synthesised from (III) and $\text{CO}(\text{NH}_2)_2$], and the substances (IV), m.p. 283° (N''-Me derivative, m.p. 177—178°), and (V), m.p. 318—320°. (III) on diazotising and heating at 100° yields 2:3'-dipyridulene 2':3'-oxide, m.p. 105.6—106.5°.

R. T.

Reactivity of the ketomethyl and ketomethylene groups. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1934, 64, 296—302).— $\text{PhN}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}_2(\beta)$ (or the *p*-Cl-compound) condenses with acetylacetone at 120° in presence of a little *HCl* to give 2- $\alpha\beta$ -naphthoquinoxalylacetone, m.p. 152° (*oxime*, m.p. 244°; *phenylhydrazone*, m.p. 211°), the constitution of which is proved by its oxidation (alkaline KMnO_4) to $\alpha\beta$ -naphthoinoxaline-2-pyruvic acid, m.p. 204°. Condensation thus takes place preferentially with the α -C atom of CH_3Ac .

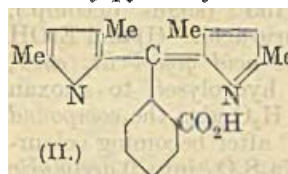
R. K. C.

Mechanism of ionic dissociation of derivatives of 2-thion-4-hydroxytetrahydroquinazoline, and the corresponding oxygen compounds. C. V. GHEORGHITU (Compt. rend., 1934, 199, 68—70; cf. A., 1933, 1171).—Salt formation, accompanied by the development of colour, probably involves rupture of

the hydroaromatic ring between positions 3 and 4, at the same time establishing an internal dipole between the 2-C and S (or O).

J. L. D.

2:4-Dimethylpyrrolephthalein. F. INGRAFFIA (Gazzetta, 1934, 64, 289—294).—Interaction of phthaloyl chloride and the *Mg* derivative of 2:4-dimethylpyrrole yields a mixture of *di*-(3:5-dimethyl-2-pyrrolyl)phthalide (I), m.p. indefinite, 180—230° (decomp.), and 3:5:3':5'-tetramethyl-2:2'-dipyrrophenylmethene-*o*-carboxylic acid (II), m.p. 182°. Dis-



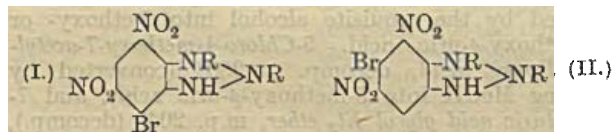
solution of (I) in hot NaOH and acidification yields (II). (II) yields ppts. with salts of *Pb*, *Hg*, *Ag*, Fe^{III} , and *Au*, but not of *Cu*, *Ba*, or *Ca*. It forms an NH_4 salt, and with *HCl* in C_6H_6 yields a *hydrochloride*.

R. K. C.

Reactions leading to syntheses of azine dyes. R. LANTZ (Ann. Chim., 1934, [xi], 2, 59—99).—Recorded syntheses of azines, oxazines, rosindulines, etc. are detailed.

R. S. C.

Condensation products of 2:4:6-trinitrobenzylidenedianiline with primary amines. S. SECAREANU and I. LUPAS (J. pr. Chem., 1934, [ii], 140, 233—239).—4:6-Dinitro-1-hydroxy-2:3-diphenyldihydrobenzotriazole is converted by *Br* in boiling *AcOH* into bromo-4:6-dinitro-2:3-diphenyldihydrobenzotriazole (I or II), m.p. 260—261°.



corresponding -*dibenzyl*-, m.p. 224—225°, -*ditolyl*-, m.p. > 280°, and -*dinaphthyl*-, m.p. > 340°, derivatives are described.

H. W.

Acetyl derivatives of uric acid. H. BILTZ and H. PARDON (J. pr. Chem., 1934, [ii], 140, 209—228).—The action of Cl_2 on uric acid suspended in Ac_2O gives 4-chloro-5-acetoxy-9-acetyldihydrouric acid (I), decomp. about 300° after becoming discoloured at 200°, hydrolysed by boiling H_2O to alloxan and $\text{CO}(\text{NH}_2)_2$, and converted by boiling *MeOH* or *EtOH* into 5-methoxy-, m.p. 202° (decomp.), and 5-ethoxy-, m.p. 228° (decomp.) - ψ -uric acid. (I) is reduced to uric acid by $\text{Na}_2\text{S}_2\text{O}_3$ and *KI* [in an individual case with an exceptionally pure Ac_2O , *Cl*, and uric acid gave (?) 4:5-di-acetoxy-9-acetyldihydrouric acid, slow decomp. > 300°]. (I) is slowly converted by H_2O at room temp. into 5-acetoxy-9-acetyl- ψ -uric acid (II), m.p. 217° (decomp.), which is unchanged by Ac_2O and H_2SO_4 at room temp. and is reduced by *HI* to ψ -uric acid. (II) and $\text{NH}_3\text{-EtOH}$ afford 5-amino-9-acetyl- ψ -uric acid, m.p. 235° (decomp.), reduced by SnCl_2 and *HCl* at 100° to uramil [in an isolated instance, (II) was transformed by dil. $\text{NH}_3\text{-EtOH}$ into 5-ethoxy- ψ -uric acid, decomp. 218°]. (I) is converted by short treatment with *MeOH* at room temp. into 4-methoxy-5-acetoxy-9-acetyldihydrouric acid, m.p. 220° (decomp.), transformed by excess of CH_3N_2 into 4-methoxy-5-acetoxy-9-acetyl-1:3:7-trimethyl-dihydrouric acid (III), m.p. 112°, reduced by *HI*-

AcOH to 1:3:7-trimethyluric acid, m.p. 335° (slight decomp.) (further identified by conversion into 8-methoxycaffeine). 5-Methoxy-1:3:7-trimethylisouric acid and Ac₂O containing a trace of H₂SO₄ give (?) *o*-methoxy-4-acetoxy-1:3:7-trimethyl-dihydrouric acid, decomp. 162°. (III) and conc. HCl at room temp. afford 5-acetoxy-9-acetyl-1:3:7-trimethyl-*ψ*-uric acid, m.p. 155° (slight decomp.), reduced to 1:3:7-trimethyluric acid. (I) and EtOH yield EtOAc and 9-acetyluric acid glycol Et₂ ether, m.p. 215° (slight decomp.), hydrolysed to alloxan tetrahydrate. (I) and KI in H₂O give the compound C₇H₆O₄N₄I₂, decomp. > 320° after becoming colourless at 280°, converted by Na₂S₂O₃ into 9-acetyluric acid (IV), slow decomp. > 320°, which is readily hydrolysed to uric acid by dil. alkali and is converted by Cl₂ in Ac₂O-AcOH into (I). Drastic treatment of (IV) with CH₂N₂-Et₂O leads to 8-methoxycaffeine whereas more moderate treatment affords 6:8-dihydroxy-2-methoxy-9-acetyl-1:7-dimethylpurine, m.p. 162° (decomp.), converted by NH₃-EtOH into 6:8-dihydroxy-2-methoxy-1:7-dimethylpurine, m.p. 282° (slight decomp.), hydrolysed by conc. HCl to 1:7-dimethyluric acid and methylated to 6:8-dihydroxy-2-methoxy-1:7:9-trimethylpurine, m.p. 186°. Attempts to prepare 7:9-diacetyluric acid are described.

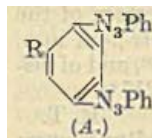
Treatment of 7-acetyluric acid or 8-acetoxy-7-acetyl-xanthine with Cl₂ in Ac₂O leads to 5-chloro-7-acetyl-Δ^{4:9}-isouric acid, slow decomp. > 250°, transformed by the requisite alcohol into 5-ethoxy- or 5-methoxy-*ψ*-uric acid. 5-Chloro-4-methoxy-7-acetyl-dihydrouric acid, decomp. > 280° (converted by boiling MeOH into 5-methoxy-*ψ*-uric acid), and 7-acetyluric acid glycol Et₂ ether, m.p. 204° (decomp.), are described. H. W.

Syntheses of 9-methylisoalloxazine. R. KUHN and F. WEYGAND (Ber., 1934, 67, [B], 1409—1413).—*o*-NH₂-C₆H₄-NHMe and alloxan monohydrate when heated in HCl-H₂O afford 9-methylisoalloxazine (I), C₆H₄<NMe-C-N-CO<N=C-CO-NH>, decomp. about 392° after darkening > 300°, which resembles closely lumilactoflavin in that the yellow solutions show an intensely green fluorescence which disappears on addition of alkali, whereas the yellow colour persists. Mineral acids cause loss of fluorescence and lightening of colour. Both phenomena are reversible. Its absorption spectrum is very analogous with those of lumiflavins (I), the main differences being between 300 and 360 mμ, in which region (II) of differing origin and prep. show most divergencies. (I) is hydrolysed by Ba(OH)₂ to CO(NH₂)₂ and 1-methyl-2-keto-1:2-dihydroquinoxaline-3-carboxylic acid, m.p. 174°. H. W.

Fluorescence of the porphyrins. III. H. FINK and W. HOERBURGER (Z. physiol. Chem., 1934, 225, 49—56; cf. A., 1933, 1173).—*p*_n-Fluorescence curves (I) are given for meso-, deuterio-, hæmato-, and tetrachloromesoporphyrin. The chief constitutional factor determining the shape of (I) is the no. and arrangement of the acid groups. J. H. B.

Supposed *in-bis*-2-phenyltriazolobenzene. K. FRIES and G. WALTNITZKI (Annalen, 1934, 511,

267—279).—The supposed 2:4-dibenzeneazo-m-phenylenediamine obtained by coupling PhN₂Cl with PhN₂·C₆H₃(NH₂)₂(*m*) (Schmidt *et al.*, A., 1921, i, 897) is actually 2:4:6-tribenzeneazo-m-phenylenediamine, m.p. 250° [reduced by SnCl₂-HCl to C₆H(NH₂)₅ and its Ac₅ derivative (Barr, A., 1888, 822)], oxidised by CuSO₄ in boiling C₅H₅N to 2:3:4:5-bis-(2'-phenyl-1':2':3'-triazolo)azobenzene (I) (A, R=N₂Ph), m.p. 217° (decomp.), converted by distillation with Zn dust into 2:5-diphenyl-1:2:3:4:5:6-benzdiazotriazole, m.p. 221° (II) (*loc. cit.*), and reduced (Zn-AcOH) to the corresponding phenylhydrazino-derivative (A, R=NH·NHPh), m.p. 307°, which is not 2:6-diphenyl-1:2:3:5:6:7-benzdiazotriazole, m.p. 334°, as previously stated (*loc. cit.*), and the existence of which is still in doubt. Reduction



of (I) with H₂-Cu-Co-Ni in Bu^oOH at 18°/100 atm. gives, with fission of NH₂Ph, 2:3:4:5-bis-(2'-phenyl-1':2':3'-triazolo)-aniline (III) (A, R=NH₂), m.p. 240° [Ac, m.p. 256°, and *o*-chlorobenzylidene (IV), m.p. 231°, derivatives], giving a Cl-free compound, m.p. > 450° (probably a dihydroacridine) with conc. HCl in some alcohols. Heated with Zn dust (III) gives (II). Addition of conc. HCl to (III) in boiling Bu^oOH gives 1:2:3:4:5:6:7:8-tetra-(2'-phenyl-1':2':3'-triazolo)-9-propyl-9:10-dihydroacridine, m.p. > 440° (oxidised by air in boiling PhNO₂ to the corresponding acridine, m.p. > 440°). The corresponding 9-Ph derivative, m.p. > 450°, is obtained from (III), PhCHO, and conc. HCl in boiling PhNO₂, and the 9-*o*-chlorophenyl derivative, m.p. > 450°, from (IV). Similar methods, but using *p*-C₆H₄Cl·N₂Cl, afford 1:3-diamino-2:4:6-tri-*p*-chlorobenzenazobenzene, m.p. 280°, converted into 2:3:4:5-bis-(2'-*p*-chlorophenyl-1':2':3'-triazolo)-*p*-chlorobenzenazobenzene (A, R=N₂·C₆H₄Cl; C₆H₄Cl instead of Ph), m.p. 273° (decomp.), and 2:3:4:5-bis-(2'-*p*-chlorophenyl-1':2':3'-triazolo)-aniline, m.p. 307° (A, R=NH₂; C₆H₄Cl instead of Ph). J. W. B.

Benzoxazolone formation in attempt to prepare mixed diacyl derivatives of *o*-aminophenol. L. C. RAIFORD and G. O. INMAN (J. Amer. Chem. Soc., 1934, 56, 1586—1590).—ClCO₂Ar (from ArOH, COCl₂, and NPhMe₂ in C₆H₆ at > 25°) and *o*-NH₂-C₆H₄·OH (2 mols.) in Et₂O give *o*-CO₂Ar·NH·C₆H₄·OH, which are converted by aq. alkali hydroxide into ArOH and *o*-C₆H₄<O>CO. Ring closure is also effected by C₆H₅N or Ac₂O (when *N*-Ac derivatives are formed). Similarly, *o*-NHbz·C₆H₄·OH and ClCO₂Ph in aq. NaOH or C₆H₅N afford PhOH and *N*-benzoylbenzoxazolone. Diacyl derivatives could not be isolated. The following are described: 2:4-dichloro-, b.p. 115—120°/16 mm., 2:4:6-tribromo-, b.p. 193—197°/34 mm., m.p. 47—50°, *o*-nitro-, b.p. 148°/15 mm., *p*-phenyl-, b.p. 173—175°/13 mm., m.p. 40—41°, 4-chloro-3-methyl-6-isopropyl-, b.p. 158—160°/34 mm., and 4-bromo-3-methyl-6-isopropyl-, b.p. 158—162°/24 mm., -phenyl chloroformates; *N*-carbophenoxy-*o*-aminophenol, m.p. 150°, -4-bromo-2-aminophenol (I), m.p. 181—182°, -4:6-dibromo-2-aminophenol (II), m.p. 158°, and -*o*-methylaminophenol, m.p. 146° (converted

by aq. alkali into *N*-methylbenzoxazolone); *N*-carboxyphenoxy- (III), m.p. 107°, *N*-carbo-*o*- (IV), m.p. 124°, and -*p*- (V), m.p. 139—141°, -*tol*xyloxy-, and *N*-carbo-*p*-diphenylxyloxy- (VI), m.p. 162—163°, derivatives of 3-bromo-5-amino-*p*-cresol. (I) and 5% KOH give 4-bromobenzoxazolone (VII), m.p. 215°; (II) affords dibromobenzoxazolone, m.p. 252° (*N*-Ac derivative, m.p. 160.5°). 6-Bromo-4-methylbenzoxazolone (VIII), m.p. 222°, is similarly obtained from (III)—(VI) and also from 3-bromo-5-amino-*p*-cresol and COCl₂ in boiling CHCl₃; the following *N*-derivatives of (VIII) are described: *Ac*, m.p. 114—115°; *Bz*, m.p. 176—176.5°; *benzenesulphonyl*, m.p. 188—189°; *carbo-methoxy*, m.p. 145° (decomp.), -*ethoxy*, m.p. 87°, -*n*-*propoxy*, m.p. 99.5°, -*n*-*butoxy*, m.p. 56°, -*phenoxy*, m.p. 145—146°, -*o*-, m.p. 168—169°, -*m*-, m.p. 149.5—150°, and -*p*-, m.p. 128—129°, -*tol*xyloxy-, -*o*-*nitro*phenoxy, m.p. 198°, -2:4-dichlorophenoxy, m.p. 165°, -2:4:6-tribromophenoxy, m.p. 202—203°, -3-methyl-6-isopropylphenoxy, m.p. 110—111°, -4-chloro-, m.p. 149°, and -4-bromo-, m.p. 156°, -3-methyl-6-isopropylphenoxy, -*p*-diphenylxyloxy, m.p. 195.5°, and -*α*-, m.p. 170°, and -*β*-, m.p. 182—183°, -*naphthoxy*. 4-Bromo-2-methylaminophenol and ClCO₂Ph in 10% NaOH give 4-bromo-2-methylbenzoxazolone, m.p. 137.5°, also prepared by methylation (MeI, MeOH-KOH) of (VII). 4:6-Dibromo-2-methylbenzoxazolone, m.p. 124—125°, is similarly obtained. *o*-Carbethoxyaminophenyl and 6-bromo-2-carbethoxyamino-4-methylphenyl, m.p. 109°, *Et* carbonates are prepared from the requisite carbethoxyaminophenol and ClCO₂Et; benzoxazolones are not produced. The following are also described: ON-*Ac*₂, m.p. 62—63°, O-*Bz*-*N*-*Ac*, m.p. 96°, *N*-*Bz*-O-*Ac*, m.p. 63—64°, and *N*-benzoyl-O-carboxyphenoxy, m.p. 103°, derivatives of *o*-NHMe-C₆H₄-OH; *N*-*Ac*, m.p. 185—185.5°, *N*-*Bz*, m.p. 174°, O-*Bz*-*N*-*Ac*, m.p. 129°, *N*-*Bz*-O-*Ac*, m.p. 109°, and ON-*Bz*₂, m.p. 137°, derivatives of 4-bromo-2-methylaminophenol (hydrochloride); *N*-*Ac*, m.p. 197°, *N*-*Bz*, m.p. 183°, O-*Bz*-*N*-*Ac*, m.p. 145°, *N*-*Bz*-O-*Ac*, m.p. 99°, and ON-*Bz*₂, m.p. 144—145°, derivatives of 4:6-dibromo-2-methylaminophenol [hydrochloride, m.p. 216° (decomp.)]. The mixed diacyl derivatives show no tendency to rearrange.

H. B.

Heterocyclic compounds. III. A. C. SIRCAR and S. C. SEN (J. Indian Chem. Soc., 1934, 11, 363—371; cf. A., 1932, 286).—3-Amino-2-hydroxyphenazine yields further ring-compounds with difficulty. Thus, by the usual methods it affords the following *N*-derivatives: *phthaloyl*, *chloroacetyl*, *benzylidene*, *o*-, *m*-, and *p*-*nitro*-, 4-hydroxy-5-methoxy-, *o*-hydroxy- and 2-hydroxy-*o*-bromo-benzylidene, *p*-anisylidene, and *furfurylidene*. However, with boiling BzCl it gives 2-phenyl-4:5-phenazino-oxazole, with boiling (COCl)₂ phenazindiketomorpholine, with SOCl₂ thioxyphe-*n*azino-oxazole, with COCl₂ phenazino-*μ*-hydroxyoxazole, with K ethylxanthate in EtOH at 200—230° *μ*-thiolphenazino-oxazole, with (CH₂Br)₂ at 180—200° phenazinomorpholine, with Ac₂O at 210—230° phenazino-*μ*-methyloxazole, and with 100% HCO₂H at 280—300° (40 hr.) phenazino-oxazole. With ClCO₂Et it gives the urethane, m.p. 231—232°. M.p. are > 300° or not stated.

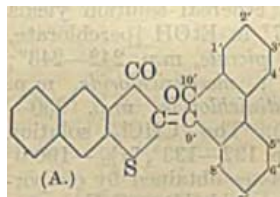
R. S. C.

Indigoid vat dyes of the isatin series. Indolethionaphtheneindigos. S. K. GUHA and H. P. BASU-MALLIK (J. Indian Chem. Soc., 1934, 11, 395—399).—The prep. of 5:7-dinitroisatin is modified. By condensation in hot AcOH indole-5'-methylthionaphtheneindigotin (I) and the following derivatives are prepared: 5-*Cl*-, 5-*Br*-, 5-*I*-, 5:7-*Br*₂-, 5-bromo-7-nitro-, 5:7-(NO₂)₂-. These dyes sublime without decomp. at > 310°. They dye wool from an acid bath and form vats with Na₂S₂O₄. Their dyeing properties and those of 2-(5-methylthionaphthene)-9'-phenanthreneindigotin are described.

R. S. C.

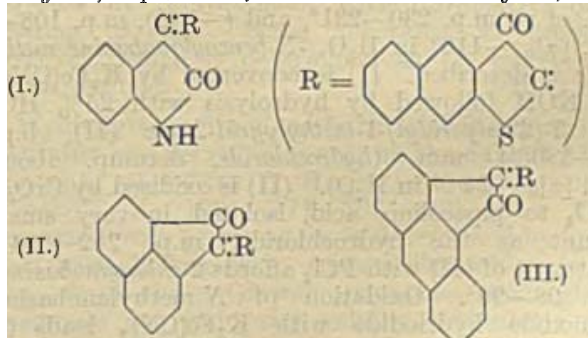
Indigoid dyes. VI. 2:3-Naphthathiophen-phenanthreneindigotin. VII. P. C. DUTTA (Ber., 1934, 67, [B], 1319—1324, 1324—1328).—The deepening of colour of isomeric thioindigoid dyes is most marked when the new symmetrical ring is attached to the thionaphthen nucleus, so that it is equidistant from CO and S, whereby it establishes an equilibrium of the mol with the auxochrome and chromophore. If the ring is displaced towards right or left, it approaches either chromophore or auxochrome, and by reason of the absence of equilibrium it exerts an unfavourable effect on the deepening of the colour.

The following compounds (A) are obtained by condensing 2:3-naphthoxythiophen with the requisite phenanthraquinone in presence of HCl-AcOH and absence of air: 2:3-naphthathiophen-9'-phenanthreneindigotin, m.p. > 290°,



and its 4'-NO₂-, m.p. > 295° after softening at 285°, 2'-NO₂-, m.p. > 300°, 4':5'-(NO₂)₂-, m.p. 255°, 2':7'-(NO₂)₂-, m.p. > 300°, 2'-Br-, m.p. > 295°, Br₂-, m.p. > 295°, Br₂-NO₂-, m.p. > 295°, Br-(NO₂)₂-, m.p. > 300°, 2'-NH₂-, m.p. > 300°, 4'-NH₂-, m.p. > 300°, 2'-OH-, m.p. > 295°, and 4'-OH-, m.p. > 300° derivatives. The prep. of 2-amino-3-naphthoic acid is described.

VII. 2:3-Naphthathiophen is condensed with the appropriate ketone to 2:3-naphthathiophen-3'-indoleindigotin (I) m.p. > 295°, -3'-5'-chloroindoleindigotin, m.p. > 295°, -3'-5'-bromoindoleindigotin, m.p.



> 295°, -3'-5'-nitroindoleindigotin, m.p. > 295° after evolving violet vapours at 290°, -2'-acenaphthyleneindigotin (II), m.p. > 290°, -2'-5'-nitroacenaphthylene-

indigotin, m.p. > 290°, 2'-5': -*dinitroacenaphthylene-indigotin*, m.p. > 290°, 1'-*aceanthryleneindigotin* (III), m.p. > 290°. *Di-2:3-naphthathiophenethylenindigotin*, CR·CH·CH:CR, m.p. > 290°, from glyoxal, 2:3'-*di-2:3-1:2-naphthathiophenindigotin*, m.p. > 300°, and 2:3'-*di-2:3-2:1-naphthathiophenindigotin*, m.p. > 290°, are described. H. W.

New alkaloid, ephedine, neutral principle, and volatile oil from Chinese *Ephedra*, Ma-huang.—See this vol., 1045.

Syntheses in the nicotine group. J. P. WIBAUT (Natuurwetensch. Tijds., 1934, 16, 106—111).—A review. The physiological activity of nicotine and kindred compounds depends on the relative positions of the pyrrole and C₅H₅N groups in the mol.

H. F. G.

Sophora alkaloids. V. Subsidiary alkaloids of *Thermopsis lanceolata*. A. OREKHOV, S. NORKINA, and H. GUREVITSCH (Ber., 1934, 67, [B], 1394—1398).—The foliage of *T. lanceolata* is percolated with C₆H₆, the percolate extracted with 5% HCl, the acid solution made alkaline with NH₃ and extracted with Et₂O, and the residual solution is treated with NaOH and extracted successively with Et₂O and CHCl₃. The first ethereal solution yields *thermopsine* (I) *homothermopsine* (II), (?) C₁₇H₂₁ON₂, m.p. 224—225°, [α]_D +86.9° in CHCl₃, and *pachycarpine* (III). The second ethereal solution yields (III), *anagryne* [α]_D —151.7° in EtOH [perchlorate, m.p. 271—272° (decomp.); *picrate*, m.p. 242—243°; *methiodide*, m.p. 263—264°; *mercurichloride*, m.p. 220—222° (decomp.); *platinichloride*, m.p. 250—251° (decomp.)], and (I). The CHCl₃ solution yields *N*-methylcytisine, m.p. 132—133°, [α]_D —190.0° in EtOH. The resinous masses obtained by evaporation of the various fractions yield (II) to C₆H₆.

H. W.

Constitution of anabasine. A. WENUSCH and R. SCHOLLER (Ber., 1934, 67, [B], 1344—1345).—Confirmation of the view that anabasine is 2-piperidyl-3-pyridine is found in its catalytic hydrogenation (Pt-sponge followed by Pt-Pd sponge in AcOH) to 2:3'-dipiperidyl (platinichloride, m.p. 238°; aurichloride, m.p. 211—215°; hydrochloride). H. W.

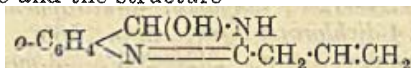
Alkaloids of *Anabasis aphylla*. IX. Oxidation of methyl- and benzoyl-anabasine methiodide. G. MENSCHIKOV, A. GRIGOROVITSCH, and A. OREKHOV (Ber., 1934, 67, 1398—1402).—The prep. of r-, m.p. 230—231°, and (—) (I), m.p. 108—109°, [α]_D —116° in H₂O, -*N*-benzoylanabasine methiodide is described. (I) is converted by K₃Fe(CN)₆ and KOH followed by hydrolysis with 25% HCl into 3-(2'-piperidyl)-1-methylpyrid-2-one (II), b.p. 181—186°/4 mm. (hydrochloride, decomp. about 260°, [α]_D —22.0° in H₂O). (II) is oxidised by CrO₃-H₂SO₄ to pipercolinic acid, isolated in very small amount as the hydrochloride, m.p. 252—254°. Treatment of (II) with PCl₅ affords 2-chloroanabasine, m.p. 98—99°. Oxidation of *N*-methylanabasine methiodide hydriodide with K₃Fe(CN)₆ leads to NN'-dimethylanabasone [3-(2'-1'-methylpiperidyl)-1-methylpyrid-2-one], m.p. 95—96°, [α]_D —100.0° in EtOH, transformed by PCl₅ into 2-chloro-3-(2'-1'-methylpiperidyl)pyridine (III), b.p. 132—135°/6 mm.,

[α]_D —119.0°, which is oxidised by KMnO₄ to chloro-nicotinic acid, m.p. 191—192°. Treatment of (III) with NaOMe-MeOH at 100° affords 2-methoxy-3-(2'-1'-methylpiperidyl)pyridine, b.p. 126—128°/4 mm., [α]_D —113.5°. H. W.

Constitution of vasicine. T. M. REYNOLDS and R. ROBINSON (Nature, 1934, 134, 142).—Allyl iodide and quinazoline form 3-allylquinazolinium iodide, which with aq. alkalis yields the carbinol base 4-hydroxy-3-allyl-3:4-dihydroquinazoline (I), m.p. 130°. Hence the formulation of vasicine, (this vol., 310), m.p. 208—210°, as (I) is incorrect.

L. S. T.

Vasicine. K. S. NARANG and J. N. RAY (Chem. and Ind., 1934, 698—699).—Reasons are advanced for considering that vasicine (I) is not identical with peganine and the structure



is tentatively advanced.

H. W.

Alkaloids of Chinese *Corydalis ambigua*, Cham. et Sch. (Yen-hu-so). V. *Corydalis-L* and -*M*. T. Q. CHOU (Chinese J. Physiol., 1934, 8, 155—158).—*Corydalis-K* (A., 1933, 652) is C₂₁H₂₅O₄N. From basic residues were further isolated *corydalis-L*, C₁₉H₂₁O₄N, m.p. 236°, [α]_D —325° in CHCl₃, and *corydalis-M*, C₂₁H₂₄O₅N, m.p. 161°, [α] 0° in CHCl₃ (hydrochloride, m.p. about 190°). F. O. H.

Asymmetric rearrangement. M. S. KHARASCH, J. K. SENIOR, D. W. STANGER, and J. A. CHENICEK (J. Amer. Chem. Soc., 1934, 56, 1646—1647).—The rotation curves of mixtures of quinine (1 mol.) and 0.1—20 equivs. of *o*-OH·C₆H₄·CO₂H, CH₂Ph·CO₂H, *o*-NO₂·C₆H₄·CO₂H, 2:4-(NO₂)₂·C₆H₃·CO₂H (I), and lauric, *o*-toluic, diphenic (II), and 4:4'-dinitrodiphenic (III) acid in CHCl₃ are given. Those for (II) and (III) resemble that of (I), indicating, in the view of the authors, that there are no grounds for assuming that quinine "dissymetrises" one of these acids and not the others (cf. Kuhn, A., 1932, 269). Quinine diphenate did not exhibit mutarotation (cf. Lesslie and Turner, this vol., 538). H. B.

Strychnine benzoates. C. F. POE and J. F. SUCHY (J. Amer. Chem. Soc., 1934, 56, 1640—1641).—The following are new: *strychnine o*-, m.p. 170° (all m.p. are on Maquenne block), *m*-, m.p. 185°, and *p*-, m.p. 251°, -*chloro*-, *o*-, m.p. 202°, *m*-, m.p. 178°, and *p*-, m.p. 252°, -*bromo*-, *o*-, m.p. 237°, *m*-, m.p. 159°, and *p*-, m.p. 241°, -*iodo*-, *o*-, m.p. 205°, *m*-, m.p. 214°, and *p*-, m.p. 266°, -*nitro*-, *m*-, m.p. 263°, and *p*-, m.p. 192°, -*hydroxy*-, *o*-, m.p. 167°, *m*-, m.p. 168°, and *p*-, m.p. 236°, -*methyl*-, *o*-, m.p. 219°, *m*-, m.p. 233°, and *p*-, m.p. 206°, -*amino*-, 2:4-, m.p. 256°, and 3:5-, m.p. 267°, -*dinitro*-, and 2:4:6-*trinitro*-, m.p. 182° (decomp.), -*benzoates*; 5-*iodo*-, m.p. 225°, 3:5-*dinitro*-, m.p. 274°, *di-iodo*-, m.p. 225°, and *acetyl*-, m.p. 142°, -*salicylates*. The benzoate and salicylate have m.p. 231° and 224°, respectively. H. B.

Optical activity of the alkaloidal salts of violuric acid. N. GHATAK (Bull. Acad. Sci. Agra and Oudh, 1933, 3, 75—78).—*Violurates* of the follow-

ing alkaloids are described, the $[\alpha]^{20}$ and λ_{\max} being given in parentheses: nicotine (-65.5° , 5695), morphine (-43.7° , 5691), brucine (-69° , 5679), strychnine (-8.3° , 5660), cinchonine ($+140.0^\circ$, 5557), quinine (-70.9° , 5537), cocaine (-12.3° , 5674). The salts have lower $[\alpha]$ than the corresponding bases.

S. C.

Arsenic trichloride and 1:4-dioxan. G. O. DOAK (J. Amer. Pharm. Assoc., 1934, 23, 541—543).—Addition of AsCl_3 to dry 1:4-dioxan gives an oxonium compound $(\text{C}_4\text{H}_8\text{O}_2)_3 \cdot 2\text{AsCl}_3$, m.p. 62° , largely dissociated in C_6H_6 or COMe_2 solution. J. W. B.

Arsenation of cholesterol and cholic acid. H. LIEB, A. VERDINO, and E. SCHADENDORFF [with, in part, A. SALLMANN] (Annalen, 1934, 512, 89—96).—*p*-Cholesterylcarbamino-phenylarsinic acid

$\text{C}_{27}\text{H}_{46}\text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$
($+\text{H}_2\text{O}$ and $+\text{EtOH}$), decomp. $> 250^\circ$ (K_2 salt), is obtained by the action of *p*-arsanilic acid on cholesteryl chloroformate in feebly acid, boiling COMe_2 containing KI. At 100° it passes into the corresponding oxide. It is reduced by H_3PO_2 in boiling AcOH to *di-p*-cholesterylcarbaminoarsenobenzene. *m*-Cholesteryl- ($+\text{H}_2\text{O}$), decomp. $> 200^\circ$, *o*-cholesteryl- ($+\text{H}_2\text{O}$), decomp. $> 170^\circ$, 4-hydroxy-3-cholesteryl- ($+\text{H}_2\text{O} : \text{Na}_2$ salt), 2-iodo-4-cholesteryl-, m.p. $> 240^\circ$ (decomp.), and 3:4-dicholesteryl- ($+\text{H}_2\text{O}$), m.p. $> 200^\circ$ (decomp.), -carbamino-phenylarsinic acid are described. Et cholate and COCl_2 in anhyd. Et_2O afford the chloroformic ester, $\text{CO}_2\text{Et} \cdot \text{C}_{23}\text{H}_{38}\text{O}_2 \cdot \text{O} \cdot \text{COCl}$, m.p. 155° (decomp.), which affords the compounds $\text{CO}_2\text{Et} \cdot \text{C}_{23}\text{H}_{38}\text{O}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NHR}$ [$\text{R} = \text{p}$ -, m.p. 261° (decomp.); m -, m.p. 253 — 254° (decomp.) after darkening and softening at 244° ; o -, m.p. 278° (decomp.) after becoming discoloured at 250° ; 4-hydroxy-3-, m.p. 236 — 237° (decomp.), -phenylarsinic acid]. The compounds have no pharmacological action. H. W.

Buffer properties of neosalvarsan. L. K. SMORODINCEVA (Z. Immunitat., 1933, 78, 239—245; Chem. Zentr., 1934, i, 417).—The p_H of different neosalvarsan (I) preps. varied from 6.1 to 8.2. The buffer capacity was $<$ that of Na_2HAsO_3 and Na_2HAsO_4 . The displacement of p_H with (I) occurs more easily than with Na_2HAsO_4 and almost as readily as with Na_2HAsO_3 . H. J. E.

Oxidation of benzene ring of arylboric acids by potassium permanganate. B. BETTMAN and G. E. K. BRANCH (J. Amer. Chem. Soc., 1934, 56, 1616—1617).—*m*- and *p*- $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{B}(\text{OH})_2$ are obtained in good yield by oxidation [alkaline KMnO_4 (I) at room temp.] of $\text{C}_6\text{H}_4\text{Me} \cdot \text{B}(\text{OH})_2$. Contrary to Koenig and Scharrnbeck (A., 1931, 244), $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{B}(\text{OH})_2$ could not be similarly prepared; o - $\text{C}_6\text{H}_4\text{Me} \cdot \text{B}(\text{OH})_2$ (1 mol.) consumes 24 equivs. of (I), showing that the C_6 ring is oxidised. o - $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ is obtained from α - and β - $\text{C}_{10}\text{H}_7 \cdot \text{B}(\text{OH})_2$; 18 equivs. of (I) are used. *m*- $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{B}(\text{OH})_2$ is oxidised slowly, but the *o*- and *p*-acids are oxidised rapidly; 24, 24, and 18 equivs., respectively of (I) are consumed. $\text{Bu} \cdot \text{B}(\text{OH})_2$ and $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{B}(\text{OH})_2$ reduce 2 equivs. of (I) rapidly; reaction then becomes slow. In the former case, BuOH is produced.

H. B.

Organo-metallic compounds. VII. Simplified preparation of tin triaryl halides. K. A. KOZESCHKOV, M. M. NADJ, and A. P. ALEXANDROV (Ber., 1934, 67, [B], 1348—1349).—Sn triaryl chlorides are obtained by heating SnCl_4 (1 mol.) with Sn tetra-aryl (3 mols.) at about 200° : $\text{SnAr}_4 + \text{SnCl}_4 = 2\text{SnAr}_2\text{Cl}_2$ and $\text{SnAr}_2\text{Cl}_2 + \text{SnAr}_4 = 2\text{SnAr}_3\text{Cl}$. Cases cited are the prep. of SnPh_3Cl , $\text{Sn}(\text{o}-\text{C}_6\text{H}_4\text{Me})_3\text{Cl}$, $\text{Sn}(\text{m}-\text{C}_6\text{H}_4\text{Me})_3\text{Cl}$, and $\text{Sn}(\text{p}-\text{C}_6\text{H}_4\text{Me})_3\text{Cl}$. H. W.

Clupein. I. Preparation and fractionation. K. E. RASMUSSEN (Z. physiol. Chem., 1934, 224, 97—115).—An improved prep. and fractionation of clupein (I) is performed mainly at 0° . (I) is extracted by dil. HCl and pptd. as picrate, which is dissolved in 67% COMe_2 and fractionally repptd. After addition of HCl, the product is extracted with Et_2O and the sulphate pptd. from the chloride solution by H_2SO_4 and EtOH . N was determined (Kjeldahl) in the various fractions after reduction of the picric acid by HCl-TiCl_3 . The four main fractions contained 90.8—91.7% of the total N as arginine-N (II), indicating that (I) is not entirely built up of clupeones, which contain two arginine to one mono- NH_2 -acid radical, corresponding with 88.9% of (II).

J. H. B.

Basic amino-acids of serum-proteins (orosins). IV. Chemical relationship between various avian orosins. Some proteins of the egg. R. J. BLOCK (J. Biol. Chem., 1934, 105, 455—461; cf. this vol., 93).—The % of histidine, arginine (I), and lysine (II) in the total coagulable protein (called orosin) (III) and the albumin, globulin, and conalbumin from the egg-whites of the hen, duck, and turkey are determined. The ratio (I):(II) is const. for the (III) of these species, but different from that of mammalian (III).

H. D.

Influence of p_H on optical rotation of proteins. H. J. ALMQUIST and D. M. GREENBERG (J. Biol. Chem., 1934, 105, 519—522).—The curves for serum-albumin, livetin, and ovalbumin are similar in form (min. $[\alpha]_D$ in isoelectric region, at p_H 4.5—10.0).

H. G. R.

Effect of dry heat and dilute alkali on the lysine content of casein. R. J. BLOCK, D. B. JONES, and C. E. F. GERSDORFF (J. Biol. Chem., 1934, 105, 667—668).—The proportion of lysine (I) formed by the acid hydrolysis of casein is unaffected by pretreatment with dil. NaOH or by heating at 150° . Some substance is produced, however, which is determined as (I) by the Van Slyke method.

H. G. R.

Hydrolytic formation of acetic acid from glucoproteins and its relationship to the carbohydrate content. O. FURTH, H. HERRMANN, and R. SCHOLL (Biochem. Z., 1934, 271, 395—413).—The AcOH separated from glucoprotein is determined by hydrolysis with boiling 25% toluenesulphonic acid and vac. distillation. Glucose, mannose, and glucosamine do not yield any volatile acid under these conditions. Zein, gelatin, caseinogen, and serum-protein, which are poor in carbohydrate, give 0.5—0.9% of volatile acid (calc. as AcOH). Ovomucoid and bile mucin give 2.4—4.0% of AcOH with 12—

15% of reducing sugar, whilst samples of ovarian mucoid give 2.6—9.4% of AcOH with 19—43% of reducing sugar. In the last two cases for each mol. of AcOH 1.5—2 mols. of sugar are also liberated.

P. W. C.

Protein structure. I. Isolation of the diketopiperazine [fraction] from protein hydrolysates. N. I. GAVRILOV and V. S. BALABUCHA-POPOVA (Biochem. Z., 1934, 271, 292—303).—An electrophoresis method for the isolation of the diketopiperazine fraction from protein hydrolysates is described.

P. W. C.

Simplified micro-analytical determination of carbon and hydrogen. J. B. NIEDERL and R. T. ROTH (Ind. Eng. Chem. [Anal.], 1934, 6, 272—274).—Improvements (some new) in the Pregl method are described. Air is not used. Org. matter is removed from cylinder- O_2 by a preheater inserted before the purification train.

R. S. C.

Micro-analytical determination of carbon and hydrogen in organic substances without the use of a catalyst. I. MAREK (Arh. Hemiju, 1934, 8, 22—29).—The author's method (A., 1928, 82) may be applied as a micro-method.

R. T.

Modifications of the ter Meulen-Heslinga semi-micro-combustion method for the determination of carbon and hydrogen. S. D. WILSON and LING-SIEN SUN (J. Chinese Chem. Soc., 1934, 2, 129—135).—The efficiency of the method is improved by the use of asbestos fibre impregnated with PbO_2 in a Pregl mortar as absorbent for oxides of N, and $PbCrO_4$ -coated CuO and Ag-coated CuO as absorbents for S and halogens, respectively.

J. W. S.

Determination of organically combined halogens. M. BUSCH (Angew. Chem., 1934, 47, 536—537).—The hydrogenation should be conducted in EtOH; in MeOH it is sometimes incomplete.

A. G.

Micro-determination of disulphide and thiol compounds. H. TOYODA (Bull. Chem. Soc. Japan, 1934, 9, 263—268; cf. A., 1930, 181).—The method, which is applicable to biological material, depends on the blue coloration given after at least 12 hr. when thiols or disulphides react with dimethyl-*p*-phenylenediamine and $Fe^{III} NH_4$ sulphate in *N*-HCl. Tyrosine, tryptophan, uric acid, creatine, and $COMe_2$ do not interfere.

J. L. D.

Determination of manganese and chromium in organic matter after nitro-sulpho-perchloric destruction.—See this vol., 982.

Determination of methylimide. R. KUHN and H. ROTH (Ber., 1934, 67, [B], 1458).—For the determination of NMe it is essential that the substance be brought into solution before the addition of HI. This can be effected by use of considerable amounts of PhOH and Ac_2O .

H. W.

Action of nitrates of various metals on mixtures of hydrocarbons. P. M. ALIEV and V. S. GUTIRIA (Ukrain. Chem. J., 1934, 9, 10—16).—Saturated and aromatic hydrocarbons (I) do not react with $Al(NO_3)_3 \cdot 9H_2O$ at 95—100°, whilst pinene and caprylene are converted into NaOH-sol. products.

This reaction is applicable to the determination of unsaturated hydrocarbons in mixtures with (I).

R. T.

Analysis of gaseous hydrocarbons. Determination of gaseous paraffins and olefines. H. TROPSCH and W. J. MATTOX (Ind. Eng. Chem. [Anal.], 1934, 6, 235—241).— N_2 , CO , O_2 , H_2 , and CH_4 are removed from the condensed gases at 0.1 mm. Subsequent fractional condensation at 1 mm. gives the following fractions: (1) —195°, C_2H_6 , C_3H_8 , C_4H_{10} , and C_5H_{12} ; (2) —135° to —140°, C_3H_8 , C_4H_{10} , C_5H_{12} , and C_6H_{14} ; (3) C_5H_{12} and higher homologues. *d* determinations by the Stark electromagnetic balance before and after removal of olefines give the ratios of each component in fractions (1) and (2). The method is rapid, cheap, accurate, and applicable to 0.5 litre of gas.

R. S. C.

Attempted adsorption indicator method for determination of alkali salts of organic acids. C. G. LYONS and F. N. APPLEYARD (Analyst, 1934, 59, 480).—Of 20 dyes examined, none was found to be suitable as an adsorption indicator for the titration of aq. $AgNO_3$ and $BaCl_2$ with the alkali salts of tartaric, citric, and benzoic acid.

E. C. S.

Determination of formaldehyde in methylols. J. BOUGAULT and J. LEBOUCC (Bull. Acad. Med., 1934, 108, 1301—1303; Chem. Zentr., 1934, i, 253).—0.05—0.1 g. is heated for 5—10 min. at 100° with 5 c.c. of H_2O and 60 c.c. of Nessler's solution. After cooling, a small excess of HCl and 20 c.c. of 0.1*N*-I solution are added, excess of I being titrated with $Na_2S_2O_3$. Methylene-methylol is first hydrolysed with 25% H_2SO_4 , distilled, and CH_2O determined in the distillate.

H. J. E.

Semicarbazides. II. *p*-Tolylsemicarbazide as a reagent for the identification of aldehydes and ketones. P. P. T. SAH and H. H. LEI (J. Chinese Chem. Soc., 1934, 2, 167—172; cf. this vol., 791).—*p*-Tolylsemicarbazones of the following compounds are described: acet., m.p. 174—175°; prop., m.p. 135—137°; *n*-but., m.p. 128—130°; isobut., m.p. 124—126°; *n*-valer., m.p. 157—168°; *n*-hex., m.p. 139—140°; *n*-hept., m.p. 151—152°; *n*-oct., m.p. 138—139°; *n*-non., m.p. 155—156°; *n*-dec., m.p. 137—138°; benz., m.p. 185—186°; *m*-nitrobenz., m.p. 228—229°; salicyl., m.p. 209—210°; and furfur., m.p. 156—157°; -aldehyde; $COMe_2$, m.p. 174—175°; $COMeEt$, m.p. 119—120°; Me hexyl ketone, m.p. 183—184°; $COPhMe$, m.p. 192—193°; $COPh_2$, m.p. 186—187°; $CH_2Ac \cdot CO_2Et$, m.p. 117—118°; Et laevulate, m.p. 116—118°; CH_2Ph laevulate, m.p. 149—150°; laevulic acid, m.p. 178—180°; and cinnamaldehyde, m.p. 184—185°.

H. N. R.

Detection and determination of pyruvic acid, methylglyoxal, trioses, and aliphatic aldehydes in very dilute solution with the help of the colour reaction with 2-methylindole and hydrochloric acid. Z. DISCHE and S. S. ROBBINS (Biochem. Z., 1934, 271, 304—308).—The reddish-violet colour given by AcCHO (I) with 2-methylindole is also obtained with acetol (II), glyceraldehyde (III), and dihydroxy-acetone (IV), the reaction in these cases being less delicate. Keeping these substances for 15 min. in alkaline reaction leads to the disappearance of with (I) and to intensification of colour with (II), (III),

and (IV) to different extents, whereas pretreatment by heating in acid solution for 15 min. leads to the formation of (I) from (III) and (IV) with intensification of colour reaction, but with (II) the reaction is unaffected.

P. W. C.

Thiocyanogen numbers. W. J. WILEY and A. H. GILL (Ind. Eng. Chem. [Anal.], 1934, 6, 298).—0.4 g. of oil and 50 c.c. of (SCN)₂ solution are required to ensure reproducible results.

R. S. C.

Micro-copper-pyridine reaction for saccharin. C. VAN ZIJP (Pharm. Weekblad, 1934, 71, 858—863).—Crystallographic and optical examination shows that the three cryst. forms of the Cu-C₅H₅N-saccharin complex, hexagonal prisms, needles, and platelets, described by Zwikker (A., 1933, 732), are different modifications of the same rhombic, holohedral crystal and not different compounds.

S. C.

[Micro-copper-pyridine reaction for saccharin.] J. J. L. ZWIKKER (Pharm. Weekblad, 1934, 71, 864—867).—A reply to van Zijp (preceding abstract). The same Cu-C₅H₅N-complex can be obtained from saccharin in the form of needles and from Na saccharinate as hexagonal platelets by working in conc. solutions, but in dil. solutions (as in A., 1933, 732) complexes are obtained which are not identical in composition.

S. C.

Colorimetric determination of rotenone. C. R. GROSS and C. M. SMITH (J. Assoc. Off. Agric. Chem., 1934, 17, 336—339).—A red coloration is produced when rotenone (I) in COMe₂ is treated with KOH-EtOH, and later with aq. HNO₃ and NaNO₂. The optimum range of the reaction is 0.05—0.30 mg. of (I) per c.c. of COMe₂. (I) can thus be determined. When applied to derris or cube roots the vals. obtained are 50—100% > by the gravimetric method, possibly owing to the presence of deguelin.

E. C. S.

Volumetric determination of furfuraldehyde in pentoses and pentosans. V. S. SADIKOV and K. S. BELIKOVA (Schr. zentr. biochem. Forschungsinst. Nahr.-Genussm., U.S.S.R., 1933, 3, 299—307).—Kullgren and Tyden's volumetric method is as accurate as, and more convenient than, Tollens' gravimetric method.

CH. ABS.

Volumetric determination of 5-bromo-2-furoic acid by bromate. (Miss) E. E. HUGHES and S. F. ACREE (Ind. Eng. Chem. [Anal.], 1934, 6, 292—293).—

This acid is determined by KBrO₃ at 21°, reaction being complete in 8—30 min.

R. S. C.

Determination of hydroxyproline. K. Lang's method. E. WALDSCHMIDT-LEITZ and S. AKABORI (Z. physiol. Chem., 1934, 224, 187—192).—Lang's method (A., 1933, 1064) determines only hydroxyproline (I), not proline (II). The colour reaction obtained with (II) (commercial prep.) is due to (I) present as impurity. The product of the reaction between NaOCl and (I) is not hydroxypyrroline but pyrrole (III), as shown by isolation of the double salt with HgCl₂. (III) is not formed from (II). The production of (III) from (II) is not quant., but if the excess NaOCl is removed by addition of NH₂-acid, preferably glutamic acid, before distillation reproducible yields (about 80% of calc.) of (III) are obtained. The reaction may therefore be used for determination of (I) colorimetrically, employing isatin-H₂SO₄ for large and *p*-NMe₂·C₆H₄·CHO for small amounts of (I). Gelatin contains 8.9—9.4% of (I), caseinogen and clupein none.

J. H. B.

Volumetric determination of methylene-blue and picric acid. A. BOLLIGER (J. Proc. Roy. Soc. New South Wales, 1933, 67, 240).—Dil. aq. solutions of methylene-blue (I) are titrated with picric acid and the sparingly sol. picrate is extracted with CHCl₃. The end-point is when the aq. layer is colourless. One part of (I) in 100,000 can be determined. Solutions of (I) are standardised by treatment with KClO₃, removal of the insol. "methylene-blue perchlorate," and determination of chloride in the filtrate. (Cf this vol., 47.)

C. M. B.

Styphnic acid. V. Its use as a reagent for the identification of alkaloids. P. P. T. SAH, T. S. MA, and V. HOO (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 245—256).—Styphnic acid is recommended as a reagent for alkaloids. The basicity of the alkaloid may be determined by titration of the styphnate with alkali. The following are described: *nicotine*, m.p. 190°; *atropine*, m.p. 180°; *cocaine*, m.p. 187°; *quinine di-*, m.p. 158°; *quinidine di-*, m.p. 149°; *cinchonine di-*, m.p. 106°; *strychnine*, m.p. 266° (decomp.); *brucine*, m.p. 266°; *morphine*, m.p. 189°; *heroin*, m.p. 222°; *dionine*, m.p. 155°; *codeine*, m.p. 115°; *pilocarpine*, m.p. 183°; *caffeine*, m.p. 199°, and *aconitine*, m.p. 120°, *styphnates*. Tables of solubility are given.

H. N. R.

Biochemistry.

Relation of respiration of fishes to environment. I. II. Behaviour of gases in solution. III. Determination of oxygen content and carbon dioxide tension of experimental water. E. B. POWERS. IV. Relation of carbon dioxide and oxygen contents of the blood to the carbon dioxide and oxygen tensions of experimental water. E. B. POWERS, F. G. HOPKINS, and T. A. HICKMAN. V. Effect of oxygen and carbon dioxide tensions of the water on the number of red corpuscles in the blood of the blue catfish. E. B. POWERS and L. M. SHIPE. VI. Oxygen and

carbon dioxide dissociation curves of whole blood. VII. Relation of the *p_H* to the carbon dioxide tension used to modify the blood. E. B. POWERS and T. A. HICKMAN. VIII. Formation of crystals in drawn blood. E. B. POWERS, L. M. SHIPE, and T. A. HICKMAN. IX. Effect of the carbon dioxide tension with which the blood has been equilibrated on the oxygen and carbon dioxide capacities of the blood. E. B. POWERS and T. A. HICKMAN. X. Mechanism of deposition of gases in the swim-bladder. XI. Summary. E. B. POWERS (Ecological Monographs, 1932, 2, 387—

389, 389—394, 394—395, 396—414, 414—420, 421—430, 430—436, 436—438, 438—442, 443—465, 465—467).
CH. ABS.

Determination of oxygen in 1 cu. mm. of blood. J. S. DONAL, jun. (Amer. J. Med. Sci., 1934, 187, 586).—Capillaries containing 1 cu. mm. of blood are broken in vac. and the dried gases passed into a chamber containing a heated W filament where positive ions form at the filament surface. The ions are collected at a negatively-charged electrode. The resulting (amplified) current $\propto [O_2]$ and is independent, over a long range, of the $[N_2]$ and $[CO_2]$. The average difference between corr. vals. and vals. obtained by Van Slyke's method was 0.56 vol.-% (max. 1.9 vol.-%).
CH. ABS.

Occurrence of two kinds of hæmoglobin in normal human blood. R. BRINKMAN, A. WILDSCHUT, and A. WITTERMANS (J. Physiol., 1934, 80, 377—387).—Study of the alkali denaturation of hæmoglobin (I) confirms that there are two kinds of (I) in human blood, the resistant type decreasing from 80% in the newborn to $> 20\%$ in the adult. The two types appear to be independent and not derived the one from the other. The difference is in the globin part of the mol.
NUTR. ABS. (m)

Personal equation in the colorimetric determination of hæmoglobin. M. ODIN and E. WERDINIUS (Acta med. scand., 1934, 81, 239—248).—In hæmoglobin determinations by the Sahli method made by different investigators on the same blood samples very different results are obtained. This is explained chiefly by variations in the time taken to dilute the sample, but a "personal equation" is also involved.
NUTR. ABS. (m)

Hæmoglobinometer without a hæmoglobin comparison standard. W. THIEL (Munch. med. Woch., 1933, 80, 499—500; Chem. Zentr., 1934, i, 254).—The Leitz abs. colorimeter is used with monochromatic radiation.
H. J. E.

Blood-iron and hæmoglobin. C. W. DOWDEN and C. McNEILL (J. Lab. Clin. Med., 1934, 19, 362—367).
CH. ABS.

Determination of hæmoglobin by the iron content method. R. L. HADEN (J. Lab. Clin. Med., 1934, 19, 406—410).—Wong's method gives accurate results.
CH. ABS.

Relation of blood-glutathione to the hæmoglobin and amount of red cells. R. J. PICKARD and C. S. MARSDEN, jun. (J. Lab. Clin. Med., 1934, 19, 395—404).—Blood-glutathione (I) is not quantitatively related to hæmoglobin. (I) is normally 20—30 mg. per 100 c.c.; in non-hæmorrhagic secondary anæmia 24.9; and after severe hæmorrhage 17.1.
CH. ABS.

Globins. III. Specificity of the protein constituent. J. ROCHE, P. DUBOULOZ, and G. JEAN (Bull. Soc. Chim. biol., 1934, 16, 757—768).—The ultra-violet absorption curves and NH_2 -acid composition of the globins of the ox, horse, dog, guinea-pig, man, rabbit, sheep, and pig, although similar, are not identical.
A. L.

Basic amino-acids of three crystalline mammalian hæmoglobins. Basic amino-acid

"Anlage" of tissue-proteins. R. J. BLOCK (J. Biol. Chem., 1934, 105, 663—666).—The mol. proportions of Fe, arginine, histidine, and lysine in horse-, sheep-, and dog-hæmoglobin were approx. const. (1 : 3 : 8 : 9), whilst for Fe, S, and cystine the vals. were 25 : 50 : 7, 25 : 100 : 14, and 25 : 75 : 21, respectively.
H. G. R.

Amino-acid composition of the respiratory pigments of invertebrates. J. ROCHE and G. JEAN (Bull. Soc. Chim. biol., 1934, 16, 769—778).—Determination of the NH_2 -acid composition (I) of the respiratory pigments of *Helix pomatia*, *H. aspersa*, *Octopus vulgaris*, *Eledone moschata*, *Sepia officinalis*, *Carcinus mænus*, *Dromia vulgaris*, *Maia squinado*, *Limulus polyphemus* (II), *Sepunculus nudus* (III), *Spirographis Spallanzanii* (IV), and *Lumbricus terrestris* (V) shows that the hæmocyanins of the Crustaceæ have (I) similar to that of (II), but different from that of the molluscs and the hæmerythrin of (III), which are similar. The (I) of the chlorocruorin of (IV) resembles that of (V), but is markedly different from that of hæmoglobin.
A. L.

Tyrosine and tryptophan contents of globulin and albumin in cows and new-born calves. D. VON DESEO, E. LAMOTH, and L. FODOR (Biochem. Z., 1934, 271, 381—384).—The tyrosine and tryptophan contents of the serum of calves show considerable individual variations and increase during the early stages of development.
P. W. C.

Composition of [serum-]proteins. A. BONOT (J. Chim. phys., 1934, 31, 383—395; cf. this vol., 789).—Serum-proteins of man, horse, dog, and ox have been analysed for total N, total org. S, and arginine (A). The ratio A/S for the total serum-proteins of each species is const. The protein micelle consists of a nucleus of polypeptide chains surrounded by more or less mobile lateral chains.
R. S.

Protein equilibrium of blood-serum. M. PIETTRE (Compt. rend., 1934, 199, 311—313).—Analytical data for myxoprotein (I) are recorded. In successive portions of horse blood drawn at intervals the proportion of serum-globulin (II) and (I) increases somewhat irregularly, whereas that of serum-albumin (III) diminishes slightly. In pathological cases the composition of serum-protein becomes modified; (I) increases and may exceed the sum of (II) and (III).
H. W.

Protein-alcohol mixtures. I. Influence of ethyl alcohol on heat-coagulation of serum-proteins. D. VON KLOBUSITZKY (Biochem. Z., 1934, 271, 385—394).—EtOH decreases the coagulation temp. of neutral fibrin-globulin (I), euglobulin, pseudoglobulin (II), serum-albumin (III), and horse-serum (IV). The abs. and relative effect of EtOH varies with the different proteins and with their concn. and that of EtOH. (I) is more finely dispersed in (IV) than in pure solution, and has therefore a greater stability. Heat-denaturation of (II) and (III) is probably a reversible process.
P. W. C.

Fractional precipitation of serum-proteins with methyl alcohol. S. C. LIU and H. YU (Chinese J. Physiol., 1934, 8, 97—110).—Denatur-

ation occurs when the proteins (I) are pptd. from sera (dog, horse, sheep, ox) at $-1 \pm 1^\circ$ by EtOH or COMe₂, but not with MeOH. Curves of pptn. of N against concn. of MeOH indicate that at approx. 10, 30, and 70% MeOH fractions of (I) corresponding with euglobulin, pseudoglobulin, and albumin, respectively, are pptd., the fractionation being superior to that by MgSO₄. Aq. dilution of the serum to $\times 10$ has no marked effect on the fractionation. The ppts. yield dry undenatured powders on repptn. with MeOH-Et₂O and washing with Et₂O. F. O. H.

Direct nesslerisation method for urea-nitrogen where commercial urease is employed. C. S. SHAPIRO (J. Lab. Clin. Med., 1934, 19, 659—666).—In determining urea-N in protein-free blood-filtrates the urease is removed after incubation by addition of H₂WO₄. The filtrate gives a stable colour with Nessler's reagent. CH. ABS.

Blood studies. VI. Organic constituents over a 12-month period in "laked" and "unlaked" blood filtrates of healthy sheep (Merino) of various ages. P. J. HAMERSMA (Onderstepoort J. Vet. Sci., 1934, 2, 153—128).—In general, the vals. for sugar, non-protein-N, urea-N, creatinine-N, uric acid-N, and NH₂-acid-N are higher in the laked than in the unlaked filtrates. The differences are small in the case of urea-N. Very little creatinine was found in sheep's blood. NUTR. ABS. (b)

Function of the placenta. C. GUTMAN and G. LEVY (Bull. Soc. Chim. biol., 1934, 16, 720—726).—The average vals. for several samples of maternal venous blood-plasma were: dry wt. 85.3, ash 7.97, total fat 7.9, total protein 62.8 g. per litre, the corresponding vals. for the foetus being 64.7, 9.25, 2.6, and 49.1, respectively. A. L.

Lipocrit method for determining blood-lipin. L. G. HERRMANN, A. AMES, and R. J. TAPKE (J. Lab. Clin. Med., 1934, 19, 411—421).—The method is described. Normal blood-lipin, after fasting for 14 hr., is independent of age or sex. CH. ABS.

Determination of blood-cholesterol. II. F. RAPPAPORT and R. KLAPHOLZ (Klin. Woch., 1934, 13, 333—334).—Blood is brought directly into NaOEt-EtOH at 3 atm., when hydrolysis of cholesteryl esters is very rapid and quant. The total cholesterol (I) is then extracted and pptd. with a known amount of digitonin (II), the excess of (II) hydrolysed, the resulting hexose determined by the Hagedorn-Jensen method, and (I) calc. from (II) used for pptn. The amount of blood required is 0.2 ml. if the (I) content is <, and 0.1 ml. if >, 500 mg. per 100 ml. NUTR. ABS. (m)

Effect of oral administration of irradiated ergosterol on blood-cholesterol. R. NAKAE (Nagoya J. Med. Sci., 1933, 7, 88—90). Continued daily oral administration of irradiated ergosterol to rabbits caused a 40% decrease in blood- and serum-cholesterol. Blood-Ca and haemoglobin were unaffected. CH. ABS.

Colorimetric determination of bile acids in body-fluids. Alleged presence in normal blood. L. D. SCOTT (J. Lab. Clin. Med., 1934, 19, 523—539).—An EtOH extract of the urinary ppt. obtained by

saturation with (NH₄)₂SO₄ is treated with Ba(OH)₂ to ppt. pigment. The extract is evaporated to dryness; a reddish-purple colour develops when the residue is treated with fructose and HCl. A solution of Na tauroglycocholate is used as standard. The presence of bile salts in blood-serum is thus demonstrable only in concn. > 5 mg. per 100 c.c.

CH. ABS.

Spectrophotometric investigation and determination of bilirubin. Effect of oxyhaemoglobin. G. E. DAVIS and C. SHEARD (J. Lab. Clin. Med., 1934, 19, 593—608).—Characteristic absorption spectra of serum-bilirubin (I) and -oxyhaemoglobin (II) and of oxygenated solutions of purified haemoglobin are given. Correction of (I) for (II) is described. Min. transmission in the most prominent absorption band is at approx. 453 and 418 mμ, respectively. CH. ABS.

Blood of normal newborn infants. II. Blood-sugar and alkali reserve. A. HOLMAN and A. MATHIEU (Amer. J. Obstet. Gyn., 1934, 27, 95—98).—Average vals. for mothers and babies are, respectively, 100.5, 95.4 mg.; 51.13, 49.72. CH. ABS.

Sugar, residual nitrogen, and alkali reserve of blood of Trakehn foals at different ages. P. LUY and A. KOSER (Arch. wiss. pr. Tierheilk., 1934, 67, 347—357).—The blood-sugar (Hagedorn-Jensen) in foals up to 2 years was 98—145 mg. per 100 ml., most vals. lying between 119 and 127 mg., i.e., > for adult horses (85 mg.). The residual N (Pincussen) of serum averaged 37.6 mg. per 100 ml. shortly after birth, falling later to 22.5 mg. and then remaining at about 29 mg. from weaning onwards. The alkali reserve (Van Slyke) (mean val. 60) in suckling foals was 49—71, in weaned foals 41—74, in yearlings 49—66, and in two-year-olds 47—66. Sex was without influence. NUTR. ABS. (b)

Comparison of blood-sugar curves when glucose is given orally and intraduodenally. E. J. MAGERS (J. Lab. Clin. Med., 1934, 19, 608—611).—No consistent differences were observed. CH. ABS.

Determination of citric acid in blood-serum by Thunberg's method. O. OSTBERG (Skand. Arch. Physiol., 1934, 67, 265—274).—By diluting the serum with aq. citric acid a difference method is obtained in which the influence of interfering substances is practically eliminated. NUTR. ABS. (m)

Determination of lactic acid in blood. E. ERNST and T. TRUKA (Biochem. Z., 1934, 272, 51—55).—Blood-plasma (2.5—3.5 c.c.) diluted with physiological aq. NaCl is treated with aq. Ca(OH)₂ and filtered. 20% aq. ZnSO₄ is added to the filtrate and the mixture is again filtered. The colourless solution obtained is treated with aq. FeCl₃ and the colour compared with that of a standard Li lactate solution. (MgO must be added and the mixture filtered if the solution is to be kept for long before addition of FeCl₃.) Tartaric, citric, β-hydroxybutyric, and oxalic acids do not interfere. W. McC.

Direct micro-determination of the water content of blood. C. HACKMANN and H. J. WOLF (Z. ges. exp. Med., 1933, 88, 96—101; Chem. Zentr., 1934, i, 254).—An ampoule containing blood is broken in

conc. aq. ZnCl_2 in a calorimeter, and the heat effect due to dilution measured. With 30—60 mg. of blood an accuracy of 0.5—1% is attained. H. J. E.

Gravimetric determination of total base in serum and blood. P. M. HALD (J. Biol. Chem., 1934, 105, 675—678).—A correction. The ppt. obtained (this vol., 201) contains a const. amount of occluded benzidine hydrochloride. A method whereby a ppt. of pure benzidine sulphate can be obtained is described. H. G. R.

Effect of inorganic salt intake on the mineral composition of the blood. V. G. HELLER and H. PAUL (J. Biol. Chem., 1934, 105, 655—661).—The changes in Na, K, Ca, Mg, and Cl in animal blood are small and become marked only as death approaches. SO_4^{--} appears to be more easily altered. H. G. R.

Partition of potassium between the serum and corpuscles in health and disease. W. S. HOFFMAN and H. R. D. JACOBS (J. Lab. Clin. Med., 1934, 19, 633—644).—Serum (I)- and erythrocyte-K are const. (19.3 and 422 mg. per 100 c.c., respectively), (I) increasing only in asthma and Bright's disease. K is determined in a protein-free filtrate prepared by treating laked blood with FeCl_3 and alkaline aq. NaOAc . CH. ABS.

Calcium and inorganic phosphorus of sheep's blood. C. H. KICK and D. S. BELL (Proc. Amer. Soc. Animal Prod., 1933, 175—177).—Blood-serum of Shropshire and Merino ewe lambs, during winter, spring, and summer feeding, contained Ca from 10.4 to 12.1 and P from 5.6 to 7.1 mg. per 100 ml. There is a tendency to lower Ca and P on spring pasture without grain, and no sp. breed difference. NUTR. ABS. (m)

Production of anti-sheep hæmolysin. M. BEATTIE (J. Lab. Clin. Med., 1934, 19, 666—667). CH. ABS.

Comparative antigenic studies on ovalbumin denatured by intense audible sound and by other means. E. W. FLOSDORF and L. A. CHAMBERS (Amer. J. Med. Sci., 1934, 187, 294). CH. ABS.

Agglutinins in mother's blood, baby's blood, mother's milk, and placental blood. J. A. TOOMEY (Amer. J. Dis. Children, 1934, 47, 521—528). CH. ABS.

Lipoid haptens. A. J. WEIL. IV. Immunisation experiments with purified haptens from alcoholic extracts of the organs. H. MERCKENS. V. Conditions of adsorption and elution of the antigen from alcoholic extracts of the organs. A. J. WEIL, B. RITZENTHALER, and H. MERCKENS (Z. Immunität., 1933, 78, 308—316, 316—322; Chem. Zentr., 1934, i, 237).—IV. Purification of antigens by pptn. with CdCl_2 and separation from cholesterol by COMe_2 gave active haptens, forming active and sp. sera.

V. Kaolin and $\text{Al}(\text{OH})_3$ will adsorb the antigen from EtOH extracts of the organ. Elution occurs readily with H_2O , aq. NaCl, EtOH, or MeOH. Purified antigen is less readily adsorbed. Further purification of the antigen is possible by repeated adsorption and desorption. H. J. E.

Separation of lipoid haptens by inorganic adsorbents. A. KLOPSTOCK and T. MISAWA (Z. Immunität., 1933, 79, 53—68; Chem. Zentr., 1934, i, 237).—Kaolin, $\text{Al}(\text{OH})_3$, and $\text{Ca}_3(\text{PO}_4)_2$ do not adsorb brain and lecithin haptens from EtOH extracts, but adsorb the Wassermann reaction lipoid hapten. The treatment of organ extracts and lecithin with kaolin entirely stops their activating function for cobra venom. In this case the other adsorbents are less active. H. J. E.

Adsorption of the Forssman heterogenetic hapten and its influence on the power of immunisation. T. MISAWA (Z. Immunität., 1933, 79, 80—98; Chem. Zentr., 1934, i, 238).—This hapten (from horse-kidney extract) is adsorbed by kaolin or collodion suspensions, but no antisera can be produced with the adsorbed antigen in the case of rabbits. Non-sp. antibodies are obtained by using C for adsorption. H. J. E.

[Determination of sugar in] skin. A. RUDY (J. Lab. Clin. Med., 1934, 19, 654—659).—50 mg. are minced and extracted with dil. aq. H_2WO_4 , sugar in the extract being determined by Folin's micro-method for laked blood. CH. ABS.

Glutathione and vitamin-C in the crystalline lens. E. I. EVANS (Nature, 1934, 134, 180—181).—The glutathione (II) content of the cryst. lenses (I) of cattle is approx. 0.330%. (I) contain no free cysteine or cystine. Although the indophenol reagent indicates the presence of much vitamin-C (III) in (I), biological assays point to the presence of small amounts only. An I-reducing substance other than (II) or (III) appears to be present in (I). L. S. T.

Tyrosine and tryptophan content of liver-proteins. O. FÜRTH, H. KAUNITZ, and F. SCHERF (Biochem. Z., 1934, 272, 88—94).—Healthy human liver contains, on the average, 4.6% of tyrosine (I) and 2.6% of tryptophan (II). In diseased livers the (I) content is sometimes very much decreased and the (II) content sometimes altered. In melanotic diseases the melanins appear to increase at the expense of (II), which decreases greatly in amount, (I) remaining unchanged. W. McC.

Adenine nucleotides in tissues. I. In striped muscle of vertebrates and invertebrates. K. LOHMANN and P. SCHUSTER (Biochem. Z., 1934, 272, 24—31).—The adenylic acid of fresh striped muscle of vertebrates (frog, rabbit) and invertebrates (lobster) occurs entirely in highly phosphorylated form (adenyl pyrophosphate). W. McC.

Leather. III. Action of potassium thiocyanate on elastin and collagen. N. I. GAVRILOV. M. M. BOTVINIK, and J. S. MOSKOVA (Biochem. Z., 1934, 272, 56—63).—Collagen (I) is more readily attacked by trypsin (II) than is elastin (III). The hydrolysis of (I) is restricted and its degradation by (II) accelerated by *N*- and 2*N*-KCNS, which, however, restricts the action of (II) on (III), this restriction being also effected by lower cons. (0.1*N*). In the absence of (II) (I) is dissolved by KCNS more readily than is (III). Tanned hide powder (IV) does not dissolve in acid (*N*) or neutral aq. KCNS, and hence the amount of untanned (I) and the rate of action of vegetable tann-

ing materials can be measured. Chrome-tanned (IV) is appreciably attacked by *N*-KCNS only if (II) is added, and the temp. raised to 50°. W. McC.

Origin of sulphur in wool. I. Sullivan technique for cystine. S. D. ROSSOUW and T. J. WILKEN-JORDEN (Onderstepoort J. Vet. Sci., 1934, 2, 361—368).—By regulating the conditions necessary for optimum colour development improvements are achieved, but since numerous substances interfere, the method is sometimes untrustworthy.

NUTR. ABS. (m)

Proteins of eggs from hens on different diets. H. O. CALVERY and H. W. TITUS (J. Biol. Chem., 1934, 105, 683—689).—There was no marked difference in the composition of the proteins of the eggs of hens on diets of wheat, maize, and soya meal. H. G. R.

Effect of variation of p_H on the process of heat-denaturation of ovalbumin. B. M. HENDRIX and P. S. WHARTON (J. Biol. Chem., 1934, 105, 633—642).—The results of Hendrix and Wilson (A., 1928, 1323) and of Booth (A., 1930, 628) indicating a loss of buffering power of ovalbumin (I) on heating at the isoelectric point have been confirmed. Heat-coagulated, unfiltered (I), heat-coagulated dried (I), and EtOH-coagulated (I) show similar titration curves, due probably to a decrease in dissociation of the free acid and basic groups. (I) heated at the isoelectric point has markedly different acid- and base-combining properties from that heated at p_H 3.0 or 7.0.

H. G. R.

Ageing of hen's eggs. A. JANKE and L. JIRAK (Biochem. Z., 1934, 271, 309—323).—During storage of eggs, H_2O is lost by the albumin (I) through the shell, the air chamber at the thick end of the egg increases, and various exchanges occur between yolk (II) and (I). The extent of ageing can be judged by the passage of PO_4''' from (II) to (I), but is best measured in terms of the difference of refractive index of the (II) of the experimental and of a freshly-laid egg.

P. W. C.

Mineral constituents and the freezing point of white and yolk of hens' eggs. J. STRAUB and C. M. DONCK (Chem. Weekblad, 1934, 31, 461—465).—Egg-white (I) contains the following osmotically active constituents expressed as mg. per 100 g. of material: K' 144.0, Na 142.0, Ca⁺⁺ 13.8, Mg⁺⁺ 15.9, Cl' 156.2, HPO_4'' 32.54, HCO_3' 201.1, lactic acid 14, glucose 500. SO_4'' is absent and NH_4^+ and NO_3^- are present only in traces. (I) contains a greater proportion of cations than of anions, agreeing with p_H 8 and isoelectric point p_H 4.7. The lowering of f. p. calc. from the above analysis, 0.435°, agrees with the experimental val. 0.45°. Egg-yolk contains K' 117.4, Na 51.7, Ca 151.3, Mg⁺⁺ 22.3, Cl' 178.0, H_2PO_4' 1787.7, glucose 250; depression of f.p. 0.60° (calc. 1.223°), the difference being due mainly to the H_2PO_4' and glucose organically combined in lecithin. S. C.

Analyses of eggs of fishes in media of differing salt content. T. BUSNITÄ and N. GAVRILESCU (Bull. Acad. Sci. Roumaine, 1932, 15, 208—215).—The eggs of *Alosa pontica* and *Cyprinus carpio* from fresh H_2O contained more ash and less fat (with a lower I val.) than those from brackish and sea- H_2O . The time of

catching has no influence on the composition of the eggs.

H. D.

Chemical composition of *Merlangus vulgaris*. A. J. J. VANDE VELDE and A. DE CLERCQ (Natuurwetensch. Tijds., 1934, 16, 81—83).—The average vals. of the protein, lipin, and ash contents of the flesh, offal, liver, and gonads of whiting in May, January, and November are recorded. The oil obtained from the liver had Wollny refraction val. 76.2, Hübl val. 125, sap. val. 229, and fatty acid val. (Hehner) 87.6 (mean vals. throughout the year).

H. F. G.

Relation between phosphorus and calcium in *Merlangus vulgaris*. A. DE CLERCQ (Natuurwetensch. Tijds., 1934, 16, 84).—The Ca contents of the flesh and offal of whiting vary from 0.10 to 0.14% (on dry wt.) and 1.01 to 1.53%, respectively, and the P contents from 0.12 to 0.22% and 0.56 to 0.77%, respectively. The P : Ca ratio in both cases rises as the wt. of the fish increases; for the flesh the ratio in males is > in females, but for the offal the reverse is true.

H. F. G.

Bound water in muscle. J. BROOKS (J. Gen. Physiol., 1934, 17, 783—790).—Bound H_2O (I) cannot be determined by freezing to -20° , as significant amounts of free H_2O are present; the temp. must be reduced to -40° to -60° . The amount of (I) in muscle at various temp. is small.

H. G. R.

Tissue-water. Its measurement and variations. M. NICLOUX (Bull. Soc. Chim. biol., 1934, 16, 822—864).—The amount of bound H_2O determined by the difference between the concn. of EtOH in the external medium (I) and in the tissue of fish (II) when these are placed in dil. aq. EtOH (0.1—0.5%), expressed as the coeff. $K=100(1-r)/s$, where r is the ratio of the concn. in (II) to that in (I), and s the dry wt.-% of the tissue, is 1.4 for the whole gudgeon, and 1.51, 1.52, and 1.47—1.52 for the muscle of the leech, carp, and frog, respectively. For the protein-tissue of the eel K , which is 1.48, becomes 1.1 when artificial sea- H_2O is used as (I), and for the gudgeon, the vals. 1.3 and 1.2 are obtained when Ringer solution of normal and double concn., respectively, is used. Asphyxiation of the animals decreases K , and heating to 60° and maceration of the tissue reduces K to 1, i.e., the bound H_2O is zero.

A. L.

Pigments from cod eggs. A. EMMERIE, M. VAN EEKELLEN, and L. K. WOLFF (Acta brev. Neerland., 1934, 4, 5—6).—Two different pigments showed absorption bands in the blue; one was probably carotene or a related pigment and the other zeaxanthin or lutein. A third pigment, probably astacene, was isolated from the saponified extract obtained in the first prep.

NUTR. ABS. (m)

Liver pigments of New Zealand oysters and toheroas. N. L. EDSON (New Zealand J. Sci. Tech., 1934, 15, 395—397).—Chemical and physical properties and absorption spectra of the pigments are recorded and compared with those of chlorophyll.

A. G. P.

Carotenoids of the hagfish, *Myxine glutinosa*, and of marine invertebrates. E. LÖNNBERG (Ark Zool., 1934, 26, A, No. 3, 1—3; No. 7, 1—36).—EtOH and Et₂O extracts of the liver and eggs of *M. glutinosa*

contain a carotenoid substance with max. absorption at 456 m μ and 490 m μ , and giving a green colour with the SbCl₃ test. Pigments with exactly similar absorption have been found only in *Anguilla anguilla* and *Raja clavata* amongst fishes; hence the nature of the carotenoids in different fishes is of no taxonomic significance, but depends on the food. The pigment of the invertebrates is extracted with distilled H₂O; it exists as a H₂O-sol. complex, of which the non-carotenoid component can be pptd. with EtOH and is probably largely protein. The absorption max. of the pigment, whether in the H₂O-sol. form or not, lies between 454—460 m μ and 487—493 m μ for all the forms examined, suggesting that it is from the xanthophyll in the food that the pigment of these animals is derived. NUTR. ABS. (m)

Lipochromes of the human body (in storage fat, adrenals, and aorta). J. G. THOMSON (Z. ges. exp. Med., 1934, 92, 692—710).—The lipochrome content (I) of the depot fat of the body varies, the fat of the extremities containing < that over the breast and abdomen. (I) depends primarily on the state of nutrition and increases at the age when a child begins to receive a mixed diet. Since emaciated individuals give a higher val. per g. of fat, particularly after losing a large amount of fat in a short time, it follows that the lipochromes are not utilised with the fat. (I) of the aorta in atheroma of the aorta is ten times, and of the normal adrenal twenty times, the val. for the body-fat, the val. for the adrenal being decreased in septic conditions. The vals. for both organs vary independently of those for the body-fats. NUTR. ABS. (m)

Isolation of the lipochrome from hen- and horse-fat. Human fat. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1934, 225, 189—195).—Carotenoid pigments were isolated from various animal fats; hen, 2 mg. per kg. of xanthophyll; horse, 1.5 mg. of β - (and a trace of α -)carotene; cow, 2 mg. of β -carotene. Human fat-pigment is of the same order. J. H. B.

Coccids produced in Japan. IV. Inorganic matter, carbohydrates, and enzymes of *Cerococcus muratae*, Kuw. V. Nitrogenous compounds and wax of *C. muratae*. M. KONO (J. Agric. Chem. Soc. Japan, 1933, 9, 775—782).—IV. Ash of the shell contains SiO₂ 87.84, Al₂O₃ 0.84, P₂O₅ 2.09, Fe₂O₃ 4.15, MgO 0.79, CaO 4.13, K₂O 4.13%. The insect contains cellulose, lignin, mannan, galactan, dextrin, *d*-mannose, and *d*-galactose, but not chitin or glucose. Cellulase, mannase, amylase, invertase, maltase, and lactase are present.

V. The shell contains 15% of a scleroprotein insol. in H₂O. The N distribution in the wax-free substance after digestion with pepsin is recorded. The wax, m.p. 77—78°, *d*¹⁵ 0.906, acid val. 25.17, sap. val. 212.79, ester val. 187.62, I val. 15.65, Ac val. 110.40, neutral fat 72.96, unsaponifiable matter 15.79, contains cerotic acid, ceryl and isoceryl alcohols, a hydrocarbon, m.p. 47.5°, and an acid, C₁₈H₃₆O₂, m.p. 12—12.5°, b.p. 145°/3 mm. CH. ABS.

Venom of the ornamented snake *Demsonia maculata*. C. H. KELLAWAY (Austral. J. Exp. Biol., 1934, 12, 47—54).—The lethal dose of the venom is

about 0.4 mg. per kg. injected intravenously into rabbits and about 0.6 mg. subcutaneously into guinea-pigs. Its hæmolytic action is relatively weak. W. O. K.

Hæmolysis by Australian snake-venoms. III. Factors which influence the action of the venom of the copperhead. H. F. HOLDEN (Austral. J. Exp. Biol., 1934, 12, 55—61).—The hæmolysis of rabbit's erythrocytes by the venom of *D. superba* is affected by variation of the *p*_H. It is accelerated by the presence of rabbit hæmoglobin, whilst native and denatured ox serum-albumin, caseinogen, and cryst. ovalbumin are inhibitory, decreasing in effect in the order named. W. O. K.

Detoxication of snake venoms and application of the resulting antigens to rapid methods of anti-venomous vaccination and serum production. E. GRASSET and A. ZOUTENDYK (Brit. J. Exp. Path., 1933, 14, 308—317).—Atoxic derivatives of viperine and colubrine venoms, obtained by means of CH₂O, are highly antigenic. CH. ABS.

Occurrence of a pigment related to vitamin-B₂ in cerebrospinal fluid. F. PLAUT and K. BOSSERT (Klin. Woch., 1934, 13, 450—451).—Some pathological and normal cerebrospinal fluids examined in darkness, with light rays which have traversed a filter of CuSO₄ + aq. NH₃ fluoresce, especially when the protein content is low. After addition of alkali, a CHCl₃-sol. substance with green fluorescence, resembling lumiflavin, is obtained from all the fluids. A similar substance is obtained from the fluid of rabbits. Flavin occurs in human and rabbit serum. The pigment is stable to H₂SO₄ and aq. Br; it is partly destroyed by boiling with alkali. NUTR. ABS. (m)

Composition of milk. G. CORNALBA (Latticini, 1934, 11, 31).—The average composition of Lombardy milk is: H₂O, 87.55; fat, 3.75; caseinogen, 2.80; albumin, 0.46; lactose, 4.80; ash, 0.80; total solids, 12.55; solids not fat, 8.80. Fat content is highest in Oct. and Nov. NUTR. ABS. (m)

Human milk during the menstrual period. G. STEINERT and G. PAPP (Orvosi Hetilap, 1934, 78, 38—39).—The milk contains less diastase than usual and inhibits growth of *Lupinus albus*. NUTR. ABS. (m)

Mineral metabolism. XXX. Iodine content of grasses at different stages of growth. Iodine content of milk. I. J. B. BLUM (Onderstepoort J. Vet. Sci., 1934, 2, 139—150).—I determinations made on five pure species of grasses cut at monthly stages of development during 12 months and on three other species, divided into leaf, stem, and flowerhead for separate analysis yielded results showing general seasonal trends in agreement with results of other investigators. In the morning and evening milk of cows all the I is sometimes present in the non-protein portion, but sometimes a considerable proportion is associated with the pptd. proteins. NUTR. ABS. (m)

Spontaneous coagulation of milk and the influence of hydrogen ions. N. L. COSMOVICI (Bull. Soc. Chim. biol., 1934, 16, 899—902; cf. A., 1925, i, 608).—For the spontaneous coagulation (1) o

milk by lactic acid fermentation, the p_H need not fall to 4.6, the isoelectric point of caseinogen. Whilst the p_H of coagulated and heated milk falls to 4.6 on keeping, the val. depends on the time elapsing between (I) and the determination. A. L.

Chemical and physico-chemical changes in milk due to pasteurisation. E. TRIA and C. ZUMMO (Boll. Soc. Ital. Biol. speriment., 1934, 9, 178—180).—The differences between raw and pasteurised milk are very small. Pasteurisation causes a decrease of 1.5% in the ultrafilterable Ca and 2% in the P. Electrical conductivity is increased 0.7%.

NUTR. ABS. (m)

Digestibility of milk *in vivo* as affected by certain physical treatments. F. N. MORTENSON (Iowa State Coll. J. Sci., 1933, 8, 211—212).—Boiled and autoclaved milk left a calf's stomach faster than raw milk, since the curd offered greater surface to the gastric juice. Similar results were obtained for man. The digestion time depends on fatigue, state of health, and individuality. CH. ABS.

Antirachitic activation of milk from the physical and biological viewpoint. G. C. SUPPLEE and M. J. DORCAS (Le Lait, 1934, 14, 1—12, 125—132).—The antirachitic activity of milk is increased and the taste unaffected by ultra-violet radiation. Milk commercially dried after irradiation retains its activity.

NUTR. ABS. (m)

Effect of removing foremilk on the fat content of the remainder of the milking. H. E. ROSS and H. WINTHER (Cornell Univ. Agric. Exp. Sta. Bull., 1934, No. 589, 7 pp.).—Exclusion of the foremilk (3—20 oz.) resulted in a slightly higher fat content (0.05—0.2%) in the remainder of the milking.

A. G. P.

Barium values of butter-fats of different animals. H. ATKINSON (Analyst, 1934, 59, 481—482).—A modified procedure for the determination of the Ba vals. (I) is described. The sap. val., (I), and volatile acid content of goat's, cow's, and gamoos' butter, samna, Indian "butter," coconut oil, and animal fat are given. E. C. S.

Camel's milk-fat. O. LAXA (Ann. Falsif., 1934, 27, 282—285).—The physical consts. are given. The % of volatile acids is unusually low for a ruminant.

E. C. S.

Fatty acids of human duodenal bile, their quantitative separation, determination, and effect of foodstuffs on their secretion. C. W. MCCLURE, M. E. HUNTSINGER, and A. T. FERNALD (Amer. J. Physiol., 1934, 107, 1—12).—The functional activities of the liver are affected differently by different types of foodstuffs. Duodenal bile contains fatty acids (I), both free and as fats and soaps, and org. and inorg. P, all of which reflect the functional activities of the liver. The differences in composition of the total (I) of bile and blood indicate that the lipins of bile are the result of secretory activity, not of mere filtration. The increase of total (I) of blood on feeding fats to man is not merely the result of accumulation in the blood of the recently absorbed (I).

NUTR. ABS. (b)

Substances in juices explain digestive advantages of fish. J. CAMPBELL (Progr. Reps. Atlantic

Biol. Stat. St. Andrews, N.B., 1934, No. 10, 9—10).—The juices from the flesh of herring, salmon, cod, and haddock were fed to a dog. Herring gave the largest vol. of gastric secretion, the others not differing greatly from each other in their effects. Glyoxaline derivatives were found in the flesh of these fish in the following relative amounts: 30:4:1:1, thus apparently explaining the more powerful activity of herring-juice. NUTR. ABS. (b)

Organic bases of fæces. H. BURCHARD (Biochem. Z., 1934, 272, 74—80).—The isolation from the fæces of healthy infants and adults of putrescine (I), cadaverine (II), and γ -butyrobetaine and of (I) and (II) from those of dyspeptic infants is described. Attempts to isolate histamine were unsuccessful.

W. McC.

Presence of lysolecithin in animal tissues in experimental acidosis. B. BRUNELLI (Arch. Farm. speriment., 1934, 58, 88—100).—Lysolecithin is present in large quantities in the brain, liver, and lungs of rabbits in which experimental acidosis has been produced, but only in traces or not at all in the kidneys and heart. R. N. C.

Lipin and amino-acid content of blood-plasma in pernicious anæmia. S. LANG and E. MOSER (Orvosi Hetilap, 1934, 78, 195—196).—The cholesterol and NH_2 -acid content was normal. NUTR. ABS. (b)

Salivary amylase in pernicious anæmia. C. P. EMERSON, jun., and O. M. HELMER (J. Lab. Clin. Med., 1934, 19, 504—506).—No deficiency was observed.

CH. ABS.

Digestion of beef proteins in the human stomach. E. J. MALTBY (J. Clin. Invest., 1934, 13, 193—207).—The rate of peptic digestion (I) varies widely in different individuals and in the same individual under different conditions. Appreciable (I) is absent in pernicious anæmia. Normally gastric contents have p_H 1.23—6.63; in anæmia it was < 5.75.

CH. ABS.

Reaction of arterial blood in cancer. S. DICKINSON and R. E. HAVARD (Brit. J. Exp. Path., 1933, 14, 394—400).—No significant difference was found. Momentary interference with the normal functioning of the respiratory centre may produce alterations in blood- p_H .

CH. ABS.

Tumour-amylase. General properties and determination of activity. F. H. SCHARLES and W. T. SALTER. **Effect of various hormones and chemical agents.** F. H. SCHARLES, P. D. ROBB, and W. T. SALTER (Amer. J. Cancer, 1934, 20, 613—624, 625—629).—(1) Aq. extracts of mouse sarcoma contain a glycogen-cleaving enzyme having optimum p_H 6.2 and temp. (*in vitro*) 48—50°, and destroyed at 60° (1 hr.) or 100° (15 min.). The apparent concn. per 100 c.c. (α -val.) is given by $10 \times \text{antilog. } (0.00175 \times \text{mg.-% of glycogen lost})$. (2) The α -val. of tumour extracts is usually 9—13 per g. of tumour, vals. increasing with age of the tumour. Subcutaneous injection of thyroxine increases, whilst that of insulin decreases and then increases, the α -val. Injection of adrenaline or fasting (24 hr.) has no effect. The activity of the extracts is unaffected by irradiation, or by addition of NaCN or $\text{CH}_2\text{I}-\text{CO}_2\text{Na}$. CH. ABS.

Changes in the serum-esterase and -fat induced by cancer and cancer-producing agents. Determination of fat in blood-serum. H. N. GREEN [with C. N. JENKINSON] (Brit. J. Exp. Path., 1934, 15, 1—14).—During the growth of Jensen rat-sarcoma serum-esterase (I) falls progressively to a very low level; liver-, lung-, and kidney-esterase are also greatly diminished. The fall in serum-phosphatase is less marked. In rats resistant to inoculation of Jensen sarcoma the serum-esterase tends to rise. Serum-fatty acid reaches a max. approaching 2% and then falls during the terminal stages of tumour growth. Rise in cholesterol is much less marked. In tar epitheliomata (mouse) and in localised human carcinomata (I) is normal, with a tendency to rise slightly. In some rabbits the application or inoculation of tar produces a rise in (I). The amount of fat in the serum is the same as that in plasma; hence serum was used for determining the degree of lipæmia. CH. ABS.

Method for testing suitability of substances for chemotherapy of carcinoma. I. II. Vitamins, hormones, and substances influencing blood-clotting. B. LUSTIG and H. WACHTEL (Biochem. Z., 1934, 271, 345—356, 357—369).—I. The power to cytolyse carcinoma (I), sarcoma (II), and normal liver-cells of some 200 substances is investigated *in vitro* in Ringer's solution in presence and absence of serum [normal, (I)]. Some substances, *e.g.*, adrenaline, cytolyse all three types of cell, others, *e.g.*, quinine, only (I) and (II) cells, whilst others, *e.g.*, œstrin and tetradecamethylenedicarboxylic acid, show a strong sp. action on (I) cells. On the other hand, many substances, *e.g.*, heterocyclic NH_2 -acids, protect (I) cells against cytotoxicity. In general, however, the power of substances to cytolyse cancer cells, to inhibit or strengthen the cytolytic action of normal serum, and to inhibit the protective action of maleic acid and of (I) serum do not always run parallel. Cytolytically active substances do not always produce inhibition of growth, but often after a short inhibition bring about accelerated growth.

II. No influence on (I) was obtained in experiments either *in vitro* or *in vivo* with vitamin- B_1 and - B_2 , oxytocin, vasopressin, thyroid extract, male sexual hormone, insulin, histamine, coagulen, and hirudin. Female sexual hormone showed a sp. and adrenaline a non-sp. activity *in vitro*, but no effect *in vivo*. The activity of the other vitamins and hormones is small and they cannot be a primary cause of (I), although they may cause slight variation of the rate of growth. P. W. C.

Halogen balance of blood, cerebrospinal fluid, and urine in patients with convulsive states on bromide-chloride therapy. J. NOTKIN, T. GARCIA, and J. A. KILLIAN (Arch. Neurol. Psych., 1933, 30, 114—122).

Industrial dermatitis. S. G. HORNER (Lancet, 1934, 227, 233—236).—A lecture. L. S. T.

Serum-lipins in diabetic acidosis. E. B. MAN and J. P. PETERS (J. Clin. Invest., 1934, 13, 237—261).

During the acute phase of recovery, serum-cholesterol, -fatty acids, and -lipin-P decreased. CH. ABS.

Carbohydrate production from fat with special reference to diabetes. M. DANN (Yale J. Biol. Med., 1933, 5, 359—372).—The view of non-combustion of carbohydrates during diabetes is supported. CH. ABS.

Changes in total content and osmolar concentration of glucose and chloride after ingestion of glucose in diabetes. F. W. SUNDERMAN and E. S. WILLIAMS (Amer. J. Med. Sci., 1934, 187, 430).—After ingestion of glucose (I) in diabetes serum-(I) increases, whilst -total fixed base and -Cl decrease. CH. ABS.

Distribution of sugar and chloride in the blood in diabetes. E. S. WILLIAMS and F. W. SUNDERMAN (Amer. J. Med. Sci., 1934, 187, 462—469).—In diabetic and normal blood the glucose is approx. equally distributed throughout the H_2O of the corpuscles and serum. Cl distribution between H_2O of cells and serum is also normal. Blood-, corpuscle-, and serum-glucose and -Cl are not consistently related. CH. ABS.

Special behaviour of diabetics during galactose assimilation. L. POLLAK and A. SELINGER (Z. klin. Med., 1933, 124, 321—342; Chem. Zentr., 1934, i, 412).—During treatment with galactose blood-glucose increases, due to a special stimulus of the liver, which is repressed by insulin in normal cases. H. J. E.

Blood-lipins in children with scarlet fever and rheumatic fever. A. D. KAISER and M. S. GRAY (Amer. J. Dis. Children, 1934, 47, 9—24).—The blood-lipin (I) at 5—16 years is const. and > for adults. Normal vals. are: total lipin 427, phospholipin 90, cholesterol 150, and residual fat 139 mg. per 100 c.c. of plasma. In rheumatism and during convalescence from scarlet fever vals. are practically normal. Sex does not affect (I). Vals. are somewhat lower in summer than in winter. CH. ABS.

Iodine content of goitrous thyroid glands. G. M. CURTIS (Anat. Rec., 1934, 58, No. 4, Suppl., 56—57).—There is great variation in the I content of histologically differing portions of goitrous thyroid glands. Diffuse hyperplastic tissue untreated by I has a low content sharply increasing after I treatment. Hæmorrhagic nodules, cyst walls, fibrosed nodules, and oedematous centres of degenerating colloid nodules have a low content. Clear cystic fluid contained 0.1 mg. per 100 ml., colloid nodules 3.8—102 mg. per 100 g. (dry basis). Lingual goitre of a dwarf cretin contained 31.6 mg. per 100 g. (dry basis), and carcinoma of the thyroid occurring within a nodular goitre contained more I than the corresponding non-malignant tissue. NUTR. ABS. (b)

Pressor substances in the blood of hypertensive subjects. O. L. V. S. DE WESSELOW and W. J. GRIFFITHS (Brit. J. Exp. Path., 1934, 15, 45—52).—Pressor substances have not been found. CH. ABS.

Relative effects of diathermy and infection on the plasma-proteins, plasma-viscosity, and suspension stability of blood in dogs. J. K. MOEN, G. MEDES, and I. CHALEK (J. Lab. Clin. Med., 1934, 19, 571—581).—In diathermy and short infection no change was observed; in prolonged infection without

marked rise in body temp. the total protein was increased. Increase in fibrinogen was $>$ that of albumin and globulin. CH. ABS.

Deficiency of vitamin- B_2 as a factor in leprosy. N. K. BASU (Z. Vitaminforsch., 1934, 3, 194—195).—Avitaminosis- B (especially $-B_2$) and protein deficiency appear to be etiological factors in leprosy. Yeast preps. have to some extent a curative action in early cases of anaesthetic leprosy. F. O. H.

Glycogen-storing disease. S. VAN CREVELD (Arch. Dis. Childhood, 1934, 9, 9—26).—In hepatomegalia glycogenica glycogen (I) in the blood (high vals.) shows marked resistance to fission on incubation for 1.5 hr. at 37° , although added (I) is hydrolysed normally. Hypoglycaemia and ketosis appear after fasting; initial insulin hyperglycaemia (II) is absent, and adrenaline does not cause (II). Blood-cholesterol is increased, whilst the ratio cholesterol:cholesteryl ester is normal. The determination of (I) in 1 c.c. of blood is described. CH. ABS.

Enzyme investigation in glycogen-storing disease. W. HERTZ (Klin. Woch., 1933, 12, 1725—1727; Chem. Zentr., 1934, i, 234).—No diastase shortage was observed. The liver-glycogen is not present in a difficultly attacked form. Blood glycolysis is normal. H. J. E.

Metabolism in hepatic diseases. I. Total and non-protein nitrogen. S. NAKAS, Y. KIN, and S. MATSUZAKI. III. Amino-acids. K. TSUSHIMA. IV. Uric acid. H. INOUE (J. Chosen Med. Assoc., 1933, 23, 1758—1786, 1348—1364, 1410—1419).—I. Blood-total N in hepatic disease (except coma and abscess; increase) is low. Ingestion of peptone or gelatin in health or hepatic disorder increases blood- and urinary N, return to normal vals. being more rapid in health. In dogs poisoned with P, or with blocked bile duct, or Eck fistula with ligated hepatic artery, blood-non-protein-N greatly increases.

III. Blood- $\text{NH}_2\text{-N}$ of the healthy Oriental is approx. the same as that of the Occidental, but urinary $\text{NH}_2\text{-N}$ is lower (average 11.82 mg. per 100 c.c.). There is no change in simple jaundice, a slight increase in cancer and cirrhosis of the liver, and a pronounced increase in coma. In hepatic disorders $\text{NH}_2\text{-N}$ vals. become normal after ingestion of protein more slowly than in health. In the dog with ligated bile duct blood- and urinary $\text{NH}_2\text{-N}$ increase. Ingestion of peptone by Eck fistula dogs produces a slight increase in $\text{NH}_2\text{-N}$, but when the hepatic artery is also ligated there is a large increase.

IV. Normal vals. are observed in hepatic disease. In leucemia and advanced cancer of the liver both blood- and urinary uric acid increase. CH. ABS.

Xanthoproteic reaction of the blood in hepatic disorders. H. INOUE (J. Chosen Med. Assoc., 1933, 23, 1178—1188).—Normal human blood has a xanthoproteic val. (Becher) of 14—24 (average 19); in hepatic disease vals. are 12—46 (22). For the normal dog vals. are 12—24 (18). CH. ABS.

Carbohydrate metabolism in obstructive jaundice. S. NISHIGAKI (J. Chosen Med. Assoc., 1933, 23, 550—563). Hypoglycaemia in jaundice is due partly to an increase in blood-bile acids, but chiefly to

hypersecretion of pancreatic hormones and decrease in liver-glycogen. CH. ABS.

Blood-plasma-cholesterol. Fluctuation due to liver injury and bile-duct obstruction. W. B. HAWKINS and A. WRIGHT (J. Exp. Med., 1934, 59, 427—439).—Hypocholesterolaemia (I), with dissociation of the normal ratio of esterified:total cholesterol, is related to chronic liver injury caused by CHCl_3 ; acute CHCl_3 injury may not affect blood-plasma-cholesterol. (I) may develop after prolonged biliary obstruction. CH. ABS.

Bile-cholesterol. Fluctuations due to diet factors, bile salt, liver injury, and haemolysis. A. WRIGHT and G. H. WHIPPLE (J. Exp. Med., 1934, 59, 411—425).—Under uniform diet conditions the normal bile fistula dog eliminates 0.5—1 mg. of cholesterol (I) per kg. in 24 hr. On diets rich in (I) the increase in output is trivial compared with the intake. Bile salt (II) alone raises (I) output $<$ a (I)-rich diet; max. output (60 mg.) is attained with (II), egg-yolk, and whole bile. Liver injury (CHCl_3) decreases (I) and (II) elimination in the bile. Blood destruction (N_2H_4) does not increase bile-(I) output. (I):(II) is normally about 1:100; the ratio is approx. reversed in circulating blood-plasma. CH. ABS.

Bile acids. I. Bile acid content of the blood of patients suffering from hepatic and biliary diseases. II. Effect of food on blood-bile acids. S. BOKU and K. GON (J. Chosen Med. Assoc., 1933, 23, 1075—1096, 1365—1381).—I. Normal vals. are: corpuscles 0.626—4.166 (average 1.298), plasma 1.080—17.856 (5.050), whole blood 0.517—10.629 (2.912) mg. per 100 c.c. In non-hepatic disease, and in hepatic and biliary disease without jaundice, vals. are normal; with jaundice, bile acids increase, but later become normal. In fatal cases they are often subnormal. Urine and cerebrospinal fluid normally contain bile acids (I).

II. Ingestion of any food diminishes blood-(I) except in hepatic and biliary disease. CH. ABS.

Blood-cholesterol and hypometabolism: adrenal and pituitary deficiency, obesity, and miscellaneous conditions. L. M. HURXTHAL (Arch. Int. Med., 1934, 53, 825—831).—Hypometabolism (I) with adrenal or pituitary insufficiency and obesity with (I) are accompanied by normal blood-cholesterol. (I) cannot be ascribed to thyroid failure in absence of hypercholesterolaemia. H. G. R.

Basal metabolism of adipose subjects during dietetic reduction of weight: under-nutrition. V. FORBECH and F. LEEGAARD (Acta med. scand., 1934, 81, 351—394).—The dietary provided 700—800 g.-cal. and contained 50—60 g. of protein, 20—30 g. of fat, and 60—80 g. of carbohydrate (I). The calc. daily metabolism averaged 50—60 g. of protein and 100—120 g. of fat. The (I) metabolism was variable and sometimes in excess of the intake. From the R.Q. vals. it was concluded that fat was changed into (I) before combustion. The metabolic anomaly causing obesity is an abnormal tendency to convert (I) into fat. The loss of wt. was never due to H_2O elimination.

NUTR. ABS. (b)

"Trypsin-poisoning" in acute pancreatic necrosis: determination of trypsin. J. BAUMANN (Z. ges. exp. Med., 1933, **91**, 120—177; Chem. Zentr., 1934, i, 65).—For the determination of trypsin the solution is diluted in a geometrical series and 1 c.c. of each dilution is kept at 37° for 30 min. with 2 c.c. of 0.1% caseinogen solution (p_H 8.5). Experimental pancreatic necrosis in dogs produced in the blood large quantities of active trypsin which is especially harmful to the kidneys and the liver. L. S. T.

Acetonæmia, and acetonæmia with parturient paresis. C. E. HAYDEN, M. G. FINCHER, and J. SAMPSON (Cornell Vet., 1933, **23**, 368—376).—In cows with (apparent) parturient paresis the blood- and urinary ketonic substances were normal. CH. ABS.

Pregnant and puerperal blood. II. Nitrogenous compounds. III. Serum-protein. IV. Water. S. KIO (J. Chosen Med. Assoc., 1933, **23**, 1019—1045, 1046—1059, 1060—1065).—II. The N distribution, serum-protein, and H_2O in the blood of the ear and uterine veins in non-pregnant, pregnant, and puerperal rabbits are recorded. CH. ABS.

Thyroid hormone content of the blood in pregnancy. W. NEUWEILER (Arch. Gynakol., 1933, **154**, 326—353; Chem. Zentr., 1934, i, 410).—No increase in the hormone was observed. H. J. E.

Lipæmia of pregnancy. E. M. BOYD (J. Clin. Invest., 1934, **13**, 347—363).—This lipæmia is due almost entirely to increase in plasma-lipins. No change in I val. of fatty acids was observed. CH. ABS.

Mineral content of the blood-serum of cows during pregnancy and after calving and of newborn calves. E. PRIBYL (Klin. Spisy Skoly Zverol. Brno, 1932, **9**, 219—286).—The Ca and inorg. P contents of the blood-serum depend greatly on the contents of those minerals in the food. A few days before and after parturition, the Ca and inorg. P in the blood-serum decrease. The mineral content of the blood-serum of new-born calves before first suckling is lower than that of their dams. The proportion of cations (Ca, Mg, Na, K) to anions (P, Cl, S), expressed in equivs., remains almost unchanged during pregnancy and puerperium. Cations are more prevalent in the blood-serum of cows than in that of new-born calves.

NUTR. ABS. (m)

Electrolyte content of the blood-serum of sheep and goats and of the blood-serum of cows in certain diseases, particularly during pregnancy and in connection with milk-fever. E. PRIBYL (Zverol. Rozpravy. Suppl. Zverol. Obzor, 1933, **7**, 61—70, 73—78).—The blood-serum of healthy sheep and goats contains (in mg. per 100 ml.): Ca, 6.2—8.34; inorg. P, 2.93—10.1; Mg, 1.0—2.74; Na, 195.6—400.0; K, 18.11—28.3; S (inorg. SO_4), 1.16—4.92. The inorg. PO_4 content is higher in young than in adult animals. A decrease in inorg. P accompanies antepartum paralysis, and retention of the placenta. In cows suffering from milk-fever, the level of Ca and inorg. P decreases, whereas the Mg content increases. The predominance of cations (Ca, Mg, Na, K) over anions (Cl, S, P), expressed in milli-equivs. per 100 ml. of blood-serum, increases on recovery. The findings

corroborate Klobouk's theory that milk-fever is Mg narcosis. NUTR. ABS. (m)

Distribution of blood-phosphorus after suppression of renal function. A. ASHLEY and G. M. GUEST (J. Clin. Invest., 1934, **13**, 219—235).—In the dog and rabbit blood-org. PO_4 , inorg. acid-sol. P (ester-P), and non-protein-N increased, whilst -Cl decreased. A reciprocal relationship exists between Cl and phosphoric esters as anions bound to alkali in the cells. CH. ABS.

Endocrine glands and rickets. E. GLANZMANN (Z. Vitaminforsch., 1934, **3**, 167—194).—Rats in which rickets (I) is induced by special diets and by keeping in the dark show definite differences from control animals in the histology of the thyroid (II), thymus, pancreas (III), and adrenal glands (IV). Administration of I or antirachitic therapy prevents the changes in (II), but only the latter prevents or cures (I). (I) is accompanied by a decrease in the area of the islets of Langerhans in (III). With (IV), the increased lipin content disappears on ultra-violet irradiation. The histological abnormalities are not corr. by small doses [e.g., with (IV), < 1000 rat units] of vitamin-D. F. O. H.

Calcium and phosphorus. VI. Treatment of late rickets with viosterol. D. H. SHELLING and K. B. HOPPER (Amer. J. Dis. Children, 1934, **47**, 61—90).—A clinical report. CH. ABS.

Calcium and magnesium content of the brains of normal guinea-pigs, and of those suffering from acute and chronic scurvy. A. MICHAUX (Compt. rend., 1934, **198**, 2285—2287; cf. this vol., 101).—The brain of normal guinea-pigs contains 0.7—2.4 mg. Ca according as the animal varies in wt. from 415 to 709 g. A 749-g. guinea-pig, starved to death, has 0.6 mg. Ca in its entire brain. Ca vals. rise considerably during chronic scurvy, but Mg does not alter appreciably. J. L. D.

Calcium content of the lungs and kidneys of guinea-pigs, normal or suffering from acute or chronic scurvy. A. MICHAUX (Compt. rend., 1934, **199**, 233—235).—In two cases of acute scurvy only, Ca in the lungs was > that observed with normal individuals. In chronic scurvy the Ca content remains normal. In acute cases, Ca in the kidneys is much > normal. H. W.

Rotatory dispersion of the serum of normal and syphilitic rabbits. M. PAIC (Compt. rend., 1934, **199**, 382—384).—There is no essential difference between the rotatory dispersion of normal and syphilitic sera. H. W.

Potentialities of extreme old age. F. G. BENEDICT and H. F. ROOT (Proc. Nat. Acad. Sci., 1934, **20**, 389—393).—A biochemical study of a nonagenarian. H. G. R.

Respiration of animal tissues. F. J. STARE and C. A. ELVEHJEM (Amer. J. Physiol., 1933, **105**, 655—664).—In normal chicks the O_2 uptake of liver, kidney, or brain is about 1000—1500 cu. mm. per g. per hr. Muscle has a much lower uptake (about 230—380 cu. mm.). With the exception of the cerebellum, wnic shows lowered O_2 uptake in vitamin- B_1 -deficient chicks,

there is little change in the respiration of tissues derived from chicks on diets deficient in vitamin-A, -B₁, or -B₂. There is no significant difference in the O₂ uptake of the livers of normal and anæmic rats. The inhibition of respiration by HCN (48—87%) is not affected by avitaminosis. NUTR. ABS. (m)

Normal respiration values of fresh animal tissue. B. KISCH (Biochem. Z., 1934, 271, 420—423).—The mean respiration vals. of slices of various organs (heart, liver, kidney, retina, Jensen sarcoma) of rat, guinea-pig, ox, sheep, pig, and goat are tabulated and discussed. P. W. C.

Energy metabolism and insensible perspiration of Australian aborigines. H. S. H. WARDLAW, H. W. DAVIES, and M. R. JOSEPH (Austral. J. Exp. Biol., 1934, 12, 63—74).—The basal metabolism and H₂O and heat loss by evaporation of Australian aborigines has been investigated and compared with that of whites under similar conditions. W. O. K.

Respiratory exchange of the Australian aborigine. C. S. HICKS, H. O. MOORE, and E. ELDRIDGE (Austral. J. Exp. Biol., 1934, 12, 79—89).—The O₂ consumption and R.Q. have been investigated. A marked sp. dynamic response to ingestion of raw meat-protein is observed. W. O. K.

Nutrition and resistance to cold. J. GIAJA and S. GELINEO (Compt. rend., 1934, 198, 2277—2278).—Resistance of warm-blooded animals to cold is measured by the % loss in wt. of the animal at death; the less is the loss in wt., the less is the resistance. Proteins have no effect on resistance, but sugars have, indicating that the latter influence the heat regulation of the body. J. L. D.

Hyperglycogenæmic curve and its dependence on the spleen. E. S. LONDON and J. B. ENTIN (Z. physiol. Chem., 1934, 225, 279—281).—Glucose orally administered to dogs produces a characteristic transient hyperglycogenæmia (I). After splenectomy, the blood-glycogen is increased and the (I) is prolonged. J. H. B.

Variations of the urea, total non-protein-nitrogen, and chloride concentration in the blood following glucose ingestion. M. BRUGER and I. A. MIRSKY [with S. MEMBER] (J. Lab. Clin. Med., 1934, 19, 474—481).—Ingestion of 100 g. of glucose (I) by 54 fasting subjects [9 with normal, 3 with low (I) tolerance, 6 with renal glycosuria, and the remainder with high or prolonged tolerance curves] produced alterations (in most subjects) in the output of urea. The non-protein-N in most cases varied with the urea clearance. There was also a reciprocal relationship between the Cl content of whole blood (or its plasma) and the concn. of blood-(I). The output of urea and non-protein-N in general was not related to the degree of diuresis produced by (I) administration. This diuresis in normal subjects was more frequent and > in those with a low (I) tolerance. The clearance of non-protein-N (principally urea) may be a compensating mechanism to maintain osmotic relationships which tend to be upset by the ingested (I). NUTR. ABS. (b)

Perfusion of the intestine and glycolysis. F. RATHERY and P. M. DE TRAVERSE (Compt. rend., 1934,

199, 378—380).—Perfusion of a solution of glucose (I) into the vessels of the intestine, except the duodenum, leads to a diminution in the content of (I). Addition of insulin (II) favours glycolysis. Perfusion of the kidney leads to less marked lowering of (I), and addition of (II) is without effect. H. W.

Lactic acid metabolism of the isolated dog's heart. H. ROLSHOVEN (Z. ges. exp. Med., 1933, 90, 225—236; Chem. Zentr., 1934, i, 415).—Either after isolation or *in situ*, the heart is able to absorb lactic acid from arterial blood continuously, and to resynthesise it. In poisoning with cyanide, lactic acid is given up to the blood passing through the heart. H. J. E.

Lactic acid and the metabolism of the heart. E. MARTINI (Boll. Soc. Ital. Biol. sperim., 1933, 6, 395—398; Chem. Zentr., 1934, i, 415).—Little lactic acid is formed in a heart poisoned with CH₂I·CO₂H. Its formation is, however, increased by exercise. H. J. E.

Fat metabolism. X. Degradation of the aliphatic chain. B. FLASCHENTRAGER, K. BERNHARD, C. LOWENBERG, and M. SCHLAFER (Z. physiol. Chem., 1934, 225, 157—167).—*n*-Octanesulphonic acid injected into a dog is largely excreted, 40% being recovered and 83% indicated by S-analysis in the urine. *p*-Toluenesulphonamide is excreted as *p*-sulphonamidobenzoic acid. On blocking the α -C the usual course of oxidation is changed. Thus with α -benzenesulphonmethyldolauric acid, m.p. 52·3° (Ca, Na salts), prepared from α -methylaminolauric acid, m.p. 208—209° (decomp.), the oxidation product is α -benzenesulphonmethyldoadipic acid (I), m.p. 171—173°. (I) was synthesised from α -benzenesulphonamidoacidic acid, m.p. 152—154°. Primary ω -oxidation is here assumed, followed by three β -oxidations. J. H. B.

Digestion of food. II. Calculation of the digestive coefficient of fat. S. SUZUKI (J. Agric. Chem. Soc. Japan, 1933, 9, 803—810).—When x is the digestive coeff. of the solid matter in the diet, and y is the Et₂O-extractive matter resulting from the fat-free diet, $\log y = 0.09345(x - 88.1)$. CH. ABS.

Feeding value of skim-milks from whole milks of different fat contents. T. GLAD (Ugeskr. Landm., 1934, 79, 52—54).—The caloric val. of skim-milk increases by about 22 g.-cal. for each 1% increase in the fat % of the whole milk from which it originates. NUTR. ABS. (m)

Formation of ethyl sulphide [in metabolism]. II. A. A. CHRISTOMANOS (Z. physiol. Chem., 1934, 225, 211—214; cf. A., 1931, 976).—In dogs receiving during consecutive 10-day periods diets of (a) bread (300 g. per day) (b) meat (600 g.), (c) bread (20 g.) + thyreoidin and adrenaline, the Et₂S excretion was lowest on (b) and highest on (c). When the intestinal tract is completely removed, the urinary excretion of Et₂S is still of the same order. This excludes Et₂S production by intestinal fermentation and indicates that it is a product of intermediary metabolism (cf. Wohlgemuth, this vol., 98). J. H. B.

Chemical reactions in muscle. J. K. PARNAS, P. OSTERN, and T. MANN (Biochem. Z., 1934, 272, 64—70).—In muscle pulp containing PO₄''' and NaF

production of NH_3 (I) is inhibited by addition of AcCO_2H or, less effectively, of phosphoglyceric acid (II), but not of lactic or glycerophosphoric acid or Harden and Young's hexose diphosphate. When $\text{CH}_2\text{I}-\text{CO}_2\text{H}$ is present (II) but not the other substances inhibit (I). These results throw light on the succession of chemical reactions in muscle, indicating that a transfer of PO_4''' from mol. to mol. in successive stages of the degradation occurs. The re-synthesis of energy-supplying N compounds in muscle is independent of the higher stages of the sugar degradation.

W. McC.

Effect of heating on the digestibility of unpolished rice. K. NAGASKA (J. Agric. Chem. Soc. Japan, 1933, 9, 1365—1370).—Fresh material was more readily digested by rats than heated (150°) or steamed material. For powdered unpolished rice the difference is small.

CH. ABS.

Digestibility of protein of soya-bean milk. W. H. ADOLPH and Y. L. WANG (Chinese J. Physiol., 1934, 8, 171—178).—The protein of fresh cow's milk (I) is more readily digested *in vitro* by trypsin (II) or (II) + pepsin (III) than is that of soya-bean milk (IV); the latter, however, is more readily hydrolysed by (III). (I) and (IV) have approx. the same optimum p_H for proteolysis. The apparent digestibility by rats is approx. the same [84.9% with (IV) and 86.6% with (I)].

F. O. H.

Blood-plasma-protein regeneration controlled by diet. I. Liver and caseinogen as protein diet factors. R. L. HOLMAN, E. B. MAHONEY, and G. H. WHIPPLE (J. Exp. Med., 1934, 59, 251—267).—When blood-plasma-protein (I) is depleted by bleeding and return of the washed red cells, regeneration of (I) can be controlled by diet; liver-protein, caseinogen, and certain vegetable proteins are effective. The normal dog has a reserve of protein-building material when (I) is depleted.

CH. ABS.

Blood-plasma-protein given intravenously utilised in body metabolism. II. Dynamic equilibrium between plasma- and tissue-proteins. R. H. HOLMAN, E. B. MAHONEY, and G. H. WHIPPLE (J. Exp. Med., 1934, 59, 269—282).—Intravenously injected blood-plasma or ingested plasma-protein is utilised by normal dogs, the former the more completely. A dynamic equilibrium between tissue- and plasma-protein, depending on the physiological needs of the moment, is indicated.

CH. ABS.

Behaviour of cystamine and cysteamine in the animal organism. H. ROBBERS (Arch. exp. Path. Pharm., 1934, 176, 29—34).—Subcutaneous injection of cystamine (I) and of cysteamine (II) (A., 1889, 870) into dogs increases the total S content of the urine. With (I), the increase in alkaline and neutral S is not due to excretion of unchanged (I) or of taurine, but probably of Et_2S . Following injection of (II), an increased excretion of neutral S occurs after 6—7 days, when the alkaline S content has decreased to normal levels; this is due to the readily oxidisable SH.

F. O. H.

Mineral growth of the human foetus. V. JOB SWANSON (Amer. J. Dis. Children, 1934, 302—306). Marked increases in the mineral con-

tent occurs in the 4th lunar month; little change occurs from the 5th to the 8th month, but Ca, P, and Mg increase gradually.

CH. ABS.

Calcium and phosphorus metabolism of rats on omnivorous and vegetarian diets. S. WAN (Chinese J. Physiol., 1934, 8, 179—188).—Rats on a general diet retain more Ca (relative to the body-wt. or the intake) than do rats on a vegetarian diet (I). The difference is less marked when fresh vegetables replace inorg. salts as a source of Ca and P in (I). The relative retentions of Ca and P depend, within certain limits, on the Ca : P ratio of the diet, but satisfactory growth can be obtained with wide variations of this ratio.

F. O. H.

Magnesium and calcium in the blood of sheep and cows. Variations in the levels of blood-magnesium and -calcium with supplementary feeding of magnesium. I. J. CUNNINGHAM (New Zealand J. Sci. Tech., 1934, 15, 414—422).—Drenching sheep with MgSO_4 solution produced a temporary increase in serum-Mg. Simultaneous administration of NaCl caused a somewhat smaller increase at the lower levels of Mg intake. The effect of MgCO_3 was < that of MgSO_4 . The serum-Ca and -Mg in treated sheep were reciprocally related. Addition of MgSO_4 to drinking- H_2O or of dolomite (I) to an ensilage ration increased the blood-Mg of cows, the effect persisting for approx. 14 days. Depression of blood-Ca with (I) administration was < that with MgSO_4 treatment, whereas the increase in Mg was more marked with (I) than with MgSO_4 . Treatment of "grass staggers" with MgSO_4 or (I) is proposed.

A. G. P.

Formation of egg-shells. Production of alkalosis and acidosis by calcium salts. J. P. MCGOWAN (Biochem. Z., 1934, 272, 9—12).—Ca administered as CaCO_3 or as salt of an org. acid causes alkalosis, which subsequently disappears as a result of the interaction, in the epithelial cells of the kidney, of CaCl_2 and NaHCO_3 , the Ca being excreted in the urine as CaCO_3 . Alternatively, in birds, CaCO_3 consumed with the food is deposited on the membranes of the egg by the cells of the egg-shell glands. If the Ca is given as salt of a strong acid (CaCl_2), $\text{Ca}_3(\text{PO}_4)_2$ is produced in the blood and excreted through the intestine. At the same time the acidosis caused is relieved by production and excretion in the urine of NaH_2PO_4 .

W. McC.

Storage of radioactive potassium isotope in animal organs. E. ERNST (Naturwiss., 1934, 22, 479).—Pptn. of the K compounds in various organs in man and animals by means of $\text{Na}_3\text{Co}(\text{CN})_6$ and examination of the radioactivity of the ppt. indicates that the radioactivity is more powerful than that of KCl. There must be, therefore, a concn. of K^{41} in these organs.

A. J.

Diffusion of nitrous oxide, ethylene, and carbon dioxide through human skin during anaesthesia. Determination of nitrous oxide in low concentrations. F. S. ORCUTT and R. M. WATERS (Anesth. and Analges., 1933, 12, 45—47).—The gas is passed through a heated unglazed porcelain tube, and then into 10% aq. KOH, nitrite being determined colorimetrically. Considerable loss of N_2O through the skin

occurs during anaesthesia. This diffusion is much > that of CO_2 and about 20 times as great as that of C_2H_4 .

CH. ABS.

Effects of narcosis on tissue-, organ-, and blood-glutathione. I. KUSHIYAMA (Japan. J. Obstet. Gynecol., 1933, 16, 360—364).—Vals. for normal rabbits are: liver 0.27, intestines 0.197, spleen 0.191, adrenal capsule 0.187, kidney 0.131, ovary 0.131, lungs 0.116, stomach 0.108, thyroid gland 0.102, pancreas 0.098, thymus gland 0.093, bone marrow 0.080, spinal cord 0.076, heart 0.071, brain 0.067, muscle 0.038, blood 0.023%. Inhalation of CHCl_3 increased vals. for heart, kidney, and blood, but decreased other vals. Immediately after Et_2O narcosis vals. for spleen, kidney, heart, and liver increased, but other vals. were unchanged.

CH. ABS.

Toxicological detection of halogenoalkanes (chloroform, carbon tetrachloride, etc.). Detection of these substances in air. KOHN-ABREST (Compt. rend., 1934, 199, 237—239).—The organs are heated on the H_2O -bath with an equal vol. of H_2O containing tartaric acid in a flask through which air is drawn. After passage through 5% AgNO_3 strongly acidified with HNO_3 , the air is led through a SiO_2 tube at 900° and then through acid AgNO_3 , in which a turbidity appears in < 1 hr. More accurate results are obtained by using 150 c.c. of the distillate obtained by the customary treatment of 1 kg. of viscera which also serves to detect CCl_3CHO . The arrangement is also adapted to the examination of air or carbonaceous gases.

H. W.

Influence of minimal narcotic doses on the respiration of erythrocytes. W. FLEISCHMANN and C. S. RAND (J. Gen. Physiol., 1934, 17, 791—795).—The respiration of mammalian erythrocytes *in vitro* is stimulated by low concns. of EtOH , but not affected by $\text{NH}_2\cdot\text{CO}_2\text{Et}$.

H. G. R.

Diurethanes as local anaesthetics.—See this vol., 993.

Effect of barbiturates in experimental nephrosis. W. S. MURPHY and T. KOPPANYI (Proc. Soc. Exp. Biol. Med., 1933, 31, 373—374).—Dogs remained anaesthetised until death, barbital being retained in the blood.

CH. ABS.

Acute barbital poisoning in dehydration and diuresis. T. KOPPANYI, W. S. MURPHY, and S. KROP (Proc. Soc. Exp. Biol. Med., 1934, 31, 451—453).—Dehydration does not prolong, nor diuresis shorten, barbital (I) narcosis in the dog. Intravenous injection of 0.5—1.0% aq. NH_4Cl accelerates urinary excretion of (I).

CH. ABS.

Diuresis. IV. Detection of anti-diuretic substances in blood. H. MARX and K. SCHNEIDER (Arch. exp. Path. Pharm., 1934, 176, 24—28; cf. this vol., 216, 804).—Treatment of human blood (I) with EtOH or MeOH yields an extract containing an anti-diuretic principle (II) [100 c.c. of (I) contain 0.005—0.01 posterior pituitary gland (III) unit]. The content is not affected by drinking, but is increased in nephritis, uraemia, diabetes insipidus, etc. Like the (I) of (III), that of (I) is resistant to heat and is readily adsorbed by silicates, from which it is eluted by alkalis but not by acids.

F. O. H.

Diuresis produced by injection of glucose. Effect on nitrogen balance and metabolism of fixed acids and bases in normal infants. K. F. WOODWARD (Amer. J. Dis. Children, 1934, 47, 513—520).—Glucose diuresis does not cause prolonged depletion of N, Cl, P, Na, or K.

CH. ABS.

Blood- and lymph-glucose in dogs under the influence of lymphagogues. Y. TAKAYANAGI (Nagoya J. Med. Sci., 1933, 7, 27—42).—Lymph: blood-sugar varies between 1.0 and 2.0; the val. is const. for an individual animal. Neither peptone nor thyroid extracts alter this ratio.

CH. ABS.

Experimental hyperglycaemia. K. FUKUDA and Y. TAKAYANAGI (Nagoya J. Med. Sci., 1933, 7, 43—52).—Intravenous injection of peptone did not affect blood-glucose in dogs fasted for 2—5 days, but well-nourished dogs exhibited hyperglycaemia. Apparently liver-sugar comprises two forms, of which only one is mobilised by peptone, and both by adrenaline.

CH. ABS.

Active principle of the amphibian organisation centre. C. H. WADDINGTON, J. NEEDHAM, W. W. NOWINSKI, D. M. NEEDHAM, and R. LEMBERG (Nature, 1934, 134, 103; cf. this vol., 551).—Stages in the purification of the crude extracts are described. Induction of neural tissue results from implantation of 9:10-dihydroxy-9:10-di-*n*-butyl-9:10-dihydro-1:2:5:6-dibenzanthracene and 1:9-dimethylphenanthrene. The naturally-occurring active principle appears to belong to a group of sterol-like compounds.

L. S. T.

Pigeon emesis and drug action. C. C. LIEB and M. G. MULINOS (J. Pharm. Exp. Ther., 1934, 51, 321—326).—Pigeon emesis may be used as a means of standardisation of ergot and digitalis if hyper-sensitive and -resistant birds are first discarded, and if the pigeons are not used more often than once a month.

H. D.

Pigeons in determination of digitalis potency. H. B. HAAG and J. D. WOODLEY (J. Pharm. Exp. Ther., 1934, 51, 360—369).—Discrepancies between the pigeon- and the cat-emesis methods are observed. A method whereby the dil. prep. is slowly administered intravenously until death occurs is described.

H. D.

Respiratory effects of morphine, codeine, and related substances. I. Effect of codeine, *iso*-codeine, *allo*- ψ -codeine and ψ -codeine on respiration of rabbit. II. Effect of dihydro-codeine, -isocodeine, -*allo*- ψ -codeine, and - ψ -codeine. C. I. WRIGHT (J. Pharm. Exp. Ther., 1934, 51, 327—342, 343—352).—I. The min. doses of codeine, *iso*-codeine, and ψ -codeine required to decrease the respiratory activity (I) of the rabbit, as measured by its response to CO_2 , are 1.6—2.4, 2.6—3.9, and 76—98 mg. per kg. of body-wt., respectively. *allo*- ψ -Codeine does not decrease (I) at < the convulsant dose.

II. The min. doses of dihydro-*isocodeine*, -codeine, -*allo*- ψ -codeine, and - ψ -codeine required to decrease (I) are 0.6—1.3, 2.5, 3.1—6.2, 73—127 mg. per kg. of body-wt., respectively. Hydrogenation of codeine reduces its convulsant action.

H. D.

Effect of codeine, dihydrocodeine, and their isomerides on blood-pressure in (a) unanæ-

thetised dogs and (b) anæsthetised cats. R. H. K. FOSTER (J. Pharm. Exp. Ther., 1934, **51**, 153—169, 170—199).—(a) In their action on the blood- and pulse-pressure and on the heart-rate the general effectiveness in decreasing order is codeine (I), dihydroalloy-codeine, dihydrocodeine, dihydroisocodeine, codeine, isocodeine, ψ -codeine, and dihydro- ψ -codeine.

(b) Morphine and (I) produce only a fall in blood-pressure; the above derivatives of (I) produce an initial rise followed by a more prolonged fall. The relation between structure and physiological action is discussed. F. O. H.

Distribution of subcutaneously injected alkaloids in different regions of central nervous system. F. VEIT and M. VOGT (Naturwiss., 1934, **22**, 492—494).—Scopolamine, atropine, mescaline, and quinine are unevenly distributed in the brain of the monkey 15—60 min. after injection, whereas apomorphine and bulbo-capnine are not. H. D.

Surface activity and spasmolytic action. B. VON ISSEKUTZ, M. LEINZINGER, and B. VON ISSEKUTZ, jun. (Arch. exp. Path. Pharm., 1934, **176**, 8—23).—With the isolated rabbit's intestine, most of the alkaloids, local anæsthetics, bile acids, etc. investigated partly or completely inhibited the pendulum motion, tonus, and the paralysis due to BaCl₂ to an extent approx. \propto their surface activity (in Tyrode solution). Fatty acids and saponins behaved anomalously, probably due to their combination with tissue-sterols. The spasmolytic action was independent of the structure and was completely reversible, thus resembling the narcosis of smooth muscle. F. O. H.

Relation between constitution and vasomotor action of pyrazole derivatives. K. HORIUCHI (Sei-i-kwai Med. J., 1932, **57**, No. 9, 1—20).—Pyrazoline causes vasoconstriction (I); pyrazole (II) and pyrazolone (III) are inactive. *N*-Ph derivatives cause (I); 3-Me derivatives of (II) and (III) produce vasodilation. CH. ABS.

Pharmacology and toxicology of benzeneazo-2:6-diaminopyridine (pyridium). R. P. WALTON and E. H. LAWSON (J. Pharm. Exp. Ther., 1934, **51**, 200—216).—Large doses (2.5—100 mg. per kg.) of pyridium, intravenously injected into animals, are well tolerated, the hydrochloride being more toxic than the free base. Oral administration may produce measurable amounts of methæmoglobin, accompanied by decrease in total pigment. F. O. H.

Mode of action of synthalin. Comparison between the action of synthalin and quinine. O. KUNG (Z. ges. exp. Med., 1933, **88**, 42—63; Chem. Zentr., 1934, i, 241).—In non-fasting dogs synthalin (I) increases the secretion of lactic acid 4- to 20-fold, according to the dose. In fasting animals the increase is less regular. Quinine (II) gave only indications of this action. In canine phloridzin diabetes (I) reduces the sugar excretion within 12 hr. A compensating increased excretion follows. Lactic acid excretion decreases. (I) increases the blood glycolysis *in vitro*. The bactericidal action of (I) is considerably > that of (II). H. J. E.

Effect of uric acid on the permeability of the hæmatoencephalic membrane. B. BRUNELLI (Arch. Farm. sperim., 1934, **58**, 60—67).—Injection of uric acid increases the permeability to electro-negative colloids such as neosalvarsan and trypan-blue. R. N. C.

Resorbability of salicyl compounds through the skin. T. BENZINGER and R. WYRSCH (Klin. Woch., 1933, **12**, 1734—1735; Chem. Zentr., 1934, i, 80).—After cutaneous application of salicylic acid 90% appears in the urine as an ester; hence in resorption experiments the ester in the urine must be hydrolysed by heating with HCl. L. S. T.

Comparative pharmacology of the three phosphoric esters of *o*-cresol. M. I. SMITH [with E. F. STOHLMAN (J. Pharm. Exp. Ther., 1934, **51**, 217—236).—In rats, rabbits, cats, and chickens, the mono-ester (I) (Na₂ salt) rapidly produces transient phenol-like symptoms of toxicity, whilst the tri-ester (II) produces no early effects, but a delayed and persistent neurotoxic action; the di-ester (III) (Na salt) has no apparent action. The rates of hydrolysis in blood and tissues give the series (I) > (III) > (II), the enzyme systems thus involved being discussed. F. O. H.

Effect of dinitrophenol fever on the degradation of tissue-proteins. O. FURTH and S. RAPAPORT (Biochem. Z., 1934, **272**, 81—87).—Administration of 2:4-dinitrophenol (I) (5—20 mg. per kg.) to dogs results in loss of wt., great decrease in excretion of urine, increase of urinary excretion of neutral S (II), increase in the ratio (II): total urinary N, and increase in urinary tyrosine. (I) initiates degradation of tissue-proteins. W. McC.

Chronic effect of trinitrotoluene and the effect of alcohol on the transformation of this substance in the body. J. TEISINGER (Arch. Gewerbe-path. Gewerbehyg., 1933, **4**, 491—499; Chem. Zentr., 1934, i, 258).—After taking EtOH (as beer or spirits) the reduction products of C₆H₂Me(NO₂)₃ (I) were detected in the urine of 38 workmen handling (I). H. J. E.

Periodical examination of workers. I. Regular blood test for lead workers. H. SERSON. II. Continuous blood tests for benzene workers. S. MEYER and A. SCHNEIDER. III. Periodical examination of Vienna workers engaged with materials containing benzene, toluene, and xylene. J. ADLER-HERZMARK (Arch. Gewerbe-path. Gewerbehyg., 1933, **4**, 465—479, 480—485, 486—490; Chem. Zentr., 1934, i, 258).—I. Symptoms of poisoning are discussed. Most Pb workers show some symptoms.

II. A series of tests enables the susceptibility of individual workers to C₆H₆ poisoning to be judged.

III. Results of tests are recorded. H. J. E.

Lead poisoning and the detection of lead. H. BOHNENKAMP and W. LINNEWIEH (Deut. Arch. klin. Med., 1933, **175**, 157—169; Chem. Zentr., 1934, i, 254).—0.1 \times 10⁻⁶ g. of Pb in urine was detected by the diphenylthiocarbazon method, which was superior to a spectrographic method. H. J. E.

Normal and pathological lead content of teeth in man and animals. F. PFRIEME (Arch. Hyg.

Bakt., 1934, **111**, 232—242).—Pb is invariably present in the teeth of normal man and animals. In man it increases with age, but no difference was found between the sexes or between city and country dwellers. The Pb content is highest in the dentine, there being only traces in the enamel and none in tartar. In Pb poisoning the Pb content of the teeth is much higher. In animals, the teeth of carnivora contain most Pb, those of herbivora least, whilst those of omnivora (e.g., the pig) are intermediate. In dogs poisoned by oral administration of white lead, there was an increase of Pb in the teeth, the amount present depending on the amount of Pb fed. NUTR. ABS. (b)

Skin diseases caused by arsenical wall-[paper] pigments. I. Storage of arsenical compounds in the animal body. M. OPPENHEIM and P. FANTL (Biochem. Z., 1934, **271**, 332—337).—After several weeks' injection of various As compounds into small animals, it was shown that whereas Na_3AsO_3 and cacodylic acid were chiefly stored in the hair and only a little appeared in the skin, myo- and neo-salvarsan are found chiefly in the skin. P. W. C.

Toxicological detection of mercury. J. MAINGARO (Arch. med. legal, 1933, **12**, 14—18; Chem. Zentr., 1934, i, 426).—Org. matter is removed by acid treatment, Hg being pptd. as HgS , dissolved in aqua regia, and pptd. from HCl on a brass spiral. Finally the Hg is treated with I vapour. The HgI_2 is dissolved in aq. KI, and Hg pptd. as HgS and determined colorimetrically. After removing org. matter the pptd. HgS may be dissolved in $\text{Br-H}_2\text{O}$ and Hg pptd. in presence of NaHSO_3 . H. J. E.

Histochemical detection of mercury. F. TMM (Z. ges. exp. Med., 1933, **88**, 191—195; Chem. Zentr., 1934, i, 254).—The section is first treated with PhBr , Hg being then converted into HgS by H_2S and HCl , and detected ultramicroscopically. H. J. E.

Acid-base balance in pathological conditions. III. Serum-electrolyte changes in acute mercuric chloride poisoning. E. MUNTWYLER, C. T. WAY, and E. POMERENE (Arch. Int. Med., 1934, **53**, 885—890).—Acute HgCl_2 poisoning is accompanied by lowering of Cl^- and total base and an increase in acid (H_3PO_4 , H_2SO_4 , and org. acid). H. G. R.

Toxic action of cations on the cells of various organs cultivated *in vitro*. C. SANNTÉ and J. VERNE (Compt. rend., 1934, **199**, 389—391).—The cells of the liver, kidney, and nerve tissue, cultivated *in vitro*, show a sp. sensibility to the toxic action of metallic chlorides which can be denoted by one or more coeffs. expressing the sp. toxicity for the fibroblasts of an organ and for the functional cells. The epithelium of the kidney is particularly sensitive to Pb and Cu and that of the liver to Zn, Co, and Ni. The low toxicity of Tl is significant for the nerve tissue. The sp. sensibilities are noted for all the chlorides of heavy metals, but disappear with the alkali and alkaline-earth metals, the toxic concns. of which are of the same order for the different tissues. Towards the heavy metals the fibroblasts of different organs exhibit a different sensitiveness. W.

Catalytic action of iron. F. EICHHOLTZ and K. HONECKER (Arch. exp. Path. Pharm., 1934, **176**, 40—

48).—An improved method for determining the catalytic action (I) of Fe in the organism with an error of $\pm 25\%$ is described (cf. this vol., 217). (I) in mice is diminished by Ca and Mg salts to 25—30%, by pituitary preps. to 30%, by adrenaline to 25%, and by As^{III} and As^{V} to 40% of its original val. Insulin and Pb enhance, whilst other hormones and heavy metals, NaCl , KCl , $\text{Na}_2\text{C}_2\text{O}_4$, and $\text{K}_2\text{C}_2\text{O}_4$ do not influence, (I). F. O. H.

Anticalcification activity of cereals. H. CHRISTIANSEN (Biochem. Z., 1934, **271**, 246—249).—Injection into rabbits of extracts of oat meal causes a slight fall in serum-Ca, but a similar fall is obtained on injecting an EtOH extract of glucose after removal of EtOH and dissolution in H_2O , and the effect must not be regarded as due necessarily to the presence of an anticalcification factor. P. W. C.

Comparative toxicity of fluorine compounds. M. C. SMITH and R. M. LEVERTON (Ind. Eng. Chem., 1934, **26**, 791—797; cf. A., 1933, 629).—14 p.p.m. of F, from whatever source (NaF , KF , NH_4F , CaF_2 ; Na, K, and Ba silicofluorides, cryolite), in the diet of rats leaves a mark on the incisors. The effect on growth, food utilisation, and damage to the teeth depends largely on the nature of the salt fed, and may be related to its solubility. E. C. S.

Stimulation of *Fundulus* by hydrochloric and fatty acids in fresh water, and by fatty acids, mineral acids, and the sodium salts of mineral acids in sea-water. J. B. ALLISON and W. H. COLE (J. Gen. Physiol., 1934, **17**, 803—816).—Stimulation of *F. heteroclitus* by mineral acids (I) is dependent on the $[\text{H}^+]$, whereas with *n*-aliphatic acids (II) the potential of the non-polar group is also concerned. (II) increase in efficiency to a limiting val. with the length of the C chain. There is very little difference in the effect of (I) in sea- and fresh H_2O , but a significant difference with (II) owing to the variation of the buffering capacities. Stimulation by salts of (I) depends on the equiv. concn., and, although the threshold is considerably higher, the efficiency is greater. H. G. R.

Acute carbon monoxide poisoning and its treatment. I. II. Inhalation therapy with oxygen and oxygen-carbon dioxide mixtures. III. Therapy of acute carbon monoxide poisoning. K. THIEL (Z. ges. exp. Med., 1933, **88**, 207—231, 233—253, 255—263; Chem. Zentr., 1934, i, 417—418).—I. With dogs arterial blood- CO_2 falls to a min., with a corresponding increase in the blood-sugar (I). Blood-lactic acid (II) also increases.

II. Inhalation of O_2 - CO_2 mixtures by dogs poisoned with CO gave better results than O_2 . The (I) is abnormally high even after complete removal of CO. Changes in (II) and in acidity are recorded.

III. The optimum treatment was intravenous injection of "hexeton" together with inhalation of O_2 - CO_2 mixtures. The effect of lobeline was too transient. H. J. E.

Physiological and bacteriological investigations with ozone. T. KUNZMANN (Zentr. inn. Med., 1933, **54**, 1057—1064; Chem. Zentr., 1934, i, 414).—An O_3 -air mixture decomposes into O_2 at the skin

surface, the O_2 entering the tissue through the sweat. Diffusion of O_2 into the veins occurs, leading to oxidation of org. acids, expulsion of CO_2 , and reduced frequency of respiration. O_3 is less effective in killing bacteria in media containing protein or carbohydrates.

H. J. E.

Actions of radiation. VI. Extension of the statistical theory of biological action of radiation. B. RAJEWSKI and H. DÄNZER. **VII.** H. DÄNZER (Z. Physik, 1934, 89, 412—420, 421—426).—VI. A more general formula is given for destruction of biological objects; this includes a recovery factor.

VII. The formula is applied to a particular case.

A. B. D. C.

Enzymes of *Solanum indicum*. H. TAUBER and I. S. KLEINER (J. Biol. Chem., 1934, 105, 679—682).—*S. indicum* contains a tryptic enzyme and several carbohydrases, including a maltase, an invertase, and a melibiase. There are two types of maltase, one which splits maltose (I) and all α -glucosides (II) and the other which splits certain easily hydrolysable (II) in addition to (I).

H. G. R.

Enzymes of *Bombyx mori*. IV. Blood-phenolases. V. Blood-saccharase and -maltase. VI. Blood-lipases. K. YAMAFUJI (Bull. Agric. Chem. Soc. Japan, 1934, 10, 15—19, 19—23, 57—60).—IV. The phenolases (I) of the blood of *B. mori* have an optimum pH 6.6; the temp. optimum for the oxidase is 40° and for the peroxidase 20° . The activity of (I) is in unhealthy > in healthy worms; it decreases during the larval, cocoon, and pupal stages and then rises rapidly to a max. in the moth stage.

V. The invertase (II) and maltase (III) of *B. mori* have an optimum 6.6. (II) is most active in the fifth larval period, and decreases in the pupal and moth periods, whilst (III) is most active during the cocoon and moth periods.

VI. The hydrolysis of tributyrin by the blood-lipase (IV) of *B. mori* is unimol. with pH 7.7 and 40° as optimal conditions. The activity of (IV) increases from the fifth larval period to a max. during cocoon spinning.

H. D.

Enzyme research as a border region between organic and physical chemistry. W. LANGENBECK (Z. Elektrochem., 1934, 40, 485—487).—A lecture.

E. S. H.

Activation of enzymes. E. WALDSCHMIDT-LEITZ (Z. Elektrochem., 1934, 40, 483—484).—A lecture.

E. S. H.

***o*-Quinones as enzyme models. XIII, XIV.** See this vol., 973.

Oxygen-carrying enzymes. O. WARBURG (Naturwiss., 1934, 22, 441—446).—A lecture.

R. K. C.

Contact and inductive function of oxidation enzymes. M. COPISAROW (Chem. and Ind., 1934, 534—535).—Since metabolic ultra-violet radiation is the result of activity of oxidation enzymes, their function represents a combination of the complementary phases contact and induction. Induction produces isomerisation in the complex mol. groupings of the genes and subsequent rhythmic coagulation of the cell-nuclear colloids leading to chromosome evolution

and cell mitosis. The somatic cell gene-mutation of cancer is due to enzymic depletion.

A. R. P.

Properties of peroxidase and its iron component. F. AXMACHER and H. OELBRACHT (Biochem. Z., 1934, 271, 441—447).—The peroxidase activity of two enzyme preps., (I) crude and (II) seventeen times as active, is followed using both leucomalachite-green and pyrogallol as substrates, and the effect on their activity of a variety of substances investigated. KCNS and $K_4Fe(CN)_6$ inhibited prep. (I) to the same extent as, $K_4Fe(CN)_6$ inhibited prep. (II) more strongly than, and KCNS more feebly than did NaCN. Pyrophosphate, $H_2C_2O_4$, and histamine hydrochloride were inactive, whilst C_5H_5N and nicotine increased the activity of (I) and (II). The active concns. of these substances were of the same order with both (I) and (II).

P. W. C.

Activation by co-enzyme of alcoholdehydrogenase in muscle, liver, and tumour. J. LEHMANN (Biochem. Z., 1934, 272, 144—152).—Horse muscle, guinea-pig liver (I), and mouse sarcoma (II) contain very labile alcoholdehydrogenase, which is active only after addition of co-enzyme. Since (I) and (II) contain other reducing substances appropriate precautions must be taken.

W. McC.

Purification of carboxylase. O. VON SCHOENEBECK (Biochem. Z., 1934, 272, 42—50).—A high degree of purification is attained by dialysis of yeast maceration juice against H_2O , acidification of the dialysate with dil. AcOH, adsorption on $Al(OH)_3$, and elution with Na_2HPO_4 .

W. McC.

Starch. II. Amylose and amylopectin. 2. S. NISHIMURA (J. Agric. Chem. Soc. Japan, 1933, 9, 767—770).—When malt-amylase solution was heated at 70° for 10 min. its amylolytic power decreased markedly. Amylose was hydrolysed more rapidly and completely than amylopectin.

CH. ABS.

Trisaccharide from the pancreatic amylolysis of erythroamylose. M. SAMBO and K. KLEMEN [with A. TEPEZ] (Bull. Soc. Chim. Yougoslav., 1934, 5, 25—30).—A trisaccharide possessing a reducing power 60—70% that of maltose is isolated by fractional pptn. with EtOH and $COMe_2$ from the products of hydrolysis of erythroamylose by pancreatic amylase.

Diastase investigation in the liver. E. H. MAJER (Z. ges. exp. Med., 1933, 90, 665—668; Chem. Zentr., 1934, i, 66).—Diastase investigations on liver pulp show that even after 18 hr. there is an extensive decomp. of glycogen, which is not increased by more extensive breakdown of the liver cells, by freezing, or by treatment with liquid air.

L. S. I.

Effect of ultra-short waves on enzymes. H. KORBER (Oesterr. Chem.-Ztg., 1934, 37, 117—118). The action of diastase on starch is increased by ultra-short waves.

H. D.

Effect of ultra-short waves on bacteria and enzymes of milk. H. KORBER (Oesterr. Chem.-Ztg., 1934, 37, 116—117).—Exposure to ultra short waves (I) for 45 min. decreases the quantity of R in a saline solution. The time of clotting of $m_1 - 18$ reduced by (I).

H. D.

Activation of yeast-invertase by ultra-violet light. G. GORBACH and H. RUESS (Biochem. Z., 1934, 271, 338—344).—Yeast-invertase solutions after irradiation for a short time show increased activity, but only after keeping. Very impure enzyme solutions (yeast autolysates, optimum irradiation 5 min.) show greatest activation, the purer solutions (dialysates, optimum irradiation 2.5 min.) smaller activation, whilst the purest preps. obtained by adsorption and subsequent elution are no longer activatable. The p_H of the enzyme solution has little influence on the activation, the best results being obtained with feebly acid or alkaline solutions. P. W. C.

Synthesis of lactose in the mammary gland. D. MICHLIN and M. LEWITOW (Biochem. Z., 1934, 271, 448—454).—Using minced mammary gland of lactating cows, an enzymic synthesis from glucose and galactose was effected of a disaccharide which was hydrolysed by emulsin and was probably lactose. P. W. C.

Role of iron in glycolysis of animal tissues. F. ZUCKERKANDL, W. FLEISCHMANN, and G. DRUCKER (Biochem. Z., 1934, 271, 435—438).— $\alpha\alpha'$ -Phenanthroline (I) does, but $\alpha\beta'$ -phenanthroline (II) does not, form stable compounds with Fe^{++} , and whereas (I) does, (II) does not, inhibit glycolysis of rat's kidney, liver, and brain tissue. Hæmin-Fe is not attacked by (I), and there must be therefore two types of Fe, one as hæmin necessary for respiration and another necessary for fermentation. Respiration of these tissues is only slightly affected by (I). P. W. C.

Co-enzyme of lactic acid formation. K. LOHMANN (Biochem. Z., 1934, 271, 278—279).—Adenylic acid (I) and creatinephosphoric acid (II) are both inactive, whilst adenylyl pyrophosphate and mixtures of (I) with (II) are active as co-enzymes of lactic acid formation. P. W. C.

Asymmetrase action of emulsin. L. ROSENTHALER (Biochem. Z., 1934, 271, 439—440).—The action of a series of carbonates (Ni, Ca, Ba, Mg, Zn, Co) on the rotation developed when emulsin acts on *dl*-mandelonitrile is recorded. P. W. C.

Structure specificity of esterase models.—See this vol., 849.

Synthesis of esters by castor-seed lipase. L. VELLUZ (Bull. Soc. Chim. biol., 1934, 17, 909—916).—The amount of esterification (I) of primary alcohols by lipase increases with mol. wt. (II), reaching a max. with BuOH. *sec.*-Alcohols are esterified only with difficulty, the *tert.*-group being unaffected. In contrast, (I) is dependent on the length of the C chain (III) and not on the (II) of the acid. With (III) $< C_7$ no (I) takes place. A. L.

Helix enzymes. I. Lipase from the intestinal juice of the vineyard-snail (*H. pomatia*). W. KUNTARA (Z. physiol. Chem., 1934, 225, 169—188).—This intestinal lipase (I) has p_H and temp. optima of 6.3—6.7 and 35°, respectively. The hydrolysis is unimol. The relative rates of fission of various substrates in descending order is: tributyrin, $PrCO_2Me$, *Me dl*-mandelate (II), castor-oil, olive-oil. The *l*-component of (II) is more readily hydrolysed. (I) is inhibited by quinine and NaF, but not by atoxyl.

3 Y*

Albumin and Ca oleate inhibit, *dl*-leucylglycylglycine does not activate. (I) is purified by adsorption on kaolin, which does not materially change its properties, although the p_H optimum is slightly raised (6.9). (I) resembles pancreatic lipase of the vertebrates in its substrate-specificity, and liver-lipase in its response to activators. The (I) of the middle intestinal glands has a p_H optimum of 9.0 and is inhibited by Ca oleate+albumin at p_H 6.7 but not at p_H 9. J. H. B.

Enzymic cleavage of acetylcholine. R. AMMON (Pflüger's Archiv, 1933, 233, 486—491; Chem. Zentr., 1934, i, 400—401).—The action of choline-esterase on acetylcholine and the effect of inhibitors have been studied. Physostigmine (0.001 mg. in 2 c.c.), prostigmine, gynergen, and muscarine inhibit strongly. Adrenaline, strychnine nitrate, and atropine sulphate act at higher concn. H. J. E.

Nuclein metabolism. I. Enzymic fission of yeast-nucleic acid with nucleotidase from rabbit's intestine. II. Enzymic fission of mononucleotides with nucleotidase from the small intestine of the rabbit. III. Splitting of the polynucleotide into mononucleotides with the intestinal enzyme. K. MAKINO (Z. physiol. Chem., 1934, 225, 147—151, 151—154, 154—156).—I. Guanosine, carmine, inosine (I), and uridine (II) were isolated from the products of fission of yeast-nucleic acid by nucleotidase from the small intestine of the rabbit. (I) and (II) are regarded as deamination products of adenosine and cytidine.

II. Fission of guanylic (I) and adenylic acid (II) by intestinal enzymes affords guanosine and inosine, respectively. (II) does but (I) does not yield NH_3 . The main degradation of (II) occurs by way of adenosine (III), since the deamination of (II) but not of (III) is inhibited by PO_4^{+++} .

III. Hydrolysis of yeast-nucleic acid with intestinal enzymes heated at 60° for 5 min. gave guanylic, adenylic, cytosylic (I), and uracylic acid (II). The H_3PO_4 fission was strongly inhibited. (II) probably arises by deamination of (I). J. H. B.

Optimum reaction of rennin. E. LUNDSTEEN (Biochem. Z., 1934, 271, 259—263).—A method is given for the isolated investigation of the enzymic phase of the reaction of rennin with caseinogen, the optimum p_H being 5.4. P. W. C.

Ultra-violet absorption spectrum of pepsin. F. L. GATES (J. Gen. Physiol., 1934, 17, 797—801).—The absorption curve is similar to that of urease and tyrosine, with a max. at 275—280 $m\mu$ and a min. near 250 $m\mu$. H. G. R.

Enzymic histochemistry. VII. Peptidase in eggs of *Psammecinus miliaris*. T. PHILIPSON. VIII. Micro-determination of lipases. D. GLICK (Compt. rend. Trav. Lab. Carlsberg, 1934, 20, No. 4, 8 pp.; No. 5, 6 pp.).—The contents of unfertilised eggs separate on centrifuging into a centrifugal fragment (which consists of two layers and contains most of the mitochondria) and a centripetal fragment which, although five times as large, possesses only an equal peptidase activity. L. D. G.

Action of hydrocyanic acid on maltin and pancreatin. V. ZANOTTI (Boll. Chim. farm., 1934,

73, 524—525).—HCN does not affect the proteolytic enzyme of pancreatin, but paralyzes the saccharifying enzymes of maltin and pancreatin to an extent \propto the amount of HCN for a const. time of action.

T. H. P.

Effect on arginase activity of cysteine, ascorbic acid, dehydroascorbic acid, lactoflavin, and metallic ions. P. KARRER and F. ZEHENDER (Helv. Chim. Acta, 1934, 17, 737—743).— Fe^{II} in larger amount causes a marked, in less amount a slight, increase of arginase (I) action; the action of Fe^{III} is similar, but less pronounced. Ca^{II} and Cu^{II} have little effect in small amount, whereas large quantities are restrictive. Cysteine at p_H 9.3 strongly inhibits the action of (I). The effect is partly compensated by small amounts of Fe^{II} and Fe^{III} , larger quantities of which increase the activity to $>$ twice that of the non-activated enzyme. Ca^{II} and Cu^{II} destroy the activity. Ascorbic acid (II) has a scarcely appreciable effect on the activity of (I), but causes strong activation in presence of Fe^{II} or Fe^{III} . Larger amounts of Ca^{II} or Cu^{II} restrict the system (I)–(II), whilst small amounts of Cu^{II} are not favourable. The action of dehydroascorbic acid is very similar to that of (II), but the influence of Fe^{II} , Fe^{III} , or Ca^{II} is less marked; Cu^{II} is strongly poisonous. Lactoflavin greatly restricts the action of (I) even in presence of Fe^{II} or Fe^{III} . The action of vitamins on enzymic processes is therefore not sp., but can be induced by materials of quite dissimilar nature, e.g., cysteine and metallic ions.

H. W.

Enzymic hydrolysis of creatinephosphoric acid and muscular contraction. K. LOHMANN (Biochem. Z., 1934, 271, 264—277).—The hydrolysis of creatinephosphoric acid (I) to creatine (II) and H_3PO_4 is not the result of the action of a sp. phosphatase, but represents the combined effect of two reactions, 1 mol. adenylyl pyrophosphate (III) first giving 1 mol. adenylic acid (IV) with $2\text{H}_3\text{PO}_4$, (IV) then reacting with 2 mols. of (I) and giving 2 mols. of (II) with regeneration of (III).

P. W. C.

Influence of thiol groups on phosphatase from different sources. A. SCHAFFNER and E. BAUER (Z. physiol. Chem., 1934, 225, 245—248).—Yeast- and kidney-phosphatase are inhibited at their optimum p_H by cysteine. The inhibition of the latter is largely removed by $\text{CH}_2\text{I}-\text{CO}_2\text{H}$.

J. H. B.

A spontaneous enzymic decomposition with negative heat of reaction. O. MEYERHOF and K. LOHMANN (Naturwiss., 1934, 22, 452).—The measured heat of the reaction hexosediphosphoric acid (I) \rightarrow 2-dihydroxyacetonephosphoric acid (II) is -33.5 g.-cal. per g. of (I), and for the reverse reaction it is $+30.5$ g.-cal. The val. for the reaction (I) \rightarrow (II) calc. from $d \log K/dT$ is -63 g.-cal. The discrepancy is probably due to difference in energy content of the components as solid and in ideal solution. R. K. C.

Mechanism of phosphorylation by yeast extracts. A. SCHAFFNER and E. BAUER (Naturwiss., 1934, 22, 464).—Glycerol extracts of dried yeast, although they possess strong phosphatase activity, do not phosphorylate glucose, but on the addition of Mg, hexose diphosphate, cozymase, MeCHO , and redoxase (from orange-pips), all of which are necessary com-

ponents, the titre of PO_4''' decreases. The synthetic activity is partly inhibited by NaF or excess of Mg, and the two enzymes are destroyed at 100° .

R. K. C.

Assimilation of growth substances by yeast from wort. N. NIELSEN (Compt. rend. Trav. Lab. Carlsberg, 1934, 20, No. 1, 17 pp.).—The growth-promoting action of wort is much reduced by shaking with yeast. The growth substance is insol. in Et_2O and is not destroyed by warming with

L. D. G.

Effect of oxygen on the alcoholic fermentation of yeast. F. WINDISCH (Z. ges. Brauw., 1933, 56, 73—74; Chem. Zentr., 1934, i, 69).—A reply to criticism (A., 1933, 428). New respiration inhibition experiments with KCN revealed no reciprocal effect between respiration (I) and fermentation (II). KCN in small concn. (0.0002—0.001M) is without effect, but at higher concns. general poisoning of the yeast occurs, and effects a corresponding inhibition in (I) and (II). O_2 immediately stimulates the fermentative power (III) of yeast. In the case of cells which can show increased growth, (III) lags behind the increasing ability to take up O_2 under aerobic conditions. No conclusions concerning the enzymic relationships between (I) and (II) could be reached.

L. S. T.

Structure of protoplasm. II. Effect of *l*- and *d*-histidine on the fermentation of *Torula utilis*. G. F. GAUSE (Biochem. Z., 1934, 272, 71—73).—The aerobic and anaerobic utilisation of glucose by *T. utilis*, cultivated on a medium containing $(\text{NH}_4)_2\text{SO}_4$ as sole N source, is unaffected by *l*- (0.01—0.1%) but greatly restricted by *d*-histidine (I) (0.001%). The fermentation is likewise restricted by (I), but not by *l*-histidine, but (I) does not appreciably restrict the fermentation when the sole N source of the medium is glycine, presumably because of the presence of an enzyme which combines with glycine.

W. McC.

Effect of monochromatic light on fermentation products of yeasts. R. MURAKAMI (Bull. Utsunomiya Agric. Coll., 1933, No. 3, 29—45).—Max. production of EtOH from koji extract by *Saccharomyces cerevisiae* and *S. ellipsoideus* occurred under light of λ 6130 Å.; that of MeCHO at 4000—5600 Å., and of acids at 4000—5000 Å. Production of acetal and esters was irregular.

CH. ABS.

Influence of viscosity of the medium on alcoholic fermentation. M. NICULESCU (Bull. Soc. Chim. biol., 1934, 16, 903—908).—Increase of the viscosity of the medium by gelatin or salep is without action on the fermentation of glucose by yeast.

A. L.

Fermentation of glyceric acid. A. LEBEDEV (Naturwiss., 1934, 22, 463).— AcCO_2H (I) is formed from glyceric acid in suspensions of yeast in a nutrient salt solution incubated at $32-34^\circ$. The yield of (I) is much increased by addition of Na_2SO_3 and still more by Na_2SO_3 +methylene-blue or Na_2SO_3 +S.

R. K. C.

Reaction between fructose and arsenic acid. A. E. BRAUNSTEIN (Biochem. Z., 1934, 271, 285—291).—The formation of labile esters of H_3AsO_4 and sucrose during fermentation in presence of this acid is not a biochemical but a purely chemical reaction, and occurs w

sucrose, glycerol, and much more rapidly with fructose, but does not occur with glucose, mannose, maltose, arabinose, lactose, galactose, or hexose diphosphate.

P. W. C.

Cozymase. III. Titration curve. K. MYRBACK (Z. physiol. Chem., 1934, 225, 199—210; cf. this vol., 927).—Cozymase in the active condition is monobasic, but on heating at 100° for 1 min. in 0.007*N*-NaOH is transformed into an inactive dibasic acid (animal adenylic acid). On longer heating in alkaline solution a further change occurs in the non-adenylic acid residue (I). In dil. acid solution the hydrolysis is much slower; inactivation is complete when 30% is hydrolysed. The (I) probably contains N and is attached by an amide linking. J. H. B.

Factor-Z of von Euler. H. BORCHARDT and H. PRINGSHEIM (Bull. Soc. Chim. biol., 1934, 16, 736—742; cf. A., 1925, i, 745).—The biocatalyst Z is conc. 100 times by extracting the lipin-free yeast with EtOH, adding H₂O to the extract, evaporating, and treating the aq. residue with AgNO₃ and H₂S. This prep. did not give the reactions for albumins, sugars, aldehydes, or phenols, and did not decolorise Br, but gave the ninhydrin reaction. A. L.

Fat and lipin metabolism of yeast. III. Sterol and fat increase in bottom-fermentation yeast. W. HALDEN (Z. physiol. Chem., 1934, 225, 249—272; cf. A., 1933, 1205).—For a Froberg-type yeast conditions were found for producing a 20-fold increase in lipins (I) and 60-fold in sterols (II). The chief factor is a reduction of the H₂O content of the suspension to < 85%. There is a parallelism in the production of (I) and (II), but on solid media the (II) content increases faster than that of the glyceride fats. The average ergosterol content of (II) was 80%. On agar media there is a rapid production of acid (to approx. 4), the glycogen content remains const., and CHAcMe·OH collects in the agar. J. H. B.

Nitrogen nutrition of yeast. H. PRINGSHEIM and H. BORCHARDT (Bull. Soc. Chim. biol., 1934, 16, 743—748).—Wine yeast, the fermenting action (I) of which had been inhibited by cultivation on media containing naphthionic acid as N source, fermented more quickly on the addition of boiled yeast extract without appreciable growth taking place. The absence of (I) in certain yeasts may be due to the lack of the factor-Z. A. L.

Purine content of yeast. F. M. KUEN and K. PURINGER (Biochem. Z., 1934, 272, 113—118).—For the liberation of purines in fresh or dried yeast hydrolysis with dil. acid (2% H₂SO₄) is the only trustworthy procedure. Purin-N amounts to 1.062—1.067% (equiv. to 13.08% of the total N). W. McC.

Carbon content of dried yeast. V. KOUDELKA (Arh. Hemiji, 1934, 8, 29—35).—The C content of dried yeasts cultivated in various media varies from 41 to 61%, and the N content from 4.4 to 14%. R. T.

Storage of sodium and calcium in the yeast cell. D. L. RUBINSTEIN and H. BURLAKOVA (Biochem. Z., 1934, 271, 324—331).—A yeast cell is able to develop in the absence of Na⁺ and Ca²⁺, but, in the presence of these elements, stores Na to a greater

extent than Ca²⁺, the process being essentially but not completely one of adsorption. P. W. C.

Electric impedance of suspensions of yeast cells. H. FRICKE and H. J. CURTIS (Nature, 1934, 134, 102—103).—The electric impedance of a 63% suspension of yeast cell in NaCl solutions of different concn. is recorded. L. S. T.

Biochemistry of *Penicillium griseo-fulvum*, Dierckx. P. SIMONART (Natuurwetensch. Tijds., 1934, 16, 58—59).—When FeCl₃ reacts with a Czapek-Dox culture medium in which *P. griseo-fulvum* (I) is cultivated at 30° instead of 25° it yields a deep blue, not a purple, coloration. When (I) is grown in a modified Czapek-Dox medium at room temp. a new acid which gives a green coloration with FeCl₃ is formed. 2:5-Dihydroxybenzoic acid is also produced. Two new compounds of unknown structure are formed in the mycelium. H. F. G.

Hydrolysis of the chitinous complex of lower fungi. O. E. MAY and G. E. WARD (J. Amer. Chem. Soc., 1934, 56, 1597—1599).—Prolonged extraction of the fat-free mycelium of *Penicillium javanicum* with boiling 10% NaOH leaves an insol. complex (C 45.04, H 6.38, N 4.34%), hydrolysed (conc. HCl) to glucosamine hydrochloride (I) (=45.5% of total N), humus-like material (II) (=7% N), and sol. non-reducing N compounds (=36.9% N); (II) is formed to the extent of 13% (wt.). (I) is decomposed to the extent of 25% by prolonged boiling with conc. HCl; 0.4% (wt.) of (II) is formed. H. B.

Chemical and physiological properties of kojic acid.—See this vol., 1007.

(a) Action of growth-promoting substances on *Mucorineae*. (b) Action of cryst. vitamin-B₁ and -B₂. (c) Presence of a growth factor in orchid pollinia. W. H. SCHOPFER (Arch. Sci. phys. nat., 1934, [v], 16, Suppl., 23—26, 26—28, 29—30).—Vegetative growth and zygote formation of *Phycomyces blakesleeana* are stimulated by traces of aq. extracts of wheat germ and of orchid pollinia, and cryst. preps. of vitamin-B₁ (C₁₂H₁₇ON₃S) and -B₂ (C₁₇H₂₀O₆N₄). In all cases the growth factor is unaffected by sterilisation with the medium. L. D. G.

Alleged influence of heavy water on mould growth. R. KLAR (Nature, 1934, 134, 104).—The increased growth reported (this vol., 806) is due probably to the presence of org. impurities and not to any stimulating effect of H₂O. L. S. T.

Alcoholic fermentation by *Rhizopus*. F. HEMMI and N. TSUKITARI (J. Agric. Chem. Soc. Japan, 1933, 9, 1371—1381).—*R. delemar*, *R. tritici*, *R. tonkinensis*, *R. oryzae*, *R. japonicus*, and *R. acidus* produce EtOH. When cultivated in koji H₂O, the first three varieties produce more EtOH; addition of CaCO₃ increases the yield of the mould, whilst addition of K₂HPO₄ increases that of EtOH. CH. ABS.

Microbiological examination of the decomposition of forest litter. I. C. STAPP and H. BORTELS (Zentr. Bakt. Par., 1934, II, 90, 28—66).—The distribution and fermentative activities of various organisms (notably *Cytophaga* spp.) are recorded. A. G. P.

Soil respiration. H. ENGEL (Zentr. Bakt. Par., 1934, II, 90, 158—161).—The CO_2 produced per unit area of soil is not necessarily a measure of the activity of soil organisms. Chemical and physical properties of the soil must also be considered. A. G. P.

Bacteria which assimilate nitrogen. I. G. ENDRES (Annalen, 1934, 512, 54—80).—The O consumption of *Azotobacter chroococcum* (I) in presence of glucose and alkali phosphate (p_H 7.3) is very small, but increases rapidly after addition of Ca^{++} almost to a limiting val. Mg^{++} behaves similarly. The occurrence of an alkali-alkaline-earth antagonism in the respiration of (I) indicates that the colloidal portions of the system are brought by a reciprocal action of K^+ , Na^+ , and Ca^{++} , Mg^{++} into a state of optimal activity with regard to swelling and degree of dispersion. With increasing age of (I) the antagonism disappears. The influence of $[\text{H}^+]$ on the substrate affinity is examined. Respiration of (I) in O_2 is much < in air and the restriction is reversible. In O_2 the restriction increases with time. Its magnitude and periodic increase are independent of the nature and concn. of the substrate. The respiratory system of (I) is unusually sensitive to HCN. The effect is reversible and diminishes with increasing glucose content. The degree of restriction in air is > in O_2 . The toxic action of Cu^{++} is of the same order of magnitude as that of HCN; it is irreversible. The respiration is not affected by a certain amount of Cu^{++} beyond which the O consumption diminishes proportionally to increase of Cu^{++} . It appears that Cu^{++} unites with a cell substance to the amount or surface of which the rate of respiration is proportional. Restriction by Cu is much more marked with bacteria which have been placed for a short time under deficiency of O_2 than with those which have always had ample access of O_2 . H. W.

Influence of aerial-earth circuit on biological activities. III. Mechanism of the influence on electrophoresis of *Azotobacter chroococcum*. A. ITANO (Ber. Ohara Inst. Landw. Forsch., 1934, 6, 255—257).—*A. chroococcum* carries a negative charge. The rate of migration is slightly depressed by the presence of excess of Ca salts in the medium (cf. A., 1933, 1207). A. G. P.

Nodule bacteria of *Astragalus sinicus* (Genge). A. ITANO and A. MATSUURA (Ber. Ohara Inst. Landw. Forsch., 1934, 6, 259—267).—The movement of the organism in soil is largely influenced by the moisture content (optimum 18%; nil < 5%), and salt concn. There is a strong chemotactic action between bacteria and Genge seeds. A. G. P.

***Corynebacterium ferreosilicicum* nov. spec.** A. BRUSSOFF (Zentr. Bakt. Par., 1934, II, 80, 162—168).—Organisms isolated from spring- H_2O produce from Fe NH_4 citrate solutions a ppt. of Fe carbonate. In agar culture accumulations of SiO_2 are also formed. A. G. P.

Origin of the deficit of nitrogen in aerobic cultures of microbes. M. LEMOIGNE and R. DESVEAUX (Compt. rend., 1934, 199, 384—386).—With cultures of *B. pyocyaneus* periodic determinations have been made of N, NH_3 , and C in the centrifuged liquid and of N and C in the culture. The deficit of N ob-

served is due to a transformation of NH_3 arising from decomp. of the proteins in the medium. This can be due only to oxidation. H. W.

***Pseudomonas Lindneri-Kluyver*. III. Metabolic balance of aerobic and anaerobic fermentation in inorganic media.** K. SCHREDER, R. BRUNNER, and R. HAMPE (Woch. Brau., 1934, 51, 241—253).—The assimilation from sugar-containing inorg. media under anaerobic conditions was always somewhat > with vigorous aeration. This is due to the increased amount of MeCHO which acts as an inhibitor. The amount of CHAcMe-OH and lactic acid produced is also greater, whilst EtOH , AcOH , and CO_2 diminish. P. G. M.

Mode of action of the dehydrogenating enzymes of lactic acid bacteria. A. BERTHO and B. VON ZYCHLINSKI (Annalen, 1934, 512, 81—88).—The objections raised by Warburg to the authors' conception of the respiratory processes of lactic acid bacilli are groundless, since Warburg's intermediate enzyme from yeast, co-enzyme of horse blood-corpuscles, and yellow-red enzyme from yeast in presence of hexose phosphate do not yield H_2O_2 in absence of HCN and much < the expected amount in its presence. (+)-Lactic acid, EtOH , AcCO_2H , and AcCHO are not oxidised by the isolated Warburg system. Attempts to separate the dehydrase system of *B. Delbrückii* from the substance of the bacteria by plasmolysis and autolysis were fruitless, the activity remaining in the solid residue. H. W.

Lactic fermentation at sub-minimal temperatures for lactic bacteria. E. W. RUNOW (Zentr. Bakt. Par., 1934, II, 90, 17—27).—Conditions influencing the activity of the organisms and the rate of acid production are examined. A. G. P.

Occurrence in bacteria of glucosidases, galactosidases, and enzymes which hydrolyse disaccharides. E. HOFMANN (Biochem. Z., 1934, 272, 133—143; cf. this vol., 927).—Many bacteria contain enzymes which hydrolyse disaccharides and glucosides, and frequently exhibit specificity. Enzymes of sulphatase bacteria (I) attack β -glucosides and β -galactosides, but those of *B. coli* and *B. Delbrückii* contain no β -glucosidase. Enzymes of *B. coli* hydrolyse maltose, but not α -phenylglucoside (II). The amount of the various enzymes in the bacteria varies with the nutrient medium used. Thus enzymes from (I) grown on beer wort with maltose agar hydrolyse α -methylglucoside and (II), but on meat extract with peptone agar only (II) is attacked. W. McC.

Mannitol-producing bacteria isolated from dry sweet potatoes. T. TAKAHASHI and T. ASAI (J. Agric. Chem. Soc. Japan, 1934, 10, 60—66). Mannitol (I) was produced from fructose (80% yield) or sucrose (31% yield) in yeast extract in presence of CaCO_3 . A mucous substance was produced with (I). Glucose affords (I), but chiefly lactic acid.

CH. ABS.

Action of certain bacteria on some simple triglycerides and natural fats, as shown by Nile-blue sulphate. M. A. COLLINS and B. W. HAMMER (J. Bact., 1934, 27, 473—485).—The red colour produced in a series of simple triglycerides (I) (agar disper-

sion) by Nile-blue sulphate decreased in intensity with rising m.p. The corresponding free acids were coloured blue. Hydrolysis of (I) by bacteria as indicated by these colour changes was not appreciably affected by the manner of dispersion of the (I), nor, within limits, by the p_H of the medium. Ease of hydrolysis of simple (I) decreased with rising mol. wt. Triolein was easily hydrolysed. A. G. P.

Types of lipolysis brought about by bacteria as shown by Nile-blue sulphate. M. A. COLLINS and B. W. HAMMER (J. Bact., 1934, 27, 487—496).—Considerable differences in the rate and manner of lipolysis (I) are shown by different species of organisms. In agar dispersions of butter, bacteria effecting uniform (I) with conspicuous lipase diffusion are more likely to cause rancidity than are the less active types. A. G. P.

Proteins of *B. tuberculosis* and the tubercular antibodies. W. SCHAEFER and G. SANDOR (Ann. Inst. Pasteur, 1934, 53, 72—92).—The proteins from a synthetic culture of *B. tuberculosis* cannot be separated from the accompanying lipins without denaturation and each gives rise to a sp. antibody (I). Protein-(I) can be separated by adsorption on defatted bacilli, whereas the lipin-(I) is only partly adsorbed. (I) is sp. when prepared from warm-blooded animals, and will not react with the cold-blooded strain or with *B. paratuberculosis*. Protein-(I) is found in all cases of human tuberculosis (II) and the lipin-(I) in cases of chronic pulmonary (II), but the quantities are very variable. H. G. R.

Bacteria. Complex carbohydrates isolated from the culture medium and its ultrafiltrate after the growth of tubercle bacilli. F. E. HOOPER, A. G. RENFREW, and T. B. JOHNSON (Amer. Rev. Tuberculosis, 1934, 29, 66—72).—*d*-Galactose, *d*-mannose, *d*-arabinose, and a small quantity of uronic acid were isolated. Crystallographic data for the phenylmethylhydrazones of these sugars are recorded. A N- and P-free polysaccharide was prepared by alkaline hydrolysis of the acetylated crude carbohydrate from the protein-free ultrafiltrate. CH. ABS.

Filterability of the tubercle bacillus. H. PLOTZ (Compt. rend., 1934, 199, 387—389).—Certain bacilli can pass through a Chamberland L_2 filter and these cause a mild disease when inoculated into animals. The behaviour of the bacilli in an electric field shows that very few have a much smaller mobility than the remainder, the virulence being less as the mobility is greater. H. W.

Directive influences in biological systems. IV. Lipase actions of type I pneumococci. G. MCGUIRE and K. G. FALK (J. Biol. Chem., 1934, 105, 669—674).—Lipase action (I) of normal and anti-pneumococcus sera was increased with the addition of beef broth (II), (II) cultures of pneumococci (III), and (II) after growth and removal of (III), but was decreased after addition of (III). The ψ -globulin fraction of the antiserum had practically no (I). H. G. R.

Diphtheria toxin and antitoxin. Determination of formaldehyde and methods by which it can be removed from anatoxin. S. SUZUKI

(Kitasato Arch. Exp. Med., 1933, 10, 267—278).—The flocculation-producing substance can be separated from diphtheria toxin by pptn. with EtOH or $(NH_4)_2SO_4$. Flocculation occurs only at a certain concn. of toxin or anatoxin. CH_2O could not be detected in purified anatoxin by the dimedon method. CH. ABS.

Concentration of diphtheria toxin and antitoxin by freezing. A. SALEMBENT and G. LOISEAU (Compt. rend., 1934, 199, 242—244).—The toxin is preserved at -7° until max. congelation has occurred and the liquid portion (I) is removed. A second portion is obtained at -2° and a third portion at room temp. The toxin is almost entirely present in (I). The antitoxin behaves similarly. H. W.

The diphtheria antitoxin-lecithin complex as an antigen. C. E. PICO and F. MODERN (Anal. Asoc. Quim. Argentina, 1934, 22, 11—14).—The effect of diphtheria toxin (I) was reduced by a 4% suspension of lecithin (II) in proportion to the amount of (II) used. Dilution of (II) inhibited its antitoxic effect. The serum of rabbits injected with mixtures of (II) and diphtheria antitoxin (III) pptd. (I) more readily than (II). (II) and (III), injected together or separately, raised the sensitivity to all antitoxins. R. N. C.

Content of reduced glutathione in the organ tissue of rabbits immunised with typhoid bacilli. F. MURATA (Sei-i-kwai Med. J., 1932, 51, No. 10, 63—91).—Reduced glutathione (I) in the liver, spleen, kidney, adrenals, testicles, lungs, heart, bone marrow, and muscle increases when the rabbit is immunised with typhoid bacilli. Immunisation after injury of endothelial cells is followed by considerable increase of (I) in the adrenals, but not in other tissues. The spleen shares in agglutinin production. CH. ABS.

Antivirus and amino-acids. C. A. SAGASTUME and A. A. SOLARI (Rev. fac. cienc. quim., La Plata, 1933, 8, ii, 15—35).—*Staphylococcus aureus* and *Es. coli* grew only slowly in sterile old cultures. Addition of glucose, fructose, lactose, maltose, or sucrose, and particularly alanine or glutamic acid, accelerated growth. Leucine, cystine, glycine, tyrosine, phenylalanine, arginine, and aspartic acid had no effect, whilst tryptophan had an inhibiting action. CH. ABS.

Viruses in relation to the aetiology of tumours. C. H. ANDREWES (Lancet, 1934, 227, 63—69, 117—123).—Lectures. L. S. T.

Protein-free suspensions of viruses. V. Nature and antigenic properties of a highly purified phage. I. J. KLIGLER and L. OLITZKI (Brit. J. Exp. Path., 1934, 15, 14—23).—Adsorption of *B. coli* phage from broth cultures on kaolin followed by elution with 0.01N-aq. NH_3 yields a potent phage relatively free from protein. The residue on the kaolin after repeated elutions has an inhibitive effect on the phage. CH. ABS.

Mechanism of bacteriophage lysis. J. BRONFENBRENNER (Amer. J. Pub. Health, 1934, 24, 398—399).—The primary effect of phage consists in the stimulation of bacterial metabolism. Lysis is a secondary phenomenon occurring as a direct result of imbibition of H_2O . CH. ABS.

Specific agglutination of bacteriophage particles. F. M. BURNET (Brit. J. Exp. Path., 1933, 14, 302—308). CH. ABS.

Anti-phage sera. I. "Percentage law." II. Properties of incompletely neutralised phage. C. H. ANDREWES and W. J. ELFORD (Brit. J. Exp. Path., 1933, 14, 367—376, 376—383). CH. ABS.

Bactericidal properties of ultra-violet-irradiated petrolatum. H. J. SEARS and N. BLACK (J. Bact., 1934, 27, 453—464).—White petrolatum after irradiation (4 hr.) becomes yellow and acquires bactericidal properties, the effect being restricted to certain vegetative forms of organisms. The active substance is probably a H_2O -insol. non-volatile oxidation product. A. G. P.

Influence of animal hormones on time of heading and accumulation of dry substance in oats. T. A. KRASNOSELSKAYA-MAXIMOVA (Bull. Appl. Bot., U.S.S.R., 1933, [iii], No. 3, 161—164).—Introduction of insulin, maserin, prolan, and ovarin into the endosperm of *Avena byzantina* increases vegetative growth and retards reproduction. CH. ABS.

Effect of spleen and various hormones on basal metabolism. I—III. M. TAKAHASHI (Sei-i-kwai Med. J., 1933, 52, No. 3, 104—132, 133—153, 154—161).—I. Spleen (mice) is synergetic with adrenaline; the synergetic substance can be extracted with NaCl solution.

II. Injection of a small amount of insulin is antagonistic, but of larger amounts synergetic, to the spleen. Thyroxine is antagonistic.

III. Pituitrin and pituglandol are antagonistic to the spleen, but hypophorin is synergetic. CH. ABS.

Influence of freezing on the therapeutic activity of glands. Powder preparations of thyroid, adrenal, gastric mucosa, and pancreas. O. BAILLY (J. Pharm. Chim., 1934, [viii], 19, 61—66).—Glands frozen for periods up to six months retain completely their therapeutic activity as indicated by the content of thyroxine-I (thyroid), adrenaline (adrenal), pepsin (gastric mucosa), and trypsin or amylase (pancreas) in derived powder preps. F. O. H.

Blood-lipase and insulin. H. TSUDZUMURA (Pflüger's Arch., 1934, 234, 250—254).—Insulin had no effect on the blood-lipase (I) of the rabbit either *in vitro* or *in vivo* unless hypoglycæmic convulsions were produced. After recovery the (I) returned to normal. The increase during convulsions was attributed to blood concn. Removal of the pancreas had no effect. Neither excess nor deficiency of insulin has a direct effect on (I). NUTR. ABS. (b)

Catalytic action of thyroxine on cell respiration. G. MANSFIELD and G. HORVATH (Naturwiss., 1934, 22, 434).—Thyroxine (I) does not increase the O_2 uptake of organ cell suspensions or slices (Warburg's technique), but in a concn. of 10^{-7} — 10^{-13} it accelerates oxidation in the Thunberg methylene-blue method or the Lipschitz $C_6H_4(NO_2)_2$ method, a necessary preliminary being an anaerobic reaction (not occurring at 0°). If cells are incubated at 37° with (I) in air and then tested by the Warburg method an increase of respiration by 15—60% is observed. (I) also increases

respiration in presence of EtNC or of KCN (yeast). A seasonal lack of susceptibility of rabbit organs was observed in February—April: thyroidectomy restored susceptibility. Anaerobic glycolysis is inhibited by (I), but when an increase in respiration is observed it is accompanied by an increase in formation of NH_3 , whilst after incubation but before oxidation an increase in residual N alone is observed. The catalytic action of (I) on respiration and the anaerobic splitting of protein are parallel. The catalytic action of (I) on respiration is an effect on the cell itself, and the oxidation-accelerating effect is due to the action of protein degradation products which are formed in presence of (I) and in absence of O_2 . R. K. C.

Estimating the functional activity of the thyroid by means of urine or serum. IV. Influence of anterior pituitary lobe. M. L. KOHR (J. Chosen Med. Assoc., 1933, 23, 1274—1281).—The thyroid function of the urine and serum of rabbits receiving daily injections of antuitrin reaches a max. in 3 days. CH. ABS.

Formation of adrenaline in the adrenal gland. Combined or virtual and free adrenaline. J. E. ABELOUS and R. ARGAUD (Compt. rend., 1934, 199, 318—320).—Only a small amount of free (I) and a much larger quantity of masked or virtual (II) adrenaline are present in the adrenal cortex, whereas in the medullary substance the proportion of (II) greatly exceeds that of (I). H. W.

Colloid-chemical action of adrenaline on protoplasm. *Paramecia*. T. WENSE (Arch. exp. Path. Pharm., 1934, 176, 49—58).—Adrenaline ($1 \times 10^{-3}\%$) increases the pulsation time of the vacuoles and the viscosity of the protoplasm of *P. caudatum*. The phenomenon, which does not depend on $[H^+]$ or salt content of the medium and occurs only in the presence of Ca^{++} , is probably due to changes in the colloidal state of the protoplasm. F. O. H.

Influence of adrenaline on chemical changes in isolated frog-muscle. A. H. HEGNAUER and G. T. CORI (J. Biol. Chem., 1934, 105, 691—703).—An increase, which is greater under anaerobic conditions, is observed in lactic acid and hexose monophosphate; neither ergotamine nor insulin antagonises this action. In anaerobic muscle there is a marked decrease in inorg. PO_4''' , but no change in adenosine triphosphate and phosphocreatine. H. G. R.

Effect of adrenalectomy on salt metabolism in rats. M. I. RUBIN and E. T. KRICK (Amer. J. Med. Sci., 1934, 187, 148).—During adrenal insufficiency there is marked loss of Ca, Mg, Na, K, P, Cl, and N from the body, resulting in most cases in a negative balance. CH. ABS.

Content and formation of the melanophore hormone of the human pituitary. A. JORES and O. GLOGNER (Z. ges. exp. Med., 1933, 91, 91—92; Chem. Zentr., 1934, i, 71).—The anterior lobe (I) contains 8 times as much of the melanophore hormone as the remainder. The pigment hormone is formed in the basophilic cells of (I). In man the pars intermedia is not functionally active. A. A. E.

Effect of pituitary products on basal metabolism. Y. ISHIKAWA and M. TAKAHASHI (Sei-i-

kwai Med. J., 1932, **51**, No. 10, 1—22).—Injection into mice of a small quantity of pituitrin reduces CO_2 production and O_2 consumption, but reduces the R.Q.; a larger quantity increases all three. A small quantity of pituglandol in both sexes, or a large quantity in the male, has the same effect as pituitrin; in the female a large quantity has no effect on CO_2 but decreases O_2 and increases R.Q. A still larger injection (0.2 c.c.) increases CO_2 and R.Q., but decreases O_2 . A small quantity of hypophorin has the same effect on the male as that of other drugs; in the female CO_2 and O_2 are scarcely affected, but R.Q. is increased. With a larger quantity CO_2 and O_2 are decreased in both sexes, but R.Q. is decreased in the male and increased in the female. CH. ABS.

Pituitary and anaerobic carbohydrate exchange. J. A. COLLAZO, J. PUYAL, and I. TORRES (Pflüger's Archiv, 1933, **233**, 503—513; Chem. Zentr., 1934, i, 409).—Medium doses of pituitary preps. diminish the lactic acid content of rabbit's blood, due perhaps to a resynthesis of sugar. Large doses produce the opposite effect. There is little effect on the blood-sugar. Pitressin, pituitrin, pitocin, and orasthin act similarly. H. J. E.

Effect of anterior pituitary preparations on growth. H. LUCKE and K. F. KINDLER (Z. ges. exp. Med., 1933, **86**, 130—143; Chem. Zentr., 1934, i, 239).—Dogs, guinea-pigs, and rats, injected with anterior pituitary preps., reached their growth limit more quickly than controls. H. J. E.

Sexual hormone of anterior pituitary from urine of pregnancy. F. HAUROWITZ, M. REISS, and J. BALINT (Z. physiol. Chem., 1934, **225**, 196).—The activation of the hormone on purification (this vol., 117) is doubtful as very variable results are obtained. J. H. B.

Loss of sensitivity to anterior pituitary-like hormone of pregnancy urine. H. SELYE, J. B. COLLIP, and D. L. THOMSON (Proc. Soc. Exp. Biol. Med., 1934, **31**, 487—488). CH. ABS.

Recognition and comparison of prolan and prol-an-like substances. H. M. EVANS, M. E. SIMPSON, and P. R. AUSTIN (J. Exp. Med., 1933, **58**, 561—568).—Prolan-like substances have been recognised in a great variety of conditions; they are widely distributed in serum and urine of non-primates. CH. ABS.

Existence of a follicle-stimulating and of a luteinising hormone in anterior lobe of pituitary body. Z. WALLEN-LAWRENCE (J. Pharm. Exp. Ther., 1934, **51**, 263—286).— COMe_2 -dried pituitary powder from sheep-glands is extracted with aq. NH_3 and pptd. with EtOH, the ppt. is extracted with dil. AcOH, and inert matter is pptd. by aq. NaOH. After adjusting to p_{H} 5 a luteinising fraction (I) which increases the follicular blood supply separates out at -6° . A fraction (II) which stimulates follicular maturation, tubal, uterine, and vaginal development is separated from the supernatant fluid by pptn. with EtOH. CH_2O titration of a mixture of (I) and (II) destroys the action of (I) only. H. D.

Absorption and excretion of folliculin in man. I. Folliculin content of the diet. H. ENG (Bio-

chem. Z., 1934, **271**, 370—377).—The average daily diet of man contains 300—400 mouse units of folliculin (I), and it is probable that the (I) content of the urine and faeces of a normal adult is derived from the diet. P. W. C.

Effect of follicular hormone on the flowering of plants. A. I. VIRTANEN, S. VON HAUSEN, and S. SAASTAMOINEN (Biochem. Z., 1934, **272**, 32—35; cf. this vol., 934).—Since crude or cryst. progynon (I) has no accelerating effect on the flowering of hyacinths or peas, the effect of yeast extract on that of peas cannot be due to the presence of (I). W. McC.

Crystalline hormone from corpus luteum. M. HARTMANN and A. WETTSTEIN (Helv. Chim. Acta, 1934, **17**, 878—882).—Treatment of extract of pig's corpus luteum, freed as far as possible from the follicular hormone, with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot 2\text{HCl}$ followed by decomp. of the disemicarbazone yields the cryst. hormone, $\text{C}_{21}\text{H}_{32}\text{O}_2$ or $\text{C}_{21}\text{H}_{30}\text{O}_2$ (possibly $\text{C}_{22}\text{H}_{34}\text{O}_2$), m.p. $175\text{—}177^\circ$ (corr.) [*dioxime*, m.p. about 240° (corr., decomp.)]. H. W.

Isolation and characterisation of the corpus luteum hormone. A. BUTENANDT and U. WESTPHAL (Ber., 1934, **67**, [B], 1440—1442).—The hormone is a ketone since highly active extracts lose their activity after treatment with $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$. Cautious hydrolysis of the crude mixture of semicarbazones followed by sublimation in vac. gives a mixture which when fractionated yields (1) a physiologically inactive *hydroxyketone*, $\text{C}_{21}\text{H}_{34}\text{O}_2$, m.p. 195° (acetate, m.p. 144.5° ; *oxime*, m.p. 224°), oxidised by cold CrO_3 to a *diketone*, $\text{C}_{21}\text{H}_{32}\text{O}_2$, m.p. 200.5° (*dioxime*, decomp. 254°); (2) a physiologically highly active *diketone* (I), $\text{C}_{21}\text{H}_{30}\text{O}_2$ or $\text{C}_{20}\text{H}_{28}\text{O}_2$, m.p. 128.5° (*dioxime*, m.p. 243°), and (3) a *substance*, m.p. 120° , closely related to (I). H. W.

Vitamin-A value of lucerne cut at different stages of maturity. S. M. HAUGE (J. Assoc. Off. Agric. Chem., 1934, **17**, 304—307).—The vitamin-A (I) val. of young lucerne (II) (10—12 in. high) is $>$ that of (II) in the bloom stage. (I) is conc. mainly in the leaves. (II) products sterilised immediately after cutting had a (I) val. $>$ that of unsterilised (II) either sun-dried or field-cured. E. C. S.

Nutritive value of marine products. VI. Vitamin-A potency of salmon-liver oil. B. E. BAILEY (Contrib. Canad. Biol. Fish., 1934, **8**, No. 21, 267—274).—Salmon-liver oils (from five species) have 2—40 times the activity of cod-liver oil. Skeena Spring varieties are the most and Chum salmon the least potent. NUTR. ABS. (m)

Nutritional value of foodstuffs of the Puerto Rican dietary. IV. Extract of the annatto seed, *Bixa orellana*: preparation and physiological properties. D. H. COOK and J. H. AXTMAYER (Amer. J. Trop. Med., 1934, **14**, 61—75).—EtOH extracts of the crude pigment from annatto seeds are active for rats as a source of vitamin-A (I). Cold extracts are more potent than hot as they contain less inert material. A petrol extract is the most potent, and contains $<$ 1000 Sherman units per g. The pigment in this extract gives the absorption bands of carotene and most of the tests for carotenoids. Cryst.

bixin, obtained from a CHCl_3 extract of the EtOH-extracted pigment, is devoid of (I). When the seeds are fried in lard all (I) passes into the lard. Vitamin-D, probably produced by the action of sunlight on the oily seed coat during drying is also present in the petrol extract. NUTR. ABS. (m)

Biological and colorimetric assay of vitamin-A in Indian fresh-water fish oils. N. C. DATTA and B. N. BANERJEE (Indian J. Med. Res., 1934, 21, 535—544).—The body oils of *ruhee*, *mirgal*, and *dhain*, used as human food in India, contain 5—50% of the vitamin-A content of cod-liver oil. The biological vals. agree fairly well with the "blue vals." NUTR. ABS. (m)

Curative method of vitamin-A assay. M. B. RICHARDS and B. W. SIMPSON (Biochem. J., 1934, 28, 1274—1292).—Discrepancies in vitamin-A (I) assay are due to differing pathological conditions of the animals at the end of the depletion period. These may be far advanced before loss of wt. gives any indication, and may persist after weeks of dosing with large amounts of (I). Restriction of the mother's intake of (I) lowers the health of the offspring in addition to lowering the (I) reserve. H. G. R.

Correspondence between biological and spectrophotometric determinations. A. CHEVALIER and P. CHABRE (Compt. rend. Soc. Biol., 1934, 115, 773—775).—For the application of the spectrophotometric method to the determination of vitamin-A in oils, the absorption at 328 m μ must be sharp, free fatty acids must be $> 1.0\%$, and carotenoid pigments must be absent. The rat unit of the U.S.P. is preferred to the international for vitamin-A, and a figure relating the U.S.P. unit to intensity of absorption at 328 m μ is given. NUTR. ABS. (m)

Comparison of some vitamin-A supplements for chick feeding. M. W. MILLER and G. E. BEARSE (Washington Agric. Exp. Sta. Bull., 1934, No. 292, 19 pp.).—Artificially dried lucerne (I) had double the vitamin-A potency of sun-cured samples even after storage for a year. The vitamin-A contents of (I) and artificially dried grass were similar and approx. 30 times that of yellow maize. A. G. P.

Diet without caseinogen for use in determination of vitamin-A. R. S. MORGAN (Biochem. J., 1934, 28, 1178—1192).—Animals fed on a vitamin-A-deficient diet (Coward, A., 1930, 269), in which the caseinogen is replaced by defatted meat meal and coconut meal (I), show a permanent arrest in growth in 4 weeks. If this diet is supplemented with vitamin-A (II) normal growth occurs. The growth response is related to the dosage of (II) by: $\text{growth} = c + k \log \text{dose}$. The limits of error using (I) are $<$ those using the Coward diet. H. D.

Comparison of extraction methods used for vitamin-A depletion diets for rats. M. L. GINDINGS and H. C. SWIM (J. Nutrition, 1934, 7, 633—646).—Continuous extraction of caseinogen with hot 95% EtOH removes max. amounts of vitamin-A without appreciable losses of vitamin-B, or -B₂. A. G. P.

Effect of vitamin-A on serum-cholesterol. H. J. JUSATZ (Klin. Woch., 1934, 13, 95—97).—Administration of a vitamin-A prep. (12.5 ml. per day for

13—19 days) to rabbits on a diet of autoclaved oats and bran results in a large increase (up to fourfold) in the serum-cholesterol. NUTR. ABS. (m)

Metabolism of carotene: possible role of the reticulo-endothelial system. B. AHMAD (Current Sci., 1934, 2, 477—478).—Mainly a discussion. Colloidal carotene injected into the blood-stream disappears rapidly from the circulation and appears to be localised in the liver and the spleen, and to a smaller extent in the lungs. L. S. T.

Paralysis and avitaminosis-A in swine. G. DUNLOP (J. Agric. Sci., 1934, 24, 435—456).—Rations of barley meal, middlings, and fish meal, or cereals, soya-bean meal, and minerals, are deficient in vitamin-A. Symptoms of paralysis develop when pigs attain approx. 150 lb. live-wt. A. G. P.

Avitaminosis-A and the chemical composition of the animal. L. EMERIQUE (Compt. rend., 1934, 199, 240—242).—In avitaminosis-A mineralisation of the bone proceeds normally until an advanced stage, and calcification then extends to the organs. The composition of the organs changes. H. W.

Effect of mineral oil administration on the nutritional economy of fat-soluble vitamins. II. Vitamin-A factor of yellow maize. III. Vitamin-D of irradiated ergosterol. R. W. JACKSON (J. Nutrition, 1934, 7, 607—616, 617—622).—Mineral oil exerts an inhibitory action on the utilisation of the vitamin-A of yellow maize by rats, but does not affect that of vitamin-D. A. G. P.

Growth and vitamin-A deficiency. J. B. ORR and M. B. RICHARDS (Biochem. J., 1934, 28, 1259—1273).—The loss of wt. in avitaminosis-A is due to the onset of pathological conditions and not to a cessation of growth. Skeletal growth continues while the animal is losing wt. H. G. R.

Vitamin-B in soya bean and the quantitative changes of vitamin-B during fermentation. T. CHACHIN (J. Agric. Chem. Soc. Japan, 1933, 9, 1297—1319).—The quantity of vitamin-B₁ decreased with progress of fermentation, becoming zero after the third month. CH. ABS.

Action of crystalline vitamin-B on *Phycomyces*. W. H. SCHOPFER (Ber. Deut. bot. Ges., 1934, 52, 308—312).—The impurity in certain samples of maltose which accelerated the growth of *P. blakesleeanus* (A., 1931, 1460) is a N compound, resistant to heat and adsorbable by animal C. Addition of vitamin-B₁ (I) and -B₂ (II) to media in which the organism failed to grow induced vigorous development. The action of (I) was much $>$ that of (II). A. G. P.

Pregnant, puerperal, and infant beri-beri. IV. Vitamin-B content of various organs and secretions of rabbits fed on diets deficient in vitamin-B. V. Vitamin-B of liver of very young rabbits. H. SHIN (J. Chosen Med. Assoc., 1933, 23, 423—440, 623—642).—IV. Non-pregnant rabbits show a decrease for liver, brain, and blood, and (less marked) for lung, heart, and urine. Pregnant and puerperal rabbits also show a great decrease, particularly for kidney and liver.

V. The vitamin-B content of livers of rabbits nursed

by a mother fed on the deficient diet for a short time during the puerperium or pregnancy is < that of young nursed by the normally fed mother.

CH. ABS.

Storage of vitamin-A in the liver of the rat. A. B. McCOORD and E. M. LUCE-CLAUSEN (J. Nutrition, 1934, 7, 557—572).—In rats receiving Sherman B diet a definite storage of vitamin-A in the liver is established in the period 54—264 days of age. Increased storage followed immediately on dosage with halibut-liver oil. The concn. of vitamin-A in blood is no indication of the amount stored in the liver.

A. G. P.

Hyperthyroidism and nutrition. I. Vitamin-B and thyroxine. B. SURE and M. E. SMITH (J. Nutrition, 1934, 7, 547—555).—In experimental hyperthyroidism protection is afforded by highly conc. preps. of vitamin-B.

A. G. P.

Quantitative change of liver-glycogen in vitamin-B₁ deficiency. T. ARIYAMA (J. Agric. Chem. Soc. Japan, 1933, 9, 1394—1403).—In pigeons fed on polished rice, McCollum salt mixture, and autoclaved yeast the liver-glycogen (I) increased 1.5—2 times. When the pigeons were fasting (I) was < normal. With administration of active oryzanin increase in (I) did not occur. In vitamin-B₁ deficiency caused by a fatty diet without carbohydrates (I) was normal, and was unaffected by addition of sucrose or EtOH to the diet.

CH. ABS.

Vitamin-B₁ and -B₂ contents of liver extract and brewer's yeast concentrate. D. K. MÜLLER and C. P. RHOADS (J. Exp. Med., 1934, 59, 315—331).—Liver extract powder = 2.5 g. of fresh whole liver daily contains enough vitamin-B₁, but not -B₂, for normal growth of rats. "Vegex" yeast concentrate also required addition of -B₂. Castle's extrinsic, anti-æmic factor is not identical with -B₂.

CH. ABS.

Vitamin-B₂ and a new flavin in ox-kidney extracts. B. C. GUHA and H. G. BISWAS (Current Sci., 1934, 2, 474—475).—A yellowish-red, hygroscopic substance (I) showing strong green fluorescence in H₂O and in acid solutions has been prepared from a conc. aq. extract of ox-kidney by absorption on fuller's earth in acid solution, elution with a mixture of C₅H₅N, MeOH, and H₂O, and purification with picric acid. An impure fraction of (I) produced good growth in vitamin-B₂-deficient rats in daily doses of 0.2—0.3 mg. (I) appears to belong to the lyochrome group of pigments and is named *renoflavin*.

L. S. T.

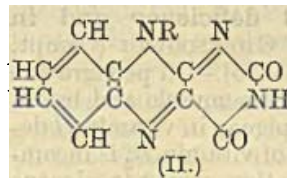
Spectrographic behaviour of photoflavin, alloxazine, and related substances. Influence of the hydrogen-ion concentration and of the two-phase reduction. E. R. HOLIDAY and K. G. STERN (Ber., 1934, 67, [B], 1352—1358).—The absorption spectra of alloxazine (I), the product of the ethylation of tolualloxazine (II), photohepatoflavin (III), and hydroxyquinoxalinecarboxylureide (IV) have been measured as well as those of the intermediate red compounds obtained by reduction of (III) with Na-Hg and of the remainder with CrCl₂. The alteration of light absorption in the (I) series (including the flavins) on transition from the holo- to the semi-quinonoid

stage corresponds with the behaviour of other types of compound at the similar stage of oxidation. The semiquinone has a more complex spectrum than the holoquinone, has a deeper colour, and shows an additional band of longer λ . If reduction is pushed to the H₂-stage, the bands of long λ disappear. In the case of (I) and (II) a small band remains in the ultra-violet. (IV) does not appear to possess sp. absorption.

H. W.

Photoflavins, a group of alloxazine derivatives.

K. G. STERN and E. R. HOLIDAY (Ber., 1934, 67, [B], 1442—1452).—Treatment of alloxan with the hydrochloride of the requisite diaminoxylene in hot H₂O leads to 6 : 7-, m.p. > 340° after darkening at 300°, 6 : 8-, slow decomp. > 300°, and 7 : 8-, m.p. 305—310° (decomp.), -*dimethylalloxazine*. Treatment of alloxazine (I) with Me₂SO₄ at 150—160° or with KMeSO₄ affords 9-methylalloxazine (II, R=Me), decomp. > 320° after darkening at 300° in a



closed tube. (I) and KPr^oSO₄ at 248° yield 9-n-propylalloxazine, m.p. about 290°, whilst 7-methylalloxazine and KEtSO₄ at 250° give 7-methyl-9-ethylalloxazine (III). The alkyl derivatives of (I) and its homologues form a closely related group of substances which differ from the alloxazines in solubility in H₂O, dil. acid, and CHCl₃, in colour, fluorescence, spectrum, and m.p. The proof that the alkyl group is at 9 is indirect. They form electro-active, reversible oxidation-reduction systems. The normal potential is relatively negative and lies in the neighbourhood of the potential of photo-derivatives of flavins. In acid solution, stepwise reduction leads to radical-like, red semiquinones. In behaviour towards alkali they resemble the natural photoflavins; thus (III) and 0.2N-Ba(OH)₂ yield CO(NH₂)₂ and a mixture of pigments sol. in CHCl₃ which can be fractionated by taking advantage of their differing basicity. So long as the identity of the photo-derivatives of the natural flavins and the exact arrangement of the alkyl group in the C₆H₄ nucleus are uncertain, it is proposed to retain the original nomenclature, e.g., lumilactoflavin (IV). The hypothetical parent of the group [the tautomeric form of (I)] is designated norphotoflavin. At present, analyses of natural photoflavins do not indicate the identity of their empirical formula, but they may be regarded as 9-alkylalloxazines. The hypothesis of Kuhn *et al.* that (IV) is a mixture is regarded as improbable, since synthetic mixtures are readily separable into their components. It appears more probable that the attack of alkali occurs in two directions, one leading to elimination of the 9-alkyl and formation of the alloxazine, the other causing fission of the pyrimidine ring. (IV) is probably a xylo-9-methylalloxazine.

H. W.

Distribution of flavins in plants. R. KUHN, T. WAGNER-JAUREGG, and H. KALTSCHMITT (Ber., 1934, 67, [B], 1452—1457).—The plant extract is subjected to a preliminary extraction with CHCl₃ from 0.5N-NaOH, and the alkaline solution is irradiated at > 20°. After 2 hr. the solution is acidified with AcOH, extracted with CHCl₃, and the lumiflavin determined

in the extract with the Pulfrich photometer, and hence the flavin content (I). (I) has been determined for a large no. of plants. Free and combined flavin is determined in green spinach and cow's milk, separation being effected by dialysis. H. W.

Isolation of the lyochrome of yolk of egg (ovo-flavin-g). P. KARRER and K. SCHOPP (Helv. Chim. Acta, 1934, 17, 735—747).—Details are given of the isolation of *ovoflavin-g* (I), $C_{17}H_{20}O_6N_4$, m.p. 284° (corr.), from yolk of egg. (I) closely resembles the other flavins and is possibly identical with one of them. Its properties are not modified by acetylation, chromatographic analysis of the Ac derivative, and subsequent hydrolysis. H. W.

Potassium and sodium content of muscles and brain-tissue in vitamin-B deficiency and in pellagra. L. BALLIF and I. GHESCOVICI (Compt. rend. Soc. Biol., 1934, 115, 75—76).—In pellagra the disturbance of metabolism of the muscle and brain-tissue is similar to that in the pigeon in vitamin-B deficiency. In pellagra the lack of vitamin-B₂ is incomplete but of several years' duration, whilst in pigeons the deficiency was complete, but lasted only a few days. NUTR. ABS. (b)

Additional substance essential to mammalian nutrition. L. N. ELLIS (Proc. Soc. Exp. Biol. Med., 1933, 31, 339—340).—With young rats on diets deficient in vitamin-B₂, some factor other than vitamin-B₂ appeared to limit growth. The missing factor was supplied by an EtOH extract of whole wheat as used in the Sherman and Bourquin basal diet, and was probably identical with vitamin-B₄. NUTR. ABS. (b)

Vitamin-C in Delicious apples before and after storage. E. L. BATCHELDER (J. Nutrition, 1934, 7, 647—653).—No loss of vitamin-C occurred after 6 months' storage at 0°. At 7.2° the loss was approx. 16% after 3 months and 25% after 6 months. A. G. P.

Chinese citrus fruits. IV. Stability of vitamin-C in orange and tangerine juices. V. Vitamin-C contents of two species of King Chu. P. P. T. SAH, T. S. MA, and V. HOO (J. Chinese Chem. Soc., 1934, 2, 175—178, 179—183).—IV. The loss of vitamin-C (I) on keeping and the change in acidity were followed. No relation between increase of acidity and loss of (I) was observed.

V. The sour variety contains more (I) than the sweet. H. N. R.

Vitamin-C content of Peiping spring vegetables. H. C. CHANG, T. S. MA, V. HOO, and P. P. T. SAH (J. Chinese Chem. Soc., 1934, 2, 184—191).—Fifty-one Chinese vegetables were examined. The richest in vitamin-C (I) were lotus root, Tientsin green turnip, and Peiping red turnip. Contrary to expectation cabbage and spinach contain only small amounts of (I). H. N. R.

Antiscorbutic efficacy of fir-needles. II, III. N. SHEPILEVSKA (Questions of Nutrition U.S.S.R., 1934, 3, No. 2, 28—40).—Supplementary (see this vol., 706). NUTR. ABS. (m)

Mandarins, dried black currants, dry carrots, mountain ash berries, and water melon as

sources of vitamin-C. N. JARUSOVA (Questions of Nutrition U.S.S.R., 1934, 3, No. 2, 42—49).—Caucasian mandarins contain 500 "units" of vitamin-C (I) per kg. of juice. Dried black currants after storage for 18 months contain 120 "units" and freshly dried black currants 150 "units." Dried carrots (3, 4, 5, 6 g. daily) do not protect guinea-pigs from scurvy, but have a deleterious effect. Mountain ash berries contain 400 "units" of (I) per kg. of expressed juice, but the product is toxic. Water-melon pulp contains 90 "units" per kg. NUTR. ABS. (m)

Antiscorbutic preparation from black-currant juice. B. JANOVSKA (Questions of Nutrition U.S.S.R., 1934, 3, No. 2, 24).—A highly active prep. of vitamin-C is obtained from black currants which have been preserved with sulphite. NUTR. ABS. (m)

Vitamin-C in the testicle. A. GIROUD and C. P. LEBLOND (Compt. rend. Soc. Biol., 1934, 115, 841—842).—The glands of the healthy mouse, rat, bull, pig, and guinea-pig (but not those of the scorbutic guinea-pig) contain vitamin-C localised in the interstitial cells. NUTR. ABS. (m)

Chemical and histological localisation of vitamin-C in the adrenal cortex. A. GIROUD and C. P. LEBLOND (Compt. rend. Soc. Biol., 1934, 115, 705—706).—Tissues from animals (rats, guinea-pigs) deprived of vitamins and tissues from which the ascorbic acid has been extracted give negative results. In the adrenal cortex the zona fasciculata and the zona reticulosa give an identical reaction, showing an even distribution of vitamin-C. The zona glomerulosa gives no reaction for ascorbic acid. The AgNO₃ test is given only by the protoplasm, the cell-nucleus being free. NUTR. ABS. (m)

Vitamin-C and the adrenals. P. E. GALVAO and D. M. CARDOSO (Compt. rend. Soc. Biol., 1934, 115, 350—352).—The adrenal gland is very rich in vitamin-C (I), 0.6—1.0 g. daily being sufficient to maintain guinea-pigs on diets deprived of (I). In guinea-pig scurvy (I) disappears from the adrenal tissue. NUTR. ABS. (m)

Antiscorbutic action of aqueous humour. H. KAWACHI (Z. physiol. Chem., 1934, 225, 273—274).—The aq. humour of the ox's eye protects guinea-pigs against scurvy (cf. A., 1933, 1213). J. H. B.

Colour reaction of ascorbic acid.—See this vol., 992.

Constitution of vitamozazone. K. TATEMATSU, K. NOGI, and A. YONEDA (Z. physiol. Chem., 1934, 225, 275—278; cf. A., 1933, 1213).—In aq. Na₂CO₃, vitamozazone (I) liberates CO₂ forming a Na salt, which on acidification regenerates (I). With CH₂N₂, (I) gives a *Me* derivative, m.p. 114—116°. Similarly, substance (II), $O < \begin{array}{c} \text{CH}_2\text{-C:N-NHPh} \\ \text{CO-C:N-NHPh} \end{array}$, m.p. 242°, by dissolution in NaOH and acidification gives a product (III), $\text{N}=\text{C} \cdot \text{CH}_2 \cdot \text{OH} \begin{array}{c} \text{N} \\ \text{CO-C:N-NHPh} \end{array}$, m.p. 151° (*Me* derivative, m.p. 134°). By reduction with Zn in AcOH and treatment with FeCl₃, (III) affords a substance resembling rubazonic acid (IV), thus confirming its pyrazolone (V) structure. (I) on similar treatment gives (IV) colour reactions, indicating that it is also

a (V). Ascorbic acid must occur naturally principally in the lactone form.

J. H. B.

Synthesis of vitamin-C by the infant. P. ROHMER, U. SANDERS, and N. BEZSSONOFF (Nature, 1934, 134, 142—143).—The human infant fed on a vitamin-C-free diet can produce vitamin-C (I) up to the age of 14 months. Excretion of (I) in the urine often ceases in sick or dystrophic infants. Curves indicating the variation of (I) in the urine of infants of different ages are given.

L. S. T.

Effects of vitamin-C deficiency on tooth-structure in guinea-pigs. E. W. FISH and L. J. HARRIS (Phil. Trans., 1934, B, 223, 489—510).—The "pulp bone" theory is discarded. Vitamin-C (I) primarily maintains the activity of certain types of cells. Effects of (I) deficiency are sequelæ of this action.

H. G. R.

Vitamin-D in cacao shell. A. W. KNAPP and K. H. COWARD (Analyst, 1934, 59, 474—478).—A sample of shell from fermented, sun-dried Gold Coast cacao contained 28 units of vitamin-D per g.

E. C. S.

Vitamins in canned foods. XIV. Calcium and vitamin-D in foods. E. F. KOHMANN, N. H. SANBORN, W. H. EDDY, and C. Z. GURIN (Ind. Eng. Chem., 1934, 26, 758—761; cf. B., 1931, 992).—Diets of raw (I), cooked (II), and canned (III) foods contained ample vitamin-D. The bone-ash content of the tibia (IV), and the general development, of rats, were better with (III) than with (I) or (II), the difference being attributed to availability of a limited Ca supply. Addition of milk gave a higher (IV) in each case. Addition of cod-liver oil to a Ca-enriched (III) diet gave no improvement.

E. C. S.

Determination of vitamin-C with removal of interfering reducing and coloured substances. A. EMMERIE and M. VAN EEKELLEN (Biochem. J., 1934, 28, 1153—1154; cf. this vol., 461).—Ascorbic acid is determined in biological fluids and plant extracts by pptn. of proteins with $\text{CCl}_3\text{-CO}_2\text{H}$ and of reducing substances and colouring matter with $\text{Hg}(\text{OAc})_2$, followed by reduction with H_2S . The titration is performed in $\text{CCl}_3\text{-CO}_2\text{H}$ solution.

H. D.

Poverty of mammalian liver in vitamin-D. S. SCHMIDT-NIELSEN and S. SCHMIDT-NIELSEN (Kong. Norske Vidensk. Selsk. Forh., 1932, 5, No. 27).—Very little vitamin-D (I) occurs in the livers of mammals or birds. The (I) content of the livers of young rats receiving 2 mg. daily of irradiated cholesterol for long periods (14 days—6 months) remains very low.

NUTR. ABS. (m)

Highly-concentrated preparations of natural vitamin-D. F. ENDER (Z. Vitaminforsch., 1934, 3, 161—163).—The light petroleum-sol. fraction of the phthalic ester prep. from a concentrate of liver oil (from *Thunnus thynnus*) (A., 1933, 1340) yields on distillation a fraction, b.p. $140\text{--}150^\circ/0.01\text{--}0.03\text{ mm.}$, the daily rat dose of which is $0.03\text{--}0.04 \times 10^{-6}\text{ g.}$

F. O. H.

Third vitamin-D. O. RYGH (Z. Vitaminforsch., 1934, 3, 164—167).—Approx. 80% of the antirachitic vitamin (I) of butter is absent from the non-saponifiable fraction (cf. this vol., 459, 704) and is found in the

fatty acids liberated from the saponifiable fraction. The same phenomenon occurs with the (I) of green plants, hay, and cow's liver oil. Human liver oil varies in the partition of (I) on saponification; this is probably due to differences in diet. C readily adsorbs (I) from irradiated ergosterol but not from the antirachitically active free fatty acids. The existence of a third vitamin-D (D_c) is postulated.

F. O. H.

Provitamin-D of cholesterol. I. Antirachitic efficacy of irradiated cholesterol. J. WADDELL (J. Biol. Chem., 1934, 105, 711—739).—Irradiated cholesterol (I) is a more powerful antirachitic agent than the equiv. no. of units of ergosterol (II), being as potent as the vitamin-D of cod-liver oil. Pure (II) mixed with (I) and irradiated is not more powerful than irradiated (II) alone; hence it is concluded that the provitamin constituent of (I) is different from (II), in disagreement with previous belief.

C. G. A.

Variability in the maize component of a rachitogenic diet. R. S. HARRIS and J. W. M. BUNKER (J. Lab. Clin. Med., 1934, 19, 390—394).—Variations, reduced by storage for 6 months after grinding, are attributed to the presence of an antirachitic substance. Variations in P content are recorded.

CH. ABS.

Influence of minerals on the course of oxidation on a vitamin-deficient diet. P. THOMAS (Biochem. Z., 1934, 271, 250—258).—Removal from and addition to an avitaminotic diet of biologically important mineral substances effects changes in the oxidational processes of the animal, and results in corresponding changes of the urinary C:N, vacate-O:N, and vacate-O:C quotients. Thus by rigorous demineralisation of vitamin-free diet, the body oxidations in the rat are so altered that the increase in the urinary C:N quotient usually found in avitaminosis is no longer obtained, and remineralisation tends to reverse this result.

P. W. C.

Respiration of plants. W. D. TREADWELL and T. ZÜRRER (Helv. Chim. Acta, 1934, 17, 886—892).—Apparatus for measuring the respiration of plants in circulating, CO_2 -free air is described. Evolution of CO_2 occurs in stages due to the heterogeneity of the cell membranes from which the evolution occurs. Irradiation lessens the discontinuity, since it is masked by the continuous assimilation. Small amounts of Et_2O vapour displace adsorbed CO_2 from the cell-tissue thus simulating a temporarily increased respiration. CO_2 (1—7%) temporarily causes marked restriction of respiration.

H. W.

Two different respiratory mechanisms in plant absorption organs. H. LUNDEGÅRDH and H. BURSTRÖM (Naturwiss., 1934, 22, 435—436; cf. A., 1933, 874).—The O_2 uptake of oat plants has been measured. The formation of "extra" CO_2 indicates that the total respiration is the sum of basal respiration and anionic respiration, the latter being largely independent of O_2 uptake, so that with lack of O_2 the quotient CO_2/O_2 may reach 2.4, falling to 1 on addition of O_2 .

R. K. C.

Rôle of fatty and essential oils in the oxidation-reduction system of plant cells. K. T. SUCHORUKOV and A. G. DRUSHININA (Sci. Mém. Univ. Saratov, 1933, 10, No. 2, 81—94).—During the process of ripen-

ing of coriander seeds dehydrogenation of fatty acids takes place, with concomitant reduction of essential oils; this oxidation-reduction system is irreversible. Only traces of glutathione are present at any stage of development. R. T.

Manometric measurements of photosynthesis in the marine alga *Gigartina*. R. EMERSON and L. GREEN (J. Gen. Physiol., 1934, 17, 817—842).—A manometric method for measuring photosynthesis (I) in marine algae is described. (I) in *G. harveyana* is similar to that in *Chlorophyceae*. H. G. R.

Influence of growth temperature on the assimilation, chlorophyll content, and transpiration of young cereal leaves. G. GASSNER and G. GOEZE (Ber. deut. bot. Ges., 1934, 52, 321—335).—Wheat and rye leaves grown at 10° showed higher assimilation (I) and transpiration (II) and chlorophyll contents (III) than those grown at 20°. A direct relationship between (III) and protein content is established. Other relationships between (I), (II), and temp. are examined. A. G. P.

Determination of chlorophyll in the leaves of *Salix fragilis* and *Populus alba*. N. T. DELEANO and J. DICK (Bull. Soc. Chim. biol., 1934, 16, 749—756).—The EtOH extract of the leaves is diluted with H₂O, the chlorophyll (I) extracted with CHCl₃, and the residue after evaporation calcined. The Mg in the ash is determined as MgNH₄AsO₄·6H₂O. The leaves of *S. fragilis* contain 0.082—0.26, of *P. alba* 0.33%, of (I). A. L.

Stimulation of growth in wheat and rice by various substances. A. RADOEFF (Compt. rend. Soc. Biol., 1933, 112, 580—582; Chem. Zentr., 1934, i, 67).—The effects of Mg and Mn salts, KMnO₄, NH₂Cl, quinol, hexylresorcinol, and various dyes have been investigated. L. S. T.

Growth hormone of plants. V. Relation of cell elongation to cell-wall formation. J. BONNER (Proc. Nat. Acad. Sci., 1934, 20, 393—397).—Elongation is not necessarily accompanied by corresponding wall deposition. H. G. R.

Plant growth substances. IX. Isolation of auxins *a* and *b* from plant materials. F. KÖGL, H. ERXLEBEN, and A. J. HAAGEN-SMIT (Z. physiol. Chem., 1934, 225, 215—229; cf. A., 1933, 1213).—One sample of maize oil and some of malt gave relatively high yields of cryst. active auxin-*a*, identical with the product from urine, and the monobasic acid auxin-*b* (I), C₁₈H₃₀O₄, m.p. 183° (decomp.), [α]_D²⁰ —2.3° → —2.8° (mutarotation) [p-phenylphenacyl ester, m.p. 174°, semicarbazone, m.p. 176°]. With MeOH-HCl, (I) affords the dimethylacetal lactone (?), C₂₀H₃₄O₄, m.p. 118°. On hydrogenation, (I) gives a tetrahydroauxin-*b*, m.p. 194° (2:4-dinitrobenzoyl derivative, m.p. 128°, [α]_D²⁰ —6.75°). (I) is decarboxylated at the m.p. and becomes inactive on keeping. The n.c.l. surfaces of the auxins and derivatives were determined by spreading in unimol. layer. J. H. B.

Detection of growth substances in woody plants. A. T. CZAJA (Ber. deut. bot. Ges., 1934, 52, 267—271).—Various species were examined by the Went technique. *Æsculus hippocastanum* is particularly rich in growth substance. A. G. P.

Formation and translocation of root hormones in roots. N. CHOLODNY (Planta [Z. wiss. Biol.], 1934, 21, 517—530).—Curvature produced in decapitated *Avena coleoptiles* (I) by contact with root tips of *Zea mais* (II) is examined. Tips of young and old roots were equally effective in this respect. Roots of other species had little or no action on (I). The ability of (II) to supply growth-promoting substance (III) is lost after 5—6 hr. unless appropriate nutrient material is supplied. The (III) in the extension zone of the roots moves only in a polar direction. A. G. P.

Ammonia and nitrate nutrition of dormant Delicious apple trees at 9°. G. T. NIGHTINGALE (Bot. Gaz., 1934, 95, 437—452).—Synthesis of simple proteins occurred in the fine fibrous roots of apple trees grown in darkness in sand cultures at 9° and supplied with (NH₄)₂SO₄ at p_H 6.0 or with Ca(NO₃)₂ at p_H 4.5. Root development was active and protein accumulated only in the roots. Synthesis of NH₂-acids (I) and asparagine (II) was more rapid and the reduction in carbohydrate content (III) more marked in roots receiving NH₄⁺. In control plants receiving no N the (III) of roots increased as a result of translocation. When the temp. was raised to 21° much (I) and (II) was translocated to buds which developed rapidly. The absorbing surfaces of fine roots in sand cultures receiving (NH₄)₂SO₄ showed p_H 4.2 and those supplied with Ca(NO₃)₂, 5.6. Changes in the p_H of the culture media throughout were >0.1 unit. With high concns. of (NH₄)₂SO₄ root surfaces and cortical cells attained p_H 2.8—3.0 and root primordia failed to emerge. In constantly stirred H₂O-cultures similar though less extensive changes occurred. Except in extreme cases when roots were injured the p_H of internal root tissues was not affected by the nutrient solution used. Starch accumulation in cells is associated with relatively acid cell contents. A. G. P.

Distribution of nitrogen between stock and scion. K. SILBERSCHMIDT (Planta, 1934, 22, 1—21).—A grafting system in which the plane of union is horizontal is utilised to confirm earlier work (A., 1933, 1092). The accumulation of N substances at the base of the scion is further examined. A. G. P.

Regularity in the biosynthesis of plants. V. I. NILOV (Plant Ind., U.S.S.R., 1933, A, No. 7, 3—34).—During the various stages of the vegetative period of *Trachispermum coticum* the oil undergoes isomerisation, accompanied by oxidation, from terpenes through p-cymene to thymol. Data are also presented for *Lavandula vera*, *L. spica*, *Rosmarinus officinalis*, and *Feniculum officinalis*. Regularity in the chemical attributes of the oils is discussed. Contrary to Blagoveshchenski, the no. of cyclic compounds does not increase with the phylogenetic ageing of the plant. CH. ABS.

Chemical study of sugar beet during the first growth year. F. KNOWLES, J. E. WATKIN, and F. W. F. HENDRY (J. Agric. Sci., 1934, 24, 368—378).—Analyses of beet at various stages of growth are recorded. Throughout the season the % of reducing sugars in the dry matter of whole plants and of sucrose and Cl in the leaves were fairly const. Assimilation

of P, Ca, and Cl, but not of N and K, ceased about a month before maturity. P and Cl were excreted by the plants during the last few weeks of growth. The importance of available N in the early stages is demonstrated.

A. G. P.

Influence of germination in sugar solutions and in glycerol on the further development of some cultivated plants. I. A. VOLKOV (Bull. Appl. Bot., U.S.S.R., 1933, [iii], No. 3, 131—139).—Growth of *Avena byzantina* is stimulated by germination in aq. sucrose (optimum 0.4*M*), glucose (0.5*M*) or glycerol (0.5*M*); that of Marquis wheat and flax is not so stimulated.

CH. ABS.

Proteins of mulberry leaves. V. Quantitative changes of total protein in fresh mulberry leaves during maturation. Y. KISHI and Y. YOKOTA (J. Agric. Chem. Soc. Japan, 1933, 9, 1358—1364).—Vals. decrease with maturity; exceptions due to varieties or conditions were observed.

CH. ABS.

Fruit development in the pecan (*Hicoria pecan*). C. L. SMITH and C. J. B. THORN (Proc. XIII Ann. Mtg. Texas Pecan Growers' Assoc., 1933, 71—76).—Most of the oil, protein, mineral, and acid-hydrolysable polysaccharide of the kernel develop during Sept., and nearly all the sugar (almost exclusively non-reducing) during the first half of Oct.

CH. ABS.

Mode of formation of the pecto-cellulosic membrane. A. DAUPHINE (Compt. rend., 1934, 199, 307—309).—The appearance and growth of cellulose are traced.

H. W.

Rate of carbohydrate condensation on a cell wall. O. L. SPONSLER (J. Amer. Chem. Soc., 1934, 56, 1599—1601).—The rate at which cell-wall material (somewhat like cellulose) is deposited during the growth of a new cross wall in a species of *Rhizoclonium* is followed microscopically. Concentric layers 0.1 micron thick are deposited (on the inner edge of a closing ring) each min. of growth irrespective of the surface area.

H. B.

Importance of carbohydrate supply in legume symbiosis. F. E. ALLISON (Nature, 1934, 134, 144).—A discussion.

L. S. T.

Relation of carotenoid pigments to sexual reproduction in plants. A. E. MURNEEK (Science, 1934, 79, 528).—*Cosmos bipinnatus*, *Salvia splendens*, and *Soja max.* exposed to a short photo-period (7—8 hr. day) and to a long period (14—15 hr. day) show marked differences in rate of growth, time of sexual reproduction, and greenness of foliage. In both cases the leaves have approx. the same concn. of chlorophyll, but plants which have changed from vegetative development to the reproductive state have an increased carotene and xanthophyll content. The concn. of the carotenoids appears to reach a max. at the time of flowering and then decreases.

L. S. T.

Soil micro-organisms; their influence on the potential difference between the plant and the soil. M. C. POTTER (Zentr. Bakt. Par., 1934, II, 90, 255—258).—Electrical energy liberated during the decomp. of manure and by chemical reactions within the plant probably sets up a definite electrical relationship between plant and soil.

A. G. P.

Micro-organisms and vitamin production in green plants. N. A. CLARK and B. H. THOMAS (Science, 1934, 79, 571—572).—In *Lemna major* grown under sterile and non-sterile conditions the absence of micro-organisms does not affect the formation of vitamin-A. Variation in illumination within limits has little effect.

L. S. T.

Effect of germination on the reducing power of *Phaseolus mung*. B. C. GUHA and A. R. GHOSH (Current Sci., 1934, 2, 390).—Germination produces a six-fold increase in the reducing power of *P. mung*, which is rich in vitamin-C. 0.5% $\text{CCl}_3\cdot\text{CO}_2\text{H}$ alone decolorises 2:5-dichlorophenol-indophenol; this can be inhibited by addition of glacial AcOH to the indicator prior to titration by the $\text{CCl}_3\cdot\text{CO}_2\text{H}$ extract.

L. S. T.

Determination of the condition of winter grains by the conductivity of their tissues. S. M. IVANOV (Plant Ind., U.S.S.R., 1933, A, No. 7, 49—60).—With injury to plants by low temp. the resistance of the juice falls, giving an early indication of injury. Plant tissue behaves similarly.

CH. ABS.

Determination of resistance of plants to drought. M. T. TIMOFEEVA (Plant Ind., U.S.S.R., 1933, A, No. 7, 69—74).—Plants having a high resistance to drought grow in sand cultures after the partly germinated seed has been kept in 2*M*-sugar solution for 6 days.

CH. ABS.

Characterisation of Black Sea *Phyllophora*. V. OPOTZKI, Z. POGREBINSKA, and A. TIULPINA (Ukrain. Chem. J., 1934, 9, 73—78).—The algae contain I 0.150—0.367, Br 0.08—0.25, KCl 0.110—0.585, Mn 0.005—0.31, ash 11—46, C 29—32.4, H 4.4, N 2.34—4.23, S 3.75—4.52, H_2O -sol. carbohydrates (I) 0.80—2.52, H_2O -insol. (I) 19.2—24.6, cellulose 7.2—8.9, protein 14.7—26.3% dry wt. The vals. vary characteristically with distance from the coast.

R. T.

Composition of three fossil woods mined from the Miocene auriferous gravels of California. R. L. MITCHELL and G. J. RITTER (J. Amer. Chem. Soc. 1934, 56, 1603—1605).—The woods [hard pine, cedrus, and sequoia (I)], obtained about 200 ft. underground, contain less extractives (hot and cold H_2O ; Et_2O ; 1% NaOH) and, except for (I), less cellulose than the normal woods. The lignin contents are abnormally high; the amount originally present has decreased to a smaller extent than any other constituent. Microscopical examination of the Cross and Bevan cellulose residues and the relation between alkali solubility and cellulose content indicate that decomp. is due to (probably) hydrolysis and not attack by fungi.

H. B.

Jugoslavian maize. M. MAUTNER (Arh. Hemiju, 1934, 8, 133—136).—The composition of Jugoslavian maize (I) is compared with that of (I) from other countries. The H_2O and starch contents vary periodically.

R. T.

Idioblasts in the *Crassulaceae*. M. PRONER (Compt. rend., 1934, 198, 1872—1874).—Idioblasts (I) are found only in the leaves and stems. MeCHO is present in the (I) of all species examined. Oxidases are very feeble or absent. Carboxylase (II) was demonstrated in 13 of the 43 species. The diurnal

variation of p_R is greatest in species with the highest no. of idioblasts, highest concn. of MeCHO, and highest (II) content. C. G. A.

Constituents of bark of *Piscidia erythrina*. P. W. DANKWORTT and E. SCHÜTTE (Arch. Pharm., 1934, 272, 701—713).—This bark (Jamaica dogwood; manaca) (I) contains *substance A*, a paraffin alcohol, $C_{17}H_{36}O$, m.p. 79° (*Ac* derivative, m.p. 62°), *substance B*, a sterol alcohol, $C_{27}H_{46}O$, + H_2O , m.p. 145° (sinters at 135°), $[\alpha]_D^{25} -51.51^\circ$ in $CHCl_3$ (*Ac* derivative; *digitonide*), a phenolic *substance E* (II), $C_{15}H_{14}O(OH)_2(OMe) \cdot CO_2H$, m.p. 157—158° (sinters at 146°) (*Ac_2* derivative, m.p. 189°; *Br_2*-derivative, m.p. 135°), a phenolic *substance F*, $C_{23}H_{24}O_9$, m.p. 180° (decomp.), an amorphous *substance G*, probably a hydrocarbon, m.p. about 70°, esters, tannins, and phlobaphens (derived from pyrocatechol), an amorphous *saponin* (0.005%) [gives glucose, galactose, and a $(OH)_2$ -acid on hydrolysis], and an amorphous *alkaloid* (0.001%), m.p. 86—87° (*hydrochloride*, m.p. 124°), and gives by hydrolysis stearic and cerotic acids. (II) contains no CH_2O_2 or CO group, with hot HCl-EtOH gives a non-acidic *substance*, $C_{14}H_{14}O_5$, m.p. 280°, with $KMnO_4$ yields only HCO_2H , on KOH fusion forms pyrocatechol, and with cold H_2SO_4 gives a *substance*, $C_{15}H_{16}O_5$, m.p. 290°. R. S. C.

Characterisation of the volatile alkaloids exuded by hemlock. J. CHAZE and M. M. JANOT (Compt. rend., 1934, 198, 2015—2017).—Coniine is exuded by hemlock seedlings. R. S. C.

Alkaloid content of medicinal and poisonous plants of U.R.S.S. A. OREKHOV (Arch. Pharm., 1934, 272, 673—691).—Of 412 medicinal or poisonous Russian plants collected (from 68 genera and 377 species) 67, hitherto unexamined, contain > 0.1% of alkaloids; 10 new alkaloid-containing genera and 24 new alkaloids are recorded, including *aloperine*, $C_{15}H_{26}N_2$ (from *Sophora alopecuroides*), *trichodesmine* (from *Trichodesma incanum*), *capparinine* (from *Capparis spinosa*), and *haplophylline* (from *Haplophyllum Sieversii*). Anabesine finds use as an insecticide and convolvine as a local anæsthetic. R. S. C.

Alkaloids of *Fagara Coco* (Gill.), England. G. V. STUCKERT (Invest. Labor. Quim. biol. Univ. nac. Cordoba, 1933, 1, 69—93; Chem. Zentr., 1934, i, 67).—The rind yields an amorphous alkaloid cocoberberine, and a yellow, N-free, pigment, *xanthofagarol*. The leaves yield α -fagarine, $C_{19}H_{22}O_4N$, m.p. 169°, an isoquinoline derivative containing Ac and 2OMe; β -fagarine (I), $C_{12}H_{14}O_3N$, m.p. 178°, containing Ac and OMe and an isoquinoline residue; γ -, $C_{15}H_{15}O_3N$, m.p. 139—140°, δ -, m.p. 136°, and X-fagarine. With HNO_3 , (I) gives a colour reaction similar to that given by brucine. L. S. T.

Colour reaction and differentiation of an alkaloid from *Fagara Coco*. R. V. DE IPOLA (Invest. Labor. Quim. biol. Univ. nac. Cordoba, 1933, 1, 94—97; Chem. Zentr., 1934, 1, 67).— β -Fagarine gives a characteristic yellow colour, changing to malachite-green on warming, with $CH_3O-H_2SO_4$. L. S. T.

Alkaloids of Chinese *Corydalis ambigua*.—See this vol., 1014.

New alkaloid, ephedrine, neutral principle, and volatile oil from Chinese *Ephedra*, Ma-huang. T. Q. CHOU and P. F. MEI (Chinese J. Physiol., 1934, 8, 161—166).—The alkaloidal residues from Ma-huang, freed from ephedrine and ψ -ephedrine, give a cryst. deposit of a neutral *substance*, $C_{10}H_{20}O_2 \cdot H_2O$, m.p. 120° (*anhyd.*, m.p. 105°), which with dil. acids at 100° yields an oil, $C_8H_{12}O$, b.p. 197°, whilst the liquors, on treatment with Na_2CO_3 and steam-distillation, yield the oil together with *ephedrine*, $C_8H_{18}O_3N_2$, m.p. 76° (*anhyd.* m.p. 87°) (*hydrochloride*, m.p. 90°; *picrate*, m.p. 190°; *platinichloride*, m.p. > 280°). All the above substances are optically inactive. F. O. H.

Alkaloids of fumariaceous plants. IX. *Dicentra formosa*, Walp. R. H. F. MANSKE (Canad. J. Res., 1934, 10, 521—526; cf. this vol., 311).—From *D. formosa* are isolated dicentrine (I), 0.10% of dried plant, glaucine (II), 0.15% [contrast the ratio (I) : (II) = 13 : 1 in *D. exima*], *d*-corydine, m.p. 142° or 148—149° (corr.) according to sample, 0.03% (triboluminescent), with which eximine (A., 1933, 990) is identical, corytuberine, > 0.02%, protopine 0.10%, alkaloid- δ (*loc. cit.*), probably $C_{21}H_{25}O_5N$, 0.002%, and fumaric acid, 0.02%. J. W. B.

***Berberis laurina*.** L. GURGUEL, O. DE A. COSTA, and R. D. DA SILVA (Boll. Assoc. Brasil. pharm., 1934, 15, 11—20).—The roots contain hydrastine 1.4, berberine 2.5%. CH. ABS.

Detection of alkaloids in plant sections. M. WAGENAAR (Pharm. Weekblad, 1934, 71, 834—840).—The sections are treated with aq. $HgCl_2$, washed, treated with aq. H_2S , and finally clarified in chloral hydrate solution; cells containing alkaloids are stained black. Alternatively the sections are treated with $K_4Fe(CN)_6$ and the pptd. alkaloid ferrocyanides subsequently stained by means of aq. $FeCl_3$. S. C.

Fundamental relationship between essential oil and alkaloid in the plant. M. WAGENAAR (Pharm. Weekblad, 1934, 71, 642—649).—From botanical, anatomical, and chemical evidence, especially on the *Umbelliferae*, it is suggested that a fundamental relationship exists between the occurrence of essential oils and alkaloids in plants. Essential oils from the seeds of *Cinchona leger* and *C. robusta* contain an indole derivative (red colour with vanillin and HCl). S. C.

Are essential oils and alkaloids causally related? C. VAN ZIJP (Pharm. Weekblad, 1934, 71, 724—726).—A criticism of Wagenaar's views (preceding abstract). S. C.

Composition of the oil of barley rootlets. A. SMEETS and E. RUPPAL (Bull. Soc. Chim. biol., 1934, 16, 865—898).—The oil (I) of barley rootlets consists of 75% of saponifiable (II) and 25% of unsaponifiable material (III). (II) is made up of lecithin and glyceryl and ceryl esters of AcOH, hexoic, palmitic, stearic, oleic, linoleic, and linolenic acids. (III) contains sitosterol and traces of ergosterol. (I) has no vitamin-A or -D. A. L.

Fatty oil from pumpkin seed. Constitution of linoleic acid. J. L. RIEBSOMER and G. A. NESTY (J. Amer. Chem. Soc., 1934, 56, 1784—1785).—The oil, extracted from the seed by Et_2O , has d_4^{20} 0.9159, n_D^{20}

1-4737, I val. (Hanus) 116-8, sap. val. 174-2, Reichert-Meissl val. 1-5, Ac val. 2-76, and acid val. 12-49; it consists of glycerides of oleic (37-5%), linoleic (42-2%), palmitic (6-5%), and stearic acids (5-4%) and contains 1-58% of unsaponifiable matter. In agreement with Haworth (A., 1929, 1040), ozonolysis indicates that linoleic acid is octadeca- $\Delta^{6,8}$ -dienoic acid. H. B.

Light petroleum- and ether-soluble constituents of cranberry pomace. K. S. MARKLEY and C. E. SANDO (J. Biol. Chem., 1934, 105, 643-653).—The light petroleum (I) extract consisted of nonacosane, $C_{29}H_{60}$, hentriacontane, $C_{31}H_{64}$, free solid fatty acids C_{16} — C_{26} , linolenic, linoleic, and oleic acids, and a small amount of glycerol. The Et_2O extract, following extraction with (I), contained free ursolic acid and an unidentified resin acid. H. G. R.

Phosphatides of wheat germ. H. J. CHANNON and C. A. M. FOSTER (Biochem. J., 1934, 28, 853-864).—Pptn. by $COMe_2$ of the oil extracted by $EtOH$ - Et_2O (1:1) from wheat germ (yield 8-5%) affords 9-2% of crude phosphatide in which phosphatidic acid, lecithin, and kephalin were present in the ratio of approx. 4:4:1. Carbohydrate (from the non-phosphatide fraction) was present, whilst choline and colamine (cf. A., 1932, 1179) were isolated. F. O. H.

Iris essence. R. THIÉBAUT (Boll. Uff. Staz. Sperim. Ind. Essenze, 1934, 9, 36-40).—Octoic, nonoic, undecoic, lauric, tridecoic (m.p. 39°), and benzoic acids are found in iris essence. T. H. P.

[Pigments of hips.] R. KUHN and C. GRUNDMANN (Ber., 1934, 67, [B], 1133).—The source of the pigment was *Rosa rubiginosa*, not *R. rubinosa*, as described (this vol., 404). H. W.

Caricaxanthin.—See this vol., 1008.

Isolation of a vegetable flavin. P. KARRER and K. SCHOPP (Helv. Chim. Acta, 1934, 17, 771-773).—The dried flowers of *Taraxacum officinale* are extracted with 80% $EtOH$ at 70° followed by removal of $EtOH$, extraction of the aq. residue with $CHCl_3$, and adsorption by frankonite in dil. $AcOH$. Elution of the adsorbate is effected with C_5H_5N - H_2O - $EtOH$. After removal of solvent the residue, dissolved in H_2O and adsorbed repeatedly by PbS , yields the flavin, m.p. 283° (corr.). H. W.

Tea-catechin II or gallocatechin from green tea.—See this vol., 1008.

Chlorinated lichen substances. A. S. PFAU (Chem. and Ind., 1934, 553).—A priority claim to the detection of monochloroatranol (2-chloro-3:5-dihydroxy-*p*-tolualdehyde) in *Buellia canescens* (A., 1933, 503). J. W. B.

Sapotoxin in *Xanthosoma atrovirens*, a tropical food-tuber. A. CLARK and R. B. WATERS (Biochem. J., 1934, 28, 1131-1134).—An acid sapotoxin isolated from tannia (*X. atrovirens*) is very toxic to rats. Consumption of these tubers may be a cause of nephritis in the W. Indies. L. D. G.

Occurrence of *d*-allantoin in *Platanus orientale*. R. FOSSE, P. E. THOMAS, and P. DE GRAEVE (Compt.

rend., 1934, 198, 1953-1955).—*dl*- and *d*-Allantoin, $[\alpha]_D^{20} +92^\circ$ in H_2O , are isolated from the leaves.

R. S. C.

Mushroom proteins. M. A. GUDLET (Schr. Zentr. Forschungsinst. Lebensm., U.S.S.R., 1933, 4, 8-19).—Although unusually resistant to acid hydrolysis the proteins are dissolved to about 80% by gastric juice with a particularly high (> 55%) yield of $(NH_2)_2$ -acids. CH. ABS.

Globulin of *Eleusine coracana* (Bessna). G. MORUZZI (Boll. Soc. ital. Biol. sperim., 1933, 6, 428-430; Chem. Zentr., 1934, i, 66).—The globulin (I) contains 15-2% N, is pptd. by conc. Na_2SO_4 solution, and is sol. in 2% $NaCl$ and $MgSO_4$ solutions. The neutral solution in 10% $NaCl$ becomes turbid at 75°, coagulates at 86°, and ppts. at 95°; acidification with $AcOH$ lowers the first temp. to 45-50° and the second to 70°. (I) gives typical protein colour reactions. L. S. T.

Albumin of *Eleusine coracana* (Bessna). G. MORUZZI (Boll. Soc. ital. Biol. sperim., 1933, 6, 431-433; Chem. Zentr., 1934, i, 66).—The albumin contains 16-1% N, is pptd. by $(NH_4)_2SO_4$ but not by NH_4Cl , and is sol. in H_2O , alkali, and dil. acids. After coagulation it is insol. in H_2O and dil. acids, and slightly sol. in cold, dil. alkali. The slightly acid ($AcOH$) solution becomes turbid at 38-40°, flocculates at 45°, and is completely coagulated at 65°. L. S. T.

Prolamin of *Eleusine coracana* (Bessna). G. MORUZZI (Boll. Soc. ital. Biol. sperim., 1933, 6, 434-436; Chem. Zentr., 1934, i, 66).—The isolated prolamin, *eleusin*, contains 14-03% N; solubility data are given. L. S. T.

Ultracentrifugal study of pomelin. L. KREJCI and T. SVEDBERG (J. Amer. Chem. Soc., 1934, 56, 1706-1711).—Pomelin (I), extracted from orange-seed meal by 0-5N- KCl , - KBr , or - KI , contains the same relative amounts of three components (II, III, IV), the sedimentation consts. of which are 2-2, 11-38, and $16-75 \times 10^{-12}$, respectively. (III) is the main constituent and is stable at p_H 3-5-12; (IV) may be a denaturation product of (III). (I) is denatured readily in solutions of low salt concn.; acid denaturation is complete at p_H 3-3. The mol. wt. of (III) is probably about 210,000. Dry (I) (Saunders, A., 1931, 661; 1932, 227) shows evidence of denaturation. H. B.

Composition of intercellular cement. H. COLIN and A. CHAUDUN (Compt. rend., 1934, 198, 2116-2118).—Successive diffusions of (sugar-freed) beet with cold H_2O give extracts the α of which gradually decreases from +200° to -25°, indicating that in the final extracts the quantity of araban (I) is > sufficient to compensate the *d*-rotation of the pectic acid (II). Subsequent extraction with either H_2O under pressure, or 0-25% HCl at 50°, affords reducing *l*-solutions 5-5-5) poor in (II) and containing large excess of (I). Contrary to Ehrlich (A., 1929, 1273) it is not considered that (I) and (II) are combined in a definite compound. J. W. B.

Properties of the polysaccharide complex extracted from a marine alga, *Chondrus crispus*. M. R. BUTLER (Biochem. J., 1934, 28, 759-769).—Aq. extracts containing the gelatinous component of *C. crispus* and prepared under standard conditions

do not contain a pure Ca salt of an ethereal sulphate of a complex carbohydrate, but chiefly a mixed Ca K H salt. By dialysis against KCl or NH_4Cl , K and NH_4 salts are obtained. The Ca salt regenerated from the K salt differs considerably from the substance in the original extract. W. O. K.

Determination of glucoside-sugars and other carbohydrate in plants, especially in *Aesculus* and *Salix*. G. KERSTAN (Planta [Z. wiss. Biol.], 1934, 21, 657—676).—Glucosides, mannose (I), etc. are removed from plant extracts by absorption on C prior to determination of monoses and sucrose. The latter are analysed by reduction methods before and after fermentation with yeast. (I) is removed from C by Et_2O . The necessity of determining residual reduction vals. at all stages of the separation is emphasised. A. G. P.

Physiological significance of glucosides of *Aesculus* and *Salix* in relation to other carbohydrates. G. KERSTAN (Planta [Z. wiss. Biol.], 1934, 21, 676—698).—Distribution of glucosides and carbohydrates in the various organs is examined. *Aesculin* (I) in twig bark does not act as a carbohydrate reserve and is not easily translocated. In *Aesculus* leaves (I) is physiologically labile and varies in amount with a day and night periodicity resembling that of carbohydrates. A. G. P.

Bog-moss. III. Composition of *Sphagnum fimbriatum*, Wils. M. WATANABE (J. Agric. Chem. Soc. Japan, 1934, 10, 67—74).—Cellulose obtained from the fibre contained 86.88% of α -cellulose (I). The resistance of (I) to 17.5% NaOH is > that of other celluloses; resistance to 30% NaOH in presence of air is < that of filter paper. CH. ABS.

Crystalline pyridine-amylose from natural potato-starch. C. RESCHKE and J. HARTMANN (Naturwiss., 1934, 22, 451—452).—When potato-starch, in which the grain-walls have been made permeable by drying at $100^\circ/14$ mm. over P_2O_5 or destroyed by grinding, or pure amylose, is soaked in 20—30% aq. $\text{C}_5\text{H}_5\text{N}$, a cryst. pyridine-amylose is formed. R. K. C.

Pecan shells as a source of *d*-xylose. C. J. B. THOR and C. L. SMITH (J. Amer. Chem. Soc., 1934, 56, 1640).—The shells are extracted with hot or cold H_2O and then hydrolysed ($\text{N-H}_2\text{SO}_4$); *d*-xylose is isolated (usual method) from the resulting syrups in 11.2—12.8% yield. H. B.

Micro-determination of sugar by Warburg's manometric method for fermentation-carbon dioxide. H. POLSTER (Planta [Z. wiss. Biol.], 1934, 21, 699—700).—Yeast fermentation of plant extracts in the presence of $\text{HPO}_4^{''}$ buffer solution records 87% of the sugar present, but with distilled H_2O 97—99% yields of CO_2 are obtained. 0.2 mg. of sugar in 1 c.c. may be determined with a fermentation period of 20 min. A. G. P.

Isolation and identification of sucrose from senega. R. BIENFANG (J. Amer. Pharm. Assoc., 1934, 23, 396—397). A. E. O.

Zymasis. VII. Determination of ethyl alcohol and acetaldehyde content of apples. J. C.

FIDLER (Biochem. J., 1934, 28, 1107—1120).—The material is steam-distilled for 2 hr. The EtOH no. is determined in one portion after oxidation to AcOH, whilst MeCHO is determined by Ripper's method in the other. H. G. R.

Presence of methyl alcohol in the leaves of vegetables: its relation to chlorophyll. M. FLANZY (Compt. rend., 1934, 198, 2118—2120).—Determination (this vol., 169) of MeOH (I) in the aq. extracts of green and etiolated leaves shows that, although there is no relationship between the amount of (I) and of chlorophyll (II) between different species, in any one plant (I) is the greater the larger is (II). J. W. B.

Simultaneous determination of citric and malic acids in plant tissue. G. W. PUCHER, A. B. VICKERY, and A. J. WAKEMAN (Ind. Eng. Chem. [Anal.], 1934, 6, 288—291).—Oxidation of malic acid by KMnO_4 in presence of KBr gives a volatile Br-compound, which with $\text{C}_6\text{H}_5(\text{NO}_2)_2\cdot\text{NH}\cdot\text{NH}_2$ forms a compound insol. in H_2O ; this is dissolved in $\text{C}_5\text{H}_5\text{N}$, poured into H_2O , and treated with NaOH; the blue colour developing is suitable for colorimetric determination. Citric acid gives $\text{CBr}_3\cdot\text{CO}\cdot\text{CHBr}_2$, which interferes, but may be removed by ligroin and determined separately. Other acids common in vegetable tissues do not interfere. NH_2 -acids from animal matter give similar ppts., but these are formed even in absence of KBr and can thus be eliminated by a blank experiment; alternatively, deamination may precede oxidation. R. S. C.

Plant sap and juice. I. A. W. BARTON. II. L. A. BRENNEN, R. DARLAND, F. M. LEE, and A. W. BARTON (Trans. Kansas Acad. Sci., 1933, 36, 72—75, 76—77).—I. Tree and herbaceous plant saps were all acid.

II. All phanerogam saps were slightly acid.

CH. ABS.
Absorption of manganese by plants. C. OLSEN (Compt. rend. Trav. Lab. Carlsberg, 1934, 20, No. 2, 34 pp.).—The Mn content of plants increases as the p_{H} of soil in which they are grown decreases. In H_2O -cultures, absorption of Mn from media of the same [Mn] is a max. at p_{H} 6—7. In media containing 0—2.5 mg. of $\text{MnSO}_4\cdot 4\text{H}_2\text{O}$ (I) per litre, absorption increases with [Mn $^{++}$]. Toxic effects occur in cultures containing 2.5 mg. of (I) per litre. In the absence of Mn leaves develop brownish spots and streaks, but are not chlorotic. H_2O plants usually have high Mn contents even when grown in neutral or alkaline media. Plants absorb Mn as Mn $^{++}$ which is stable in acid soils. A. G. P.

Manganese content of grasses and lucerne from grazed plots. D. W. BOLIN (J. Agric. Res., 1934, 48, 657—663).—Mn is determined in plant material by fusion with anhyd. Na_2CO_3 , followed by reduction of all Mn to MnSO_4 with NaHSO_3 , and subsequent use of the KIO_3 method. Vals. are > by the official method. Analyses of various grasses are recorded. Marked differences are shown by different species in the ability to utilise Mn from soil. A. G. P.

Physiological acidity and alkalinity of inorganic nitrogenous compounds in solution cultures. J. P. CONRAD (J. Amer. Soc. Agron., 1934, 26, 364—

372).—Reaction changes in single-salt culture solutions containing NO_3^- or NH_4^+ produced by the growth of maize and sorghum plants are compared with those in N-free media containing the corresponding anions or cations. The residual titratable acidity of $(\text{NH}_4)_2\text{SO}_4$ solutions (after all N had been absorbed by plants) was $>$ that produced in H_2SO_4 cultures. The residual titratable alkalinity (A) of NaNO_3 solutions was $<$ that in corresponding NaHCO_3 solutions. The A vals. of HNO_3 , NH_4NO_3 , and NH_4HCO_3 solutions after complete absorption of all N were approx. the same and equal to that produced in H_2O . The data are discussed in relation to the theory of the synthesis of protein from NH_4OH or HNO_3 . The energy required by plants to secure the OH^- necessary for the assimilation of NH_4^+ or the H^+ for the assimilation of NO_3^- is qualitatively related to the rates of absorption of NH_4^+ or NO_3^- from solutions of different p_{H} . A. G. P.

Effect of colloids on the assimilation of magnesium and ammonium chlorides by the roots of plants. B. NIKLEWSKI (Biochem. Z., 1934, 271, 111—122).—The absorption of Cl^- and still more of NH_4^+ and Mg^{++} by the roots of plants (sugar-beet, mustard) is increased by addition of colloidal material (I) (solution from stable manure, suspension of loam), although occasionally this procedure diminishes uptake of Cl^- . (I) acts directly on the plasma.

W. McC.

How does water penetrate the interior of [cereal] grains? K. G. SCHULZ (Woch. Brau., 1934, 51, 201—204).—The dorsal half of barley grains takes up H_2O rather more rapidly than the ventral half. The germ end of the grain absorbs H_2O almost twice as rapidly as the central portion or the apex, absorption by these last two portions being about the same. The greatest absorption seems to take place in the micropylar region, but the husk permits entry of H_2O all over the surface, although to a relatively smaller extent.

I. A. P.

Influence of sodium nitrate solutions on the permeability of protoplasm to water. I. DE HAAN (Natuurwetensch. Tijds., 1934, 16, 131—139). Plasmolysis and deplasmolysis of the epidermal cells of the inner epidermis of *Allium cepa* with sucrose solutions (I) shows that whereas pretreatment with NaNO_3 reduces the permeability of the protoplasm, $\text{Ca}(\text{NO}_3)_2$ has no effect. If, however, NaNO_3 is added to (I) (without altering the osmotic pressure), the permeability of membranes pretreated with NaNO_3 increases.

H. F. G.

Accumulation of electrolytes. VI. Effect of external p_{H} . A. G. JACQUES and W. J. V. OSTERHOUT (J. Gen. Physiol., 1934, 17, 727—750). Although KCl is present in the sap of *Valonia*, under normal conditions it penetrates chiefly as KOH . The rate of entrance of KOH is increased in photosynthesis by an increase in the p_{H} just outside the protoplasm.

G. R.

Influence of radium on the cultural yields of certain plants. A. LÉPAPE and R. TRANNOY (Compt. rend., 1934, 199, 316—318).—In moderate doses, Ra does not appear to have any influence on the yields of eight plants cultivated in different localities. The

yields are invariably lower if the Ra content of the soil is 1000 times $>$ normal.

H. W.

Vital staining with chrysoidine. H. D. WULFF (Planta, 1934, 22, 70—79).—Changes occurring in pollen tubes (e.g., decomp. of fat, formation of starch, intermixing of colloids) and in generative cells (accumulation of lipins) may be examined by the use of chrysoidine, which is sol. in plasma-colloids.

A. G. P.

Use of tannic acid and ferric chloride for staining cell-walls in meristematic tissue. A. S. FOSTER (Stain Tech., 1934, 9, 91—92).—The prep. is treated successively with aq. tannic acid, FeCl_3 , and EtOH-safranin solutions after appropriate washings. When destained and cleared meristematic tissues of *Carya* so treated display intensely black cell-walls, violet-pink cytoplasm, blue spindle fibres, and red nucleoli and chromosomes.

H. W. D.

Use of picric acid with the Gram stain in plant cytology. F. H. SMITH (Stain Tech., 1934, 9, 95—96).—A saturated solution of picric acid in EtOH is used in the dehydration following the application of gentian-violet I. Clove oil is used for differentiation. Chromosomes are stained more distinctly than with the usual Gram stain, and do not fade.

H. W. D.

Metachromatic staining of plant tissues. II. Basic dyes. A. T. CZAJA (Planta [Z. wiss. Biol.], 1934, 21, 531—601; cf. A., 1931, 402).—Differential absorption of acid and basic dyes in H_2O and EtOH solution is explained by the negative charge on the cell-wall in contact with H_2O and its positive charge when in contact with EtOH. Effects of the encrusting layers of lignin, cutin, and corky matter are examined and discussed.

A. G. P.

Changes in plant-food intake caused by a population of *Heterodera marioni* (Cornu), Goodey, on *Ananas comosus*. O. C. MAGISTAD and J. M. OLIVEIRA (Phytopath., 1934, 24, 276—283).—Dry-matter production in pine-apple plants was reduced by inoculation with *H. marioni*. Manuring increased the N content of all plants, but improved growth occurred only in non-infected plants. The N intake was reduced 40—50% by the nematodes.

A. G. P.

Toxin produced by *Bacterium tabacum* and its relation to host range. E. E. CLAYTON (J. Agric. Res., 1934, 48, 411—426).—Certain chemical reactions of the thermostable, non-filterable toxin (I) are examined. Typical "wildfire" lesions are produced in plants other than tobacco by inoculation with (I), which is rapidly inactivated by alkalis.

A. G. P.

Susceptibility reactions of *Pinus sylvestris* to Woodgate rust. R. P. TRUE (Phytopath., 1934, 24, 19—20).—Comparison of cellulose, lignin, pectin, starch, fat, oil, tannin, resin, and terpene contents of infected and healthy areas of trees shows the former to contain relatively more reserve food materials and tannins.

A. G. P.

Possible chemical nature of tobacco mosaic virus. C. G. VINSON (Science, 1934, 79, 548—549). Virus preps. have not yet been obtained free from N (cf. this vol., 230).

L. S. T.

Physiology of virus diseases in plants. I. Movement of the virus agent in tobacco and tomato. II. Effects of mosaic on the metabolism of tomato. J. CALDWELL (Ann. Appl. Biol., 1934, 21, 191—205, 206—224).—Diseased plants had decreased contents of dry matter and carbohydrates, but that of N was not appreciably affected. The CO_2 output of diseased tissue expressed in terms of fresh or dry wt. or residual N was $>$ normal. Respiration in O_2 or N_2 produced similar results. A. G. P.

Action of trypsin on tobacco-mosaic virus. W. M. STANLEY (Phytopath., 1934, 24, 18).—Addition of trypsin to juice of diseased plants rendered this non-infective. No digestion of protein was apparent. The infectivity of virus-trypsin solutions increased on dilution, with keeping, or with moderate heating. Addition of globin and trypsinogen, having isoelectric points near to that of trypsin, produced similar effects. Pepsin, gelatin, and ovalbumin having isoelectric points in the acid area were non-effective. A. G. P.

Factors affecting the inactivation rate of the virus of tomato spotted wilt. J. G. BALD and G. SAMUEL (Ann. Appl. Biol., 1934, 21, 179—190).—Loss of virulence of spotted wilt inoculum (I) was accelerated by aeration, but bubbling N_2 through (I) produced only a very small change. The rate of inactivation was increased by treatment with chloramine-T, H_2O_2 , FeSO_4 , tannic acid, quinol, and cystine hydrochloride, and retarded by Na_2S and (slightly) by NaNO_2 . A. G. P.

Search for mitogenetic radiation by means of a photo-electric method. E. LORENZ (J. Gen. Physiol., 1934, 17, 843—862).—No mitogenetic radiation could be observed, using a photo-electric counter tube with Cd as the photo-electric metal, with biological materials supposed to be excellent radiators. H. G. R.

Protein determinations and colloid chemistry. C. LANGE (Kolloid-Z., 1934, 68, 69—82).—The nephelometric method is unsuitable for abs. determinations. The influence of dispersity is discussed. E. S. H.

Rapid colorimetric multiple determination of uric acid. G. KEIGHLEY and H. BORSOOK (J. Lab. Clin. Med., 1934, 19, 650—654).—A spectrophotometric modification of Morris and Macleod's method is described. CH. ABS.

Colorimetric determination of tyrosine and tryptophan by the method of Folin and Marenzi. D. VON DESSEO (Biochem. Z., 1934, 271, 142—151; cf. A., 1929, 1093).—The method is improved by hydrolysing the protein with 20% aq. NaOH for 2 hr. at 2—8 atm. and employing a formula different from that of the authors named. In the tyrosine determination (error ± 3 to $\pm 6\%$) turbidity is avoided by addition of 14N- H_2SO_4 . 3 hr. suffices for pptn. of the tryptophan (average error 4—5%). W. McC.

Determination of histidine with the step photometer. R. KAPELLER-ADLER (Biochem. Z., 1934, 271, 206—208; cf. A., 1933, 1094).—The step photometer is used in conjunction with the method previously described. W. McC.

Determination of reductones and thiol compounds. C. MARTIUS and H. VON EULER (Biochem. Z., 1934, 271, 9—14).—The velocities of reduction (I) of 2 : 6-dichlorophenol-indophenol (II) by ascorbic acid (III), reductone, dihydroxymaleic acid, glutathione (IV), and cysteine (V) exhibit max. at the following p_H , respectively: 6.5—7.5, 5.0—7.0, 5.0—6.0, 5.5, and 5.5. The min. for the first three substances are at p_H 11, 12, and 12.5, respectively. (I) by (III) is not affected by the presence of (IV) or (V). For titration of (III) with (II) in presence of thiol compounds p_H should be 2.5. 2 : 6-Dibromophenol-indophenol behaves exactly like (II), but with phenol-indophenol the max. occur 1 p_H unit lower. W. McC.

Determination of lactic acid by the method of Mendel and Goldscheider. R. NORDBO (Biochem. Z., 1934, 271, 213—215; cf. A., 1926, 212).—For each amount of acid there is an optimum amount of veratrole. To 0.5 c.c. of the solution (0.005—0.02 mg. of lactic acid) heated at 100° for 4 min. with 3 c.c. of H_2SO_4 and then cooled to 0° , 0.05 c.c. of a 1 : 800 solution of veratrole in 96% EtOH is added. After 1 hr. the colour comparison is made. Blood may be deproteinised with $\text{HCl} + \text{HgCl}_2$ or with HPO_3 . Results are 6—7 mg. of lactic acid per 100 c.c. $<$ those given by the gasometric method (for blood). W. McC.

Lactic acid determination. H. J. FUCHS and J. BRÜGGEMANN (Z. physiol. Chem., 1934, 225, 35—40).—Improvements in lactic acid determination (cf. this vol., 56) in blood relate to removal of protein with CuSO_4 -NaOH and sugar with CuSO_4 - $\text{Ca}(\text{OH})_2$, filtration through glass-wool, and use of H_3AsO_3 for the iodometric titration. J. H. B.

Elements in tissues. IX. Spectroscopic determination of manganese. W. GERLACH and K. RUTHARDT (Virchow's Archiv, 1934, 292, 52—54).—0.0001 mg. of Mn can be detected and determined (accurate to $\pm 10\%$) by adding $\text{Pb}(\text{NO}_3)_2$ and comparing the intensities of the Pb and Mn lines in pairs with those of standards. NUTR. ABS. (m)

Micro-determination of potassium as potassium hydrogen tartrate in biological material. A. BOLLIGER (Austral. J. Exp. Biol., 1934, 12, 75—78).—The material is digested with HClO_4 , HNO_3 , and H_2O_2 (cf. A., 1932, 978) and the perchlorates left after evaporation are extracted with a mixture of BuOH and EtOAc, KClO_4 and NH_4ClO_4 remaining undissolved. The latter is removed by heating, when it partly decomposes, whilst the KClO_4 is dissolved in warm H_2O and K pptd. by adding < 10 vols. of a cold saturated EtOH solution of tartaric acid. The crystals of K H tartrate are separated by centrifuging, washed with EtOH, dissolved in a small quantity of H_2O , and titrated with NaOH, a composite indicator of Me-red and methylene-blue being employed. W. O. K.

Mineral metabolism. XXVIII. Micro-determination of iodine in biological material. I. J. B. BLOM (Onderstepoort J. Vet. Sci., 1934, 2, 123—130).—Dry oxidation in a closed system and open ashing in a Ni dish give comparable results if the ashing temp. is $> 300^\circ$. By either method $> 80\%$ of the total I can be recovered. NUTR. ABS. (m)

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1934.

General, Physical, and Inorganic Chemistry.

Origin of anomalous displacements in the Stark effect of hydrogen. W. STEUBING and P. JAKEL (Z. Physik, 1934, 90, 112—132).

A. B. D. C.

Demonstration of the axiality of light emission of the ultra-violet hydrogen lines 1025 and 1215 Å. R. FRERICHs and H. BOMKE (Physikal. Z., 1934, 35, 549—551).—For the 1025 Å. line, with parallel emission, the ratio of the intensity of the long-wave to that of the short-wave component is 1:2. An approx. val. of 1:1.5 is obtained for opposite emission. For the 1215 Å. line, the components have the same intensity in both parallel and opposite emission.

A. J. M.

Nuclear spin of deuterium. G. M. MURPHY and (Miss) H. JOHNSTON (Physical Rev., 1934, [ii], 46, 95—98).—Determination of the alternating intensities in emission of the $\Delta v=0$ sequence of the Fulcher bands leads to a nuclear spin of unity.

N. M. B.

Direct proof of the existence of metastable molecules in active nitrogen. J. KAPLAN (Nature, 1934, 134, 289).—The bands 2760.6 and 2603.8 Å. appear in the N afterglow and provide direct proof of the existence in it of metastable mols.

L. S. T.

Situation of the A ($^3\Sigma$) level in the nitrogen molecule. E. T. S. APPLEYARD, N. THOMPSON, and S. E. WILLIAMS (Nature, 1934, 134, 322—323).

L. S. T.

Measurements of intensity distribution and width of predissociation lines of the AlH molecule. II. H. C. BURGER and P. H. VAN CITTERT (Z. Physik, 1934, 90, 70).—Polemical against Farkas and Levy (this vol., 823).

A. B. D. C.

Further band systems of aluminium hydride. W. HOLST (Nature, 1934, 134, 322).—The band system at 4950 Å. (this vol., 715) belongs to a $^1\Sigma^{***} \rightarrow ^1\pi$ transition.

L. S. T.

Continuous emission spectra of atomic origin. G. BALASSE (J. Phys. Radium, 1934, [vii], 5, 304—308).—Spectra excited by electrodeless discharge have been photographed for the neutral atoms of K, Rb, Cs, Zn, Hg, P, As, Bi, S, and I, and for the ionised atoms of Hg, S, and I. Properties and mechanism of emission are discussed. The coincidence of certain lines with the continuous spectrum is explained by anomalous dispersion (see this vol., 935).

Deepest terms in ions of the isoelectronic sequences Ni I to Kr IX and Pd I to Xe IX. P. G. KRUGER and W. E. SHOUFF (Physical Rev., 1934, [ii],

46, 124—129).—Radiations corresponding with energy differences between terms have been found, and new lines of Kr IX and Xe IX are predicted.

N. M. B.

Spectrum of nickel hydride. A. G. GAYDON and R. W. B. PEARSE (Nature, 1934, 134, 287).—Details of a spectrum attributed to the mol. NiH are given.

L. S. T.

Spectrum of zinc. L. BLOCH and E. BLOCH (J. Phys. Radium, 1934, [vii], 5, 289—298).—The spark spectrum in vac. revealed the new Zn IV order of < 120 lines in the range 4000—2500 Å. The high-frequency electrodeless discharge allowed the separation of the orders Zn II, giving < 50 new lines, Zn III, and Zn IV. Data for about 800 lines are tabulated.

N. M. B.

Band spectrum of Se₂. E. OLSSON (Z. Physik, 1934, 90, 138—144).—Bands near 3700 and 3900 Å. were investigated; Se⁸⁰ has no nuclear spin.

A. B. D. C.

Second spark spectrum of tellurium. S. G. KRISHNAMURTY (Nature, 1934, 134, 255).—The fundamental intervals $5p^3P_0-5p^3P_1$, $5p^3P_2-5p^3P_2$, and $5p^3P_2-5pD_{1/2}^1$ are 4751, 3410, and 9198 cm.⁻¹, respectively. The calc. third ionisation potential of Te is approx. 29.5 volts.

L. S. T.

Excitation and ionisation of mercury atoms in columns of the rare gases containing mercury. F. M. PENNING (Physica, 1934, 1, 763—769).—From spectrograms of the positive columns of the rare gases at a pressure of 10 mm. and at 0° and 19°, in presence and absence of Hg, it is concluded that at 19° the positive ions are mainly Hg⁺ formed by direct electron collision, whilst at 0° excitation of rare gases is necessary.

H. S. P.

Initial stages of spark discharges in gases. H. J. WHITE (Physical Rev., 1934, [ii], 46, 99—106).—Using the electro-optical shutter, a study in N₂, H₂, O₂, CO₂, He, and A at atm. pressure and gaps < 1 cm. shows four types of spark breakdown characterised by the appearance and growth of luminous streamers; the velocity of the latter in H₂ and N₂ is approx. 10⁷ cm. per sec., agreeing with calc. electron velocities under breakdown conditions. Results indicate that the current at breakdown is carried mainly by electrons, which come from the cathode rather than from ionisation in the gas. The space charges causing breakdown arise from differences in mobility velocity of electrons and positive ions.

N. M. B.

Interior radiation of the electric arc. T. PECZALSKI (Compt. rend., 1934, 199, 405—407).—Using hollow C electrodes it has been shown that the

spectrum of the internal layers of an arc salted with CaF_2 includes Ca, C, N_2 , and O_2 bands, whilst the radiation from the exterior consists principally of CaF_2 bands. J. W. S.

Thermal mechanism in the column of the arc. L. S. ORNSTEIN and H. BRINKMAN (*Physica*, 1934, 1, 797—824).—Theoretical. The formation and destruction of excited particles in the ordinary arc is due chiefly to collisions between atoms and mols. Near the electrodes and at low pressures, excitation and ionisation due to electron collision may occur, so that the thermal mechanism of the arc changes into the electron mechanism of the glow discharge. H. S. P.

Formation of hydrogen in a vacuum. M. POSEJPAL (*Compt. rend.*, 1934, 199, 186—188; cf. this vol., 236, 471).—It has been shown that H_2 pre-existing in the discharge tube cannot account for the development of H_2 in a vac. during discharge, described previously. Measurable vols. of H_2 are developed in a vac. tube which contains 30 thin Pt wires (12 connected to the cathode and 18 to the anode), but H_2 is not developed when the same current is passed but with no wires in the tube. The vols. produced are about twice those which are formed by the same current during electrolysis, in agreement with the author's theory. J. W. S.

Emission of low-penetrating radiation by charged insulators. G. REBOUL (*J. Phys. Radium*, 1934, [vii], 5, 329—343).—Charged insulators emit, in losing their charge, a highly absorbable radiation which ionises gases, affects a photographic plate, and gives rise to invisible phosphorescence phenomena. Certain anomalies which are shown by insulators and can be explained by the emission, and the properties, nature, and origin of the radiation are examined and discussed. N. M. B.

X-Ray dispersion in nickel by the method of total reflexion. A. J. LAMERIS and J. A. PRINS (*Physica*, 1934, 1, 881—888; cf. A., 1931, 1105).—The hump found by Kiessig in the dispersion curve near to the Ni K edge is not confirmed. The results obtained do not agree with Honl's theoretical curve. H. S. P.

Fine structure of X-ray absorption edges of the polyatomic vapours GeCl_4 and AsCl_3 . D. COSTER and G. H. KLAMER (*Physica*, 1934, 1, 889—894).—The fine structure of the K absorption edge of Ge and As in the vapours of GeCl_4 and AsCl_3 , respectively, has been measured, and found to extend for several hundred volts from the edge. For GeCl_4 fine structure agrees with theory (see following abstract); for AsCl_3 it indicates that the distance of the Cl atoms from the As atom is about 2.20 Å. H. S. P.

Theoretical calculation of the fine structure for the K absorption band of Ge in GeCl_4 . D. R. HARTREE, R. DE L. KRONIG, and H. PETERSEN (*Physica*, 1934, 1, 895—924).—Mathematical. H. S. P.

K Series X-ray emission lines of iron in several compounds. S. TANAKA and G. OKUNO (*Japan. J. Physics*, 1934, 9, 75—79).— $K\alpha_2$, $K\beta$, and $K\beta'$ lines of Fe were investigated for Fe, Fe_2O_3 , FeS, FeS_2 , and $\text{K}_3\text{Fe}(\text{CN})_6$ by means of the secondary method. Separ-

ation of $K\beta'$ from $K\beta_1$ was obtained for Fe_2O_3 and FeS. Displacement of the $K\beta_1$ lines of the compound relative to that of the pure element was detected especially for FeS_2 . With Fe and the other compounds investigated $\Delta\lambda$ for the $K\alpha$ doublet is 4, whereas FeS_2 has the corresponding $\Delta\lambda$ 3.82. W. R. A.

Quadrupole lines in the K series of ruthenium. E. WILHELMY (*Physical Rev.*, 1934, [ii], 46, 130—132).—The Ru $K\beta_4$ ($K-N_{IV}N_V$) and $K\beta_5$ ($K-M_{IV}V$) lines have been observed with a double crystal spectrometer; the wave-lengths are 0.55974 and 0.56668 Å., respectively. $K\beta$ appears to be a doublet; the width of the single components is < 11 volts; $K\beta_4$ is 28 volts. The intensity ratios are: $K\beta_4/K\alpha_1=1/160$, $K\beta_5/K\alpha_1=1/400$. A very faint line ($K\beta_6/\lambda\alpha_1=1/2000$) of λ 0.558 Å. has been observed. N. M. B.

Intensity measurements of X-ray spectral lines. M. BÖTZKES (*Z. Physik*, 1934, 89, 667—681).—Relative intensities are given for Ta L lines. A. B. D. C.

Determination of atomic scattering factors for X-rays in the region of L absorption edges. J. BRENTANO and A. BAXTER (*Z. Physik*, 1934, 89, 720—735).—Observations were made for W and Al. A. B. D. C.

L Absorption discontinuities of bismuth. L. H. CARR (*Physical Rev.*, 1934, [ii], 46, 92—95).—Using balanced cells containing $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in dil. HNO_3 and dil. HNO_3 , respectively, μ/ρ was measured at 20 wave-lengths in the range 0.56—1.54 Å. Equations to the branches of the curve and the magnitudes of discontinuities were deduced. N. M. B.

Experiment showing the dark current of alkali cells due to a glow electron current. R. SCHULZE (*Z. Physik*, 1934, 90, 63—69).—The dark current is shown as exponentially dependent on temp., and must be due to a glow electron current. A. B. D. C.

Form of discharge in gas-filled photo-cells. F. ROTHER and H. BOMKE (*Physikal. Z.*, 1934, 35, 703—705).—In the gas-filled cell a form of discharge occurs well below the breakdown potential. It is not a glow discharge, but is an accompaniment of the increase in the photo-current brought about by ionisation by collision. The nature of the discharge does not vary with the type of anode. A. J. M.

Secondary emission of tantalum. R. WARNECKE (*J. Phys. Radium*, 1934, [vii], 5, 267—282).—The variation of the no. of secondary electrons ejected from a Ta target as a function of the speed of the primary electron in the range 0—1000 volts has been investigated. Distribution curves show that secondary electron speeds lie between zero and that of the primary electron. N. M. B.

Ratio of the dia- and para-magnetism of an electron gas as a function of the strength of field. K. F. NIESSEN (*Physica*, 1934, 1, 783—796).—Mathematical. This ratio is not const. With stronger fields the Landau diamagnetic effect increases relatively to the Pauli paramagnetic effect. H. S. P.

Proton production in the low-voltage arc. E. S. LAMAR and O. LUHR (*Physical Rev.*, 1934, [n],

46, 87—91).—An improved design of tube gave proton current/total current as high as 98% at 0.3—0.4 mm. pressure. N. M. B.

Diffusion of positive ions of salts through copper, silver, and gold at high temperature. Mass spectrograph analysis of emitted ions. J. CICHOCKI (Ann. Physique, 1934, [xi], 2, 160).—A correction (cf. this vol., 125). N. M. B.

Effect of the electric field on alkali metal atoms in atomic ray experiments. H. SCHEFFERS and J. STARK (Physikal. Z., 1934, 35, 625—627).—Experiments with at. rays of K, Li, and Cs in electrical fields of various strengths show that a moment is produced \propto the field strength, the proportionality factors being 4.2, 3.4, and 1.2 (all $\times 10^{-23}$), respectively. A. J. M.

Revision of at. wt. of niobium. Analysis of niobium pentachloride. O. HONIGSCHMID and K. WINTERSBERGER (Z. anorg. Chem., 1934, 219, 161—177).—Methods for the prep. of pure Nb_2O_5 are described. Nb_2S_5 was prepared by the action of H_2S and CS_2 on Nb_2O_5 at 1000° . NbCl_5 was formed by the action of Cl_2 on Nb_2S_5 and purified by fractional sublimation in vac. The at. wt. of Nb is 92.91 (Ag 107.880, Cl 35.457), in good agreement with the val. obtained by the mass spectrograph. M. S. B.

Thermal data and at. wt. of xenon. W. HEUSE and J. OTTO (Physikal. Z., 1934, 35, 628—629).—The 0° isotherm and the expansion and potential coeffs. of Xe have been determined. The at. wt. determined from the density of the gas is 131.22 ± 0.02 . A. J. M.

Radioactivity of samarium. HERZSFINKEL and A. WRONBERG (Compt. rend., 1934, 199, 133—135).—The max. penetration of α -particles emitted by Sm_2O_3 , measured by an ionisation chamber and electroscopes method, was 1.67 cm., confirming the val. found by Curie and Joliot (Mader, this vol., 713). 1 g. of Sm emits 67 particles per sec. B. W. B.

Actinium-uranium ratio in radioactive minerals. (MLLE.) E. GLEDITSCH and E. FOEY (Compt. rend., 1934, 199, 412—414).—The mean Ac:U ratio for a no. of minerals from different sources is calc. as 0.243:1. This, combined with the accepted val. for Io:U (0.53:1), indicates Ac:U 0.128:1. For every 100 atoms of U, 4 disintegrate into Ac. It is concluded that if Ac is derived from an isotope of U the half-life period of the latter should not differ from that of U-I. J. W. S.

Ultimate origin of the actinium series. H. J. WALKE (Phil. Mag., 1934, [vii], 18, 256—262; cf. this vol., 471).—It is suggested that the Ac series arises from the disintegration of the heavy U isotope (called protactino-uranium PrAcU) of at. wt. 239, and not as a result of branching of the main U series. PrAcU is stated to lose an α -ray to form a product (U-Z_1) of mass 235, at. no. 90, which loses a β -ray to yield U-Z. The latter by a β -ray change yields AcU and thence by another α -ray change U-Y. The latter passes to Pa and thence to Ac by β - and α -ray changes, respectively. J. W. S.

Ionisation curves for polonium α -radiation in pure xenon and krypton. R. NAIDU (J. Phys.

Radium, 1934, [vii], 5, 343—346).—Bragg curves and data are given. The ranges at 15° are: $R_{\text{Kr}} 3.03 \pm 0.01$, $R_{\text{Xe}} 2.17 \pm 0.01$ cm. The absorbing powers relative to air are Kr 1.227, Xe 1.785. The total ionisation relative to air is Kr 1.45, Xe 1.40, and relative to He, Kr 1.263, Xe 1.221, air 0.873. The % ionisation energy losses are 30 in Kr, 40 in Xe, and 49 in air. N. M. B.

Measurements of the absorption of γ -rays by the method of coincidences. Radiation from excited beryllium. P. AUGER (Compt. rend., 1934, 199, 414—416).—The radiation from a tablet of Be bombarded with α -rays from a 10-millicurie Po source has been studied with oxidised steel and Al counters, mounted in coincidence. The variation of the no. of impacts with the nature and thickness of interposed metallic screens is shown graphically. 21 mm. of Pb reduced the intensity to one half, corresponding with an absorption coeff. of 0.34 cm^{-1} . J. W. S.

Theory of nuclear transformations and the classification of light elements. G. PETIAU (J. Phys. Radium, 1934, [vii], 5, 426—430).—A more detailed consideration of work already noted (this vol., 323, 578).

Range- and resonance-groups of protons from nuclear transformations by α -particle collisions. H. POSE (Physikal. Z., 1934, 35, 633—636).—The excitation functions of nuclear proton groups of Al, Na, F, N, and B have been investigated. The absorption curves indicate definite range groups, and resonance groups occur for protons from all the above with the possible exception of B. The facts can be explained by Gamow's theory. A. J. M.

Ranges of nuclear protons produced by the transformation of nitrogen by polonium α -rays. H. STEGMANN (Physikal. Z., 1934, 35, 636—637).—Three groups of protons are liberated; two groups, with ranges of 56 and 101.5 mm., respectively, are due to a resonance effect, whilst the third, with a range of 81.5 mm., is due to a normal excitation process. A. J. M.

H-Rays from aluminium using radium-B+C as source. G. ORTNER and G. STETTER (Z. Physik, 1934, 89, 708—712).—Artificial disintegration with this source gives four broad groups of H-rays. A. B. D. C.

"Nuclear photo-effect": disintegration of the dipton by γ -rays. J. CHADWICK and M. GOLDHABER (Nature, 1934, 134, 237—238).—Exposure of H^2 to γ -radiation from Ra-Th produces an effect which must be attributed to protons (I) resulting from the splitting of the dipton, probably according to the scheme ${}_1\text{H}^2 + h\nu \longrightarrow$. The mass of the neutron calc. from an estimate of the energy of (I) is 1.0080 ± 0.0005 and the binding energy of the dipton is 2.1×10^6 ev. The cross-section for disintegration of a dipton by a γ -ray of 2.62×10^6 ev. is 10^{-28} cm^2 . Lea's suggestion of the capture of neutrons by (I) (this vol., 235) is criticised. L. S. T.

Intense sources of protons, applicable to [the study of] transmutations. H. HULUBEI (Compt. rend., 1934, 199, 199—201).—Hydrogenated Pd forms a convenient source of protons, the wall of a Pd tube

being introduced between a source of H_2 and the vessel for acceleration of the protons, and being kept warmed either by the Joule effect alone or with auxiliary heating. J. W. S.

Radioactivity induced by neutron bombardment. T. BJERGE and C. H. WESTCOTT (*Nature*, 1934, **134**, 286).—Using neutron sources of $Rn+Be$ many of Fermi's results have been confirmed. Additional results are: F gives an approx. 40-sec. period; the longer period exhibited by Zn is approx. 6 hr. and the active body is an isotope of Cu; Cu gives a 6-hr. period and the active body is probably the same as that obtained from Zn; Na gives a weak effect of the same period (approx. 10 hr.) as the long periods of Mg and Al; the active body in each case is probably $^{11}Na^{24}$. L. S. T.

Spontaneous emission of neutrons from radioactive isotopes. H. J. WALKER (*Nature*, 1934, **134**, 215).—A discussion. Goldhaber's view (this vol., 826) is supported. γ -Radiation of high energy, the neutron, and the positron emission observed by Curie, Joliot, and Preiswerk (*ibid.*) all result from the β -ray activity of the unstable nuclei, $^{13}Al^{28}$ and produced (cf. this vol., 939). L. S. T.

Complex neutron. H. MARGENAU (*Physical Rev.*, 1934, [ii], **46**, 107—110).—The unsatisfactory results of assuming that the neutron is a combination of a proton and an electron, with a modified potential near the proton, are demonstrated on the basis of the theories of Dirac and of Schrodinger. N. M. B.

Induced positron radioactivity. F. H. NEWMAN and H. J. WALKER (*Nature*, 1934, **134**, 288—289).—Theoretical. Radioactivity induced by proton, dipion, neutron, and α -particle bombardment can be explained on the hypothesis that the nuclear structure of stable isotopes consists of α -particles, neutrons, and dipions. L. S. T.

Experimental proofs of the annihilation of positive electrons. F. JOLIOT (*J. Phys. Radium*, 1934, [vii], **5**, 299—303; cf. this vol., 126, 127). N. M. B.

Limits of the energy spectra of positrons and electrons from artificial radio-elements. A. J. ALICHANOV, A. J. ALICHANIAN, and B. S. DZELEPOV (*Nature*, 1934, **134**, 254—255).—The end-points of the spectra of radio-N, radio-P, and radio-Al are 1450, 3700, and 3050 kv., respectively. L. S. T.

Photographic investigations with positrons. L. BEWLOGUA and K. R. DIXIT (*Physikal. Z.*, 1934, **35**, 699—702).—A photographic method for the identification of positrons, similar to that used by Rutherford for the investigation of the secondary β -radiation, is described. The distribution of electrons and positrons was investigated, the ratio of positrons to electrons increasing with the at. no. The absorption of electrons and positrons at Ag and Pb foils was also investigated by this method. A. J. M.

Estimated electron affinities of the light elements. G. GLOCKLER (*Physical Rev.*, 1934, [ii], **46**, 111—114).—Empirical extrapolation of the Moseley $I\lambda^2/Z$ curves gives for the affinities, in e.v.: H (+0.7), He (−0.5), Li (+0.3), Be (−0.6), B (+0.1),

C (+1.37), N (+0.04), O (+3.8), F (+3.9), Ne (−1.20), Na (+0.1), Mg (−0.9), Al (−0.2), Si (+0.6), P (+0.2), S (+2.1), Cl (+3.7), A (−1.0), Ni (+0.3), Cu (+1.2), Ag (+1.0), Hg (+1.8). N. M. B.

Radiation emitted by the retardation of fast electrons. F. SAUTER (*Ann. Physik*, 1934, [v], **20**, 404—412).—Theoretical. Wave-mechanical formulæ, which include the relativity correction, have been derived for the spectral intensity of the radiation emitted when an electron collides with an at. nucleus, and for the total energy radiated. R. S. B.

Diamagnetism of the Dirac electron. T. MUTO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 165—170).—Mathematical. J. W. S.

Classical theory of the spinning electron. H. A. KRAMERS (*Physica*, 1934, **1**, 825—828).—Mathematical. The ratio e/mc of the magnetic moment and angular momentum of the electronic spin is classically derived without reference to a detailed classical model of the constitution of the electron. H. S. P.

Exchange in the Thomas-Fermi atom. H. JENSEN (*Z. Physik*, 1934, **89**, 713—719).—Theoretical. A. B. D. C.

Wave equation of the photon. L. DE BROGLIE (*Compt. rend.*, 1934, **199**, 445—448; cf. this vol., 236).—Mathematical. J. W. S.

Is the Lorentz contraction dependent on refractive index? L. COURVOISIER (*Z. Physik*, 1934, **90**, 48—62).—This contraction of a ponderable body is independent of the refractive index of itself or of its medium. A. B. D. C.

Reflecting power of aluminised surfaces. B. K. JOHNSON (*Nature*, 1934, **134**, 216).—Data for reflexion throughout the ultra-violet spectrum are given for Al deposited on glass by the new evaporation method. L. S. T.

Simple and general relationship between molecular spectra and the electrons and electron rings of the constituent atoms. H. DESLANDRES (*Compt. rend.*, 1934, **199**, 393—397; cf. this vol., 823).—The theory previously put forward is extended and shown to be in accordance with the Raman spectra of H_2 (gas), C_2 (crystal), and C_2H_2 (gas), the absorption spectra of H_2 (gas), Li_2 (gas), and C_2H_2 (gas), and the Swan spectrum of C_2 (gas). J. W. S.

Transparency of the lower atmosphere and its content of ozone. D. CHALONGE and E. VASSY (*J. Phys. Radium*, 1934, [vii], **5**, 309—319).—Using an improved spectrograph the coeffs. of atm. absorption in the ultra-violet were obtained by photometric measurement of the absorption of 1200—1400 m. of air for continuous H radiation. Two spectra compared, photographed at distances of 400 and 1600—1800 m., show for wave-lengths >2700 Å. absorption attributed to O_3 , and consisting of bands, followed below 2421 Å. by a continuous spectrum. Outside the region of absorption the O_3 content is deduced. Data for simultaneous determinations at two localities are given. N. M. B.

Suppression of certain bands of the ozone spectrum under the action of cold. (MME.) L.

LEFEBRE (Compt. rend., 1934, 199, 456—457).—The ultra-violet absorption spectrum of O_3 is much sharper at -80° than at 20° . The spectrum can be classified into bands which become more intense, and those which almost disappear, these bands being attributed to electron jumps from a state of zero vibration and finite vibrational states, respectively. J. W. S.

Significance of the O_4 spectrum and existence of polyatomic polarisation molecules. W. FIN-KELNBURG (Z. Physik, 1934, 90, 1—10).—Solid, liquid, and high-pressure O_2 spectra are shown, similar to those of diat. polarisation mols., and give dissociation energies for excited O_4 states to corresponding O_2 states, as several hundredths of a volt.

A. B. D. C.

Significance of the O_4 spectrum and existence of polyatomic polarisation molecules. H. SALOW (Z. Physik, 1934, 90, 11).— O_2 absorption between 2400 and 2900 Å. increases progressively in presence of He, Ne, A, N_2 , and CO_2 . A. B. D. C.

Zeeman effect in triplet bands. Influence of magnetic fields on lines of the third positive carbon monoxide bands. R. SCHMID (Z. Physik, 1934, 89, 701—707). A. B. D. C.

Band spectrum of CO^+ . H. BULTHUIS (Physica, 1934, 1, 873—880).—The rotational structure of the combination bands $B^2\Sigma^- \Pi$, (0, 3), and (0, 4) has been analysed. With the aid of these and of the $B^2\Sigma^- \rightarrow X^2\Sigma$ and $A^2\Pi^-$ band lines, the combination principle was tested and the intensity relations were found to agree qualitatively with theory.

H. S. P.

Spectrum of gallium oxide. (MISS) M. L. GUERNSEY (Physical Rev., 1934, [ii], 46, 114—116).—The spectrum has been photographed and a band system in the region 3800—4200 Å. is identified as a $^2\Sigma^- \rightarrow ^2\Sigma$ transition. Wave-nos., quantum assignments, and intensities are tabulated, and an equation for the band heads is given.

N. M. B.

Absorption and fluorescence spectra of some hydrocarbons with two benzene nuclei. R. TITEICA (Compt. rend., 1934, 199, 458—460).—Data are recorded for EtOH solutions of Ph_2 , CH_2Ph_2 , $[CH_2Ph]_2$, and $CH_2Ph \cdot C_6H_4Ph$. The spectra frequently show a periodicity of 400—500 cm^{-1} , this frequency difference decreasing with increasing complexity of the mol. The heavier is the mol., the further is the fluorescence spectrum displaced towards the visible region.

J. W. S.

Absorption spectra of single crystals of polynuclear hydrocarbons. K. S. KRISHNAN and P. K. SESHAN (Current Sci., 1934, 3, 26—27).—The absorption of single crystals of anthracene, phenanthrene, 1 : 2-benzophenanthrene, 1 : 2 : 5 : 6-dibenzanthracene (I), fluorene, fluoranthene, and pyrene is more intense when the incident light vibrations are parallel to than when normal to the C_6H_6 planes in the mols. Details are given for (I).

L. S. I.

Ultra-violet absorption spectra of gen-alkaloids. V. BRUSTIER and P. BLANC (Bull. Soc. chim., 1934, [v], 1, 702—712).—The *N*-oxides of atropine, hyoscyamine, and scopolamine have seven absorption

bands (maxima between 2410 and 2715 Å.) which are less intense and of slightly shorter λ than the corresponding bands of the parent alkaloids. The absorption of morphine *N*-oxide (I) is similar to that of morphine (II), but the band of (I) is at a slightly shorter λ and the intensity is $<$ that of (II). The absorption systems of strychnine and its *N*-oxide (III) are almost identical, but that of the benzoate of (III) is modified, the bands being more intense and at longer λ .

J. G. A. G.

Spectrum of heavy water in the photographic infra-red. G. HERZBERG and H. VERLEGER (Physikal. Z., 1934, 35, 622).—Four bands were found, two due to HH^2O and two to H_2^2O . The HH^2O band at 9400 Å. and the H_2^2O band at 11,600 Å. were very strong. The former corresponds approx. with the strong H_2O band at 9400 Å.

A. J. M.

Infra-red spectrum of magnesium oxide. J. FOCK (Z. Physik, 1934, 90, 44—47).—Investigation of this spectrum from 2.8 to 200 μ gives a fundamental at 17.3 μ , near the val. deduced from sp. heat.

A. B. D. C.

Short-wave infra-red [spectra] of silicates. K. WIRTZ (Physikal. Z., 1934, 35, 649—651).—The structure of the silicates is considered. There is similarity between the short-wave infra-red spectrum of a sulphate and a silicate such as titanite, $(CaO, Ti)SiO_4$, both giving two bands. Similar spectra are given by diopside and albite, and can be ascribed to the SiO_4 group. Silicates containing single Si-O groups with metal atoms in the crystal lattice give essentially similar spectra.

A. J. M.

Transformation of ammonium salts: influence of the NH_4 radical on anions. J. FOCK (Z. Physik, 1934, 90, 38—43).—The transformation effect observed in the 9 band of SO_4 in $(NH_4)_2SO_4$ does not occur in Na_2SO_4 or in K_2SO_4 , and is due to a coupling effect of the NH_4 radical.

A. B. D. C.

Infra-red absorption spectrum of formaldehyde. I. H. H. NIELSEN (Physical Rev., 1934, [ii], 46, 117—121; cf. Patty, A., 1932, 558; Dieke, this vol., 238).—Further investigation to beyond 11.0 μ revealed additional bands at 5.7, 6.7, 7.5, 8.6, and 9.6 μ . Data and resolution into rotational components are tabulated and plotted.

N. M. B.

Normal frequencies of sulphur hexafluoride. A. EUCKEN and H. AHRENS [with E. BARTHOLOME and L. BEWLOGUA] (Z. physikal. Chem., 1934, B, 26, 297—311).—In measurements with gaseous and liquid SF_6 the Raman lines 775, 645, and 525 cm^{-1} have been observed (cf. this vol., 830). These are taken to correspond with the simple totally symmetrical frequency, ν_1 , ν_2 , and ν_3 , respectively. The infra-red spectrum exhibits the frequencies 617 (ν_5) and 965 cm^{-1} (ν_6). The last of the frequencies theoretically to be expected has been found by measurement of the mol. heat, C_p , of the gas at 210—340° abs. to be 363 cm^{-1} (ν_4), which is optically inactive. The other bands in the infra-red spectrum are accounted for as combination vibrations of the above by applying the selection rules for an octahedral model.

R. C.

Raman spectrum of water. I. M. MAGAT (J. Phys. Radium, 1934, [vii], 5, 347—356).—Bands at

500 and 200 cm^{-1} were found and separated from the satellite lines of Hg in the range 30—240 cm^{-1} . No band was found at λ 3630. Intramol. vibrations of H_2O and of complex quasi-mols. were identified. Full data and frequencies are tabulated. N. M. B.

Intensity measurements in the Raman spectrum of carbon dioxide. (MISS) I. HANSON (Physical Rev., 1934, [ii], 46, 122—123).—A simple photographic method of measuring Raman intensities is described. The ratio of the intensities of the strong CO_2 doublet is corr. to 0.572. An exposure of 24 days brought out three new lines corresponding with shifts 1244 ± 10 , 1426 ± 8 , 1528 ± 15 cm^{-1} , as predicted by Dennison (cf. A., 1933, 661). N. M. B.

Rotational Raman effect in liquids. I. Benzene. S. BHAGAVANTAM and A. V. RAO (Indian J. Physics, 1934, 8, 437—443; cf. this vol., 345).—The intensity of the diffuse wings accompanying the Rayleigh lines in C_6H_6 starts from a max. at or near the centre and decreases rapidly for about 20 cm^{-1} , thence gradually for about 130 cm^{-1} . Discussion of results indicates that the wing cannot be explained as due only to mol. rotation. N. M. B.

Dispersion of polarisation of Raman lines. S. C. SARKAR (Indian J. Physics, 1934, 8, 415—423).—The dependence of polarisation of Raman lines of some liquids on the frequency of the exciting radiation has been investigated. Liquids having their absorption bands in the near ultra-violet show considerable dispersion in the polarisation. If ρ is the ratio of the intensity of the weak to the strong component, the val. of ρ for excitation by λ 5461 and 4358 is 4 : 5 in the case of PhNO_2 , and for CS_2 the ratio of vals. of ρ for excitation by λ 5461, 4358, and 4046 is 1 : 0.85 : 0.75. For liquids having absorption bands farther in the ultra-violet, ρ is practically independent of the frequency of the exciting line. N. M. B.

Raman spectra of isomeric alcohols. G. V. NEVGI and S. K. K. JATKAR (Indian J. Physics, 1934, 8, 397—414).—Full data are tabulated for various isomerides of butyl, amyl, and octyl alcohols. An explanation of the large shifts 2870—2930 cm^{-1} is suggested. The frequency 1450 cm^{-1} is probably due to the transverse vibration of H in $\text{-CH}_2\text{-}$; 1300 cm^{-1} is attributed to the bending vibration of H in straight C chains. The shifts 750—1030 cm^{-1} are due to the outer vibrations of OH against the rest of the mol. groups, decreasing as homologous series are ascended, and in passing from primary and *sec.* to *tert.* alcohols; these assignments are confirmed by thermal data. Heats of dissociation tend to decrease in a homologous series, and more markedly in passing from primary to *tert.* alcohols. N. M. B.

Raman effect and constitution of molecules. VII. Depolarisation of Raman frequencies of *cis*- and *trans*-isomeric compounds. Raman frequencies of CH_2Br_2 and their polarisation. B. TRUMPY (Z. Physik 1934, 90, 133—137; cf. this vol., 583).—Polarisation of Raman lines of *cis*- and *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ distinguish between the two isomerides. Data for CH_2Br_2 are compared with those for CH_2Cl_2 (*loc. cit.*). A B D C

Raman effect of the hydroxyl radical. L. MEDARD (Compt. rend., 1934, 199, 421—423; cf. this vol., 583).—With an Hg arc, filtered through a solution of CoCl_2 and a Corning No. 306 filter, and by further filtering the scattered light from the liquid under test through a solution of NaNO_2 , the continuous background normally encountered with org. OH-compounds is suppressed. HCO_2H shows a weak Raman band at 2950—3300 cm^{-1} ; $[\text{CH}_2\text{-OH}]$, shows a broad band at 3300—3500 cm^{-1} , and a narrower, more intense band at 3700 cm^{-1} . NH_2OH freshly prepared shows a broad band at 3300 cm^{-1} superimposed on the NH_2 bands. Anhyd. glycerol yielded only continuous backgrounds. J. W. S.

Raman effect. XXXV. Raman spectra of some acetyl and acetonitrile compounds. H. C. CHENG (Z. physikal. Chem., 1934, B, 26, 288—296).—Ten compounds have been studied. The behaviour of the frequencies of the CH and CCl linkings in the groups CH_2Cl , CCl_3 , and CHCl_2 and the effect of Cl substitution on the CO frequency are discussed. The CN group has an inner vibration frequency at 2250 and a second frequency at 150—200 cm^{-1} . R. C.

Light scattering by binary liquid mixtures. S. PARTHASARATHY (Indian J. Physics, 1934, 8, 275—313).—A mol. theory of the scattering of light by binary liquid mixtures is developed, in which account is taken of the optical anisotropy of the mols. and of the influence of the Lorentz polarisation field on the effective mol. optical anisotropy. Tabulated data for 25 binary liquid mixtures giving the variation of the depolarised scattering with concn. are in agreement with the theory. Anisotropic and density scattering and magnetic and electric birefringence are discussed in relation to the theory. N. M. B.

Polarisation of fluorescence. II. Dyes in solution. S. M. MITRA (Indian J. Physics, 1934, 8, 445—450).—In order to determine whether variations of polarisation of substances previously reported (cf. this vol., 346) were due to the solvent, investigations were repeated for the solid dyes and in sugar solutions, castor oil, glycerol- H_2O mixtures, and gelatin as solvents. The % polarisation differed in each case, and its sign continued to be negative for λ 3131 excitation. N. M. B.

Sensitisation of phosphors. S. ROTHSCHILD (Physikal. Z., 1934, 35, 557—560).—A CaS-Sm phosphor can be sensitised by a trace of Bi; Cu, Pb, and Mn are not effective. The explanation is discussed. A. J. M.

Electrical conductivity of Ag_2HgI_4 . Mechanism of conduction in solids of high conductivity. J. A. A. KETELAAR (Z. physikal. Chem., 1934, B, 26, 327—334).—Conductivity measurements at 18—93° have shown that α - Ag_2HgI_4 is a good conductor, and transport measurements that conduction is purely cationic, principally by Ag^+ . The high conductivity of the α -form, by far the highest yet observed in a solid with solely electrolytic conductivity, and its small temp. coeff. are ascribed to the energy of release of the metal ions being zero owing to 25% of the points in the metal ion lattice being vacant. The same explanation may be extended to other similar

solid conductors, *e.g.*, α -AgI and α -CuI. The transformation α - β -Ag₂HgI₄ may be partly continuous. R. C.

Dipole moments and physico-chemical properties. IV. A. E. VAN ARKEL (Chem. Weekblad, 1934, 31, 470—474).—The observed b.p. of many liquids agree closely with the vals. calc. on the basis of London's views. The influence of structure, and in particular of the presence of dipoles, on b.p. is discussed; calc. and observed influences of dipoles in various CH₄ derivatives are in agreement. Unsaturated hydrocarbons are considered, and the influence of the nature and orientation of substituents in the C₆H₆ ring is discussed. H. F. G.

Anomalous absorption and dispersion of primary alcohols in the ultra-short wave range. K. KRAUSE (Physikal. Z., 1934, 35, 684—691).—The absorption and dispersion of alcohols (BuⁿOH, Bu^tOH, *n*-amyl alcohol) and ethereal oils (eugenol, bay oil, linalool) and of alcoholic solutions with various viscosities were determined in the wave-length range 2—5 m. A new differential process for the absorption experiments, and a modified Drude's method for the determination of the dielectric const., are described. The dependence of the absorption max. on viscosity confirms theory. The dielectric const. of the three oils is independent of frequency. A. J. M.

Dipole moment of non-associated gaseous hydrogen fluoride. C. H. D. CLARK (Physikal. Z., 1934, 35, 622—623).—The dipole moments of the hydrogen halides are considered. The moment of non-associated HF is calc. as 1.58 Debye units, and the nuclear separation 0.864 Å. A. J. M.

Effect of solvent on the moment of a molecule containing movable dipoles. A. E. STEARN and C. P. SMITH (J. Amer. Chem. Soc., 1934, 56, 1667—1670).—The dipole moment of EtCl in heptane, C₆H₆, CS₂, CCl₄, CHCl₃, and Et₂O and their binary mixtures has been determined at temp. between -70° and 90°. Complexes appear to be formed in Et₂O and C₆H₆. A dipole in the interior of a mol. may have no detectable effect on the internal potential energies of adjacent mols., although the mol. field may alter the moment of an adjacent EtCl mol. E. S. H.

Dipole moments of phosgene, hydrogen cyanide, and certain substituted methanes. C. P. SMITH and K. B. MCALPINE (J. Amer. Chem. Soc., 1934, 56, 1697—1700).—The dipole moments calc. from measurements of the dielectric consts. of COCl₂, HCN, MeNO₂, and CCl₃·NO₂ vapours conform with those calc. on the assumption of a central tetrahedral C atom. E. S. H.

Variations in refractive index of CO₂-free dry air, and a statistical correlation with solar activity. L. W. TILTON (J. Res. Nat. Bur. Stand., 1934, 13, 111—124).—Examination of published data has shown a correlation of refractivity of air with sunspot no. E. S. H.

Refractive index of gaseous "heavy water." C. CUTHBERTSON (Nature, 1934, 134, 251).— $\mu_{5462.23}^{25}$ for gaseous heavy H₂O (approx. 30% H₂O) is 1.000256 compared with 1.000255 for ordinary H₂O. L. S. T.

Molecular refractivity and association of liquids containing the hydroxyl group. R. P. ALLARD and H. H. WENZKE (J. Amer. Chem. Soc., 1934, 56, 1693—1694).—Changes in mol. refractivity of AcOH on dilution with C₆H₆ or dioxan show that such changes do not constitute a simple test of association of OH compounds. E. S. H.

Principal optical polarisabilities of the naphthalene molecule. K. S. KRISHNAN (Indian J. Physics, 1934, 8, 431—436; cf. A., 1933, 10).—From the Lorentz refraction const., the depolarisation factor of light scattering, and the Cotton-Mouton const., the calc. vals. of the polarisabilities along the three principal axes are 26.8, 14.1, and 11.5 (all $\times 10^{-24}$) c.g.s., *e.s.u.* N. M. B.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. VIII. **Magneto-optical dispersion of *n*-butyl, methyl, and ethyl acetate.** G. E. JONES and E. J. EVANS (Phil. Mag., 1934, [viii], 18, 386—400; cf. A., 1931, 24; this vol., 349).—Ordinary dispersion and magneto-optical dispersion data are tabulated for the region 2700—7000 Å. Verdet's const. and the vals. of e/m are calc. and their variation with mol. wt. is discussed. J. W. S.

Paramagnetic rotation in a variable magnetic field. G. ZANOTELLI (Atti R. Accad. Lincei, 1934, [vi], 19, 718—722).—The paramagnetic part of Verdet's const. in an oscillating field (frequency, n , 3.2—5.5 $\times 10^6$ cycles per sec.) does not differ by > one sixth from the val. in a steady field. With aq. CeCl₃, the rotation at any given field strength is independent of n and there is no detectable hysteresis. D. R. D.

Complexes between metals of the first transitional series and dipyrindyl and phenanthroline. L. CAMBI and A. CAGNASSO (Atti R. Accad. Lincei, 1934, [vi], 19, 458—461).—The susceptibility-temp. curves, between 291° and 84° abs., of [Ni(dipyrindyl)₃]Br₂·3H₂O and [NiR₃]Br₂·2H₂O, and of [CoR₃]Br₂·2H₂O and [MnR₂]Cl₂ (R=phenanthroline) are practically coincident. H. F. G.

Structure of the nitro-group. H. O. JENKINS (Nature, 1934, 134, 217).—The finite vals. found for the differences $\infty P_2 - {}_E P_2$ are due in the case of *p*-C₆H₄(NO₂)₂ (I) and *s*-C₆H₃(NO₂)₃ (II) to sp. solvent effects of C₆H₆ and C₁₀H₈ on the dissolved nitro-compounds. The vals. of $\infty P_2 - {}_F P_2$ for (I) and (II) in CHCl₃ are zero. Hence both (I) and (II) are non-polar and the NO₂ group is symmetrical, a resonance existing between — and — L. S. T.

Magneto-chemical investigations. IX. **Nickel oxide.** W. KLEMM and K. HAAS (Z. anorg. Chem., 1934, 219, 82—86).—Variable vals. for the magnetic susceptibility, χ , of NiO are due to partial splitting up into Ni and a higher oxide at > 400°. Above an O content between NiO_{1.003} and NiO_{1.008}, χ is practically const. independently of field strength. In apparently pure NiO the proportion of metallic Ni is 0.3—0.6%. χ for the NiO phase increases linearly with rise of temp., contrary to the Curie or Weiss law. At low temp. the vals. are much < those

for salts, and the relation between those for NiO and NiS is similar to that found for Cu. M. S. B.

Magnetic properties of rare-earth salts. E. H. WILLIAMS (Physical Rev., 1934, [ii], 46, 133—134).—The susceptibility reciprocal-abs. temp. curve for GdCl_3 , $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ is a broken line; the last named, when carefully dried, gives a straight line through the origin. N. M. B.

Diamagnetism of organic compounds and influence of temperature and constitution. II. R. CARRERA and H. FAHLENBRACH (Z. Physik, 1934, 89, 682—700; cf. A., 1933, 1233).—Susceptibilities are given between -50° and 140° for laboratory glass, Jena apparatus glass 20, uviole and quartz glass, cetyl alcohol (I), hexane, C_6H_6 , AcOH , *o*- and *p*-cresol, *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{NO}_2$, and *p*- $\text{C}_6\text{H}_4\text{Cl} \cdot \text{OH}$, and at room temp. for isoamyl alcohol and sugar charcoal. Abrupt change of susceptibility was observed at each m.p., the magnitude of the change being exponentially related to the dipole moment of the substance, and probably brought about by deformation of the electron cloud. Apart from this change only (I) showed variation of susceptibility with temp. Pascal's λ -theory is discussed. A. B. D. C.

Diamagnetism of organic liquid mixtures. S. R. RAO (Indian J. Physics, 1934, 8, 483—501; cf. A., 1932, 678).—Using an improved method, data are tabulated and plotted for $\text{COMe}_2 \cdot \text{CHCl}_3$, $\text{COMe}_2 \cdot \text{PhNO}_2$, $\text{COMe}_2 \cdot \text{C}_6\text{H}_6$, $\text{C}_6\text{H}_6 \cdot \text{AcOH}$, $\text{C}_6\text{H}_6 \cdot \text{PhNO}_2$, $\text{COMe}_2 \cdot \text{AcOH}$, and $\text{COMe}_2 \cdot \text{NH}_2\text{Ph}$. In all cases the additive law of mixtures is obeyed. Evidence indicates that for $\text{COMe}_2 \cdot \text{CHCl}_3$ and $\text{COMe}_2 \cdot \text{PhNO}_2$ association produced no change in the sp. diamagnetic susceptibility. N. M. B.

"Electron motion" in limited crystal lattices. S. RIJANOV (Z. Physik, 1934, 89, 806—819).—The energy spectrum and proper functions for a two-dimensional lattice are discussed. A. B. D. C.

Determination of the variation of the inner potential of a crystal lattice from the deviations from Bragg's law of electron diffraction. II. V. E. LASCHKAREV (Z. Physik, 1934, 89, 820—825; cf. this vol., 126).—The periodic variation of this potential through the lattice is estimated for MoS_2 . A. B. D. C.

Distance between micelles in viscose rayon. N. MATSUMOTO (J. Soc. Chem. Ind. Japan, 1934, 37, 356B).—The X-ray val. 65 \AA . was given by several fibres spun under similar conditions but with diameters ranging from 7 to 36μ . G. H. C.

Study of chemical systems by variations of weight during regular temperature variation. M. GUICHARD (Compt. rend., 1934, 199, 138—140).—The interpretation of wt.-temp. curves of substances undergoing thermal decomp. or dehydration is complicated by the occurrence of fusion or solidification. B. W. B.

Valency angle of oxygen. G. M. BENNETT, D. P. EARP, and S. GLASSTONE (J.C.S., 1934, 1179—1180).—It is inferred from measurements on solutions in CCl_4 , cyclohexane, and C_6H_6 that the dipole moment of

diphenylene dioxide is 0, indicating an angle of 120° between the O valency linkings in this compound. R. S. B.

Chemical linking. I. Interpretation of valency on the basis of wave-mechanics and band spectra. R. F. HUNTER and R. SAMUEL (J.C.S., 1934, 1180—1186).—Current theories of valency are criticised in the light of spectroscopic and wave-mechanical evidence. In particular it is emphasised that the "lone pair" of electrons (s^2) cannot form a chemical linking without fission and transference of at least one electron to a *p* group. The octet rule leads to incorrect formulation (*e.g.*, in O_2 the octet is actually not closed, the lowest level is $^3\Sigma$, and the mol. should be written —O—O—), and in many cases stable structures are formed with incomplete octets. A theory is proposed in which there is only one type of chemical linking (covalent) the polarisation of which may vary between 0 (in H_2) and the val. in a true salt. Chemical union results in the formation of a closed group or sub-group, which may or may not contain 8 electrons. Any atom may act as the + partner, and the max. no. of + valencies = the no. of electrons in the outer shell. The formulæ $\text{—N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ and $\text{—N} \begin{smallmatrix} \oplus \diagup \text{O} \\ \oplus \diagdown \text{O} \end{smallmatrix}$ are

regarded as physically inadmissible, the 5 links in —N(=O) , (correct formulation) arising from 5 identical *p* electrons (excited N). KF , HF , and complexes formed by B and Al trihalides and Be dihalides with amines etc. are considered to be formed by dipole association. It is inferred that CO contains a double linking. R. S. B.

Energy relations in the periodic system of chemical compounds of the type $A_m B_n$. H. G. GRIMM (Angew. Chem., 1934, 47, 594—601).—It is shown for several substances (halogens, alkali halides, CuCl , C, N., alkali metals, etc.) that the type of mol. actually formed is the one to be expected from energetics, other types of mol. requiring the absorption of additional energy. Valency is similarly treated. A. G.

Parachor and ring structure. S. K. RAY (J. Indian Chem. Soc., 1934, 11, 499—501).—From measurements on 15 compounds it is found that $\text{C}_5\text{H}_5\text{N}$ derivatives have the same structural contribution as the corresponding C_6H_6 derivatives, and that in 5-membered rings unsaturated N lowers the contribution due to the ring by about 5.5 units, but not when saturated. The mutual condensation of 5- and 6-membered rings lowers the parachor by 2.5 units. R D

Nature of the recrystallisation process. H. G. MULLER (Physikal. Z., 1934, 35, 646—649).—Recrystallisation is a self-diffusion process. For the origination of recrystallisation nuclei, a special centre-formation is not required. A. J. M

Kinetic deduction of rate of formation of nuclei. R. KAISCHEV and I. N. STRANSKI (Z. physikal. Chem., 1934, B, 26, 317—326).—Expressions giving the rate of formation of liquid nuclei from supersaturated vapour, crystal nuclei (with the simple cubic lattice) from supersaturated vapour, and gas nuclei from superheated liquid have been derived. All contain

the factor $e^{-F\sigma/3kT}$, $F\sigma/3$ being the work of formation of a nucleus. R. C.

Mechanism of equilibrium of small crystals. III. I. N. STRANSKI and R. KAISCHEV (Z. physikal. Chem., 1934, B, 26, 312—316; cf. this vol., 946).—The Gibbs-Wulff condition for the equilibrium of a small crystal, i.e., that the central distances for the equilibrium form shall be proportional to the corresponding sp. surface energies, is equiv. to the condition that the mean work of separation, ϕ , shall be the same for each face of the equilibrium form. Only those faces can appear in the equilibrium form for which ϕ depends on the extent of the face. The possible faces in the equilibrium form of a cubic face-centred and closest-packed hexagonal lattice are enumerated. R. C.

Investigation of surface area and lattice changes of crystalline salts by Hahn's emanation method. F. STRASSMANN (Z. physikal. Chem., 1934, B, 26, 353—361; cf. A., 1931, 890).—The val. for the surface area of a specimen of cryst. $\text{Ba}(\text{NO}_3)_2$ deduced from its emanating power agrees with the val. obtained by direct microscopic measurement, although there is appreciable diffusion of Rn from within the crystals through the surface. The emanation method may also be used qualitatively to follow the formation of $\text{Ba}(\text{NO}_3)_2 \cdot 2\text{KNO}_3$ in the solid eutectic mixture of KNO_3 and $\text{Ba}(\text{NO}_3)_2$ at room temp. R. C.

Investigation of connexion between lattice structure and permeability to gases of organic salts by Hahn's emanation method. F. STRASSMANN (Z. physikal. Chem., 1934, B, 26, 362—372).—The emanating power, E , of org. Ba salts is independent of the hardness and d of the crystals, but is decisively influenced by the constitution of the salt. It is deduced that a considerable proportion of the emanation (Rn or thoron) given off diffuses from within the crystal and that the diffusibility is influenced by the structure of the crystal. Diffusion seems to occur particularly readily along glide-planes. A method of determining a very small E for thoron with a precision of $\pm 5\%$ is described. R. C.

Crystallisation of metals from sparse assemblages. E. N. DA C. ANDRADE and J. G. MARTINDALE (Nature, 1934, 134, 321—322).—When Au or Ag crystals grow slowly from a film in which the amount of available material is small, the first stage of crystallisation appears to be the formation of an aggregate of spherulitic nature, in which the individual cryst. fibres behave as if uniaxial. L. S. T.

Helicoidally rolled spherulites of the allantoin and their artificial coloration. P. GAUBERT (Compt. rend., 1934, 199, 213—215).—These spherulites are formed when supersaturated solutions of or *r*-allantoin are placed in a thin layer on glass. The rolling of the cryst. particles forming the radial fibres occurs around the *b* crystallographic axis. Addition of a trace of coal-tar dye favours the formation of this structure. Spherulites coloured with methylene-blue are polychroic. J. W. S.

Diffuse scattering of X-rays from sodium fluoride. III: Using sensibly monochromatic radiation. P. S. WILLIAMS (Physical Rev., 1934, [ii], 46, 83—86; cf. A., 1932, 979).—A comparison of the classical scattering of Mo $K\alpha$ lines by NaF with that by paraffin is in agreement with previous results using a band of wave-lengths, but shows appreciable divergence from the predictions of quantum theory. N. M. B.

Powder figures of magnetised single iron crystals. S. KAYA (Z. Physik, 1934, 89, 796—805).—Powder figures on the cubic face are directly related to the condition of magnetisation.

A. B. D. C.

X-Ray researches on thin nickel films. R. RIEDMILLER (Ann. Physik, 1934, [v], 20, 377—403).— d for thin films of Ni evaporated in a vac. on to a microscope cover-slip has been calc. from the wt. and thickness, l (X-ray interferometric), and is 20—25% < the val. for Ni in bulk for most of the films of $l=400$ —1750 Å., owing to loosening in the crystallite structure, or to increase in the lattice const. The sp. electrical resistance in vac. decreases rapidly as l increases, and then reaches a const. val. 35—40 times the normal for $l > 1000$ Å., up to 2250 Å. The refraction coeff., $\delta=1-n$, has been measured by means of X-rays; $\delta/d=\text{approx. const.}=2.66 \times 10^{-6}$ (theoretical val. 2.58×10^{-6}). Calculation shows that in two cases 1 O_2 mol. is present with 4 and 10 Ni atoms. R. S. B.

X-Ray investigation of calcium at higher temperatures. II. L. GRAF (Physikal. Z., 1934, 35, 551—557).—The change taking place in the structure of Ca at 450° was investigated. The phase stable above 450° may occur either as space-centred cubic or hexagonal close-packed lattices. The purity of the Ca decides the form of the lattice, which is hexagonal with pure Ca. Another transition occurs at 300°, where sudden changes occur in some of the properties of the metal. With very pure Ca a further transition point at 218° seems probable.

A. J. M.

Lattice structure of the oxides, sulphides, selenides, and tellurides of lithium, sodium, and potassium. E. ZINTL, A. HARDER, and B. DAUTH (Z. Elektrochem., 1934, 40, 588—593).—The following vals. for lattice const. and ionic distance, respectively, are given (in Å.): Li_2O 4.619, 2.00; Li_2S 5.708, 2.47; Li_2Se 6.005, 2.60; Li_2Te 6.504, 2.82; Na_2O 5.55, 2.40; Na_2S 6.526, 2.83; Na_2Se 6.809, 2.95; Na_2Te 7.314, 3.17; K_2O 6.436, 2.79; K_2S 7.391, 3.20; K_2Se 7.676, 3.32; K_2Te 8.152, 3.53.

E. S. H.

Lattice constant of OsS_2 . K. MEISEL (Z. anorg. Chem., 1934, 219, 141—142).—X-Ray measurements on OsS_2 give a 5.6075 \pm 0.0006 Å. and d 9.57 \pm 0.01. M. S. B.

Structure of the pseudo-halogens and their compounds. I. Thallous thiocyanate. M. STRADA (Gazzetta, 1934, 64, 400—409).—TICNS is of the tetragonal system, ditetragonal pyramidal class, group T_d , symmetry C_4 or C_{2v} ; a 4.766, c 3.78 Å.; one mol. per unit cell, $d_{\text{calc.}}$ 5.06. The electronic structure of the CNS ion is similar to that

of the halogen ions, and in TICNS the C, N, and S atoms are in a straight line forming the polar axis of the crystal. H. F. G.

Fibrous structure in ionic lattices. II. G. R. LEVI and M. TABET (*Atti R. Accad. Lincei*, 1934, [vi], 19, 723—725; cf. this vol., 479).—Threads of AgCl and AgBr formed under pressures of 2000—7500 atm. show fibrous structure, the crystallites being oriented along the (111) axis at room temp. and along the (100) at higher temp. (e.g., 280°). The transition temp. varies with the pressure and is lower for AgBr than for AgCl. Breaking stresses of the threads have been measured. Laminae of AgCl and AgBr show marked fibrous structure. D. R. D.

Crystal structure of nickel bromide and iodide. J. A. A. KETELAAR (*Z. Krist.*, 1934, 88, 26—34).—The sublimed salts have the CdCl₂ structure with a_0 3.715, c_0 18.30, and a_0 3.895, c_0 19.63 Å., respectively, referred to hexagonal cells. Non-sublimed NiBr₂ exhibits the "alternating" structure (cf. this vol., 16). The difference between these structures and those of the corresponding Co compounds is unexpected. B. W. R.

Crystal structure of the low-temperature modification of ammonium bromide. J. A. A. KETELAAR (*Nature*, 1934, 134, 250—251).—At low temp. NH₄Br has a tetragonal lattice and at -100° a is 6.007 ± 0.006 Å. and c 4.035 ± 0.004 Å.; probable space-group D_{4h}^+ . L. S. T.

Quantitative spectrometric studies of ammonium and potassium cupric chloride dihydrate, (NH₄)₂CuCl₄·2H₂O and K₂CuCl₄·2H₂O. L. CHROBAK (*Z. Krist.*, 1934, 88, 35—47).—Fourier projections, based on intensity measurements from shaped crystals and corr. for extinction, are used to differentiate between the conflicting suggestions which have been made for the structure of these compounds. No conclusion is reached for the NH₄ salt; for the K salt, definite evidence in favour of one is obtained. B. W. R.

Crystal structure of the alums. C. A. BEEVERS and H. LIPSON (*Nature*, 1934, 134, 327).—Details are given. L. S. T.

Atomic arrangement in ammonium and caesium persulphate, (NH₄)₂S₂O₈ and Cs₂S₂O₈, and the structure of the persulphate group. W. H. ZACHARIASEN and R. C. L. MOONEY (*Z. Krist.*, 1934, 88, 63—81).—The X-ray data from these two isomorphous compounds, in relation to the very different scattering powers of the constituent atoms, allow the at. parameters to be separately determined. The cell consts. are a_0 7.83, b_0 8.04, c_0 6.13 Å., β 95° 9', and a_0 8.13, b_0 8.33, c_0 6.46 Å., β 95° 19', respectively; space-group C_{2h}^2 . The persulphate group appears as two tetrahedral SO₄ groups (S at the centre) joined by an oblique covalent linking. B. W. R.

Fine-structure researches on boracite. M. MEHMEL (*Z. Krist.*, 1934, 88, 1—25).—Above 265° α -boracite (Mg₃Cl₂B₁₄O₂₆) is cubic; a_0 12.1 Å., 4 mols. in the cell. Below this temp. the α -modification is rhombic, a_0 17.07, b_0 17.07, c_0 12.07 Å., 8 mols. in the cell. The space-group cannot be fixed. The

$\beta \rightarrow \alpha$ transition is exhibited by a discontinuity in the expansion coeff. B. W. R.

Crystal structure of enargite, Cu₃AsS₄. L. PAULING and S. WEINBAUM (*Z. Krist.*, 1934, 88, 48—53).—The structure is orthorhombic, a_0 6.46, b_0 7.43, c_0 6.18 Å., space-group C_{2v} , analogous to that of wurtzite (ZnS), each As and Cu being tetrahedrally surrounded by S. B. W. R.

Crystal structure of binnite, (Cu,Fe)₁₂As₄S₁₃. L. PAULING and E. W. NEUMAN (*Z. Krist.*, 1934, 88, 54—62).—The cell is cubic with a_0 10.19 Å., space-group T_2^7 . From intensity considerations satisfactory at. positions are found, which are probably also applicable to the tetrahedrite minerals (CuZn)₁₂Sb₄S₁₃. B. W. R.

Effect of temperature on the crystalline spacing of certain normal diacids. F. D. LA TOUR and A. RIEDBERGER (*Compt. rend.*, 1934, 199, 215—217; cf. A., 1932, 1192).—The interplanar distance $a/2 \sin \beta$ (A., 1929, 126) for the higher dibasic acids with an even no. of C atoms increases rapidly with rise of temp. This is due principally to expansion along the a axis. Expansion along the b axis is very slight. Discontinuities in the temp. coeff. of expansion along the a axis occur between C₁₂ and C₁₄ and between C₁₈ and C₂₀. The abnormal variation of the interplanar distance $c \sin \beta$ is attributed to a variation in β depending on the attractions between the CO₂H groups. J. W. S.

Structure of thin celluloid films. III. E. T. JONES (*Phil. Mag.*, 1934, [vii], 18, 291—302; cf. A., 1933, 1236).—Structures of celluloid films are discussed with reference to the patterns obtained by passing cathode rays through them. J. W. S.

Casein.—See this vol., 1119.

Variation of the thermal and electrical conductivity of a single bismuth crystal in a magnetic field. H. REDDEMANN (*Ann. Physik*, 1934, [v], 20, 441—448).—The thermal (Λ_T) and sp. electrical (Λ_E) conductivities of a single Bi crystal (rod) have been determined from -193.92° to 23.3°; the Wiedemann-Franz-Lorenz no. $L - \Lambda_T/T\Lambda_E$ varies from 10.99×10^{-8} to 4.17×10^{-8} . In a magnetic field (H) of 5900 gauss transverse to the axis of the crystal rod at -183.5° Λ_E , for the most favourable angle (θ) between the field and the axis of the rod, is approx. 0.1 its former val. Λ_T is unaffected by a variation in θ , and in H is 0.83 its former val. The high val. of L is due to the contribution of lattice conduction to Λ_T . R. S. B.

[Electrical] conductivity of tellurium. C. H. CARTWRIGHT and M. HABERFELD (*Nature*, 1934, 134, 287—288).—Curves showing the decrease in resistance of Te produced by the addition of Cu or Sb are discussed. The addition of 0.2% of Sb or Bi increased the conductivity of Te 100-fold and changed the temp. resistance coeff. from negative to positive. L. S. T.

Dependence of the conductivity of very thin metallic layers on the electrostatic field. R. DEAGLIO (*Naturwiss.*, 1934, 22, 525—526).—Thin metallic layers sputtered or vaporised show a consider-

able increase in conductivity on application of an electrostatic field. With vaporised layers, the effect is symmetrical, and independent of the sign of the charge, but for layers formed by sputtering the effect is unsymmetrical, and the increase in conductivity is $>$ when the layer is positively charged.

A. J. M.

Change of resistance of thin metallic layers on charging. A. DEUBNER (Ann. Physik, 1934, [v], 20, 449—462).—An apparatus for determining very small changes of resistance is described. For Ag layers about 40 atoms thick, and a charge of 5000 volts, a change of 10^{-4} of the resistance was measurable (cf. this vol., 588). For Au about 0.1 of this could be found, whilst for Cu and Bi there was no detectable change. The connexion between the resistance change and the optical absorption of the layers is discussed.

A. J. M.

Thermal variation of the structural demagnetisation factor in nickel and cobalt. T. KAHAN (Compt. rend., 1934, 199, 349—351).—The structural demagnetisation factor decreases with rise of temp., being distinguished in this way from the geometrical factor, which does not vary with temp.

A. J. M.

Magnetic properties of iron-cobalt single crystals. J. W. SHIH (Physical Rev., 1934, [ii], 46, 139—142).—The direction for easiest magnetisation changes from $\langle 100 \rangle$ to $\langle 111 \rangle$ as the amount of Co increases, the transition occurring at about 42% Co. The theory of Fowler and Powell is contradicted (cf. A., 1931, 791). The magnetisation curve of a 70% Co specimen agrees with Akulov's theory.

N. M. B.

Unsymmetrical hysteresis loop. S. S. SIDHU (Indian J. Physics, 1934, 8, 451—467).—A general investigation of the magnetic properties of different grades of Sisteel and 50% Ni steel, when symmetrically and unsymmetrically magnetised, is described.

Magnetism of tin. S. R. RAO (Nature, 1934, 134, 288).—As the particle size of colloidal white Sn decreases, the small paramagnetic susceptibility (I) changes to diamagnetic which then increases as particle size decreases. The (I) of white Sn appears to depend on the crystal structure and not to be an at. property.

L. S. T.

Dependence of magnetic induction on the magnetic field in superconducting lead. G. N. RJABININ and L. W. SHUBNIKOW (Nature, 1934, 134, 286—287).

L. S. T.

Refractive index of thin films of potassium. B. MUKHOPADHYAY (Current Sci., 1934, 3, 25).—A discussion of the discrepancy between calc. (this vol., 231) and experimental (A., 1933, 1096) vals.

L. S. T.

Optical properties of thin films. M. BLACKMAN (Phil. Mag., 1934, [vii], 18, 262—272).—Theoretical.

J. W. S.

Dispersion of the phase jump for reflexion of light at thin metallic layers. J. BAUER (Ann. Physik, 1934, [v], 20, 481—501).—The experiments were carried out by Fabry and Buisson's method (J. Physique, 1908, [iv], 7, 417), with Ag, Au, and Pt

obtained by cathodic sputtering or vac. vaporisation. The phase-jump increases as the absorption coeff. of the layer decreases. For non-homogeneous layers, the course of the phase-jump varies over the layer. The two modifications of Ag found by Fabry and Buisson are identical with those of Ritschl (A., 1931, 888).

A. J. M.

Condensation of thin metallic films: some reflecting observations. T. V. STARKEY (Phil. Mag., 1934, [vii], 18, 241—256).—A method for correlating structural characteristics with reflecting power is developed, and is applied to films condensed from a mol. beam of Cd vapour on a target cooled with liquid air. Owing to surface irregularities and uneven contamination, active centres exist on the target and become occupied in a time short in comparison with the time of growth of the film, the final vols. of the aggregates formed at these centres ranging about a mean vol. according to the Gaussian law of errors. Because of mechanical trapping, a permanent sensitisation of the surface occurs, which persists in spite of acid cleaning of the surface and increases on each repetition of the process. The growth of the aggregates is favoured by the migration of small particles, probably mols., to the active centres, and the no. of aggregates per unit area is independent of the rate of growth of the film and of the residual air pressure.

J. W. S.

Velocity of propagation of sound in carbon dioxide near the critical state. V. SCHPAKOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 26—34).—Measurements were made at 15—50° at pressures from 1 to 85 atm. in a gas column by the method of resonance. An increase in the mol. thermal capacity at const. vol. was observed with increasing pressure, attributed to the formation of cybotactic groups in the gas.

H. J. E.

Norbury relationship for thermal resistance of metals. H. REDDEMANN (Ann. Physik, 1934, [v], 20, 502—512).—The extent to which the law of the linear isothermal ($\Delta w = \Delta \rho / ZT$), connecting thermal resistance (w), electrical resistance (ρ), and temp. (T), holds for alloys of Cu, Al, Au, Ag, Pt, and Pd with other metals is investigated. The const. Z is almost independent of the added metal up to a certain val. of ρ_{sp} . The law holds satisfactorily up to this limit, and may be used to calculate w from ρ . As long as $\rho \propto w$, the Norbury relationship (connecting the increase of resistance of alloys with the positions of the metals in the periodic system) holds for both.

A. J. M.

Theory of liquids. T. S. WHEELER (Current Sci., 1934, 3, 23—24).—Theoretical. Vals. of surface tension and internal latent heat calc. for He, H₂, Ne, A, and N₂ are in agreement with those observed for the liquid state.

L. S. T.

Calorimetric studies at very low temperatures. W. H. KEESOM (J. Phys. Radium, 1934, [vii], 5, 373—384).—A lecture.

N. M. B.

Specific heats of zinc and silver at liquid helium temperatures. W. H. KEESOM and J. A. KOK (Physica, 1934, 1, 770—778).—It is shown experimentally that the rapid descent of the $TC^{1.3}T$

curve below 5° abs. is not due to absorption of He at the surface of the metal. The effect is attributed to the heat capacity of the free electrons (I), and below 3.0° abs. the supplementary at. heat for Ag agrees with (I) calc. by Sommerfeld's formula. With Zn the agreement is less satisfactory. H. S. P.

Specific heats of gases at high temperatures. W. T. DAVID and A. S. LEAH (Phil. Mag., 1934, [viii], 18, 307—321).—From the temp. reached in explosions of H_2 and O_2 and CO and O_2 in various proportions and diluted with other gases, and from the known vals. of the sp. heats at lower temp., it is concluded that the theoretical vals. of the sp. heats of CO, N_2 , and CO_2 , and probably those of H_2 and O_2 , are accurate up to 2500° . The theoretical vals. for H_2O show inaccuracies only above 2000° . J. W. S.

Determinations with condensed heavy hydrogen. K. CLUSIUS and E. BARTHOLOME (Naturwiss., 1934, 22, 526—527).—The sp. heat of pure H_2 in the solid and liquid states at 10° and 23° abs., the heat of fusion, triple point pressure, and density of the liquid H_2 have been determined. In the solid state, H_2 and D_2 have practically the same sp. heat below 14° abs. The mol. vol. of H_2 at the triple point is about 11.5% < that of D_2 , a difference which remains at 0° abs. A statistical calculation of the abs. entropy of H_2 at 298.2° abs. gives 38.98 entropy units, in sufficiently good agreement with the experimental val. (38.76). A. J. M.

Isotopic ratio in hydrogen : general survey by precise density comparisons on water from various sources. H. J. EMELEUS, F. W. JAMES, A. KING, T. G. PEARSON, R. H. PURCELL, and H. V. A. BRISCOE (J.C.S., 1934, 1207—1219).— d for various samples of rigorously purified H_2O has been determined to within 2×10^{-7} g. per c.c. by observing the flotation temp. of a SiO_2 float. London tap- H_2O (I) of const. d served as a standard. The following results for d relative to (I) at 20.335° were obtained for the sources given; the unit $= 1 \gamma d = 10^{-6}$ g. per c.c., heavier than the standard $= +$: natural waters, -0.63 to $+2.52$; minerals, $+2.52$ to $+6.30$; fruits, -0.8 to $+4.41$; sucrose, $+8.61$; *Salix caprea*, sap $+3.67$, wood, $+3.15$; animal fluids, -0.84 to $+2.52$; electrolyte baths, $+30.4$ to $+19.9$; other industrial liquids, -5.04 to $+4.62$. The H_2O from rasorite ($Na_2B_4O_7 \cdot 4H_2O$ $\Delta \gamma d = \pm 6.30$) is distinctly heavier than that from tincal ($Na_2B_4O_7 \cdot 10H_2O$ $\Delta \gamma d = +2.73$ mean). Thermophilic cotton fermentation gives no change in d . On freezing H_2O , $H_2^{18}O$ crystallised preferentially, which may explain the difference in d between natural and artificial ice. The crystallisation of K alum and of Na_2SO_4 caused no separation between the two isotopes. H_2O adsorbed on SiO_2 gel and charcoal gave $\Delta \gamma d = +0.4$ and $+0.2$. Distillation effected a considerable concn. of $H_2^{18}O$. It is inferred that in the absence of local influences the abundance ratio of the two isotopes is const. over the earth's surface. R. S. B.

Adiabatic cooling of magnetic substances. W. J. DE HAAS and E. C. WIERSMA (Physica, 1934, 1, 779—780).—A method of obtaining a homogeneous

temp. as low as 0.031° abs. in 66 g. of K Cr alum is described. H. S. P.

Phenomenon of fusion in relation to a new equation of state and the lattice structure of solids. I. S. FRANCHETTI (Atti R. Accad. Lincei, 1934, [vi], 19, 713—718).—Theoretical. An equation of state is evolved from the relationships previously deduced by the author. D. R. D.

Vapour pressures of metals of high b.p. I. Determinations by b.-p. method. J. FISCHER (Z. anorg. Chem., 1934, 219, 1—16).—Experiments with Hg in a graphite crucible show that, in Greenwood's method for the determination of the b.p. of a metal, a disturbance of the molten metal has been mistaken for boiling at a temp. much < the true b.p. The extent of the deviation depends on the nature of the gas flowing through the outer vessel containing the porous crucible (graphite, sintered corundum, or ZrO_2) and, above a certain min., is not affected by the velocity of flow of the gas, but the phenomenon does not occur in the absence of the gas stream. The effect is due to effusion. By heating to const. temp. the true b.p. may be obtained. The b.p. found for Pb is $1750 \pm 10^\circ$ and for Ag $2150 \pm 20^\circ$. The v.p. const. for Pb is in good agreement with the theoretical val. and the Trouton const. is normal. The shape, size, and distribution of the pores in graphite have been studied. M. S. B.

Formula and tables for the pressure of saturated water vapour in the range $0-374^\circ$. N. S. OSBORNE and C. H. MEYERS (J. Res. Nat. Bur. Stand., 1934, 13, 1—20).—The tables are computed from a formula which represents an adjusted composite appraisal of the available published data. E. S. H.

Continuation of the vapour-pressure curve above the critical point. A. EUCKEN (Physikal. Z., 1934, 35, 708—711; cf. this vol., 723).—Theoretical. It is shown that it is possible to demonstrate the continuation of the v.-p. curve above the crit. point on the basis of certain analytical criteria. A. J. M.

Dependence of "vapour pressure" on temperature above the critical point. M. TRAUZ (Physikal. Z., 1934, 35, 711).—A reply to Eucken (preceding abstract). A. J. M.

Vapour pressure of solid and liquid deuterium and the heats of sublimation, of fusion, and of vaporisation. G. N. LEWIS and W. T. HANSON, jun. (J. Amer. Chem. Soc., 1934, 56, 1687—1689).—V.-p. data for H_2^2 (containing < 0.03% H_2) are recorded between 20° and 15° abs. The presence of small amounts of H_2 affects the vals. markedly. The following are some of the data : heat of vaporisation 308.3 (liquid), 357.2 (solid); heat of fusion 48.9 g.-cal. per mol.; triple point 18.66° abs.; b.p. 23.6° abs. E. S. H.

Vapour pressure of hydrogen and deuterium fluorides. W. H. CLAUSSEN and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1934, 56, 1820).—The v.-p. of H^1F between 5 and 76 cm. is given by $\log_{10} P_1(\text{cm.}) = 6.3739 - 1316.79/T$ and of H^2F by $\log P_2(\text{cm.}) = 6.2026 - 1261.16/T$. E. S. H.

Thermal expansion of artificial graphite and carbon. P. HEDNERT (*J. Res. Nat. Bur. Stand.*, 1934, 13, 37—51).—Over the range 20—1000° the expansion coeffs. of transverse sections are > those of longitudinal sections of artificial graphite, and the vals. increase with rising temp. The coeffs. appear to be influenced by the grain size. The expansion coeffs. of C rods made with lampblack are > those made with petroleum coke, indicating that the latter is more suitable for the low-expanding element of temp. regulators. E. S. H.

Viscosity of esters of saturated aliphatic acids. A. H. GILL and F. P. DEXTER (*Ind. Eng. Chem.*, 1934, 26, 881).— η for various esters from MeOAc to $C_5H_{11}\cdot CO_2C_5H_{11}$ has been determined at 25°, and is approx. the same for esters containing the same no. of C atoms. It is suggested that a satisfactory substitute for porpoise-jaw oil (I), used for delicate machinery, could be made from an isomeride of $Bu^iCO_2C_{12}H_{25}$ contained in (I), and a saturated fatty acid. R. S. B.

Problems of the liquid state. H. KUDAR (*Physikal. Z.*, 1934, 35, 560—563).—Theoretical. The phenomena of melting, temp. coeff. of fluidity, thermal expansion of liquids, and self-diffusion and conductivity of solid electrolytes are considered. A. J. M.

Thermal diffusion in gas mixtures. G. BLUM and O. BLUM (*Z. Physik*, 1934, 90, 12—37).—An interferometer has been used to follow diffusion in H_2 - CO_2 and H_2 - N_2 mixtures at -185°, -80°, and 170°. In addition to attractive forces there are repulsive forces inversely \propto at least the 5th power of the mol. separation. A. B. D. C.

Chart for the rapid calculation of mixtures. J. S. BAKER (*Ind. Eng. Chem.*, 1934, 26, 910).—A chart is described by which the amounts of mixtures of two components required to give a desired concn. may be read off. R. S. B.

V.p. of binary systems. I. Benzene and acetic acid. F. HOVORKA and D. DREISBACH (*J. Amer. Chem. Soc.*, 1934, 56, 1664—1666).—Theoretical considerations show that the system C_6H_6 -AcOH is not azeotropic. E. S. H.

Tests for accuracy of vapour-liquid equilibrium data. H. A. BEATTY and G. CALINGAERT (*Ind. Eng. Chem.*, 1934, 26, 904—909).—Simple rules, derived from the Duhem-Margules equation (I), are given for testing the accuracy of v.p. data for non-ideal binary systems. The partial pressures p_1 and p_2 are plotted against the mol. fractions x and $1-x$; then the ratio of the slope of the curve $(dp_1/dx$ for component 1) to the slope of the line joining the point to the origin (p_1/x) will be the same for the two components at the same val. of x , or $(dp_1/dx)/(p_1/x) = [dp_2/d(1-x)]/[p_2/(1-x)]$. If for a particular val. of x the tangent to one partial pressure curve passes through the origin, the same relation will be shown by the tangent to the second curve. Linear portions of the curves which extrapolate to the origin lie over the same range for the two curves. Other rules involving activity coeffs. are deduced, and data which have passed these tests may be further examined

by graphical integration of (I), using activity coeffs.; one partial pressure curve is calc. from the other and then compared with experiment. Examples from isobaric and isothermal data are given. R. S. B.

X-Ray studies on the diffusion of metals in copper. C. MATANO (*Japan. J. Physics*, 1934, 9, 41—47).—The coeffs. of diffusion of Al, Zn, Mn, Ni, Sn, Pd, Pt, and Au in Cu have been determined at 400° and 950°. Previous treatment influences the coeff. greatly at 400° but not at 950°. W. R. A.

Dipole theory and the size of molecules. J. W. WILLIAMS (*Trans. Faraday Soc.*, 1934, 30, 723—728; cf. A., 1933, 447).—Theoretical. The Debye equations are developed to apply to a binary mixture. H. J. E.

Dipole moments of the halogen hydrides in solution. F. FAIRBROTHER (*Trans. Faraday Soc.*, 1934, 30, 862—870).—The dipole moment of HCl, HBr, and HI has been measured in C_6H_6 and CCl_4 solution. In each case the val. is > that in the gaseous state. The solute mol. is changed from its covalent state (as gas) to a mol. of the ion pair type under the polarising influence of the dipoles induced in the solvent by the fields of the solute dipoles. H. J. E.

Polarity and the association of liquids. A. R. MARTIN (*Trans. Faraday Soc.*, 1934, 30, 759—762).—The dielectric consts. of mixtures of C_6H_6 with PhCl, PhCN, and BzOH have been measured, and are correlated with the partial v.p. For the C_6H_6 -PhCl and C_6H_6 -PhCN mixtures deviations from the ideal v.p. relation are accounted for by interdipole forces (I) and van der Waals forces. In C_6H_6 -BzOH mixtures (I) is the predominating factor. H. J. E.

Temperature solution method and the atom polarisation. H. O. JENKINS (*Trans. Faraday Soc.*, 1934, 30, 739—745).—The polarisation of $PhNO_2$ in decahydronaphthalene has been measured at 25° and 142.4°. The experimental val. at 142.4° is > that calc. from the Debye linear law. The discrepancy is attributed to the influence of temp. on the dielectric const. of the solvent, and, as a result, on its interaction with the solute. The accuracy of estimates of at. polarisation based on the temp-solution method is questioned. H. J. E.

Dielectric behaviour of concentrated solutions of dipole substances. A. E. VAN ARKEL and J. L. SNOEK (*Trans. Faraday Soc.*, 1934, 30, 707—719).—Measurements have been made for $PhNO_2$ in C_6H_6 , PhMe, and CS_2 , for C_5H_5N in C_6H_6 , and for MeCN and its Cl-derivatives in C_6H_{14} , CCl_4 , and C_6H_6 . The polarisation decreases with increasing concn., especially when the dipole moment is large. H. J. E.

Influence of the solvent on dipole moments. F. H. MULLER (*Trans. Faraday Soc.*, 1934, 30, 729—734).—The total polarisation of various mols. has been measured in a range of solvents of different dielectric const. (I). Only the polarisation due to orientation changes with the solvent. Mols. without moment (e.g., CCl_4 or CS_2) show no change. The total moment causes the solvation effect. Generally the dipole moment decreases regularly with increasing (I) of the solvent. This is true when (I) for a given

solvent is varied by change of temp. $C_2H_4Cl_2$, I, and some ketones are exceptional. H. J. E.

Energy absorbed in dielectrics with polar molecules. P. DEBYE (Trans. Faraday Soc., 1934, 30, 679—684).—A crit. discussion. The relaxation times (I) of $m-C_6H_4Cl_2$, $PhNO_2$, and $CHCl_3$ in C_6H_{14} , CS_2 , C_6H_6 , CCl_4 , and $C_{10}H_{18}$ are 1.2—3.6, 1.9—5, and 2.3—3.9 (all $\times 10^{-12}$) sec., respectively. The vals. of (I) for a given polar substance in different non-polar solvents are not \propto their viscosities. H. J. E.

Dielectric constant measurements in aqueous solution and *cis-trans* isomerism. G. DEVOTO (Z. Elektrochem., 1934, 40, 641; cf. this vol., 1093).—Measurements are recorded for aq. solutions of betaines of the cinnamic acid series. The elevation of the dielectric const. of H_2O per mol. of dissolved *trans-m*- $NMe_3 \cdot C_6H_4 \cdot CH : CPh \cdot CO_2^-$ is $>$ that for the *cis* compound. For $m-NH_2 \cdot C_6H_4 \cdot CH : CH \cdot CO_2H$ there is an equilibrium between the polar and non-polar forms. H. J. E.

Dielectric investigations of cellulose derivatives in organic liquids. I. Dipole moment and solvation of glucose penta-acetate and cellobiose octa-acetate. II. Dipole moments of cellulose acetates and their solvation. I. SAKURADA and S. LEE (J. Soc. Chem. Ind. Japan, 1934, 37, 331—334B, 334—337B).—I. The dipole moments of β -glucose penta-acetate (I) in C_6H_6 and in $CHCl_3$, and of cellobiose octa-acetate (II) in $CHCl_3$ are 2.43, 1.99, and 2.40 e.s.u., respectively. The mol. polarisation of (I) in $CHCl_3$ is $<$ in C_6H_6 , and the solvation with $CHCl_3$ is 0.74 or 1.48 mol. per mol., according to whether the fall in orientation polarisation is ascribed wholly to the $CHCl_3$ or to both the $CHCl_3$ and to (I).

II. The dipole moments (on C_6 basis) in $CHCl_3$ of two preps. of cellulose acetate of widely different viscosities were found to be 1.98 and 1.95, respectively. Their solvation is probably about the same as that of (I) and (II) (0—0.3 c.c. per c.c.) and the high viscosity is due to mechanical trapping of solvent. A. G.

Dielectric capacity of albumin solutions. W. J. SHUTT (Trans. Faraday Soc., 1934, 30, 893—897).—A Pt ellipsoid of rotation with mirror attached is suspended from a torsion head (I) in the liquid between two external Pt discs. Application of an alternating field rotates the suspended system, which is then adjusted to zero by (I). The effect with an unknown solution is compared with that for H_2O , from which the dielectric const. (II) of the former is calc. The val. of (II) for 2.5% aq. albumin has a max. at p_H 4.9, and min. at p_H 4.4 and 5.25. The val. of (II) \propto albumin concn. H. J. E.

Dipole moments and physico-chemical properties. V. A. E. VAN ARKEL (Chem. Weekblad, 1934, 31, 490—492).—Dissolution is too complicated a phenomenon for the influence of dipoles to be calc. quantitatively, but it is shown qualitatively that, e.g., the solubilities of Cl-derivatives of CH_4 and C_2H_6 are in accordance with theory. H. F. G.

Influence of viscosity on the decrease in fluorescent power of the solutions of certain dyes as a function of concentration. J. BOUCHARD (Compt. rend., 1934, 199, 460—462).—The fluorescent

power of solutions of dyes in H_2O -glycerol mixtures has been studied as a function of concn. and viscosity, η . The fluorescent power for infinite dilution is independent of the η . The fluorescence in aq. sucrose or glucose solution is equal to that in aq. glycerol solution of equal η . The results are in agreement with the view that the variation of fluorescence with concn. is due to the velocities of diffusion in the solution. J. W. S.

Relation between the dissolution properties of organic liquids and the viscosity of cellulose ester solutions. I. SAKURADA and M. SHOJINO (Kolloid-Z., 1934, 68, 300—305).—The solvent power of 11 org. liquids for cellulose esters has been examined by comparing the form of the solubility curves of the esters in liquid mixtures, of which one component is a non-polar, indifferent liquid, such as C_6H_6 . Parallel viscosity measurements show that η decreases as solvent power increases. E. S. H.

System aluminium-zinc. E. SCHMID and G. WASSERMANN (Z. Metallk., 1934, 26, 145—150).—X-Ray measurements at 20—400° show that the composition of the saturated γ -phase varies from 5% Zn at 160° to 48% Zn at 350°, and that the β -phase has a similar face-centred cubic structure to the γ -phase. No evidence of the existence of Al_2Zn_3 at any temp. has been obtained. The β -phase appears to be a continuation of the γ -phase, the two regions being separated by a miscibility gap, although it is possible that at $> 350^\circ$ the two phases merge into one another without interruption, which would indicate that the accepted solidus line needs modification. The eutectoidal structure produced by the decomp. of β is the result of recrystallisation caused by a far-reaching diffusion process. A. R. P.

Thermal analysis of the system rubidium-mercury. Mercurides of the alkali metals. W. BILTZ, F. WEIBKE, and H. EGGERS (Z. anorg. Chem., 1934, 219, 119—128).—The phase diagram shows the existence of $RbHg_6$, m.p. 132°, and the compounds $RbHg_2$, m.p. 256°, almost black; Rb_3Hg_7 , m.p. 197°; Rb_2Hg_8 , peritectic decomp. 157°, and Rb_3Hg_4 (brass-coloured), Rb_5Hg_{18} , Rb_2Hg_9 , and $RbHg_9$ with peritectic or eutectic points at 170°, 194°, 162°, and 67°, respectively. Comparison with the other alkali metals indicates that the thermal stability of compounds with Hg increases from Li to Cs, and that the lower mercurides of the lighter metals and the higher mercurides of the heavier metals are those more readily formed. M. S. B.

Equilibrium diagrams of the systems lead-thallium and lead-thallium-cadmium. E. JANECKE (Z. Metallk., 1934, 26, 153—155).—From a review of the evidence obtained in recent work the existence of the compound $PbTl$ is indicated. A. R. P.

Cadmium-lithium alloys. A. BARONI (Z. Elektrochem., 1934, 40, 565).—Polemical (cf. this vol., 356). E. S. H.

Crystallographic structure of the intermediate phase Au_2Pb . H. PERLITZ (Keemia Teated, 1934, 2, 11—16).—From X-ray examination of Au - Pb alloys the existence is inferred of an intermediate

phase with a narrow range of homogeneity in the region 66.6 at.-% Au. The lattice is face-centred cubic, and the unit cube of edge 7.910 Å. contains 24 atoms. It is inferred that 16 Au atoms occupy the positions 16*b*, and 8 Pb atoms the position 8*g*, of Wyckoff's tables, a structure identical with that of MgCu₂ and KBi₂.
R. S. B.

Electrical conductivity and equilibrium diagram of binary alloys. XIII. Formation of solid solutions in the system magnesium-tin. G. GRUBE and H. VOSSKUHLE. **XIV. System lithium-thallium.** G. GRUBE and G. SCHAUFLE (Z. Elektrochem., 1934, 40, 566—570, 593—600; cf. this vol., 724).—**XIII.** Measurements of electrical conductivity and thermal expansion in Mg-rich alloys show a sharp fall in the solid solution region as the Sn content is increased, reaching a min. at the composition Mg₂Sn. The solubility limit is 3.5% Sn at the eutectic temp. and 0.5% Sn at 440°.

XIV. Thermal analysis and conductivity-temp. curves indicate the existence of LiTl, Li₂Tl, Li₅Tl₂, Li₃Tl, and Li₄Tl.
E. S. H.

Formation of metallic hydrides by atomic hydrogen. II. System tantalum-hydrogen. E. PIETSCH and H. LEHL (Kolloid-Z., 1934, 68, 226—230; cf. A., 1933, 1020).—By the action of at. H on Ta a new solid phase is formed, having a cubic body-centred lattice with *a* 3.42 Å. Excess of H produces a solid solution in which *a* increases to 3.44 Å.
E. S. H.

Continuous transition and critical point between two solid phases. U. DEHLINGER (Z. physikal. Chem., 1934, B, 26, 343—352; cf. A., 1933, 896).—Theoretical. It is deduced that in the transformation (cubic → tetragonal) of the superstructure of the alloy AuCu, the connexion between the regularity of the at. distribution and the tetragonal axial ratio will depend on the pressure. Calculation of the thermodynamic equilibria, introducing an entropy term depending on the lattice symmetry, shows that at low pressures a discontinuous transition, and at high pressures a continuous transition, which is a phase change of the second order, are to be expected; between the two will be a crit. point. The possibility of continuous transition depends on the presence of electrons not necessary either for the general electron gas or the co-ordination of the first sphere.
R. C.

Temperature-structure-composition behaviour of certain crystals. M. J. BUEGER (Proc. Nat. Acad. Sci., 1934, 20, 444—453).—Theoretical considerations relating to two-component crystals are discussed.
H. F. G.

Adsorptive inclusion and mixed crystal formation. A. SMEKAL (Physikal. Z., 1934, 35, 643—646).—The conditions for the formation of mixed crystals of two substances are discussed. The decisive factor for complete miscibility is the energy, and not necessarily a similarity of lattice dimensions. Criteria for distinguishing between the inclusion of small quantities of a foreign substance in a crystal by adsorption or by the formation of mixed crystals are examined. The first or second of these methods will

occur according as there is, or is not, a localisable electron linking in the foreign atom. Various applications are described.
A. J. M.

Principles of gas exsorption. II. A. GUYER, B. TOBLER, and R. H. FARMER (Chem. Fabr., 1934, 7, 265—269; cf. this vol., 592).—The rate of loss of gas from saturated H₂O droplets moving downwards is very great compared with stationary drops and stirred solutions, owing probably to eddies within the drops. The fractional loss *A* and apparent "evasion coeff." *B* (loss of gas in mg. per min. per sq. cm. from a 0.1% solution at zero external partial pressure of the gas) are nearly linear functions of the time of formation of the drops. With increase of the size of the drops *A* diminishes rapidly but *B* is unchanged, whilst with increase of the distance of fall *A* increases; *B* is independent of the distance and the rate of fall. With rise of temp. *A* increases, but only ∝ the change in the rate of diffusion of the gas within the liquid. Reduction of pressure increases the rate of loss of gas to a greater degree than in the case of bulk solutions.
H. F. G.

Permeability to hydrogen of nickel, copper, and some of their alloys. W. BAUKLOH and H. KAYSER (Z. Metallk., 1934, 26, 156—158).—Curves showing the permeability to H₂ (I) at 600—900° are given for Ni, Ni + 1% Cr, Ni + 2% Cr, 33.3:66.6 Ni-Cu alloy, 75:25 Cu-Ni alloy, Armo Fe, and pure Cu. (I) decreases in the order given and the slope of the curves (except that of Fe) also decreases in this order.
A. R. P.

Diffusion of water in a zeolite crystal. Mobility of adsorbed molecules. A. TISELIUS (Z. physikal. Chem., 1934, 169, 425—458; cf. this vol., 249).—In the diffusion of H₂O in single crystals of heulandite the diffusion coeff., *D*, is not const., except for very small concn. gradients, but falls rapidly with the concn. (*c*). From the variation of *D* with temp. the energy of activation of diffusion has been calc., and this indicates that the diffusing mols. even in positions intermediate between the two lattice points are bound to the lattice by strong forces. The variation of *D* with *c* seems to be a consequence of the deviation of the sorbed state from the ideally dissolved state. *D* varies considerably with direction, which is partly explained by what is known of the lattice structure. Sorption isobars and the variation of the double refraction and angle of extinction with the H₂O content have been determined.
R. C.

Penetration of copper into rock salt by electrolysis and diffusion. S. ARZIBISCHEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 20—26).—Cu diffuses into a NaCl crystal pressed between two copper plates and heated to 760°. Diffusion of other metals could not be detected. The effect with Cu is attributed to the approx. equality of the ionic radii of Cu and Na. Similar diffusion with resultant red coloration of the crystal occurs in an electric field, or in a NaCl crystal coloured blue by immersion in Na at 700°. From absorption measurements the red-coloured crystals are shown to contain colloidal Cu.
H. J. E.

Liquid-liquid equilibria involving heavy water. N. F. HALL, H. R. WENTZEL, and T. SMITH (J. Amer.

Chem. Soc., 1934, **56**, 1822).—Addition of H_2O depresses the lower crit. solution temp. of nicotine- H_2O mixtures and raises the crit. solution temp. of $\text{PhOH-H}_2\text{O}$ mixtures. In the latter case the temp. rise \propto the amount of H_2O added. E. S. H.

Separation of crystals and gases from super-saturated solutions. R. FRICKE (Kolloid-Z., 1934, **68**, 165—168).—A review of published work.

E. S. H.
Solubility of calcium laevulate in water. G. J. COX, M. L. DODDS, and C. CLASPER (J. Amer. Pharm. Assoc., 1934, **23**, 662—664).—The solubility is given by $p = 27.58 + 0.173t + 0.0031t^2$, where p is g. of $\text{Ca}(\text{C}_5\text{H}_7\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ per 100 g. of solution and t is temp. in $^\circ\text{C}$. C. G. A.

Cinchonine solubility. R. A. HATCHER (Amer. J. Pharm., 1934, **106**, 244—249).—The solubility of cinchonine in H_2O is said to depend on the method of measurement. R. S. B.

Solubility of magnesium ammonium phosphate in some salt solutions. K. L. MALJAROV and V. B. MATSKIEVITSCH (Z. anal. Chem., 1934, **98**, 31—33).—The solubility of MgNH_4PO_4 increases with the concn. of NH_4^+ or Na^+ salt present; this is particularly marked with $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The solvent effect of salts increases in the order NaCl , NH_4NO_3 , Na_2SO_4 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The use of NH_4NO_3 instead of NH_4Cl in separating Ca and Mg is therefore recommended. A. R. P.

Solubility of the phosphoric acid of different phosphates. F. MACH and P. LEDERLE (Z. Pflanz. Dung., 1934, **A**, 34, 323—340).—Various Ca phosphates are more sol. in H_2O than in aq. $\text{Ca}(\text{HCO}_3)_2$ (I) containing free CO_2 . The solubility is lowered if the (I) is substantially free from CO_2 , and is still lower in soil extracts. The conclusion of Wilhelmj (B., 1931, 455) could not be substantiated. SiO_2 sol increases the solubility of phosphates, but SiO_2 gel is without effect. A. G. P.

Influence of salt- or acid-type hydrophilic colloids on the solubility of sparingly soluble acids and bases. I. Gum arabic and its free acid. H. BRINTZINGER and H. G. BEIER (Kolloid-Z., 1934, **68**, 271—275).—The solubility of BzOH , salicylic and sulphanilic acids is increased by gum arabic, but not by arabic acid (I), whilst the solubility of strychnine and of *o*-, *m*-, and *p*- $\text{NO}_2\text{-C}_6\text{H}_4\text{-NH}_2$ is increased by (I). These influences are attributed to salt formation. E. S. H.

Solubility of gluten. W. H. COOK and R. C. ROSE (Nature, 1934, **134**, 380—381).—Gluten (I) is completely dispersed by 10 and 12% solutions of Na salicylate (II). Higher concns. are slower in their action. 8% (II) and 24% $\text{CO}(\text{NH}_2)_2$ are min. concns. for complete dispersion of (I). L. S. T.

Distribution of chloroacetic acids between two non-miscible liquid phases. N. A. DE KOLOSOVSKI and F. S. KULIKOV (Z. physikal. Chem., 1934, **169**, 459—471).—The distribution ratio of the chloroacetic acids between H_2O and twelve org. solvents has been determined at 25° over a wide range of concn. R. C.

Formation of fog in the absorption of hydrogen chloride by liquids. H. REMY [with W. OWE] (Kolloid-Z., 1934, **68**, 246—253).—The absorption of fumes of moist SO_3 and of HCl (obtained by passing air through a conc. solution or by passing H_2 over heated AgCl) in H_2O , EtOH , aq. 1% gelatin, aq. KOH , BaCl_2 , or AgNO_3 has been determined. Absorption of HCl is almost complete, although in some cases a slight fog remains above the absorbent liquid. Absorption of SO_3 is $\leq 67\%$ in any of the systems examined, and varies with the concn. of SO_3 in the fumes. E. S. H.

Sorption of sulphur dioxide by active charcoal. I. Relation between sorption, temperature, and pressure. K. ARII (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 853—867).—The adsorption isotherms of SO_2 on active coconut charcoal have been determined at 0 — 50° , the results being in agreement with Freundlich's formula. The relation between amount adsorbed per c.c. (a), pressure (p), and temp. (t) is given by $\log a = \log a_0 - (0.006790 - 0.0006742 \log p)t$, where a_0 is the amount adsorbed at 0° . The differential isosteric heat of adsorption is also calc. J. W. S.

Adsorption of ether vapour from vapour-air mixture by active charcoal powder [in relative motion]. E. BOYE (Kolloid-Z., 1934, **68**, 367—371).—Adsorption isotherms at 20° have been determined, using two kinds of finely-divided active C. E. S. H.

Adsorption of acids by animal charcoal. S. CASPE (J. Indian Chem. Soc., 1934, **11**, 439—440).—The loss in acidity of aq. HCl and AcOH on treatment with animal C is due to reaction between these acids and phosphates present in the C, and not to adsorption as is commonly supposed. D. R. D.

Influence of acidity on the adsorption of metal salts by active charcoal. H. LEUNG (Z. anorg. Chem., 1934, **219**, 178—180).—Adsorption of $\text{Hg}(\text{NO}_3)_2$ from aq. HNO_3 , FeCl_3 from aq. HCl , and $\text{K}_2\text{Cr}_2\text{O}_7$ from aq. H_2SO_4 of different concn. shows that increasing acidity reduces the amount of salt adsorbed, but that, above a certain definite concn., the acid has no further influence. M. S. B.

Effect of p_{H} on the adsorption and deamination of alanine by charcoal. E. BAUR and K. WUNDERLY (Biochem. Z., 1934, **272**, 1—8; cf. this vol., 594).—Low acidity stimulates and high acidity restricts the adsorption and deamination of alanine by charcoal, the quant. relationships being exactly similar to those between activity and p_{H} in fermentation. The production of complex ions which are expelled from the adsorbent by $[\text{H}^+]$ is assumed. W. McC.

Absorption of alkali metals on metal surfaces. I. Formation and adsorption of ions; potential curves. J. H. DE BOER and C. F. VEENEMANS (Physica, 1934, **1**, 753—762).—Theoretical. Alkali metal atoms are transformed into positive ions by adsorption at a metal surface, if the sum of the energies of adsorption of the ions (Q_i) and of escape of electrons from the metal ($\epsilon\phi_0$) $>$ energies of adsorption (Q_a) and of ionisation (I_a) of the atoms. If in addition $\epsilon\phi_0 > I_a$, the absorbed ions are vaporised

at higher temp. The adsorption phenomena may be compared with the formation of chemical compounds as is shown by the potential curves. H. S. P.

Activated adsorption of water vapour by alumina. H. S. TAYLOR and A. J. GOULD (J. Amer. Chem. Soc., 1934, 56, 1685—1687).—Pptd. Al_2O_3 has a very high adsorptive capacity for H_2O vapour at high temp. The lower temp. at which activated adsorption of H_2O vapour occurs and the lower heat of adsorption, as compared with the corresponding data for H_2 , explain the dehydrating characteristics of Al_2O_3 . E. S. H.

Adsorption of sulphate ion by thorium hydroxide sol dialysed to different degrees. N. V. KAREKAR and A. M. PATEL (Kolloid-Z., 1934, 68, 286—289).—Using K_2SO_4 , MgSO_4 , and $\text{Al}_2(\text{SO}_4)_3$ as the added electrolytes the adsorption of the cations increases with increasing valency and decreases with progressive dialysis of the sol. The adsorption of SO_4^{2-} in K_2SO_4 and MgSO_4 is reduced, but in $\text{Al}_2(\text{SO}_4)_3$ is slightly increased, by the addition of MeOH , EtOH , or Pr^nOH . E. S. H.

Absorption of acetone by cellulose nitrates. M. MATHIEU and C. KURYLENKO (Compt. rend., 1934, 199, 427—428).—The absorption spectrum of cellulose trinitrate- COMe_2 combinations is quantitatively influenced by the amount of H_2O in the COMe_2 used and is markedly different if H_2O is rigidly excluded. Further, absorption of COMe_2 is reversible without loss of structure. It is concluded that no definite compounds are formed. R. S. C.

Exchange adsorption and adsorption indicators. I. M. KOLTHOFF (Kolloid-Z., 1934, 68, 190—200).—A discussion of the conditions for exchange adsorption and for true adsorption. The action of adsorption indicators is explained on the basis of exchange adsorption. E. S. H.

Theory of phenomenon of liquid drops on the surface of the same liquid. M. KATALINIĆ (Kolloid-Z., 1934, 68, 372—373).—Polemical (cf. A., 1933, 1113). E. S. H.

Reciprocal solubility and surface tension. V. SEMENTSCHENKO and E. DAVIDOVSKAJA [with S. GRATSCHIEVA] (Kolloid-Z., 1934, 68, 275—286).—The influence of additions of BuCO_2H , $\text{C}_5\text{H}_{11}\cdot\text{CO}_2\text{H}$, $\text{C}_6\text{H}_{13}\cdot\text{CO}_2\text{H}$, $\text{C}_7\text{H}_{15}\cdot\text{CO}_2\text{H}$, and amyl alcohol on the interfacial tension and crit. solution temp. of the system MeOH -hexane has been determined at 2°, 7°, 12°, 17°, and 22°. Similar data have been obtained for the system nicotine- H_2O with the above and other additions. The results show that substances which lower the interfacial tension cause the region of partial miscibility to contract, and *vice versa*. E. S. H.

Spreading of cellulose and its derivatives on solids and liquids. I, II. T. NAKASHIMA and M. NEGISHI (J. Soc. Chem. Ind. Japan, 1934, 37, 327—331b).—The spreading coeff. of solutions of cellulose nitrate or acetate (I) in COMe_2 or of (I) in MeOAc depends greatly on the quality of the prep. and on the concn. It is only slightly affected by the surface tension, but is probably a function of the viscosity. A. G.

Mechanical properties of unimolecular films. I. LANGMUIR (J. Franklin Inst., 1934, 218, 143—171).—A lecture, dealing mainly with the author's own work and including unpublished work [with (Miss) K. B. BLODGETT] on unimol. films of stearic acid at a H_2O -hydrocarbon interface. Bimol. and more composite films are dealt with in addition to unimol. films. D. R. D.

Surface films of ergosterol and its irradiation products. J. F. DANIELLI and N. K. ADAM (Biochem. J., 1934, 28, 1583—1591).—Surface pressure and potential measurements on unimol. films of ergosterol and its irradiation products show considerable changes in the tilt of the mols. as irradiation proceeds, probably due to stereochemical changes altering the angle of tilt of the OH group to the ring system. The position of the double linking probably alters, also, during irradiation. Position 3 for OH is favoured. C. G. A.

Mechanism of deformation of thread-like materials. II. Arrangement of the micelles of films. O. KRATKY (Kolloid-Z., 1934, 68, 347—350; cf. A., 1933, 902).—Consideration of published work on the double refraction of stretched cellulose nitrate films suggests that the micelles exist either as groups of parallel units or as bundles. E. S. H.

Wetting phenomena with hydrophilic and hydrophobic powders in a system of two immiscible liquids. IV. Influence of acids on the wetting of lead glance powder with different flotation reagents. E. BERL and B. SCHMITT (Kolloid-Z., 1934, 68, 350—361; cf. A., 1933, 1114).—The wetting curves of sulphated PbS in presence of different inorg. and org. acids and K Et xanthate are described. The cause of the observed max. is ascribed to preferential adsorption of the acid in dil. and conc. solutions at active, sulphated centres. With increasing degree of sulphation of PbS the max. is displaced in the direction of higher acid concn.; in absence of sulphate, org. acids having no hydrophilic groups can act as flotation reagents. E. S. H.

Heat of wetting charcoals of graded activity, in relation to adsorptive capacity and retentivity. S. H. BELL and J. C. PHILIP (J.C.S., 1934, 1164—1169).—The increase of available surface of either birchwood or sugar charcoal, and the decrease of bulk density on activation by air at 700—900°, are accompanied by a steady rise in the heat of wetting, which seems to be more definitely related to the retentivity than to the adsorption. Air treatment seems to reduce adsorptive power in the early stages, probably due to clogging by hydrocarbons which are removed by the subsequent treatment. No appreciable adsorption of dissolved substances of large mol. dimensions, e.g., methylene-blue, occurs with sugar C until a late stage in the air-activation of the C. The rise in the adsorption val. with increase in period of activation is then comparatively rapid. M. S. B.

Precipitation phenomena in the drying of dilute solutions. H. FLOOD and L. TRONSTAD (Kolloid-Z., 1934, 68, 333—335).—The formation of annular and spiral periodic structures in the evaporation in vac. of very dil. NaOH - Na_2CO_3 solutions is described. E. S. H.

Mosaic structure of crystals and heterogeneous equilibrium. D. BALAREV (Kolloid-Z., 1934, 68, 266—271).—A discussion of the effect of the heterogeneous structure of crystals on equilibrium in reactions involving a solid phase, with reference to sp. examples.

E. S. H.

Compressibility of dilute solutions of electrolytes. A. SZALAY (Physikal. Z., 1934, 35, 639—643).—The compressibility was investigated by the Debye-Sears optical diffraction method employing ultrasonic waves. A linear increase in the velocity of sound with the ionic concn. in H_2O was found. The compressibility decreases linearly with increasing concn. Ions with the same charges produce approx. the same effect, but the effect increases with valency $>$ corresponds with a linear law, but $<$ for a quadratic law.

A. J. M.

Viscosity of solutions of strong electrolytes. V. D. LAURENCE and J. H. WOLFENDEN (J.C.S., 1934, 1144—1147).—The relative viscosities of aq. $LiCl$, $LiBr$, LiI , $LiIO_3$, $LiOAc$, Li picrate, KI , KIO_3 , $KOAc$, $AcOH$, NEt_4Br , and NEt_4 picrate have been determined at 25° at concns. down to approx. $0.005N$ in some cases. The A and B coeffs. of the Jones-Dole equation $\eta = 1 + A\sqrt{c} + Bc$ have been calc. The A vals. are in good agreement with the Falkenhagen-Dole equation. The B vals. for the inorg. salts are approx. additive, being made up of independent components characteristic of the two ions, but this is not so for salts containing the NEt_4 and picrate ions. Comparison of B for OAc' and $AcOH$ shows that the val. of B is increased by an electric charge.

M. S. B.

Surface tension of Debye-Huckel electrolytes. L. ONSAGER and N. N. T. SAMARAS (J. Chem. Physics, 1934, 2, 528—536).—Wagner's formula for the surface tension of electrolytes is simplified. The limiting law $\sigma = \sigma_0 + \text{const.} \times c \log (\text{const.}/c)$ is obtained. The theory accounts fairly well for the observed σ up to concns. of $0.2N$. The available data for uni-univalent electrolytes indicate that Coulomb's law is valid for distances $>$ a mol. diameter (3×10^{-8} cm.) from the surface.

M. S. B.

Superficial electric moments of particles [dispersed] in a liquid medium. (MLLE.) N. CHOUCROUN (Compt. rend., 1934, 199, 36—38; cf. A., 1933, 461).—A micro-electrophoresis apparatus is described for use on a microscope stage, with which superficial electric moments of gamboge, mastic, and powdered glass were measured as functions of p_H . The double layers were found to cover only approx. 0.01% of the surfaces. The surfaces of bacteria and of yeasts were found to be non-uniformly electrified, definite orientation occurring in the applied field. Groups of bacteria may be separated by differential electrophoresis. The charges on yeasts varied periodically with time, and may be related to the vital processes.

B. W. B.

Mechanical properties of disperse systems and surface layers. II. Elastic properties and dispersity of foams. Experimental test of theory. D. DERJAGUIN and E. OBUCHOV (Kolloid-Z., 1934, 68, 243—246; cf. A., 1933, 777).—Data for

0.02% aq. saponin are in complete agreement with the theory previously outlined.

E. S. H.

Limits of applicability of ultrafiltration to the recognition of the colloid state. B. ERSCHLER (Kolloid-Z., 1934, 68, 289—298).—Collodion membranes have the power to retain crystalloids. With non-electrolytes the amount retained is independent of the concn. and is generally ≈ 2 — 3% . With electrolytes the amount retained is greater for dil. solutions, but less for conc. solutions. The charge on the membrane is discussed as a factor.

E. S. H.

Anomalous turbulence in sols. W. O. OSTWALD [with V. TRAKAS and collaborators] (Kolloid-Z., 1934, 68, 211—226).—In sols of Congo-red, benzopurpurin 4B, cotton-yellow, geranin, and 2% gum arabic turbulence is observed at very low velocities of flow.

E. S. H.

Preparation of colloidal manganese dioxide. E. CHIRNOAGA (Kolloid-Z., 1934, 68, 298—300).— MnO_2 sols are prepared by the slow reduction of $0.01N$ - $KMnO_4$ at room temp. with $EtOH$, Et_2O , $CHCl_3$, CS_2 , $PhMe$, xylene, etc. The sol is negatively charged and is readily coagulated by electrolytes, but is remarkably stable after boiling.

E. S. H.

Cohesion in the system sand + colloidal silicic acid and ferric hydroxide, dried at 110° . A. GLAZUNOV and V. PETAK (Chem. Listy, 1934, 28, 191—194).—Grains of sand are agglutinated by heating at 110° with colloidal $Fe(OH)_3$ (I); cohesion augments with (I) content up to 4% , thereafter diminishing. This effect is due to saturation of the sand surface with (I) at 4% , above which excess of (I) remains unadsorbed, and yields a non-cohesive powder on drying. SiO_2 gel has no agglutinative action, and if present together with (I) prevents cohesion.

R. T.

Magnetic birefringence in mercurisulphosalicylic acid sols. S. PRAKASH and L. N. BHARGAVA (J. Indian Chem. Soc., 1934, 11, 449—454).—Addition of KCl causes a decrease in the magnetic birefringence (B) of these sols; $Ba(NO_3)_2$ and KNO_3 increase B , and with KBr B passes through a min. For $FePO_4$ and $Zr(OH)_2$ sols, $B=0$.

D. R. D.

Vanadium pentoxide jellies. A. RABINERSON (Kolloid-Z., 1934, 68, 305—316).—Thixotropic V_2O_5 gels containing electrolytes, especially at higher concns., become non-thixotropic on keeping. The change is accelerated by shaking. Thixotropic gels are attributed to oriented coagulation. The setting time is retarded by previously heating the sol. Fresh thixotropic gels are liquefied by warming, probably through destroying the oriented coagulation.

S H

Formation of a ruby-red jelly of zirconium sulphosalicylic acid. S. PRAKASH and L. N. BHARGAVA (J. Indian Chem. Soc., 1934, 11, 419—420).—If Zr sulphosalicylic acid gel (cf. A., 1933, 1011) is allowed to set in presence of $Al(NO_3)_3$ or HNO_3 , it acquires a ruby-red colour. With $NaNO_3$, the colour is bright yellow. The rate of development of colour in presence of $Al(NO_3)_3$ has been followed using a Nutting photometer.

D. R. D.

Ageing of gel-like basic zinc salts. Topochemical reactions of compact disperse systems.

W. FEITKNECHT (Kolloid-Z., 1934, 68, 184—190).—X-Ray examination of gelatinous basic Zn salts, produced by hydrolysis, shows that (a) with basic ZnCl_2 a definite diagram for a $\text{Zn}(\text{OH})_2$ -rich form is given together with other variable forms, (b) with basic ZnBr_2 three characteristic forms are shown, and (c) with basic ZnSO_4 the structure varies with the $\text{Zn}(\text{OH})_2$ content. E. S. H.

Structure of cellulose solutions. S. GLIKMANN (J. Chim. phys., 1934, 31, 458—468).—The viscosity of solutions of cellulose nitrate (I) and acetate and of ethyl- and benzyl-cellulose in different org. solvents, the pptn. of COMe_2 solutions of (I) by aq. CaCl_2 , the variation of the ζ -potential of (I) with concn., and the appearance of (I) under the ultramicroscope after fractionation, may all be explained by assuming the existence of reversible aggregates of the cellulose derivatives which dissociate almost entirely in dil. solution, and form a gel-like structure in conc. solution. M. S. B.

Kinetics of slow coagulation. S. GHOSH (Kolloid-Z., 1934, 68, 316—324).—A crit. review of published work. E. S. H.

Action of "zwitterions" on colloids. E. WEITZ and W. CONRAD (Kolloid-Z., 1934, 68, 230—233).—Zwitterions of the nature of aliphatic or aromatic NH_2 -acids have little or no coagulating effect on positively-charged $\text{Fe}(\text{OH})_3$ sols or negatively-charged Au sols. The zwitterions stabilise $\text{Fe}(\text{OH})_3$ sols, but sensitise Au and As_2S_3 sols, towards coagulation by other electrolytes. E. S. H.

Lyotropic effects. E. M. BRUINS (Chem. Weekblad, 1934, 31, 479—480).—It is shown graphically that there is a crit. cation (anion) for which the lyotropic series of the anions (cations) comes to an end; for di-univalent salts the crit. lyotropic nos. are 14.9 and 0.01 for the anion and cation, respectively. H. F. G.

Lyophilic colloids. II. Solvation problem. S. LIEPATOV and S. PREOBRAZHENSKAJA (Kolloid-Z., 1934, 68, 324—333; cf. this vol., 144).—Measurements of the viscosity and osmotic pressure at different concn. and temp., and of the heat of dissolution of cellulose acetate in MeOAc have been made. The results are discussed in relation to the main theories of lyophilic colloids, and the conclusion is reached that solvation is a complex phenomenon which cannot be explained on purely chemical grounds. E. S. H.

Lyophilic colloids. XXII. Heat-coagulation of ovalbumin. H. R. KRUYT and J. R. DE JONG (Kolloid-Beih., 1934, 40, 55—86; cf. this vol., 27).—Sols of ovalbumin undergo a decrease of viscosity (η) between 0° and 20° , which is attributed to a diminution of the degree of hydration. Between 20° and 90° η increases, especially in the case of isoelectric sols; the change is less as the sol diverges from the isoelectric point, and when a sufficient charge on the particles is attained the sol obeys the Hagen-Poiseuille law; these phenomena are attributed to changes in the degree of aggregation. At const. temp. $> 20^\circ$ some decomp. occurs, causing a decrease of η . The effect of adding EtOH is similar to that of raising the temp. E. S. H.

Role of lipins in the changes of state of proteins. W. PAULI and M. A. OMAR (Kolloid-Z., 1934, 68, 203—211).—The prevention of the heat-coagulation of ovalbumin by removal of lipins is due to a strong displacement of p_H in the alkaline direction, and can be overcome by electro-dialysis. The lipin content does not affect the behaviour of albumin towards H^+ , OH^+ , $\text{CO}(\text{NH}_2)_2$, or Na salicylate. E. S. H.

Structural changes taking place during the ageing of freshly-formed precipitates. II. Free mobility of lead ions in amicroscopic crystals of lead sulphate. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1934, 56, 1658—1661; cf. this vol., 840).—Rates of exchange between ageing inactive PbSO_4 and radioactive Pb^{++} solution and between radioactive PbSO_4 and inactive Pb^{++} solution are identical. The rate of exchange is diminished by a large excess of $\text{Pb}(\text{NO}_3)_2$ in the supernatant liquid. The homogeneous distribution of Th-B throughout the system is explained by the assumption that the Pb^{++} ions can move freely in the primary amicroscopic PbSO_4 crystals, even in a ppt. 50 min. old. E. S. H.

Colloidal behaviour of sericin. III. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 283—302; cf. B., 1934, 878).—The cataphoretic velocity (v) of sericin particles has been measured over a range of p_H 3.6—5. From 10° to 40° $\log v = a + bt$, where t is temp. and a and b are consts. The influence of salts and of pre-heating the sericin on v has been studied. v decreases on keeping owing to gelatinisation. Two forms of sericin have been prepared by adding to a lukewarm solution an equal vol. of saturated $(\text{NH}_4)_2\text{SO}_4$; on keeping sericin-A (transparent, long fibres) flocculates on the surface and sericin-B (white, granular) slowly ppts. from the solution. Other precipitants, and separation by an electric current and by freezing, are described. The average N contents of sericin-A and -B are 16.36 and 16.11%. Flocculation vals. have been determined for many salts, the controlling factor being the charge on the cation; pptn. with alcohols and COMe_2 has also been studied. In an electric field the A form predominates at the anode and the B form at the cathode. In all cases batches from different silk cocoons are compared. R. S. B.

Ostwald's isocolloid theory and the explanation of the fine structure of resins. R. HOUWINK (Kolloid-Z., 1934, 68, 371—372).—A correction. E. S. H.

Physical chemistry of the dehydration processes of bakery colloids. Physico-chemical foundations of moisture determination. A. I. GERSCHON (Kolloid-Z., 1934, 68, 361—366).—A study of the dehydration of flour, dough, and bread at different temp. shows that the moisture content is a linear function of temp., whilst at const. temp. the rate of dehydration follows an unbroken curve, which at lower temp. is in accordance with a unimol. reaction. No clear distinction between the free and bound H_2O can be made. E. S. H.

Physical chemistry of starch and bread-making. XX. Connexion between the changes in starch in the staling of bread and the changes

in the retrogression of starch paste. J. R. KATZ. XXI. Connexion between changes in the X-ray diagram, on the one hand, and changes in the swelling capacity and amount of soluble amylose, on the other, in the retrogression of wheat starch in the first stage of peptisation (judged by experiments on the retardation of the staling of bread). J. R. KATZ and A. WEIDINGER (Z. physikal. Chem., 1934, 169, 321—338, 339—360; cf. this vol., 961).—XX. In the staling of bread and the ageing of starch paste the same process occurs, but not with the same intensity. In staling, the change in the starch is retrogression from the first stage of peptisation, whilst in the ageing of starch the change is retrogression from the second stage. In both cases a substance with a *B* X-ray diagram is formed. In the first stage of peptisation a *V* diagram is obtained, in the second an amorphous diagram. Wheat starch heated with 20—50% of H_2O yields an *A* with a superimposed *V* diagram, but with < 20% of H_2O an unchanged *A* diagram only, and heated with 50—60% of H_2O a pure *V* diagram. The starch in fresh bread is attacked more rapidly by malt diastase than that in stale bread, and the latter more rapidly than native starch not heated with H_2O .

XXI. Heating at 40—70°, cooling at -185°, the presence of too little or too much H_2O , and the presence of aldehydes or certain alkaline substances, but not of ketones, delay or prevent the staling of bread. The effect of each of these factors on the X-ray diagram runs parallel with the effect on the swelling capacity, as measured by the vol. of decantate, and usually with the effect on the amount of sol. amylose (I). It seems that the decline on staling in the amount of (I) and in swelling capacity are closely related, but are not manifestations of the same fundamental change. These results confirm the hypothesis that in retrogression from the first stage of the peptisation of starch the fall in swelling capacity is due to transformation of the starch into a modification of lower swelling capacity. R. C.

Theory of the equation of state. I. G. SCHWEIKERT (Z. Physik, 1934, 90, 355—372).—An equation of state of the van der Waals type has been derived from a consideration of mol. vol. and time of collision. The equation is utilised in the calculation of sp. heats. A. B. D. C.

Thermodynamical theory of the equation of state. V. JACZYNA, S. DEREVJANKIN, A. OBNORSKI, and T. PARFENTJEV (Z. Physik, 1934, 90, 331—341).—Experimental data show almost complete agreement with the thermodynamic equation. A. B. D. C.

The liquid state. J. H. HILDEBRAND (Science, 1934, 80, 125—133).—A lecture. L. S. T.

Spectral physics and thermodynamics. Calculation of free energies, entropies, specific heats, and equilibria from spectroscopic data and the validity of the third law. H. ZEISE (Z. Elektrochem., 1934, 40, 662—669).—A further review (cf. A., 1933, 1245).

Activities of life and the second law of thermodynamics. F. G. DONNAN and E. A. GUGGENHEIM (Nature, 1934, 134, 255; cf. this vol., 733). L. S. T.

Thermodynamic properties of steam at high temperatures. A. R. GORDON (J. Chem. Physics, 1934, 2, 549).—Vals. for the thermodynamic properties of steam, calc. from Mecke's spectroscopic data, are given for temp. 1500—3000° abs. M. S. B.

Exchange reaction of hydrogen and deuterium oxide. R. H. CRIST and G. A. DALIN (J. Chem. Physics, 1934, 2, 548).—New corr. vals. are given for the equilibrium const. of the reaction $H^1H^2O + H^1 \rightleftharpoons H^2O + H^1H^1$. For temp. 300—900° abs. *K* is 0.35—0.83 (cf. this vol., 962). M. S. B.

Equilibrium $H_2O + HD = HOD + H_2$ and its rôle in the separation of the hydrogen isotopes. A. FARKAS and L. FARKAS (J. Chim. Physics, 1934, 2, 468—469).—The separation of H^1 and H^2 by various processes, such as electrolysis, decomp. of dil. acids by metals etc., is governed by the vals. of the possible equilibria, especially $H^1O + H^1H^2 \rightleftharpoons H^1H^1O + H^2$, by the rate of establishment of the equilibria which may be catalysed by different substances, especially metals, and by the rate of reaction of the different individuals, H^1O , H^1H^2O , and H^2O . M. S. B.

Equilibrium constants of the vapour-phase hydration of ethylene, propylene, and the butylenes. H. M. STANLEY, J. E. YOE, and J. B. DYMCK (J.S.C.I., 1934, 53, 205—208r).—Equilibrium consts. for the following gaseous reactions have been determined at 1 atm. by a flow method in the temp. range specified: (1) $CH_2=CH_2 + H_2O \rightleftharpoons EtOH$ (145—250°); (2) $CHMe=CH_2 + H_2O \rightleftharpoons CHMe_2OH$ (175—250°); (3) $[CHMe]_2$ or $CHEt=CH_2 + H_2O \rightleftharpoons CHMeEtOH$ (150—250°); (4) $CMe_2=CH_2 + H_2O \rightleftharpoons CMe_2OH$ (150° and 175°). In every case, the vals. of $K_p = [p_{alcohol}/(p_{olefine} \times p_{H_2O})]$ diminish with rising temp. The heat of hydration of C_2H_4 is calc. as +9600 g.-cal. per mol. At a given temp. the equilibrium is most favourable for alcohol production in the case of C_2H_4 and least favourable in the case of the *n*-butylenes, whilst C_3H_6 and isobutylene occupy an intermediate position.

Calculation of the equilibria in keto-enol tautomerism. G. W. WHELAND (J. Chem. Physics, 1934, 2, 482).—A correction (cf. this vol., 28). M. S. B.

Acid-base function in non-aqueous solvents. I. Colorimetric investigations in *n*-cresol. J. N. BRÖNSTED, A. DELBANCO, and A. TOVBORG-JENSEN (Z. physikal. Chem., 1934, 169, 361—378).—From measurements of extinction spectra of solutions of indicators in *n*-cresol (I) and extinction of mixed solutions of indicators and protolytic buffers the scale of strength consts. of electroneutral and cation acids in (I) has been determined. The graph of the rational acid const. in (I) against the conventional acid const. in H_2O consists of two parallel straight lines, one corresponding with neutral carboxylic acids of the AcOH type, the other with cation acids of the NH_3Ph type, such that if a simple positive acid and an electroneutral acid are equally strong in H_2O , the former is > 1000 times as strong as the latter in (I). This ratio agrees qualitatively with theory (this vol., 962). Piperidine and certain aliphatic amines are more or less completely protolysed in dil. (I) solution. Judged by

these results (I) is a much more strongly acid medium than H_2O and the alcohols. R. C.

Dissociation constants of boric acid from 10° to 50°. B. B. OWEN (J. Amer. Chem. Soc., 1934, 56, 1695—1697).—The first dissociation const. of H_3BO_3 and the corresponding heat of dissociation have been determined at 10—50°. At 25°, $K=5.80 \times 10^{-10}$ and $\Delta H=3360$ g.-cal. E. S. H.

Thermodynamics of aqueous barium chloride solutions from electromotive force measurements. E. A. TIPPETTS and R. F. NEWTON (J. Amer. Chem. Soc., 1934, 56, 1675—1680).—E.m.f. measurements of cells of the type Ba (two-phase amalgam)| $BaCl_2(m)$ | Hg_2Cl_2 |Hg have been made at 0°, 15°, 25°, 35°, and 45°, and the activity coeffs., relative partial mol. heat contents, and heat capacities of $BaCl_2$ in aq. solution calc. therefrom. E. S. H.

Iodine cations. W. A. NOYES (J. Amer. Chem. Soc., 1934, 56, 1819).—Evidence for the existence of I^+ in aq. solution is adduced. E. S. H.

Activity of sodium and potassium dissolved in gallium. E. S. GILFILLAN, jun., and H. E. BENT (J. Amer. Chem. Soc., 1934, 56, 1661—1663).—The solubility of Na in Ga at 30° is about 0.001 wt.-%; the activity of Na corresponds with an e.m.f. of 0.70 volt. The solubility of K in Ga at 32° is about 4×10^{-6} wt.-%; the activity corresponds with an e.m.f. of 0.76 volt. E. S. H.

Physico-chemical studies of complex acids. XII. Precipitation of the normal and complex tungstates and molybdates of the alkaline earths and of silver. H. T. S. BRITTON and W. L. GERMAN (J.C.S., 1934, 1156—1160).—The reaction between the hydroxides of Ca, Sr, and Ba and aq. $NaWO_3$ containing HCl has been studied conductometrically and electrometrically, and the ppts. formed at different stages have been analysed. Normal tungstates are formed in presence of excess of tungstic acid. The action of normal, para-, and meta-tungstates and -molybdates on $BaCl_2$ and $AgNO_3$ has also been examined. The solubility products of Ag_2WO_4 and Ag_2MoO_4 have been determined. In general ppts. obtained with the para- and meta-salts vary in composition with the amount of precipitant employed, and there seems no evidence for the existence of complex para- and meta-salts. M. S. B.

Symbols in the phase rule and in electrochemistry. E. LANGE (Z. Elektrochem., 1934, 40, 655—661).—A system of nomenclature is developed to represent phase conditions and equilibria. H. J. E.

System mercuric chloride-potassium chloride-ethyl alcohol. M. PERNOT (Compt. rend., 1934, 199, 478—480).—KCl and $HgCl_2$ in 95% or 100% EtOH at 34° afford the compound, $5HCl.6HgCl_2.2EtOH$, which when exposed to air yields the substance, $5KCl.6HgCl_2.4H_2O$. H. W.

Systematic relationships. LXI. Osmium sulphides. R. JUZA (Z. anorg. Chem., 1934, 219, 129—140).—The reversible decomp. of OsS_2 has been studied tensimetrically. No stable lower sulphide exists and Os and OsS_3 are only very slightly sol. in one another. The g.-mol. heat of formation from Os and

S_2 vapour is 62 kg.-cal. at 1020°. On heating the amorphous pptd. OsS_2 in vac. it glows at 560—570° and crystallisation suddenly takes place. Oxy-sulphides are produced by the action of H_2S on OsO_4 solutions. M. S. B.

Heat of dilution of heavy water. E. DOEHLE-MANN, E. LANGE, and H. VOLL (Naturwiss., 1934, 22, 526).—The heat of dilution of H_2O containing varying amounts of H^1H^2O has been measured by means of a differential calorimeter. The concns. were determined by a refractometer. The strong intermol. forces of H_2O are shown in the negative vals. of the heat of dilution. The heat of dilution is approx. \propto the initial concn. of H^1H^2O . A. J. M.

Determination of gradation of polarity of amino-nitrogen in organic compounds. D. RADULESCU and O. JULA (Z. physikal. Chem., 1934, B, 26, 390—394; cf. A., 1930, 1087).—The heat of neutralisation, U , of several org. bases with three anhyd. org. acids and two aq. mineral acids has been determined. For each acid the bases fall into approx. the same order in respect of the gradation of U , which is taken to be the order of polarities. Sp. heats of the acids and bases are recorded. R. C.

Heats of combustion and of formation of the normal paraffin hydrocarbons in the gaseous state, and the energies of their atomic linkings. F. D. ROSSINI (J. Res. Nat. Bur. Stand., 1934, 13, 21—35).—From vals. obtained for the heats of combustion (I) of simple n -paraffins (A., 1931, 433, 1236; this vol., 966) the (I) of all other n -paraffins in the gaseous state are deduced. When the no. of C atoms (n) is >5 , at 25° and 1 atm. (I) = $60.40 + n(157.00 \pm 0.08)$ kg.-cal. per mol. In any org. mol. containing a n -alkyl group ($n > 5$), the addition of CH_2 increases (I) by 157.00 ± 0.08 kg.-cal. per mol. The heats of formation of all the n -paraffins in the gaseous state at 25° C. and 0° abs. from H_2 , β -graphite, and diamond, respectively, have been calc. The energy of dissociation of gaseous n -paraffins into gaseous C and H at 0° abs. is a linear function of n , when n is >6 . The energy evolved in the reaction $C(gas) + 2H(gas) + C_nH_{n+2}(gas) = C_{n+1}H_{2n+4}(gas)$ at 0° abs., when n is >5 , is $(20.8 \pm 0.9) + D_{CO}$ kg.-cal. per mol., where D_{CO} is the energy of dissociation of CO at 0° C. E. S. H.

Hydration of normal Mg^{++} , Ca^{++} , Sr^{++} , and Ba^{++} solutions. J. BABOROVSKY and O. VIKTORIN (Chem. Listy, 1934, 28, 188—191).—Measurements of the transport nos. of N -chloride solutions indicate Mg^{++} 20, Ca^{++} 16—17, Sr^{++} 16, and Ba^{++} 11 H_2O . R. T.

Conductivity of methoxides and ethoxides. G. E. M. JONES and O. L. HUGHES (J.C.S., 1934, 1197—1207).—The electrical conductivity of the methoxides and ethoxides of Li, Na, and K has been determined in MeOH and EtOH at 25°; in order to ascertain the effect of impurities, the conductivity of the Me and Et carbonates of Li, Na, and K, and of CO_2 and NH_3 in both alcohols, and finally of $Ca(OMe)_2$ in MeOH has also been measured. The following mobilities are recorded: OMe' 53.3; OEt' 24.5; $MeCO_3'$ 45.4; $EtCO_3'$ 20.7. The dissociation consts. of CO_2 and NH_3 in MeOH are 2×10^{-10} and 2×10^{-6} and in EtOH

6×10^{-12} and 1.5×10^{-7} , respectively. A method for the correction of the conductivity data for bases on account of the presence of CO_2 is worked out.

M. S. B.

Velocity of establishment of potential. J. J. BIKERMAN (Compt. rend., 1934, 199, 453—455).—Assuming that the effects of applying a potential between two electrodes immersed in an electrolyte are (a) displacement of charges within the mols., (b) orientation of the mols., and (c) accumulation of anions and dissipation of cations at the anode, and *vice versa* at the cathode, it is concluded that the e.m.f. should show a dispersion at frequencies of 10^7 to 10^8 per sec. The anomalies observed in electrode capacities under a.c. cannot be due, therefore, to the slowness of the formation of the double layer, but are more probably due to alteration in the dielectric const. and viscosity of the solvent in the electrolyte-electrode interface or to secondary causes.

J. W. S.

Potentials of bismuth oxides and the alkaline bismuth cell. E. BAUR and W. LATTMANN (Z. Elektrochem., 1934, 40, 582—585).—Measurements of potential of the electrode $\text{Bi}|\text{Bi}_2\text{O}_3, N\text{-NaOH}$ in presence of oxidising agents reveal the existence of B_2O_4 and B_4O_7 . The cell $\text{Bi}|\text{Bi}_2\text{O}_3, N\text{-NaOH}, \text{Bi}_2\text{O}_3, \text{Ni}$ has e.m.f. 1.035 volts.

E. S. H.

Periodic changes of potential of iron in chromic-sulphuric acid solutions. II. M. KARSCHULIN (Z. Elektrochem., 1934, 40, 559—564; cf. this vol., 601).—Addition of HCl , NaCl , CuSO_4 , K_2SO_4 , or KNO_3 reduces the frequency and amplitude of the periods and causes the Fe to become more active. When the system is in a steady state, the potential of Fe being positive to the calomel electrode, periods are induced by adding the above salts or by cathodic polarisation. During such "positive" periods the Fe is covered with a black, magnetic oxide.

E. S. H.

Reduction of permanganate in buffered solution: potentiometric titration with hydrogen peroxide. W. PUGH (J.C.S., 1934, 1150—1151).—Using silicofluorides as buffers the potentiometric titration of KMnO_4 with H_2O_2 can be carried out completely to the Mn^{2+} stage in neutral solution. Typical titration curves indicating definite stages in the reduction are given.

M. S. B.

Reversibility in the oxidation of certain derivatives of carbohydrates, especially ascorbic acid. R. WURMSER and J. A. DE LOUREIRO (J. Chim. phys., 1934, 31, 419—432; cf. this vol., 367).—An oxidation-reduction system, with a potential in the neighbourhood of the reduction potential of indophenols, is present in cellular tissue. For a similar system in reduced carbohydrates the name "redoxine" is proposed. The substance has not been isolated, but its potential in neutral and acid media has been determined. The ultra-violet absorption spectrum has a band at 2780 \AA . in a solution of p_H 7 and at 2650 \AA . in p_H 1. The structure of ascorbic acid is discussed and the potential in acid, neutral, and alkaline solution has been determined. The instability of the oxidised form increases considerably with increase of p_H . Reductone also forms a reversible oxidation-reduction system.

M. S. B.

Influence of polarisation on photo-voltaic effects. (MLLE.) M. THEODORESCO (J. Chim. phys., 1934, 31, 433—438).—The variations of photo-sensitivity observed on polarising Cu electrodes covered with CuO , Cu_2O , or a mixture of the two, in solutions of different electrolytes, have been studied. The effect is reversible, and after suppression of the polarising current the electrode returns gradually to the initial condition. Stirring has no influence. The polarisation e.m.f. corresponding with the max. effect depends on the concn. of electrolyte in the same way as the electrolytic decomp. potential. Inversion of the photovoltaic behaviour of Cu_2O occurs after a sufficiently positive polarisation. The formation of a deposit of Cu on the Cu_2O plate has been observed after negative polarisation. The results are discussed in relation to Audubert's theory of the photovoltaic effect.

M. S. B.

Theory of passivity. XXIV. Film passivity and chemical passivity [caused] by anodic treatment of iron in sulphuric acid. W. J. MULLER and E. LÖW. XXV. Chemical passivity and its electronic interpretation. W. J. MULLER (Z. Elektrochem., 1934, 40, 570—577, 578—582; cf. this vol., 602).—XXIV. An Fe anode goes into solution in H_2SO_4 at 0.7 volt as Fe^{2+} , at 0.8—1.4 volts as Fe^{3+} , whilst at 1.4 volts O_2 is discharged. At < 0.5 volt a white, non-birefringent film, probably of basic salt, forms on the anode, whilst at higher potentials a transparent oxide film forms. The time required for the film transformation varies with initial c.d. in an analogous way to the time required for formation of the primary film. There is a small time interval between the formation of the oxide film and the evolution of O_2 .

XXV. An explanation of the difference between the author's concepts of film passivity (in which the metal goes into solution at its lower valency) and chemical passivity (in which the ions entering the solution have a higher valency).

E. S. H.

Passage of current in an electrolyte without electrolysis. V. KARPEN (Compt. rend., 1934, 199, 480—483).—The e.m.f. of polarisation for different permanent currents passing between Pt electrodes in a solution of KI (50 g.) and I (30 g.) in H_2O (1000 c.c.) has been measured. For a given e.m.f. of polarisation the currents passing are incomparably > in the absence of I. The atoms of I in contact with the cathode receive an electron, and the resultant ions pass to the anode, where they become atoms with resulting increase of [I]. The view that the movement of I from cathode to anode is due to diffusion is supported by the observed effect of the relative positions of anode and cathode and of the temp.

H. W.

Crystal structure and conductivity of silver mercuric iodide. J. A. A. KETELAAR (Chem. Weekblad, 1934, 31, 442—445; cf. this vol., 1056).

H. F. G.

Change of velocity of an explosion wave with pressure. A. SOKOLIK and K. SCHTSCHELKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 102—103).—In a $2\text{H}_2 + \text{O}_2$ mixture the velocity of explosion, measured photographically, changes from 2630 to 2830 m. per sec. with a pressure change from 200 to

760 mm.; for $\text{CH}_4 + 2\text{O}_2$ from 2040 to 2350 m. per sec. for a pressure change of 80 to 760 mm. In a $\text{H}_2 + \text{Cl}_2$ mixture the velocity was const. at 1730—1740 m. per sec. at 200—760 mm. The change with pressure is attributed to dissociation in the wave front.

H. J. E.

Kinetics of the thermal decomposition of acetaldehyde vapour. M. LETORT (Compt. rend., 1934, 199, 351—353).—The true order of the reaction $\text{MeCHO} = \text{CH}_4 + \text{CO}$ is 1.5. The val. 2, usually given, is obtained when the walls of the quartz containing vessel have become poisoned.

A. J. M.

Flame temperatures in methane-air mixtures. W. T. DAVID and J. JORDAN (Phil. Mag., 1934, [vii], 18, 228—236; cf. A., 1932, 25; this vol., 258).—The temp. obtained by the Na-line reversal method (A., 1932, 127) are much > those from a Pt-Rh resistance thermometer, probably owing to the Na atoms being raised to a temp. > that corresponding with the mean mol. translational energy of the flame gases. The temp. obtained by the latter method show a max. at about 9.4% CH_4 , but, as with CO, they are 250—300° < the calc. temp., indicating a latent energy of about 15% of the heat of combustion.

J. W. S.

Kinetics of the reduction of hydrogen peroxide by the halides. A. MOHAMMAD and H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1934, 56, 1680—1685).— H_2O_2 is reduced by Cl' or Br' according to the rate law $-d[\text{H}_2\text{O}_2]/dt = k_1[\text{H}_2\text{O}_2][\text{X}'] + k_2[\text{H}_2\text{O}_2][\text{X}'][\text{H}']$, which is known also to hold for reduction with I. The effects of k_1^0 and k_2 on temp. variation have been determined. The mechanism is discussed.

E. S. H.

Reactivity of thiol group. III. N. HELLSTRÖM (Z. physikal. Chem., 1934, 169, 416—424; cf. A., 1933, 259).—The rate of reaction of $\text{Zn}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2$ (I) with $\text{CH}_3\text{I}\cdot\text{CO}_2\text{Na}$ (II) and $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Na}$ (III), and of $\text{Hg}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2$ with (II) in aq. solution at 25° has been measured. Thiodiglycolic acid is formed, and the reduction-oxidation reaction which occurs in the action of $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ or (II) on the SH group of $\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (IV) is absent. The velocity coeffs. for the reaction of (II) with the Hg-SH linking, the SH group, and the SH ion of (IV) are approx. in the ratio 1.5 : 1 : 10,000, whilst for the Zn compound the ratio is 150 : 1 : 10,000.

R. C.

Kinetics of hæmoglobin. IV. General methods and theoretical basis for the reactions with carbon monoxide. V. Combination of carbon monoxide with reduced hæmoglobin. VI. Competition of carbon monoxide and oxygen for hæmoglobin. VII. Reactivity of freshly reduced hæmoglobin. F. J. W. ROUGHTON (Proc. Roy. Soc., 1934, B, 115, 451—464, 464—473, 473—495, 495—503).—IV. The Hartridge-Roughton rapid reaction technique is extended to the study of (a) the combination of CO with reduced sheep hæmoglobin (Hb), (b) the displacement of O_2 by CO from combination with Hb, and (c) the displacement of CO by O_2 from combination with Hb. The velocity equations deduced for reaction (a) from the Hufner theory (I) and Adair's intermediate compound theory (II)

(A., 1925, i, 851) are identical, but differ from that based on Hill's equation (III). When < three of the four available groups of Hb are already occupied by O, or CO, theory (II) leads to the velocity equation $d[\text{COHb}]/dt = m'[\text{CO}][\text{O}_2\text{Hb}]/[\text{O}_2] - m[\text{COHb}]$ for reactions (b) and (c).

V. The velocity of reaction (a) is approx. 0.1 of that of the O_2 -Hb reaction under similar conditions, and this observation is utilised in a more accurate method especially applicable to dil. solutions. Even beyond the early stages of the reaction $d[\text{COHb}]/dt = k[\text{CO}][\text{Hb}]$ is obeyed, and the effects of varying the concns. of reactants are inconsistent with (III). The velocity at $p_{\text{H}} 10$ is 50% > at $p_{\text{H}} 5.6$ —7.2, and the temp. coeff. is 1.8 (approx.) in the range 7.2—33.3°. Light displaces the equilibrium $\text{CO} + \text{Hb} \rightleftharpoons \text{COHb}$ to the left, but does not accelerate the forward reaction.

VI. The trustworthiness of the methods used in this and earlier work is confirmed and the absence of significant photochemical "after-effects" in the "light method" is demonstrated. In the p_{H} range 5.6—10.0, the data for reaction (b) accord with the equation $d[\text{COHb}]/dt = m'[\text{CO}][\text{O}_2\text{Hb}]/[\text{O}_2]$ over a twenty-fold range of concn. (< 0.6 millimol. per litre), and m' increases only slightly with decrease of p_{H} . The data for reaction (c) conform to the equation $-\text{[COHb]}/d = m[\text{COHb}]$ at high $[\text{O}_2]$. Change of p_{H} has little effect on m , but the temp. coeff. is 4 (approx.) per 10°. The unexpectedly small variations of m' and m with change of p_{H} are discussed, especially with reference to the view that in the exchange of O_2 for CO, three of the four available linkings of Hb are already saturated with gas mols., and the possibility that Hb and its compounds when freshly formed have different reactivities from the "old" mols. The kinetic data are inconsistent with (III), and since theory (I) is not in accord with dissociation curve data, theory (II) is adopted as the best working hypothesis.

VII. The rate of combination at $p_{\text{H}} 10$ and 15° of CO with Hb freshly reduced from O_2Hb by $\text{Na}_2\text{S}_2\text{O}_4$ is twice as great as with Hb > 2 sec. old. The difference disappears at 33° and at $p_{\text{H}} 6.6$ (room temp.). The O_2 -Hb reaction does not show a similar phenomenon. The dissociation, by dilution, of 90% O_2Hb at $p_{\text{H}} 6.3$ leads to an equilibrium established 0.5—0.7 sec. after mixing with 45% O_2Hb followed by a slowly established equilibrium with 20% O_2Hb . This was not due to inactivation of the Hb. At $p_{\text{H}} 10$ the equilibrium val. does not fall below the initial val. of 50—60% O_2Hb . These results are consistent with the above anomalies (Part VI).

J. G. A. G.

Change of reactivity and dissolution velocity of sulphur at the transition temperature. J. A. HEDVALL, A. FLOBERG, and P. G. PALSSON (Z. physikal. Chem., 1934, 169, 75—80; cf. A., 1931, 582).—The reactivity and rate of dissolution in AcOH of S are much greater during the transition rhombic-monoclinic than at temp. either below or immediately above the transition temp.

R. C.

Active oxides. LXXVI. Kinetics of thermal decomposition of magnesite and the chemical

compounds intermediately formed. G. F. HUTTIG, W. NESTLER, and O. HNEVKOVSKY (Ber., 1934, 67, [B], 1378—1387).—Study of the rate of decomp. of MgCO_3 in vac. when used in powder form, as a film obtained by spreading a paste of $\text{MgCO}_3\text{-MeOH}$ (or EtOH) on glass and subsequently heating, or mixed with a metallic powder of high thermal conductivity, shows that the true rate of decomp. (dissociated from factors such as thermal conductivity and diffusion of gas) is best measured under the conditions last named, provided so much powder is used that the particles of it are in contact with one another throughout the mass. At 530° equal weights of MgCO_3 are decomposed in equal intervals of time, and the change cannot be represented as of the $2/3$ order. At 510° breaks in the decomp. isotherm occur corresponding with the compounds $4\text{MgCO}_3\cdot 3\text{MgO}$, (?) $2\text{MgCO}_3\cdot 3\text{MgO}$, and $\text{MgCO}_3\cdot 3\text{MgO}$. At 520° the existence of the substance $\text{MgCO}_3\cdot 2\text{MgO}$ is indicated. At 490° , decomp. is slow, but the characteristics of the 510° isotherm are probably emphasised. H. W.

Topochemical processes in materials. H. STAGER (Kolloid-Z., 1934, 68, 137—146).—A discussion including examples of the corrosion of metals.

E. S. H.

Topochemical aspect of the corrosion of metals. U. R. EVANS (Kolloid-Z., 1934, 68, 133—137).—A review.

E. S. H.

Transmission of detonations in a vacuum. A. BELIAEV and J. B. CHARITON (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 166—167).—The initiating crystal of PbN_6 (wt. 1—2 mg.) was placed over a small hole in a metal disc (I) 1 mm. thick at the centre of a glass bulb. The initiated crystal was placed below (I) on a mica slip. In air at normal pressure the detonation was transmitted approx. 1.5 cm. In vac. the lower crystal of PbN_6 could be detonated when at 40—45 cm. from (I), the energy reaching its surface being approx. 500 ergs per sq. cm.

H. J. E.

Application of the laws of chemical kinetics to secondary processes of electrolysis. S. A. PLETENEV and V. N. ROSOV (Z. Elektrochem., 1934, 40, 600—604).—The velocity of dissolution of Cu in aq. CuCl_2 and $\text{Fe}_2(\text{SO}_4)_3$ and the velocity of anodic oxidation of FeSO_4 have been measured. The results are discussed in relation to the kinetic laws. E. S. H.

Hydrolysis of starch by acid. A. P. SCHULZ and W. HÖNSCH (Chem.-Ztg., 1934, 58, 640—642, 671).—Results are given of 4 hydrolyses with HCl of 2 different concns. and at 2 different temp. The products were analysed in terms of amyloses (I), glucose (II), and maltose (III), and the results, represented according to both rectangular (IV) and triangular co-ordinates, are compared especially with those of Rolfe and Defren (A., 1898, i, 7). All the curves (IV) show a marked max. in the (III) content. Under approx. technical conditions, formation of (III) is more rapid than its decomp. The intersection points of the (I) and (II) curves give measures of the hydrolysis and show that at 100° the velocity of reaction approx. \propto the acid concn., whilst at higher temp. (pressure boiling) the increased effect is $< \propto$ the increase in acid concn.

T. H. P.

Rate of reaction between organo-magnesium halides and esters. G. VAVON, M. BARBIER, and G. THIEBAUT (Bull. Soc. chim., 1934, [v], 1, 806—814).—The benzoates of the following are described: $\text{CHPr}^2\cdot\text{OH}$, b.p. $146\text{—}147^\circ/14$ mm., $\text{CHPr}^2\cdot\text{OH}$, b.p. $141\text{—}142^\circ/15$ mm., methylpseudobutylcarbinol, b.p. $125^\circ/12$ mm., neomenthol, b.p. $181^\circ/16$ mm. The rate of reaction, of ROBz ($\text{R}=\text{Et}$, Bu) with $\text{MgEtBr} > \text{MgPr}^2\text{Br} > \text{MgBuBr} > \text{MgPhBr}$, and $\text{MgBuCl} > \text{MgBuBr} > \text{MgBuI}$. With MgR'Br , the val. of x when R is a primary grouping $> \text{sec.} > \text{tert.}$ and $\text{CHPr}^2\cdot\text{O} > \text{CHPr}^2\cdot\text{O}$, $\text{CHMeBu} > \text{CHMe}\cdot\psi\text{-Bu}$, and menthyl $>$ neomenthyl, thus demonstrating the effects of the structure of R . The vals. of x for Et esters increase with the strength of the acid; thus, with substituted EtOBz , $o\text{-Cl} > o\text{-Br} > o\text{-I}$ and $o\text{-MeO}$ (I) $> m > p$, and a steric factor is involved, since the x for Et valerate $>$ Et pivalate, $\text{EtOBz} > o\text{-C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{Et} > s\text{-C}_6\text{H}_4\text{Me}_3\cdot\text{CO}_2\text{Et}$, and $\beta > \alpha$ -naphthate. The exceptionally high val. of x for (I) is attributed to a complex Mg oxonium compound being formed with the O of the OMe.

J. G. A. G.

Solubility of cadmium in some organic acids. P. FORTNER and H. LUKAS (Pharm. Zentr., 1934, 75, 557—562).—The rates of dissolution of Cd (I) in 0.1N-lactic, -succinic, -tartaric, -citric, and -oxalic acids have been determined at room temp., 35° , and 60° . Dissolution is approx. four times as rapid in Pt as in glass, owing to electrolytic action. The solubility of (I) in wine is $>$ that calc. from the acidity. The following new normal salts are described, the solubilities % at 40° being given in parentheses: lactate (10.11), succinate (0.367), tartrate (0.100), citrate (0.23), oxalate (0.009).

S. C.

Inter-relations of hydrogen and deuterium molecules. A. J. GOULD, W. BLEAKNEY, and H. S. TAYLOR (J. Chem. Physics, 1934, 2, 362—373).— H_2O in a Pyrex or soft-glass vessel does not affect the concn. of $\text{H}_2\text{-H}^2$ mixtures. No effect is produced by stop-cock grease. Diffusion through Pd without circulation produces very little change, but diffusion with circulation results in a residual mixture containing H_2 , H^1H^2 , and H_2^2 in approx. equilibrium proportions, indicating that the diffusion process is at. Desorption from charcoal at liquid air temp. is a mol. process, and there is no reaction between H and H_2^2 . Hg and glass at room temp. also produce no reaction. Cr_2O_3 and a Ni-kieselguhr surface promote reaction between $-\text{H}_2$ and H_2^2 and a Pd surface at 270° . Any surface promoting the reaction between H_2 and H_2^2 will also promote the ortho-para conversion of H_2 , but the converse is not true. The vals. of the equilibrium const. $[\text{H}^1\text{H}^2]^2/[\text{H}_2][\text{H}_2^2]$ between $-\text{H}_2$ and 270° are in good agreement with those calc. from statistical mechanics. The calc. val. at 270° is 3.67.

M. S. B.

Explosion of mixtures of combustible gases with air by nuclear drops of water and other nuclei and by X-rays. I. Explosion of gaseous combustible mixtures passing through vitreous and steel combustion tubes, by nuclear drops of water. II. Explosion of hydrogen-air mixtures by X-rays. R. O. KING. III. Explosion of hydrogen-air mixtures by stone dust. IV. Ex-

plosion by nuclear drops of water of ethylene-air mixtures passing through a nickel-steel combustion tube. R. O. KING and G. MOLE (J. Inst. Petroleum Tech., 1934, 20, 791—805, 806—812, 812—815, 816—820).—I. H_2O droplets were injected axially down a rising column of gas in a heated vertical tube 1.25 in. diam. The ignition and explosion of the central stream of H_2 -air mixture by H_2O droplets ["nuclear" ignition (I)] occur at temp. $> 585^\circ$, and hence the length of tube heated by the furnace (6 in.) and the rate of gas flow ($F=100$ c.c. per min.) were so chosen that the boundary layer did not ignite ["self-ignition" (II)] at lower temp. and that flameless surface combustion was, relatively, not so rapid as to deplete the central core of gas sufficiently to make it non-inflammable. In Pyrex tubes, the nuclear ignition temp., T_N , coincided with that of (II), T_S , with mixtures containing 12—50% H_2 , but with richer mixtures T_N was $< T_S$ and such explosions were feeble and localised. With a new Cr-Ni-steel tube (II) was limited to 18—45% H_2 -air mixtures at $< 700^\circ$ and 50 c.c. per min., but H_2O injected into richer mixtures produced (I). Ageing of the tube catalysed surface combustion and the central column of gas became too impoverished to explode. The effect was diminished by increasing F , and T_N was then $< T_S$. (I) is due to H_2O droplets and not steam passing through the gas phase. The process is physical, since injected refractory particles lowered the ignition temp., T .

II. X-Rays lowered the T of air- H_2 rich mixtures in new Pyrex tubes to vals. $< T_S$, but the effect disappeared when the tube had been exposed to O_2 -rich mixtures. The lowering by X-rays is attributed to increased electrification of the layers of gas moving slowly over the surface, and this effect is counterbalanced by rapid steam formation when the surface becomes oxidised. X-Rays produced no significant effects when the Fe tube was used, since surface oxidation-reduction equilibria were rapidly established.

III. Dust (chiefly Al_2O_3) depressed $T >$ did H_2O droplets, but T_N , T_S , and the dust T decreased and converged as F was increased. The phenomenon is contrasted with the action of dust in inhibiting explosions in coal mines.

IV. The effect of the surface of the Fe tube on the 5—10% C_2H_4 -air mixture was $<$ and more reproducible than with H_2 -air mixtures. At 50 c.c. per min. (II) was not observed, but H_2O injections produced (I) with $> 6\%$ C_2H_4 . T_N decreased linearly with increase of $[\text{C}_2\text{H}_4]$. With $F > 100$ c.c. per min., (II) was observed, and as F was further increased T_S decreased to the approx. const. vals. of T_N . The results are interpreted in terms of the fog produced during hydrocarbon oxidations providing a sufficient concn. of nuclei to cause explosion. J. G. A. G.

Acid-base reactions involving deuterium. W. F. K. WYNNE-JONES (J. Chem. Physics, 1934, 2, 381—385).—Measurements have been made of the rate of neutralisation of the ψ -acid nitroethane in H_2O . The results indicate that the rates of ionisation of H^1 and H^2 are as 10 : 1. The importance of this in the catalysis of sucrose inversion by acids and bases in H_2O is discussed. The effect of H_2O on the acid catalysis of the mutarotation of α -glucose

has been studied, and the results show that the catalytic activity of H_2O is 3.8 times that of H_2O , whilst the activity of $(\text{OH}^1)^*$ is only 1.33 times that of $(\text{OH}^2)^*$. The mechanism of the reaction is discussed. It is suggested that the exchange of H^2 and H^1 atoms in a homogeneous phase at room temp. is essentially an acid-base-catalysed reaction, and is probably most readily brought about by adding acid and alkali alternately. M. S. B.

Catalytic activity of deuterium ion (H_3O^+). E. A. MOELWYN-HUGHES (Z. physikal. Chem., 1934, B, 26, 272—280; cf. this vol., 607).—The ratio of the catalytic coeff. of H_3O^+ for the mutarotation of glucose in H_2O to the catalytic coeff. of H_3O^+ for the mutarotation in H_2O is < 1 and rises with the temp., T , whilst the corresponding ratio for the inversion of sucrose is > 1 and falls with rising T . Arrhenius' equation is valid for the mutarotation, the energy of activation for H_3O^+ being $>$ for H_3O^+ by 1250 g.-cal.; both vals. agree with the theoretical vals. To explain the greater activity of H_3O^+ compared with that of H_3O^+ in the sucrose inversion it is suggested that the intermediate sugar-catalyst complex is more stable. R. C.

Iodide ion catalysis of hydrogen peroxide in heavy water. E. ABEL, O. REDLICH, and W. STRICKS (Naturwiss., 1934, 22, 525).—The catalytic decomp. of H_2O_2 in a solution containing H_2O by KI was investigated by an interferometric method. For a solution containing 60 mol.-% H_2O there is a decrease in the velocity coeff. of 20% compared with the val. for pure H_2O . Similarly the velocity coeff. of the reaction between H_2O_2 and HI is decreased when H_2O is used. A. J. M.

Action of inhibitors on the decomposition of hydrogen peroxide. D. RICHTER (J.C.S., 1934, 1219—1224).—The inhibition by 18 substances (I) of the photochemical decomp. of 0.1M- H_2O_2 at p_H 6.8 by light of λ 300 m μ did not, in general, increase in direct proportion to the concn. of inhibitor. 33—38 mols. of H_2O_2 were decomposed per quantum absorbed in the presence of 5—10 $\times 10^{-4}$ M- $\text{CH}_2\text{Ph}\cdot\text{OH}$, -resorcinol, and -PhOH. (I) have only small inhibiting effects on the decomp. of H_2O_2 catalysed by liver catalase, yeast catalase, and haematin, and it is therefore inferred that the enzymic decomp. does not involve reaction chains of the type occurring in the photochemical decomp. J. G. A. G.

Catalysed decomposition of nitroamide. V. Catalysis in *m*-cresol. J. N. BRONSTED, A. L. NICHOLSON, and A. DELBANCO (Z. physikal. Chem., 1934, 169, 379—387; cf. A., 1933, 471).—The decomp. in protolytic buffers in *m*-cresol solution at 20° proceeds in accordance with the protolytic theory of acidic and basic catalysis. With electroneutral bases (I) the velocity is not affected by addition of acid, but with anion bases (II) the velocity coeff. falls with increasing acid concn. The graph of the logarithm of the mol. catalysis const., k , against the logarithm of the protolytic strength const., K , of the base in *m*-cresol consists of two straight lines, one corresponding with (I), the other with (II), and the equations connecting k and K are exactly similar to those for the decomp. in aq. and $\text{C}_5\text{H}_{11}\cdot\text{OH}$ solutions. The

catalysis is determined, not by the hypothetical "internal basicity" of the catalyst, but by the practical scale of basicity corresponding with the medium. R. C.

Temperature coefficient of the sucrose inversion. E. A. MOELWYN-HUGHES (*Z. physikal. Chem.*, 1934, **B**, 26, 281—287).—The unimol. law is valid for the acid-catalysed inversion only within certain limits of temp. and acid concn. At higher temp. there are deviations indicating that there is a further reaction, which becomes increasingly evident as the temp., T , rises. The nature of this reaction is unknown. The apparent heat of activation calc. by Arrhenius' equation falls as T rises, and it is suggested that corresponding with the possibility of several simultaneous reactions the sucrose mol. has several heats of activation (cf. A., 1933, 910). At higher temp. sucrose reacts with pure H_2O giving org. acids and unidentified products. R. C.

Oxidation of thiol compounds by hydrogen peroxide at room temperatures in presence of inorganic catalysts. I. Oxidation of cystine and dithioglycollic acid in presence of molybdic acid and tungstic acid sols. J. C. GHOSH and B. C. KAR (*J. Indian Chem. Soc.*, 1934, **11**, 485—497).—These sols exert a strong catalytic action particularly in presence of small concns. of Cu^{II} , Fe^{II} , Cr^{III} , or Ce^{III} sulphates or $MnCl_2$. KCN has no effect; this shows that catalysis is not due to traces of Fe salts etc. The reaction follows a unimol. law in any single experiment, but the velocity coeff. (I) increases with the initial concn. of H_2O_2 ; the temp. coeff. of (I) is 2—2.3 per 10° . With molybdic acid, (I) increases with p_H ; with tungstic acid it has a max. at low p_H (p_H 1.13 for cystine, 1.62 for dithioglycollic acid), a min. at 2.5, and then rises again. Beyond p_H 5, spontaneous decomp. of the H_2O_2 prevented measurements. (I) also increases with the concn. of the sol, the deviation from direct proportionality being ascribed to the change in the surface/mass ratio with the larger particles in the conc. sols. D. R. D.

Action similar to that of oxidase with metallic complex salts. X. Y. SHIBATA and K. YAMASAKI (*Bull. Chem. Soc. Japan*, 1934, **9**, 273—283).—The O_2 uptake of $p\text{-OH}\cdot C_6H_4\cdot NHMe$ sulphate (I) in slightly alkaline solution has been measured at 25° , alone (α), in the presence of cobaltammines (II), and Cr complex salts (III). (II) form a black ppt. with (I) and decrease α , (III) form no ppt. and scarcely affect α . In the case of (II) the stronger oxidisers of the polyphenols give the smallest O_2 uptake, and the ppt. appears sooner than in the case of the weaker oxidisers. (III) do not affect the polyphenols. The addition of KCN and (III) to (II) tends to remove the retarding influence of (II) on α . NH_2OH considerably increases, but only slightly influences the effect of (II) on α . R. S. B.

Synthesis of esters by castor seed lipase.—See this vol., 1033.

Exchange reaction between deuterium and water vapour on surfaces. H. S. TAYLOR and H. DIAMOND (*J. Amer. Chem. Soc.*, 1934, **56**, 1821—1822).—In contact with catalytic hydrogenating sur-

faces, such as Cr_2O_3 and ZnO , H_2^3 reacts with adsorbed H_2O and may be replaced completely by H_2 .

E. S. H.

Hydrogenation-dehydrogenation catalysts. K. PACKENDORFF and L. LEDER-PACKENDORFF (*Ber.*, 1934, **67**, [B], 1388—1391).—A powerful dehydrogenating catalyst results when H_2 is passed over the carrier, impregnated with H_2PtCl_6 , at $100\text{--}150^\circ$. Such catalysts are unsuitable for hydrogenation. Typical dehydrogenating catalysts can dehydrogenate at $170\text{--}180^\circ$, that is at a temp. lower than that usually regarded as the optimum for hydrogenation. Conversely, a typical hydrogenating catalyst can convert C_6H_6 into C_6H_{12} to the extent of 30% at 310° . Since dehydrogenating catalysts are obtained at $150\text{--}180^\circ$ and hydrogenating agents at $0\text{--}10^\circ$, the characteristic properties of the former are ascribed to its lower activity. In confirmation, a hydrogenating can be converted into a dehydrogenating catalyst by P, but not by S. Activity in a catalyst is probably associated with a small granule irregularly formed and inactivity with coarse, regularly formed granules. H. W.

Optical asymmetric catalysis at quartz crystals. G. M. SCHWAB, F. ROST, and L. RUDOLPH (*Kolloid-Z.*, 1934, **68**, 157—165).—Ppts. of Ni or Pt on optically active quartz have the power to catalyse preferentially the dehydration or oxidation of one of the optical isomerides of racemic *sec.*-BuOH. A "specificity" of 10% has been observed, the optimal condition being a loose, monat. coating of metal. E. S. H.

Active oxides. LXXIX. Kinetics of dehydration of Kohlschutter's topochemical aluminium hydroxide. G. F. HUTTIG and O. STEFFEL [with O. HNEVKOVSKY] (*Kolloid-Z.*, 1934, **68**, 178—184; cf. this vol., 606).—Dehydration isotherms at 120° , 150° , and 180° show that the loss of H_2O proceeds as a zero order reaction to the composition Al_2O_3 , whilst the dependence of velocity coeff. on temp. is in accordance with Arrhenius' equation. Further dehydration is in accordance with a unimol. reaction. E. S. H.

Active oxides. LXXVII. Dependence of the catalytic activity of different magnesium oxides on their mode of preparation and previous history. B. STEINER and G. F. HUTTIG (*Kolloid-Z.*, 1934, **68**, 253—260; cf. this vol., 850).—The catalytic effect of 18 different preps. of MgO on the reaction $2CO + O_2 \rightarrow 2CO_2$ has been investigated at $240\text{--}495^\circ$ and with different amounts of catalyst. The results show that the catalysts are characterised by the quantity and quality of active centres. MgO prepared from $Mg(OH)_2$ ages slowly, the no. of active centres increasing while the quality decreases; MgO from MgC_2O_4 ages more rapidly with the same result; MgO from basic $MgCO_3$ has a small no. of highly active centres. The sources of MgO fall in the following order with regard to the catalytic activity of MgO at 460° : magnesite, MgC_2O_4 , $Mg(OH)_2$, basic $MgCO_3$, $Mg(NO_3)_2$. E. S. H.

Formation of ammonia at highly dispersed metals. D. P. DOBYTSCHIN and A. V. FROST (*Elektrochem.*, 1934, **40**, 585—587).—Polemical (cf. this vol., 371). E. S. H.

Poisoning of ammonia catalysts by gases containing oxygen. P. V. USSATSCHEV, V. I. TARAKANOVA, and V. A. KOMAROV (*Z. Elektrochem.*, 1934, 40, 647—653).—On poisoning technical NH_3 catalysts by small additions of CO_2 , CO , SO_2 , N_2O , NO , or H_2O to the N_2 - H_2 mixture, the NH_3 concn. in the issuing gas first rose and then fell, due to displacement of adsorbed NH_3 from the catalyst surface. The no. of active centres on the catalyst and the time of contact of NH_3 mols. with the surface are greater at lower temp. The reaction rate is controlled by the rate of NH_3 desorption. H. J. E.

Catalytic interchange of hydrogen between water and ethylene and between water and benzene. J. HORIUTI and M. POLANYI (*Nature*, 1934, 134, 377—378).—After H_2O containing 3 at.-% of H^2 is heated with C_2H_2 or C_6H_6 in a sealed tube in presence of a Ni catalyst, the C_2H_2 and C_6H_6 contain H^2 . L. S. T.

Kinetics and mechanism of the catalytic exchange of chlorine for the amino-group. N. N. VOROSHOV and V. A. KOBELEV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 3, 108—114).—In the reaction between PhCl and aq. NH_3 at 200° with CuCl as a catalyst, the rate $\propto [\text{CuCl}]$ and, over a limited range, $\propto [\text{NH}_3]$. The rate is determined by the formation of the complex $\text{PhCl}\cdot\text{Cu}(\text{NH}_3)_2^+$, which reacts rapidly with NH_3 , OH' , and NH_2Ph . H. J. E.

Passivation and activation of cadmium. T. PIERZCHALSKI (*Rocz. Chem.*, 1934, 14, 295—300).— HCNS , $\text{CS}(\text{NH}_2)_2$, CS_2 , I , and As catalyse the dissolution of Cd in 7*N*- HCl , whilst HCN and $\text{CO}(\text{NH}_2)_2$ are without effect. HCNS exerts a max. action at 0.0025*N* concn., whilst that of the remaining catalysts increases with their concn. R. T.

Contact method of conversion of acetylene into acetone.—See B., 1934, 792.

Catalysis by liquid metals. E. W. R. STEACIE and E. M. ELKIN (*Canad. J. Res.*, 1934, 11, 47—52).—There is no abrupt change in the rate of decomp. of MeOH on a Zn surface when the Zn is melted nor in the order (0—0.5) of the reaction, and it is therefore doubtful whether the catalysis can be ascribed to a limited part of the solid surface. The products of decomp. are mainly H_2 and CO , and the heat of activation is 30,000 g.-cal. A. G.

Influence of certain organic hydroxy-compounds on the oxidation of ferrous hydroxide by dissolved oxygen. W. S. PATTERSON (*J.S.C.I.*, 1934, 53, 298—299T).— EtOH , $[\text{CH}_2\text{OH}]_2$, glycerol, erythritol, and mannitol inhibit the oxidation $\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_3$ by dissolved O_2 . The effect increases for equimolar proportions of inhibitor with increasing % OH in the org. compound. A possible explanation is suggested due to the adsorption of the org. compound in the $\text{Fe}(\text{OH})_2$ gel, which is thus in some measure protected.

Oxidation of glucose by air in presence of iron pyrophosphate. A. GOERNER (*J. Biol. Chem.*, 1934, 105, 705—709).—Bacterial contamination was eliminated by the use of germicides and shown not to be the cause of the oxidation. Glucose solutions containing pyrophosphate (I) or phosphate buffers do not yield

appreciable amounts of CO_2 in absence of Fe . Increasing amounts of (I) do not inhibit the catalytic action of Fe . C. G. A.

Electrolytic concentration of the heavy hydrogen isotope in water. L. TRONSTAD and J. BRUN (*Z. Elektrochem.*, 1934, 40, 556—558).—Contrary to a recent report (this vol., 612) H_2^2O can be conc. by electrolysing H_2SO_4 solutions with Pb electrodes. Failures are attributed to the formation of spongy Pb at the cathode, whereby diffusion of fresh electrolyte is hindered. E. S. H.

Concentration of deuterium by electrolysis of sulphuric acid solutions. T. TITANI, K. KURANO, and M. HARADA (*Bull. Chem. Soc. Japan*, 1934, 9, 269—271).—Commercial H_2SO_4 diluted to 10% with tap H_2O has been electrolysed in fractions using Pb electrodes (10×4 cm.) and 4 amp. d.c. The loss of H^1 and H^2 by electrolysis is expressed by $-dN_1 - (k_1 + k)N_1 dt$, $-dN_2 = (k_2 + k)N_2 dt$, where N_1 and N_2 are the total mols. of H^1 and H^2 , k_1 and k_2 are consts. for the electrolysis proper, and k is a const. for the loss due to evaporation and spray. It follows that the total separation factor α , $(\log N_{10} - \log N_1) / (\log N_{20} - \log N_2)$, where N_{10} and N_{20} refer to the start, is related to the electrolytic separation factor $\alpha_e = k_1/k_2$, according to $\alpha = \alpha_e / [1 - b(\alpha_e - 1)]$, where $b = k/k_1$. The final concn. of H^2 varies from 0.08 to 0.9%, α from 2.2 to 2.7, α_e from 1.50 to 1.58, and b from 0.62 to 0.78. The results are compared with those of other workers, and it is suggested that α may depend on the initial content of H^2 . R. S. B.

Concentration of deuterium by electrolysis of neutral salt solutions. I. T. TITANI, K. OKABE, and M. HARADA (*Bull. Chem. Soc. Japan*, 1934, 9, 272—273).—0.25*M*- Na_2SO_4 has been electrolysed in fractions between a Ni cathode and a Pb anode (10×4 cm.) using 2.5 amp. $\alpha = 1.58$ (cf. preceding abstract), $b = 0.58$, and $\alpha_e = 2.3$; the product contains 0.085% of H^2 . When Na_2SO_4 is replaced by 0.5*M*- NaOH with Ni electrodes and 3 amp., $\alpha = 1.52$, $b = 0.88$, and $\alpha_e = 2.8$; the product contains 0.08% of H^2 . The use of Na_2SO_4 dispenses with neutralisation, and the same electrolyte can be used throughout. R. S. B.

Alkaline storage battery. V. Alkali zincate storage battery.—See B., 1934, 802.

Electrolysis of methyl alcohol solutions of zinc and cadmium chlorides. E. GUILLERMET (*Compt. rend.*, 1934, 199, 191—193; cf. this vol., 154).—Electrolysis of a 5% MeOH solution of ZnCl_2 with a c.d. of 1.3—5 amp. per sq. dm. yields compact deposits adhering well to a Pt cathode. At 3—5 amp. per sq. dm. there is a tendency for trecing at the edges of the cathode. The deposit is almost pure with c.d. 3—5 amp. per sq. dm., with c.d. 1 amp. per sq. dm. during 4 hr. runs, or with acid solutions, but in other cases it is contaminated with oxychloride. The yields reach 95% with a Zn anode, but are less with a Pt anode, decreasing with increasing time of electrolysis, or c.d., and decreasing distance between the electrodes. Use of a diaphragm increases the yield. The Zn anode is attacked uniformly, but there is chemical as well as electrochemical attack. Electro-

lysis of 0.7—0.9% MeOH solutions of CdCl_2 with a c.d. of 0.5—3 amp. per sq. dm. yields, not an adherent deposit, but a black spongy mass. With a Cd anode this deposit contains white particles of an oxychloride containing MeOH, and the same material is formed in suspension in the solution. With a Pt anode the solution becomes acid and the white compound disappears, the deposit turning greyish and cryst. Since the total yields with a Cd anode are 100%, the formation of the white product is attributed to an electrochemical process, probably discharge of CdCl ions. With a Pt anode the yields are < 100%, are increased by use of a diaphragm, and decreased by using an acid solution. There is no chemical, as distinct from electrochemical, attack on a Cd anode. J. W. S.

Electrolytic deposition of iron-nickel alloys.—See B., 1934, 801.

Electrometallurgy of aluminium. P. DROSSBACH (Z. Elektrochem., 1934, 40, 605—608).—Evidence is adduced to show that the primary process in electrolysing molten cryolite is the decomp. of NaF.

E. S. H.

Substitute for platinum as anode material in electrolytic oxidation processes. I. Tungsten anodes. G. ANGEL (Z. Elektrochem., 1934, 40, 641—647).—In the electrolysis of conc. aq. NaClO_3 (with or without addition of aq. $\text{Na}_2\text{Cr}_2\text{O}_7$) with a W or Mo anode, a protective oxide film forms. Electrolysis occurs with > 70 volts applied potential, the anodes being strongly attacked. If a Pt lead is used for the W electrode, practically all of the current is carried by the Pt, NaClO_4 being formed normally, with high current efficiency. The W is unattacked.

H. J. E.

Electrodeposition of rhodium.—See B., 1934, 801.

Kinetics of photosynthesis. R. EMERSON and L. GREEN (Nature, 1934, 134, 289—290).—A crit. discussion (cf. this vol., 497).

L. S. T.

Measurement of doses of very soft X-rays (limit rays). R. JAEGER (Physikal. Z., 1934, 35, 665—682).—Modifications in the method for hard X-rays make it applicable for soft rays. A. J. M.

Limit of the variation of the relation between intensity and velocity of photochemical reactions. W. V. BHAGWAT (J. Indian Chem. Soc., 1934, 11, 443—447).—The velocity of the reaction usually \propto , or else increases less rapidly than, the intensity of illumination. In the few cases where it increases more rapidly, the effect is due to the destruction of inhibitors by the light. Proportionality to the square root of the intensity is more probable with high than with low frequency. D. R. D.

Kinetics of reactions of heavy hydrogen. I. H. W. MELVILLE (J.C.S., 1934, 1243—1250).—The data refer to the Hg-photosensitised reduction by H_2 and 66% H_2 of O_2 , N_2O , and C_2H_4 . At 20°, when H^1 is in excess, the zero order reaction velocities are not affected by isotopic composition, but when O_2 is in excess, the reaction becomes of first order with respect to H and the velocity with H_2 is < with H^1 , owing to a collision frequency factor. A similar effect would

be expected with excess of N_2O and C_2H_4 . Consistent with $\text{H} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{OH}$ (slower) and $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$, there is no isotope effect in the reaction with excess of H_2 at appropriate pressure and 250°, and hence quantum-mechanical leakage of H atoms is negligible. In $2\text{H}_2 : \text{O}_2$ mixtures at 4.6 mm. and 246—421°, chain lengths of about 30 were found and the reaction velocity with H_2 is < with H^1 , but this difference diminishes as the temp. is raised. This is consistent with the initial formation of HO_2 followed by $\text{HO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{OH}$, to the activation of which the different zero-point energies of H_2 and H^1 contribute. In presence of Pd-black and excess of H , the reactions at 20° are of zero order at pressures > sp. limiting vals. Experiments at 20° and 339° show that the quantum yield in the hydrogenation of C_2H_4 is independent of temp. and the H isotope used; hence a chain mechanism is excluded and the second step in the reaction is probably between Et and H . In no case could the difference between the rates of reaction of the two isotopes be attributed to the leakage of atoms through potential barriers.

J. G. A. G.

Initiation of the hydrogen-chlorine reaction by X-rays. S. GOTZKY and P. GUNTHER (Z. physikal. Chem., 1934, B, 26, 373—389).—The relation between reaction velocity and concns. is represented by Bodenstein and Dux's equation (A., 1913, ii, 1039). The reaction chains are initiated by dissociation of Cl_2 and 7.8 g.-cal. of energy of secondary electrons is required for the formation of 1 mol. of HCl . The energy of the secondary electrons is insufficient to cause concurrently chemical excitation and ionisation in the reaction mixture; the act of excitation is causally related to the appearance of ions. Each ion is associated with three or four acts of excitation. The energy of recombination of the ions seems to be of no account for the excitation of the reaction. These results agree with Lind's cluster theory (cf. this vol., 975). Cu surfaces irradiated with X-rays retard the reaction, whilst Ag surfaces have no effect. R. C.

Mercury-photosensitised decomposition of the deuteroammonias. J. C. JUNGERS and H. S. TAYLOR (J. Chem. Physics, 1934, 2, 373—380).—Samples of $\text{N}(\text{H}^1\text{H}^2)_3$ in which H^1 was replaced by H^2 to the extent of 68, 90, and 99%, respectively, have been prepared by treating different samples of Mg_3N_2 with H_2O vapour. These varying compositions showed that stable amido- and imido-compounds had been present in the original Mg_3N_2 . The physical properties of NH_3 (99% H^2) have been determined and contrasted with those of NH_3 (in parentheses): d 1.174 (1); f.p. 199° (193.2°) abs.; b.p. 242.3° (239.75°) abs.; v.p. at 238.6° abs. 628 (714) mm.; latent heat of vaporisation from v.-p. curve 5990 (5797) g.-cal. Substitution of H^2 for H^1 displaces the ultra-violet absorption bands towards shorter wave-lengths. The absorption curves also give an indication of the three possible $\text{N}(\text{H}^2\text{H}^1)_3$ present. The Hg-photosensitised decomp. of NH_3 is > 10 times slower than that of NH_3 by H_2 . It is also inhibited more strongly by H^1 than that of NH_3 by H_2 . There is a qual., but not quant., resemblance in the kinetics of decomp. of NH_3 and NH_3 . The nature of the collisions involved

on decomp. is discussed on the basis of the data on the quenching of Hg resonance radiation by $N(H^2H^1)_3$.

M. S. B.

Influence of water on the photolysis of ozone at λ 280, 254, and 210 m μ . G. S. FORBES and L. J. HEIDT (J. Amer. Chem. Soc., 1934, 56, 1671—1675).—In the photolysis of O_3 at partial pressures 10 mm.—1 atm. in presence of saturated H_2O vapour at 2° and 20°, the quantum yields, ϕ , range from 1.6 to 130, indicating a chain mechanism. ϕ is raised by increase in p_{O_3} , but depressed by increase in total pressure or in p_{H_2O} , and at any given wave-length is inversely proportional to a fixed power of the light intensity: $\phi \propto \sqrt{[H_2O]}$.

E. S. H.

Photochemical reduction of carbon dioxide on surfaces. M. QURESHI and S. S. MUHAMMAD (J. Osmania Univ. Coll., 1933, 1, Reprint; cf. A., 1932, 1006).— CO_2 was bubbled at 25—30° through an irradiated aq. suspension of electrolytic $NiCO_3$, activated by heating at 120—140° or by irradiation. No CH_2O or carbohydrate was formed.

H. J. E.

Formation of silver bromide emulsion for photography. VII—X. M. MIYATA (J. Soc. Chem. Ind. Japan, 1934, 37, 299—303b).—Washing the emulsion results in the removal of adsorbed Br^- and its replacement by Cl^- derived from the H_2O . The sensitivity (I) of an emulsion increases with the $[Cl^-]$ of the wash H_2O up to 0.01N, and it is also increased by the addition of $AgCl$ by other methods. $AgCl$ is more sensitive to light than $AgBr$, and its (I) is increased by a small proportion of $AgBr$ or of AgI , which behave like optical sensitizers. The increase in (I) during digestion is probably due to the nuclei of $AgCl$ increasing in size and approaching the AgI within the grains.

A. G.

So-called photochemical antagonism. M. TRAUTZ and H. E. HAAS (Z. wiss. Phot., 1934, 33, 81—93).—A crit. survey is given of the theories of reactions which are reversible (I), or variable in equilibrium point (II), by exposure to light or to lights of different λ . For (I), the action of infra-red light approximates to the thermal equilibrium, but the behaviour to ultra-violet light depends on the intensity. For (II), particularly when contrasting reactions in the dark and in the light, a difference in mode of reaction (although producing the same end-products) is postulated.

J. L.

Herschel effect. O. BARTELT and H. KLUG (Z. Physik, 1934, 89, 779—785).—This is due to re-formation of Ag ions from Ag atoms of the latent image.

A. B. D. C.

Theory of photographic development. I. Adsorption theory.—See B., 1934, 813.

Theory of photographic development. II. Adsorption of quinol on colloidal silver. A. J. RABINOWITSCH and S. PEISSACHOWITSCH (Z. wiss. Phot., 1934, 33, 94—104; cf. B., 1934, 813).—Mixtures of Ag sols containing gelatin with varying amounts of quinol (I) were analysed by titration with I_2 before and after ultra-filtration. Some of the (I) is adsorbed on the Ag particles, and some is oxidised, the remainder being found in the filtrate. The surface of the Ag particles must be larger than expected from

counting the no., as an average of 5 mols. of (I) are adsorbed per Ag atom.

J. L.

Photodissociation of molecules in the Schumann ultra-violet. A. TEREININ and H. NEUJMIN (Nature, 1934, 134, 255).—In photochemical reactions induced in gases by light in the Schumann region the emission of OH and CN accompanying the photodissociation of more complex mols. has been observed. The observed processes are $h\nu + H_2O \longrightarrow H + OH^*$, $h\nu + MeOH \longrightarrow Me + OH^*$ and $h\nu + MeCN \longrightarrow Me + CN^*$, where OH^* and CN^* are excited radicals emitting the bands at 3062 and 3883 Å., respectively.

L. S. T.

Influence of circularly polarised light on the velocity of mutarotation of some sugars. P. SOUTY (Compt. rend., 1934, 199, 198—199).—Relative to laevorotatory circularly polarised light of the same intensity, dextrorotatory circularly polarised light accelerates mutarotations which lead to increased positive rotations (mannose, maltose, etc.), and retards mutarotations which lead to increasing negative rotations (glucose, lactose, etc.). Certain frequencies are more effective than others, monochromatic illumination of λ 5461 Å., but not 5890—5896 Å., affecting the mutarotation of glucose.

J. W. S.

Photosensitising action of iodine. Isomeric transformation of allocinnamylideneacetic acid into the normal form. I. J. C. GHOSH, D. S. N. MURTHI, and D. N. DAS GUPTA. II. J. C. GHOSH and D. S. N. MURTHI (Z. physikal. Chem., 1934, B, 26, 255—266, 267—271; cf. A., 1931, 180).—I. The velocity coeff. of the transformation in C_6H_6 solution sensitised by I_2 is given by $(1/t) \log_e [A/(4 \times x)]$, where t is the time and A the initial concn. of *allo*-acid multiplied by an empirical const. (1.33). It increases with $[I_2]$, at first rapidly, then more slowly, and \propto the square root of the energy of the radiation absorbed. These results are accounted for by supposing the primary act to be the photo-dissociation of I_2 mols. into atoms, followed by a chain reaction: $I + A \longrightarrow IA$, $IA \longrightarrow I + B$, $I + B \longrightarrow IB$, and $IB + A \longrightarrow I + B + B$ ($A = \text{allo-acid}$, $B = \text{normal acid}$). The activation energy calc. on the assumption that a collision between two I atoms in presence of C_6H_6 mol. always gives I_2 agrees with the val. calc. from the temp. coeff.

II. The kinetics of the transformation in CCl_4 solution can be accounted for by the above mechanism.

R. C.

Induced and photochemical oxidation of sodium tartrate by air and its use in diabetes and prolonged fasting. C. C. PALIT and N. R. DHAR (J. Indian Chem. Soc., 1934, 11, 471—477).—Na tartrate is oxidised directly by air in presence of Na_2SO_3 , $Ce(OH)_2$, $NaOH$, Na_2CO_3 , $NaHCO_3$, and $Fe(OH)_2$, the activity of the catalyst falling in approx. this order. The activity of $Ce(OH)_2$ and $Fe(OH)_2$ is increased by addition of traces of $Cu(OH)_2$ and decreased by larger quantities. The action is accelerated by light. K oleate and Na tartrate mutually retard the oxidation of each other by air. The results suggest that Na tartrate should be of use in the treatment of diabetes and inanition, and that traces of Cu salts should be added to the Fe salts in the treatment of anæmia.

D. R. D.

Products of irradiation of ergosterol with ultra-violet rays. A. V. TRUFANOV (Khim. Farm. Prom., 1933, 253—256).—Irradiation of a 2% solution in C_6H_6 for 4 hr. gave the best results (50% activated).

CH. ABS.

Interchangeability of hydrogen atoms in organic compounds with the hydrogen atoms of water. R. KLAR (Z. physikal. Chem., 1934, B, 26, 335—342).—There is no interchange of H atoms between heavy H_2O and $NaOAc$ or C_6H_6 . With $MeCHO$ there is slow interchange and with CH_2O , $COMe_2$, and CH_3Ac_2 all the H atoms are interchangeable. With $COMe_2$ interchange occurs by way of enolisation; it is very slow in neutral, more rapid in acid, and very rapid in alkaline solution. The quotient of the ratio $H^2:H$ in the org. compound by that in the H_2O is < 1 .

R. C.

Heavy water. H. ERLÉNMEYER and H. GARTNER (Nature, 1934, 134, 327).—By crystallising Na_2SO_4 from H_2O containing 4—5% H_2O , normal and heavy H_2O are divided practically equally in the H_2O of crystallisation and the solution. Within this concentration Et_2O dissolves H_2O and H_2O in equal quantities. When the Et_2O drops are allowed to rise through this solution of heavy H_2O , dissolving mainly H_2O out of the interfaces H_2O-Et_2O , then the interfaces are enriched in H_2O . $[Co(NH_3)_6](NO_3)_3$ but not KH_2PO_4 exchanges its H for H^2 in this solution. L. S. T.

Separation of heavy water from ordinary water. G. BRUNI and M. STRADA (Atti R. Accad. Lincei, 1934, [vi], 19, 453—458).—Methods of separation based on freezing the H_2O and on fractional crystallisation of hydrated salts are discussed. From 1500 litres of H_2O , 21 g. having a H_2O content of 0.37%, corresponding with an enrichment of about 20 times, were obtained after 7 cycles of freezing. Fields of snow which had been repeatedly thawed and re-frozen exhibited a surface layer about 2 cm. thick containing 0.055% of H_2O . Large crystals of carnallite from the Stassfurt and Beienrode deposits yielded on distillation H_2O containing up to 0.0412% of H_2O , compared with 0.027—0.029% for the adjacent mass of crystals.

H. F. G.

Silver difluoride. H. JOCKUSCH (Naturwiss., 1934, 22, 561).—The reaction between powdered Ag and F_2 at room temp. gives rise to yellow AgF_2 , which is rapidly decomposed by H_2O giving Ag_2O and an oxidising solution. The easily decomposable fluorate may be formed (A., 1933, 797). It reacts with $EtOH$ forming $MeCHO$ and $AcOH$, becoming reduced to Ag. It does not react with CCl_4 at 0° , but if dissolved reducing agents, e.g., $EtOH$, $PhMe$, are present, it is reduced to AgF .

A. J. M.

Reaction between hypophosphorous acid and silver nitrate. T. AJELLO (Gazzetta, 1934, 64, 351—359).—Contrary to statements in the lit., equimol. quantities of H_3PO_2 and $AgNO_3$ react without evolution of gas and with only partial oxidation of the former. The AgH_2PO_2 first formed decomposes to yield Ag and H_2PO_2 groups, and the latter react with H_2O to form H_3PO_3 and O ; finally, the O oxidises, although incompletely, the H_3PO_3 to H_3PO_4 and H_3PO_4 .

H. F. G.

Combination of silver and copper with fluorine. O. RUFF and M. GIESE (Z. anorg. Chem., 1934, 219, 143—148).—The compound, AgF_2 , has been prepared by the action of F_2 at $150-200^\circ$ on Ag halide, on mol. Ag prepared by reducing Ag_2O with CH_2O , or on fine Ag gauze. It is dark brown, highly reactive, and strongly paramagnetic; X-ray examination shows it to be rhombic, a 6.24, b 5.480, c 4.86 Å., d calc. for 4 mols. 5.4; d (pyknetric in CCl_4) 4.57—4.78; the dissociation pressure is 1 atm. at $435-450^\circ$. AgF_2 might be used as a fluorinating agent. Its formation explains the catalytic action of Ag salts in the decomp. of gases by F_2 . No fluoride of Cu higher than CuF_2 could be prepared by similar methods. M. S. B.

Preparation and explosion temperatures of some complex cupric chlorates, perchlorates, and nitrates formed with ethylenediamine. J. AMEL (Compt. rend., 1934, 199, 201—203).—By slow treatment of $Cu(ClO_3)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 6H_2O$ with 75% $(CH_2 \cdot NH_2)_2$ (en), the compounds, $Cu(ClO_3)_2 \cdot 2en \cdot H_2O$ (I); $Cu(ClO_3)_2 \cdot 3en \cdot H_2O$ (II); $Cu(ClO_4)_2 \cdot 2en \cdot H_2O$ (III); $Cu(ClO_4)_2 \cdot 3en \cdot H_2O$ (IV); $Cu(NO_3)_2 \cdot 2en$ (V); and $Cu(NO_3)_2 \cdot 3en \cdot H_2O$ (VI) have been obtained. On keeping for 60 hr. in a vac. desiccator at 20° , (II) loses 10% of its en, (IV) is almost unchanged, and (VI) passes almost completely into (V). All are insol. in Et_2O and almost so in $EtOH$. (III) and (IV) are slightly sol. in $COMe_2$. The aq. solutions vary in colour from blue to purple; they are decomposed by acids, and excess of KOH ppts. CuO on prolonged boiling. All explode on heating, generally after melting with decomp. The induction periods before explosion are given as functions of the temp. in graphical form. (I) and (II) explode readily, and (III) and (IV) less readily on striking with a hammer; (II) and (VI) also explode on contact with H_2SO_4 .

J. W. S.

Thermal dehydration or decomposition of certain minerals and salts. A. F. GILL (Canad. J. Res., 1934, 10, 703—712).—By the use of a combined calcining furnace and weighing balance, data have been obtained for the course of the decomp. up to $800-1000^\circ$ of magnesite, hydromagnesite, magnesitic dolomite, dolomite, serpentine, asbestos, $Ca(OH)_2$, $Mg(OH)_2$, gypsum, $MgSO_4 \cdot 7H_2O$, $AlCl_3 \cdot 6H_2O$, pyrites, and coal.

H. S. P.

Technical preparation of calcium silicon alloys. R. WEINER (Z. Elektrochem., 1934, 40, 624—629).—A Ca—Si alloy (approx. 30% Ca) has been prepared by heating CaC_2 , SiO_2 , and C in a 20-kw. electric furnace, using mainly resistance heating. The alloy, as formed, should be removed from the hottest zone, in which it is unstable. A similar product is formed from CaO , SiO_2 , and C.

H. J. E.

Crystals of calcium carbonate. T. NODA (J. Soc. Chem. Ind. Japan, 1934, 37, 319—322B).—When aq. $(NH_4)_2CO_3$ is added to aq. $CaCl_2$ the formation of rhombic as opposed to acicular crystals of $CaCO_3$ is favoured by low temp., low $[NH_3]$, and high concn. of reactants. Below 35° spherulitic crystals appear.

A. G.

Effects of fluorides on thermal synthesis of calcium silicates. S. NAGAI and M. MIYASAKA (

Soc. Chem. Ind. Japan, 1934, **37**, 303—306B).—The addition of CaF_2 to mixtures of CaCO_3 or CaO with SiO_2 lowers the temp. of combination by about 200° , and diminishes the proportion of CaO in the silicate when heating is prolonged. A. G.

Effects of fluorides on the thermal synthesis of calcium silicates. II. S. NAGAI and M. MIYASAKA (J. Soc. Chem. Ind. Japan, 1934, **37**, 419—421B).—The presence of increasing amounts of CaF_2 increases the rate of the reaction $2\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2$ at 1200° ; at 1300° the conversion produces some $3\text{CaO} \cdot \text{SiO}_2$. Part of the CaF_2 is removed by evaporation during the reaction. T. W. P.

Disperse structure of the real crystal system, and the temperature of the beginning of grey glow. D. BALAREV and N. KARABASCHEV (Kolloid. Z., 1934, **68**, 261—266).—The temp. at which the grey glow appears on heating BaSO_4 is lowered by the presence of impurities in the crystals. The result is attributed to the liberation of free energy from the inhomogeneous crystal structure. E. S. H.

Action of mercuric oxide on ferric chloride solutions. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 814—815).—By agitating HgO with aq. FeCl_3 , HgCl_2 and $\text{Fe}(\text{OH})_3$ are formed, the last being soluble in excess of FeCl_3 . With increase of HgO , HgCl_2 is deposited, and finally Hg oxychlorides appear. J. G. A. G.

Hydrated phosphates and arsenates of trivalent elements. I. Hydrates of boron phosphates and arsenates. E. GRUNER (Z. anorg. Chem., 1934, **219**, 181—191).—X-Ray examination shows that sol. BPO_4 and the insol. form obtained by heating this at 1000° are identical. By isothermal dehydration at 20° hydrates with 6, 5, 4, and $3\text{H}_2\text{O}$ have been shown to exist. The only hydrates of BAsO_4 indicated by isobaric decomp. at 11 mm. are $\text{BAsO}_4 \cdot 6\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$. No ammoniates have been obtained, but the compounds $\text{BPO}_4 \cdot 3\text{H}_2\text{O} \cdot \text{NH}_3$ and $\text{BAsO}_4 \cdot 3\text{H}_2\text{O} \cdot \text{NH}_3$, prepared by extracting any of the hydrates with liquid NH_3 , appear to be acid salt complexes of phospho- and arseno-boric acid, $\text{H}_2[\text{BPO}_3(\text{OH})_4]$ and $\text{H}_2[\text{BASO}_3(\text{OH})_4]$. The higher hydrates appear to be hydrates of these acids. Potentiometric titration indicates that, in aq. solution, a mixture of H_3BO_3 and H_3PO_4 or H_3AsO_4 is obtained. M. S. B.

Boric acid and alkali borates. VI. Nature and thermal decomposition of ammonium perborate. W. KRETZSCHMAR. VII. Constitution of perborates and polyborates. H. MENZEL (Z. anorg. Chem., 1934, **219**, 17—34, 35—41).—VI. $\text{NH}_4\text{BO}_3 \cdot 0.5\text{H}_2\text{O}$, dried in the air, can be kept unchanged in a closed vessel at room temp. for a considerable time. Long exposure causes a very gradual loss of NH_3 and active O, and a slight increase of H_2O . By drying in vac. the anhyd. salt is obtained without decomp. X-Ray analysis of the two compounds shows that there are definite differences of crystal structure which indicate that they are separate chemical individuals. The constitutional formula of NH_4BO_3 is discussed. NH_4BO_3 is decomposed by heat, and the proportions of the products at different

temp. between 120° and 250° have been determined. The chief products are NH_3 , N_2 , O_2 , and (above 150°) N_2O . The character of the decomp. process is discussed and, in connexion with it, the thermal decomp. of NH_4NO_3 , regarded as an intermediate product, has been investigated.

VII. There is no reason to regard $\text{NH}_4\text{BO}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{KBO}_3 \cdot 0.5\text{H}_2\text{O}$ as fundamentally different from $\text{NaBO}_3 \cdot 0.5\text{H}_2\text{O}$ and $\text{LiBO}_3 \cdot 0.5\text{H}_2\text{O}$. They are all substitution products of H_2O_2 . Different structural formulæ, put forward for the polyborates, are discussed. M. S. B.

Change of true specific gravity of kaolin by heating. T. NAKAI and Y. FUKAMI (J. Soc. Chem. Ind. Japan, 1934, **37**, 430—432B).—The changes in d of two samples of kaolin on heating to increasingly higher temp. were measured by Yoshida's method. Over the ranges, room temp. to 400° , and 1200 — 1500° , the samples differed through small differences in impurities. In both the d fell sharply over the range 400 — 600° , corresponding with the conversion kaolinite $\rightarrow \text{Al}_2\text{O}_{3(\text{amorph.})} + \text{SiO}_{2(\text{amorph.})} + \text{H}_2\text{O}$, but rose from 600° to 1200° . The conversion $\text{Al}_2\text{O}_{3(\text{amorph.})} \rightarrow \gamma\text{-Al}_2\text{O}_3$ between 900° and 1000° , and the reaction $3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite) between 1100° and 1200° , cause changes of slope in d -temp. curve. T. W. P.

Compounds of gallium and indium. IX. Density of solid indium halides. W. KLEMM and F. DIERKS. X. Chalcogenides of gallium and indium [and thallium]. W. KLEMM and H. U. VON VOGEL (Z. anorg. Chem., 1934, **219**, 42—45, 45—64).—IX. Earlier vals. of d for InX_3 ($\text{X} = \text{Br}$ or I), InCl_3 , and InI have been confirmed and vals. for InX_2 and InX are also given. Space increments of In^{3+} , In^{2+} , and In^+ in the different halides are compared with the theoretical vals. The agreement is better for the first two than for the last.

X. The existence and methods of prep. of the oxides and sulphides of Ga and In already recorded have been confirmed. By the thermal analysis of the systems Ga-Te and In-Te the existence of the following tellurides is demonstrated: GaTe , m.p. $824 \pm 2^\circ$, black, soft, friable leaflets; Ga_2Te_3 , m.p. $790 \pm 2^\circ$, hard, brittle, and black; InTe , m.p. $696 \pm 2^\circ$, silver-grey fused mass when hot, steel-blue when cold; In_2Te_3 , m.p. $667 \pm 2^\circ$, hard, brittle, and black. The following selenides have been prepared by synthesis: Ga_2Se , black; GaSe , m.p. $960 \pm 10^\circ$, dark reddish-brown leaflets; Ga_2Se_3 , m.p. probably $> 1020 \pm 10^\circ$, black, hard, and brittle, red on grinding; In_2Se , black and soft; InSe , m.p. $660 \pm 10^\circ$, black and friable, In_2Se_3 , m.p. $890 \pm 10^\circ$, black and rather soft. d , magnetic susceptibilities, and m.p. of many of the compounds of Ga, In, and Tl are recorded. Gradations of colour and other properties are discussed. Ionic vols. have also been compared. M. S. B.

Change of form of graphite crystals on burning. N. BACH and I. LEVITIN (Kolloid-Z., 1934, **68**, 152—157).—The appearance of etch-like figures on the surface of graphite when heated in CO_2 is described. Addition of HCl to the atm. transforms the rounded figures into hexagonal. The reaction with CO_2 at 1000° is catalysed by the ash components of the graphite

or by adding K. In pure C, only the unsaturated outer atoms in the hexagonal basal planes are able to react.

E. S. H.

Reduction of graphite oxide by hydrogen sulphide. U. HOFMANN and A. FRENZEL (*Kolloid-Z.*, 1934, 68, 149—151).— H_2S penetrates between the layers of C atoms and substitutes S for O. The product decomposes rapidly with separation of S.

E. S. H.

Primary processes in the oxidation of graphite. L. MEYER (*Z. Elektrochem.*, 1934, 40, 640—641).—Polemical against Sihvonon (cf. this vol., 978).

H. J. E.

Morphology and mode of reaction of natural organic growths. (Topochemical reactions.) K. HESS and C. TROGUS (*Kolloid-Z.*, 1934, 68, 168—175).—Published work on the chemical, X-ray, and microscopical examination of the reaction of ramie threads with various reagents is discussed from the topochemical viewpoint.

E. S. H.

Mineral colours. J. HOFFMANN (*Z. anorg. Chem.*, 1934, 219, 197—202).—The natural quartz colours are ascribed to the presence of silicates, e.g., $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$, grey, and $\text{Na}_2\text{O} \cdot \text{SiO}_2$, amethyst. CO_2 and CO from Na_2CO_3 may also give a grey colour. Citrine colouring is probably due to $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3$. The coloration of rock-salt is attributed to the formation of various NaCl complexes through the action of light.

M. S. B.

Corrosion figures on glass. J. HERBERT (*Compt. rend.*, 1934, 199, 369—371).—The resemblance of the corrosion figures obtained by etching glass with HF to the silicofluorides of Na and Ca is very marked. Figures having the form of crystals of CaSiF_6 have been obtained by depositing crystals of this salt on glass not containing Ca, and etching the glass with HF. Chemical composition of the glass has a great effect on the form of the figures, as has also the concn. of the corrosive liquid. The rapidity with which the molten glass has been cooled is without effect on the form of the figures.

A. J. M.

Preparation of cerium and its alloys. A. KARL (*Bull. Soc. chim.*, 1934, [v], 1, 871—877).—Anhyd. CeCl_3 has been prepared (1) by heating the hydrous chloride (I) in a current of dry HCl (traces of oxychloride remain), (2) by passing COCl_2 at 350—400° over (I) previously heated until dry, (3) by passing HCl over dry $\text{Ce}_2(\text{CO}_3)_3$ at 450°, and (4) by dehydrating (I) mixed with CaCl_2 , the final stage being in an atm. of HCl. Ce is not obtained by heating CeO_2 with CSi, but a reactive Ce—Mg alloy is obtained with Mg. About 85% of the calc. yield of 97% Ce is obtained by lowering 70 g. of Ca into a molten mixture of 1 part by wt. of CeCl_3 with 2.5 parts of CaCl_2 in a vertical Fe tube. Fe added to the melt yields an Fe—Ce alloy. CeF_3 and Ca do not afford Ce; Al does not react with CeCl_3 , but Mg forms a Ce—Mg alloy.

J. G. A. G.

Synthesis of ammonia under very high pressures above 1000 kg. per sq. cm. J. BASSET (*Compt. rend.*, 1934, 199, 205—208).—The reaction of a $\text{N}_2 + 3\text{H}_2$ mixture has been studied at pressures of 1000—4500 kg. per sq. cm. and at 0—1000°.

Above 2000 kg. per sq. cm. the reaction occurs irrespective of the material of the container, and the velocity of the reaction is so increased that the presence of a special catalyst is no longer required. At const. partial pressure the formation of NH_3 is independent of the presence of impurity. The optimum temp. is 800—1000°. Under the experimental conditions used, the production capacity is 10 g. per hr. per c.c. of space at 850° and 4500 kg. per sq. cm., only 2—3% of the gases not combining.

J. W. S.

Hydrolytic fission of amines. W. J. HICKINBOTTOM (*J. Amer. Chem. Soc.*, 1934, 56, 1820—1821).—The induced polarity theory of Lapworth and Robinson is applied to reactions of this type.

E. S. H.

Reactions between nitrogen compounds and phenols. II. Solubility product and complex formation. R. LABES and T. BREITENSTEIN (*Arch. exp. Path. Pharm.*, 1934, 175, 372—395; cf. this vol., 446).—The combination between a phenol (I) and a N compound (II) is mainly governed by the affinity between the acidic phenolic OH and a suitable basic N. (II) which are strong bases readily forming cations in aq. solution, take up H^+ and consequently do not unite readily with (I); similarly the influence of a proximate $\text{CO} \cdot \text{NH} \cdot \text{CO}$ group (e.g., veronal and luminal) or of a free NH_2 (e.g., NH_2Ph) decreases the affinity. Many heterocyclic (II) (e.g., $\text{C}_5\text{H}_5\text{N}$, quinoline, antipyrine, pyrimidine, caffeine, alkaloids) are very active. Combination is influenced by the no. and hydrophobic character of lipophilic groups which produce a high Langmuir residual affinity and thereby form complexes at low concns. of the components. The solubility of the complexes formed partly depends on the degree of dissociation of groups not participating in the combination. The bearing of the data obtained on the pharmacological action of drugs is discussed.

F. O. H.

Oxygen isotope separation by chemical reaction. H. S. TAYLOR and A. J. GOULD (*J. Amer. Chem. Soc.*, 1934, 56, 1823).—Fractional thermal decomp. of PbO_2 does not cause any appreciable separation of O^{16} and O^{18} , but by treating 30% H_2O_2 at room temp. with colloidal Pt the first fractions of O_2 collected are enriched in O^{16} .

E. S. H.

Action of hydrochloric acid on sulphates and alums. N. D. COSTEANU and A. S. COCOȘINSCHI (*Bull. Acad. Sci. Roumaine*, 1934, 16, 122—130).— Na_2SO_4 and K_2SO_4 when evaporated with HCl and dried at 200—210° increase in wt. to an extent which does not alter on repetition of the treatment, the product being, probably, $3\text{M}_2\text{SO}_4 \cdot 2\text{HCl}$. With K and NH_4 alums the increase of wt. increases with each repetition of the evaporation.

H. F. G.

Polythionates. IV. Function of arsenic compounds in the formation of polythionates from thiosulphates and acids. C. J. HANSEN (*Ber.*, 1934, 67, [B], 1418—1420).—Mainly a reply to Kurt-nacker *et al.* (this vol., 160).

W.

Formation of sulphuric acid and hydrogen sulphide by the decomposition of sodium thiosulphate. P. W. SCHENK (*Z. anorg. Chem.*, 1934, 219, 87—88).—The views put forward by Foerster and

M. S. B.

C. G. A.

M. S. B.

J. G. A. G.

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J. G. A. G.

Influence of substituents in bases and anions on the co-ordination index of a metal. V. Additive products of pyridine with the nickel salts of substituted acetic acids. A. ABLOV (Bull. Soc. chim., 1934, [v], 1, 731—738).—The following compounds are described: $\text{Ni}(\text{OAc})_2 \cdot 2\text{C}_5\text{H}_5\text{-N} \cdot 2\text{H}_2\text{O}$; $\text{Ni}(\text{OAc})_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 0.5\text{H}_2\text{O}$;

$\text{Ni}(\text{CH}_2\text{Ph}\cdot\text{CO}_2)_2, 2\text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$;
 $\text{Ni}[\text{CHPh}(\text{OH})\cdot\text{CO}_2]_2, 2\text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$;
 $\text{Ni}[\text{CPh}_2(\text{OH})\cdot\text{CO}_2]_2, 2\text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$;
 $\text{Ni}(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2, 6\text{H}_2\text{O}$; $\text{Ni}(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2, 3\text{C}_5\text{H}_5\text{N}, 2\text{H}_2\text{O}$;
 $\text{Ni}(\text{CHCl}_2\cdot\text{CO}_2)_2, 4\text{C}_5\text{H}_5\text{N}$; $\text{Ni}(\text{CCl}_3\cdot\text{CO}_2)_2, 4\text{C}_5\text{H}_5\text{N}$;
 $\text{Ni}(\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2)_2, 4\text{C}_5\text{H}_5\text{N}, \text{H}_2\text{O}$;
 $\text{Ni}(2\text{-C}_{10}\text{H}_7\cdot\text{SO}_3)_2, 3\text{C}_5\text{H}_5\text{N}, 3\text{H}_2\text{O}$. The existence of several salts recorded in the lit. was not confirmed. There is a parallelism between the strength of the acid and the no. of mols. of base co-ordinated, and in the comparison with the corresponding Cu salts (cf. this vol., 13) the effect of the sp. affinity of Cu for $\cdot\text{CN}$ is emphasised. The results are interpreted in terms of a sp. affinity of the acid residue (I) for the metal arising from a polarisation of the cation by (I). The term "index of co-ordination" loses its precise significance in so far as it is not always possible to distinguish whether the anion is in the interior or exterior zone of the central cation. J. G. A. G.

Amphoteric hydroxides as isopoly-bases. K. JAHR (Przemysł Chem., 1934, 18, 127—129).—A lecture. R. T.

Significance of isopoly-acids in the formation and structure of isopoly-compounds. Hydrolysis and aggregation of isopoly-bases. G. JANDER (Przemysł Chem., 1934, 18, 125—126, 126—127).—Lectures. R. T.

X-Ray method of chemical analysis. E. WAINER (J. Amer. Chem. Soc., 1934, 56, 1653—1657).—A crit. study of procedure and the variables involved. The log time-density is a more suitable function for defining the plate characteristic for X-ray exposure than the usual log intensity-density. E. S. H.

Determination by extraction methods. P. BALAVOINE (Mitt. Lebensm. Hyg., 1934, 25, 82—86).—Errors and their elimination are discussed. Woy's formula is modified mathematically, the wt. of substance sought which is removed from x g. of sample being $4b-a$; thus, $2x$ and x g. of sample are well mixed separately with the same sufficient vol. of solvent, the residues after evaporation of half of the supernatant liquid being weighed (a and b , respectively). An application to fat in chocolate is described. J. G.

Calculation of the results of conductometric titrations. J. MIKA (Z. anal. Chem., 1934, 98, 3—12).—Mathematical expressions are given by the use of which more accurate results can be obtained than by the graphical method. A. R. P.

Measurement of hydrogen-ion concentration. I. SORAGTO (Ind. Sacc. Ital., 1933, 26, 511—517).—The Hellige comparator method is suitable for colourless and slightly coloured solutions where an accuracy of 0.2—0.3 p_H suffices; for darker solutions, and where higher accuracy is required, the potentiometric method must be used. Sb rods cooled slowly after casting are more suitable than plates obtained by the electrolysis of the chloride in COMe_2 solution. J. P. O.

Improvement of Mohr's titration by changing the form of the silver chloride precipitate. A. LOTTERMOSER and W. LORENZ (Kolloid-Z., 1934, 68, 201—203).—Addition of 5—10 c.c. of 0.1% agar solu-

tion to the titrated liquid prevents the formation of large clots of AgCl in conc. Cl' solutions. E. S. H.

Determination of free iodine. P. LISBOA E COSTA (Bol. assoc. brasil. pharm., 1934, 15, 57—65).—5% aq. PhOH is added and the HI formed is titrated with 0.1N- $\text{Na}_2\text{B}_4\text{O}_7$. CH. ABS.

Determination of small quantities of fluorides in water.—See B., 1934, 782.

Determination of sulphate in waters and mineral waters. O. HACKL (Z. anal. Chem., 1934, 98, 1—3).—Removal of SiO_2 by evaporation is unnecessary before pptn. of the SO_4^{2-} with BaCl_2 . A. R. P.

Automatic detection and control of hydrogen sulphide.—See B., 1934, 755.

Potentiometric determination of selenocyanate in presence of thiocyanate. P. SPACU (Z. anal. Chem., 1934, 98, 26—31).—In neutral solution using a Ag-wire indicator electrode KCNSe and KCNS can be determined successively by titration with AgNO_3 , but a small positive error is always obtained for KCNSe and a corresponding negative error for KCNS . A. R. P.

Devarda's method. E. CATTELAINE (J. Pharm. Chim., 1934, [viii], 20, 118—121).—Details are given for the exact determination of NO_3' as NH_3 by Devarda's method. C. G. A.

Iodometric determination of nitric oxide by Mayrhofer's method.—See B., 1934, 798.

Gasometric micro-determination of phosphoric acid. E. KIRK (J. Biol. Chem., 1934, 106, 191—201).— H_3PO_4 (0.005—0.02 mg. of P) is determined (within $\pm 0.5\%$ for > 0.01 mg. of P) by a modified pptn. as strychnine phosphomolybdate, purification by washing, dissolution in COMe_2 , and evaporation, and gasometric determination of C in the residue by Van Slyke's wet combustion method. R. S. C.

Production of arsenic mirrors in Marsh's apparatus and the determination of small amounts of arsenic. J. GANGL and J. V. SÁNCHEZ (Z. anal. Chem., 1934, 98, 81—96).—The wide mirror-deposition tubes used in the standard apparatus may lead to loss of As. In a new apparatus the metal is deposited in a spiral capillary of quartz; it is dissolved out with a solution of ICl and the liberated I titrated with HCN and KIO_3 (cf. Kubina, A., 1929, 163). D. R. D.

Electrolytic conductivity method for determining carbon dioxide dissolved in water.—See B., 1934, 767.

Continuous determination and recording of the carbon dioxide content of gas mixtures.—See B., 1934, 798.

Potentiometric determination of cyanate. R. RIPAN-TILICI (Z. anal. Chem., 1934, 98, 23—26).—The solution is titrated very slowly at 0° with 0.1% AgNO_3 using a Ag-wire indicator electrode and applying a correction factor for the solubility of AgCNO . A. R. P.

Purification and physical properties of organic compounds. Specific heat of solids just below the m.p. as a criterion of purity. E. L. SKAU (J. Chim. phys., 1934, 31, 366—382).—Theoretical. The sp. heats of mixtures of C_6H_6 with small amounts of $C_{10}H_8$ are calc. The vals. increase rapidly near the m.p., whereas the sp. heat of pure C_6H_6 shows little variation until the m.p. is attained. Traces of impurity can be detected in this way, but a eutectic mixture would show the same behaviour as a pure solid.

R. S.

Determination of potassium as perchlorate. J. D'ANS [with T. KANAKOWSKY] (Angew. Chem., 1934, 47, 583—586).—The sample is dissolved in dil. HCl and treated at 20° with conc. aq. $NaClO_4$ nearly saturated (at 20°) with $KClO_4$. The cryst. ppt. is washed with 1% $HClO_4$ in EtOH followed by EtOH, dried, and weighed. A small correction factor for the amount of $KClO_4$ sol. in the final mixture is applied. The maintenance of a const. temp. is important. $NaCl$, Na_2SO_4 , $MgCl_2$, or $MgSO_4$ does not interfere; hence the method is applicable to kainite etc. When NH_4 salts are present the sample is treated with aq. NaOH or, alternatively, NH_4ClO_4 is quantitatively removed from the ppt. by heating at 380—450° for 20—30 min. A rough technique suitable for mines is described.

F. O. H.

Separation of barium from calcium by the sulphate method. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anal. Chem., 1934, 98, 12—22).— $BaSO_4$ can be pptd. free from $CaSO_4$ from solutions of the two chlorides containing 2—5 c.c. of N -HCl in 200 c.c. by slow addition of 0.2*N*- H_2SO_4 at room temp. with vigorous stirring; the ppt. should be filtered next day, washed with hot 1% H_2SO_4 , then with H_2O , and ignited apart from the paper.

P

Determination of magnesium in aluminium and duralumin.—See B., 1934, 800.

Determination of zinc in presence of uranium. W. R. WIGGINS and C. E. WOOD (J.S.C.I., 1934, 53, 254r).—Two methods for the determination of Zn, viz., pptn. of Zn-8-hydroxyquinoline in alkaline tartrate or in alkaline malate solution, were compared. In each case the ppt. was brominated to the 5:7- Br_2 -derivative volumetrically, and close agreement between experimental and theoretical vals. obtained.

[Electrolytic] determination of zinc.—See B., 1934, 764.

Application of quantitative spectrographic analysis to metallurgical problems.—See B., 1934, 764.

Determination of copper with [ammoniacal] potassium cyanide solution. HARBAUER and GEORGI (Chem.-Ztg., 1934, 58, 712—713).—In the titration of Cu^{++} with KCN results are low unless at least 5 g. of NH_4 salt are present in 150—200 c.c. of the solution. A large excess of free NH_3 must be avoided and the KCN solution standardised on a known Cu solution. It will then remain unaltered for some weeks if kept in a cool, dark place. Metals which form CN complexes or insol. metal salts must

be absent. With care as to these points the method is almost equal to the electrolytic one for accuracy.

C. I.

Mercurimetry and its applications in chemical and biochemical analyses. A. IONESCO-MATIU (Bull. Soc. Chim. biol., 1934, 16, 970—992).—A lecture.

Volumetric determination of mercuric and mercurous iodides. D. KOSZEGI and N. TOMORI (Pharm. Zentr., 1934, 75, 532—535).—1—1.3 g. are boiled with 10 c.c. of 2*N*-KOH and 3 c.c. of 40% aq. CH_2O ; the mixture is cooled, diluted to 200 c.c., and filtered. In the approved method, 10 c.c. of filtrate (I) are acidified with AcOH, treated with 30 c.c. of $Cl-H_2O$, boiled for 20 min., and the resulting KIO_3 is determined by titration with 0.1*N*- $Na_2S_2O_3$ after adding 0.5 g. of KI and excess of HCl. Alternatively, the I⁺ in (I) may be determined titrimetrically with $AgNO_3$ or $KBrO_3$ solutions.

S. C.

Electrometric titration of manganese according to Volhard. E. I. ACHUMOV and B. B. VASILIEV (Zavod. Lab., 1934, 3, 407—409).—Minor modifications of Brann and Clapp's method (A., 1929, 286) are proposed.

R. T.

Determination of the "true" and apparent manganese dioxide content of pyrolusite. H. DITZ (Z. anorg. Chem., 1934, 219, 113—118).—The methods proposed for the determination of the different stages of oxidation of Mn in pyrolusite, and the influence on the result of the amount and nature of the oxides of Fe present, are discussed.

M. S. B.

Vogel's thiocyanate test for cobalt in presence of iron. H. DITZ and R. HELLEBRAND (Z. anorg. Chem., 1934, 219, 97—104).—By substituting $COMe_2$ for $C_5H_{11}OH-Et_2O$ mixtures in Vogel's reaction the test for Co becomes much more sensitive, but the sensitivity in presence of a little Fe is much < for Co alone, independently of the method used for the preliminary separation of Fe.

M. S. B.

Rapid determination of small amounts of tungsten in ores etc.—See B., 1934, 800.

Measurement of strong polonium preparations. G. ORTNER and G. STETTER (Physikal. Z., 1934, 35, 563—564).—The method uses an ionisation chamber filled with pure N_2 .

A. J. M.

Volumetric determination of titanium. E. TSCHIECH (Pharm. Zentr., 1934, 75, 513—515).—The solution containing $Ti(SO_4)_2$ and H_2SO_4 is run through a Jones reductor into aq. $Fe_2(SO_4)_3$, and the Fe^{II} produced titrated with aq. $KMnO_4$. Fe in the Ti is determined by reducing a separate portion with $NaHSO_3$ or $SnCl_2$ and titrating back, and its equiv. is deducted from the Ti found.

A. G.

Determination of bismuth in copper.—See B., 1934, 764.

Determination of niobium and tantalum in wolframite. J. A. TSCHERNICHOV and (MISS) M. P. KARSAJEVSKAJA (Z. anal. Chem., 1934, 98, 97—107).—The usual method of removing W by aq. NH_3 is not satisfactory, since appreciable amounts of W are found with the earth acids. In the new procedure, heavy metals are removed by successively digesting the mineral with HCl, aqua regia, and aq. $NH_3-NH_4NO_3$,

then evaporating the residue with H_2SO_4 and HF , followed by treatment with aq. NH_3 and washing with NH_4NO_3 ; it is then fused with $\text{K}_2\text{S}_2\text{O}_7$, and extracted with tartaric acid. The solution is pptd. with H_2S and then with cupferron. This ppt. is fused with Na_2CO_3 , W extracted with H_2O , and the residue fused with $\text{K}_2\text{S}_2\text{O}_7$. It is then treated by the method of Schoeller (A., 1929, 1160; 1932, 356). D. R. D.

Construction of thermostats and cryostats. A. LALANDE (J. Chim. phys., 1934, 31, 439—457).—The principles which should govern the construction and regulation of baths of const. high or low temp. are discussed. M. S. B.

Automatic cryostat. A. I. SCHATTENSTEIN (Z. Elektrochem., 1934, 40, 653—655; cf. A., 1930, 1394).—A 2.5-litre Dewar vessel containing EtOH , fitted with stirrer and thermo-regulator (I), is cooled by a thick Cu strip, one end of which is in a large insulated vessel containing solid CO_2 . An electric heating coil operates in conjunction with (I). A temp. const. to 0.005° is attained down to -70° . H. J. E.

Micro-burner. W. STAHL (Chem.-Ztg., 1934, 58, 682). E. S. H.

Kerr effect, and light distribution with the Kerr cell. A. NARATH (Kinotech., 1933, 15, 395—399).—Theoretical deductions are supported by experiment. The Kerr const. for PhNO_2 (546.1 $\text{m}\mu$; 20°) is 3.61×10^{-5} . CH. ABS.

Technique of measurement of radiation by the rectifying layer selenium cell. R. SEWIG (Physikal. Z., 1934, 35, 564—565).—The use of rectifying layer Se cells for meteorological investigations is discussed (cf. this vol., 272). A. J. M.

Technique of measurement of radiation by the rectifying layer selenium cell. W. GRUNDMANN and L. KASSNER (Physikal. Z., 1934, 35, 566—567; cf. preceding abstract).—Reasons for the unsuitability of these cells for meteorological work are given. A. J. M.

Metal contact photo-electric cell. P. SELENYI (Physica, 1934, 1, 781—782).—A question of priority (cf. de Boer and van Geel, this vol., 624). H. S. P.

Optical factors in caesium-silver oxide photo-electric cells. H. E. IVES and A. R. OLPIN (J. Opt. Soc. Amer., 1934, 24, 198—205).—The emissive power is greater at the red end of the spectrum. The photo-electric emission behaves as though it originates in a thin surface layer. C. W. G.

Valve action and photo-effect of the silicon carbide detector. P. SPECHT (Z. Physik, 1934, 90, 145—165).—The barrier layer effect which appears only with small currents has a large valve action, whilst the vol. effect is small. The photo-effect, which shows saturation with increasing light intensity, is a max. at points of max. valve action. A. B. D. C.

Design and construction of photo-electric cells. R. V. JONES (J. Sci. Instr., 1934, 11, 247—257).—The principles of design are discussed, and the construction of a simplified form is described. C. W. G.

Quantitative photographic photometry. W. H. E. BANDERMANN (Z. Physik, 1934, 90, 266—278). A. B. D. C.

Reflectivity of intermetallic systems. J. WULFF (J. Opt. Soc. Amer., 1934, 24, 223—226).—Measurements on a no. of Mg systems are recorded. C. W. G.

Source of ultra-violet continuous radiation. O. S. DUFFENDACK and J. H. MANLEY (J. Opt. Soc. Amer., 1934, 24, 222).—A low-voltage arc in H_2 is satisfactory. C. W. G.

Determination of the dielectric constant of dilute aqueous solutions by means of high-frequency oscillations. F. P. HENNIGER (Ann. Physik, 1934, [v], 20, 413—440).—The dielectric const. (ϵ) of aq. solutions of CuSO_4 , $\text{La}(\text{NO}_3)_3$, and $\text{K}_4\text{Fe}(\text{CN})_6$ has been determined at 20° by means of a resonance method for a range of concns. The electrolyte solution is compared with aq. KCl of equal conductivity. The frequency, 2×10^{-7} ($\lambda = 15.02 \pm 0.02 \text{ m.}$), falls in the region of greatest variation of ϵ with λ . Results are in good agreement with the theory of Debye and Falkenhagen. R. S. B.

Mass spectrograph. J. MATTAUCH and R. HERZOG (Z. Physik, 1934, 89, 786—795). A. B. D. C.

Investigation of ionisation chambers and production of rays of given range. G. DIECK (Z. Physik, 1934, 90, 71—111). A. B. D. C.

Crystal detectors. J. N. FRERS (Z. Elektrochem., 1934, 40, 612—624).—Current-voltage characteristics were studied for the systems $\text{Pt}|\text{CuBr}$; $\text{Pt}|\text{Ag}_2\text{S}$; $\text{Pt}|\text{Cu}_2\text{S}$; $\text{Pt}|\text{PbS}$; $\text{Pt}|\text{MoS}_2$; $\text{Pt}|\text{FeS}_2$; $\text{Pt}|\text{ZnO}$; $\text{FeS}_2|\text{PbS}$; $\text{ZnO}|\text{PbS}$; $\text{ZnO}|\text{FeS}_2$, the detector being heated, if necessary, to secure conduction. The mechanism of crystal detector action is discussed. H. J. E.

Apparatus for exact dosage of volatile liquids in gaseous form. O. EICHLER (Arch. exp. Path. Pharm., 1934, 175, 399—400).—The liquid (e.g., CHCl_3) is heated in an apparatus whereby the source of heat is controlled by the v.p. of the volatilised fluid. The vapour escapes through a capillary tube of known dimensions and mixes with air in calculable amounts. F. O. H.

Oxidation of sulphurous acid. I. Dilatometric technique. R. C. HOATHER and C. F. GOODEVE (Trans. Faraday Soc., 1934, 30, 626—629).—A dilatometric apparatus is described for following the reaction $\text{SO}_2(\text{aq.}) + 0.5\text{O}_2(\text{aq.}) = \text{SO}_3(\text{aq.})$ by observing the diminution in vol. R. S. B.

Efficiency of laboratory condensers. J. FRIEDRICH and H. VON KRUSKA (Chem. Fabr., 1934, 7, 284—287).—Details are given of the cooling surfaces, heat transfer coeffs., k , and limiting rates of condensation of Et_2O vapour of a no. of different types of laboratory condenser (I). The West (I) has the highest k (0.85) of those studied, and although large sizes are not practicable it is excellent for fractionations. The Dimroth (I) ($k=0.75$) may be made with a very large surface, but fractions easily mix, it is recommended for extraction. Other vals. of

arc: spiral 0.62, Allihn 0.56, Mach 0.55, Liebig 0.47.
H. F. G.

Use of mica in place of platinum wire in analytical work. V. I. PODGORBUNSKI and I. F. SCHITSCHPETUNIN (Sovetsk. Zolotoprom., 1933, No. 3—4, 20—22).—Muscovite and phlogopite micas are satisfactory.
CH. ABS.

Vapour density determinations by an optical method. M. WEISS (Ann. Physik, 1934, [v], 20, 557—568).—A method of determining v.d. of gases and vapours to within 0.1% is based on the fact that the mol. refractivity of a gas is independent of pressure, within wide limits. It has been used to determine the v.d. of air, CO₂, Et₂O, EtCl, and EtNO₂ at 20° and 100°. The mol. refractions and polarisabilities of these substances and C₆H₆ were also determined.
A. J. M.

Sensitive float method for the determination of small changes in the density of liquids, particularly water. H. MOSER (Physikal. Z., 1934, 35, 682—683).—A trustworthy and comparatively rapid method for determining changes in d , accurate to $\pm 6 \times 10^{-7}$, is described. The method requires 140 c.c. of the liquid, and has been chiefly used in the examination of the isotopic constitution of H₂O.
A. J. M.

Measurement of deposited dust from the atmosphere. H. W. GONELL (Chem. Fabr., 1934, 7, 300—303).—Rain-H₂O drains off a slightly inclined Zn tray into a 1-litre vessel in which entrained dust deposits. The tray is painted internally with lubricating oil; this is finally dissolved in C₆H₆, which is added to the H₂O. The apparatus is finally cleaned with Et₂O. A wire gauze of 2 mm. mesh over the

tray keeps off leaves, insects, etc. An exposure of 1—2 weeks affords sufficient dust for microscopical study.
C. I.

Copper apparatus for the determination of m.p. C. F. LINSTROM (Chem. Fabr., 1934, 7, 270).—The block is so designed that the substance may be observed from a direction perpendicular to the direction of the incident light, which is provided by a small electric lamp and focussed through a hole in the block by means of a condenser. Evolution of gas, changes of colour, etc. during heating may be clearly detected.
H. F. G.

Use of dioxan as solvent in the determination of mol. wt. by the cryoscopic method. A. E. OXFORD (Biochem. J., 1934, 28, 1325—1329).—Specially purified dioxan (b.p. 101.4°, f.p. 11.67°) is suitable for use as solvent in the cryoscopic determination of mol. wt. ($K=47$) of many cryst. org. compounds, but cannot accurately be used for sugars and NH₂-acids owing to low solubility, for substances containing H₂O of crystallisation (these sharing their H₂O with the solvent), or for carolic acid. A semi-micro-method of determination has been devised.
I. A. P.

Micro-determination of mol. wt. of volatile liquid compounds. A. F. COLSON (Analyst, 1934, 59, 529—531).—The method is based on that of Blackmann (A., 1910, 643).
E. C. S.

Nomenclature of the hydrogen isotopes and their compounds. E. J. CRANE (Science, 1934, 80, 86—89).
L. S. T.

Ancient Indian iron. S. C. BRITTON (Nature, 1934, 134, 238—240, 277—279).
L. S. T.

Geochemistry.

Atmospheres of the stars. H. N. RUSSELL (J. Franklin Inst., 1934, 218, 127—142).—A review of existing knowledge of stellar spectra and of the deductions which can be made therefrom concerning the composition, temp., and general conditions prevailing in the atm. of stars.
D. R. D.

Vertical distribution of ozone in the atmosphere. F. W. P. GÖTZ, A. R. MEETHAM, and G. M. B. DOBSON (Proc. Roy. Soc., 1934, A, 145, 416—446).—Spectroscopic observations of the light from the zenith blue sky while the sun is rising or setting have been made at Arosa for a year. The height and distribution of the O₃ have been found under various meteorological conditions for different seasons of the year. The average height of the O₃ in Switzerland is about 22 km. above sea-level, and this is distributed mainly between the ground and 35 km. The main changes in O₃ content are centred at a height of about 10—20 km. The form of the vertical distribution depends chiefly on the total O₃ present.
L. L. B.

Transparency of the lower atmosphere and its content of ozone.—See this vol., 1054.

Waters of Mt. Meru, Tanganyika. D. STURDY, W. E. CALTON, and G. MILNE (J. E. Africa Uganda

Nat. Hist. Soc., 1932, No. 45—46, 1—38).—Analytical data for the H₂O and for lake-edge salt deposits are recorded.
CH. ABS.

Absorption of light by sea-water. E. B. STEPHENSON (J. Opt. Soc. Amer., 1934, 24, 220—221).—In the formula $I = I_0 \times 10^{-\gamma D}$, where I is in foot-candles and D is in ft., $\gamma = 0.008 \pm 0.001$ for clear open sea, and 0.030 in Panama Bay.
C. W. G.

Mud of Lake Canieris. J. KUPZIS (Latvian Univ. Raksti, 1934, 2, 357—382).—The mud is strongly alkaline and is rich in CaSO₄, Fe, Al, sulphide-S, and amines.
A. G.

San Francisco Mountains meteorite. S. H. PERRY (Amer. J. Sci., 1934, [v], 28, 202—218).—An analysis (Fe 91.91, Ni 7.83%) and full description are given.
C. W. G.

Quantitative study of pleochroic haloes. I. G. H. HENDERSON and S. BATESON. II. G. H. HENDERSON and L. G. TURNBULL (Proc. Roy. Soc., 1934, A, 145, 563—581, 582—591).—I. A recording microphotometer has been constructed for measuring the amount of darkening in pleochroic haloes. Records of U haloes in biotite are given. The ranges of all

the α -particles, including U-I, agree with the features of the halo.

II. A biotite from Renfrew, Ontario, has been studied by the above method. The ring radii agree with the known ranges of the α -particles of the U and Ac families. No evidence is found of any change in the ranges of the α -particles in the course of geological time. L. L. B.

Dickite in the Rôseki deposits in Shôkôzan. B. YOSHIKI (Proc. Imp. Acad. Tokyo, 1934, 10, 417—420).—An analysis and dehydration phenomena are recorded. C. W. G.

Chemical formula of basaltic hornblende. Y. KAWANO (Proc. Imp. Acad. Tokyo, 1934, 10, 349—352).—Analyses of hornblende from Korea and Lukow lead to the formulæ $(\text{O}, \text{OH}, \text{F})_{2.0}(\text{Ca}, \text{Na}, \text{K})_{2.8}(\text{Mg}, \text{Fe}^{\text{II}}, \text{Mn}, \text{Fe}^{\text{III}}, \text{Ti})_{5.1}[(\text{Si}, \text{Al})_{4.0}\text{O}_{11.0}]_2$ and $(\text{O}, \text{OH}, \text{F})_{2.0}(\text{Ca}, \text{Na}, \text{K})_{3.1}(\text{Mg}, \text{Fe}^{\text{II}}, \text{Mn}, \text{Fe}^{\text{III}}, \text{Al}, \text{Ti})_{5.0}[(\text{Si}, \text{Al})_{4.0}\text{O}_{11.0}]_2$. C. W. G.

Escape of helium from minerals and rocks. B. G. CHLOPIN, E. K. GERLING, and E. M. JOFFE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 121—127).—He is given off more readily from the minerals uraninite and chlopinite by heating to 400—600° in presence of H_2 , which penetrates into the mineral and is adsorbed. The results suggest that the He is held in the mineral in at least two forms. CH_4 , C_2H_4 , and their homologues are more effective than H_2 at 600—700°. They probably form active H. A gas reacting chemically with the mineral and changing its structure should also accelerate the loss of He. H. J. E.

Chromium. III. Occurrence of chromium in certain soils and plants in the province of Quebec. A. DINGWALL and H. T. BEANS (J. Amer. Chem. Soc., 1934, 56, 1666—1667). E. S. H.

Distribution of chromium and manganese. G. VON HEVESY, A. MERKEL, and K. WURSTLIN (Z. anorg. Chem., 1934, 219, 192—196).—The Cr and Mn content of a no. of rocks has been determined by X-ray spectroscopy. Deep-lying rocks have the largest Cr content and Essexite the least. The mean val. for volcanic rock is 1 part in 2000. Essexite is also poorest in Mn and diorite richest, the mean val. being 1 part in 1000. M. S. B.

Determination of the age of certain minerals. G. H. HENDERSON (Proc. Roy. Soc., 1934, A, 145, 591—598).—The presence of Ac in pleochroic haloes of the U types leads to a new method of determining the age of certain minerals. The method is applied to three biotites. L. L. B.

Microscopical study of the siliceous sand of Kliwa; its origin and the conditions of deposition. M. G. FILIPESCO (Bull. Acad. Sci. Roumaine, 1932, 15, 141—146).—The sand consists of a mixture (10 : 1) of angular and rounded particles, the former being marine and the latter air-borne. The heavy minerals are derived from metamorphic rocks, and the quartz grains are associated with fragments of quartzite. The quartz and grits of Kliwa are all derived from the Dobruja ridge, which contains, *inter alia*, quartzitic rocks and schists. H. F. G.

X-Ray and colloid-chemical study of clay. W. HOFMANN, K. ENDELL, and D. WILM (Angew. Chem., 1934, 47, 539—547).—A detailed review of work carried out during the past decade. H. F. G.

X-Ray diagrams of different peranthracites and true anthracites. P. CORRIEZ (Compt. rend., 1934, 199, 410—412).—Anthracites show a foliated structure similar to that of graphite, but the separation between successive layers is slightly > in the latter case. A few of these layers form the unit cell of anthracite. The development of the lattice in other directions, however, varies from sample to sample, the degree of organisation increasing as the amounts of gas developed from the sample on heating decrease, finally reaching graphite structure in peranthracite from Areches. X-Ray methods afford a method of distinguishing between anthracites and peranthracites. J. W. S.

Free alumina in soils. F. HARDY (Nature, 1934, 134, 326—327).—Further evidence of the presence of free gibbsitic alumina in bauxites, laterites, and lateritic soils and its absence from most tropical red earths and kaolinitic earths has been obtained by determinations of heats of wetting. This test may be a quicker and simpler alternative to the alizarin test for detecting free Al_2O_3 in the products of rock weathering and in soils. L. S. T.

Organic Chemistry.

Physico-chemical problems of organic chemistry. E. HERTEL (Z. Elektrochem., 1934, 40, 405—413).—A lecture. E. S. H.

Spacial configuration of organic molecules and molecular aggregates. H. MARK (Z. Elektrochem., 1934, 40, 413—424).—A lecture. E. S. H.

Experimental problems resulting from a rational system of organic compounds. H. G. GRIMM (Z. Elektrochem., 1934, 40, 460—462).—A lecture (cf. Naturwiss., 1929, 17, 535, 557). E. S. H.

Symmetrical disubstituted methanes from members of optically active homologous series of disubstituted carboxylic acids and their de-

rivatives. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1934, 106, 173—178; cf. this vol., 55).—The conversion of *l*- β -methylhexoic acid into δ -methylheptane (I) is described. Optically inactive (I) is also obtained from *d*- α -bromo- δ -methylheptane. Optically inactive ε -methylnonane is derived from (–)- β -methylheptoic acid and from (–)- α -bromo- ε -methylnonane. 1- Δ^8 -Hepten-8-ol, b.p. 157°/760 mm., $[\alpha]_D^{20}$ –0.8° (*H phthalate*, $[\alpha]_D^{20}$ –1.25° in C_6H_6), is converted into inactive *di-n-propylcarbinol*, b.p. 152°/760 mm. H. D.

Peroxide effect in addition of reagents to unsaturated compounds. VIII. Addition of hydrogen iodide to ethylene compounds. M. S.

KHARASCH and C. HANNUM (J. Amer. Chem. Soc., 1934, **56**, 1782—1784).—Addition of anhyd. HI to C_3H_6 in presence of ascaridole (I) or $NHPh_2$ (in a vac.) gives Pr^2I (the "normal product," i.e., the product analogous to that obtained using HBr in presence of antioxidant) in each case. Similarly, Δ^a -butene affords *sec.*- BuI , whilst $\delta\delta$ -dimethyl- Δ^a -pentene gives (cf. Whitmore and Homeyer, this vol., 54) β -iodo- $\delta\delta$ -dimethylpentane. Allyl bromide and HI at -38° or room temp. in presence of (I) give a good yield of $CH_2Br\cdot CHMeI$ (II); at -38° in presence of $NHPh_2$ and in a vac., addition does not occur, whilst at 0° a poor yield of (II) (accompanied by much tar and some Pr^2I) results. H. B.

Rearrangement during pyrolysis of butenes. C. D. HURD and A. R. GOLDSBY (J. Amer. Chem. Soc., 1934, **56**, 1812—1815).—When Δ^a -butene (I) is passed through a Pyrex tube (contact time 9—12 sec.) at 600° , 650° , and 700° , the extent of decomp. is 10, 57, and 87%, respectively. The gaseous products formed are H_2 , CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , butadiene (trace), and (at 650° and 700° , but not at 600°) Δ^b -butene (II) (63 : 37 mixture of *cis*- and *trans*-forms). The extent of decomp. of (II) at 650° and 700° is 44 and 80%, respectively, with contact time 12—13 sec. Rearrangement into (I) occurs, and the recovered (II) has the same composition as the original material; the other gaseous products are as above. *iso*Butene is not produced from (I) or (II). Mixtures of C_4H_{10} , C_4H_8 , and C_4H_6 are separable with a Frey-Hepp column (B., 1933, 581). H. B.

Polymerisation of butadiene, isoprene, dimethylbutadiene, and cyclohexadiene. N. D. ZELINSKI, Y. I. DENISENKO, M. S. EVENTOVA, and S. I. KHROMOV (Sintet. Kauchuk, 1933, No. 4, 11—14).—In contact with $AlCl_3$, $\beta\gamma$ -dimethylbutadiene polymerises in 24 hr. to a substance different from that obtained on slow polymerisation. Isoprene behaves similarly. Pure butadiene (I) does not polymerise readily, but (I) containing 20—50% of other hydrocarbons polymerised rapidly. 1 : 3- and 1 : 4-*cyclo*Hexadiene polymerise only when heated.

CH. ABS.

Oxygen additive compounds of acetylenes. C. A. YOUNG, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, **56**, 1822—1823).— $CH\cdot CR$, $CR\cdot CR'$, and $CR\cdot CHal$ (R and R' are alkyl and aryl) acquire oxidising properties after contact with air or O_2 ; peroxide formation probably occurs. H. B.

Addition of methyl alcohol to vinylacetylene. D. B. KILLIAN, G. F. HENNTON, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, **56**, 1786—1787). $CH_2\cdot CH\cdot C\cdot CH$ and MeOH in presence of BF_3 (prep.: A., 1933, 932), HgO , and $CCl_3\cdot CO_2H$ give the *Me_2* acetal, b.p. 63 — $65^\circ/25$ mm., of *Me* β -methoxyethyl ketone, b.p. 139 — $140^\circ/745$ mm. H.

Addition of organic acids to alkylacetylenes. F. HENNION and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, **56**, 1802—1803).— $CH\cdot Calk$ and RCO_2H in presence of $BF_3\cdot Et_2O$ (prep.: A., 1933, 932), HgO , and MeOH give $CH_2\cdot Calk\cdot O\cdot COR$ (I) and varying amounts of $COMeAlk$ (II). (I) are hydrolysed ($EtOH\cdot KOH$) to (II). The following are described :

α -methylvinyl, b.p. 92 — $94^\circ/736$ mm., and α -n-amylinyl, b.p. 92 — $94^\circ/40$ mm., acetates; α -n-butylvinyl acetate, b.p. 74 — $75^\circ/39$ mm., chloroacetate, b.p. 100 — $101^\circ/20$ mm., and benzoate, b.p. 147 — $149^\circ/21$ mm.

H. B.

Chlorofluoro-ethanes and -ethylenes. E. G. LOCKE, W. R. BRODE, and A. L. HENNE (J. Amer. Chem. Soc., 1934, **56**, 1726—1728).—*Pentachlorofluoroethane* (I), b.p. 137.9° (corr.)/760 mm., m.p. 101.3° , *s-tetrachlorodifluoroethane* (II), b.p. 92.8° (corr.)/760 mm., m.p. 24.65° , $\alpha\alpha\beta$ -trichloro- $\alpha\beta\beta$ -trifluoroethane (III), b.p. 47.7° (corr.)/760 mm., m.p. -36.4° , *s-dichlorotetrafluoroethane* (IV), b.p. 3.8° (corr.)/760 mm., $CCl_2F\cdot CF_3$, b.p. about -2° (corr.)/760 mm., and $CClF_2\cdot CF_3$, b.p. -38° (corr.)/760 mm., are obtained from C_2Cl_6 and $SbCl_5F_3$ (Midgley and Henne, B., 1930, 651). $CCl_3\cdot CClF_2$, b.p. 91.5° (corr.)/760 mm., m.p. 40.6° (lit. 52°), and $\alpha\alpha\alpha$ -trichloro- $\beta\beta\beta$ -trifluoroethane, b.p. 45.8° (corr.)/760 mm., m.p. 13.2° , are prepared by chlorination of $CHCl_2\cdot CHF_2$ and $CH_2Cl\cdot CF_3$, respectively. (I) and Zn in EtOH give *trichlorofluoroethylene*, b.p. 72.1° (dibromide, m.p. 122.5°); (II) similarly affords *cis*-, b.p. 21.1° , m.p. -130.5° , and *trans*-, b.p. 22° , m.p. -110.3° , $\alpha\beta$ -dichloro- $\alpha\beta$ -difluoroethylenes; (III) yields $CClF\cdot CF_3$, m.p. -23° (dibromide, b.p. 92.9°); (IV) furnishes $CF_2\cdot CF_2$, b.p. -78.4° (dibromide, b.p. 46.4° , m.p. -112°). *s-Dichlorodibromodifluoroethane* has b.p. 139.7° , m.p. 32.5° . Numerous other physical data are given. H. B.

Allylic transformations. III. Dichloropropyl- enes. A. KIRRMANN, PACAUD, and H. DOSQUE (Bull. Soc. chim., 1934, [v], 1, 860—871; cf. A., 1932, 600).—The following reactions indicate that compounds, $CHX\cdot CH\cdot CH_2X$, are tautomeric with, but more stable than, $CH_2\cdot CH\cdot CHX_2$ (X =halogen), but that the latter have an independent existence. Acetaldehyde and PCl_5 give γ -chloroallyl chloride (I) (32%), acrylidene dichloride (II) (16%), some $CHCl_2\cdot CH_2\cdot CH_2Cl$ (III), b.p. 143 — 144° (also obtained from $CH_2Cl\cdot CH_2\cdot CHO$ and PCl_5), and (?) $\alpha\alpha\epsilon$ -trichloro- β -chloromethylpentan- γ -ol, b.p. 135 — $137^\circ/19$ mm. (I) with hot NaOMe or NaOEt gives γ -chloroallyl Me ether (IV), b.p. 107 — 108° , and Et ether; b.p. 126 — 127° , respectively. (II) gives (IV) more slowly, with traces of derivatives of (II). $CHCl\cdot CH\cdot CH_2I$ and $MgPrBr$ at -10° give a mixture, containing probably a little cyclohexene. (II) with $MgPhBr$ gives a poor yield of the mixture obtained from (I). (I) with $NHET_2$ in cold Et_2O gives slowly *dimethyl- γ -chloroallylamine*, b.p. 57 — $58^\circ/17$ mm. (picrate, m.p. 91° ; *platinichloride*, m.p. 169 — 170°); (II) gives a poor yield of a base (picrate, m.p. 91°). (I) or (II) with NaOAc in AcOH at 110° gives a 50% yield of γ -chloropropenyl acetate, b.p. $57/15$ mm., hydrolysed by cold NaOH to γ -chloroallyl alcohol (V), b.p. $57^\circ/14$ mm. (phenylurethane, m.p. 75°), which with PCl_3 gives (I). (I) and Ag_2O in cold H_2O give (V) and *di- γ -chloroallyl ether*, b.p. 88 — $91^\circ/15$ mm. (tetrabromide, b.p. $197^\circ/19$ mm.), obtained in lower yield also from (II) and $CHBr\cdot CH\cdot CH_2Br$. $CaBr_2$ and hot (I) give much $CHCl\cdot CH\cdot CH_2Br$ (VI). CaI_2 reacts more rapidly with (I) than with (II). γ -Chloroallyl iodide has b.p. $157^\circ/760$ mm., $51^\circ/16$ mm. (I) does not react with Zn in hot $COMe_2$ or Mg, but with "mol." Na violently gives

gaseous products. (VI), however, reacts with Mg to give a mixture. (III) with NaOAc in AcOH gives $\gamma\gamma$ -dichloropropyl acetate (78%), b.p. 85°/18 mm., hydrolysed by cold 0.2*N*-NaOH to $\gamma\gamma$ -dichloropropyl alcohol, b.p. 82—83°/20 mm. R. S. C.

Saturated solid alcohol from the urine of pregnant mares.—See this vol., 1126.

Synthesis of higher alcohols from water-gas under pressure. E. M. BOTSCHAROVA and B. N. DOLGOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 115—120).—41% of oily products (higher alcohols 67, esters 7.2, acids 4.7, hydrocarbons 1%) are obtained by passing 1:1 CO-H₂ over 4ZnO-V₂O₅-KOH catalyst at 350—450°/220 atm. Many other catalysts gave less satisfactory results. R. T.

Action of polyhydric alcohols on periodic acid and alkali periodates. L. MALAPRADA (Bull. Soc. chim., 1934, [v], 1, 833—852).—For elucidation of these reactions the following analytical methods are used. Org. and mineral acids are titrated with NaOH in presence of HIO₄ using thymolphthalein, as this changes to blue when the HIO₄ is converted into Na₂H₃IO₆. Aldehydes are determined by a modification of Dœuvre's method or by the NaHSO₃ method using KIO₃ in dil. AcOH for oxidation of the excess SO₃ (aldehyde-H sulphite compounds do not reduce KIO₃-dil. AcOH). The accepted course of the HIO₄ oxidation is verified by these methods for inositol, tartaric, gluconic, and saccharic acids, glucose, and dihydroxyacetone. By use of a deficiency of HIO₄ it is shown that the reaction proceeds stepwise, thus: (a) OH·CHR·CHR'·OH \longrightarrow RCHO + R'CHO; (b) if R or R' = R''·CH·OH, then OH·CHR''·CHO \longrightarrow R''CHO + HCO₂H, and so on. HIO₄ also oxidises ketones, which is interpreted by means of the hydrated forms of the latter. HIO₄ oxidation is thus generalised in the equation OH·CRR'·CR'R''·OH + O \longrightarrow R·CO·R' + R''·CO·R' + H₂O, in which R and R'' = H or alkyl, and R' = H or OH. NaIO₄ and K₂H₃IO₆ (I) react similarly to HIO₄ in all respects, but more slowly, and, being readily purified, can be used for determination of polyhydric alcohols (II). (I) may form additive compounds with (II). R. S. C.

Rapid qualitative test for ethylene glycol and its application in presence of glycerol. A. W. MIDDLETON (Analyst, 1934, 59, 522—524).—The aq. alcohols are treated with HNO₃, whereby [CH₂·OH]₂ (I) yields H₂C₂O₄, isolated as the Ba salt and detected by decolorisation of warm aq. KMnO₄. 0.1 g. of (I) can be detected in the absence of glycerol (II), and 0.3 g. in the presence of 0.7 g. of (II), but the test fails when (II) forms > 75% of the mixture. E. C. S.

d-Sorbitol. New source, method of isolation, properties, and derivatives. H. H. STRAIN (J. Amer. Chem. Soc., 1934, 56, 1756—1759).—Details are given for the isolation (in about 2.5% yield) of d-sorbitol (I), m.p. 91—93° (corr.), [α]_D²⁰ -2.5° in H₂O (compound, m.p. 89°, with 1 mol. of C₅H₅N), from the fruit of *Photinia arbutifolia*, Lindl. The following derivatives of (I) are described: hexa-acetate, m.p. 101—102° (corr.) (lit. 99°), [α]_D²⁰ +10.6° in COMe₂; benzylidene, m.p. 195—196.5°; trisopropylidene, b.p. 140°/1—2 mm., m.p. 45—46°, [α]_D²⁰ +15.8° in EtOH;

tri(methylene), m.p. 213—214° (corr.) (lit. 206—209°), [α]_D²⁰ -32.8° in C₅H₅N. (I) is not epimerised by heating with C₅H₅N. H. B.

Tests for purity of ether. II. A. WØHLK (Dansk Tidsskr. Farm., 1934, 8, 226—232).—Aldehydes in Et₂O can be best detected by Ag₂O-aq. NH₃, and removed by adding solid KOH to the moist Et₂O. R. P. B.

Autoxidation of diethyl ether and chemistry of its decomposition products. II. R. NEU (Pharm. Zentr., 1934, 75, 529—532; cf. A., 1932, 1017).—Et₂O free from aldehydes undergoes rapid autoxidation in presence of colloidal Fe or blood charcoal (Fe₂O₃) and in clean sheet-Fe containers in the dark. The action of light is of secondary importance. S. C.

Unsaponifiable matter from oils of elasmobranch fish. X. Structure of batyl alcohol and synthesis of β-octadecyl glyceryl ether. W. H. DAVIES, I. M. HEILBRON, and W. E. JONES (J.C.S., 1934, 1232—1235).—Crystallisation of the crude solid αγ-benzylideneglycerol (Hill *et al.*, A., 1928, 1213) after keeping affords a geometrical isomeride (I), m.p. 62.5—63° (labile *Bz* derivative, m.p. 80—81°, readily passing into the stable form, m.p. 103°), which with Ag₂O-Mel affords a β-*Me* ether, b.p. 145—148°/5 mm., hydrolysed to Hill's glyceryl β-*Me* ether. With *n*-C₁₈H₃₇I the *K* derivative of (I) in C₆H₆ gives its β-octadecyl ether, m.p. 43—44°, hydrolysed by aq. EtOH-HCl to glyceryl β-octadecyl ether (II), m.p. 62—63° [*di*(phenylurethane), m.p. 83—84°], depressed by admixture with batyl alcohol (III) (the α-ether). Condensed films of (II) on H₂O occupy approx. 6 Å.² more area at all pressures than do those of natural or synthetic (III) (Adam and Harding). Similar reactions afford the β-cetyl ether of (I), m.p. 34—35°, hydrolysed to glyceryl β-cetyl ether, m.p. 60—61° [*di*(phenylurethane), m.p. 82—83°]. J. W. B.

Methyl hydrogen phosphates. V. HARLAY (J. Pharm. Chim., 1934, [viii], 20, 160—167).—The prep., isolation, and properties of MeH₂PO₄ and Me₂HPO₄ and their determination in presence of H₃PO₄ are described. E. H. S.

Determination of aliphatic nitrates by titration. J. W. H. OLDHAM (J.S.C.I., 1934, 53, 236r).—A method for the determination of org. nitrates by means of aq. Ti₂(SO₄)₃ is described and examples are given.

Preparation and properties of β-monoglycerides. B. F. STIMMEL and C. G. KING (J. Amer. Chem. Soc., 1934, 56, 1724—1725).—αγ-Benzylideneglycerol and the appropriate acyl chloride in C₅H₅N at 20° give αγ-benzylideneglyceryl decoate, m.p. 32°, laurate, m.p. 46.6°, myristate, m.p. 62°, palmitate, m.p. 63.5°, and stearate, m.p. 69°, which when reduced (H₂, Pd-black, EtOH) (cf. Bergmann and Carter, A., 1930, 1555) afford glyceryl β-decoate, m.p. 40.4°, β-laurate, m.p. 51.1°, β-myristate, m.p. 61°, β-palmitate (I), m.p. 68.5°, and β-stearate, m.p. 74.4°, respectively. (I) rearranges to the α-palmitate in 0.05*N*-EtOH-HCl during 24 hr. at room temp.; little or no change occurs in solutions < 0.005*N*. Similar results are found with aq. EtOH-NH₃ (concn. about twice that of HCl).

Prolonged heating of (I) induces a change which does not involve complete transition; short heating has little or no effect.

H. B.

Acetoacetic ester condensation. VII. Condensation of alkyl acetates. N. FISHER and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, **56**, 1766—1769).—The yields of $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{R}$ obtained in 2—32 hr. from 1.2 mols. of ROAc ($\text{R}=\text{Me}, \text{Et}, \text{Pr}^a, \text{Pr}^s, \text{Bu}^a, \text{Bu}^s, \text{Bu}^v, \text{sec.-Bu}$) and 0.2 mol. of NaOR (preps. described) at a temp. (57—115°) capable of maintaining, where possible, homogeneity of the reaction mixture are usually 50—80%. The high yields indicate (cf. A., 1931, 1035) that NaOR is the active condensing agent. NaOPh fails to condense PhOAc ; the enolic form of the β -CO-ester cannot decompose the salt of the more acidic phenol, thus preventing condensation (cf. this vol., 756). Pr^a , b.p. 78°/11 mm., Pr^s , b.p. 69°/11 mm., Bu^a , b.p. 90°/11 mm., Bu^s , b.p. 84.5°/11 mm., sec.-Bu , b.p. 79.1°/11 mm., and Bu^v , b.p. 71.5°/11 mm., *acetoacetates* are new.

H. B.

Action of iodoacetic acid on mercaptans and amines. L. MICHAELIS and M. P. SCHUBERT (J. Biol. Chem., 1934, **106**, 331—341).—Tri(carboxymethyl)amine (I) is prepared from glycine and $\text{CH}_2\text{I}\cdot\text{CO}_2\text{H}$ (II) in aq. KOH solution at 80°. The titration curve of (I) shows two pK , one at 3 and one near 10. K_2 salts of di(carboxymethyl)-(α -carboxyethyl)-amine, carboxymethyl-di-(α -carboxyethyl)amine, tri-(α -carboxyethyl)amine, and tetracarboxymethyl-p-phenylenediamine, m.p. 165°, are prepared similarly. K tetracarboxymethylcystine diacetate (III) is prepared from cystine and (II) in aq. KOH at 90° by pptn. with EtOH . (III) gives dicarboxymethylcystine acid with Br . Reduction of (III) with Sn in HCl and pptn. of the product from AcOH with EtOH gives K dicarboxymethylcystine acetate. Cysteine and $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ in aq. KOH give S -carboxymethylcysteine, and thiolacetanilide and (II) give carboxymethylthiolacetanilide, m.p. 99—100°. Glutathione and (II) neutralised with Na_2CO_3 form S -carboxymethylglutathione at room temp. The rate of reaction of (II) with SH is $>$ that with NH_2 . At physiological p_H the reaction is slow.

H. D.

Constitution of linoleic acid.—See this vol., 1046.

Synthesis of ascorbic acid and its analogues: addition of hydrogen cyanide to osones. W. N. HAWORTH, E. L. HIRST, J. K. N. JONES, F. SMITH, and (in part) R. W. HERBERT and C. E. WOOD (J.C.S., 1934, 1192—1197).—Mainly a more detailed account of results already published (this vol., 633). The mechanism of the formation and reactions of iminoglucoascorbic acid is given. Similarly from galactosone and NaCN is obtained iminogalactoascorbic acid, m.p. 190° (decomp.), $[\alpha]_D^{25}$ —95° in H_2O , +25° in $N\text{-HCl}$ (absorption band at 275 μ , ϵ approx. 18,000), hydrolysed by $N\text{-HCl}$ at 15° to galactoascorbic acid.

J. W. B.

Physiological activity of synthetic ascorbic acid. W. N. HAWORTH, E. L. HIRST, and S. S. ZILVA (J.C.S., 1934, 1155—1156).—In comparative tests (guinea-pigs) the physiological, physical, and chemical properties of highly purified natural ascorbic

acid and of the synthetic material (A., 1933, 936) are identical.

J. W. B.

Reversibility in the oxidation of certain derivatives of carbohydrates, especially ascorbic acid.—See this vol., 1072.

Derivatives of glycuronic acid. IV. Synthesis of methyl α - and β -tetra-acetylglycuronates and of methyl 1-chlorotriacetylglycuronate. W. F. GOEBEL and F. H. BABERS (J. Biol. Chem., 1934, **106**, 63—69; cf. A., 1933, 808).— $\text{Me } d\text{-glycuronate}$, from MeI and the Ag salt, gives a mixture of $\text{Me } \alpha\text{-(I)}$, m.p. 111—112° (corr.), $[\alpha]_D^{25}$ +98.0° in CHCl_3 , and $\beta\text{-(II)}$, m.p. 178° (corr.), $[\alpha]_D^{25}$ +8.7° in CHCl_3 , -tetra-acetylglycuronate. With Ac_2O and ZnCl_2 or $\text{C}_5\text{H}_5\text{N}$ (I) and (II) give $\text{Me } 1\text{-chlorotriacetylglycuronate}$, m.p. 150.5—151.5° (corr.), $[\alpha]_D^{25}$ —16.7° in CHCl_3 , with AcCl and HCl .

H. D.

Keten. I. Preparation and reactions. F. O. RICE, J. GREENBERG, C. E. WATERS, and R. E. VOLBRATH (J. Amer. Chem. Soc., 1934, **56**, 1760—1765).—Secondary factors in the prep. of keten (I) from COMe_2 (by passage through a quartz tube) are: (i) packing the tube with quartz or Pyrex glass, (ii) furnace temp. (if $<$ 600°), (iii) contact time, (iv) dilution of the COMe_2 vapour with an inert gas. The essential condition for a good yield (based on COMe_2 decomposed) is the decomp. of only a small fraction of the COMe_2 used. The yield is diminished considerably by the presence of 0.1 mol.-% of MeI , Me_2S , Me_2SO_4 , PbEt_4 , and isoamyl nitrite, and to a slight extent by MeCHO , NH_3 , CHPh_3 , and azoisopropane. As usually prepared, (I) contains 5—10% of C_2H_4 , which is separable by distillation in a vac.-jacketed still. Pure (I), b.p. —41°/760 mm., m.p. —134.6°, is stable at —80° provided it is freed (by distillation) from C particles and resinous material. (I) is a powerful acetylating agent; Ac derivatives are obtained from various alcohols, ArOH , and NH_2Ar , provided these can be liquefied or dissolved in an inactive [to (I)] solvent. Polymerisation of the (I) can usually be avoided by slow passage into the compound (kept relatively conc.) at as high a temp. as possible. Bu^vOH reacts very slowly; $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (at 225°) gives resinous material and Ac_2O ; NH_2Bz (at 180°) affords PhCN and Ac_2O .

H. B.

Crystalline methyl- d -ribose. J. MINSAAS (Annalen, 1934, **512**, 286—289).—Methyl- d - β -ribose, m.p. 83—84° (corr.), $[\alpha]_D^{20}$ —113.6°, is obtained by heating ribose with 0.25% HCl-MeOH .

H. W.

Acetone [isopropylidene] derivatives of d -ribose. II. P. A. LEVENE and E. T. STILLER (J. Biol. Chem., 1934, **106**, 421—429).—Methylribopyranoside (I) on acetylation (A., 1933, 1145) gave an isopropylidene derivative (II), b.p. 84—86°/0.05 mm. Methylisopropylidenemethylriboside, b.p. 68—69°/0.04 mm., on hydrolysis with 0.02N- HCl at 100° shows a change of $[\alpha]_D$ from —64.5° to —22° in 30 min. and the product (III) contains 46% of a monomethylpentose. Exhaustive methylation of (III) gave trimethylmethylriboside, which with 0.02N- HCl at 100° showed a fall in $[\alpha]_D$ and an increased reducing power to a max. of 52%. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ with (II) gave

a mixture of 2:3-isopropylidenemethylribofuranoside 5-*p*-toluenesulphonate (IV), m.p. 83—84°, $[\alpha]_D^{25}$ —35.5° in EtOH, and isopropylidenemethylribofuranoside 4-*p*-toluenesulphonate (V), m.p. 144—145°, $[\alpha]_D^{25}$ —114.9° in EtOH, separated by recrystallisation from EtOH. (V) is hydrolysed by 5% H_2SO_4 to methylribofuranoside 4-*p*-toluenesulphonate, m.p. 124°, $[\alpha]_D^{25}$ —40° in CHCl_3 . (IV) gave an I-derivative with NaI (Oldham, A., 1932, 254), whilst (V) did not. It is concluded that on acetylation (I) partly rearranges to furanose. H. D.

Reactions of carbohydrates. II. Reactions with *m*-dinitrobenzene and alkali hydroxides. L. EKKERT (Pharm. Zentr., 1934, 75, 515—516).—Reducing carbohydrates (I) give a violet colour when a few drops of the solution are added to 5 mg. of $\text{m-C}_6\text{H}_4(\text{NO}_2)_2$ in 5 drops of EtOH and warmed after adding 1—3 drops of *N*-NaOH. Non-reducing (I) remain colourless. A. G.

Synthesis of aldehydo-sugar acetates. M. L. WOLFROM, L. W. GEORGES, and S. SOLTZBERG (J. Amer. Chem. Soc., 1934, 56, 1794—1797).—The product from β -glucose tetra-acetate and $\text{EtOH-NH}_2\text{OH}$ is acetylated (Ac_2O , $\text{C}_5\text{H}_5\text{N}$ at room temp.) to aldehydoglucoseoxime hexa-acetate (A., 1931, 467), hydrolysed ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in MeOH) to the penta-acetate (*loc. cit.*), which is converted by HNO_2 (cf. Claisen and Manasse, A., 1889, 584) into aldehydoglucose penta-acetate (I), $[\alpha]_D^{25} +10.6^\circ$ in MeOH. Acetylation (Ac_2O , $\text{C}_5\text{H}_5\text{N}$) of glucosesemicarbazone dihydrate gives (mainly) aldehydoglucosesemicarbazone penta-acetate (II), m.p. 154.5—155.5°, $[\alpha]_D^{25} +96.6^\circ$ in CHCl_3 (cf. A., 1929, 1043), and smaller amounts of an isomeric penta-acetate (III), m.p. 236—237°, $[\alpha]_D^{25} -16^\circ$ in CHCl_3 , a tetra-acetate, m.p. 171—172°, $[\alpha]_D^{25} -9^\circ$ in CHCl_3 [acetylated further to (III)], and a hexa-acetate, m.p. 110—111.5°, $[\alpha]_D^{25} -100^\circ$ in CHCl_3 . (II) is converted by HNO_2 into (I). Acetylation (Ac_2O , $\text{C}_5\text{H}_5\text{N}$) of galactoseoxime gives β -galactoseoxime hexa-acetate and a H_2O -insol. product, which is hydrolysed ($\text{MeOH-H}_2\text{C}_2\text{O}_4$) to a mixture (A), m.p. 92—96°, $[\alpha]_D^{25} +36.6^\circ$ in CHCl_3 , of approx. equal amounts of aldehydogalactoseoxime penta-acetate hydrate (IV) and galactonitrile penta-acetate (V). HNO_2 converts (A) into a mixture of (V) and aldehydogalactose penta-acetate (VI), which are more easily separated than are (IV) and (V). (VI) is also obtained by the action of HNO_2 on the mixture obtained by acetylation (Ac_2O , $\text{C}_5\text{H}_5\text{N}$ at 55°) of galactosesemicarbazone. H. B.

Comparative action of periodic acid on hexoses and the artificial heterosides derived therefrom. H. HERISSEY, P. FLEURY, and (Mlle.) M. JOLY (J. Pharm. Chim., 1934, [viii], 20, 149—160; cf. A., 1933, 596).—Hexoses treated with HIO_4 consume 5 O and liberate 1 mol. of CH_2O . The derived α - and β -heterosides require only 2 O and no CH_2O is formed. E. H. S.

Additive compounds of the carbohydrates. I. Potassium hydroxide-glucose and related compounds. E. G. V. PERCIVAL (J.C.S., 1934, 1160—1164).—With NaOR in dry ROH glucose (I) forms compounds, $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{NaOR}$ ($\text{R}=\text{Me}$ or Et), but if a trace of H_2O is present or with aq. EtOH-KOH

the compound (II), $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{KOH}$ is obtained. With dry Me_2SO_4 at 45—70°, (II) affords much unchanged (I) and, after acetylation, cryst. β -methylglucoside tetra-acetate together with its syrupy mixture with the α -compound. (II) is assigned the structure

$$\text{OH} \cdot \text{CH} < \frac{\text{CH}(\text{CH}_2\text{OH}) - \text{O}}{\text{CH}(\text{OH}) \cdot \text{CH}(\text{OH})} > \text{CH} \cdot \text{OH} \leftarrow \text{OH} \cdot \text{K}.$$

With dil. aq. EtOH-KOH cellobiose (III) forms the compound $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{KOH}$ [similarly converted by Me_2SO_4 into unchanged (III), β -methylcellobioside hepta-acetate and its α -isomeride], but in more conc. solutions there is evidence that $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{KOH}$ (giving a monomethylmethylcellobioside with Me_2SO_4) is formed. Maltose appears to give $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{KOH}$ in conc. alkaline solution. J. W. B.

Optical rotatory dispersion in the carbohydrate group. III. Tetramethyl- α -methylglucopyranoside and tetramethyl- α -methylmannopyranoside. R. W. HERBERT, E. L. HIRST, and C. E. WOOD (J.C.S., 1934, 1151—1155).—Although α -methylmannopyranoside exhibits complex rotatory dispersion, its Me_4 derivative (I) shows simple dispersion in H_2O , EtOH , and CHCl_3 , the rotation being controlled by an absorption band in the region of λ 1600. In agreement with this, (I) shows no selective absorption down to λ 2100. The complex rotatory dispersion of α -methylglucopyranoside is enhanced in its Me_4 derivative (II), which can be represented by a two-term Drude equation with terms of opposite sign, k_1 of the high-frequency term (contributed by a band at approx. λ 1500) being $> k_2$ of the low-frequency term (λ 2500 for H_2O and CHCl_3 ; 2300 for EtOH). The absorption curve of (II) is characterised by a step-out in the region of λ 2600, the cause of which is discussed. The ratio k_2/k_1 is dependent on the solvent, being —0.0198 for H_2O , —0.0484 for EtOH , and —0.0248 for CHCl_3 . J. W. B.

Synthesis of 2:3:6-tribenzoyl- α -methylglucoside. D. J. BELL (J.C.S., 1934, 1177—1179).— α -Methylglucoside 2:3-dibenzoate (I) with 1.2 mol. of BzCl in $\text{C}_5\text{H}_5\text{N}$ affords the 2:3:6-tribenzoate (II), m.p. 132—133°, $[\alpha]_D^{19} +141.1^\circ$ [4-*p*-toluenesulphonyl derivative (III), m.p. 158—160°, $[\alpha]_D^{19} +104.2^\circ$, unattacked by NaI in COMe_2], the constitution of which is established by the following observations. With excess *p*- $\text{C}_6\text{H}_4\text{Me-SO}_2\text{Cl}$ and $\text{C}_5\text{H}_5\text{N}$, (I) affords its 2:6-di-*p*-toluenesulphonyl derivative, m.p. 122—124°, $[\alpha]_D^{19} +94.58^\circ$, converted by NaI-COMe into 6-iodo- α -methylglucoside 2:3-dibenzoate 4-*p*-toluenesulphonate, m.p. 136°, $[\alpha]_D^{19} +90.9^\circ$, which with $\text{AgNO}_3\text{-MeCN}$ followed by Zn-Fe-AcOH gives α -methylglucoside 2:3-dibenzoate 4-*p*-toluenesulphonate, m.p. 179—180°, $[\alpha]_D^{19} +106.3^\circ$, benzylation of which gives (III). α -Methylglucoside 2:3:4-tribenzoate 6-*p*-toluenesulphonate [Helferich *et al.*, A., 1925, i, 9; depresses m.p. of (III)] is similarly converted into the 6-*I*-compound, and α -methylglucoside 2:3:4-tribenzoate, m.p. 140—142°, depressed by (II). All $[\alpha]_D^{19}$ vals. are in CHCl_3 . J. W. B.

Reaction between fructose and arsenic acid.—See this vol., 1034.

Structure of *d*-glucoheptulose hexa-acetate. M. L. WOLFROM and A. THOMPSON (J. Amer. Chem.

Soc., 1934, **56**, 1804—1806).—Glucoseptulose (I) is acetylated [Austin's method (A., 1932, 724); Ac_2O and ZnCl_2 at room temp.; Ac_2O (excess) and cold $\text{C}_5\text{H}_5\text{N}$] to the hexa-acetate (II), m.p. 115—116°, $[\alpha]_D^{25} + 87.6^\circ$ in CHCl_3 , converted by HBr in AcOH — Ac_2O into α -aceto-bromo-d-glucoseptulose (III), m.p. 97—98°, $[\alpha]_D^{25} + 134.5^\circ$ in CHCl_3 . Acetylation [Ac_2O and $\text{C}_5\text{H}_5\text{N}$ (excess) at 0° and then at room temp.] of (I) gives the penta-acetate, m.p. 114—115°, $[\alpha]_D^{25} + 49^\circ$ in CHCl_3 [acetylated (Ac_2O , NaOAc) to (II)], which contains glucosidic OH, since it is also obtained from (III) and Ag_2CO_3 in aq. COMe_2 . (II), EtSH , ZnCl_2 , and sol. anhydrite (Hammond and Withrow, A., 1933, 1266) give a compound, $\text{C}_{11}\text{H}_{18}\text{O}_5\text{S}_2\text{Ac}_4$, m.p. 92—93°, $[\alpha]_D^{25} + 65^\circ$ in CHCl_3 [in which 2 OAc groups of (II) have been replaced by 2 EtS], which is a thioglycoside. This result shows (cf. this vol., 636) that (II) is a cyclic compound (cf. Austin, loc. cit.). H. B.

Karakin, the glucoside of *Corynocarpus laevigata*. M. S. CARRIE (J.S.C.I., 1934, **53**, 288—289T).—The alcoholic extract of karaka kernels contains sugars, consisting of 95% of sucrose and 5% of glucose (I), an oil, hydrolysed to stearic and oleic acids, and karakin (II), $(\text{C}_5\text{H}_7\text{O}_5\text{N})_3$, m.p. 122°. (II) is hydrolysed by HCl in cold COMe_2 to 1 mol. of (I) and 3 mols. of heptagenic acid. H. W.

Strophanthin. XXX. Ultra-violet absorption spectra of trianhydrostrophanthidin and trianhydroperiplogenin derivatives. R. C. ELDERFIELD and A. ROTHEN (J. Biol. Chem., 1934, **106**, 71—78).—The curves for ultra-violet absorption (I) of mono- (II) and di- (III) -anhydrodihydrostrophanthidin in EtOH show max. at 3030 Å. due to CHO. At shorter λ (I) increases rapidly and continuously. Octahydrotrianhydrostrophanthidin shows slight (I). The (I) of dihydrotrianhydrostrophanthidin (IV) has a strong band between 2790 and 2500 Å. absent in (II) and (III) if the presence of the CHO is allowed for, indicating a C_6H_6 ring in (III). The (I) of trianhydrostrophanthidin (V) is similar to that of (IV) indicating the presence of an allylbenzene linking (Hillman, A., 1934, 345). The (I) of trianhydroperiplogenin has a band from 2600 to 3000 Å., but in the higher λ the curve is displaced from those of (IV) and (V). H. D.

Ivory-nut mannans. II. Constitution of mannan-B. F. KLAGES (Annalen, 1934, **512**, 185—194; cf. this vol., 514).—Mannan-B gives by methylation and hydrolysis the same products as does mannan-A (I), and is thus similarly constituted. Oxidation of methylated (I) by I is a secondary reaction, since tetramethyl- β -methylglucoside is similarly oxidised. R.

Size and structure of the cellulose molecule. A. AF EKENSTAM (Svensk Kem. Tidskr., 1934, **56**, 157—167).—Cellulose (I) may be dissolved in aq. HCl , H_2SO_4 , or H_3PO_4 for mol. wt. determinations by Staudinger's viscosity method. On account of the decomp. which occurs, the vals. must be extrapolated to zero time. The vals. agree with those obtained by other methods. If (I) is dissolved in conc. H_2SO_4 , the electrical conductivity increases with time. R. P. B.

Adsorption of acetone by cellulose nitrates.—See this vol., 1067.

Reaction of amines with ethyl β -bromopropionate and *n*-butyl bromide. W. V. DRAKE and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, **56**, 1810—1812).—The extent and course of the reaction of $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ (I) and Bu^nBr (II) with various NHR_2 (III) and NR_3 (IV) are determined at 90°, essentially as previously described (A., 1931, 494). The basicity of (III) is the factor controlling elimination of HBr from (I), but there is a considerable difference [undoubtedly due to steric factors associated with the structure of (III)] in the subsequent addition of (III) (of similar strength) to the resulting $\text{CH}_2\text{CH}\cdot\text{CO}_2\text{Et}$. The formation of NBuR_2 from (II) and (III) is not related to the basicity of (III); thus, for the same time, NHPhMe reacts to a greater extent than 2-methylpiperidine and NHET_2 . The variation in reactivity is probably due to steric factors. The extent of the reaction between (I) and (IV) is related to the basicity of (IV); some steric factor appears to be involved in the elimination reaction, since the *N*-alkylpiperidines (approx. the same basicity) show widely differing amounts of reaction (the reactivity decreases with increase in the size of alkyl). Considerable amounts of quaternary salt are obtained from (I) and $\text{C}_5\text{H}_5\text{N}$ and NPhMe_2 . Quaternary salt formation from (II) and (IV) is also independent of the basicity of (IV). H. B.

Determination of hexamethylenetetramine by precipitation of its uranyl double sulphate. FOUCRY (J. Pharm. Chim., 1934, [viii], **20**, 168—170).—The pptn. is quant. and occurs in a solution containing 0.04 mg. of $(\text{CH}_2)_6\text{N}_4$ in 2 c.c. E. H. S.

Application of dielectric constant measurements in aqueous solution to organic chemistry. G. DEVOTO (Z. Elektrochem., 1934, **40**, 490—493).—A review of published work. E. S. H.

Synthesis of glycine from glyoxylic acid. P. DESNUELLE and C. FROMAGEOT (Bull. Soc. chim., 1934, [v], **1**, 700—702).—Hydrogenation (colloidal Pd) of $\text{CHO}\cdot\text{CO}_2\text{H}$ in an excess of aq. NH_3 gives an 8% yield of glycine. R. S. C.

Synthesis of *dl*-lysine. J. C. ECK and C. S. MARVEL (J. Biol. Chem., 1934, **106**, 387—391).—cycloHexanone (I) is converted into the oxime and rearranged by Ruzicka's reaction (A., 1921, i, 591) to 2-ketohexamethyleneimine. Hydrolysis and benzoylation gives ϵ -benzamidohexoic acid, which is converted into *dl*-lysine (II) by the method of von Braun. 500 g. of (II) are prepared from 1000 g. of (I). H. D.

Labile hydrogen (Wieland) in the catalytic oxidation of thiol compounds by heavy metals. R. BRDIČKA (Biochem. Z., 1934, **272**, 104—112).—The existence of labile H in complex compounds of cysteine with Co and Ni is demonstrated by Heyrovsky's method. The activation of H of SH results from co-ordination of SH with Co or Ni, a dipole containing loosely bound H being formed. An explanation is thus provided of the mechanism (I) of the catalysis by heavy metals of the oxidation of SH compounds, direct transference of the activated H of these compounds to the H acceptor being

assumed. The views of Warburg and Wieland concerning the inhibition of autoxidation of cysteine by substances containing Fe in complex combination are harmonised by (I). W. McC.

Determination of cystine. Use of the Zeiss photometer. J. H. BUSHILL, L. H. LAMPITT, and L. C. BAKER (Biochem. J., 1934, 28, 1293—1304).—Using light of λ 530 m μ the extinction coeff. with the Sullivan technique (A., 1926, 1266) varies up to $\pm 25\%$ and the Lugg modification (I) (A., 1933, 814), taking precautions to prevent oxidation, to $\pm 8\%$. Cystine can be determined with an error of $\pm 4\%$, indicating that an error is introduced in its reduction in the process. The colour is affected considerably by O₂, particularly in (I). H. G. R.

Synthesis of cystinyldiglycine and cystinyldialanine. J. WHITE (J. Biol. Chem., 1934, 106, 141—144).—Dicarbobenzyloxy cystinyl dichloride, prepared by the action of PCl₅ on dicarbobenzyloxy cystine in Et₂O, gives dicarbobenzyloxy cystinyldiglycine (II), m.p. 161—163°, on treatment with glycine in N-NaOH at 0° and subsequent acidification. (II) on hydrolysis with conc. HCl gave cystinyldiglycine (III). Cystinyldialanine (IV) is prepared similarly. The Sullivan reaction is positive for both (III) and (IV). H. D.

Synthesis of pentocystine and homomethionine. V. DU VIGNEAUD, H. M. DYER, C. B. JONES, and W. J. PATTERSON (J. Biol. Chem., 1934, 106, 401—407).—Et₂ sodiophthalimidomalonate and trimethylene bromide condense to give Et₂ phthalimido- γ -bromopropylmalonate (I). Refluxing an EtOH solution of (I) with NaSH and extracting the evaporated residue with Et₂O yields Et₂ phthalimido- γ -thiolpropylmalonate, which on alkaline hydrolysis gives Na phthalimido- γ -thiolpropylmalonate. Oxidation of the Na salt with FeCl₃ gives bis- δ -phthalimido- δ -dicarboxybutyl disulphide (II). Hydrolysis of (II) with conc. HCl and extraction with 0.5N-HCl gives $\delta\delta'$ -diaminodi-n-butyl disulphide- $\delta\delta'$ -dicarboxylic acid (pentocystine), m.p. 269—272° (decomp.) (III). Di-formylpentocystine has m.p. 122°. (III) gives negative -SH and Sullivan tests and positive -S-S- and ninhydrin tests. Reduction of (III) with Na in liquid NH₃ and addition of CH₂PhCl gives S-benzylpentocystine, m.p. 219—222° (decomp.). α -Amino- δ -methylthiolvaleric acid (homomethionine) (IV), m.p. 272—274° (formyl derivative, m.p. 122—123°), is produced by addition of Na to a liquid NH₃ solution of (III) and addition of MeI. Excess of NH₃ is removed, the residue dissolved in H₂O, and the solution neutralised with 10% HI. Pptn. of (IV) is completed with EtOH. H. D.

Formation and synthetic use of amido- and imido-chlorides. J. VON BRAUN (Angew. Chem., 1934, 47, 611—615).—A crit. summary of the reactions of imidochlorides NR:CR'/Cl (R and R'=aryl or aliphyl). J. W. B.

Diazomethanes. I. Action of sodium triphenylmethyl on aliphatic diazo-compounds. E. MULLER and H. DISSELHOFF. II. Action of acids on the sodium derivative of diazomethane. E. MULLER and W. KREUTZMANN (Annalen, 1934,

512, 250—263, 264—275).—I. Addition of a small excess of CH₂N₂ to a solution of CPh₃Na causes immediate decolorisation and formation of a whit ppt. (I) which could not be analysed on account of its explosive nature, but is regarded as CHN₂Na. Hydrolysis of (I) with H₂O gives up to 35% of CH₂N₂; N₂H₄, CN', or HCO₂H could not be detected. With BzBr at >20° (I) gives a compound BzN<CH

$\begin{array}{c} \text{N} \\ \text{N} \\ \text{CH} \end{array} \text{O} \rangle \text{CPh}$, or NHBz.N:C, m.p. 35—37°, hydrolysed by alkali through NH₂.NHBz to N₂H₄, BzOH, and HCO₂H. I in Et₂O is immediately decolorised by (I) with evolution of a small amount of C₆H₆, but not N₂, and production of CHI₃ with minor amounts of liquid I-compounds. CHPhN₂ causes decolorisation of CPh₃Na, but gives only smearable products. With Na, Ph diphenyl ketone CHPhN₂ yields 3:4-diphenylosotriazole, m.p. 138—139°, the initial formation of CPhN₂Na being followed by addition of a second mol. of CHPhN₂ and liberation of Ph diphenyl ketone. CHN₂.CO₂Et and CPh₃Na react with evolution of gas and formation of ill-characterised products. CPh₃N₂ caused immediate decolorisation of CPh₃Na without evolution of N₂. Hydrolysis of the product with H₂O gives triphenylmethylbenzhydrylidenehydrazine, m.p. 171° (also obtained from CPh₃Cl and benzophenonehydrazine in C₆H₅N at 100°), hydrolysed to CPh₃, N₂H₄, and CPh₃.OH.

II. Treatment of the compound derived from CH₂N₂ and CPh₃Na with anhyd. AcOH in presence of Et₂O gives the expected amount of NaOAc, but no CH₂N₂ or MeOAc; the ethereal solution becomes yellow due to an unstable material regarded as isodiazomethane (I), (I) and BzOH afford

benzoylformylhydrazine (II), m.p. 158—159°, also obtained from NHBz.NH₂ and boiling anhyd. HCO₂H. (II) is transformed by successive treatment with boiling KOH-MeOH and PhCHO into benzoylbenzylidenhydrazine, m.p. 204°, and HCO₂H. It contains 2 active H (Zerevitinov). With PhNCO it affords the compound C₁₅H₁₃O₃N₃, m.p. 141° (turbid), becoming clear at 170°. It does not react with aldehydes. (I) and m-NO₂.C₆H₄.CO₂H yield m-nitrobenzoylformylhydrazine, m.p. 208° (also derived from m-NO₂.C₆H₄.NH.NH₂ and HCO₂H), hydrolysed and converted by PhCHO into benzaldazine and m-nitrobenzoylbenzylidenhydrazine. Picrylformylhydrazine, m.p. 188.5° (decomp.), obtained similarly by both methods, affords a semicarbazide derivative C₁₄H₁₀O₈N₆, m.p. 157.5—158° (decomp.). (I) and o-C₆H₄(CO₂H)₂ give a substance C₉H₈O₄N₂, m.p. 160°. BzBr and (I) yield a compound C₈H₇ON₂Br, m.p. 192° (slight decomp.), transformed by successive action of NaHCO₃ and PhCHO into benzaldehydebenzoylhydrazine, m.p. 206°. (I) and saccharin give the product C₈H₇O₃N₃S, m.p. 229° (decomp.). Formylhydrazine and BzOH in boiling Et₂O do not anion (II). H. W.

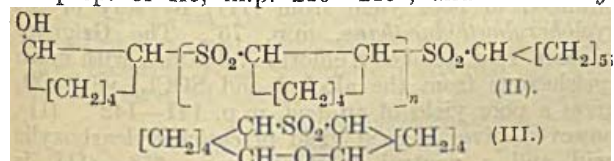
Magnesium for Grignard reagents. N. W. CUSA and F. S. KIPPING (J.S.C.I., 1934, 53, 213—214r).—Attention is directed to the great influence of the quality of the Mg on the yields of Grignar

reagents obtained with *cyclohexyl* chloride and bromide. H. W.

Preparation of thallium triethyl, triisobutyl, and triphenyl. S. F. BIRCH (J.C.S., 1934, 1132—1136).—A simplified apparatus is described for the prep. of Tl triaryls and trialkyls by the action of the appropriate Li alkyl or aryl (prep. by the method of Gilman *et al.*, A., 1932, 728) on TlR_2Cl in Et_2O or C_5H_{12} , or on TiCl_4 direct: $3\text{LiR} + 3\text{TiCl}_4 \rightarrow \text{TiR}_3 + 2\text{Ti} + 3\text{LiCl}$, all operations being carried out in N_2 . Thus from the appropriate pairs are obtained *Tl triphenyl* (60% yield), m.p. 188—189°, decomp. 215—216°, giving TiPh_2O in air, and TiPh_2OAc with $\text{AcOH} \cdot \text{C}_6\text{H}_6$: *Tl triethyl*, b.p. 50—51°/1.5 mm. (66%), similarly converted into TiEt_2OAc , which with aq. KCN gives the corresponding *cyanide*, darkens 240°, not melting at 310°; and *Tl triisobutyl*, b.p. 74—76°/1.6 mm. (73%), converted into *disobutylthallium acetate*, m.p. 215° (decomp.). From LiBu^β and TiEt_2Br a compound, b.p. 50—65°/3.2 mm., probably $\text{TiEt}_2\text{Bu}^\beta$, was obtained, but was not purified.

J. W. B.
Rupture of pentamethylene rings with conversion into paraffin hydrocarbons by platinum catalysts in presence of hydrogen. N. D. ZELINSKI and B. A. KAZANSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 168—170).—When heated with H_2 at 305—310° (Pt-C) methyl-, ethyl-, and propyl-*cyclopentane* yield mixtures of paraffin hydrocarbons, consisting chiefly of the *iso*-isomerides. R. T.

Reaction between sulphur dioxide and olefines. *cycloHexene*. D. S. FREDERICK, H. D. COGAN, and C. S. MARVEL (J. Amer. Chem. Soc., 1934, 56, 1815—1819).—*cycloHexene* (I) and liquid SO_2 in a little 95% EtOH and 2% H_2O_2 at 25—30° give (cf. Seyer and King, A., 1933, 1013) an amorphous compound (II; $n \approx$ about 39), softens and decomp. $> 200^\circ$, which is sol. only in CHCl_3 , $\text{C}_2\text{H}_2\text{Cl}_4$, PhNO_2 , and dioxan. Other methods of prep. of (I) are investigated. The presence of OH in (II) is proved by the prep. of *Ac*, m.p. 210—215°, and *chloroacetyl*,



m.p. 215—220°, derivatives, both of which have *M* about 6000. (II) is degraded by 17% NaOH to (I), *dicyclohexenyl sulphone*, m.p. 75°, and complex S-compounds, by 5% NaOH to *dodecahydrophenoxthine dioxide* (III), m.p. 138°, and a little (I), and by 90% KOH at 250° to (I), a *dicyclohexenyl*, b.p. 234° (*tetra-bromide*, m.p. 158°) [reduced (H_2 , PtO_2) to *dicyclohexyl*], *cyclohexene-sulphinic* or *-sulphonic acid* (*Ag* salt), and K_2SO_3 ; these compounds are probably formed from the intermediate di-2-hydroxycyclohexyl sulphone. H. B.

Influence of negative groups on reactions between nitrosobenzene and unsaturated compounds. A. POLVERINI (Gazzetta, 1934, 64, 409—415).—A change of colour to chestnut-yellow when a compound is mixed with PhNO in a neutral solvent

occurs with compounds containing two double linkings (*citral*, *geraniol*, *pyrrole*, *isoprene*, α -*ionone*, *linoleic acid*), more slowly when negative groups are present in crit. positions (*sorbic acid*). Compounds with only one double linking also react (CMe_2CHMe , *oleic acid*, *ricinoleic acid*, *pinene*, *terpineol*), more slowly when one negative group is present (*dihydrocarvone*, *atropic acid*, $\text{CHPh}:\text{CHAc}$, *cinnamaldehyde*, *coumarin*), or not at all when two such groups are present (*piperic*, *cinnamic*, *crotonic*, *fumaric acids*, *stilbene*).

R. K. C.

Molecular rearrangements involving spontaneous cleavage. C. B. WOOSTER and R. A. MORSE (J. Amer. Chem. Soc., 1934, 56, 1735—1737).— CNaPh_3 in liquid NH_3 and $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$ in Et_2O give $\gamma\gamma\gamma$ -*triphenylpropyl Et ether*, m.p. 111.5—112°, which with HI (const. b.p.) in N_2 affords $\gamma\gamma\gamma$ -*triphenylpropyl iodide* (I), m.p. 174.5—175°. Treatment of (I) with Na in liquid NH_3 , decomp. of excess of Na with NH_4NO_3 , and subsequent hydrolysis (H_2O) gives some CHPh_3 ; a mol. rearrangement involving spontaneous cleavage appears to take place. The probable mechanism is discussed. (I) and $\text{CPh}_3 \cdot \text{CH}_2\text{Cl}$ (cf. A., 1930, 762; 1932, 838) are unaffected by NaNO_3 in liquid NH_3 . H. B.

Influence of solvent on the course of reactions of organic molecules. H. LUTGERT (Z. Elektrochem., 1934, 40, 499—501).—A discussion of published work on the influence of dielectric const. and dipole moment. E. S. H.

Magneto-chemistry and the biradical formula. E. MULLER (Z. Elektrochem., 1934, 40, 542).—A discussion of magnetic susceptibility as a means of characterising substances of the type R_2 . E. S. H.

Supposed isomerisation of retene by sulphur. J. R. HOSKING and W. T. MCFADYEN (J.S.C.I., 1934, 53, 195—196t).—The suggestion (Beath, B., 1934, 43) that retene is isomerised by heating with S is shown to be without foundation. The hydrocarbon obtained from crude retene (from *abietene* or *colophony*) is *pimanthrene* (I), m.p. 86° (*picrate*, m.p. 131°; *styphnate*, m.p. 159°), and not an isomeride of retene. It is suggested that the “*isoretene*,” m.p. 86—87° (*picrate*, m.p. 127°), obtained by S dehydrogenation of *rimuene* (*loc. cit.*), and considered to be 1-methyl-6-*iso*-propylphenanthrene, is (I). The production of (I) is ascribed to the presence of *d*-*pimaric acid* or a congener in the crude resin acid products (cf. Rimbach, A., 1897, i, 254).

Preparation of s-acylarylcarbamides. N. PALIT (J. Indian Chem. Soc., 1934, 11, 479—483).— $\text{NH}_2 \cdot \text{CO} \cdot \text{NHAc}$ and NH_2Ph at 170—175° (5 hr.) give NH_3 , *s-acetylphenylcarbamide* (I), m.p. 183° (68.5%), $\text{CO}(\text{NHPh})_2$ (11.4%), and NH_4Ac (14.2%). *p*- $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ gives similarly (3 hr.) nearly pure *s-acetyl-p-tolylcarbamide* (II), m.p. 199—200°, but longer heating gives much *di-p-tolylcarbamide*. *p*-*Anisidine* gives (2 hr.) *s-acetyl-p-anisylcarbamide*, m.p. 220—221° (69%), *di-p-anisylcarbamide*, m.p. 235—237° (10%); more after longer heating), *anisylcarbamide*, and a substance, $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_2$, m.p. 220—221°. $\text{NH}_2 \cdot \text{CO} \cdot \text{NHBz}$ and NH_2Ph at 170° give NH_3 and *s-benzoylphenylcarbamide* (III), m.p. 204—205°; longer

heating gives much $\text{CO}(\text{NHPh})_2$. *s*-Benzoyl-*p*-tolyl-, m.p. 228—229°, and *p*-anisyl-carbamide, m.p. 219°, were similarly prepared. (I), (II), and (III) were previously assigned *as*-formulae. R. S. C.

Thio-*o*-toluidine. Preparation by synthesis and by the action of sulphur on *o*-toluidine in presence of litharge. H. H. HODGSON and H. V. FRANCE (J.C.S., 1934, 1140—1141).— $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ (I) and S yield mainly products in which S is *ortho* to NH_2 , whereas if PbO is present the chief product is 2 : 2'-diamino-5 : 5'-ditolyl sulphide (II), m.p. 96° (dihydrochloride, m.p. 248—249°; dipicrate, m.p. 186°; Ac_2 , m.p. 220°, and Bz_2 , m.p. 233°, derivatives; bisazo-compound with $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, m.p. 258°); highly-coloured by-products are kept at a min. by using an excess of (I) and keeping the temp. as low as possible. 5-Bromo-2-nitrotoluene (III) and the Na salt of 2-amino-5-tolyl mercaptan in EtOH yield 2'-nitro-2-amino-5 : 5'-ditolyl sulphide, m.p. 104° (hydrochloride, m.p. 187°; Ac , m.p. 143°, and Bz , m.p. 119°, derivatives; corresponding *azo*- β -naphthol, m.p. 194°), reduced by Fe dust and very dil. HCl to (II). (III) and Na_2S in boiling H_2O give 2 : 2'-dinitro-5 : 5'-ditolyl sulphide, m.p. 164°. 2 : 2'-Dinitro-5 : 5'-ditolyl disulphide, m.p. 163°, is obtained from (III) and Na_2S_2 in EtOH. 2 : 2'-Diamino-5 : 5'-ditolyl disulphide is unchanged when boiled with (I) alone or in presence of PbO. 5-Bromotoluene-2-azo- β -naphthol has m.p. 172°. H. W.

Chemistry of the Knoevenagel and similar reactions. L. H. SMITH and K. N. WELCH (J.C.S., 1934, 1136—1140).— CH_2Bz_2 and $p\text{-NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$ (I) at 155—170° in presence of a trace of NEt_3 yield $\alpha\alpha$ -dibenzoyl- β -*p*-dimethylamino-phenylethane, m.p. 132—133°. (I) and the respective phenol afford 4-dimethylamino-4'-hydroxydiphenylmethane, m.p. 107—108°, 2' : 4'-dihydroxydiphenylmethane, m.p. 172.5°, 1-dimethylaminobenzyl- β -naphthol, m.p. 143°, and 4-dimethylaminobenzyl- α -naphthol, m.p. 148—149°. Condensation with *m*-2-xylenol led only to a glassy solid, whilst quinol did not react. Reactions with phenols do not proceed in this direction in the presence of a trace of acid, probably owing to autocondensation of the alcohol; change does not proceed smoothly in $\text{C}_6\text{H}_5\text{N}$. With $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ and NHPh_2 , (I) yields *p*-tolyl-*p*-dimethylaminobenzylamine, m.p. 101°, and diphenyl-*p*-dimethylaminobenzylamine, m.p. 80—81°, respectively, whereas $o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ affords methylenebis-*o*-nitroaniline, m.p. 195°. NPhMe_2 and (I) readily give 4 : 4'-tetramethyldiaminodiphenylmethane (II); contrary to von Braun *et al.* (A., 1912, i, 968) (I) is probably an intermediate in the formation of (II) from NPhMe_2 and CH_2O . The experiments suggest that the function of *sec.* bases as catalysts in Knoevenagel's reaction is due to the formation of substances of the type $\text{NR}_2\cdot\text{CHR}'\cdot\text{OH}$ and an electronic theory is discussed. H. W.

Derivatives of 4 : 4'-tetramethyldiaminodiphenylmethane. D. C. R. JONES and F. A. MASON (J.C.S., 1934, 1190—1192).—Chlorination of $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ (I) in AcOH containing NaOAc gives the 3 : 3'- Cl_2 -derivative, b.p. 265°/20 mm. (picrate, m.p. 173°). The corresponding 2- Cl -, m.p. 63°, and 2- Br -, m.p. 68°, -derivatives are obtained from

the very unstable 2-diazonium compound by the Sandmeyer-Gattermann reaction. The 2 : 2'- Cl_2 -, m.p. 96°, and 2 : 2'- Br_2 -, b.p. 265°/20 mm., m.p. 103°, -derivatives are derived from the 2 : 2'-bisdiazonium compound. The I- or I_2 -compounds could not be prepared similarly. Bromination of (I) in AcOH affords the 3 : 3'- Br_2 -derivative (II), b.p. 274—279°/20 mm. (picrate, m.p. 188°), whereas attempted monobromination in AcOH, CHCl_3 , CCl_4 , or $\text{C}_2\text{H}_2\text{Cl}_4$ led to (II) and unchanged (I). ClSO_3H and (I) in $\text{C}_2\text{H}_2\text{Cl}_4$ yield 4 : 4'-tetramethyldiaminodiphenylmethane-2 : 2' (?) -disulphonic acid (Na salt). $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$, Me_2SO_3 , and NaOH give diphenylmethane-3 : 3'-bistrimethylammonium iodide, m.p. 228°. H. W.

Reduction of some oximes and their acetyl derivatives by aluminium amalgam. V. CERCHEZ and (MME.) DUMITRESCO-COLESIU (Bull. Soc. chim., 1934, [v], 1, 852—856).—Oximes or their Ac derivatives (I) with Al-Hg give > 50% yields of the amines or acetamides. In some cases partial hydrolysis of Ac occurs, because (I) exists partly as *O*-Ac compound. In this way are obtained heptyl-, benzyl- (and its Ac derivative), *o*-hydroxy- and *o*-methoxybenzyl- (and its Ac derivative), and benzhydrylamine (and its Ac derivative). $\text{CPh}_2\cdot\text{N}\cdot\text{OH}$ has m.p. 71° (cf. lit.). R. S. C.

Compounds of ethyl iodoacetate with benzyl-dimethylamine and ethylpiperidine. (MME.) M. CHALEIL (Bull. Soc. chim., 1934, [v], 1, 738—742).—The gel forms of the methiodide, m.p. 129—130° (decomp.), of Et benzylmethylaminoacetate [from $\text{CH}_3\text{Ph}\cdot\text{NMe}_2$ and $\text{CH}_2\text{I}\cdot\text{CO}_2\text{Et}$ (I)] and ethiodide, hygroscopic, cryst. (not obtained pure), of *N*-carbethoxymethylpiperidine [from (I) and ethylpiperidine] do not give Liesegang rings. NHMe_2 removes halogen acids from cyclohexyl bromide (II) or iodide. 4-Methylcyclohexyl iodide (from the alcohol and PI_3), b.p. 86.5—87.5°, loses HI slowly when heated with NNaAcPh in xylene. cyclohexylcarboxylamide (III) and NaOCl give a poor yield of cyclohexylamine, also obtained in poor yield from (III) by way of the cyclohexylmethylurethane, m.p. 75°. The Grignard reagent from cyclohexyl chloride (obtained with much cyclohexene from the alcohol and SOCl_2) with CO_2 gives a poor yield of an acid, m.p. 141—142°. (II), however, gives a good yield of cyclohexylcarboxylic acid and a neutral substance, m.p. 65°. (III) is obtained in good yield from the NH_4 salt in gaseous NH_3 at 120—180°. The 2- and 4-methyl homologues are similarly prepared, the former giving only the *cis*-amide, m.p. 152—153°. R. S.

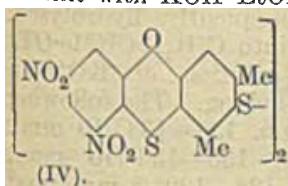
Isomeric *p*-aminoazoxybenzenes. D. VORLANDER and H. SCHUSTER (J. pr. Chem., 1934, [II], 140, 193—208).—The separation of the *a*-, m.p. 138—139°, and *b*-forms, m.p. 136° (corr.) (cf. lit.), *o*-*p*-aminoazoxybenzene (I) is improved. The ing derivatives are prepared, the m.p. given being that of the *a*-form: benzylidene, m.p. 10, 134°; anisylidene (II), m.p. 132° (215°), 124° (201°); cinnamylidene (III), m.p. 126°, 133°; *p*-phenylbenzylidene (IV), m.p. 174° (274°), 179° (273°); *p*-terephthalylidene (bis-derivative) (V), m.p. 227° [293° (decomp.)], 200° [282° (decomp.)]. (II), (III), (IV), and (V) form

liquid crystals, the m.p. given in parentheses being those of anisotropic melting. The corresponding derivatives of *p*-aminoazobenzene have m.p. 131°, 151° (185°), 143°, 208° (250°), and 251° (285°), respectively, the last four forming liquid crystals. Both forms of (I) give colourless hydrochlorides, wherefore formulae of the type, $\frac{NR}{NR'} > O$ are suggested. R. S. C.

Normal aryl sulphates. L. DENIVELLE (Compt. rend., 1934, **199**, 211—213).—ClSO₂·OPh and PhOH in C₆H₅N at 120° yield *Ph₂ sulphate*, b.p. 144—146°/1 mm.; *guaiacyl*, b.p. 98°/1 mm., m.p. 54°, *p*-tolyl, b.p. 114—116°/14 mm., m.p. 64—65°, *m*-tolyl, b.p. 115°/14 mm., m.p. 58.5°, and *Ph p*-tolyl, m.p. 57°, sulphates are similarly obtained. H. W.

Preparation of *p*-iodophenol and its derivatives. F. B. DAINS and F. EBERLY (Trans. Kansas Acad. Sci., 1933, **36**, 114—117).—Noelting and Wrzesinsky's method (Ber., 1875, **8**, 820) has been modified. Benzyl, m.p. 62°, and *p*-nitrobenzyl, m.p. 145°, *p*-iodophenyl ethers; methylene, m.p. 114°, ethylene, m.p. 175—177°, and trimethylene, m.p. 149°, di-*p*-iodophenyl ethers are described. CH. ABS.

Derivatives of *s*- and *as*-*m*-xyleneols. E. KATSCHER and H. LEHR (Monatsh., 1934, **64**, 236—246).—The orientation of the *m*-5-xylenoldisulphonyl chloride (I), m.p. 117—119° (A., 1931, 83), as the 2:4-disulphonyl chloride (disulphonamide, m.p. 206—208°) is shown by the following data. (I) with 20% aq. NaOAc in COMe₂ gives *m*-xylene-2:5-sulphoquinone-4-sulphonyl chloride, decomp. > 300°. Addition of HCl and 30% H₂O₂ to the filtrate from the prep. of (I) from *m*-5-xyleneol and OH·SO₂Cl affords a trichloro-*m*-xyleneol (II), m.p. 175—177°; similar treatment of the KOH hydrolysis product of (I) gives (II) and the *K* salt, decomp. > 300°, of a dichloro-*m*-xyleneolmonosulphonic acid. Reduction of (I) with Zn-AcOH-HCl affords 2:4-dithiol-*m*-5-xyleneol (III), m.p. 75° [*Bz₂* derivative, m.p. 160—161°; *Ac₂* derivative, m.p. 124—125°, also by boiling Zn-AcOH-Ac₂O-NaOAc on (I)], converted by picryl chloride in EtOH at 100° into a dipicryl derivative, m.p. 237—238° (positive FeCl₃ reaction), converted by treatment with KOH-EtOH *in situ* into bis-2:4-dinitro-



5:7-dimethylphenoxethin 6:6'-disulphide (IV), m.p. 255—257°. With aq. CH₂Cl·CO₂Na (V) at 100° the *K* salt of (III) affords *m*-5-xyleneol-2:4-di-(thioglycollic acid), m.p. 151°.

m-4-Xyleneol-5-sulphonyl chloride (*loc. cit.*) [O-Ac derivative, m.p. 62°; sulphonanilide, m.p. 142—143° (O-Ac derivative, m.p. 105°), converted by CH₃N₂ into the sulphonmethylanilide, m.p. 111—112°] with 2*N*-KOH, with dry NH₃ in Et₂O solution, or with 20% NaOAc in COMe₂ affords 1:3:1':3'-tetramethyldiphenyl-4:5:4':5'-sulphonyl-ide, no decomp. at 300°. Reduction (Zn-HCl-AcOH) of (VI) affords 5-thiol-*m*-4-xyleneol, m.p. 91—93° (*Bz₂*, m.p. 72°, liquid Ac., and monopicryl, m.p. 164°, derivatives). (VI) with 1 mol. of (V) gives *m*-4-xyleneol-5-thioglycollic acid, m.p. 155° (VII), the 4-carboxymethyl ether, m.p. 190—192°, of which is obtained

when an excess of (V) is used. With OH·SO₂·Cl (VII) gives a substance which is probably a thio-indigotin derivative. J. W. B.

Molecular rearrangements involving optically active radicals. V. Rearrangement of optically active phenyl alkyl ethers. M. M. SPRUNG and E. S. WALLIS (J. Amer. Chem. Soc., 1934, **56**, 1715—1720).—PhOBu^β and H₂SO₄-AcOH at 105—108° give (cf. Niederl and Natelson, A., 1932, 510) C₄H₈, Bu^βOAc, PhOH, C₆H₄Bu^β-OH (I) (yield about 8.5%) (acetate, m.p. 112°), *o*- and *p*-OH·C₆H₄·COMe, and OH·C₆H₄·SO₃H; a better yield of (I) is obtained when rearrangement is effected with ZnCl₂ in AcOH. *m*-C₆H₄Me·OBu^β and H₂SO₄-AcOH afford C₄H₈, *m*-C₆H₄Me·OH, *m*-cresolsulphonic acid, (probably) 4-acetyl-*m*-cresol, 4-sec.-butyl-*m*-cresol, and phenolic material of b.p. 260—275°/760 mm.; *p*-tolyl Bu^β ether, b.p. 97—99°/14 mm., similarly affords C₄H₈, Bu^βOAc (trace), *p*-C₆H₄Me·OH, *p*-cresolsulphonic acid, 3-acetyl-*p*-cresol, 3-sec.-butyl-*p*-cresol, m.p. 44—44.5° (acetate, m.p. 80—81°), and (probably) some dibutylcresol. Similar rearrangement of *d*-PhOBu^β, b.p. 86—90°/16 mm., [α]_D²⁵ +30.02°, *d*-*m*-C₆H₄Me·OBu^β, b.p. 103—108°/17 mm., [α]_D²⁵ +27.35°, and *d*-*p*-C₆H₄Me·OBu^β, b.p. 97—100°/14 mm., [α]_D²⁵ +23.14° [prepared from Bu^βBr, [α]_D²⁵ -19.77°, and the (hydrated) NaOAr at 110—120°], gives dextrorotatory alkylphenols; partial racemisation occurs. Possible mechanisms are discussed. H. B.

I. Influence of the position of thiol and methylthiol groups on the colour of monosubstituted β -naphtholazo-dyes. E. JUSA and G. BREUER. **II. Influence of position isomerism and *S*-methylation on the colour of thiol- α -naphtholazo-dyes.** E. JUSA and L. GRUN (Monatsh., 1934, **64**, 247—266, 267—286).—I. Reduction (Zn-HCl-EtOH) of *O*-carbethoxy- β -naphthol-8-sulphonyl chloride gives the corresponding 8-thiol compound, b.p. 225—235°/20 mm. [picryl derivative, m.p. 164°; *Me* thioether (I), b.p. 235—245°/25 mm.], oxidised by FeCl₃ to the 8:8'-disulphide (II), m.p. 95°, and hydrolysed by aq. EtOH-KOH to 8-thiol- β -naphthol (III), m.p. 92° (*Ag* and picryl, m.p. 179°, derivatives), converted by CH₂Cl·CO₂Na-KOH into β -naphthol-8-thioglycollic acid, m.p. 146°. Hydrolysis (aq. EtOH-KOH) of (II) gives bis- β -naphthol 8:8'-disulphide, m.p. 196°, and (I) gives 8-methylthiol- β -naphthol (IV), m.p. 96°. (III) and (IV) when coupled with *p*-NO₂·C₆H₄·N₂Cl give, respectively, 1-*p*-nitrobenzeneazo-8-thiol- and -8-methylthiol- β -naphthol. By similar methods from *O*-carbethoxy- β -naphthol-7-sulphonyl chloride (PCl₅ on the *K* sulphonate) are obtained the corresponding 7-thiol compound, m.p. 109° (picryl derivative, m.p. 152°; *Me* thioether, m.p. 87°), the 7:7'-disulphide, m.p. 129°, 7-thiol- β -naphthol, m.p. 148° (*Ag*, picryl, m.p. 203°, and *Bz₂*, m.p. 159°, derivatives; *Me* thioether, m.p. 109°), β -naphthol-7-thioglycollic acid, m.p. 149°, bis- β -naphthol 7:7'-disulphide, m.p. 205°, and 1-*p*-nitrobenzeneazo-7-thiol- and -7-methylthiol- β -naphthol. Similarly are obtained 6-thiol-*O*-carbethoxy- β -naphthol (picryl derivative, m.p. 159°), 6-thiol- β -naphthol (picryl, m.p. 243°, and *Bz₂*, m.p. 211°, derivatives), β -naphthol-6-thioglycollic

acid, m.p. 157°, and 1-p-nitrobenzeneazo-6-thiol- and -6-methylthiol- β -naphthol.

II. By application of similar methods to various α -naphtholsulphonic acids are obtained, from α -naphthol-3-sulphonic acid (Gebauer-Fülneegg *et al.*, A., 1929, 1440), *Et O-carbethoxy- α -naphthol-3-sulphonate*, m.p. 66° [3-sulphonanilide, m.p. 119°, from the sulphonyl chloride (V), hydrolysed by boiling KOH-EtOH to α -naphthol-3-sulphonanilide, m.p. 172°]. Reduction (Zn-HCl-AcOH) of (V) gives 3-thiol-*O-carbethoxy- α -naphthol*, b.p. 178°/4 mm. (*Me thioether*, b.p. 200°/15 mm.; *picryl* derivative, m.p. 167°), hydrolysed by aq. EtOH-KOH (N₂) to 3-thiol- α -naphthol, m.p. 108° (*Me thioether*, m.p. 63°), and oxidised by FeCl₃ to the 3:3'-disulphide, m.p. 113°, hydrolysed to bis- α -naphthol 3:3'-disulphide, decomp. 240°. α -Naphthol-3-thioglycollic acid, m.p. 133°, 2-p-nitrobenzeneazo-3-thiol- and -3-methylthiol- α -naphthol are also obtained. Similarly from α -naphthol-4-sulphonic acid and the derived 4-thiol-*O-carbethoxy- α -naphthol* (VI) (*picryl* derivative, m.p. 160°) and 4-thiol- α -naphthol (1: derivative, m.p. 154°) are obtained: α -naphthol-4-thioglycollic acid, m.p. 125°, and [with excess of CH₂Cl·CO₂Na on (VI)] 1-carboxymethoxy-naphthalene-4-thioglycollic acid, CO₂H·CH₂·O·C₁₀H₆·S·CH₂·CO₂H, m.p. 223°, 2-p-nitrobenzeneazo-4-thiol- and -4-methylthiol- β -naphthol. From α -naphthol-5-sulphonic acid are prepared *Et O-carbethoxy- α -naphthol-5-sulphonate*, m.p. 77°, and the corresponding 5-thiol compound (*picryl* derivative, m.p. 158°), the *Bz₂* derivative, m.p. 193°, of 5-thiol- α -naphthol, α -naphthol-5-thioglycollic acid, m.p. 135°, 2-p-nitrobenzeneazo-5-thiol- and -5-methylthiol- α -naphthol. The tinctorial properties of these azo-dyes are tabulated, methylation of SH deepening the colour tone. J. W. B.

Formation of an intermediate product in the nitration and simultaneous demethylation of 6:7-dimethoxy-1:2:3:4-tetrahydronaphthalene. H. J. LEWIS and R. ROBINSON (J.C.S., 1934, 1253—1255).—6:7-Dimethoxy-1:2:3:4-tetrahydronaphthalene, b.p. 125°/1 mm., m.p. 53—54°, obtained by reduction of 6:7-dimethoxy-1-keto-1:2:3:4-tetrahydronaphthalene with Zn-Hg and HCl, is converted by HNO₃ (d 1.4) in AcOH at > 10° into 9-nitro-6-keto-7-methoxy-1:2:3:4:6:9-hexahydronaphthalene (I), m.p. 92—93° (decomp.) according to the rate of heating. In boiling EtOH (I) passes rapidly into 5(or 8)-nitro-6-hydroxy-7-methoxy-, m.p. 133°, transformed by Me₂SO₄ into 5-nitro-6:7-dimethoxy-, m.p. 88—89°, -1:2:3:4-tetrahydronaphthalene. The bearing of this observation on theories of the mechanism of aromatic substitution is discussed. H. W.

Aromatic sulphides. C. LEFEVRE and C. DESGREZ (Compt. rend., 1934, 199, 300—302; cf. this vol., 886).—Application of the authors' method to polyhydroxy-compounds containing two C₆H₅ rings at about 150° generally gives disulphides in which the ·S·S· group unites the two aromatic nuclei at positions *para* to OH or NH₂. Trihydroxybenzophenone, however, gives the compound, [OH·C₆H₄·CO·C₆H₄(OH)₂·S]₂. o-OH·C₆H₄·SO₃H with PhOH and *m*-C₆H₄(OH)₂ affords dihydroxy- and trihydroxy-diphenylsulphone,

respectively, whilst aminohydroxy- and aminodihydroxy-diphenylsulphone are obtained by similar treatment of *m*-NH₂·C₆H₄·SO₃H. H. W.

Transpositions in the cyclohexane series. The aptitude of the wandering radical towards migration is influenced by its position in space. M. TIFFENEAU and B. TCHOUBAR (Compt. rend., 1934, 199, 360—362).—2-Chloro-1-methylcyclohexanol-A, b.p. 75—76°/14 mm. (from MgMeI and chlorocyclohexanone), and -B, b.p. 87—88°/14 mm. (from methylcyclohexene and HOCl), are de-halogenated by Mg to 2-methylcyclohexanone with a little acetylcylopentane (I), and (I), respectively. 2-Chloro-1:4-dimethylcyclohexanol-A, b.p. 92—94°/17 mm. (from MgMeI and 2-chloro-4-methylcyclohexanone), and -B, b.p. 101—102°/18 mm. (from HOCl and 1:4-dimethyl- Δ^1 -cyclohexene), similarly afford 2:4-dimethylcyclohexanone with a little 1-acetyl-3-methylcyclopentane (II), and (II), respectively. 2-Chloro-1:5-dimethylcyclohexanol-A, b.p. 88—90°/14—15 mm. (from MgMeI and liquid 2-chloro-5-methylcyclohexanone), and -B, b.p. 83—84°/13—14 mm. (from MgMeI and cryst. 2-chloro-5-methylcyclohexanone), give 2:5-dimethylcyclohexanone with a little 3-acetyl-3-methylcyclopentane (III), and (III), respectively. The aptitudes of the CH₂ and Me towards migration are thus influenced by their position in space. H. W.

Oxidation of 1-methyl- Δ^1 -cyclohexene by selenium dioxide. E. URION (Compt. rend., 1934, 199, 363—365).—The main product of the oxidation of 1-methyl- Δ^1 -cyclohexene, b.p. 110—111°/760 mm., by SeO₂ in AcOH is 2-methyl- Δ^2 -cyclohexenyl acetate, b.p. 84°/23 mm. (2-methyl- Δ^2 -cyclohexenol, b.p. 80°/18 mm.), whilst in EtOH 1-ethoxy-2-methyl- Δ^2 -cyclohexene, b.p. 61—62°/15 mm., mainly results. In H₂O 2-methyl- Δ^2 -cyclohexenone, b.p. 69—70°/16 mm., 178—179°/760 mm., is the chief product. H. W.

Synthesis of hydroxyalkyl- (α -hydroxyethyl)-benzenes and of the corresponding ethers. R. QUELET (Compt. rend., 1934, 199, 483—485).—Compounds, C₆H₄R·CHClMe, are converted into substances, C₆H₄R·CHMe·OH, when heated with a dil. solution of NaOH or KOH in H₂O·COMe₂ or when transformed by NaOAc in AcOH into the corresponding acetates, which are subsequently hydrolysed. C₆H₄R·CHClMe is converted into C₆H₄R·CHMe·OEt by gradual addition to a solution of KOH in EtOH at 80° and subsequent boiling. The following are new: *p*- α -acetoxyethyl-, b.p. 136—138°/16 mm., 5-methyl-2- α -acetoxyethyl-, b.p. 135—136°/10 mm., 2-methyl-5- α -acetoxyethyl-, b.p. 128—129°/8 mm., and 2-methyl-4- α -acetoxyethyl-, b.p. 131—132°/10 mm., -anisole: methoxy-4- α -methoxyethyl-, b.p. 105°/15 mm., -4- α -ethoxyethyl-, b.p. 114—115°/15 mm., -4- α -isopropoxyethyl-, b.p. 118—119°/16 mm., 3-methoxy-1-methyl-4- α -methoxyethyl-, b.p. 116—117°/16 mm., -methoxy-1-methyl-4- α -ethoxyethyl-, b.p. 126°/18 mm., 2-methoxy-1-methyl-4- α -methoxyethyl-, b.p. 126°/16 mm., 2-methoxy-1-methyl-4- α -ethoxyethyl-, b.p. 128—129°/16 mm., 1-methoxy-2-methyl-5- α -methoxyethyl-, b.p. 16 mm., 1-methoxy-2-methyl-5- α -ethoxyethyl-, b.p. 18 mm., 2-methoxy-1-methyl-5- α -methoxyethyl-4-isopropyl-, b.p. 139—140°/16 mm., and 2-methoxy-1-

methyl-5- α -ethoxyethyl-4-isopropyl-, b.p. 132—133°/9 mm., -benzene. H. W.

Mechanism of anionotropic change and the fate of the mobile anion. H. BURTON (J.C.S., 1934, 1268—1269).—Under the same conditions of temp., time, and concn. as those used for the production of cinnamyl acetate (I) and *p*-nitrobenzoate (II) from α -phenylallyl *p*-nitrobenzoate (III), and $\text{NMe}_4\cdot\text{OAc}$ (IV) in Ac_2O (A., 1928, 880), (II) and (IV) in Ac_2O afford very little (I), thus proving that (II) is not an intermediate in the change (III) \rightarrow (I) and confirming the mechanism previously deduced for anionotropic change (*loc. cit.*). J. G. A. G.

Tetraphenylmethane dyes. II. R. N. SEN and M. M. GHOSH (J. Indian Chem. Soc., 1934, 11, 455—461; cf. A., 1931, 840).—By condensation of malachite-green or crystal-violet with NaOAc and the appropriate amine, phenol, or ether at 160—180° are prepared *hexa-* (I), m.p. 115—116° (*Ac* derivative, m.p. 66—68°), and *octa-methyltetra-amino-*, m.p. 102—104°, *hexamethyltri-amino-p-hydroxy-*, m.p. 102° (*Ac* derivative, m.p. 84—85°), -2:4-dihydroxy-, m.p. > 270° (Bz_2 derivative, m.p. 117—119°), -*p*-methoxy-, m.p. 140—144°, -2:4-dimethoxy-, m.p. 122°, and -4-hydroxy-3-methyl-, m.p. 95° (*Ac* derivative, m.p. 64—65°), *tetra-* (II), m.p. 102° (*Ac* derivative, m.p. 90°), and *hexa-methyltri-amino-*, m.p. 107—110°, *tetramethyldi-amino-p-hydroxy-*, m.p. 75° (*Ac* derivative, m.p. 93—95°), -2:4-dihydroxy-, m.p. 124—126° (Bz_2 derivative, m.p. 113°), -*p*-methoxy-, m.p. 90—95°, -2:4-dimethoxy-, m.p. 85—87°, and -4-hydroxy-3-methyl-tetraphenylmethane, m.p. 113—115° (*Ac* derivative, m.p. 90—91°). (I) and (II) led to *p*-(*hexamethyltri-*, m.p. 116—117°, and *p*-(*tetramethyldi-amino*triphenylmethyl)benzeneazo- β -naphthylamine, m.p. 160—162°. The colours produced on dyeing are listed. R. S. C.

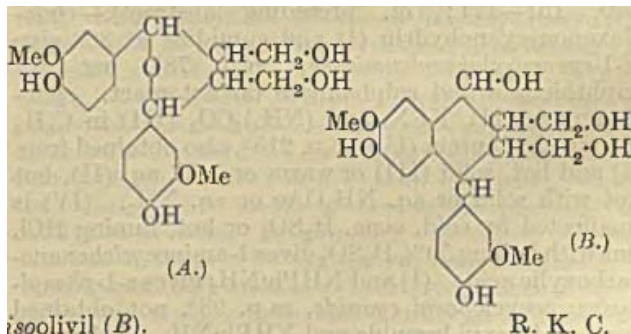
Cholesterols. T. RUEMELE (Pharm. Zentr., 1934, 75, 562—565).—A review. S. C.

Merino fleece. II. Rapid method of separating cholesterol and "ischolesterol" of wool wax. M. R. FRENEY (J.S.C.I., 1934, 53, 289—290r).—The Tswett method of separating closely related coloured compounds by chromatographic adsorption in an Al_2O_3 column has been applied to the separation of the colourless sterols of wool wax. By this method preps. with characteristics closely resembling those of cholesterol (I) and ischolesterol (II) were obtained with comparative ease. The laevorotatory (I) was retained in the upper portions of the column, whilst the dextrorotatory (II) was washed down into the lower layers.

Salts of ergosteryl sulphate: preparation and antirachitic activity on irradiation in aqueous medium. S. NATELSON, A. E. SOBEL, and B. KRAMER (J. Biol. Chem., 1934, 105, 761—765).—*K*, m.p. 225° (decomp.), *Na*, m.p. 186° (decomp.), and *Li*, m.p. 170° (decomp.), ergosteryl sulphates and *Li* cholesteryl sulphate, m.p. 150° (decomp.), were prepared by the action of the corresponding hydroxide on the pyridine steryl sulphate. The *Li* salts are the most sol., giving soapy solutions in H_2O . The ergosteryl salts become antirachitic on irradiation. An aq. solution of the irradiated *Li* salt, administered sub-

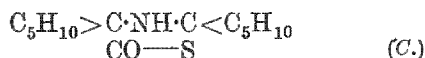
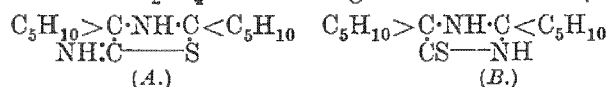
cutaneously, intravenously, or orally, cures rickets in rats. C. G. A.

Constitution of olivil. Products of oxidation of isoolivil. B. L. VANZETTI and P. DREYFUS (Gazzetta, 1934, 64, 381—399; cf. A., 1929, 1064).—Oxidation of the alkyl derivatives of isoolivil with $\text{KMnO}_4 + \text{KOH}$ (11 O) yields two classes of substances, (a) neutral substances (phthalides) and (b) sparingly sol. acids. Certain of these and derived products have been identified in the case of dimethylisoolivil with compounds previously synthesised (A., 1931, 226), and in the case of the *Me Et* and *Et*, derivatives with compounds now described. Ethylvanillic acid and SO_2Cl_2 yield the *chloride* (I), m.p. 73°, b.p. 173—174°. Condensation of (I) with veratrole in presence of AlCl_3 yields 3:4:3'-trimethoxy-4'-ethoxybenzophenone (II), m.p. 107.5—108°, whilst with ethylguaiaicol it yields 3:3'-dimethoxy-4:4'-diethoxybenzophenone, m.p. 108—109°, and 4:3'-dimethoxy-3:4'-diethoxybenzophenone (III), m.p. 125°. Ethylisovanillic acid (improved prep.) yields the *chloride*, b.p. 275—280°, which condenses with veratrole to give 4:3':4'-trimethoxy-3-ethoxybenzophenone (IV), m.p. 129—129.5°, or with ethylguaiaicol to give (III) and 4:4'-dimethoxy-3:3'-diethoxybenzophenone, m.p. 135—136.5°. Dimethylisoolivil yields (a) 4:5-dimethoxy-2-(3':4'-dimethoxyphenyl)phthalide, m.p. 188° (not 238°, as previously given), and (b) 4:5:3':4'-tetramethoxy-2-benzoylbenzoic acid, m.p. 223° (*Me* ester, m.p. 161.5°). The latter yields the corresponding benzylbenzoic acid (c) by reduction, 3:4:3':4'-tetramethoxybenzophenone (d) when heated with *Cu* powder, and 2:3:6:7-tetramethoxyanthraquinone (e) on treatment with 80% H_2SO_4 . Ethylated methylisoolivil, m.p. 189°, yields the homologous 5:3':4'-trimethoxy-4-ethoxy-derivatives: (a), m.p. 176—177°, (b), m.p. 184°, (c), m.p. 158.5—159.5°, (d), (IV), and (e) 2:3:6-trimethoxy-7-ethoxyanthraquinone, m.p. 290° (V). Methylated ethylisoolivil, m.p. 168°, yields the homologous 4:5:3'-trimethoxy-4'-ethoxy-derivatives: (a), m.p. 148°, (b), m.p. 219—220°, (c), m.p. 167°, (d) (II), and (e) the anthraquinone derivative (V). Diethylisoolivil yields the homologous 5:3'-dimethoxy-4:4'-diethoxy-derivatives: (a), m.p. 169°, (b), m.p. 213°, (c), m.p. 187°, (d), (III), m.p. 128—128.5°, and (e) 2:6-dimethoxy-3:7-diethoxyanthraquinone, m.p. 288°. Provisional formulæ are suggested for olivil (A) and



Cyanohydrins. H. T. BUCHERER and W. BRANDT (J. pr. Chem., 1934, [ii], 140, 129—150).—*cyclo*-Hexanecyanohydrin (I) is partly decomposed by distillation at 27—49 mm. With conc. HCl at room

temp. and then at 100° it gives an 83% yield of 1-hydroxycyclohexane-1-carboxylic acid (II), or, under other conditions, 39.2% of (II), 19.6% of the amide (III) of (II), and 26.5% of a compound, $C_{13}H_{21}O_2N$, m.p. 195°. The NH_4 salt, m.p. 178—198° (closed tube), of (I) gives at 150—160° NH_3 , (I), and (III). (II), cyclohexanone, and hot conc. HCl give a poor yield of a substance, m.p. 39°, b.p. 160—167°/20 mm. [probably Δ^1 -cyclohexenyl 1-hydroxycyclohexanecarboxylate, since it is insol. in cold NaOH, but hydrolysed by hot KOH-EtOH to (I)], also obtained as a by-product in the hydrolysis of (I). (II) with $SOCl_2$ gives a poor yield of (?) 1-carboxycyclohexyl 1-hydroxycyclohexanecarboxylate, m.p. 156—158°, but with PBr_3 only an oil. (I) and dry NH_3 give the amino-nitrile, m.p. 186—195° (50% yield), hydrolysed by hot 50% H_2SO_4 to 1-aminocyclohexanecarboxylic acid, m.p. 320° (closed tube) (lit. 334—335°), and giving, when diazotised, (II) and an oil. (I) and solid $(NH_4)_2CO_3$ give 1:1-pentamethylenehydantoin, m.p. 215° (see following abstract); similar substances, m.p. 210—214°, and 174—175°, are obtained from 3-methylcyclohexanone- and acetone-cyanohydrins, respectively. 1-Phenylhydrazino-1-cyanocyclohexane and H_2SO_4 , under certain conditions only, give a 16% yield of the amide, m.p. 124—128°, and with hot conc. HCl give tetrahydrocarbazole. 1- β -Naphthylaminocyclohexyl cyanide and H_2SO_4 give the amide, m.p. 184—187° (hydrochloride, m.p. 210—222°). (I) and NH_4HS under various conditions give an oil, an indefinite substance, m.p. about 70—75°, or a substance, m.p. 225° (hydrochloride, m.p. 270—271°), probably (A) or (B), which with conc. H_2SO_4 at 50—60° gives the substance (C),



m.p. 105°, and with hot 10% H_2SO_4 gives 1-aminocyclohexanecarboxylic acid. Substances similar to (A) or (B), m.p. 169—176°, 155—156°, and 58—63° (hydrolysed to the corresponding NH_2 -acid), were obtained from 3-methylcyclohexanone-, acetone-, and Me Et ketone-cyanohydrins, respectively. R. S. C.

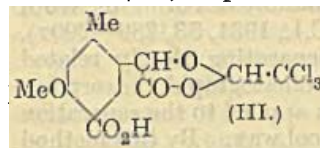
Hydroxy-nitriles from cyclic ketones. H. T. BUCHERER and H. BARSCH (J. pr. Chem., 1934, [ii], 140, 151—171; cf. preceding abstract).—cyclo-Hexanonecyanohydrin (I) and cumidine at 80° give N-1-cyanocyclohexylcumidine, m.p. 78°, but Na naphthionate and sulphanilate do not react. cyclo-Hexanone (II), KCN, and $(NH_4)_2CO_3$ (III) in C_6H_6 give the hydantoin (IV), m.p. 215°, also obtained from (I) and hot, solid (III) or warm or cold, aq. (II), but not with solid or aq. NH_4OAc or aq. NH_3 . (IV) is unaffected by cold, conc. H_2SO_4 or hot, fuming HCl, but with boiling 50% H_2SO_4 gives 1-aminocyclohexanecarboxylic acid. (I) and $NHPh \cdot NH_2$ gives s-1-phenylhydrazinocyclohexyl cyanide, m.p. 98°, not obtained from cyclohexyl bromide and $NHPh \cdot NH_2$. 1-Anilino-cyclohexyl cyanide and 50% H_2SO_4 at 90—100° give the anilino-acid, the hydrochloride of which gives amorphous substances with Ac_2O , but at 211—220° yields NH_2Ph . (I) and cold, fuming HCl give a sub-

stance (V), $C_{13}H_{21}O_2N$, m.p. 195.5—196°, the 1-OH-acid (VI), and a compound, m.p. 85° (probably a mixture), which with aq. Na_2CO_3 gives a substance, m.p. 130°. (I) and cold EtOH-HCl give (V) and (VI). (V) is also obtained from (I) and cold, conc. H_2SO_4 , is stable to conc. H_2SO_4 , but with hot, conc. HCl gives (VI). (VI) and NH_2Ph or $NHPh \cdot NH_2$ at 100° give the anilide, m.p. 167°, and phenylhydrazide, m.p. 185°, respectively. (VI) and $SOCl_2$ give a substance, m.p. 153°. The NH_4 salt of (VI) at 140—160° gives a substance, m.p. 85—92°. 3-Methylcyclohexanone affords a cyanohydrin, which with NH_2Ph with or without KCN yields resins; 2-methylcyclohexanone-cyanohydrin, however, affords 1-anilino- (both methods), m.p. 126°, and 1-p-toluidino-2-methylcyclohexyl cyanide, m.p. 135°, and with solid (III) a substance, m.p. 207°, but yields indefinite substances with fuming HCl. R. S. C.

Polar structure of aromatic betaines. G. DEVOTO (Gazzetta, 1934, 64, 371—380).—Measurements are recorded of the dielectric const. of the following betaines: o-, m-, and p- $NMe_3^+ \cdot C_6H_4 \cdot CO_2^-$, o-, m-, and p- $NMe_3^+ \cdot C_6H_4 \cdot O^-$, trans-p- $NMe_3^+ \cdot C_6H_4 \cdot CH \cdot CH \cdot CO_2^-$, m- and p- $NMe_3^+ \cdot C_4H_4 \cdot SO_3^-$, and of o- $NMe_2 \cdot C_6H_4 \cdot CO_2H$ (I), $NHPh \cdot CH_2 \cdot CO_2H$, and $NMe_2Ph \cdot CH_2 \cdot CO_2^-$. The results confirm the amphoteric polar formulæ for the betaines and (I) is predominantly in the polar form [K_z (ratio zwitterion/uncharged mols.)=10]. For o-, m-, and p- $NH_2 \cdot C_6H_4 \cdot CO_2H$ (cf. A., 1933, 777) vals. of K_z are 0.6—0.8 (?), 3—4, and 0.1—0.2, respectively. There is no evidence of deformation of the mols. in solution. R. K. C.

Preparation of amylbenzoic acids.—See B., 1934, 752.

Derivatives of m-cresotic acid. N. M. SHAH and R. L. ALIMCHANDANI (J. Indian Chem. Soc., 1934, 11, 467—469).—5-Carboxy-4-methoxy-2-methylmandelic acid (I), $CCl_3 \cdot CH(OH) \cdot$ (II), and H_2SO_4 give the chloralide (III), m.p. 178—179°, the structure of which



is proved by hydrolysis by hot, aq. $Ba(OH)_2$ to (I), oxidation to α -coccinic acid, and reduction (Zn dust-AcOH) to $\beta\beta$ -dichloroethoxy-5-carboxy-4-methoxy-2-methylphenylacetic acid, m.p. 195—196°, stable to Br, but giving with conc. H_2SO_4 at 100 HCl and 5-carboxy-4-methoxy-2-methylbenzaldehyde. 5-Carboxy-4-hydroxy-2-methylmandelic acid gives with (II) a product which could not be purified. Condensation of m-cresotic acid with (II) in the m-position is thus improbable (cf. A., 1921, i, 111). R. S.

Condensation of pyruvic acid with aldehydes. R. N. SEN and B. K. SEN (J. Indian Chem. Soc., 1934, 11, 411—418).— $AcCO_2H$ and the appropriate aldehyde, best with 20% KOH-EtOH, give rapidly good yields of the following benzylidenepyruvic acids: benzylidene- (K salt; dibromide and phenylhydrazones, cryst.; with Ac_2O and $NaOAc$ at 180—190 β -naphthaquinone, p-, yellow (I) [changes at 165° to a red form, which reverts to (I) in hot, aq. EtOH and at 175—180° gives a neutral ring com-

pound, m.p. > 230° (also obtained by hot Ac_2O) (*K* salt; *dibromide*, softens at 95°; *phenylhydrazone*, m.p. 186°), m., m.p. > 260°, red (*K* salt, hygroscopic; *dibromide* and *phenylhydrazone*, cryst.), and *o*-nitrobenzylidene-, cryst. (formed with 10% of indigotin and a small amount of a red substance), *cinnamylidene*-, orange-red, m.p. 74°, changes to yellow form, m.p. 104° when kept [*K* salt; *dibromide*, m.p. 114°; *phenylhydrazone*, m.p. 152°; with Ac_2O and NaOAc at 200—210° gives the diketone, $\text{R} < \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{CH} \\ \text{CO} \cdot \text{CO} \cdot \text{CH} \end{smallmatrix}$ (II; $\text{R} = \text{C}_6\text{H}_4$), red, m.p. 223°], 3 : 4-methylenedioxy-, yellow, at 70° or with cold HCl gives an orange-red form, m.p. 162—163° [*K* salt; *dibromide*, m.p. 102°; *phenylhydrazone*, m.p. 174°; gives the diketone (II; $\text{R} = 3 : 4\text{-CH}_2\text{O} \cdot \text{C}_6\text{H}_2$), m.p. 160°], *p*-methoxybenzylidene- (*K* salt; *dibromide*, m.p. 82—85°; *phenylhydrazone*, m.p. 158°; gives a red ring compound, $\text{C}_{11}\text{H}_8\text{O}_3$), *furfurylidene*-, m.p. 110° [*K* salt; *phenylhydrazone*, m.p. 162° (decomp.)], *p*- (by HCl), an oil, and *o*-hydroxybenzylidene-pyruvic acid (by HCl or KOH), yellow, decomp. 185—190° (obtained with much red lactone, m.p. > 235°). β -Resorcyraldehyde (conc. HCl at 200—220°) gives the derived lactone, red. Glucose (HCl - EtOH ; room temp.) gives slowly a 90% yield of $\delta\epsilon\zeta\eta\theta$ -pentahydroxy- α -keto- n - Δ^8 -noneno- δ -lactone (6- $\alpha\beta\gamma\delta$ -tetrahydroxybutyl-3-keto-3 : 6-dihydro- α -pyrone), m.p. > 240°. R. S. C.

Synthesis of kynurenine. I. Decarboxykynurenine. T. YORITAKA (Z. physiol. Chem., 1934, 226, 29—31).—Reduction of the oxime, m.p. 129—130°, of *o*-nitrobenzylidenepyruvic acid with SnCl_2 gave *o*-aminostyryl- α -aminoacetic acid (hydrochloride; sulphate; picrate, decomp. 195°; picrolonate, m.p. 232—236°; phosphotungstate; platinichloride).

J. H. B.

Stereochemistry of diphenyls. XXXV. Effect of 3'-substituents on rate of racemisation of 2-nitro-2'-methoxydiphenyl-6-carboxylic acid. S. L. CHIEN and R. ADAMS (J. Amer. Chem. Soc., 1934, 56, 1787—1792).—Me 2-bromo-3-nitrobenzoate (I), 3-iodopyrocatechol Me_2 ether, b.p. 124—125°/4 mm. (from the 3- NH_2 -derivative), and Cu bronze at 220—250° give (after hydrolysis) 2 : 2'-dinitrodiphenyl-6 : 6'-dicarboxylic acid (II) and 17.2% of 2-nitro-2' : 3'-dimethoxydiphenyl-6-carboxylic acid, m.p. 199—200° (all m.p. are corr.), resolvable into the *l*-acid, m.p. 199—201°, $[\alpha]_D^{25} - 66.7^\circ$ (initial) in EtOH [strychnine salt (+1.5 H_2O), m.p. 143.5—147.5°, m.p. (anhyd.) 208—210°]. 2-Chloro-6-iodoanisole, m.p. 94—95° [from 6-chloro-*o*-anisidine, m.p. 179—180° (decomp.), obtained by reduction (H_2 , PtO_2 , 95% EtOH) of the NO_2 -compound], and (I) similarly afford (II) and 7.9% of 3'-chloro-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 172—173°, resolvable into *d*-, m.p. 170.5—172°, $[\alpha]_D^{25} + 14.2^\circ$ in EtOH (strychnine salt, m.p. 149.5—162°, $[\alpha]_D^{25} - 51.7^\circ$ in CHCl_3), and *l*-forms, m.p. 171.5—173°, $[\alpha]_D^{25} - 41.5^\circ$ (initial) in EtOH [strychnine salt, m.p. 150.5—153.5° (decomp.), $[\alpha]_D^{25} + 42.8^\circ$ in CHCl_3]. 2-Bromo-6-iodoanisole, m.p. 92—93° [from 6-bromo-*o*-anisidine, b.p. 157—159°/30 mm., prepared by reduction (Fe powder, dil. HCl) of the NO_2 -compound (from the bromo-nitrophenol, Me_2SO_4 , and K_2CO_3 in xylene)], and (I)

give (II) and 3.7% of 3'-bromo-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 182—183°, resolvable into the *l*-acid, m.p. 180.5—182.5°, $[\alpha]_D^{25} - 38^\circ$ (initial) in EtOH (cinchonine salt, m.p. 201—206°). 6-Iodo-2-nitroanisole (from the phenol, Me_2SO_4 , and K_2CO_3 in xylene) and (I) afford (II) and 15.5% of 2 : 3'-din-2-nitro-2'-methoxydiphenyl-6-carboxylic acid, m.p. 173—173.5°, resolvable into *d*-, m.p. 169.5—171.5°, $[\alpha]_D^{25} + 12.9^\circ$ in EtOH [brucine salt (+2 H_2O), m.p. 192—195.5°, $[\alpha]_D^{25} - 116.4^\circ$ in CHCl_3], and *l*-forms, m.p. 170.5—172.5°, $[\alpha]_D^{25} - 13.4^\circ$ (initial) in EtOH [brucine salt (+2.5 H_2O), m.p. 140—147.5° (decomp.), $[\alpha]_D^{25} + 100^\circ$ in CHCl_3]. 6-Iodo-2-methylanisole, b.p. 124—126°/22 mm. (cf. Robinson, J.C.S., 1916, 109, 1084), and (I) at 240—280° similarly give (II) and 18.7% of 2-nitro-2'-methoxy-3'-methyldiphenyl-6-carboxylic acid, m.p. 189—193°, resolvable into the *l*-acid, m.p. 191—193°, $[\alpha]_D^{25} - 100.2^\circ$ (initial) in EtOH [cinchonine salt, m.p. 226—229° (decomp.)]. The half-life periods of the *l*-acids in EtOH and COMe , at 25° increase in the order : 3'-substituent = OMe , Me , Cl , Br , NO_2 ; the acids are much more stable than the isomeric 5'-derivatives (A., 1933, 63). The Na salts racemise more readily in EtOH than in H_2O ; in both cases racemisation usually occurs more readily than with the acids in org. solvents. H. B.

Action of magnesium phenyl bromide on the anhydride and phenylimide of cyclobutane-1 : 2-dicarboxylic acid. E. ELLINGHOE and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1777—1779).—cyclobutane-1 : 2-dicarboxylic anhydride and MgPhBr (I) (1 mol.) in Et_2O give *trans*-2-benzoylcyclobutane-1-carboxylic acid; with 2 mols. of (I), the lactone (II), m.p. 116—117°, of 2- α -hydroxybenzhydrylcyclobutane-1-carboxylic acid results. (II) and $\text{NH}_2\text{Ph} \cdot \text{HBr}$ at 160—170° afford the lactam (III), m.p. 136—137°, of 2- α -anilinobenzhydrylcyclobutane-1-carboxylic acid. *N*-Phenylcyclobutane-1 : 2-dicarboxylimide and (I) (1 mol.) in Et_2O give *cis*-2-benzoylcyclobutane-1-carboxylanilide, m.p. 149.5—150.5°, converted by cold dil. EtOH - NaOH into the *trans*-form (A., 1932, 746). 2- α -Hydroxybenzhydrylcyclobutane-1-carboxylanilide (IV), m.p. 193.5—194.5°, is obtained from 2 mols. of (I). (IV) is dehydrated in boiling xylene containing a little KHSO_4 to (III) and is converted by Ac_2O , EtOH - H_2SO_4 , or EtOH - NaOH into (II). H. B.

Syntheses of cyclic compounds. XI. Thermal decomposition of *trans*-hexahydrohydrindene- and of *trans*-decahydronaphthalene-2 : 2-diacetic acids. R. J. TUDOR and A. I. VOGEL (J.C.S., 1934, 1250—1253).—Thermal decomp. of *trans*-cyclohexane-1 : 2-diacetic acid (improved prep.) gives *trans*-hexahydro-2-hydrindone (83%) and *trans*-1-methylcyclohexane-2-acetic acid (*Ag* salt), whilst somewhat higher yields of ketone are obtained by catalytic decomp. in presence of cryst. baryta. Thermal decomp. of *trans*-decahydronaphthalene-2 : 2-diacetic acid and *trans*-hexahydrohydrindene-2 : 2-diacetic acid under comparable conditions affords 48% and 35.5% of the corresponding :CH_2 compounds (A., 1933, 1049), indicating a real difference in the condition of strain of the parent systems. H. W.

Synthesis of 5-chloro-3 : 4-dimethoxybenzoic acid. R. M. HANN (J. Washington Acad. Sci., 1934,

24, 329—331).—With $\text{NH}_2\text{OH}\cdot\text{HCl}\cdot\text{NaHCO}_3$, 5-chloroveratraldehyde (by methylation of 5-chlorovanillin) affords its anti-oxime, m.p. 90° (Ac derivative, m.p. 84°), the unstable hydrochloride, m.p. 117° , of which is converted by HCl into the syn-oxime, m.p. 112° , converted by Ac_2O into 5-chloroveratronic nitrile, m.p. 103° , from which the corresponding acid, m.p. 191° , is obtained by hydrolysis with 20% NaOH. All m.p. are corr. J. W. B.

Action of chlorosulphonic acid on naphthalene. G. WALTER (Monatsh., 1934, 64, 287—288).—When C_{10}H_8 is heated with ClSO_3H at 180° , tetrachlorophthalic anhydride, m.p. 255° , is obtained. It gives a "glyptal" resin when heated with glycerol at 100 — 170° . J. W. B.

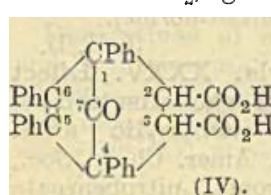
Action of maleic anhydride on anthracene derivatives. E. DE B. BARNETT, N. F. GOODWAY, A. G. HIGGINS, and C. A. LAWRENCE (J.C.S., 1934, 1224—1227).—The formation of an adduct from maleic anhydride (I) and an anthracene derivative is independent of the presence of Bz substituents, but may be hindered by the presence of two meso-substituents, and does not occur with dianthranyl or with heterocyclic compounds formally similar to anthracene. Although adducts are easily formed from anthranyl acetates and anthranyl Me ethers, the corresponding OH compounds appear incapable of existence, since attempted hydrolysis is accompanied by loss of maleic acid, and the halogen atoms in the adducts from 9-bromo- and 9:10-dichloro- and -dibromo-anthracene are unaffected by KOH-EtOH. (I) adds to an anthrone giving the anthronylsuccinic anhydride. If Cl is in the *peri* position to the succinic acid residue, this residue is lost on reduction; otherwise the anthranylsuccinic acid is formed, although the anthranylsuccinic acids are exceptional in the facile reduction by Zn and alkali to the H_2 -acids. The following are described: $\alpha\beta$ -endo-9:10-dihydroanthraquinyl-9:10-succinic anhydrides (cf. II): 9-Ph, m.p. 252° ; 9- CH_3Ph , m.p. 223° ; 9-Br-, m.p. 255° ; 9-OAc-, m.p. 240° ; 9:10-(OMe) $_2$ -, m.p. 259° ; 1:5- Cl_2 -9-OAc, m.p. 244° ; 1:8- Cl_2 -9-OAc, m.p. 227° ; 4:5- Cl_2 -9-OAc, m.p. 249° ; β -benzoyl- $\alpha\beta$ -endo-9:10-dihydroanthraquinylpropionic acid (cf. III), m.p. 234° ; anthranylsuccinic anhydride (cf. IV), m.p. 215° ; its 1:5- Cl_2 -, m.p. 212° ; 1:8- Cl_2 -, m.p. 215° ; 4:5- Cl_2 -, m.p. 237° ; 1:3- Me_2 -, m.p. 197° ; 1:4- Me_2 -, m.p. 210° ; 2:3- Me_2 -, m.p. 240 — 260° ; 2:4- Me_2 -, m.p. 230 — 235° , derivatives; anthranylsuccinic acid, m.p. 219° ; its 1:4- Me_2 -, m.p. 228° ; 2:4- Me_2 -, m.p. 235° ; 2:3- Me_2 -, m.p. 235° , derivatives and the corresponding anhydrides, m.p. 200° , 235° , 240° , and 192 — 194° , respectively; 9:10-dihydroanthranylsuccinic acid,

m.p. 247° (decomp.). 10-Methoxyanthrone, KOH, and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ yield anthraquinyl Me_2 ether. Anthraquinyl diacetate is obtained by gradual addition of Zn dust to a boiling solution of anthraquinone in $\text{C}_5\text{H}_5\text{N}$ and Ac_2O . 1:5- and 1:8-Dichloroanthraquinyl diacetate have m.p. 310° (decomp.) and m.p. 249° , respectively. H. W.

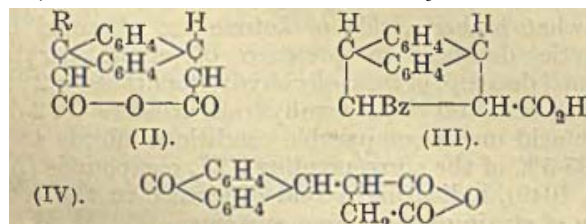
Synthesis in the cestrin group. J. C. BARDHAN (Nature, 1934, 134, 217).—Condensation of β -1-naphthylethyl bromide with methyl sodio- β -keto-adipate gives a keto-ester, cyclised in presence of H_2SO_4 to 2-carboxy-3:4-dihydrophenanthrene-1-propionic acid, m.p. about 226 — 227° . Distillation with Ac_2O gives an cestrus-producing product, $\text{C}_{17}\text{H}_{14}\text{O}$, m.p. 210° . L. S. T.

Synthesis of dicyclic terpenes. Synthesis of ethyl cyclohexanone-2:6-dicarboxylate. P. C. GUHA and N. K. SESHARDINGAR (Current Sci., 1934, 3, 20—21).—Et cyclohexanone-2:6-dicarboxylate, b.p. 140 — $142^\circ/1$ — 1.5 mm. (hydrolysed and decarboxylated to cyclohexanone), is obtained by the action of NaOEt on Et trimethylenedimalonate (I). (I) and COBr_2 afford Et, cyclohexanone-2:2:6:6-tetracarboxylate, b.p. $175^\circ/2$ — 3 mm. (acid, m.p. 246°). By use of Et ethylene- and methylene-dimalonates derivatives of cyclopentanone and cyclobutanone are obtained. H. W.

Tetraphenylcyclopentadienone in the diene synthesis. C. F. H. ALLEN and L. J. SHEPS (Canad. J. Res., 1934, 11, 171—179; cf. A., 1933, 1164).—The endo-ketonic substances obtained by diene syntheses from tetraphenylcyclopentadienone (I) readily lose first CO to yield derivatives of tetrahydrophthalic acid, and then H_2 , giving substituted phthalic acids.



Maleic anhydride (II) and (I) (cf. Diltthey *et al.*, this vol., 62) at 155 — 160° yield the anhydride (III), m.p. 220° , of cis-1:4-endoketo-1:4:5:6-tetraphenyl-1:2:3:4-tetrahydrophthalic acid (IV), m.p. 190 — 191° (decomp.) [Ag salt, decomp. 185 — 190° ; Me_2 ester, decomp. 155°]. At 240° (III) gives 3:4:5:6-tetraphenyl-1:2-dihydrophthalic anhydride (V), m.p. 255° (corresponding cis- Me_2 ester, m.p. 149 — 150°). Prolonged heating at 250° of (I) and (II) or of (III) or (V) at 270° , alone or with S, yields 3:4:5:6-tetraphenyl-o-phthalic acid, m.p. 287° [Na salt; Me_2 ester (VI), m.p. 250 — 251° , also from Me maleate and (I)]. With Me fumarate at 170° , (I) yields trans- Me_2 1:4-endoketo-1:4:5:6-tetraphenyl-1:2:3:4-tetrahydrophthalate, m.p. 214 — 215° (decomp.); prolonged heating at 225° gives trans- Me_2 3:4:5:6-tetraphenyl-1:2-dihydrophthalate, m.p. 157° . (I) and $[\text{C}\cdot\text{CO}_2\text{Me}]_2$ give (VI); with $[\text{C}\cdot\text{CO}_2\text{Et}]_2$ (I) yields Et 3:4:5:6-tetraphenylphthalate, m.p. 187 — 188° . (I) and $\text{CBz}\cdot\text{CPh}$ at 195° yield 2:3:4:5:6-pentaphenylbenzophenone, m.p. 340 — 341° . (I) does not react with Ph styryl ketone, trans-dibenzoyl ethylene, or $\text{CPh}_2\cdot\text{CO}$. Anhydroacetonebenzil and (II) at 131° give 1:4-endoketo-5:phenyl-1:2:3:4-tetrahydrophthalic acid, (VII), m.p. 186 — 187° (Ag salt, m.p. 198 — 199° ; K salt; oxime, m.p. 219 — 220°). On heating (VII) passes into 4:5-



m.p. 211° (decomp.) [anhydride, m.p. 169°]; 10-bromo-anthranylsuccinic acid, m.p. 255° (decomp.) [anhydride,

diphenyl-1 : 2-dihydrophthalic acid (VIII), m.p. 235—243° (decomp.) (Ag salt, m.p. 205°). With (II), (VII) and (VIII) yield the dianhydride previously described (*loc. cit.*, IX). All of the endoketonic products described are unaltered by treatment with PhN_3 .

H. N. R.

Bile acids. XLIII. M. SCHENCK (Z. physiol. Chem., 1934, 226, 45—52; cf. this vol., 653).—Elimination of the ketoxime group from the oximinolactamhydroxamic acid (I) (*loc. cit.*) by 20% HCl at 100° affords a *ketolactamhydroxamic acid* (II), $\text{C}_{24}\text{H}_{36}\text{O}_8\text{N}_2$, decomp. 238°. With HNO_3 , (II) gives a *ketolactamtricarboxylic acid*, $\text{C}_{24}\text{H}_{35}\text{O}_8\text{N}$, two forms, m.p. 200—205°, and decomp. 262°, respectively (cf. A., 1928, 1007). When (II) is hydrolysed with HCl and the solution evaporated to dryness, the NH_2OH recombines yielding the oximinoaminotetracarboxylic acid, $\text{C}_{24}\text{H}_{38}\text{O}_9\text{N}_2$, decomp. 228°. Reduction of the nitro-oximinohydroxamic acid, $\text{C}_{24}\text{H}_{35}\text{O}_9\text{N}_3$, with Zn

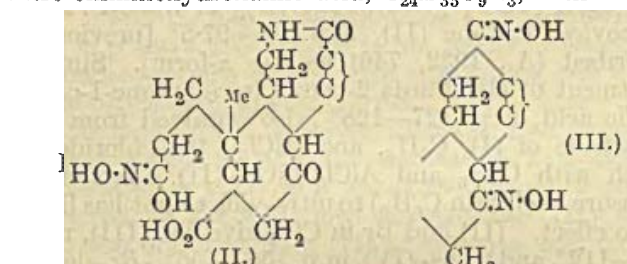
on (I)] or other NH_2Ar ; the following mechanism is suggested (cf. A., 1927, 761): $\text{CHPh:NPh} + \text{MeNO}_2 \xrightarrow{\text{PhOH}} \text{NO}_2\text{-CH}_2\text{-CHPh:NHPh} \xrightarrow{\text{PhOH}} \text{CHPh:CH}\cdot\text{NO}_2 + \text{CHPh:NPh} + \text{H}_2\text{O}$. (III) is decomposed rapidly by mol. equivs. of NH_2R and NHR_2 . H. B.

Jute lignin. III. Action of nitric acid on lignin. P. B. SARKAR (J. Indian Chem. Soc., 1934, 11, 407—410; cf. A., 1933, 1050).—Jute lignin with HNO_3 (0.25N—fuming) gives $\text{H}_2\text{C}_2\text{O}_4$ (more with conc. than with dil. acid, and at 100° than at 30°), a mixture of NO_2 -compounds (I), and a little AcOH . (I) has 8.27—10.2% of OMe. $\text{CO}(\text{NH}_2)_2$ reduces, but does not destroy entirely, the oxidising power of HNO_3 . R. S. C.

Chemical formula of lignin. P. KLASON (Svensk Kem. Tidskr., 1934, 46, 140, 168—169; cf. this vol., 408).—A reply to criticisms. R. P. B.

Many-membered ring-systems. IV. Synthesis of *dl-muscone*. K. ZIEGLER and K. WEBER (Annalen, 1934, 512, 164—171; cf. this vol., 894).— α - κ -Dibromodecane and $\text{CHNa}(\text{CO}_2\text{Et})_2$ (I) in EtOH give *Et*₂ κ -bromodecylmalonate, b.p. 123°/0.02 mm., which with MeI and NaOEt yields *Et*₂ methyl- κ -bromodecylmalonate, b.p. 128°/0.02 mm. This with (I) forms *Et*₂ tridecane- $\alpha\mu\mu$ -tetracarboxylate, an oil, yielding by KOH-MeOH and subsequent heating at 100° tridecane- $\alpha\mu$ -dicarboxylic acid, m.p. 83—84°, the *Et*₂ ester, b.p. 176°/0.9 mm., of which with Na and amyl alcohol gives β -methyltridecane- $\alpha\epsilon$ -diol (30% yield), m.p. 46—47°. This afforded $\alpha\epsilon$ -dibromo- β -methyltridecane, b.p. 135°/0.002 mm., and thence β -methyltridecyl $\alpha\epsilon$ -dicyanide, b.p. 165°/0.3 mm., which is cyclised to *dl-muscone*, b.p. 128°/1.2 mm. (semicarbazone, m.p. 133.5—134.5°). R. S. C.

Addition reactions of phenyl vinyl ketone. IV. Termolecular products. C. F. H. ALLEN and A. C. BELL (Canad. J. Res., 1934, 11, 40—46; cf. A., 1933, 950).—Owing to the reactivity of the primary products $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, and $\text{CH}_2(\text{CN})_2$ give termol. additive products with Ph vinyl ketone (I), whilst 1 mol. of MeNO_2 condenses with 3 mols. of (I). $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ (even in excess) with (I) in presence of NaOMe in MeOH gives *Me di- β -benzoyl ethylcyanoacetate* (II), m.p. 144° [disemicarbazone, m.p. 220° (decomp.)]. (II) and HBr in AcOH yield *Me di-(β -benzoyl ethyl)malonamate* (III), m.p. 224°, reconverted into (II) by P_2O_5 ; (III) cannot be converted into the Me_2 ester, but yields *di-(β -benzoyl ethyl)malonamic acid* (IV), m.p. 280°, with aq. KOH followed by HCl. With HBr in CHCl_3 , (II) gives the *imide-bromide*, $(\text{CH}_2\text{Bz}\cdot\text{CH}_2)_2\text{C}(\text{CO}_2\text{Me})\cdot\text{CBr}\cdot\text{NH}$, m.p. 165° (decomp.), readily hydrolysed to (IV). (IV) with AcOH yields *Me 2-bromo-6-phenyl-3- β -benzoyl ethyl-3 : 4-dihydropyridine-3-carboxylate*, m.p. 144°; this is also hydrolysed to (IV) by HBr. *Di-(β -benzoyl ethyl)cyanoacetic acid*, m.p. 161°, from (II), on heating loses CO_2 , giving γ -cyano- $\alpha\epsilon$ -dibenzoylpentane (V), m.p. 100° [monosemicarbazone, m.p. 202° (decomp.)]. This yields a *dimeride*, m.p. 265°, with HBr in AcOH, conc. HCl, or 50% H_2SO_4 ; with conc. H_2SO_4 (V) isomerises to Δ^5 -2-keto-6-phenyl-3- β -benzoyl ethyltetrahydropyridine, m.p. 141°, sometimes accompanied by a substance, $\text{C}_{20}\text{H}_{21}\text{O}_3\text{N}_2$, m.p. 137°.



dust and aq. NH_3 yields a *dioximinohydroxamic acid* (III), $\text{C}_{24}\text{H}_{37}\text{O}_8\text{N}_3$, decomp. 270°. Beckmann inversion (90% H_2SO_4) of (III) gives (I). (III) did not give the expected blue nitroso-compound, $\text{C}_{24}\text{H}_{33}\text{O}_3\text{N}$, with HNO_3 . J. H. B.

Two syntheses of norpinic acid. K. N. GAIND and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 421—425).—Kerr's synthesis (A., 1929, 445) of norpinic acid does not give the yield claimed. The Na-derivative of *Et*₄ isopropylidenedimalonate (improved prep.) and CH_2I_2 or the Na₂-derivative of *Et*₄ methyl-enedimalonate (improved prep.) and CMe_2Cl in dry C_6H_6 (8 hr.) at 140° give, after hydrolysis, 1 : 1-di-methylcyclobutane-2 : 2 : 4 : 4-tetracarboxylic acid, m.p. 200°, which at 220—240°, or, better, in hot 50% H_2SO_4 , gives norpinic acid, m.p. 146° (softens at 137°). R. S. C.

Knoevenagel reaction and synthesis of unsaturated nitro-compounds. D. E. WORRALL (J. Amer. Chem. Soc., 1934, 56, 1556—1558; cf. Hann and Lapworth, J.C.S., 1904, 85, 46).— β -Nitro- α -phenyl-ethyl alcohol (I) is formed from PhCHO , MeNO_2 , and a little NEt_3 . Reaction occurs much more slowly when NH_2Bu or *n*-amylamine (II) is the condensing agent; the Schiff base is first produced, but $\text{CHPh:CH}\cdot\text{NO}_2$ (III) is the final product. This is probably formed by way of (I) [which is shown to decompose in presence of NH_2Alk into (III) and H_2O]. *sec*-Amines are least suitable for the condensation. *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ and *m*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ react much more readily than PhCHO in presence of NEt_3 ; reaction occurs very slowly in presence of (II), probably owing to the greater stability of the intermediate Schiff base. (III) is also formed from PhCHO , MeNO_2 , and NH_2Ph [which has no action

With Br in AcOH (V) is dibrominated and isomerised to 2-bromo-6-phenyl-3- β -bromo- β -benzoyl-ethylpyridine, m.p. 151°. With $\text{CH}_2(\text{CN})_2$ (I) gives di-(β -benzoyl-ethyl)malononitrile, m.p. 215°; (I) and $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ yield di- β -benzoyl-ethylcyanoacetamide, m.p. 200—201°. McNO_2 with (I) gives nitrotri- β -benzoyl-ethylmethane, m.p. 132°. The prep. of Et 4-benzoylpyrazoline-5-carboxylate, m.p. 140°, is described. H. N. R.

Properties of adipoin, a cyclic sugar. G. P. G. MOEYS and N. SCHOORL (Pharm. Weekblad, 1934, 71, 1026—1029).—Adipoin, 2-hydroxycyclohexanone, gives all the analytical reactions for a sugar. It reduces Trommer's, Luff's, and Fehling's solutions in the cold, gives a positive test with Bosc's reagent (A., 1932, 499) at a dilution of 1:2000, and forms phenylosazones [*p*-bromo-, m.p. 183—185° (decomp. at 170°), *p*-nitro-, m.p. 236—237°]. S. C.

Phenanthrene series. VII. 3-Hydroxyacetylphenanthrenes and amino-ketones and -alcohols derived from them. Aminohydroxyphenanthrenes. A. BURGER and E. MOSETTIG (J. Amer. Chem. Soc., 1934, 56, 1745—1747).—3-Hydroxy-6-acetylphenanthrene (I) (cf. A., 1933, 951) is converted (no details) into 3-methoxyphenanthrene-6-carboxylic acid [hydrazide, m.p. 193—194° (all m.p. are corr.)] and thence (Curtius degradation) into 6-amino-3-methoxyphenanthrene, m.p. 125° [$\text{N}\cdot\text{CO}_2\text{Et}$ derivative, m.p. 134—135° (the main reaction product is a substance, m.p. 117°); hydrochloride, m.p. 263—264° (decomp.)]. 6-Hydroxy-3-methoxyphenanthrene, m.p. 135—136°, is methylated to 3:6-dimethoxyphenanthrene [picrate, m.p. 154.5° (decomp.)], thus establishing the constitution of (I). 3-Methoxy-9-acetylphenanthrene (II) (cf. *loc. cit.*) is similarly converted into 3-methoxyphenanthrene-9-carboxylic acid [hydrazide, m.p. 234° (decomp.)] and thence into 9-amino-3-methoxyphenanthrene, m.p. 117—118° [$\text{N}\cdot\text{CO}_2\text{Et}$, m.p. 147°, *Cl*-, m.p. 128—129° (Ac_2 derivative, m.p. 134—135°), and Ac derivative, m.p. 148.5—150° [described by Werner (A., 1902, i, 437) as the Ac derivative]], thus establishing the structure of (II). ?Chloro-9-amino-3-ethoxyphenanthrene (Ac_2 derivative, m.p. 122°) has m.p. 120—123°. 9-Nitro-3-acetoxypheanthrene, m.p. 159° [from the 3-OAc-derivative and HNO_3 (d 1.5) in AcOH], is hydrolysed (dil. NaOH) to the 3-OH-derivative, m.p. 188—189°, reduced (alkaline $\text{Na}_2\text{S}_2\text{O}_4$) to 9-amino-3-hydroxyphenanthrene, m.p. 265—267° (decomp.) (hydrochloride). 10-Amino-3-methoxyphenanthrene, m.p. 116—116.5° (Ac_2 , m.p. 122.5—123.5°, and $\text{N}\cdot\text{CO}_2\text{Et}$, m.p. 136.5—137.5°, derivatives), is obtained by Curtius degradation of 3-methoxyphenanthrene-10-carboxylic acid (*Me* ester, m.p. 93°; hydrazide, m.p. 243—244°). The Ac derivative, m.p. 249—250°, of 9-amino-10-methoxyphenanthrene, m.p. 68—69°, is prepared by methylation (CH_3N_2 or Me_2SO_4) of 9-acetamido-10-hydroxyphenanthrene (*Et* ether, m.p. 247°). 4-Acetamido-3-hydroxyphenanthrene, m.p. 197° (*Me*, m.p. 208—209°, and *Et*, m.p. 159°, ethers), is obtained by hydrolysis of the Ac_2 derivative (Fieser, A., 1929, 930). (II) and Br in Et_2O and sunlight give 3-methoxy-9-bromoacetylphenanthrene, m.p. 115.5—116.5°, which with NHMe , in C_6H_6 and H_2 affords 3-methoxy-9-dimethylaminoacetylphenanthrene [hydrochloride (III), m.p. 190—191° (decomp.); perchlorate, m.p.

198—199°]. (III) is reduced (H_2 , PtO_2 , EtOH) to the hydrochloride, m.p. 207—208° (decomp.), of 3-methoxy-9- β -dimethylamino- α -hydroxyethylphenanthrene [picrate, m.p. 229° (decomp.); benzoate hydrochloride, m.p. 168—170° (decomp.)]. 3-Acetoxy-6-bromoacetyl-, m.p. 160°, -6-diethylaminoacetyl- (perchlorate, m.p. 199—200.5°), and -6- β -diethylamino- α -hydroxyethylphenanthrene [hydrochloride, m.p. 173—174° (decomp.)] are similarly prepared. 3-Hydroxy-6- β -diethylamino- α -hydroxyethylphenanthrene [hydrochloride, m.p. 186—187° (decomp.); dibenzoate hydrochloride, m.p. 190—191°] has m.p. 125°. H. B.

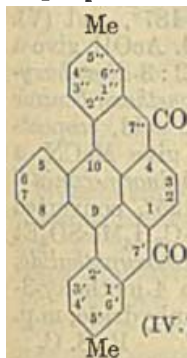
1:2-Dibenzoylcyclobutanes. E. ELLINGBOE and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 1774—1777).—Successive treatment of the mixture of *cis*-(I) and *trans*-cyclobutane-1:2-dicarboxylic acids obtained from cyclobutane-1:1:2-tricarboxylic acid (modified prep.; cf. A., 1929, 794) at 150°, with SOCl_2 and $\text{C}_6\text{H}_6 + \text{AlCl}_3$ gives about 75% of *trans*-1:2-dibenzoylcyclobutane (II), m.p. 96—97.5° [previously described (A., 1932, 746) as the α -form]. Similar treatment of (I) affords 2-benzoylcyclobutane-1-carboxylic acid, m.p. 127—128° [also obtained from the anhydride of (I), C_6H_5 , and AlCl_3], the chloride of which with C_6H_6 and AlCl_3 gives (II). Prolonged exposure of (II) (in C_6H_6) to ultra-violet light has little or no effect. (II) and Br in CCl_4 give *cis*-(III), m.p. 111—112°, and *trans*-(IV), m.p. 155—156°, - Br_2 -derivatives (cf. *loc. cit.*), both of which are converted (at differing rates) by KI in EtOH into 1:2-dibenzoyl- Δ^2 -cyclobutene (V), m.p. 96—97.5°. (V) and Br in CCl_4 afford (III) only. Reduction (H_2 , PtO_2 , EtOH) of (V) gives *cis*-1:2-dibenzoylcyclobutane (VI), m.p. 121—122° (dioxime, m.p. 174—175°), previously described (*loc. cit.*) as the β -form, and a compound, m.p. 222—223°. (VI) is readily converted into (II) by warm conc. HCl or cold $\text{EtOH}\cdot\text{NaOH}$; bromination gives (III) and (mainly) (IV). H. B.

Isomeric forms of 3-phenyl-2:3:5:6-tetramethyl- Δ^5 -cyclohexene-1:4-dione. H. M. CRAWFORD (J. Amer. Chem. Soc., 1934, 56, 1803—1804).—3-Phenyl-2:3:5:6-tetramethyl- Δ^5 -cyclohexene-1:4-dione, m.p. 142° (A., 1928, 523), is converted by heating with fused NaOAc in EtOH into a geometrical isomeride, m.p. 72° (cf. *loc. cit.*), which is oxidised (KMnO_4 , COMe_2) to the more fusible form of α -phenyl- $\alpha\alpha'$ -dimethylsuccinic acid (this vol., 294). H. B.

Perylene derivatives. XLII. Degradation of 3:9-dibenzoylperylene. O. BENNDORF and W. SORNS (Monatsh., 1934, 64, 167—172).—Oxidation of 3:9-dibenzoylperylene with $\text{CrO}_3\cdot\text{AcOH}$ affords its 4:10-quinone (I), m.p. 279° (previous darkening) (*di*-*o*-diazine with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in PhMe), reduced to the hydroquinol, m.p. 266—267°, together with 2-benzoylanthraquinone-1:5-dicarboxylic acid + 2 EtOH and solvent-free, m.p. 315° [also by direct oxidation of (I)], decarboxylated by sublimation in a vac. (CO_2) to 2:6-dibenzoylanthraquinone, m.p. 283—284°.

W B
Tautomerism of anthraquinone- α -carboxyl chlorides. V. Tautomerism of anthraquinone-1:4-dicarboxyl dichloride and synthesis of the ring-system of the homocordianthrone series

(4 : 5 : 6 : 7 : 8 : 9-tribenzopyrene-3 : 10-quinone). R. SCHOLL and K. MEYER [with A. KELLER]. VI. Tautomerism of 3-methyl- and 2 : 4-dimethyl-anthraquinone-1-carboxyl chloride. R. SCHOLL, J. DONAT, and O. BOTTGER (Annalen, 1934, 512, 112—124, 124—130; cf. this vol., 1006).—V. 1 : 4-Dimethylantraquinone and MgPhBr (1 mol.) in cold Et₂O-C₆H₆ give a little 9-phenyl-1 : 4-dimethylloxanthrone, m.p. 198°, whereas 10 mols. of MgPhBr and subsequent heating afford a 55% yield of 9 : 10-dihydroxy-9 : 10-diphenyl-1 : 4-dimethyldihydroanthracene, m.p. 221—222°. Anthraquinone-1 : 4-dicarboxyl dichloride (I) (best from the acid and boiling SOCl₂), m.p. 203—205°, with C₆H₆ and AlCl₃ in PhNO₂ at 50—60° gives 9-phenylloxanthrone-1 : 4-dicarboxylic acid (40% yield) (probably cyclised by H₂SO₄ and Cu powder), also obtained in poorer yield together with 1 : 4-dibenzoylanthracene (7%), m.p. 225°, by use of FeCl₃. (I), PhMe, and a little FeCl₃, when heated, give 9-hydroxy-9-p-tolylloxanthrone-1 : 4-dicarboxylic acid, m.p. 194—195° (stable to hot AcOH or Na₂S₂O₄, but undergoes ring-closure with H₂SO₄-Cu), and 1 : 4-di-p-tolylanthraquinone, cryst. (I), PhMe, and AlCl₃ in cold PhNO₂, however, afford 9 : 10-dihydroxy-9 : 10-di-p-tolyl-9 : 10-dihydroanthracene-1 : 4-dicarboxylomonolactone (II), m.p. about 260° (rapid heating), converted by hot Ac₂O into the dilactone (III), m.p. 253°, also obtained from (II) at the m.p. and reconverted into (II) by hot AcOH. (II) or (III) with conc. H₂SO₄, faster with Cu powder, undergoes ring-closure, and with HI-AcOH gives 9 : 10-di-p-tolylanthracene-1 : 4-dicarboxylic acid, cryst., which with conc. H₂SO₄ at 70—80° rapidly affords 5' : 5''-dimethylhomocærdianthra-7' : 7''-dione (5' : 5''-dimethyl-4 : 5 : 6 : 7 : 8 : 9-tribenzopyrene-3 : 10-quinone) (IV), blue, cryst., is oxidised by CrO₃ to the colourless 9 : 10-(OH)₂-compound, which is rapidly auto-reduced to (IV). Similarly are prepared 1 : 4-di-(2' : 4'-dimethylbenzoyl)- (by FeCl₃ or AlCl₃), m.p. 237—238°, 1 : 4-di-(2' : 4' : 6'-trimethylbenzoyl)- (by AlCl₃), m.p.



209—210°, and 1 : 4-di-p-anisoyl-anthraquinone (by FeCl₃), m.p. 243—245°, 9 : 10-di-p-anisylanthracene-1 : 4-dicarboxylic acid, cryst. (obtained by HI from the dihydroxydihydrodilactone or dilactone, which were not isolated pure), and 5' : 5''-dimethoxyhomocærdianthrone, cryst.

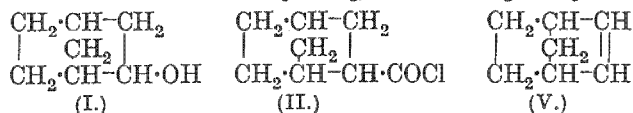
VI. 1 : 3-Dimethylantracene and pptd. MnO₂ in H₂SO₄-H₂O at 60—80° give 3-methylantraquinone-1-carboxylic acid (87% yield), m.p. 277° (cf. lit.), the constitution of which is proved by reduction (Zn dust-aq. NH₃), distillation, and oxidation to 2-methylantraquinone. This acid with PCl₅ in C₆H₆ affords the chloride, which with C₆H₆ and FeCl₃ yields 3-benzoyl-1-methylantraquinone, m.p. 224.5—226°, and the lactone of 9-phenyl-3-methyloxanthrone-1-carboxylic acid (not obtained pure), reduced by Zn dust and KOH to 9-phenyl-3-methylanthracene-1-carboxylic acid, m.p. 295.5—297°. m-Xylene affords similarly 84% of 1-(2' : 4'-dimethylbenzoyl)-3-methylantraquinone, m.p. 196.5—198°, and a little amorphous lactone. Anthraquinone-1 : 3-dicarboxylic acid (modified prep.)

gives (SOCl₂) the dichloride, cryst., which with C₆H₆ and FeCl₃ affords 1 : 3-dibenzoylanthraquinone, m.p. 212—214°, and the lactone of 3-benzoyl-9-phenyloxanthrone-1-carboxylic acid, not obtained pure. 1-Cyano-2 : 4-dimethylantraquinone (62% yield from the 1-NH₂-compound), m.p. 225—226°, affords 2 : 4-dimethylantraquinone-1-carboxylic acid, m.p. 241.5—242.5°, the chloride, m.p. 155—158°, of which leads to 9-phenyl-, m.p. 198—199°, and 9-m-xyl-2 : 4-dimethyloxanthrone-1-carboxylolactone, m.p. 202—204°, and 1-(2' : 4'-dimethylbenzoyl)-2 : 4-dimethylantraquinone, m.p. 193—194°. The lactones with H₂SO₄-Cu gives coeranthranols. The relative yields of lactones and diketones accord with expectation. 2-Methylantraquinone-1-carboxyl chloride has m.p. 196—198° (no decomp.; cf. lit.). R. S. C.

The "hydrosulphides" of carvone and 1 : 4-isopropyl-Δ²-cyclohexen-1-one. P. L. HOOPER, A. K. MACBETH, and J. R. PRICE (J.C.S., 1934, 1147—1150).—d-Carvone hydrosulphide forms a bis-2 : 4-dinitrophenylhydrazone, m.p. 222°, [α]_D²⁰ -172.2° in CHCl₃. 1 : 4-isoPropyl-Δ²-cyclohexen-1-one (2 : 4-dinitrophenylhydrazone, m.p. 137.5—138°) in EtOH with H₂S gives a hydrosulphide, m.p. 206—207°, [α]_D²⁰ -127.6° in CHCl₃ (bis-2 : 4-dinitrophenylhydrazone, m.p. 238—239°, [α]_D²⁰ +6.35° in CHCl₃). The hydrosulphide dinitrophenylhydrazones cannot be oxidised and with MeI in Et₂O-HgCl₂ yield those of the parent ketone. The structure of the compounds is discussed; the presence of two keto-groups is indicated.

F. R. S.

Norcamphor group. I. G. KOMPFA and S. BECKMANN (Annalen, 1934, 512, 172—185).—α-Norborneol (I), m.p. 149—150° (phenylurethane, m.p. 159—160°), is obtained from norcamphor by hydrogenation (colloidal Pd) in HCl-aq. EtOH or reduction with Na-EtOH. 1 : 2 : 2-dicycloheptanecarboxyl chloride (II), b.p. 200—202°/750 mm., 80—81°/8 mm. (obtained from the acid by PCl₅), with NaN₃ in xylene



at 120—140° gives β-norbornylcarbimide, b.p. 71—72°/9 mm. [NN'-di-β-norbornylcarbamide, m.p. 257—259° (decomp.)], hydrolysed by conc. HCl to β-norbornylamine, b.p. 156—157°, m.p. 75—80° [hydrochloride, m.p. about 260° (decomp.)]; aurichloride, m.p. 211—212° (decomp.); platinumchloride, decomp. > 200°; carbamide, m.p. 196—197°; phenylthiocarbamide, m.p. 154—155°; picrate, m.p. 174—175°, also obtained less well by Hofmann degradation of the amide from (II). This base with HNO₃ yields β-norborneol (III), m.p. 127—128°, b.p. 176—177° (phenylurethane, m.p. 145—146°; H phthalate, m.p. 102—103°; acetate, b.p. 89—90°/20 mm.), oxidised by K₂Cr₂O₇-H₂SO₄ to norcamphor. The corresponding chloride (obtained by PCl₅), b.p. 160—162°, or bromide (IV), b.p. 81—83°/30 mm., with Na and EtOH gives norbornylane (1 : 2 : 2-dicycloheptane), m.p. 86—87°. (III) and P₂O₅ or (IV) and boiling quinoline give norbornylene (V), m.p. 51—53° (dibromide, an oil; nitrosochloride, m.p. 157—158°; PhN₃-compound, m.p. 101—102°), which is oxidised only by KMnO₄. R. S. C.

Terpenes. I. Action of oxalic acid on *d*- α -pinene. T. KUWATA (J. Soc. Chem. Ind. Japan, 1934, 37, 312—315B).—*d*- α -Pinene and $\text{H}_2\text{C}_2\text{O}_4$ in COMe_2 at 50—90° afford *d*-borneol, *d*-isoborneol, *d*- α -terpineol (and their oxalates), dipentene, and a small amount of polyterpenes. The acid is assumed to attack the 1- and 7-positions. R. S. C.

Preparation of camphene from bornyl chloride. T. KUWATA (J. Soc. Chem. Ind. Japan, 1934, 37, 389—392B).—The activity of phenols in the removal of HCl from bornyl chloride by NH_2Ph (I) increases with the no. of OH groups. In presence of $\text{NH}_2\text{Ph}\cdot\text{HCl}$, the condensation of camphene (II) and (I) to give bornylaniline (III) is reversible. When bornyl chloride is distilled with (I), (II) is removed and (III) decomposes into (I) and (II). A. L.

Preparation of camphorquinone. J. ALLARD (Bull. Inst. Pin, 1934, 127—128; cf. this vol., 299).—Borneol and SeO_2 at a high temp. afford camphorquinone (60%). J. L. D.

Use of nitrogen dioxide in the terpene series. R. DULOV (Bull. Inst. Pin, 1934, 129—139).—Mainly a review. Benzylidenecamphor (cf. A., 1891, 1498) with N_2O_4 in Et_2O below 0° affords a nitrosite, m.p. 185—186°, which is hydrolysed (KOH) to camphorquinone. J. L. D.

Rotatory powers of disubstituted camphor-anilic acids. M. SINGH and B. SINGH (J. Indian Chem. Soc., 1934, 11, 433—440).— $[\text{M}]_{5780}$ and $[\text{M}]_{5461}$ in MeOH, EtOH, COMe_2 , and COMeEt are given for 2'-methyl-5', m.p. 206° (211.8°), 4', m.p. 221—222° (174.7°), and 3'-chloro-, m.p. 219° (145.5°), 4'-methyl-2'-chloro-, m.p. 206—207° (76.3°), and 2'-methoxy-5'-chloro-camphoranilic acid, m.p. 176—177°, the figures quoted in parentheses being $[\text{M}]_{5780}$ in MeOH. R. S. C.

cis- and trans-Isomerides of myrtanol. G. DUPONT and W. ZACHAREWICZ (Compt. rend., 1934, 199, 365—367).—Catalytic hydrogenation (PtO_2) of *d*-myrtenol (I) or *d*-myrtenal (II) leads to *d*-isomyrtanol (III), b.p. 122°/20 mm., $[\alpha]_D +20.67^\circ$ [from (II)] or b.p. 113—113.8°/14 mm., $[\alpha]_D +18.0^\circ$ [from (I)]. 1-isoMyrtanol has $[\alpha]_D -24.48^\circ$ (*H* phthalate of active alcohol, m.p. 124—124.5°, $[\alpha]_D -5.6^\circ$, and of *r*-alcohol, m.p. 126.5—127.5°). *d*-isoMyrtanyl acetate has b.p. 132.5—133.5°/26 mm., $[\alpha]_D +15.30^\circ$. Reduction of the requisite myrtenol by Na in xylene affords 1-myrtanol (IV), b.p. 126.5—127.5°/22 mm., $[\alpha]_D -26.06^\circ$ (*H* phthalate, m.p. 108.5—109°, $[\alpha]_D -15.0^\circ$; acetate, b.p. 127.5—128.5°/19 mm., $[\alpha]_D -21.51^\circ$), and *r*-myrtanol, b.p. 122—123°/19 mm. (*H* phthalate, m.p. 114.5—116°). Comparison of the Raman spectra indicates that (III) and (IV) are *cis*- and *trans*-forms, respectively, when the results are considered in conjunction with those obtained for bornel and isoborneol etc. H. W.

Colour reactions of blue sesquiterpenes. S. SABETAY and H. SABETAY (Compt. rend., 1934, 199, 313—316).—Hydrolysis of Bourbon geranium oil followed by fixation of the alcohols as borates and distillation leads to a sesquiterpene, b.p. 117—120°/5 mm., $\alpha +11.40^\circ$ (*l*-1), which gives a yellow colour with SbCl_3 and an intense blue with $\text{Br}\cdot\text{CHCl}_3$, with

$\text{HNO}_3\cdot\text{AcOH}$, or when heated with S. The reaction with $\text{Br}\cdot\text{CHCl}_3$ appears sp. for "blue" sesquiterpenes which give less satisfactory colorations with I, HI, H_2SO_4 , or HNO_3 . H. W.

Opianic acid and its derivatives. V. M. RODIONOV and S. J. KANEVSKAJA with (in part) M. SCHEMJAKIN, DAVANKOV, and (MLLES.) FEDOROVA, ABLETZOVA, and KUPINSKAJA (Bull. Soc. chim., 1934, [v], 1, 653—678).—The separation of opianic acid (I) from hemipinic acid (II) is modified (two methods). K opianate with $\text{CH}_2\text{Cl}\cdot\text{COMe}$ or $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ at 100° gives acetonyl (III), m.p. 104—106°, and carbethoxymethyl opianate [both α -(carboxylic) esters], m.p. 86—87° (semicarbazone, m.p. 186°). Me α -opianate with $\text{KOH}\cdot\text{MeOH}$ at 0° gives the ψ -ester. (I) and PhOH at 120° form the *Ph* ψ -ester, m.p. 145—147°; (III) with KOH , piperidine, or NaOAc in hot EtOH gives Et ψ -opianate. (I), NH_3 , and $\text{CH}_2(\text{CO}_2\text{H})_2$ in hot EtOH yield meconinacetic acid and β -amino- β -2-carboxy-3:4-dimethoxyphenylpropionic acid, m.p. 132—134°, which at 140—150° gives 3:4-dimethoxyphthalimidoacetic acid, m.p. 174—175°, but $\text{CH}_2(\text{CO}_2\text{Et})_2$ gives Et₂ meconinmalonate [*Et*₂ dimethoxyphthalidomalonate], m.p. 74—75°. (I) gives (Cannizzaro) meconin (IV) and (II). Hemipinimide, KOH , and KOC at 15—60° give a mixture of 2-aminoveratric and 3:4-dimethoxyanthranilic acid, m.p. 98—99°. The latter acid yields 2:3-dimethoxybenzoic (*o*-veratric) acid (V), m.p. 120—123°. Et guaiacol-*o*-carboxylate and $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ yield, after hydrolysis, an acid, m.p. 184—187°, and (V). (II), NaOH , and $\text{Hg}(\text{OAc})_2$ in hot, dil. AcOH give a mixture of 6-anhydrohydroxymercuri-2:3-dimethoxy- and 2-anhydrohydroxymercuri-5:6-dimethoxy-benzoic acid, hydrolysed to *o*- and *m*-veratric acid, respectively. (IV) and KCN at 180—185° give MeCN, a substance, m.p. 86—88°, and "methylnormeconin" (3-hydroxy-4-methoxyphthalide), m.p. 125°, converted into (IV) by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ and by $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Et}$ and $\text{KOH}\cdot\text{MeOH}$ into 4-methoxy-3-ethoxyphthalide, m.p. 68—69°, oxidised by KMnO_4 to 4-methoxy-3-ethoxyphthalic acid, m.p. 175—176° (anhydride, m.p. 105°). R. S. C.

Esterification in presence of alkali. Esterification of nitro-opianic acid by means of silver oxide. M. SCHEMJAKIN (Bull. Soc. chim., 1934, [v], 1, 689—691).—Nitro-opianic acid and Ag_2O or the pre-formed Ag salt in 55% aq. MeOH at room temp. give the Me ψ -ester, probably by way of the α -(carb-oxylic) ester. R. S. C.

Mechanism of geometrical inversion in regard to coumarins and coumaric acids. T. R. SESHADRI (Current Sci., 1934, 3, 19—20).—Two factors control the *cis* to *trans* inversion from coumarin (I) to coumaric acid (II), viz., addition at the double linking which renders rotation of the groups into the required position possible, and repulsion between the negatively-charged O and CO_2 which forms the driving force of the change. For the reverse change sunlight appears as effective as ultra-violet light and a mechanism is suggested. In the conversion of acids and esters into (I) by HCl, HBr, or H_2SO_4 at 100°, the removal of H_2O or EtOH is the first stage; the dipole that is formed supplies the necessary energy

for the inversion, and the rotation of the groups is facilitated by the temporary addition of the acids at the double linking. Transformation at the m.p. is initiated by loss of alcohol, and the combined effect of CO and the positive charge on the C atom occasioned by loss of OR eliminates the effect of the double linking. H. W.

Influence of substituents on the mercuration of coumarins. K. G. NAIK and A. D. PATEL (J.C.S., 1934, 1043—1047).—Substituted coumarins are only mercurated by Hg acetamide and acetate in presence of 5% NaOH, the results being mainly alike. Hg enters positions 6 and 8, monomercuration taking place if one position be occupied. NO₂ in position 6 is removed. Other groups also influence the course of reaction. Mercuration (Hg acetate) of coumarin gives 6:8-bishydroxymercuricoumarin, which with HCl forms the *chloromercuri*-compound, and with H₂SO₄ yields the *sulphatomercuri*-compound. Coumarin and Hg acetamide afford 6:8-bisacetoxymercuricoumarin, which with Na₂S₂O₃ gives a compound, C₁₈H₈O₄Hg₂. 7-Hydroxy-6:8-bisacetoxymercuri-4-methylcoumarin and I afford a product, m.p. 172°. F. R. S.

Synthesis of 5-hydroxyflavone. S. SUGASAWA (Proc. Imp. Acad. Tokyo, 1934, 10, 338—340).—2:6-Dimethoxybenzonitrile is converted by MgMeI in PhOMe into 2:6-dimethoxyacetophenone, b.p. 135—136°/2 mm., m.p. 68—69°, demethylated by AlCl₃ in PhMe to 2:6-dihydroxyacetophenone (I), m.p. 156—157°, also obtained in better yield but poorer quality from 6-methylumbelliferone acetate. (I), NaOBz, and Bz₂O at 180—190° yield 5-hydroxyflavone, m.p. 156—157° (acetate, m.p. 145°), whereas at 205—210°, 2-benzoyl-5-hydroxyflavone, m.p. 173—174° (acetate, m.p. 189—190°), is the main product. H. W.

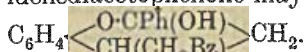
Synthesis of anthocyanins. XXI. 3-β-Glucosidyl delphinidin chloride. (Miss) T. M. REYNOLDS and R. ROBINSON (J.C.S., 1934, 1039—1043).—Tribenzoylgalloyl chloride and CH₂N₂ give ω-diazo-, m.p. 169° (decomp.), converted by HCO₂H into ω-formoxy-, m.p. 116—117°, and by AcOH into ω-acetoxy-3:4:5-tribenzoyloxyacetophenone, m.p. 138—140°; the formoxy-compound could not be hydrolysed. ω-Diazo-3:4:5-triacetoxyacetophenone (I) with *p*-toluenesulphonic acid forms ω-*p*-toluenesulphonoxo-, m.p. 134°, and with Br in COMe₂ yields ω-bromo-3:4:5-triacetoxyacetophenone, m.p. 123°; the ω-Cl-derivative has m.p. 114.5°. These compounds do not condense satisfactorily with glucose 2:3:4:6-tetra-acetate. (I) and HCO₂H yield ω-formoxy-3:4:5-triacetoxyacetophenone, m.p. 99—100°, hydrolysed to the ω-OH-compound, m.p. 87—88°. The OH-compound condenses with tetra-acetyl-α-glucosidyl bromide to ω-tetra-acetyl-β-d-glucosidoxy-3:4:5-triacetoxyacetophenone, m.p. 87—88° and 141—142°, [α]_D²⁰ green -26.0° in CHCl₃, which with 2-O-benzoylphloroglucinaldehyde and HCl yields benzoylacetylglucosidyl delphinidin chloride, hydrolysed by Ba(OH)₂ MeOH (air-free) to 3-β-glucosidyl delphinidin chloride (+0.8H₂O), purified through the picrate (+2.5H₂O). The anthocyanin has been characterised by colour reactions, absorption spectra, and distribution no. F. R. S.

Constitution of tannins. II. Structure and synthesis of bis-(5:7:3':4'-tetrahydroxy)flavipinacol. A. RUSSELL and J. TODD (J.C.S., 1934, 1066—1070).—Reduction (Zn-AcOH) of chalkone gives a bis-compound the properties of which have been examined. Measurements of H₂ absorbed (2 equivs.) during reduction of 2-hydroxychalkones indicate polymerisation. Phloracetophenone tribenzoate, protocatechualdehyde dibenzoate, and HCl yield 2:4:6:3':4'-pentabenzoyloxy-chalkone, hydrolysed to the -hydroxy-compound, m.p. 245°, which is reduced to bis-(5:7:3':4'-tetrahydroxy)flavipinacol. The properties of this substance have been compared with those of natural hemlock tannin and show that phlobatannins must be constituted similarly to the reduction products of 2-hydroxychalkones.

F. R. S.

Chromone group. XII. Synthesis of 7-hydroxyisoflavone and of α- and β-naphthaisoflavone. H. S. MAHAL, H. S. RAI, and K. VENKATARAMAN (J.C.S., 1934, 1120—1122).—2:4-Dihydroxyphenyl CH₂Ph ketone and CH₂PhCl give 2-hydroxy-4-benzoyloxyphenyl benzyl ketone, m.p. 111°, which with HCO₂Et and Na forms 7-benzoyloxy-, m.p. 171°, hydrolysed to 7-hydroxy-isoflavone, m.p. 215° (Ac derivative, m.p. 139°). 2-Phenylacetyl-α-naphthol, HCO₂Et, and Na yield 3-phenyl-1:4-α-naphthapyrone, m.p. 187°; the 1-phenylacetyl compound behaves similarly (cf. A., 1932, 1140). F. R. S.

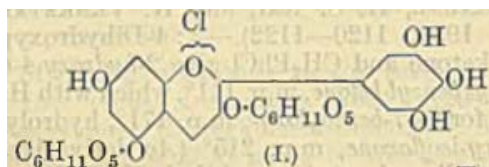
Reactions of o-hydroxybenzylidenediacyetophenones. I. Reaction with acids. D. W. HILL (J.C.S., 1934, 1255—1258).—o-Hydroxybenzylidenediacyetophenone (I) when preserved in cold or treated for a short time with hot AcOH affords 4-phenacylflavene (II), m.p. 96°, whilst it is converted by more prolonged treatment with boiling AcOH into 4-phenacylideneflavene (III), m.p. 128°, the corresponding substituted hydrochalkone, and C₆H₅Me. The yield of (II) indicates that the transformation of (I) into (III) proceeds entirely through (II). 2-Hydroxy-4-methoxybenzylidenediacyetophenone, m.p. 181°, from 2-hydroxy-4-methoxybenzaldehyde, C₆H₅Me, and NaOH in H₂O-EtOH, is converted similarly into 7-methoxy-4-phenacylflavene, m.p. 85—86°, and 7-methoxy-4-phenacylideneflavene, m.p. 153°, accompanied by Ph β-2-hydroxy-4-methoxyphenylethyl ketone (semicarbazone, m.p. 177—178°). 2-Hydroxy-5-methoxybenzylidenediacyetophenone (improved prep.) yields 6-methoxy-4-phenacylflavene, m.p. 118—119°, and 6-methoxy-4-phenacylideneflavene, m.p. 146—147°. The analogy between these reactions and the conversion of certain chromanols into chromenes by AcOH suggests that o-OH-derivatives of benzylidenediacyetophenone may be formulated



H. W.

Synthesis of anthocyanins. XXII. Isolation of an anthocyanin of *Salvia patens* termed delphin, and its synthesis. (Miss) T. M. REYNOLDS, R. ROBINSON, and (Miss) R. SCOTT-MONCRIEFF (J.C.S., 1934, 1235—1243).—A delphinidin diglycoside has been isolated as delphin chloride or O-3:3-diglucosidyl delphinidin chloride (I) from the flowers of *S. patens*, in which it may occur in an acylated form. In

purification the Ac group is removed and the resulting anthocyanin is named *delphin*; it is probably widely distributed. (I) is hydrolysed to delphinidin chloride [hydrate (+3.5H₂O)] and glucose. ω -Tetra-acetyl- β -glucosidoxy-3:4:5-triacetoxyacetophenone (II) and 2-O-tetra-acetyl- β -glucosidylphloroglucinaldehyde (III) condense (HCl) and yield with difficulty (I). 2-O-Tetra-acetyl- α -glucosidyl-4-O-benzoylphloroglucinaldehyde, m.p. 72—74°, obtained from (III) and BzCl condenses with (II) to give 7-benzoyloxy-3':4':5'-triacetoxy-3:5-di(tetra-acetyl- β -glucosidoxy)flavylum chloride (?). The colour reactions, absorption in the visible region, and distribution no. of (I) have been determined and the natural and synthetic pigments compared. The autocondensation product of 2-O-benzoylphloroglucinaldehyde (EtOAc-HCl) gives a cryst. substance, C₁₈H₁₅O₇Cl.3H₂O.0.1HCl, which after hydrolysis gives a *chloride* and a *picrate*. The condensation product of (III) could not be isolated.



F. R. S.

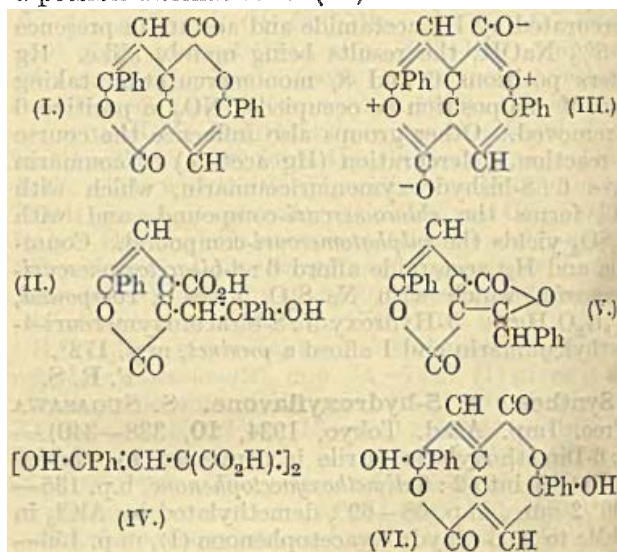
Synthesis of cœroxonones. F. E. KING (J.C.S., 1934, 1064—1066).—The Na salt of resorcinol Me ether (I) and 1-chloroanthraquinone (II) give *erythroxyanthraquinone 3'-methoxyphenyl ether*, m.p. 130—131°, which with H₂SO₄ yields *cœroxonone-3:9*, m.p. 310°. (I) and 1:5-dichloroanthraquinone (III) similarly form *anthrarufin di-3'-methoxyphenyl ether*, m.p. 177—178°, and *cœrdioxonone-3:11* (+H₂SO₄), a strong vat dye. The Na salt of pyrogallol Me₃ ether (IV) and (II) give *erythroxyanthraquinone 2':3'-dimethoxyphenyl ether*, m.p. 165°, which with H₂SO₄ gives 4-hydroxy-cœroxonone [Ac derivative, m.p. 235—240° (decomp.)], a weak green dye unaffected by NH₂Ph. (III) and (IV) afford *anthrarufin bis-2':3'-dimethoxyphenyl ether*, m.p. 183°, forming with H₂SO₄ 4:12-dihydroxycœrdioxonone-3:11 (+0.5H₂SO₄), a maroon dye.

F. R. S.

Formation of "Pechmann's dye" and some derivatives thereof. Constitution of "Pechmann's dye," C₂₀H₁₂O₄. C. DUFRAISSE and P. CHOVIN (Bull. Soc. chim., 1934, [v], 1, 771—789, 790—796).—Addition of PCl₅ (2 mols.) to CH₂Bz.CO.CO₂Et (1 mol.) at 10°, removal of excess of PCl₅ by cyclohexanone, and subsequent heating at 155° gives Pechmann's dye (I), C₂₀H₁₂O₄, m.p. 317° (block) (2.5—6.5%) [obtained only in the same yield from CHBz.CH.CO₂Et (cf. lit.)], characterised by its absorption (max. at λ 5050 and 5400). (I) is unchanged by Ac₂O, H₂O₂, or cold, conc. HCl, but with CrO₃ gives BzOH. (I) with cold 20% KOH-EtOH gives a yellow acid (II), C₂₀H₁₄O₅ + H₂O, m.p. 214°, and an orange substance (III), C₂₀H₁₄O₅, m.p. 332°. (II) is also obtained from (III) by 10% KOH-EtOH; when dissolved in NaHCO₃ and pptd. by acid it gives the yellow acid (IV), C₂₀H₁₂O₄ + 2H₂O, m.p. 221°, of Bogert and Ritter. When heated alone or with Ac₂O, (IV) gives (III), and when dissolved in KOH-EtOH and pptd. by acid gives (II). (III)

and HNO₃ (13%) give a neutral, yellow substance (V), C₂₀H₁₂O₄, m.p. 335°. (I) in C₆H₆ and HNO₃ (13%) give a colourless dicarboxylic acid (VI), C₂₀H₁₄O₆, m.p. 224° (block), which at 200° gives CO₂ (nearly 1 mol.) and 10% of (I). (V) with Fe-AcOH gives a neutral, yellow substance, C₂₀H₁₄O₄, m.p. 333° (block). (I) is assumed to be formed by disproportionation.

The following formulæ are assigned, the dilactonic formula for (I) being discarded. The ketonic form is a possible alternative for (IV).



R. S. C.

Thiophen derivatives. XXVI. Isomeric bromothiophens and the constitution of thiophendisulphonic acids. W. STEINKOPF, H. JACOB, and H. PENZ (Annalen, 1934, 512, 136—164; cf. A., 1933, 512).—Substituents in the α -position in thiophen are more labile than those in the β -position. Thus, sulphonation of α -halogenothiophens leads to some replacement of halogen by SO₃H, α -nitrothiophens afford tetrabromothiophen, α -bromothiophens react with Mg (in presence of much MeBr, which is often effective also in the C₆H₆ series), and α -sulphothiophens are desulphonated by an excess of Na-Hg. Many data recorded in the lit. are superseded by those given below, where all the constitutions cited are rigidly proved. Mesitylenedisulphonyl chloride and *o*-C₆H₄(SO₂Cl)₂ with *o*-C₆H₄(NH₂)₂ give the *di-p-aminoanilides*, m.p. 200° (decomp.) and 261° (decomp.), respectively. 2-Iodothiophen and ClSO₃H at -15° give 2-iodothiophen-5-sulphonyl chloride (I), m.p. 51—52° (sulphonamide, m.p. 165°), and thiophen-5-sulphonyl chloride (II). (I) and H₂SO₄-SO₃ (33%) at < 35° afford 2-iodothiophen-3:5-disulphonyl chloride, m.p. 87—88°, converted by a little Na-Hg into thiophen-2:4-disulphonyl chloride, but by an excess into thiophen-3-sulphonyl chloride. 2-Bromothiophen affords 2-bromothiophen-5-sulphonyl chloride, m.p. 44—46° (sulphonamide, m.p. 144° [converted into (II)]), and -3:5-disulphonyl chloride, m.p. 98—101° (ar-sulphonamide, m.p. 214°). Thiophen-2:4-disulphonyl chloride and Na-Hg give thiophen-3-sulphonyl chloride. Tetrabromothiophen (III) (modified prep.), m.p. 117—118° (lit. 114°), b.p. 170—173°/13 mm., and Mg-MgMeI give 2:3:4-tribromo- (IV) (50%

m.p. 43—46°, and some 3:4-dibromo-thiophen, b.p. 221—222°. (IV) affords 2:3:4-tribromo-5-nitrothiophen, m.p. 96—98°. (III) leads similarly to 3:4:5-tribromothiophen-2-carboxylic acid, m.p. 259°, and 2:3:4-tribromo-5-iodothiophen, m.p. 126°. Tetrachlorothiophen gives similarly 2:3:4-trichlorothiophen, b.p. 203—208° (5- NO_2 -derivative, m.p. 73—76°), and 3:4:5-trichlorothiophen-2-carboxylic acid, m.p. 224° after sintering. 2:5-Dichlorothiophen gives the 3:4-(NO_2)₂-derivative, m.p. 88—91°. 3:4-Dibromothiophen, m.p. 4·5°, b.p. 221—222°, obtained in 30% yield from (III) or as a by-product together with (IV), leads to the 2- NO_2 - (prepared in Ac_2O), m.p. 115—116°, 2:5-(NO_2)₂-, m.p. 128°, and 2-HgCl-derivatives, m.p. 191°, 3:4-dibromo-2-acetothienone, m.p. 83—85°, *Ph* 2-(3:4-dibromothiophenyl) ketone, m.p. 107—109° [oxime, m.p. 155—156°; converted by Br into (III)], 3:4-dibromothiophen-2-sulphonyl chloride, m.p. 118°, and -2:5-disulphonyl chloride, m.p. 169°, and 3-bromothiophen-4-carboxylic acid, m.p. 150—152°. (IV) leads to 3:4-dibromothiophen-2-carboxylic acid (poor yield), m.p. 198° (with Br gives the 3:4:5- Br_3 -acid), and 3:4-dibromo-2-iodothiophen, m.p. 60°. 2:3:5-Tribromothiophen (V) gives (Grignard etc.) 3-bromothiophen (VI), b.p. 157—158°, 2:3-, m.p. -15·5°, b.p. 214° (5-HgCl-, decomp. 240°, and 5- NO_2 -derivative, m.p. 75°), and 2:4-dibromothiophen, m.p. -30° to -25°, b.p. 210° [5-HgCl-, m.p. 184—187°, 5- NO_2 -, m.p. 79—80°, and 3:5-(NO_2)₂-derivative, m.p. 102°]. These compounds lead to 2:3:2':3'-, nom.p., and 2:4:2':4'-tetrabromo-5:5'-dichloromercuridithienyl, m.p. 195—200°, 4:5-, m.p. 85—86°, and 3:5-dibromo-2-acetothienone, m.p. 45°, *Ph* 5-(2:3-dibromothiophenyl) ketone, m.p. 80° (also obtained from *Ph* 2-thienyl ketone and Br), 2:3-dibromothiophen-5-sulphonyl chloride, m.p. 80° (debrominated by Na-Hg), and 2:4-dibromothiophen-3:5-disulphonyl chloride, m.p. 157° (debrominated by Na-Hg). (V) gives (Grignard, CO_2) 4:5-, m.p. 227—228° (lit. 222°), and 3:5-dibromothiophen-2-carboxylic acid, m.p. 180—188° (affording the 3:4:5- Br_3 -acid), and by a Grignard reaction with I 2:3-dibromo-5-iodothiophen, m.p. 59°. (VI) gives the 2-HgCl-derivative, m.p. 120·5—123°, 3:3'-dibromo-2:2'-dichloromercuridithienyl, m.p. 154°, 3-bromo-(?)2-nitro-, m.p. 81—83° after sintering, and two ??-dinitro-thiophens, m.p. 110—111° and 167°, respectively, 3-bromo-(?)2-acetothienone, b.p. 130°/11 mm., and 3-bromothiophen-2-carboxylic acid, m.p. 190°. 5-Bromothiophen-2-carboxylic acid, m.p. 141—142°, prepared from 2:5-dibromothiophen (VII) and thiophen-2-carboxylic acid (VIII), yields 4:5-dibromothiophen-2-carboxylic acid, m.p. 228—229·5°. (VIII) and Cl_2 in cold AcOH give the 5- Cl -acid, m.p. 146—147°. (VII) and $\text{H}_2\text{SO}_4\text{-HNO}_3$ at < 40° give 2:5-dibromo-3-nitrothiophen, m.p. 60—61°, also obtained from 3-nitrothiophen and Br. 2-Bromothiophen with fuming HNO_3 in Ac_2O gives the (?)2- NO_2 -derivative, m.p. 48—49°. (VII) gives (Grignard, I) 2-bromo-5-iodothiophen, b.p. 116°/13 mm. (IV), (III), and (V) all afford 3:4:5-tribromo-2-acetothienone, m.p. 131°, the yields decreasing in the order given. 2:5-Dibromothiophen-3:4-disulphonyl chloride (modified prep.) gives the dianilide, m.p. 175°. 2:5-Thioxen and fuming H_2SO_4 form 2:5-thioxen-3:4-disulphonic anhydride, decomp. 200° (darkening

at 170°) (disulphonyl chloride, m.p. 146°). Similarly are obtained 2:4-thioxen-3:5-disulphonyl chloride, m.p. 74°, and 2:3-thioxen-5-sulphonamide, m.p. 137—139° after sintering. The Grignard reagent from (III) with anhyd. CuCl_2 gives (IV) and 2:3:4:2':3':4'-hexabromodithienyl, m.p. 125°. Chlorobromothiophens could not be obtained by Grignard reactions.

R. S. C.

Diphenylene sulphides. C. COURTOT (Compt. rend., 1934, 198, 2260—2263).—The following sulphones are prepared by interaction of the sulphide with H_2O_2 in AcOH . 5-Chloro- (I), m.p. 249°; 5-bromo- (II), m.p. 266—267° (sulphide, m.p. 126°); 5:5'-dichloro-, m.p. 340° (sulphide, m.p. 212°), and 5:5'-dibromo-diphenylene sulphone, m.p. 361—362° (sulphide, m.p. 229°). Diphenylene sulphone mono-(+ H_2O , m.p. 276°; sulphonyl chloride, m.p. 234—235°; sulphonyl chloride of sulphide, m.p. 141°), and disulphonic acid [disulphonyl chloride, m.p. 333—340° (decomp.)]. The monosubstituted sulphones with NaOH at 195—230° afford hydroxydiphenylene sulphone, m.p. 256—258° (*Ac* and *Bz* derivatives, m.p. 269° and 176°, respectively), and some hydroxydiphenyl-2-sulphonic acid. The disubstituted sulphones give some dihydroxydiphenylene sulphone, m.p. 331° (*Bz* derivative, m.p. 227—228°), but mainly dichloro- (sulphonyl chloride, m.p. 202°) and dibromo-diphenyl-2-sulphonic acid (cf. A., 1931, 1406). The orientation of the halogens (cf. A., 1931, 1406; this vol., 900) is shown by the conversion of 5-chloro-2-aminodiphenyl (A., 1927, 236) through the diazonium compound into the sulphonic acid, m.p. 102°, the chloride of which is cyclised in PhNO_2 containing AlCl_3 to (I). Similarly, 5-bromo-2-aminodiphenyl affords (II).

J. L. D.

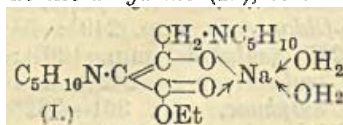
Preparation and identification of 2:5-dimethylpyrrole. C. F. H. ALLEN and D. M. YOUNG (Canad. J. Res., 1934, 10, 771—773).—A new, convenient method for preparing 2:5-dimethylpyrrole (I) is to reflux $[\text{CH}_3\text{Ac}]_2$ with $(\text{NH}_4)_2\text{CO}_3$. The identification of (I) is discussed; (I) with 2:4-dinitrophenylhydrazine in aq. $\text{EtOH-H}_2\text{SO}_4$ gives acetonylacetone-2:4-dinitrophenylhydrazone, m.p. 262°, and *Et* 3-acetyl-2:4-dimethylpyrrole-5-carboxylate similarly gives a 2:4-dinitrophenylhydrazone, m.p. 264°.

H. N. R.

Bacteriostatic azo-compounds. I. OSTROMISLENSKY (J. Amer. Chem. Soc., 1934, 56, 1713—1714).— $\text{C}_5\text{H}_5\text{N}$ and NaNH_2 in NPhMe_2 give (cf. Tschitschabin and Zeide, A., 1915, i, 590) a mixture (A) of 2:6-(I) and 2:4-diaminopyridines. (A) and diazotised NH_2Ph afford (cf. B., 1929, 493) a mixture (B) of (probably) 2:4-diamino-5-benzeneazopyridine, m.p. 203°, and 2:6-diamino-3-benzeneazopyridine (II) [the dihydrochloride, from (I) and PhN_2Cl in 8% HCl , passes into the free base when heated to 100°]. 2:6-Diamino-3-p-hydroxy- (III), m.p. 214—215°, -3-p-methoxy-, m.p. 192°, -3-p-ethoxy- (IV), m.p. 176—177°, and -3-o-carboxy-, decomp. slowly at 270°, -benzeneazopyridine are prepared from (I) and $\text{C}_6\text{H}_4\text{R.N}_2\text{X}$. The bacteriostatic index (max. dilution preventing growth of *S. albus*, *S. aureus*, and *Str. haemolyticus* on agar media) of the hydrochlorides of (B), (II), (III), and (IV), *m*-phenylenedisazobis-*m*-phenylenediamine

hydrochloride, 4- β -naphthaleneazo-*m*-phenylenediamine hydrochloride, and 2:4-diaminoazobenzene hydrochloride has been determined. H. B.

Acetoacetic ester condensation. VIII. Condensation of ω -piperidino-esters. W. B. THOMAS and S. M. McELVAIN (J. Amer. Chem. Soc., 1934, 56, 1806—1809).—Et piperidinoacetate (I) and NaOEt (0.5 mol.) at 110—115°/37 mm. give EtOH (83%) and 52% of Et sodio- α -dipiperidinoacetoacetate [isolated as the dihydrate (II), softens at about 100° and then decomposes on further heating, by addition of H₂O to the Et₂O-C₆H₆ solution of the reaction mixture]. (II) is hydrolysed (aq. EtOH-NaOH in N₂) to *s*-dipiperidinoacetone [dihydrochloride, m.p. 175—195° (decomp.)]. Similar condensation of Et β -piperidinopropionate, γ -piperidinobutyrate (III), b.p. 128—130°/19 mm., and δ -piperidinovalerate, b.p. 132—134°/10 mm., followed by hydrolysis (20% HCl), gives 53—68% of di- β -piperidinoethyl ketone (semicarbazone, m.p. 96—97°; dihydrochloride, m.p. 212—214°), di- γ -piperidinopropyl ketone, b.p. 188—190°/3 mm. (semicarbazone, m.p. 82—83°; dihydrochloride, m.p. 241—242°), and di- δ -piperidinobutyl ketone, b.p. 220—221°/2 mm. (semicarbazone, m.p. 88—89°; dihydrochloride, m.p. 222—223°), respectively, together with some β -piperidinopropionic (hydrochloride, m.p. 206—209°), γ -piperidinobutyric (IV), b.p. 162—164°/2 mm., m.p. 71—72° (hydrochloride, m.p. 189—190°), and δ -piperidinovaleric acid (hydrochloride, m.p. 198—200°), respectively. The above condensations do not proceed satisfactorily at atm. pressure; thus, (III) affords EtOH (71%) and (after treatment with AcOH in Et₂O-C₆H₆) (IV) and tarry material. EtOH is also eliminated from Et 3-carbethoxypiperidinoacetate and NaOEt (0.5 mol.) at 110—115°/20 mm.; no condensation occurs (cf. A., 1924, i, 417) with Na at 150° or with Na or NaOEt in xylene. (I) does not react with Na at 150°, whilst (III) does so. The presence of an α -piperidino-group inhibits the reaction with Na (cf. *loc. cit.*); in view of the ready condensation with NaOEt, further evidence is thus obtained that Na is not the active condensing agent in the acetoacetic ester condensation. H. B.

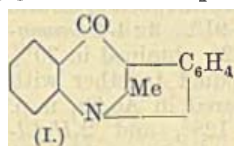


decomposes on further heating, by addition of H₂O to the Et₂O-C₆H₆ solution of the reaction mixture]. (II) is hydrolysed (aq. EtOH-NaOH in N₂) to *s*-dipiperidinoacetone [dihydrochloride, m.p. 175—195° (decomp.)]. Similar condensation of Et β -piperidinopropionate, γ -piperidinobutyrate (III), b.p. 128—130°/19 mm., and δ -piperidinovalerate, b.p. 132—134°/10 mm., followed by hydrolysis (20% HCl), gives 53—68% of di- β -piperidinoethyl ketone (semicarbazone, m.p. 96—97°; dihydrochloride, m.p. 212—214°), di- γ -piperidinopropyl ketone, b.p. 188—190°/3 mm. (semicarbazone, m.p. 82—83°; dihydrochloride, m.p. 241—242°), and di- δ -piperidinobutyl ketone, b.p. 220—221°/2 mm. (semicarbazone, m.p. 88—89°; dihydrochloride, m.p. 222—223°), respectively, together with some β -piperidinopropionic (hydrochloride, m.p. 206—209°), γ -piperidinobutyric (IV), b.p. 162—164°/2 mm., m.p. 71—72° (hydrochloride, m.p. 189—190°), and δ -piperidinovaleric acid (hydrochloride, m.p. 198—200°), respectively. The above condensations do not proceed satisfactorily at atm. pressure; thus, (III) affords EtOH (71%) and (after treatment with AcOH in Et₂O-C₆H₆) (IV) and tarry material. EtOH is also eliminated from Et 3-carbethoxypiperidinoacetate and NaOEt (0.5 mol.) at 110—115°/20 mm.; no condensation occurs (cf. A., 1924, i, 417) with Na at 150° or with Na or NaOEt in xylene. (I) does not react with Na at 150°, whilst (III) does so. The presence of an α -piperidino-group inhibits the reaction with Na (cf. *loc. cit.*); in view of the ready condensation with NaOEt, further evidence is thus obtained that Na is not the active condensing agent in the acetoacetic ester condensation. H. B.

2:6-Diamino-4-benzeneazopyridine. A. E. CHICHIBABIN (TSCHITSCHIBABIN) and E. D. OSSETROWA (J. Amer. Chem. Soc., 1934, 56, 1711—1713, and Bull. Acad. Sci. U.R.S.S., 1934, 615—622).—4-Phenylhydrazinopyridine-2:6-dicarboxylic acid (+EtOH), m.p. 231° (from the 4-Cl-acid and NHPhNH₂ at 130—133°), is oxidised (air in feebly alkaline solution) to 4-benzeneazopyridine-2:6-dicarboxylic acid (+0.5AcOH), m.p. 270° (decomp.), the Me ester, m.p. 175°, of which with N₂H₄.H₂O at 200° gives the phenylhydrazino-dihydrazide, which on recrystallisation is oxidised to 4-benzeneazopyridine-2:6-dicarboxyhydrazide, m.p. 228°. This is converted into the diazide, m.p. 110°, which with boiling EtOH affords the corresponding diurethane, m.p. 182°, hydrolysed (EtOH-KOH) to 2:6-diamino-4-benzeneazopyridine (I), m.p. 170—171°, and the corresponding monourethane, m.p. 143°. (I) is not obtained from

2:6-diaminopyridine and diazotised NH₂Ph (cf. Ostromislensky, B., 1929, 493). H. B.

Action of acetylsalicylyl chloride on magnesyloindoles. C. TOFFOLI (Gazzetta, 1934, 64, 364—371).—Interaction of Mg 2-methylindolyl bromide (2 mols.) with acetylsalicylyl chloride (1 mol.) yields *o*-hydroxyphenyl 3-(2-methylindolyl) ketone, m.p. 167° (hydrobromide, m.p. 180°). From equimol. quantities



the products are 3-acetyl-2-methylindole, *o*-3-(2-methylindolyl)phenyl 3-(2-methylindolyl) ketone, m.p. 197° (hydrobromide, m.p. 187°; picrate, m.p. 190°), and *o*-1:3-phenylene-2-methyl-4-ketoquinoline (I) m.p. 236° (hydrobromide, m.p. 236°; picrate, m.p. 233°). R. K. C.

New reactions of phenylcarbimide. III. Benzylidenearminoindoles. A. NERI (Gazzetta, 1934, 64, 420—438).—2- α -Anilinobenzyl-3-methylindole (A., 1933, 615) condenses with PhNCO to give α -(phenyl-2-methyl-3-indolylmethyl)- α - β -diphenylcarbamide, m.p. 116°, readily decomposed on attempting recrystallisation or hydrolysed by 20% HCl to benzylidene-2:2'-dimethyl-3:3'-di-indole (I), m.p. 246°. 3- α -*o*-Nitroanilinobenzyl-2-methylindole, m.p. 187°, yields α -(*o*-nitrophenyl-2-methyl-3-indolylmethyl)- α - β -diphenylcarbamide, m.p. 198—199°. 2-Methylindole (II) and benzylidene-*m*-nitroaniline yield only (I). (II) with NH₃ and 1 or 2 mols., respectively, of *o*-nitrobenzaldehyde yields 3- α -amino-*o*-nitrobenzyl-2-methylindole, m.p. 182°, or 3- α -*o*-nitrobenzylidene-amino-*o*-nitrobenzyl-2-methylindole, m.p. 132°. (II), NH₃, and PhCHO yield benzylidenedi-indole. R. K. C.

Modification of Skraup's synthesis of quinoline. G. I. MIKHAILOV (Khim. Farm. Prom., 1933, 344—347).—PhNO₂ (2.32 kg.), NH₂Ph (0.56 kg.), and glycerol (1.23 kg.) are treated in a special apparatus with H₂SO₄ (0.31 kg.), with stirring. The temp. is kept at 147—149° for 2 hr., 0.94 kg. of H₂SO₄ being slowly added. H₂O and PhNO₂ begin to distil. When the acid is added the temp. is kept at 148—149° for 1.5 hr., then slowly raised to 152° and kept so for 15 min. The mixture is cooled to 120°, freed from PhNO₂, diluted with H₂O (4.5 litres), cooled to 10°, and neutralised. The bases are distilled with steam, poured into 0.9 litre of HCl (*d* 1.14), cooled to -5°, and diazotised with NaNO₂. The diazonium salt is decomposed, and the quinoline (0.7 kg.) separated with steam from the alkaline liquid. CH. ABS.

Direct introduction of amino-group into aromatic and heterocyclic nucleus. I. Reaction of quinoline with alkali and alkaline-earth amides in liquid ammonia. F. W. BERGSTROM (J. Amer. Chem. Soc., 1934, 56, 1748—1751).—2-Aminoquinoline (I) is not obtained from quinoline (II) and KNH₂ (in liquid NH₃ at 20—130°) or NaNH₂ or LiNH₂ (at 20°), resinous material is formed, not only in liquid NH₃, but also in NH₂Bu⁺ and NEt₃. (II) and in liquid NH₃ containing Hg give 5—11% of (I). (I) is obtained in good yield from (II) and Ba(NH₂)₂ in liquid NH₃ at room temp.: reaction is accelerated by Ba(NO₃)₂, Ba(CNS)₂, LiNO₃, and Sr(NO₃)₂. A

(I) is produced from (II) and $\text{Sr}(\text{NH}_2)_2$; $\text{Ca}(\text{NH}_2)_2$ is unreactive. Of the various complex ammonio-salts investigated, $\text{Ba} \cdot \text{NK} \cdot 2\text{NH}_3$ only reacts with (II) to give (I); slight dissociation into KNH_2 and $\text{Ba}(\text{NH}_2)_2$ probably occurs.

H. B.

Synthesis of *Bz*-tetrahydroquinolines. U. BASU (Annalen, 1934, 512, 131—135).—2-Hydroxy-methylenecyclohexanone (or its acetate) and *Et* β -aminocrotonate give *Et* 2-methyl-5:6:7:8-tetrahydroquinoline-3-carboxylate, b.p. $158^\circ/11$ mm. (picrate, m.p. 147° ; HgCl_2 -compound, m.p. 116°), hydrolysed to the corresponding acid, m.p. 228° (decomp.), which, when distilled with soda-lime, affords 2-methyl-5:6:7:8-tetrahydroquinoline, b.p. $225^\circ/762$ mm. (methiodide, m.p. 121° ; picrate, m.p. 157° ; platinumchloride, m.p. 198° ; dehydrogenated by distillation over Pb). Similarly were prepared *Et* 2:7-(I), b.p. $163^\circ/11$ mm., and 2:6-dimethyl-5:6:7:8-tetrahydroquinoline-3-carboxylate, an oil (picrate, m.p. 129° ; HgCl_2 -compound, m.p. 122°), the acid from (I), m.p. 243 — 244° (decomp.), and 2:7-dimethyl-5:6:7:8-tetrahydroquinoline, b.p. $237^\circ/762$ mm. (methiodide, m.p. 184° ; picrate, m.p. 152° ; platinumchloride, m.p. 195°). 2-Hydroxymethylene-5-methylcyclohexanone and benzoylacetoneimine in hot *EtOH* give 3-benzoyl-2:7-dimethyl-5:6:7:8-tetrahydroquinoline, m.p. 77° (picrate, m.p. 177°).

R. S. C.

Synthesis of isoquinoline derivatives. III.

Synthesis of corydaldine. L. M. MOHUNTA and J. N. RAY (J.C.S., 1934, 1263—1264).—The azide, obtained from the hydrazide of β -3:4-dimethoxyphenylpropionic acid, m.p. 132° , in *PhMe* solution gives the carbimide (I), cyclised to corydaldine and a neutral substance (II). (I) condenses with various bases to give carbamides, $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NHR}$, which with POCl_3 form bases, 1-arylimino-6:7-dimethoxy-1:2:3:4-tetrahydroisoquinolines: carbamide ($\text{R} = \text{Ph}$), m.p. 154° , and base, m.p. 139° ; carbamide ($\text{R} = p\text{-C}_6\text{H}_4\text{Me}$), m.p. 155° , and base, m.p. 126° ; carbamide ($\text{R} = m\text{-C}_6\text{H}_4\text{Me}$), m.p. 150° , and base, m.p. 188° ; carbamide ($\text{R} = o\text{-C}_6\text{H}_4\text{Me}$), m.p. 153° ; and carbamide ($\text{R} = p\text{-C}_6\text{H}_4 \cdot \text{OEt}$), m.p. 152° , and base. Condensation of (I) with *NHPhMe* leads to 1-phenylmethylamino-6:7-dimethoxy-3:4-dihydroisoquinoline, m.p. 150° , reduced (Al-Hg) to a base, m.p. 155 — 158° . (I) and Ac_2O in *PhMe* yield *s*-bis-(β -3:4-dimethoxyphenylethyl)carbamide, m.p. 152° , identical with (II).

F. R. S.

Substituted tetrahydroisoquinoline hydrochlorides. J. S. BUCK (J. Amer. Chem. Soc., 1934, 56, 1769—1771).—6-Methoxy-, m.p. 236° , 5:6-dimethoxy-, m.p. 232° , and 6:7-dimethoxy-, m.p. 253° , tetrahydroisoquinoline hydrochlorides are obtained from the appropriate $\text{CH}_2\text{Ar} \cdot \text{CH}_2 \cdot \text{NH}_2$ and 40% CH_2O , and subsequent cyclisation (23% HCl) of the $\text{CH}_2\text{Ar} \cdot \text{CH}_2 \cdot \text{N} \cdot \text{CH}_2$. They are demethylated (conc. HCl at 170°) to 6-hydroxy-, m.p. 233° , 5:6-dihydroxy-, m.p. 246° , and 6:7-dihydroxy-, m.p. 262° , tetrahydroisoquinoline hydrochlorides, respectively. 6-Methoxy-, m.p. 170° , 5:6-dimethoxy-, m.p. about 210° , and 6:7-dimethoxy-, m.p. 215° , *N*-methyltetrahydroisoquinoline hydrochlorides, prepared similarly from $\text{CH}_2\text{Ar} \cdot \text{CH}_2 \cdot \text{NHMe}$, are demethylated (52% HI) to

6-hydroxy-, m.p. 236° , 5:6-dihydroxy-, m.p. 255° (decomp. 139°), and 6:7-dihydroxy-, m.p. 276° , *N*-methyltetrahydroisoquinoline hydrochlorides, respectively. Application of the above reaction to homopiperonylamine and its *N*-Me derivative gives (? 5:6)-methylenedioxy-, m.p. $> 315^\circ$, and (? 5:6)-methylenedioxy-*N*-methyl-, m.p. 315° (to red liquid), tetrahydroisoquinoline hydrochloride, respectively. 6:7-methoxy-*N*-methyltetrahydroisoquinoline and *N*-methyltetrahydroisoquinoline hydrochloride have m.p. 75 — 77° and 228° , respectively.

H. B.

Attempts to find new antimalarials. VIII.

Derivatives of 8-aminoalkylaminoquinoline.

A. W. BALDWIN and R. ROBINSON. IX. 8- δ -

Aminobutylamino-6-ethoxyquinoline. W. MEI-

SEL and R. ROBINSON (J.C.S., 1934, 1264—1267,

1267—1268).—VIII. 8-Amino-6-ethoxyquinoline and

β -bromoethylphthalimide condense to 8- β -phthalimido-

ethylamino-6-ethoxyquinoline, m.p. 178 — 179° , hydro-

lysed to 8- β -aminoethylamino-6-ethoxyquinoline di-

hydrochloride, m.p. 247° . 8-Aminoquinoline and γ -

bromopropylphthalimide (I) yield 8- γ -phthalimido-

propylaminoquinoline, m.p. 111° , hydrolysed to 8- γ -

aminopropylaminoquinoline dihydrochloride ($+\text{H}_2\text{O}$).

2-Nitro-4-*n*-butoxyaniline, m.p. 66° , is converted into

8-nitro-6-*n*-butoxyquinoline, m.p. 92° , reduced to the

8-amino-compound, m.p. 59° , which with (I) gives

8- γ -phthalimidopropylamino-6-*n*-butoxyquinoline, m.p.

75 — 80° . $(\text{CH}_2\text{Cl} \cdot \text{CH}_2)_2\text{O}$, $o\text{-C}_6\text{H}_4(\text{CO})_2\text{NH}$, and K_2CO_3

yield diphtalimidodiethyl ether, m.p. 157° , and

phthalato- β -(β' -chloroethoxy)ethylamide, m.p. 72° , which

with KI yields the corresponding I-compound, m.p.

83 — 84° . The I-compound and 8-amino-6-methoxy-

quinoline (II) give 8- β -(β' -phthalimidoethoxy)ethyl-

amino-6-methoxyquinoline, m.p. 145° , hydrolysed

to 8- β -(β' -aminoethoxy)ethylamino-6-methoxyquinoline

hydrochloride, m.p. 224° . 5-Nitro-2-methoxy-*m*-xylene,

m.p. 91° , is reduced to 2-methoxy-*m*-5-xylydine, m.p.

61° , which is converted into 6-methoxy-5:7-dimethyl-

quinoline, m.p. 58° , nitrated to the 8- NO_2 -compound,

m.p. 100 — 5° . 8- γ -*n*-Propyl-, b.p. 225 — $230^\circ/0.1$ mm.,

and -butyl-aminopropylamino-6-methoxyquinoline, b.p.

$216^\circ/0.1$ mm., are obtained from the appropriate amine

and (II). The substances have been tested for thera-

peutic activity.

IX. 8-Amino-6-ethoxyquinoline and 8-bromobutyl-

phthalimide give 8- δ -phthalimidobutylamino-6-ethoxy-

quinoline, m.p. 114 — 115° (hydrobromide, m.p.

143 — 144°), hydrolysed to 8- δ -aminobutylamino-6-

ethoxyquinoline dihydrochloride ($+\text{H}_2\text{O}$), m.p. 196 —

197° , which shows promising results in therapeutic ex-

periments. 8-Amino-6-methoxyquinoline and succinic

anhydride condense to 8- β -carboxypropionamido-6-

methoxyquinoline, m.p. 143 — 144° . F. R. S.

3-Acetylcarbazole and carbazole-3-carboxylic

acid. S. G. P. PLANT and S. B. C. WILLIAMS (J.C.S.,

1934, 1142—1143).—9-Acetylcarbazole and AlCl_3

give 3-acetylcarbazole (I), m.p. 167° , which with

AcCl forms 3:9-diacetyl-, m.p. 153° , and with Me_2SO_4

yields 3-acetyl-9-methylcarbazole, m.p. 102° . (I) is

reduced (Zn-Hg and HCl) to 3-ethylcarbazole, m.p.

142° , also obtained by oxidation with S in quinoline

of 6-ethyl-1:2:3:4-tetrahydrocarbazole, m.p. 78° ,

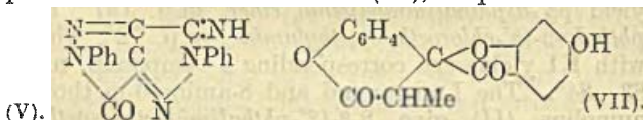
derived by Fischer's reaction from the condensation

product of $p\text{-C}_6\text{H}_4\text{Et}\cdot\text{NH}\cdot\text{NH}_2$ and cyclohexanone. Fusion of (I) with KOH leads to carbazole-3-carboxylic acid, m.p. 276—278° (*Et* ester, m.p. 165°). The compounds obtained by Borsche and Feise (A., 1907, i, 242) are the 2-Ac compounds. 9-Benzoylcarbazole, AlCl_3 , and AcBr give 9-benzoyl-2-acetylcarbazole, m.p. 153°, hydrolysed to 2-acetylcarbazole (II) (oxime, m.p. 278°; lit. 253°). (II) forms 2-acetyl-9-methyl-, m.p. 122° (oxime, m.p. 217°), and 2-ethyl-carbazole, m.p. 225°.

F. R. S.

Helicoidally rolled spherulites of the allantoin.—See this vol., 1059.

Condensation of esters and aliphatic nitriles. W. BORSCHÉ and R. MANTEUFFEL (Annalen, 1934, 512, 97—111).— $\text{Et}_2\text{C}_2\text{O}_4$ (I), MeCN (II), and KOEt in EtOH— Et_2O give an improved yield of the *K* salt of *Et* β -cyanopyruvate (III) (2:4-dinitrophenylhydrazine, m.p. 128.5°), best identified by coupling with PhN_2Cl and NaOAc to give the β -benzeneazo-derivative (IV), m.p. 149—150° [2:4-dinitrophenylhydrazine, m.p. 251—252° (decomp.)]. (IV) with $\text{NH}_2\cdot\text{NHPh}$ under various conditions gives 3-cyano-1-phenyl-4:5-diketopyrazoline-4-hydrazine, m.p. 189—191°, the osazone, $\text{NHPH}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{NHPh}$, m.p. 132.5° [when kept in EtOH forms (?) 3-carbethoxy-5-imino-1-phenyl-4:5-diketopyrazoline-4-phenylhydrazine, m.p. 105.5—107.5°], and a substance, probably (V), m.p. 149°. (III) gives similarly the *p*-bromobenzeneazo-derivatives (VI), m.p. 156—157°



(decomp.) (2:4-dinitrophenylhydrazine, m.p. 249—250°), the *di*-*p*-bromo-osazone, m.p. 156—157°, 3-cyano-1-bromophenyl-4:5-diketopyrazoline-4-phenylhydrazine, m.p. 203°, a substance, m.p. 262—263°, and [from (IV) and $\text{NH}_2\cdot\text{NHPh}$] the ester, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{N}\cdot\text{NHPh}$, m.p. 156—157°. *Et* β -cyano- α -ketobutyrate (2:4-dinitrophenylhydrazine, m.p. 149.5—150.5°) is hydrogenated (Adams) to *Et* β -cyano- α -hydroxybutyrate, b.p. 130—132°/16 mm., and with resorcinol gives mainly *Et* 7-hydroxy-3-methylcoumarin-4-carboxylate, m.p. 195°, and a small amount of the substance (VII), m.p. 241° (Me_2 ether, m.p. 183—184°). (I) and *n*-heptonitrile give a 35% yield of *Et* β -cyano- α -keto-octoate, b.p. 112—114°/2 mm. (2:4-dinitrophenylhydrazine, m.p. 115° after sintering; β -*p*-anisylazo-derivative, m.p. 96.5—97.5°). Adiponitrile (VIII) gives a 90% yield of β -dicyano- α -keto-hexaoate, m.p. 83—84° (*K* salt; 2:4-dinitrophenylhydrazine, m.p. 145°; phenylhydrazine, m.p. 93°; *Me* ether of the enolic form, b.p. 200—205°/17 mm.). (I) and *cis*- or *trans*-crotononitrile yield similarly 75—80% of *Et* 8-cyano- α -keto- Δ^5 -pentenoate, unstable (*K* salt; *Bz* derivative, b.p. 160—165°/2 mm.), probably by way of $\text{CH}_3\cdot\text{CH}=\text{CH}\cdot\text{NK}$ and $\text{CO}_2\text{Et}\cdot\text{C}(\text{OK})(\text{OEt})\cdot\text{CH}_2\cdot\text{CH}=\text{CH}\cdot\text{C}(\text{NK})\cdot\text{OEt}$. The dinitrile of sorbic acid affords *Et* ζ -cyano- α -keto- Δ^7 -heptadienoate (90% yield), solid, unstable (*K* salt; *Bz* derivative, b.p. 175—178°/2 mm.). (II) and HCO_2Et give $\text{CN}\cdot\text{CH}_2\cdot\text{CHO}$ (*K* and *Na* salts), which with $\text{NH}_2\cdot\text{NHPh}$ yields the phenylhydrazine, m.p.

166—168°, and a substance, m.p. 125—126°, and with $p\text{-C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{NH}_2$ the *p*-bromophenylhydrazine, m.p. 193—195°, and *pp'*-dibromophenylformazyl cyanide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{N}:\text{C}(\text{CN})\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Br}$, m.p. 259—260° (decomp.), but with NH_2Ph in AcOH affords by polymerisation the anil, $\text{CN}\cdot\text{CH}_2\cdot\text{CH}:\text{C}(\text{CN})\cdot\text{CH}:\text{NPh}$, m.p. 153°. EtCN affords α -cyanopropaldehyde (*Na* salt; anil, m.p. 154°; 2:4-dinitrophenylhydrazine, m.p. 145—146°). (VIII) gives similarly α -dicyano-*n*-valeraldehyde (*Na* salt; anil, m.p. 101—102°; 2:4-dinitrophenylhydrazine, m.p. 138.5—139.5°; *p*-bromophenylhydrazine, m.p. 111.5—112.5°). R. S. C.

Derivatives of piperazine. II. Utilisation in identification of fatty acids. C. B. POLLARD, D. E. ADELSON, and J. P. BAIN (J. Amer. Chem. Soc., 1934, 56, 1759—1760).—The following salts of piperazine are described: *H* oxalate, m.p. > 300° (all m.p. are corr.); *H* succinate, m.p. 205—206° (decomp.); *H* adipate, m.p. 244—245° (decomp.); *H* sebacate, m.p. 166—168°; *di*(*H* glutarate), m.p. 152°; *di*(chloroacetate), m.p. 145—146°; *di*trichloroacetate, m.p. 121—121.5°; diacetate, m.p. 208.5—209°; dipropionate, m.p. 124—125°; dibutyrate, m.p. 121—122°; diisobutyrate, m.p. 89.5—90°; divalerate, m.p. 112.5—113°; diisovalerate, m.p. 139—140°; dihexoate, m.p. 111—111.5°; diheptoate, m.p. 95—96°; dilactate, m.p. 96—96.5°.

H. B.

Optically active barbituric acids. E. C. KLEIDERER and H. A. SHONLE (J. Amer. Chem. Soc., 1934, 56, 1772—1774).—*Et* *d*-, b.p. 123—124°/10 mm., $[\alpha]_D^{25} + 11.62^\circ$, and *l*-, b.p. 123—124°/10 mm., $[\alpha]_D^{25} - 11.02^\circ$, ethyl-(α -methylbutyl)malonates, prepared (usual method) from *d*-, b.p. 116—118°, $[\alpha]_D^{25} + 29.9^\circ$, and *l*-, b.p. 116—118°, $[\alpha]_D^{25} - 29.9^\circ$, $\text{CHMePr}\cdot\text{Br}$, with $\text{CO}(\text{NH}_2)_2$ and NaOEt give *d*-, m.p. 120—121°, $[\alpha]_D^{25} + 4.93^\circ$ and *l*-, m.p. 120—121°, $[\alpha]_D^{25} - 4.73^\circ$, α -ethyl-5- α -methylbutylbarbituric acids. *dl*- α -Cyano- α -ethylisoxoic acid, b.p. 145—147°/14 mm. [obtained by hydrolysis ($\text{EtOH}\text{--KOH}$) of the *Et* ester, b.p. 122—123.5°/14 mm. (from Bu^nBr , $\text{CN}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, and NaOEt)], is resolved by Fischer and Flatau's method (A., 1909, i, 628) into *d*-, b.p. 148—149°/14 mm., $[\alpha]_D^{25} + 7.03^\circ$, and *l*-forms, b.p. 148—149°/14 mm., $[\alpha]_D^{25} - 6.85^\circ$; the corresponding *Et* esters (prepared from the acid chlorides) with $\text{NHMe}\cdot\text{CO}\cdot\text{NH}_2$ and NaOEt give [after hydrolysis (HCl)] *d*-, m.p. 75°, $[\alpha]_D^{25} + 3.5^\circ$, and *l*-, m.p. 74.5°, $[\alpha]_D^{25} - 3.4^\circ$, 1-methyl-5-ethyl-5-*n*-butylbarbituric acids. Differences in the pharmacological action of the above active acids and their *dl*-forms are noted. *dl*- α -Cyano- α -ethylisoxoic acid, b.p. 153.5°/14 mm. (*Et* ester, b.p. 128—131°/14 mm., from isoamyl bromide and $\text{CN}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$), is similarly resolved into *d*-, b.p. 156—158°/14 mm., $[\alpha]_D^{25} + 6.71^\circ$, and *l*-forms, b.p. 156—158°/14 mm., $[\alpha]_D^{25} - 7.73^\circ$, convertible (as above) into *d*-, m.p. 99°, $[\alpha]_D^{25} + 1.5^\circ$, and *l*-, m.p. 10°, $[\alpha]_D^{25} - 1.56^\circ$, 1-methyl-5-ethyl-5-isoamylbarbituric acids, which (like the *dl*-form, m.p. 72°) have no anaesthetic action.

H. B.

Correlation of ultra-violet absorption and chemical constitution in various pyrimidine and purines. F. F. HEYROTH and J. R. BOUROW (J. Amer. Chem. Soc., 1934, 56, 1728

cf. A., 1931, 1308).—The ultra-violet absorption curves of aq. solutions of the following are given: thymine glycol, alloxantin, isodialuric acid, 5:5-diethylbarbituric acid, dialuric acid, alloxan, uracil, thymine, cytosine, isocytosine, isobarbituric acid, barbituric acid, pyrimidine, 2:6-dichloropyrimidine, 2:6-dichloro-4-methylpyrimidine, adenine, adenine thiomethylpentose, and guanine [the absorption of which is affected by p_H (cf. Holiday, A., 1930, 1088)]. Loss of selective absorption accompanies saturation of the nuclear double linkings, whilst the magnitude of the absorption is lessened by introduction of a second or third double linking. The effects of substituents are discussed. The relation of the absorption of the ring-compounds present in nucleic acid to that of the acid itself is discussed.

H. B.

Partial synthesis of ribose nucleotides. I. Uridine-5-phosphoric acid. P. A. LEVENE and R. S. TIRSON (J. Biol. Chem., 1934, 106, 113—124).—*isopropylideneuridine* (I), m.p. 159—160°, $[\alpha]_D^{25}$ —15.8 in MeOH (from uridine, H_2SO_4 , and $CuSO_4$ in $COMe_2$), with $-C_6H_4Me \cdot SO_2Cl$ in C_6H_5N gives *isopropylideneuridine 5-p-toluenesulphonate*, $[\alpha]_D^{25}$ +17.4° in $COMe_2$, converted into *iodoisopropylideneuridine*, m.p. 164°, $[\alpha]_D^{25}$ —16.3° in $COMe_2$. Methylation gives *5-methoxyisopropylideneuridine*, m.p. 223—225°. It is concluded that (I) is 2:3-*isopropylideneuracilribofuranoside* (A., 1933, 957). (I) is phosphorylated in C_6H_5N with $POCl_3$ at —30° to —35° and the Ba salts are fractionated by their solubility in H_2O . After hydrolysis with 5*N*- H_2SO_4 at 75° for 2 hr. the Ba salt of *uridine-5-phosphoric acid* (II), $[\alpha]_D^{25}$ +3.44° in 10% HCl, was separated, differing in its solubility in H_2O from Ba uridyate. The Ba salt of (II) was hydrogenated catalytically to the salt of *dihydrouridine-5-phosphoric acid* (III). The *brucine* salt of (II) has m.p. 200°, $[\alpha]_D^{25}$ —68.8° in C_6H_5N . The curves of hydrolysis of the Ba salts of uridine-3-phosphoric acid, (II), and (III) are compared.

H. D.

Pyrrole-indole group. XIX. Methane derivatives and methene bases from indoles. B. ODDO and C. TOFFOLI (Gazzetta, 1934, 64, 359—363; cf. A., 1923, i, 715; 1924, i, 1346).—Mg indolyl bromide and MeCHO yield 3:3'-*di-indolylmethylmethane*, m.p. about 160°, converted in air in presence of HCl into 3-indolyl-3'-indolidenemethylmethane, m.p. 210°. 3:3'-*Di-(2-methylindolyl)methylmethane*, m.p. 192.5°, and 3-(2-methylindolyl)-3'-(2-methylindolidenemethylmethane, m.p. 222°, are obtained similarly.

R. K. C.

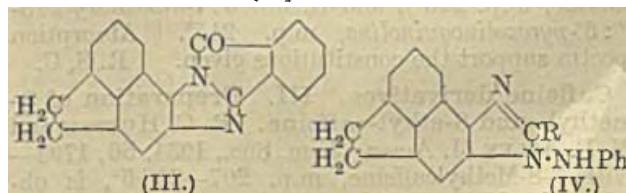
Complex salts of 2:2'-dipyridyl with bivalent iron. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 333—336).—When cryst. $FeSO_4$ is heated with the theoretical quantities of dipyridyl (dip) (I), and then extracted with boiling MeOH, there are formed three impure salts, probably $Fe(dip)_nSO_4 \cdot mH_2O$, where $n=1, 2, 3$, and correspondingly $m=3, 4, 5$. On treatment with $BaCl_2$ and $Ba(OH)_2$ to take up any excess of H_2SO_4 all three salts give predominantly, dark red hexagonal tables of $[Fe(dip)_3]Cl_2 \cdot 7H_2O$, rhombic bipyramidal, $a:b:c=0.8886:1:0.7717$. When the (I) is partly substituted by H_2O , the cryst. form remains the same.

H. S. P.

Residual affinity and co-ordination. XXXIV. 2:2'-Dipyridyl platinum salts. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1934, 965—971).—*Bis-2:2'-dipyridyl platinumochloride*, prepared from 2:2'-dipyridyl, HCl, and K_2PtCl_4 , with H_2O at 100° gives 2:2'-dipyridyl hydrochloride and the yellow form of β -2:2'-*dipyridylplatinous chloride* (I), which also exists in a red form. Both forms give the same chemical reactions and are probably due to difference of cryst. structure: (I) with Cl_2 affords β -2:2'-*dipyridylplatinic chloride*, with $AgNO_3$ forms β -2:2'-*dipyridylplatinous nitrate*, and also gives the bromide, iodide, and hydroxide. A solution of bis-2:2'-dipyridylplatinous chloride is obtained from (I) and excess of 2:2'-dipyridyl and with KI forms *bis-2:2'-dipyridylplatinous iodide dihydrate* and with K_2PtCl_4 yields the *platinochloride*, oxidised by Cl_2 to *bis-2:2'-dipyridyldichloroplatinic platinumochloride*. With C_6H_5N and K_2PtCl_4 , (I) forms a *plato-salt*, whilst in presence of Cl_2 , 2:2'-*dipyridylpyridinotrichloroplatinic chloride dihydrate* is obtained. With aq. NH_3 , (I) yields 2:2'-*dipyridyldiamminoplatinous chloride dihydrate*, which with EtOH gives a *monohydrate*, with KI forms an *iodide hydrate*, with H_2O affords 2:2'-*dipyridylamminoplatinous chloride* (+2.5*H*₂O) (II), and with Cl_2 leads to 2:2'-*dipyridyldiamminodichloroplatinic chloride dihydrate (monohydrate)*. (II) with KI forms 2:2'-*dipyridylamminoplatinous iodide hydrate*, and with Cl_2 yields 2:2'-*dipyridylamminotrichloroplatinic chloride hydrate*, which with Cl_2 gives a complex explosive compound in which the H of the NH_3 is partly replaced by Cl. (I) and $[CH_2 \cdot NH_2]_2$ give 2:2'-*dipyridylethylenediaminoplatinous chloride*, which with conc. HCl yields the red form of (I), or with dil. HCl the yellow form, with Ag_2CO_3 and HBr forms 2:2'-*dipyridylethylenediaminoplatinous bromide dihydrate*, and with Cl_2 affords 2:2'-*dipyridylethylenediaminodichloroplatinic chloride pentahydrate* (this gives a complex compound with Cl_2). (I) and ethylene Me_2 disulphide lead to 2:2'-*dipyridylethylenedimethyldisulphineplatinous chloride*, converted by K_2PtCl_4 into the *plato-salt*.

F. R. S.

Affinity of the arylazo-group. G. B. CRIPPA and G. PERRONCITO (Gazzetta, 1934, 64, 415—420).—4-Benzencazo-5-aminoacenaphthene (I) reacts with o - $C_6H_4(CO)_2O$ to give the *phthalimido-derivative* (II), m.p. 250°, and the $Ph \cdot N_2$ -group is, therefore, more strongly bound than in 1-benzencazo- β -naphthylamine (A., 1929, 181; 1933, 59). Reduction of (II) by Zn and AcOH gives 1':2'-*benzoyleneacenaphtho-4:5-imino-4-azole* (III), m.p. 280°. (I) condenses with MeCHO, PhCHO, o - $C_6H_4Me \cdot CHO$, and



m - $NO_2 \cdot C_6H_4 \cdot CHO$, respectively, to give the following substituted *N*(4)-*anilidoacenaphtho-4:5-iminoazoles*: μ -methyl-, m.p. 222°, μ -phenyl-, m.p. 233°, μ -*p*-tolyl-, m.p. 245°, and μ -*m*-nitrophenyl-, m.p. 252° (as IV).

R. K. C.

Preparation of carbocyanine dyes.—See B., 1934, 794.

Conditions and region of validity of the flavin synthesis. R. KUHN and F. WEYGAND (Ber., 1934, 67, [B], 1459—1460).—The production of flavins from alloxan and derivatives of o - $C_6H_4(NH_2)_2$ occurs smoothly when the base is present as salt, more slowly and less completely when the free bases are used in solvents of high b.p., e.g., $PhNO_2$. HCl may be replaced by H_2SO_4 , H_3PO_4 , HNO_3 , $H_2C_2O_4$, or AcOH. Anhyd. solvents are very suitable if opportunity is given for salt formation (AcOH). o - $NH_2 \cdot C_6H_4 \cdot NHMe$ and the $NaHSO_3$ compound of methylalloxan in boiling dil. HCl afford 3 : 9-dimethylflavin [3 : 9-dimethylisalloxazine], m.p. 320—325° (decomp.), which does not yield a Ag salt and cannot be removed by $CHCl_3$ from its solution in dil. alkali. H. W.

Synthesis of lumilactoflavin. R. KUHN, K. REINEMUND, and F. WEYGAND (Ber., 1934, 67, [B], 1460—1462).—Condensation of 4-amino-5-methylamino- o -xylene hydrochloride with alloxan tetrahydrate leads to 6 : 7 : 9-trimethylflavin [6 : 7 : 9-trimethylisalloxazine]. Its identity with lumilactoflavin (I) is established by direct comparison of the compounds and by alkaline hydrolysis to the same ketocarboxylic acid, $C_{12}H_{12}O_3N_2$, and "sublimate," $C_{11}H_{12}ON_2$, and further by the identity of synthetic 3 : 6 : 7 : 9-tetramethylflavin with the product of the action of Me_2SO_4 on (I). H. W.

Quinoline derivatives. II. Pyrazolinoquinolines. K. S. NARANG, J. N. RAY, and A. SINGH (J. Indian Chem. Soc., 1934, 11, 427—431; cf. A., 1933, 1060).—1-Phenyl-3-methylpyrazolone, o - $NO_2 \cdot C_6H_4 \cdot CHO$, and $NaOAc$ at 150° give 4- o -nitrobenzylidene-1-phenyl-3-methylpyrazolone, m.p. 162°, reduced by Zn dust and AcOH or HCl-EtOH or by Al-Hg in moist Et_2O to a mixture of 1-hydroxy-2 : 3-4' : 5'-pyrazolinotetrahydroquinoline (I), m.p. 142° (hydrochloride, m.p. 251—252°), and 4- o -hydroxylamino-1-phenyl-3-methylpyrazolone, m.p. 101—102°. o -Nitropiperonal and 6-nitroveratraldehyde give similarly 4- o -nitropiperonylidene- (II), m.p. 190°, and 4- o -nitroveratrylidene-1-phenyl-3-methylpyrazolone (III), m.p. 183°. (II) with Zn dust and HCl or Al-Hg gives 4- o -aminopiperonylidene-1-phenyl-3-methylpyrazolone, m.p. 186° (trihydrochloride, m.p. 243°), cyclised at 150° in H_2 to 6 : 7-methylenedioxy-2 : 3-4' : 5'-pyrazolinoquinoline (poor yield), m.p. 185° (picrate). (III) with Zn dust and AcOH gives o -aminoveratrylidene-1-phenyl-3-methylpyrazolone, m.p. indefinite (trihydrochloride, m.p. 226°), and thence 6 : 7-dimethoxy-2 : 3-4' : 5'-pyrazolinoquinoline, m.p. 215°. Absorption spectra support the constitutions given. R. S. C.

Caffeine derivatives. III. Preparation of 8-methyl- and 8-ethyl-caffeine. R. C. HUSTON and W. F. ALLEN (J. Amer. Chem. Soc., 1934, 56, 1793—1794).—8-Methylcaffeine, m.p. 207—208.5°, is obtained in 10.8—67.5% yield from 8-methoxy- (I), 8-ethoxy- (II), 8- n -propoxy-, 8- n -butoxy-, or 8- iso -amyloxy- (III)-caffeine (this vol., 906) and Ac_2O at 260—270° (sealed tube). 8-Ethylcaffeine, m.p. 186—187.5°, is similarly prepared in 7.2—19% yield from (II), (III), or 8-isopropoxy- [but not (I)] or hydroxy-

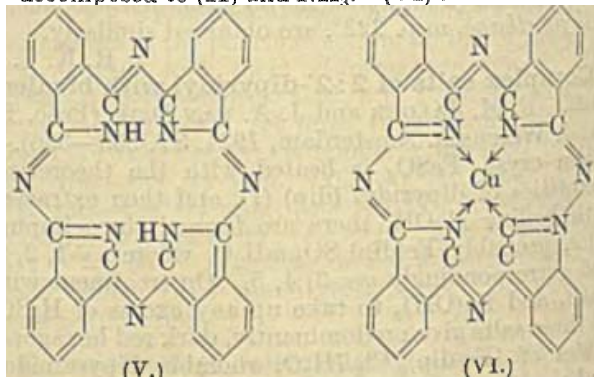
caffeine and $(EtCO)_2O$ at 295—360°. 8- n -Propyl- and - n -butyl-caffeines could not be prepared by the same procedure. H. B.

Phthalocyanines. I. New type of synthetic colouring matters. R. P. LINSTAD. II. Preparation of phthalocyanine and some metallic derivatives from o -cyanobenzamide and phthalimide. G. T. BYRNE, R. P. LINSTAD, and A. R. LOWE. III. Preparation of phthalocyanines from phthalonitrile. R. P. LINSTAD and A. R. LOWE. IV. Copper phthalocyanines. C. E. DENT and R. P. LINSTAD. V. Mol. wt. of magnesium phthalocyanine. R. P. LINSTAD and A. R. LOWE. VI. Structure of the phthalocyanines. C. E. DENT, R. P. LINSTAD, and A. R. LOWE (J.C.S., 1934, 1016—1017, 1017—1022, 1022—1027, 1027—1031, 1031—1033, 1033—1139).—I. By passing NH_3 into molten o - $C_6H_4(CO)_2O$ in Fe vessels, crude Fe phthalocyanine (I) is obtained. It is decomposed by HNO_3 to o - $C_6H_4(CO)_2NH$ (II) and the Fe^{III} salt, by H_2SO_4 at 100° to o - $C_6H_4(CO_2H)_2$, (II), $FeSO_4$, and $(NH_4)_2SO_4$, and with soda-lime to $PhCN$ and NH_3 . With NH_2Ph , it affords the aniline compound. The general properties of (I) are described. (I) is probably produced by dehydration of (II) and fixation of NH_3 and the metal.

II. o -Cyanobenzamide (III) reacts with many metals at 250° to yield strongly coloured substances : the metals are Mg (metal or oxide) Fe (metal, oxide, or sulphide), Co, Ni, Sb. The reactions are exothermic and the precursor of the compounds is iminophthalimidine. MgO , (III), and $C_{10}H_8$ yield Mg phthalocyanine, $(C_8H_4N_4)Mg \cdot 2H_2O$ (IV), which with H_2SO_4 forms phthalocyanine, $C_{32}H_{18}N_8$ (V). Fe, Ni, and Co give stable metallic phthalocyanines. Sb and (III) afford a product which contains only a trace of metal.

III. o - $C_6H_4(CN)_2$ (VI) combines very readily with metals and their derivatives to yield phthalocyanines. (IV) is prepared from (VI) and is formulated as a dihydrate, containing $2H_2O$, or $H_2O + C_9H_7N$, or $H_2O + C_5H_5N$, depending on the solvent. Na amyloxyde and other reagents containing Na react with (VI) to yield products which lose Na, giving (V).

IV. (VI) and Cu at 190—210° yield Cu phthalocyanine (VII), which is very stable, subliming at 580 without decomp., the Cu being stable to H_2SO_4 . It may be obtained from Cu and (V) at high temp. and is decomposed to (II) and NH_3 . (VI) and CuCl combine



to give (VII) and $CuCl_2$, whilst (VI) and $CuCl_2$ give HCl and Cu monochlorophthalocyanine, $C_{32}H_{15}N_8Cu$, the Cl being in one of the C_6H_6 nuclei.

V. The mol. wt. of (IV) has been determined by the ebullioscopic method in $C_{10}H_8$, using a Pt-resistance thermometer. The val. (551) confirms the formula of (IV).

VI. The reagents which react with (VI) do not give similar products with *m*- or *p*- $C_6H_4(CN)_2$, *o*-xylenylene dicyanide, *o*-cyanocinnamionitrile, and 2:2'-diphenonitrile. The evidence for the structure of the compounds is summarised and the formulæ (V) and (VI) are advanced.

Oxidation of (IV), (V), and (VI) with $Ce(SO_4)_3$ shows that the metallic derivatives are formed from (V) by replacement of 2 H by 1 atm. of bivalent metal. The stereochemistry of the phthalocyanines and their relationship to the porphyrins are briefly discussed.

F. R. S.

Purification of chlorophylls-*a* and -*b*; their absorption spectra; evidence for the existence of a third component of chlorophyll. F. P. ZSCHEILE, jun. (Bot. Gaz., 1934, 95, 529—562).—Earlier methods do not completely separate chlorophyll-*a* and -*b*. Modified methods are described. A third component of chlorophyll possesses properties intermediate between those of *a* and *b*. A. G. P.

Unsaturation and tautomeric mobility of heterocyclic compounds. IV. Methylation and bromination of a series of 2-*p*-substituted anilino-thiazoles. R. F. HUNTER and E. R. PARKEN. V. **Benzoxazoles.** R. D. DESAI, R. F. HUNTER, and A. R. K. KHALIDI (J.C.S., 1934, 1175—1177, 1186—1190).—IV. Condensation of the appropriate substituted phenylthiocarbamide with CH_3AcCl yields 2-*p*-chloro-, m.p. 147°, -bromo-, m.p. 162°, -iodo-, m.p. 168—169°, -ethoxy-, m.p. 135—136°, -hydroxy-, m.p. 220°, and -nitro-anilino-4-methylthiazole, m.p. 181—182°. Methylation (MeI) of these compounds shows that they react in the amino-aromatic form yielding 2-*p*-chloro-, m.p. 138—139°, -bromo-, m.p. 154°, and -iodo-anilo-3:4-dimethyl-2:3-dihydrothiazole picrate, m.p. 154—155°, and 2-*p*-ethoxy-, m.p. 114—115°, -hydroxy-, m.p. 189—190°, and -nitro-anilino-4-methylthiazole, m.p. 151°, identical with the corresponding condensation products of CH_3AcCl and the *s*-aryl-methylthiocarbamides (*s*-*p*-hydroxy-, m.p. 186°, and -nitro-phenylmethylthiocarbamide, m.p. 183—184°). Bromination of the compounds leads to substitution products: hydro-penta-, m.p. 128—129° (decomp.), and hydro-tri-bromide, m.p. 124—126° (decomp.), of 5-bromo-2-*p*-chloroanilino-4-methylthiazole, m.p. 126—127° (decomp.); hydro-penta-, m.p. 114—115° (decomp.), and hydro-tri-bromide, m.p. 118—119°, of 5-bromo-2-*p*-bromoanilino-4-methylthiazole, m.p. 137; 2-*op*-dibromoanilino-4-methylthiazole, m.p. 136—137°; hydrotribromide, m.p. 119—120°, of 5-bromo-2-*p*-hydroxyanilino-4-methylthiazole, m.p. 136—137°; hydroethoxyanilino-4-methylthiazole, m.p. 113—114° (decomp.), of 5-bromo-penta-bromide, m.p. 121—122°, of 5-bromo-2-hydroxyanilino-4-methylthiazole, m.p. 131—132° (decomp.); and hydrotribromide, m.p. 127—128°, of 5-bromo-anilo-3:4-dimethyl-2:3-dihydrothiazole, m.p. 123. 2-Phenylmethylamino-4-methylthiazole picrate has m.p. 113—114°.

V. 1-Aminobenzoxazole (I) (picrate, m.p. 224) is

4 D

methyated (MeI) to 1-imino-2-methyl-1:2-dihydrobenzoxazole, m.p. 96° (picrate, m.p. 189—190°; Ac derivative, m.p. 92°); the isomeric 1-methylamino-benzoxazole (Ac derivative, m.p. 91°), obtained from 1-thiolbenzoxazole and NH_2Me , is not formed during methylation. Bromination of (I) yields the hydrobromide, m.p. 245°, and hydrodibromide, m.p. 232° (decomp.), of 5(?) -bromo-1-aminobenzoxazole, m.p. 194—195°. Methylation of 1-anilino-benzoxazole (picrate, m.p. 188°) gives a mixture of the picrate, m.p. 156°, of 1-anilo-2-methyl-1:2-dihydrobenzoxazole and the picrate, m.p. 176°, of 1-phenylmethylamino-benzoxazole, also obtained from 1-thiolbenzoxazole and $NHPhMe$. 1-Hydrobenzoxazole is methylated to 1-keto-2-methyl-1:2-dihydrobenzoxazole, m.p. 87—88°, and brominated to a hydrobromide of 5(?) -bromo-1-hydroxybenzoxazole, m.p. 190°. 1-Thiolbenzoxazole with HgO forms a mercuric salt, m.p. 204°, with Br yields a compound, m.p. 128° (decomp.), decomposed to 5(?) -bromo-1-thiolbenzoxazole, m.p. 200°, and with Me_2SO_4 followed by $HgCl_2$ affords a compound, m.p. 162°, of $HgCl_2$ with 1-methylthiolbenzoxazole. 1-Thio-2-methyl-1:2-dihydrobenzoxazole has m.p. 134—135°, and 1-*p*-toluidinobenzoxazole, m.p. 178°. *o*-Aminophenol, $PhCHO$, and $AcOH$ yield 1-phenylbenzoxazole.

F. R. S.

Oxacyanines. (MISS) N. I. FISHER and (MISS) F. M. HAMER (J.C.S., 1934, 962—965).—2:1- $C_{10}H_6(NH_2) \cdot OH, HCl$ with $Ac_2O-NaOAc$ gives 1-methyl- α -naphthoxazole, m.p. 36—37°, b.p. 178—201°/18—20 mm., which forms a methiodide (I), m.p. 202° (decomp.), and ethiodide, m.p. 215° (decomp.). 2-Methyl- α -naphthoxazole, m.p. 25°, gives a methiodide, m.p. 212—213° (decomp.), and ethiodide, m.p. 202—203° (decomp.). (I), Ac_2O , and amyl nitrite give 2:2'-dimethyloxacyanine iodide, m.p. > 310° [diethyl-compound, m.p. 301° (decomp.)], which with SO_2 in $MeOH$ forms 2:2'-dimethyl-5:6:5':6'-dibenzoxacyanine iodide, m.p. > 320° (diethyl-compound, m.p. > 315°). The products obtained in the 2-Me series are 2:2'-dimethyl-, m.p. 291° (decomp.), and 2:2'-diethyl-3:4:3':4'-dibenzoxacyanine, m.p. 283° (decomp.). The yields of oxacyanines vary from 14 to 26%. The absorption lies further into the more refrangible region of the spectrum than does that of any known kind and of cyanine dye, the simplest oxacyanines giving colourless solutions. The dibenzoxacyanines act as photographic sensitisers to gelatin-AgCl emulsions.

F. R. S.

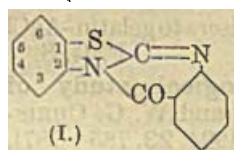
Preparation and bacteriological study of thiazole-azo-dyes. W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 785—787). 2-Aminothiazole (from thiocarbamide and $\alpha\beta$ -dichloroethyl ether), m.p. 88.5—90.5°, is diazotised (with difficulty) and coupled with resorcinol, *m*-cresol, and *m*- $C_6H_4(NH_2)_2$ to give the dyes (I), (II), and (III) (not obtained pure), respectively. (I) and (II) have no germicidal action, but inhibit the growth of *B. typhosus* and *Staphylococcus* at 1:8000 and 1:16,000, respectively.

R. S. C.

Thiomorpholine derivatives. L. A. BURROWS and E. E. REID (J. Amer. Chem. Soc., 1934, 56, 1720—1724).— $S(CH_2CH_2Br)_2$ (I) and $NH_2 \cdot CH_2 \cdot CH_2 \cdot OH$ (II) (3 mols.) in C_6H_6 give 4- β -hydroxyethylthiomorpholine,

$S < \text{CH}^2 \cdot \text{CH}^2 > \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, b.p. $130^\circ/10$ mm., m.p. $35\text{--}5^\circ$ [hydrochloride, m.p. $162\text{--}163^\circ$; acetate, b.p. $144^\circ/15$ mm., $269^\circ/757$ mm. (hydrochloride, m.p. $149\text{--}5^\circ$); propionate, b.p. $155^\circ/15$ mm., $277\text{--}7^\circ/757$ mm., m.p. -1° (hydrochloride, m.p. $132\text{--}6^\circ$); butyrate, b.p. $166^\circ/15$ mm., $284\text{--}7^\circ/757$ mm. (hydrochloride, m.p. 129°); valerate, b.p. $176\text{--}6^\circ/15$ mm., $291^\circ/757$ mm. (hydrochloride, m.p. $128\text{--}3^\circ$); hexoate, b.p. $186\text{--}8^\circ/15$ mm., $297^\circ/757$ mm. (hydrochloride, m.p. $121\text{--}5^\circ$); heptoate, b.p. $196\text{--}6^\circ/15$ mm. (hydrochloride, m.p. $118\text{--}6^\circ$); benzoate, m.p. $66\text{--}67^\circ$ (hydrochloride, m.p. 224°); p-nitrobenzoate, m.p. 63° (hydrochloride, m.p. 219°); p-aminobenzoate, m.p. 136° (dihydrochloride, m.p. 237°)]. (I) and $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ in CHCl_3 similarly afford 4- γ -hydroxypropylthiomorpholine, m.p. 55° [hydrochloride, m.p. 188° ; acetate hydrochloride, m.p. 145° ; benzoate hydrochloride, m.p. $183\text{--}5^\circ$; p-nitrobenzoate, m.p. 77° (hydrochloride, m.p. 218°); p-aminobenzoate dihydrochloride, m.p. 219°]. 4- β -Hydroxyethylthiomorpholine 1-oxide, m.p. 45° (hydrochloride, m.p. $173\text{--}174^\circ$; acetate hydrochloride, m.p. $135\text{--}136^\circ$); propionate hydrochloride, m.p. $161\text{--}162^\circ$; butyrate hydrochloride, m.p. $158\text{--}5^\circ$; valerate hydrochloride, m.p. $149\text{--}150^\circ$; hexoate hydrochloride, m.p. 140° ; heptoate hydrochloride, m.p. $156\text{--}157^\circ$, and 4- β -hydroxyethylthiomorpholine 1:1-dioxide, m.p. 54° [hydrochloride, m.p. $175\text{--}5^\circ$; acetate, m.p. $22\text{--}3^\circ$ (hydrochloride, m.p. 147°); propionate, m.p. $43\text{--}44^\circ$ (hydrochloride, m.p. $183\text{--}184^\circ$); butyrate, m.p. $21\text{--}6^\circ$ (hydrochloride, m.p. 146°); valerate, m.p. 25° (hydrochloride, m.p. 144°); hexoate, m.p. 25° (hydrochloride, m.p. $141\text{--}142^\circ$); heptoate, m.p. 27° (hydrochloride, m.p. $142\text{--}5^\circ$); benzoate, m.p. $125\text{--}5^\circ$ (hydrochloride, m.p. 174°); -nitrobenzoate, m.p. 167° (hydrochloride, m.p. 222°); p-aminobenzoate, m.p. $148\text{--}6^\circ$ (dihydrochloride, m.p. 238°)], are prepared from (II) and $\text{SO}(\text{CH}_2 \cdot \text{CH}_2 \text{Br})_2$ and $\text{SO}_2(\text{CH}_2 \cdot \text{CH}_2 \text{Br})_2$, respectively. All b.p. and m.p. are corr. The aromatic esters possess local anaesthetic properties similar to those of the corresponding morpholine derivatives. H. B.

Benzthiazoloquinazolines. P. K. BOSE and K. B. PATHAK (J. Indian Chem. Soc., 1934, **11**, 463—465).—2-Chlorobenzthiazole and $o\text{-NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, when heated, give benzthiazoloquinazoline (I), m.p. 189° (NO_2 -derivative, m.p. $279\text{--}280^\circ$), hydrolysed by



hot 5% KOH-EtOH to N-2-benzthiazolylantranilic acid (2-o-carboxyanilinobenzthiazole) or 2-benzthiazolynideneantranilic acid, m.p. 187° (Na salt, m.p. 273°), reconverted into (I) by Ac_2O . The 5-, m.p. 226° [NO_2 -, m.p. 304° , and (NO_2)₂-derivatives, m.p. 280°], and 4-Me-derivative, m.p. 180° , of (I) were similarly prepared and led to the acids, m.p. $188\text{--}189^\circ$ (Na salt, m.p. 280°) and 189° , respectively. 2-Chloro-*lin*-(α)-naphthothiazole, m.p. 75° , gives *lin*-(α)-naphthothiazoloquinazoline, m.p. 261° . 1-Chloro-3-methylthiazole could not be obtained by Hofmann's or Hunter's method and only in poor yield from the aminothiazole (Sandmeyer).

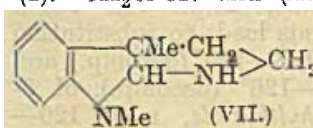
R. S. C.

Ergot alkaloids. III. Lysergic acid. W. A. JACOBS and L. C. CRAIG (J. Biol. Chem., 1934, **106**,

393—399).—The hydrochloride, m.p. $208\text{--}210^\circ$, and H sulphate, m.p. 220° , of lysergic acid (I), obtained by the hydrolysis of ergine (this vol., 538), were prepared. Oxidation of (I) with HNO_3 gave a product resembling that obtained similarly from the acid $\text{C}_{14}\text{H}_9\text{O}_8\text{N}$. Reduction of (I) with Na in amyl alcohol, extraction with hot EtOH, and pptn. with AcOH gave dihydrolysergic acid, m.p. 336° (decomp.), $[\alpha]_D^{20} -88^\circ$ in $\text{C}_5\text{H}_5\text{N}$ (Me ester, m.p. 182°). H. D.

Photosynthesis of nicotine. H. E. WATSON and B. K. VAIDYA (J. Indian Chem. Soc., 1934, **11**, 441—442).—2% aq. CH_2O , 6-2N- NH_3 , and CuCO_3 in ultra-violet light give NH_2Me , but no nicotine (I) [cf. Bhargava *et al.* (A., 1933, 1256), whose method of working leads to total loss of (I)]. R. S. C.

Indole series. II. Alkylation of 3-formyl-1-methyloxindole and synthesis of the basic ring structure of physostigmine. P. L. JULIAN, J. PIKL, and D. BOGGESE (J. Amer. Chem. Soc., 1934, **56**, 1797—1801).—1-Methyloxindole and HCO_2Et in EtOH-NaOEt give 3-formyl-1-methyloxindole (I), m.p. 192° (lit. 186°), which with MeI (> 2 mols.) in MeOH-NaOMe (> 2 mols.) affords 1:3:3-trimethyloxindole (II), b.p. $131\text{--}132^\circ/11$ mm., m.p. 50° , also prepared from α -bromoisobutyryl-N-methylanilide and AlCl_3 at $120\text{--}125^\circ$. 1:3-Dimethyloxindole (III), b.p. $136\text{--}138^\circ/11$ mm., m.p. 27° and 55° (stable), is obtained similarly using 1 mol. of NaOMe; further methylation gives (II). (III) is also obtained from α -bromopropion-N-methylanilide and AlCl_3 . In the above methylation of (I), 3-formyl-1:3-dimethyloxindole is probably first produced and then cleaved to (III). The Na salt (IV) of (I) and MeI in COMe_2 give a compound, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N} \cdot 0.5\text{NaI}$, m.p. 213° , hydrolysed (H_2O) to 2-methoxy-3-formyl-1-methylindole (V), m.p. 138° , converted by prolonged boiling with EtOH into 2-ethoxy-3-formyl-1-methylindole (VI), m.p. 78° . (IV) and EtI in COMe_2 similarly give a compound, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N} \cdot 0.5\text{NaI}$, m.p. 167° , also prepared from (VI) and NaI in COMe_2 . (V) and (VI) are readily hydrolysed (3% HCl; dil. alkali) to (I); attempted prep. of the semicarbazones, phenylhydrazones, and anils gave the corresponding derivatives of (I). $\text{CH}_2\text{Cl} \cdot \text{CN}$ and (III) in EtOH-NaOEt afford



1:3-dimethyloxindolyl-3-acetonitrile, b.p. $194\text{--}196^\circ/14$ mm., m.p. 58° (-3-acetic acid, m.p. 178°), reduced (Na, EtOH) to β -1:3-dimethyloxindolyl-3-ethylamine (picrate, m.p. 113°) and (mainly) deoxynoreseroline (VII), b.p. $154^\circ/17$ mm. (picrate, m.p. 158° ; Bz derivative, m.p. 168°). (vII) and MeI in Et_2O give deoxyseroline (picrate, m.p. 177°). H. B.

Dehydrogenation of yohimbine. R. MAJIMA and S. MURAHASI (Proc. Imp. Acad. Tokyo, 1934, **10**, 341—344).—The action of Pd-black on a boiling aq. solution of yohimboic acid and maleic anhydride leads to fumaric acid, $[\text{CH}_2 \cdot \text{CO}_2\text{H}]_2$, and tetrahydro-yohimboic acid, decomp. 335° (hydrochloride, decomp. 325°), transformed by CH_3N_2 or HCl-MeOH in tetrahydro-yohimbine, $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_2$, m.p. $256\text{--}265^\circ$ (decomp.), $[\alpha]_D^{20} +289\text{--}9^\circ$ in AcOH, transformed to

KOH in amyl alcohol into harman and *m*-toluic acid. *Et tetrahydro-yohimboate* has m.p. 281—282° (decomp.), $[\alpha]_D^{25} + 245.2^\circ$ in AcOH. Deoxy-yohimboic acid similarly yields *tetrahydrodeoxy-yohimbine*, m.p. 251—252° (decomp.) (*hydrochloride*, decomp. 302°). *Yohimbylamine* (I), $C_{19}H_{25}ON_3$, m.p. 177—178°, is obtained from yohimbine by the Curtius reaction. The *dihydrochloride* (+3.5H₂O), decomp. 293°, and *sulphate* (+1.5H₂O), m.p. 314°, are described. (I) affords *tetrahydro-yohimbylamine dihydrochloride*, $C_{19}H_{21}ON_3 \cdot 2HCl \cdot 0.5H_2O$, decomp. 342°. The $ZnCl_2$ double salt, decomp. 330—332°, *perchlorate*, decomp. about 278° after blackening at 260°, and the *sulphate* (+3H₂O), decomp. 345°, are described. H. W.

Alkaloids of fumaraceous plants. X. *Dicentra oregana*, Eastwood. R. H. F. MANSKE (Canad. J. Res., 1934, 10, 765—770).—By the procedure used previously (A., 1933, 728) 3% of alkaloids may be isolated from the roots of *D. oregana*, viz., *dicentrine*, *glaucine*, *corydine*, *protopine*, α -*allocryptopine* (found for the first time in a species of *Dicentra*), and two other alkaloids (δ and ϵ) which have been partly characterised. The phytochemical significance of the *glaucine*:*dicentrine* ratio is discussed. Alkaloid δ appears to be that found in *D. eximia* and *D. formosa* (A., 1933, 990). Alkaloid ϵ , $C_{19}H_{21}$ or $23O_4N$, m.p. 230° (previous sintering), is phenolic and probably contains one NMe and two OMe. H. N. R.

Oxidation of harmaline to harmine by nitric acid. S. ELGAZIN (Khim. Farm. Prom., 1933, 270—271).—Harmaline nitrate (I) is prepared by agitating harmaline (1 kg.) in H₂O (8 litres) at $\geq 15^\circ$ while 5% HNO₃ is added. The excess of HNO₃ is neutralised, the mixture heated at 75°, clarified with C, filtered, and cooled; (I), m.p. 230—232°, crystallises. (I) (1 kg.) is dissolved in 96% EtOH (10 litres) at 50°, treated with HCl (*d* 1.19, 1 kg.), and the temp. slowly raised to 56—60°. After 20 min. the solid mass is cooled, filtered, washed with EtOH, and dried. Harmine cryst. from 85% EtOH has m.p. 257—259°. Yield about 80%. CH. ABS.

Cinchonine solubility.—See this vol., 1066.

Water of crystallisation of quinine sulphate. H. WALES (J. Amer. Pharm. Assoc., 1934, 23, 793—795).—V.-p. measurements show that quinine sulphate forms an octahydrate, which in air reverts to the dihydrate. No heptahydrate is formed. R. S. C.

Strychnine and brucine. BRUSTIER and P. BLANC (Bull. Soc. chim., 1934, [v], 1, 712—719). Brucine (I) has only two absorption bands with max. at 2666.7 and 3059.2 Å. Since strychnine (II) has three bands, it is probably constituted differently from (I). The absorption of (II) resembles that of C_5H_5N , whilst that of (I) and quinoline are similar. (I) and (II) also give ozonisation products with different absorptions. S.

Reduction in morphine series. II. Isomeric phenolic dihydro- ψ -codeines. R. E. LUTZ and L. SMALL (J. Amer. Chem. Soc., 1934, 56, 1741—1744).—Reduction (H₂, Pd-CaCO₃, 80% EtOH) of ψ -codeine (I) gives (mainly) the phenolic *arhydro- ψ -codeine-B* (II), m.p. (+x EtOH) 125—127°, $[\alpha]_D - 14.1$

in EtOH, m.p. (anhyd.) 174.5—175.5° (from EtOAc) and 196—197° (sublimation and crystallisation from C_6H_6) [*hydrochloride* (+H₂O), m.p. 265—266° (corr.); *salicylate*, m.p. 225—226° (corr.), m.p. (+x EtOH) 130—132° (corr.)], dihydro- ψ -codeine-A, and tetrahydro- ψ -codeine (III). (II) is reduced (H₂, PtO₂, dil. AcOH) to (III). The *methiodide* (+3H₂O), m.p. 222—223° (corr.) (after melting partly at 131—132°), of (II) is decomposed by conc. aq. KOH to *dihydro- ϵ -methylmorphimethine-B*, m.p. 188.5—189.5°; $[\alpha]_D^{25} + 28^\circ$ in CHCl₃, which is reduced (H₂, Pd-CaCO₃, EtOH) to hexahydro- ϵ -methylmorphimethine (IV). Contrary to Speyer and Krauss (A., 1923, i, 1115), electrolytic reduction of (I) gives mainly (II) and not *dihydro- ψ -codeine-C* (+EtOH) (V), m.p. 100—116° (decomp.) and 167.5—168° (corr.) [*hydrochloride* (+0.5H₂O), m.p. 253° (corr.); *salicylate*, m.p. 232—234° (corr.)]. (V) is formed together with a mixture of dihydrodeoxycodeine-B and -C (see following abstract) by reduction (Na, EtOH in N₂) of (I). The *methiodide* (+H₂O), m.p. 238—239° (corr.), of (V) is converted (aq. KOH) into *dihydro- ϵ -methylmorphimethine-C*, m.p. 150°, $[\alpha]_D^{25} + 62.5^\circ$ in CHCl₃ [*hydriodide* (+H₂O), m.p. 137—138° (corr.)], also obtained in small amount by reduction (Na, EtOH) of ϵ -methylmorphimethine, which is reduced further to (IV). The reductions in the methine series parallel those of the parent ψ -codeine derivatives. Structures are suggested for most of the above compounds. H. B.

Deoxycodine. V. So-called dihydrodeoxycodeine-A. L. SMALL and R. E. LUTZ (J. Amer. Chem. Soc., 1934, 56, 1738—1740).—Reduction (Na, EtOH) of α -chlorocodide (I) or deoxycodine-A (II) gives a 1:3-mixture (III), m.p. 120—125° or 157° (according to solvent), of dihydrodeoxycodeine-B (IV), m.p. 131—133°, m.p. (anhyd. ?) 173—173.5° (obtained by sublimation), and dihydrodeoxycodeine-C (V), m.p. 108—111°, $[\alpha]_D^{25} + 5.6^\circ$ (lit. -61.6°) in EtOH, and not dihydrodeoxycodeine-A (A., 1931, 1077). Treatment of the methiodide from (III) with TIOH in H₂O, evaporation of the resulting solution to dryness in a vac., and sublimation of the residue at 140°/0.001 mm. gives *de-N-methyldihydrodeoxycodeine-B*, m.p. 114.5—145.5°, $[\alpha]_D^{25} + 9.5^\circ$ in CHCl₃ [similarly prepared with $[\alpha]_D^{25} + 7.4^\circ$ in CHCl₃ from (IV)], and *de-N-methyldihydrodeoxycodeine-C*, m.p. 175—176°, $[\alpha]_D^{25} - 13.8^\circ$ in CHCl₃ [also prepared from (V)]. The above reduction of (I) undoubtedly gives (II); subsequent 1:2- and 1:4-addition of H₂ occurs. (V) is also obtained by electrolytic reduction of chlorodihydrocodide and by reduction (Na, EtOH in N₂) of deoxycodine-C. Structures are suggested for (IV) and (V). Contrary to previous results (*loc. cit.*), vigorous reduction (Na, EtOH) of dihydrodeoxycodeine-D gives only 5% of tetrahydrodeoxycodeine. H. B.

Alkaloids of *Alstonia* barks. II. *A. macrophylla*, Wall., *A. somersetensis*, F. M. Bailey, *A. verticillosa*, F. Muell., *A. villosa*, Blum. T. M. SHARP (J.C.S., 1934, 1227—1232).—*A. verticillosa* contains sterols and echitamine; *A. macrophylla* contains *villalstonine* (I), $C_{40}H_{50}O_4N_4$, *macralstonine* (II), $C_{44}H_{54}O_5N_4$, *macralstonidine* (III), $C_{41}H_{50}O_3N_4$, and base M in small amount; *A. somersetensis* contains (I) and (III); and *A. villosa* contains (I) and base V in

small amount. (I) has m.p. 218—260°, and is isolated as the *oxalate*, m.p. 235° (decomp.), $[\alpha]_D +31.2^\circ$ in $\text{C}_6\text{H}_5\text{O}_2$; it forms a *hydrochloride* ($+4\text{H}_2\text{O}$), m.p. 270° (decomp.), $[\alpha]_D +56.3^\circ$ in H_2O , a *sulphate* ($+6\text{H}_2\text{O}$), m.p. above 310°, $[\alpha]_D +52.94^\circ$ in H_2O , a *hydrobromide* ($+4\text{H}_2\text{O}$), m.p. 293° (decomp.), a *hydriodide*, m.p. 286° (decomp.), a *dimethiodide*, m.p. 287° (decomp.), and a *N-benzyl* derivative, m.p. 246° (decomp.). (I) and KOH yield a *substance*, $\text{C}_{39}\text{H}_{48}\text{O}_4\text{N}_4$, m.p. 291—293° (decomp.), which does not contain OMe. (I) has one OMe present as ester and two NMe. (II) has m.p. 293° (decomp.), $[\alpha]_D +27.5^\circ$ in CHCl_3 , and forms a *sulphate*, m.p. about 263° (decomp.), $[\alpha]_D -36.8^\circ$ in H_2O . Base *M* has been obtained as the *sulphate*, m.p. about 257°, $[\alpha]_D -71.9^\circ$ in H_2O . (III) decomposes about 270° and has $[\alpha]_D +174.5^\circ$ in C_6H_6 ; it forms a *hydrochloride*, m.p. 326° (decomp.), $[\alpha]_D +136.5^\circ$ in H_2O . It contains two NMe but no OMe and appears to contain a CH_2O_2 . Base *V* has m.p. 273° (decomp.), $[\alpha] +54.6^\circ$. All the alkaloids give colour reactions suggesting indole derivatives. F. R. S.

Ultra-violet absorption spectra of gen-alkaloids.—See this vol., 1055.

Reactivity of nuclear chlorine in 2-chloro-5-nitrophenylarsinic acid. M. J. HALL and C. S. HAMILTON (J. Amer. Chem. Soc., 1934, 56, 1779—1782).—5-Nitro-2-*anilino*-, m.p. 182—184°, -2-*isobutylamino*-, m.p. 189—190° (decomp.), -2-*n*-, m.p. 135—137°, and -*iso*-, m.p. 186° (decomp.), -*amylamino*-, and -2- β -*hydroxyethylamino*-, m.p. 146—147°, -*phenylarsinic acids*, prepared from 2-chloro-5-nitrophenylarsinic acid (I), the requisite NH_2R , anhyd. K_2CO_3 , and a little Cu in amyl alcohol, are reduced $[\text{Fe}(\text{OH})_2]$ to the corresponding 5- NH_2 -derivatives, m.p. 195° (decomp.), 192° (decomp.), 178—179° (decomp.), 186° (decomp.), and 154—155° (decomp.), respectively. (I) and $[\text{CH}_2\text{NH}_2]_2$ similarly give 5-nitro-2- β -*aminoethylamino*-phenylarsinic acid, m.p. 250—251° (decomp.), or 4 : 4'-*dinitro- α - β -dianilinoethane-2 : 2'-diarsinic acid*, decomp. 228—229° (darkens at 225°) [corresponding 4 : 4'-(NH_2) $_2$ -derivative, m.p. 200—201° (decomp.)]. 5-Nitro-2-*phenoxy*-, m.p. 231—232°, -2-*p-chlorophenoxy*-, m.p. 225—230°, -2-*o*-, m.p. > 250°, and -*p*-, m.p. 245—246°, -*tolyl*-, and -2-*o*-, m.p. 229° (decomp.), and -*p*-, m.p. > 250°, -*carboxyphenoxy-phenylarsinic acids* are similarly prepared from (I) and the requisite ArOH [except for the CO_2H -derivatives, which are formed by oxidation (KMnO_4) of the Me compounds]; these are reduced to the corresponding 5 NH_2 -derivatives, m.p. 203°, > 250°, > 250°, 224° (decomp.), 227° (decomp.), and > 250°, respectively. *o*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{OH}$ and (I) similarly afford 3-nitrodiphenylene oxide-1-arsinic acid, m.p. 203—205° (32% yield) [corresponding NH_2 -derivative, decomp. 218° (darkens at 210°)]. The Cl atom of (I) is less reactive than that in 4-chloro-3-nitrophenylarsinic acid (cf. A., 1932, 1049). H. B.

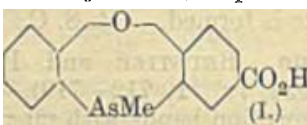
3-Nitro-4-hydroxyphenylarsinic acid from p-chloroaniline [and from 2-nitrodiphenylamine-4-arsinic acid]. V. A. IZMAILSKI and A. M. SIMONOV (Khim. Farm. Prom., 1933, 317—326).—*p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$ is transformed (Bart-Schmidt) into *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{AsO}_3\text{H}_2$ (yield 80%). 4 : 3- $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{AsO}_3\text{H}_2$ (I) is then made by nitration

with H_2SO_4 and excess of KNO_3 at 100°. (I) (14 g.) is stirred at 85° for 10 hr. with 40% NaOH (50 g.); H_2O (30 c.c.) and HCl (25 c.c.) are added, the solution is filtered with C at 80°, acidified with HCl (15 c.c.), and crystallised, affording 3 : 4- $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OH})\cdot\text{AsO}_3\text{H}_2$ in 64% yield. Alternatively, 3 : 4- $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NHPh})\cdot\text{AsO}_3\text{H}_2$ is prepared from the 4-Cl-compound by boiling for 10 hr. with *N*-NaOH and fresh NH_2Ph . Excess of NH_2Ph is removed with steam and the ppt. washed, dried, and hydrolysed for 8 hr. with 25% NaOH. CH. Abs.

Thermal decomposition of the aryltrihydroxy-arsonium chlorides. J. PRAT (Compt. rend., 1934, 199, 208—210; cf. A., 1932, 1049; 1933, 962).—The thermal decomp. of $[\text{AsPh}(\text{OH})_3]\text{Cl}$ and $[\text{CHPh}_2\cdot\text{As}(\text{OH})_3]\text{Cl}$ follows the general course $2[\text{AsR}(\text{OH})_3]\text{Cl} \rightarrow 2\text{RCl} + 2\text{As}(\text{OH})_3 \rightarrow 2\text{RCl} + \text{As}_2\text{O}_3 + 3\text{H}_2\text{O}$. (I) With $[p\text{-C}_6\text{H}_4\text{Me}\cdot\text{As}(\text{OH})_3]\text{Cl}$, however, this reaction does not predominate, the principal course of the reaction being $[p\text{-C}_6\text{H}_4\text{Me}\cdot\text{As}(\text{OH})_3]\text{Cl} \rightarrow \text{C}_6\text{H}_4\text{Me}\cdot\text{AsO}_3\text{H}_2 + \text{HCl} \rightarrow \text{PhMe} + \text{H}_3\text{AsO}_4 + \text{HCl}$ (II). The H_3AsO_4 oxidises part of the PhMe. The decomp. of $[\text{Cl}(\text{NH}_3\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})_3)]\text{Cl}\cdot\text{H}_2\text{O}$ follows the course (II), except in the presence HCl which tends to make it proceed by mechanism (I). In a current of dry HCl $[p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})_3]\text{Cl}$ decomposes slowly and incompletely according to mechanism (I).

J. W. S.

Configuration of heterocyclic compounds. I. Optical resolution of 10-methylphenoxarsine-2-carboxylic acid. (MISS) M. S. LESSLIE and E. E. TURNER (J.C.S., 1934, 1170—1174).—*o*-Aminophenyl *p*-tolyl ether is converted into 2-*p*-tolylphenylarsinic acid, m.p. 192—193°, which with H_2SO_4 yields 2-methylphenoxarsinic acid, m.p. 245—246°. Oxidation of the Me compound with KMnO_4 leads to 2-carboxyphenoxarsinic acid, m.p. 280—281°, which forms 10-chloro-, m.p. 280—281°, converted by MgMeI into dl-10-methyl-phenoxarsine-2-carboxylic acid (I), m.p. 202—203° [methiodide, m.p. 250°, and its hydrate, m.p. about 250° (decomp.)]. Fractional addition of strychnine to (I) leads to strychnine d., $[\alpha]_{D}^{20} +33.7^\circ$, dl., $[\alpha]_{D}^{20} -18.2^\circ$, and l-10-methylphenoxarsine-2-carboxylate, $[\alpha]_{D}^{20} -51.7^\circ$ in CHCl_3 . The acids obtained from these salts are the d., m.p. 135—136°, $[\alpha]_{D}^{20} +95.8^\circ$ in EtOH, and l-10-methylphenoxarsine-2-carboxylic acid, m.p. 135—136°, $[\alpha]_{D}^{20} -96.0^\circ$. The acids are optically stable. The dissymmetry of the mol. is ascribed preferably to a folded structure, but an explanation based on the presence of an asymmetric As atom is not excluded.



Mercury derivatives of nitro-*m*-cresol. See B., 1934, 781.

Nitration of phenyl derivatives of mercury, thallium, lead, bismuth, tin, and iodine. F. CHALLENGER and E. ROTHSTEIN (J.C.S., 1934, 1258—1263).—The extent of nitration of the compounds is: HgP nitrate 50, Tl Ph $_2$ oxide, 74, Tl Ph $_2$ nitrate, 75, Tl Ph $_2$ hydroxynitrate, decomp. 268°, 80, Pd Ph $_2$ nitrate, triphenylbismuthine dinitrate, 85, Sn Ph $_2$ oxide, and diphenyliodonium nitrate, 82.5%. The ntra

product was treated with Br, and the proportion of resulting mixed bromonitrobenzenes determined by two independent methods. The results show that the effect of variation of phenylcationic charge in the compounds nitrated needs to be considered for purposes of comparison.

F. R. S.

Diphenylene selenide. C. COURTOT and A. MOTAMEDI (Compt. rend., 1934, **199**, 531—533).— Ph_2SeO (A., 1894, i, 89) [prepared from Ph_2Se (A., 1932, 762)] and NaNH_2 in C_6H_6 give *diphenylene selenide* (I), $\text{O}^-\text{C}_6\text{H}_4^-\text{Se}$, m.p. 74.5° (corr.) [*dichloride*; *di-bromide*, m.p. 121.5° (corr.)], and phenylseleninic acid, m.p. $122\text{--}124^\circ$ (corr.). Treatment of halogenated (I) with 3% aq. NaOH affords *diphenyleneseleninone*, m.p. $215\text{--}216^\circ$, oxidised by KMnO_4 to *diphenyleneselenone*, m.p. 282° .

F. O. H.

Sensitisation of silver halide emulsions.—See B., 1934, 781, 782.

Manufacture of dyes and their intermediates.—See B., 1934, 753.

Heat-coagulation of caseinogen. I. The role of phosphorus cleavage. G. R. HOWAT and N. C. WRIGHT (Biochem. J., 1934, **28**, 1336—1345).—Heating Na or Ca caseinogenate at 120° in closed tubes transforms the whole of the P from the Na salt and 80% from the Ca salt into the acid-sol. form, whilst some non-protein-N is liberated. Heat-dephosphorised (I) and alkali-dephosphorised (II) caseinogen differ from one another and from untreated caseinogen (III) in base-binding capacity; acid-binding properties are also affected, but less so. In presence of enough $\text{Ca}(\text{OH})_2$ to give approx. neutral solutions, (I) and (II) coagulate more rapidly at 120° than (III), whilst excess of Ca^{++} accelerates coagulation of (I) and (III). Thus, Ca^{++} liberated during dephosphorisation increases the heat-sensitivity of the products. Factors other than those indicated are probably also involved in heat-coagulation.

I. A. P.

Casein. C. PORCHER, H. VOLKRINGER, and J. BRIGANDO (Compt. rend., 1934, **199**, 249—252).—Examination of the absorption spectra of Na caseinate (I) and paracaseinate (II) and of the protein (III) obtained by addition of CaCl_2 to a solution of Ca caseinate at $p_{\text{H}} > 7$ shows that the absorption of (I) and (II) begins at about λ 2950 Å. and presents a broad band between 2900 and about 2600 Å. General absorption then begins in the neighbourhood of 2500 Å. The curves for (I) and (II) appear identical, the apparently systematic differences between 2800—2920 and 2400—2450 Å. probably lying within the experimental errors. A max. of absorption is observed at 2765 Å., the band being completely analogous with that found for albumins and NH_2 -acids. A second max. appears at 2840 Å. The reactions of Voisenet and Millon are positive with (I) and (II), but negative with (III).

H. W.

Fractionation of caseinogen. J. GRÓH (Z. physiol. Chem., 1934, **226**, 32—44).—Caseinogen (I) was fractionally pptd. by three methods: from solution in (a) aq. carbamide by EtOH, (b) fused PhOH at 70° by EtOH, (c) dil. aq. NH_3 containing 70% of EtOH by dil. HCl. All methods finally gave only two

distinct fractions with 7.8 and 3.9% tyrosine content, $[\alpha]_{\text{D}} +91^\circ$ and $+129^\circ$ in 1% aq. borax, respectively. These preps. are not derivatives, but constituents of (I) and occur in approx. equal amount. J. H. B.

Reversibly oxidisable substance from irradiated protein. M. LAMPERT and P. WELS (Arch. exp. Path. Pharm., 1934, **175**, 554—557).—The SH-compound formed by ultra-violet irradiation of aq. ovalbumin (I) (A., 1933, 1063) cannot be separated by ultra-filtration or by deproteinisation with colloidal $\text{Fe}(\text{OH})_3$, methods by which added glutathione, cysteine, α -thiolactic and thioglycollic acid are readily separated from (I). Hence the substance is probably of high mol. wt.

F. O. H.

Gold sol reaction in irradiated proteins and protein derivatives. M. SPIEGEL-ADOLF (Biochem. J., 1934, **28**, 1201—1208).—Irradiation with a Hg-arc lamp causes loss of protective power and production of pptg. power towards Au sols in the case of gelatin, arginine, histidine, lysine, proline, and thymonucleic acid, possibly due to decarboxylation. Glycine and cyclic NH_2 -acids were not altered. Irradiation of histamine does not destroy its Au-pptg. power as rapidly as its biological activity.

C. G. A.

Composition of [serum-]proteins.—See this vol., 1018.

Role of lipins in the change of state of proteins.—See this vol., 1069.

Semi-micro-apparatus for the determination of carbon and hydrogen. G. KOMPFA and W. ROHRMANN (Chem. Fabr., 1934, **7**, 239—240).—Improvements have been made in the apparatus previously described (A., 1933, 731) whereby the accuracy and the no. of determinations per charge are increased, explosion hazard is reduced by the use of an asbestos plug between the boat and the Cu spiral, and drying out of the soda-lime by the CaCl_2 is prevented by the interposition of a tap between the two absorption tubes; if the tap is closed between determinations infrequent filling only is necessary.

H. F. G.

Microdetermination of bromine in organic substances. T. LEIPERT and O. WATZLAWEK (Z. anal. Chem., 1934, **98**, 113—116).—The products of combustion of the substance are collected in $N\text{-NaOH}$. Br is determined by oxidation to bromate and titration with $\text{Na}_2\text{S}_2\text{O}_3$ (cf. van der Meulen, A., 1931, 325). The presence of 1 drop of NH_4 molybdate solution accelerates the iodide-bromate reaction in feebly acid solution.

D. R. D.

Oxidation of organic sulphur applied to its determination. C. LEFEVRE and M. RANGIER (Compt. rend., 1934, **199**, 462—464).—Org. S, if not combined with O, is determined by oxidation with boiling alkaline KMnO_4 . Otherwise the substance is burnt in dry O_2 , the vapours being passed over Pt-10% Rh heated to bright redness and collected in aq. NaOBr. The solution and washings of the tube are united, acidified with HCl, boiled, and pptd. with BaCl_2 .

J. W. S.

p-Benzoquinone as amine reagent. M. FOUCRY (J. Pharm. Chim., 1934, [viii], **20**, 116—118).—5 c.c.

of a solution of 1 g. of *p*-benzoquinone in 100 g. of EtOH and 5 g. of AcOH boiled and cooled in presence of neutral or slightly acid solutions of amines give a red colour, immediately with conc. solutions and on keeping with dil. solutions. Conc. NH_4 salt solutions give a positive reaction, as do some NH_2 -acids (glycine, alanine). C. G. A.

Determination of weak organic acids (phenols). W. MUNCH (Z. anal. Chem., 1934, 98, 107—113).—Cresol is determined by adding it to a solution in equilibrium with $\text{Ca}(\text{OH})_2$. The increase in Ca content of the solution (conveniently determined by pptn. of CaC_2O_4 and titration with KMnO_4) is a measure of the cresol added owing to the formation of the sol. Ca compound. A correction factor of 1.1 is needed because of the hydrolysis of the compound. Other phenolic compounds may be treated similarly.

D. R. D.

Potassium mercury iodide reagents for alkaloids. J. TRAVELL (J. Amer. Pharm. Assoc., 1934, 23, 689—698).—Red HgI_2 dissolved in 10% aq. KI solution is 5—15 times as sensitive as Mayer's reagent, detecting morphine sulphate at 1:7000 and quinine sulphate at 1:1,500,000. The sensitivity to proteins

is similar. The alkaloid, but not the protein, mercuriiodides are sol. in 10% KI or EtOH. C. G. A.

Determination of total sulphur in keratin. J. BARRITT (J.S.C.I., 1934, 53, 291—294r).—The Mackay method (B., 1930, 626) for the determination of total S in rubber and similar materials is unsatisfactory as a standard method for determining S in keratin (I). Two simple and comparatively rapid methods described, involving (1) wet oxidation and (2) dry oxidation, give consistent results which agreed well with vals. obtained by the Carius method. In (1) the (I) sample is refluxed with HNO_3 (*d* 1.42), oxidation being completed with Benedict-Denis reagent (II). In (2) the sample is fused with Na_2O_2 in the Hodsman bomb (A., 1921, ii, 345). Examination of the method in which the (I) is dissolved in HCl before treatment with (II) showed that on hydrolysis with HCl wool evolved H_2S in amount > is accounted for by the slow decomp. of cystine under similar conditions. The work of Hoffman and Gortner (A., 1922, i, 427) on the decomp. of cystine on boiling with HCl was repeated and the very slow evolution of H_2S confirmed.

Reactions between nitrogenous compounds and phenols. II.—See this vol., 1082.

Biochemistry.

Spectrophotometric characteristics of hæmoglobins. I. Ox blood- and muscle-hæmoglobins. J. H. SHENK, J. L. HALL, and H. H. KING. II. Hæmoglobin of fowls. D. E. KLEIN, J. L. HALL, and H. H. KING (J. Biol. Chem., 1934, 105, 741—752, 753—760).—I. Solutions of muscle-hæmoglobin (I) show absorption curves similar to those of blood-hæmoglobin (II), but displaced towards the red. Equal concns. of (I) and (II) do not display equal absorption. The ratio of the densities of the max. absorption in the yellow and in the green, the ratios of both max. to the min. between them, and the ratio of the densities at 5770 and 5820 Å. are const.; a method for determining the relative % of (I) and (II) in the same solution is based on the last-named ratio. The points of max. absorption for blood-oxyhæmoglobin are at 5420 and 5770 Å. and the min. is at 5620 Å., the vals. for muscle-oxyhæmoglobin being 5430, 5820, and 5640 Å., respectively. The acid-hæmatin fractions are apparently identical. Animals on pasture have a higher (I) content than dry-lot fed animals.

II. The absorption factors calc. from spectrophotometric measurements and Van Slyke determinations on 100 chicken-blood samples are variable, although most fall at 1.20 mg. of hæmoglobin per c.c. Turkey blood also gave inconsistent results, but ox blood was const. at 1.165 mg. per c.c. C. G. A.

Determination of the isoelectric and isoionic points of hæmoglobin from measurements of membrane potentials. G. S. ADAIR and M. E. ADAIR (Biochem. J., 1934, 28, 1230—1258).—The isoelectric points (I) are determined by equilibrating conc. protein solutions with dil. buffer solutions at 0°. The isoionic point (II) is determined from

the distribution of salts across membranes. The (II) of cryst. hæmoglobin is at p_H 7.6; in NH_4 phosphate buffers of ionic concn. 0.02, 0.04, and 0.07 the (I) were 7.16, 6.91, and 6.70, respectively. The min. osmotic pressure is at p_H vals. between (I) and (II). The distribution of NH_4^+ and PO_4^- between protein crystals, protein solution, and dialysate is investigated. The effect of salts on (I) may be due to a reaction $+X^- + \text{Na}^+ + \text{Cl}^- \rightarrow [\text{ClX}]^- + \text{Na}^+$, where $+X^-$ is a zwitterion. C. G. A.

Kinetics of hæmoglobin. IV—VII.—See this vol., 1073.

Certain conditions of existence of fishes, especially as concerning their internal environment. E. B. POWERS (Ecology, 1934, 15, 69—79).—The isoelectric point of the hæmoglobin (I) of the yellow catfish is reached in an atm. containing 0.344% of CO_2 . The affinity of (I) for O_2 increases as CO_2 rises from 0.344 to 1.4%, but subsequently declines with higher vals. The form of the O_2 -affinity curve is influenced by the alkali reserve of the blood. Epidemics of fish mortality in ponds may be attributed to sufficient rise in CO_2 to reach the isoelectric point of the blood. A. G. P.

Mol. wt. of erythrocrucorin. II. T. SVEDBERG and I. B. ERIKSSON-QUENSEL (J. Amer. Chem. Soc., 1934, 56, 1700—1706; cf. A., 1933, 965; this vol., 92).—Erythrocrucorin (I) from *Planorbis corneus* has a sedimentation const. ($s \times 10^{13}$) of 33.7 and is stable at p_H 3—7.8. Gradual decomp. occurs at p_H > whilst at < 3, three smaller components (all stable at p_H 0.7—2) are formed. The mol. wt., calc. from measurements of sedimentation equilibrium, is about 1,300,000 (a footnote states that a more accurate method has given a val. of 1,600,000). The (I) from

Daphnia pulex contains 2 components; the major constituent has $s \times 10^{13} = 16.3$ and is stable at p_H 4.5–10.5 (at p_H 11.5–12.1, the original minor constituent is the sole product present). The mol. wt. and $s \times 10^{13}$, respectively, of the (I) from the following are given in parentheses: *Arca pexata* (33,600; 3.5); *Notomastus latericius* (36,400; 2.1); *Chironomus plumosus* (31,400; 2); *Thyone briareus* (23,600; 2.6); *Myxine glutinosa* (23,100; 2.3); *Petromyzon fluviatilis* (19,100; 1.9); all the (I) have isoelectric points between p_H 5 and 6. The relationship between the mol. wts. of different types of red blood-proteins is discussed briefly.

H. B.

Chlorohæmatoprostheticin. A. HERZOG (Biochem. Z., 1934, 272, 13–20).—Criticisms (this vol., 426) are rebutted and confirmation of the formula $C_{33}H_{32}O_4N_4ClFe$ is provided.

W. McC.

Isoelectric flocculation of porphyrins. H. FINK and W. HOERBURGER (Japan. J. Med. Sci., Biochem., 1934, 2, 371).—Okahara's results (this vol., 203) confirm previously published data (A., 1929, 879, 1340; 1930, 225; 1933, 959, 1173).

F. O. H.

Cataphoresis of mammalian erythrocytes. F. O. HOWITT (Biochem. J., 1934, 28, 1165–1170).—The cataphoretic velocity (I) of erythrocytes (II) of the rat, rabbit, mouse, and guinea-pig, determined by a macro-method (A., 1930, 568) in $M/15$ PO_4''' at p_H 7.37 and 25° was 1.45, 0.60, 1.42, and 1.16 μ per sec. volt cm., respectively, in agreement with Abramson (A., 1929, 1094). The (I) of (II) from mice in hypoglycæmic convulsions was lower and that of (II) from blood containing As, 0.1% glucose, or 0.1% glucose + 0.02% insulin was unchanged. In hæmolysed blood the intact (II) migrated independently of the hæmoglobin, which showed no marked (I).

H. D.

Light-filtering index of blood-serum. G. L. ROHDENBURG and R. SCHLEUSSNER (J. Lab. Clin. Med., 1934, 19, 705–712).—Clinical application is discussed.

CH. ABS.

Origin of blood-proteins. R. JURGENS and F. GEBHARDT (Arch. exp. Path. Pharm., 1934, 175, 558–571).—Intravenous injection of a pyretic substance into geese produces an increase in fibrinogen (I) and globulin (II) even after hepatectomy, which normally causes a disappearance of (I) and a decrease in (II). Hence (I) and (II) are at least partly of extra-hepatic origin. The blood-forming tissues, especially bone-marrow, appear to be the site of plasma-protein formation.

F. O. H.

Coagulation of serum-proteins by lactic acid. W. KOPACZEWSKI (Compt. rend., 1934, 198, 2282, 2285; cf. this vol., 547).—Serum-protein fractions, separated by $COMe_2$, when dissolved in 0.8% NaCl or $N/60$ -NaOH are pptd. by lactic acid (I), globulins (II) more easily, and albumins less easily, than myxoproteins. Dialysis gives only a small yield of (II), relatively free from inorg. constituents, which are more slowly pptd. than those obtained by the $COMe_2$ method. Serum, after dialysis, is pptd. by (I) only if a trace of $CaCl_2$ is added, although the action of Ca salts is not sp. (II) in NaOH neutralised with HCl are not pptd. by (I). Factors which influence the coagulation

of serum have similar effects on the coagulation of solutions of (II) (cf. this vol., 792), which suggests that they represent the portion of the serum which is responsible for its coagulation.

J. L. D.

Catalytic fission of serum-albumin by 3% sulphuric acid. V. S. SADIKOV, V. N. MENSCHIKOVA, R. G. KRISTALLINSKAJA, E. V. LINDKVIST-RISAKOVA, E. G. CHALETZKAJA, A. G. PESINA, and L. N. RUBEL (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 569–572).—Hydrolysis of serum-albumin (I) for 2 hr. at 180° with 3% H_2SO_4 yields gaseous (II), liquid (III), and solid products. (II) contains NH_3 , CO_2 , H_2S , and org. substances, the total N content being 13% of that of (I). (III), before and after hydrolysis with 25% HCl, contains 4.83 and 3.72% of tyrosine, 0.74 and 0.65% of tryptophan, and 2.10 and 1.3% of cystine, respectively. (III), which contains mainly substances with no free NH_2 (cyclopeptides or proline derivatives), can be fractionated by extraction with Et_2O , $CHCl_3$, or $EtOAc$, Et_2O yielding a fraction which, on crystallisation from AcOH or $EtOAc$, affords cyclopeptides, m.p. 273° , 223° , and 202° . Data for the N distribution and constituents of such fractions are given.

F. O. H.

Pigment-binding power of various albumin fractions. E. KYLIN (Arch. exp. Path. Pharm., 1934, 175, 711–718).—Serum-albumin consists of fractions which migrate cataphoretically at different velocities and which have different binding power (I) with dyes (naphthol-yellow-S). That different sera vary in (I) was confirmed (cf. A., 1928, 127; this vol., 541).

F. O. H.

Recovery of guanidine from blood-stream after injection. J. A. SAUNDERS (Biochem. J., 1934, 28, 1157–1159).—The method for guanidine (I) determination in shed blood previously described (A., 1932, 890) is used. (I) injected into dogs is recovered from their blood up to 10 min. after injection.

H. D.

Volumetric micro-determination of uric acid in urine and blood. I. RUSZNYÁK and E. HATZ (Orvosi Hetilap, 1933, 77, 200–202).—Uric acid is pptd. from urine by aq. Ag lactate, centrifuged, and dissolved in aq. NaCN, the tube being washed with aq. Na_2CO_3 . 5 c.c. of aq. phosphotungstic acid are added; an aliquot part is treated with 10% aq. NaOH and titrated with 0.01M- $K_3Fe(CN)_6$ (I). Folin's method is used for blood. Li oxalate is used to prevent coagulation. The final titration is performed with 0.005M-(I).

CH. ABS.

Determination of blood-urea by direct nesslerisation of a sodium tungstate-sulphosalicylic acid filtrate. D. F. EVELETH (J. Lab. Clin. Med., 1934, 19, 783–786).—The filtrate is prepared by treating 2 c.c. of oxalated blood, which has been incubated with 1 c.c. of urease solution for 15 min. at 50° , with 13 c.c. of H_2O , 2 c.c. of 10% Na_2WO_4 , and 2 c.c. of 25% sulphosalicylic acid.

CH. ABS.

Gasometric micro-determination of lipins in plasma, blood-cells, and tissues. E. KIRK, I. H. PAGE, and D. D. VAN SLYKE (J. Biol. Chem., 1934, 106, 203–234).—Total cholesterol (I) in plasma (0.15–3 c.c.) is determined ($\pm 0.5\%$) by extraction with $EtOH-Et_2O$, hydrolysis, pptn. with digitonin, and

manometric micro-combustion of the ppt. The total lipins in blood (0.05 c.c.) are determined by extraction ($\text{EtOH-Et}_2\text{O}$; evaporation at 60° ; dissolution in ligroin) and determination of total non-volatile C, the free (I) by digitonin pptn., the lipin $\text{NH}_2\text{-N}$ by emulsification in H_2O and determination of aliphatic $\text{NH}_2\text{-N}$ by the micromanometric HNO_2 method, and the total phosphatides (I) by the P content. Determination of (I) by $\text{COMe}_2\text{-MgCl}_2$ gives low results owing to formation of a diaminophosphatide which is insol. in moist Et_2O ; micro-combustion of the whole ppt. gives accurate results.
R. S. C.

Comparison of the content of chlorine, fructose, etc. in the blood of wild and domestic ducks. H. OKAMURA (Japan. J. Med. Sci., Biochem., 1934, 2, 323—339).—The following vals. (g. per 100 c.c.) were obtained for wild and domestic ducks, respectively: Cl (as NaCl), 0.465, 0.452; total sugar (as glucose), 0.116, 0.114; fructose, 0.005—0.007, 0.005—0.007; total residual N, 0.033, 0.036; urea-N, 0.0076, 0.0053; uric acid, 0.0067, 0.0056.
F. O. H.

Blood of normal chickens. H. M. DYER and J. H. ROE (J. Nutrition, 1934, 7, 623—626).—Analyses are recorded.
A. G. P.

Sugar in arterial and venous blood. I. BLITSTEIN (Arch. internat. Med. exp., 1933, 8, 25—46).—The venous blood-sugar (I) level is usually lower, sometimes by as much as 50 mg. per 100 ml. of blood, but is more uniform than arterial (I).
NUTR. ABS. (b)

Presence of sugars other than glucose in blood. H. OKAMURA (Japan. J. Med. Sci., Biochem., 1934, 2, 313—321).—Dog's blood with a sugar content of 0.145% contains fructose [0.0054% by the cryogenin colour reaction (I) (A., 1933, 737) and 0.006% by the NHPh_2 method] which can be isolated as the phenyl-methylhydrazone. Ox-blood contains 0.003—0.006%. Modifications in (I) are suggested.
F. O. H.

Light-filter for micro-determination of blood-sugar. J. W. MULL (J. Lab. Clin. Med., 1934, 19, 667).
CH. ABS.

Effect of changes in blood-sugar concentration on the blood-oxalic acid level. Glucose as a source of oxalic acid. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 401—411).—The blood- $\text{H}_2\text{C}_2\text{O}_4$ level in the rabbit (normally 0.0029—0.0035%) rises during the hyperglycæmia due to fright or ingestion of glucose, falls on administration of AcCO_2H , and is not influenced by intravenous injection of hexose monophosphate. $\text{H}_2\text{C}_2\text{O}_4$ appears to play a part in carbohydrate metabolism.
F. O. H.

Relation of blood-oxalic acid to food. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 373—379).—Ingestion of protein- or fat-rich diets has no marked influence on the blood- $\text{H}_2\text{C}_2\text{O}_4$ (I) in man, whilst green foods produce an increase which is not due to preformed $\text{H}_2\text{C}_2\text{O}_4$. Fasting for 7 days in rabbits does not affect (I); longer periods produce a fall. Ox-bile contains 0.007—0.009% of $\text{H}_2\text{C}_2\text{O}_4$.
F. O. H.

Influence of amino-acids on the production of oxalic acid by the animal organism. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 413—425).—

The blood- $\text{H}_2\text{C}_2\text{O}_4$ of rabbits is increased by intravenous injection of aspartic acid, asparagine, and, to a slight extent, by that of $l(+)$ - (but not of d -) amino-butyric acid; glycine, alanine, and glutamic, butyric, and succinic acids have no appreciable effect. A sample of commercial gelatin contained 0.00115% of $\text{H}_2\text{C}_2\text{O}_4$.
F. O. H.

Oxalic acid in the blood of various species of animals. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 427).—The following vals. (mg. per 100 c.c.) were obtained: ox, 2.84—3.96; pig, 2.90—3.01; dog, 1.89—1.90; carp (after fasting), 1.30—3.12, (normal), 3.10—3.42; sea-bass, 2.98—3.67; salmon, 3.15—3.38.
F. O. H.

Oxalic acid in blood. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 291—303).—A modification of the method of Izumi (this vol., 201) for the determination of $\text{H}_2\text{C}_2\text{O}_4$ in blood (I) (2 ml.) is given. Human (I) contains 3—4 and the plasma 4—6 mg. per 100 c.c. On keeping (I), the level increases and then decreases owing to pptn. of insol. derivatives, e.g., CaC_2O_4 .
F. O. H.

Thunberg's method of citric acid determination: some further results. A. LENNER (Skand. Arch. Physiol., 1934, 67, 221—225).—The mean error of the method is $\pm 0.525 \times 10^{-6}$ g. After ingestion of citric acid (I) or NaHCO_3 the (I) content of human serum rises, after NH_4Cl it falls, and after fat or glucose it remains unchanged. The serum val. remains normally fairly const., but in women there are variations corresponding with the menstrual cycle. During pregnancy there is little change, but a considerable rise occurs during parturition, followed by a fall and a gradual return to normal. The urine of new-born infants contains (I).
NUTR. ABS. (m)

The first acid change in whole blood. E. P. LAUG (J. Biol. Chem., 1934, 106, 161—171).—On removal from the body the p_{H} of whole blood decreases by about 0.008 in 5 min. This is not affected by KF (up to 1—2%) and is probably due to lactic acid production.
H. G. R.

Acid-base condition of the blood. III. Value of pK' in the Henderson-Hasselbalch equation for human and dog sera, determined with the Simms electrode. H. W. ROBINSON, J. W. PRICE, and G. E. CULLEN (J. Biol. Chem., 1934, 106, 7—27).—Methods for the determination, with increased accuracy, of pK' for saturation of sera (I) with known CO_2 tensions and of the alkali reserve are described. pK' vals. for human and dog (I) are identical (6.09 ± 0.008) and are not appreciably altered by abnormal pathological conditions.
H. G. R.

Influence of sodium and potassium content of the diet on the sodium concentration of human centrifuged red blood-cells. A. M. BUTLER and E. M. MACKAY (J. Biol. Chem., 1934, 106, 107—112).—With variations in the ratio Na : K in the diet, there is no change in the serum val. As the ratio is decreased, the Na concn. in the cells becomes lower. Mg in cells is in an inverse relation to the Na : K ratio in the diet.
H. G. R.

Determination of iron in blood-plasma. F. S. FOWWEATHER (Biochem. J., 1934, 28, 1160—1164).—Fe in plasma, showing a negative benzidine test for hæmoglobin, is determined colorimetrically with KCNS after ashing with H_2SO_4 and H_2O_2 . The vals. so obtained are > those found in the determination on protein-free filtrates. H. D.

Biochemistry of copper. III. Distribution between corpuscles and plasma. U. SARATA. IV. Content of red and white blood-cells. A. SUZUKI and U. SARATA. V. Effect of hæmorrhage on the blood-copper. U. SARATA and A. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 305—308, 309—312, 341—354; cf. this vol., 202).—III. Serum or plasma contains 3.28—3.52 (ox), 3.41—4.14 (horse), 3.08—5.01 (rabbit), and 3.48—4.47 (man) $\times 10^{-2}$ mg. Cu per 100 c.c. Most of the blood-Cu (approx. 80% in rabbits) is in the corpuscles.

IV. The erythrocytes (I) and leucocytes (obtained as a paste by centrifuging) of horse's blood contain, respectively, 0.882 and 0.282 mg. Cu per 100 g. The stromata and cell contents of (I) have approx. the same Cu content.

V. Acute hæmorrhage in rabbits produces a rapid increase in the blood-Cu followed by a rapid fall, after which the level slowly diminishes to the normal; reticulocyte formation (II) follows a parallel course. The increase in Cu content in (I) is > in the plasma. The role of Cu in (II) and anæmia is discussed.

F. O. H.

Zinc content of isolated nuclei [of blood-corpuscles]. A. KOGA (Keijo J. Med., 1934, 5, 80—96).—The Zn contents [determined by polarographic analysis of the Ca zincate ppt. (A., 1907, ii, 53)] of the cytoplasm and nuclei (the latter contaminated by cell stromata) of blood-corpuscles are, respectively, 3.0, 8.3 (goose), 6.9, 20.5 (tortoise); 8.8, 34.9 (toad); 1.3, 4.0 (fish, *Ophicephalus argus*, Cantor) mg. per 100 g. of dried substance (cf. A., 1933, 965). Hæmolysis by various salts at different temp. is discussed.

F. O. H.

Inorganic phosphorus of horse serum. Effect of age and nutrition. P. B. PEARSON (J. Biol. Chem., 1934, 106, 1—6).—With increasing age of the growing animal there is a decrease in the inorg. P (I) of the serum, which tends to become const. at maturity. Grazing on dry forage gives a val. for (I) < that of animals receiving grain, green feed, and liberal hay. Recovery from dietary hypophosphoræmia occurs within 8 days on changing to a normal diet.

H. G. R.

Colorimetric determination of nitrite in blood. E. J. STIEGLITZ and A. E. PALMER (J. Pharm. Exp. Ther., 1934, 51, 398—410).—A quant. reaction for NO_2' detects it at a concn. of 0.2 p.p.m. For determination of NO_2' in blood, 8 c.c. are mixed with 20 c.c. of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (4.5%), 1 c.c. of $N\text{-NaOH}$ is added, and to 8 c.c. of the clear protein-free filtrate are added 8 c.c. of saturated aq. $\alpha\text{-C}_{10}\text{H}_7\text{-NH}_2$ and 8 c.c. of a solution of 2:6:8- $\text{NH}_2\text{-C}_{10}\text{H}_5(\text{SO}_3\text{H})_2$ (1 drop of a 32.6% commercial solution of the Na_2 salt of amino G" acid added to 50 c.c. of H_2O and acidined with 10 c.c. of glacial AcOH). The colour developed after heating to a definite temp. (< 100°) is compared with a

standard solution of NaNO_2 similarly treated. Normal human blood contains 0.5—1.6 $\times 10^{-6}$ g. of NO_2' per 100 c.c. (mean approx. 10^{-6} g.). W. O. K.

Water content of normal human blood. K. KURODA (Keijo J. Med., 1934, 5, 111—121).—The H_2O content [determined by a micro-method (A., 1933, 1094)] of the blood of 34 men (varying from 76 to 81%, average 78.74%) and 45 women (varying from 77 to 84%, average 80.21%) is tabulated.

F. O. H.

Water content of the blood of mice during growth. K. KURODA (Keijo J. Med., 1934, 5, 140—150).—During the first two weeks of life the H_2O content (I) decreases from 83.5 to 81.3%, after which it rises to approx. 83% at 5 weeks and then falls to an approx. steady val. of 79—80.5% during the 7th to 35th weeks, a second and less marked max. occurring during the 18th week. Slight differences occur in the age-(I) curves of the two sexes. F. O. H.

Glutathione and blood-coagulation. J. KUHNAU and V. MORGENSTERN (Naturwiss., 1934, 22, 509—510).—Reduced glutathione (I) in a concn. < 0.02M always inhibits coagulation. Down to 0.002M it has the effect of inhibiting coagulation at $p_{\text{H}} < 7.4$ (A-effect) and of accelerating it at $p_{\text{H}} > 7.4$ (B-effect). Oxidised glutathione has little or no A-effect, but a strong B-effect. (I) thus inhibits coagulation in circulating blood and induces it in shed blood, which becomes alkaline by loss of CO_2 . The action is directly on thrombin, and is inhibited by substances which react with the SH group. Cu in low. concn. increases the A-effect and does not affect the B-effect. Fe^{II} reduces the A-effect and increases the B-effect. Substances forming complexes with Cu or Fe^{II} have a corresponding influence on the A- and B-effects, and the action of (I) is regarded as a Cu-anticatalysis at $p_{\text{H}} < 7.4$ and a Fe-catalysis at $p_{\text{H}} > 7.4$. HCN and L-ascorbic acid influence thrombin like (I). Analogous effects recorded with proteolytic ferments are in accordance with the assumption that thrombin is one of this class.

R. K. C.

Heparin and blood-coagulation. J. MELLANBY (Proc. Roy. Soc., 1934, B, 116, 1—9).—Heparin (I) prevents the coagulation of oxalated plasma (II) by thrombase (III) in conjunction with the neutral salt content, since it has no action on dialysed (II). The antithrombase action of (I) is annulled by thrombo-kinase, but the conversion of prothrombase into (III) is not affected. (I) does not act as antiprothrombase.

H. G. R.

Changes in [blood]-cell volume produced by varying concentrations of different anticoagulants. V. G. HELLER and H. PAUL (J. Lab. Clin. Med., 1934, 19, 777—780).—The cell-vol. is decreased by increasing the concn. of the Na, K, and Li salts used as anticoagulants, and increased by increasing the concn. of NH_4 salts. A mixture of $\text{K}_2\text{C}_2\text{O}_4$ (40%) and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ gives a min. variation in cell vol.

CH. ABS.

Hæmolytic action of silver occurring as impurity in "chemically pure" sodium chloride. E. G. BALL (Biol. Bull., 1933, 64, 277—288).—Ag (10^{-3} to $10^{-4}\%$) from Ag-lined vessels caused rapid

haemolysis of fish erythrocytes when the NaCl was used to prepare physiological saline solutions.

CH. ABS.

Complement action of blood-serum. M. DOLADILHE (Compt. rend., 1934, 199, 539—541).—The complement action of serum-globulin (I) partly depends on the presence and physico-chemical state of albumin (II) from the same or different serum. Thus heating (II) for 25 min. at 53° influences both the dispersive power of (II) (this vol., 912) and the haemolysis of sensitised red corpuscles by (I).

F. O. H.

Changes in the protein of the antiserum during the precipitin reaction and the composition of the precipitate. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 283—294).—Samples of serum-albumin and -globulin (I) were isolated using rabbits both before and after immunisation by parenteral administration of horse serum and also from the horse serum itself. The corresponding ppt. was also isolated. The various fractions were then injected subcutaneously into rabbits, and tables summarise the biological reactions obtained. (I) of horse and of immunised rabbit serum are different in biological reaction, as are also (I) of normal and immunised rabbit. The ppt., although showing some differences, closely resembles (I) of the immune serum.

P. W. C.

Keratins. I. Lead sulphide reaction. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1934, 64, 183—190).—Unbleached horn or wool is coloured brown (due to formation of PbS) when heated with aq. Pb(NO₃)₂ or Pb(OAc)₂, but no such action occurs after bleaching with H₂O₂. The formation of PbS is, however, restored and intensified by irradiation of the bleached samples. The reaction is probably due to the presence of S'' (confirmed by the greatly increased N₂ evolution with Feigl's I-azide reagent), produced by irradiation, but removed by oxidation to SO₄'' with H₂O₂. Feathers, bristles, and light horse-nair do not give the reaction.

J. W. B.

Sulphur in keratin.—See this vol., 1120.

Use of the Hagedorn-Jensen method in determination of skin-glucose. D. M. PILLSBURY and G. V. KULCHAR (J. Biol. Chem., 1934, 106, 351—356).—All glucose is extracted in 3 min. from sliced skin by the ZnSO₄-NaOH mixture at 100°; no appreciable amount of non-glucose reducing substances is extracted in this time. Increase in reducing substances obtained on longer extraction is due to non-fermentable substances. Recovery of added glucose is satisfactory. Similar results are obtained by the Somogyi-Shaffer-Hartmann method.

C. G. A.

Mineral content of elastic ligaments. E. HEISCHKEL (Biochem. Z., 1934, 272, 235—245).—Fresh ox ligamentum nuchæ contains 52% H₂O and 0.5% mineral matter, the latter consisting of Na > 64; K > 69; Ca > 33; Mg 4; Cl > 72; PO₄ > 69; SO₄ > 132; SiO₂ 32; Fe > 5 mg. per 100 g. The high SO₄ and Ca contents and the excess of Na (equiv.) over K are characteristic.

P. W. C.

Inorganic constituents of the crab's shell. P. E. H. JONES (Z. physiol. Chem., 1934, 226, 1—2).—

The Ca, Mg, P, and org. matter contents of *Potamobius fluviatilis*, L. (thorax), are 28.7, 0.20, 1.57, and 20.1, of *Astacus gammarus*, L. (thorax), 28.0, 0.38, 2.44, and 19.3, (claws) 30.7, 0.32, 1.30, and 18.9%, respectively, calc. on dry wt.

J. H. B.

Distribution of iron in tissues, particularly liver, during peptic digestion and autolysis. W. D. McFARLANE (J. Biol. Chem., 1934, 106, 245—266).—43—60% of the Fe in perfused rat-liver tissue (I) is in non-hæmatin form (reacts with dipyridyl after reduction by Na₂S₂O₄). All the Fe in a CCl₃·CO₂H filtrate (II) reacts with KCNS after oxidation by H₂O₂. Only 40% of the non-hæmatin Fe is in (II). 50% of the total Fe in (II) is pptd. by Pb(OAc)₂. All the Cu in (I) is in (II). Pepsin at 2.0 increases fivefold the Fe in (II) from foetal calf-liver, (I), and rat-muscle tissue (max. in 40 hr.). Decomp. of org. Fe compounds (? proteinates) occurs during autoprolytic changes in liver and spleen at *p*_H 4.5, is accelerated by H₂S, and inhibited by Cu. During prolonged autolysis Fe recombines with org. substances.

R. S. C.

Organic phosphorus compounds in octopods. S. SUZUKI (Japan. J. Med. Sci., Biochem., 1934, 2, 355—357).—The org. P compounds from the tentacles of the octopus yield a small pyrophosphate fraction which contains traces of adenylic acid, but no adenylyl pyrophosphate. No creatine- and only small amounts of arginine-phosphoric (?) acid are present (cf. A., 1932, 532; this vol., 96).

F. O. H.

Weight and chemical composition of *Euchæta norvegica*. Boeck. A. P. ORR (Proc. Roy. Soc. Edinburgh, 1934, 54, 51—55).—The amounts of chitin, fat, protein, and ash of male and female animals at various stages of their life cycle are given.

W. O. K.

Spontaneous formation of lysolecithin in dried animal organs. M. FRANCIOLI (Fermentforsch., 1934, 14, 241—249).—Heart, liver, spleen, muscle, brain, adrenal, pituitary, thymus, prostate, and kidney contain lecithase-A, which is not destroyed when these organs are preserved by drying and is able at room temp. to split off an unsaturated fatty acid mol. from lecithin to give lysolecithin.

P. W. C.

Origin of hydrogen sulphide evolved on boiling hen's flesh. V. S. SADIKOV, A. F. SCHOSCHIN, K. M. STARUCHINA, and M. I. LIVSCHITZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 39—43).—Total S falls from 0.935 to 0.806, cystine (I)-S from 0.414 to 0.327, methionine (II)-S from 0.251 to 0.196, and glutathione-S from 0.051 to 0% of ash- and fat-free muscle after cooking for 25 hr. at 100°. The reactions (I)+H₂ → cysteine (III), (I)+H₂O → serine+ ν , (III)+S → (I)+H₂S, and (II)+H₂O → homocystine+MeOH are postulated.

Glutathione and vitamin-C in the crystalline lens. T. W. BIRCH and W. J. DANN (Nature, 1934, 134, 383).—A reply to criticism (this vol., 1020).

L. S. T.

Press-fluid from heated beef muscle. A. M. CHILD and M. BALDELLI (J. Agric. Res., 1934, 40, 1127—1134).—The % of Et₂O extract and H₂O in juice obtained by pressure for 5 min. were approx.

the same as, but the N content was significantly $>$, when pressure was applied for 20 min. A. G. P.

Internal and external secretions of glands. P. LIVRAGA (Arch. exp. Path. Pharm., 1934, 175, 572—587).—Ligature of a part of the pancreas in cats (the blood-supply being maintained) results in degenerative changes in both the acinar and islet tissue (I) of the separated part, whilst (I) of the intact portion enlarges. The histological changes in the pancreatic and other tissues are correlated with the decrease in liver-glycogen and the variations in blood-sugar, growth, etc. F. O. H.

Formation of a hæmatopoietic substance in concentrated human gastric juice. P. J. FOUTS, O. M. HELMER, and L. G. ZERFAS (Amer. J. Med. Sci., 1934, 187, 36—49).—Whereas gastric juice conc. by ultrafiltration is not potent in pernicious anaemia, that treated by vac. distillation gives rise to a reticulocytosis (I). Juice conc. first by vac. distillation and then by ultrafiltration gives a moderate (I), and that part of the juice which passes through the filter gives a more marked response after further vac. distillation. Material in the juice, which can be activated by vac. distillation, is held back by preliminary ultrafiltration. During vac. distillation, the intrinsic factor present in the juice acts on some extrinsic factor also present, thus conferring potency. NUTR. ABS. (m)

Chemical and physical relation between blood-serum and body-fluids. II. D. R. GILLIGAN, M. C. VOLK, and H. L. BLUMGART (New Engl. J. Med., 1934, 210, 896—905).—Cerebrospinal fluid does not appear to be a dialysate or simple ultrafiltrate. The distribution of Ca, Mg, Cl, HCO_3^- , inorg. $\text{PO}_4^{'''}$, non-protein-N, and reducing substances between serum and cerebrospinal fluid differs from that between serum and oedema fluid. CH. ABS.

Sugar and fructose contents of human amniotic fluid. M. IIZUYO (Japan. J. Med. Sci., Biochem., 1934, 2, 359—369).—As pregnancy progresses the % of reducing fermentable sugar decreases (from $> 0.09\%$ at 2—3 months to 0.014—0.025% at full term), whilst the abs. content increases. Approx. 10% is fructose. F. O. H.

Determination of bile-pigments. E. A. PETERMAN and T. B. COOLEY (J. Lab. Clin. Med., 1934, 19, 723—735).—The time required to complete the change of colour from yellow to deep blue in the oxidation of bilirubin (I) depends on the HNO_3 used, and on the application of heat and light. The total (I) can be determined at any stage of oxidation by determining both the blue and yellow components of the colour by means of light filters and suitable dichromatic standards. CH. ABS.

Use of hydrogen peroxide in the determination of bilirubin in bile. E. A. PETERMAN and T. B. COOLEY (J. Lab. Clin. Med., 1934, 19, 743—748).— H_2O_2 is used instead of HNO_3 . Colorimetric readings are made at the stage of max. intensity of blue, using Nile-blue as standard. CH. ABS.

Relationships between the constituents of milk. A. BLACK and LE R. VORIS (J. Agric. Res.,

1934, 48, 1025—1032).—Statistical examination of detailed analyses is recorded. A. G. P.

Rapid determination of total proteins and non-protein-nitrogen in human and cow's milk. L. D. SCOTT (Biochem. J., 1934, 28, 1193—1197).—The protein (I) is pptd. by $\text{Zn}(\text{OH})_2$, digested with syrupy H_3PO_4 and H_2SO_4 , and the solution nesslerised. The non-protein-N is determined by the digestion of the supernatant liquid from (I) and aeration into standard acid. C. G. A.

Human milk. XV. Non-protein-nitrogen constituents. B. N. ERICKSON, M. GULICK, H. A. HUNSCHER, and I. G. MACY (J. Biol. Chem., 1934, 106, 145—159).—The non-protein-N (I) and $\text{NH}_2\text{-N}$ were practically the same in the first and the last halves of lactation, but varied from a max. in the evening to a min. in the morning. In the early stages and in fever, the vals. were irregular and high. Under normal conditions (I) is similar to that of the blood, and may be used clinically as an index of abnormal disturbances. H. G. R.

Phosphatides of milk. W. DIEMAIR, B. BLEYER, and M. ÖRT (Biochem. Z., 1934, 272, 119—132).—The phosphatide extracted from milk powder by MeOH is chiefly a monoaminophosphatide the components of which are palmitic, stearic, and oleic acids, colamine, and choline. A diamminophosphatide is also extracted. W. McC.

Fat of human milk. A. W. BOSWORTH (J. Biol. Chem., 1934, 106, 235—244).—The fat of human milk was hydrolysed and the Me esters of the acids (I) were fractionated. A relatively large fraction was obtained corresponding with dodecoic acid (cf. cow's milk). (I) include tetra- and hexa-decenoic, oleic, linoleic, and (probably) decenoic acids, unsaturated acids with $> 18\text{C}$, and two highly unsaturated acids of the arachidonic type. R. S. C.

Fat percentage of milk as affected by feeding fats to dairy cows. N. N. ALLEN (J. Dairy Sci., 1934, 17, 379—395).—The increased fat content of milk from cows receiving butter-fat, lard, tallow, and various vegetable oils averaged 10—20% of the additional fat intake. Milk yields were not affected except in the case of coconut oil, which reduced yields when fed in large amounts. The effect of the fats was apparent 12—24 hr. after feeding and persisted 30—42 hr. after cessation of the additional ration. A. G. P.

Factors influencing the initial induction period in the oxidation of milk-fat. J. L. HENDERSON and C. L. ROADHOUSE (J. Dairy Sci., 1934, 17, 321—330).—Modifications of Greenbank and Holm's photochemical method (B., 1933, 275) for determining susceptibility to oxidation (S) are described. Exposure to light and to the action of Cu increased the S of milk-fat. Ni had a slight effect, but a Cr-Ni alloy was without influence. Milk from animals utilising body-fat while supplied with sub-maintenance rations had higher proportions of unsaturated fats and greater S. A. G. P.

Dialysis of milk. II. Factors influencing the distribution of calcium and phosphorus. L. H. LAMPITT and J. H. BUSHILL (Biochem. J., 1934, 28,

1305—1312).—An increase in the dialysable Ca and inorg. P, but no effect on org. P, results from both an increase (by dilution) and a decrease (by bacterial action) in p_H . Pasteurisation decreases the amount of sol. P and Ca. The results for fresh, pasteurised, and separated milks are: dialysable Ca 25—33%, dialysable P 43—51%, dialysable inorg. P 33—41%.

H. G. R.

Zinc content of human, cow's, and goat's milk at various stages of lactation. A. KOGA (Keijo J. Med., 1934, 5, 106—110).—Colostrum (human) contains 3—9 and normal milk 0.6—2.1 (human), 3.4—3.6 (cow), and 2.6—4.2 (goat) mg. Zn per kg. (cf. A., 1919, i, 420).

F. O. H.

Vitamins. XX. Effect of various methods of pasteurisation on the vitamin- B_1 and - B_2 contents of cow's milk. R. A. DUTCHER, N. B. GUERRANT, and J. G. McKELVEY (J. Dairy Sci., 1934, 17, 455—466).—Losses of vitamin- B_1 and - B_2 occurred in all methods of pasteurisation, but were min. when the milk was boiled for 10 min. under reflux. When pasteurised under diminished pressure losses were > under normal pressure.

A. G. P.

Irradiated milk: transmission and antirachitic activation of milk films by ultra-violet radiations. G. C. SUPPLEE and M. J. DORCAS (J. Dairy Sci., 1934, 17, 433—443).—The antirachitic potency imparted to milk by ultra-violet irradiation is not \propto fat content. Penetration of radiations of 2500—2850 Å. is small and synthesis of vitamin-D in treated milk occurs substantially at the surface.

A. G. P.

Relative value of irradiated yeast and irradiated ergosterol in the production of vitamin-D milk. W. C. RUSSELL, D. E. WILCOX, J. WADDELL, and L. T. WILSON (J. Dairy Sci., 1934, 17, 445—453).—When supplied at the rate of 60,000 units daily the efficiencies of irradiated yeast and ergosterol were approx. the same with respect to vitamin-D production in milk, but the former is the more effective when fed in larger amounts. In both cases < 2% of the ingested vitamin-D appeared in the milk. Additions of quinol increased the effectiveness of ergosterol, especially at the lower level of intake.

A. G. P.

Detection of milk from cows infected with mastitis. W. H. HALVERSEN, V. A. CHERRINGTON, and H. C. HANSEN (J. Dairy Sci., 1934, 17, 281—296).—In addition to characteristic bacterial and leucocyte counts, milk from cows infected with mastitis (acute) shows a high catalase content, high p_H , low curd tension, and usually > 0.14% Cl'.

A. G. P.

A saturated solid alcohol from the urine of pregnant mares. G. A. D. HASLEWOOD, G. F. MARRIAN, and E. R. SMITH (Biochem. J., 1934, 28, 1316—1320).—The alcohol ($C_7H_{12}O$)_n, m.p. 303—304.5°, —44° (acetate, m.p. 168°), has been isolated from the neutral, Et₂O-sol. fraction of mare's urine.

H. G. R.

Urinary composition in marine fish. R. F. PITTS (J. Cell. Comp. Physiol., 1934, 4, 389—395).—Urinary Cl' was low or zero in all cases examined.

Artificially induced diuresis is accompanied by additional excretion of Cl', SO_4^{--} , and Mg^{++} . The sculpin can excrete a supersaturated solution of $MgHPO_4$ in its urine.

A. G. P.

Fæcal "fat": its relation to fat in the diet. A. KRAKOWER (Amer. J. Physiol., 1934, 107, 49—54).—The fæcal fats of normal individuals receiving test diets containing small and large amounts of fat have similar I vals. (I), although (I) of the fats fed vary (8.2—125.8). There is little relationship between the amount of fat fed and the amount in the fæces.

NUTR. ABS. (m)

Nature of calcium, magnesium, and phosphorus compounds excreted by the gut and their proportion in the fæces. J. MAREK, O. WELLMANN, and L. URBANYI (Biochem. Z., 1934, 272, 277—283).—Ca is excreted by the intestine as normal and acid phosphate and as carbonate, as soaps (with a fat-rich diet), and as org. and P-containing H_2O -sol. and -insol. compounds. The ratio of these compounds varies with the diet. With a P-rich diet, sol. alkali phosphate may also be excreted in considerable amounts. Mg excreted in the fæces is partly H_2O -sol. and partly insol. Administration of excess Ca does not notably decrease the PO_4^{---} supply of the body and vice versa.

P. W. C.

Cholesterol saturation of blood in allergic diseases. B. PAUL (Orvosi Hetilap, 1933, 77, 444—446).—Blood-serum in allergy during attacks is saturated or supersaturated with cholesterol.

CH. ABS.

Amount of material effective in pernicious anæmia present in dog liver. M. B. STRAUSS and W. B. CASTLE (Proc. Soc. Exp. Biol. Med., 1933, 31, 360—363).—In pernicious anæmia daily intramuscular injection of extract equiv. to 20 g. of dog liver produced no response, whereas daily injections equiv. to 20 g. of hog liver produced a reticulocyte crisis. Daily injections equiv. to 100 g. of dog liver produced a satisfactory response. The content of potent material in canine liver only is about one fifth of that in hog liver, because of the low amount of intrinsic factor in dog's gastric juice.

NUTR. ABS. (m)

Influence of disease, sex, and age on the content of the human liver in metals. H. LUNDGARDH (Naturwiss., 1934, 22, 572).—Liver (from both sexes) has an average content ($\times 10^{-2}$ g. per kg.) of Mn 0.2, Cu 0.5, Sr 0.6, Rb 1.4, Al 3.0, Ca 3.4, Zn 3.9, Mg 14.0, Fe 20.0, Na 118.0, and K 194.0. In some cases Ag, Pb, Sn, Ba, Cd, and B were detected. Marked increases of the Mn content occur with diabetes, of Ca, Fe, and Na with pernicious anæmia, and of Zn with cancer. The average vals., excepting that of Na, are somewhat lower in women. Certain changes occur with age, and these also are to a certain extent characteristic of the sex.

F. O. H.

Changes in creatine and creatinine excretion in progressive muscular atrophy following ingestion of glycine. A. G. SCHOO and J. BOER (Nederland. Tijds. Geneesk., 1934, 78, 34).—After ingestion of 1 g. of creatine, excretion of creatine and creatinine is considerably greater in children (1) suffering from the disease than in healthy children. Administration of 4 g. of glycine (II) daily for 6 weeks

brings the excretion of creatine in (I) within normal limits. After discontinuing (II) excretion of ingested creatine is again $>$ in healthy children. (II) changes the metabolic processes in the muscles.

NUTR. ABS. (m)

Blood-sugar in cancer patients after ingestion of glucose. B. LEVIE (Nederland. Tijds. Geneesk., 1934, 78, 265).—In some but not all cases (carcinoma and sarcoma) examined, high blood-sugars were found following ingestion of 50 g. of glucose, with a late max. and delayed return to normal.

NUTR. ABS. (b)

Spectrographic study of the occurrence of chromium and molybdenum in carcinoma of the human breast. A. DINGWALL and H. T. BEANS (Proc. Nat. Acad. Sci., 1934, 20, 416—420).—In 60 cases of carcinoma of the breast either Mo or Cr was detected; in only one of these were both present. These elements may have a definite significance in the metabolism of the tumour cell.

P. G. M.

Relationship of internal secretions to the metabolism of malignant tumour tissue. O. O. MEYER and C. McTIERNAN (Amer. J. Cancer, 1934, 20, 96—116).—Subcutaneous injection of thyroxine into tumour-bearing animals appears to inhibit tumour growth. Insulin, theelin, prolan, thymus extract, and adrenal cortex extract have no effect.

CH. ABS.

Acceleration of respiration of normal and tumour tissue by thionine (Lauth's violet). F. DICKENS (Nature, 1934, 134, 382—383).—Addition of thionine (I) to a lactate-containing medium increases respiration of the kidney of the rat. Respiration in presence of glucose is also increased. With Jensen rat-sarcoma, (I) increases respiration in $\text{PO}_4^{'''}$ - and HCO_3^- -media containing glucose; in media containing lactate (I) and pyocyanine both produce a decrease in respiration. (I) has little or no effect on aerobic glycolysis.

L. S. T.

Effect of 2:6-dichlorophenol-indophenol on tumour and kidney respiration. K. A. C. ELLIOT (Nature, 1934, 134, 254).—In the absence of glucose, respiration of cancer tissue is practically completely inhibited by $1.3 \times 10^{-3} M$ 2:6-dichlorophenol-indophenol; in presence of glucose there is little, if any, effect. No inhibition of glycolysis occurs. With kidney cortical tissue inhibition is practically complete in both cases.

L. S. T.

Role of 1:2:5:6-dibenzanthracene in the production of fowl tumours. J. G. CHALMERS (Biochem. J., 1934, 28, 1214—1218).—As determined by spectroscopic examination the compound disappears from the breast muscle of chickens within a few days of injection, a time short compared with that required for the production of malignant symptoms. It is not transferred to the liver.

C. G. A.

Comparison of the action of polycyclic aromatic hydrocarbons in producing tumours of the connective tissue. G. BARRY and J. W. COOK (Amer. J. Cancer, 1934, 20, 58—69).—Subcutaneous injection of chrysene and 5:6-cyclopenteno-1:2-benzanthracene in lard produces tumours. Application of oleic acid, mouse fat, or solutions of chrysene to the skin does not produce epithelioma.

CH. ABS.

Influence of pathological processes (tumours, cachexia, and X-irradiation) on the constitution of tissue-proteins. E. G. SCHENCK (Arch. exp. Path. Pharm., 1934, 175, 401—405; cf. A., 1933, 1328).—The changes in the content and constitution of the proteins of tissues (heart, muscle, liver) due to the presence of growing tumours in rats are tabulated. Similar data for the changes due to X-irradiation of normal and diseased tissue and of the tumours themselves are also given.

F. O. H.

Composition of nucleic acids of malignant tumours. K. STERN and R. WILLHEIM (Biochem. Z., 1934, 272, 180—188).—The nucleic acid of human malignant tumours contains considerably less N than normal, but no difference can be detected in the distribution of N between purine and pyrimidine bases.

P. W. C.

Blood-urea-, -uric acid, and -cholesterol in meningitis and cerebral diseases. L. RICCITELLI (Klin. Woch., 1932, 11, 2155—2156; Chem. Zentr., 1934, i, 72).—In cerebral diseases, blood-urea, -uric acid, and -cholesterol are often increased. These changes are also produced by stimulation of the floor of the fourth ventricle, which is assumed to contain a regulating centre for these substances.

L. S. T.

Changes in carbohydrate metabolism in disease of the mid-brain. D. ADLERSBERG and R. FRIEDMANN (Z. ges. exp. Med., 1934, 93, 316—349).—The disease is characterised by two types of reaction: (1) cerebrohepatic, with disturbance of glucose (I) and occasionally galactose (II) tolerance, marked sensitivity to insulin (III) and normal H_2O metabolism, (2) cerebral, with normal (I) and (II) tolerance, reduced sensitivity to (III), and marked disturbance of H_2O metabolism.

NUTR. ABS. (m)

Blood-sugar [in diabetes]. E. SCHILLING (Z. ges. exp. Med., 1934, 93, 257—264).—In mild cases all types of adrenaline (I) curve are observed, whilst in moderately severe cases the curves are higher, and in very severe cases much flatter, than normal. In all cases except the very mildest the curve after glucose is higher than normal. In severe cases injection of (I) is of val. in overcoming hypoglycaemia.

NUTR. ABS. (m)

Fruit as source of carbohydrate in the diet in diabetes, liver disease, and obesity. A. DEINDL (Deut. Arch. klin. Med., 1934, 176, 311—329).—After four types of test meal, namely 600 g. of apples (I), a mixture of glucose, fructose, and sucrose equiv. to the sugar content of the apples, and equiv. amounts of glucose and fructose administered to persons with diabetes, obesity, or liver disease there is marked similarity in the glycæmic curves obtained, showing the close connexion between these pathological conditions. There is a more marked and prolonged rise in blood-sugar (II) (most pronounced in the diabetics) than occurs in normal subjects after similar meals. Although after (I), (II) does not attain so high a val. as after the mixed sugars, its return to normal is much more delayed (due to slower digestion and absorption). Hence the observed unfavourable influence of fruit on sugar tolerance in diabetes.

NUTR. ABS. (m)

Utilisation of various carbohydrates by the depancreatized dog. J. L. BOLLMAN and F. C. MANN (*Amer. J. Physiol.*, 1934, **107**, 183—189).—In depancreatized dogs on a daily diet (I) of 150 g. meat, 50 g. pancreas, 50 g. cracker meal, and 200 ml. milk with 6 units of insulin, the daily excretion of glucose is 2—25 g. The increased excretion of sugar which follows addition of 50 g. of glucose to (I) is about 50 g.; results are similar with galactose, and maize-starch if allowance is made for the unhydrolysed starch in the faeces. Fructose (II) appears to be partly utilised for several days under these conditions, the average daily excretion after addition of 50 g. to (I) being about 20 g. This apparent utilisation is soon lost and the total sugar added then appears in the urine. Sucrose and inulin act like (II).

NUTR. ABS. (m)

Jerusalem artichoke in the treatment of diabetes. L. K. CAMPBELL (*Arch. Int. Med.*, 1934, **54**, 82—87).—There is no difference in the utilisation of Jerusalem artichoke in diabetes from that of an equiv. amount of oatmeal.

H. G. R.

Effect of pregnancy on the insulin requirement of the diabetic. G. G. DUNCAN and F. FETTER (*Amer. J. Med. Sci.*, 1934, **187**, 347—351).—During pregnancy (I) the insulin requirement increases during the first three months, remains const. during the second, again increases in the third three months, and finally decreases suddenly after parturition. (I) need not permanently impair the diabetic's tolerance, and diabetes *per se* is not a contraindication to (I).

NUTR. ABS. (m)

Induced and photochemical oxidation of sodium tartrate by air and its use in diabetes and prolonged fasting.—See this vol., 1079.

Bactericidal action of diabetic serum. E. KESTERMANN and A. KNOLLE (*Deut. Arch. klin. Med.*, 1933, **176**, 64—80).—Artificial increase of blood-sugar to a high level results in reduction of bactericidal power (I) towards *B. coli* but not towards staphylococci (II) or streptococci (III). Serum from less severe cases of diabetes has (I) similar to that of normal serum, although it is more easily exhausted. In severe cases the activity is reduced. There is a relationship between the severity of the illness and the degree of diminution of serum activity (IV). A similar but much smaller difference shows when (II) and (III) are used. Treatment with diet and insulin is followed by an improvement in (I). Similar decrease in (IV) is noted in cachexia following other diseases.

NUTR. ABS. (m)

Retention of sodium chloride during artificially-produced fever. S. LANG (*Arch. exp. Path. Pharm.*, 1934, **175**, 406—408).—During the fever produced in dogs by intramuscular injection of milk the urinary excretion of NaCl increases. F. O. H.

Goitre in New Zealand. Relation between incidence of goitre and iodine content of soil and water. R. A. SHORE and R. L. ANDREW (*Bull. Office internat. d'Hyg. publ.*, 1934, **26**, 252—254).—There is direct relationship between the I content (I) of the soil of New Zealand and the frequency (II) of goitre, the max. incidence occurring where (II) is

lowest. There is no relation between (I) of drinking H₂O and (II).

NUTR. ABS. (m)

Action of 3:5-di-iodotyrosine in hyperthyroidism. E. DELCOURT-BERNARD (*Rev. belge Sci. med.*, 1934, **6**, 1—27).—In hyperthyroidism, di-iodotyrosine (I) usually lowers, but sometimes raises, the metabolism. The effects of (I) differ from those of Lugol's I, which has a greater effect on ventilation than on O₂ consumption. (I), when it lowers the metabolic level, lowers mainly O₂ consumption; when it raises the metabolism, it raises both ventilation and O₂ consumption.

NUTR. ABS. (m)

Potassium metabolism in hyperpiesia. L. ARMENTANO (*Orvosi Hetilap*, 1934, **78**, 96—98).—In healthy subjects or in arteriosclerosis, following intravenous injection of 5% aq. KCl, the K content of the blood rises 10—15 mg. per 100 ml. in the first 10 min. and falls within 30 min. to or below its original level. In hyperpiesia immediate fall in the K level occurs. Decerebration in dogs diminishes blood-K.

NUTR. ABS. (m)

Starvation ketonuria in infants. H. BEUMER and H. PETERS (*Z. Kinderheilk.*, 1934, **56**, 61—63).—Administration of alkali accelerates appearance of hunger acetoneuria (I) and increases the output of CO₂. The occurrence of (I) following an injection of adrenaline during fasting is confirmed.

NUTR. ABS. (m)

Utilisation of ingested sugar in glycogen-storing disease. H. BIEDERMANN and W. HERTZ (*Deut. Arch. klin. Med.*, 1934, **176**, 267—271).—In one case, ingestion of 100 g. of glucose (I), 30 g. of fructose (II), or 25 g. of galactose caused no glycosuria. After (I) the hyperglycemia was more prolonged and > normal, although the fasting blood-sugar (III) was very low (46—61 mg. per 100 ml.). The glycaemic response to (II) was normal. After (I) or (II) the output of urinary inorg. P was increased. Another case, which had (III) 53—83 mg. per 100 ml., gave similar results, but showed after (II) an increased and prolonged rise in (III). Combustion of ingested sugar is delayed in this disease.

NUTR. ABS. (m)

Value of salmon oil in treatment of infantile rickets. M. M. ELIOT, E. M. NELSON, S. P. SOUTHER, and M. K. CARY (*J. Amer. Med. Assoc.*, 1932, **99**, 1075—1082).—Varieties are compared as regards vitamin-A potency.

CH. ABS.

Beryllium rickets. II. Prevention and cure. H. D. KAY and D. I. SKILL (*Biochem. J.*, 1934, **28**, 1222—1227).—Be rickets can be prevented if glycerophosphate is administered parenterally at the same time as the Be diet. Be-rachitic animals transferred to a normal diet rapidly recover, the phosphoric ester content of the liver and erythrocytes increasing.

C. G. A.

Phosphoric ester content of the red cells and liver, and the phosphatase of the kidney in experimental osteoporosis in young rats. D. I. SKILL and H. D. KAY (*Biochem. J.*, 1934, **28**, 1228—1229).—In osteoporosis caused by a low-Ca, high-P diet the phosphoric ester content of the red cells and liver is lowered. As in experimental rickets the phosphatase activity of the kidney is diminished.

C. G. A.

Phosphorus partition in chicken blood as related to diet and bone maladies. V. G. HELLER, B. ZIMMERMAN, and R. B. THOMPSON (Poultry Sci., 1934, **13**, 141—147).—Doubt is thrown on reported total inorg. P contents of serum and on the use made of these vals. in interpreting the mineral and vitamin status of foods. A. G. P.

Phosphatase. III. Serum-phosphatase in diseases of the bone. A. BODANSKY and H. L. JAFFE (Arch. Int. Med., 1934, **54**, 88—110).—Serum-phosphatase (I) is not affected by destruction of bone (II), but is high in cases of excessive formation of abnormal (II). Determinations of (I) may be used as an indication of effective therapy in rickets and in the differential diagnosis of other bone diseases. H. G. R.

Tissue respiration and certain reducing substances in chronic fluorosis and scurvy in the guinea-pig. P. H. PHILLIPS, F. J. STARE, and C. A. ELVEHJEM (J. Biol. Chem., 1934, **106**, 41—61).—The rate of O_2 uptake (I), the inhibiting effect of CN' , and the decolorisation time of methylene-blue for the liver tissues of guinea-pigs are not affected by scurvy (II) or by fluorosis (III), whereas the indophenol-oxidase content is diminished and the glutathione increased in both (II) and (III). In the adrenals, (I) is about 50% of the normal val. in (II) and (III), whereas (I) is low in (II) and high in (III) and in general \propto the vitamin-C content of the tissue. The similarity between (II) and (III) has been confirmed and extended. H. G. R.

Silica content of normal and silicotic lungs. Silicosis. F. S. FOWWEATHER (Chem. and Ind., 1934, 713—716).—The degree of pulmonary fibrosis resulting from silicosis (I) is not related to the SiO_2 content of the lungs; the nature of the inhaled SiO_2 and the condition of the tissue are probably important factors. Silicates slowly decompose in the lungs to form active SiO_2 ; hence the long interval frequently occurring between exposure to SiO_2 and death. A severe type of (I) is produced by inhalation of siliceous soap powder. F. O. H.

Pathogenesis and clinical features of non-tropical sprue. L. DUNNER, H. HIRSCHFELD, and M. GERALDY (Klin. Woch., 1934, **13**, 138—141).—The bile and pancreas function normally, but loss of fatty acids and Ca soaps occurs. The Ca content of blood and tissues becomes insufficient. NUTR. ABS. (b)

Precipitation of ox-heart antigen by cerebrospinal fluid of neurosyphilitic patients. B. S. LEVINE (Amer. J. Syphilis Neurol., 1934, **18**, 239—248).—Globulins have been conc. and freed from $(NH_4)_2SO_4$ sufficiently to raise the sensitivity of the pptn. reaction to a level comparable with that of complement fixation. CH. ABS.

Gaseous metabolism of small animals. H. R. KANITZ and J. APITZSCH (Biochem. Z., 1934, **272**, 189—196).—Apparatus is described. P. W. C.

Respiratory exchanges. M. ZAPAN (Bull. Acad. Sci. Roumaine, 1934, **16**, 147—157).—Physical fatigue is manifested by an increase in expired CO_2 , which \propto the work done, but is \neq 6.9%. The amount

of CO_2 expired does not always correspond with the O_2 used and, after heavy work, about 6 hr. is necessary to reach normal equilibrium. H. G. R.

Influence of temperature on the chemical composition of anaerobically fatigued muscle. C. LUTWAK and W. MOZOLOWSKI (Biochem. Z., 1934, **272**, 157—166).—The behaviour of P compounds of muscle stimulated anaerobically at 4° to fatigue is similar to that at 18°, whereas the formation of lactic acid and NH_3 is much greater at the higher temp., the lactic acid max. and the rate of its formation being different. Creatine- and adenosine-phosphoric acids are almost completely decomposed in fatigued muscle. P. W. C.

Relation of cystine and cysteine to muscle overstrain. M. ITAGAKI, M. ODAGIRI, and Z. KABUKI (Japan. J. Med. Sci., Biochem., 1934, **2**, 381—399).—Muscular activity in rabbits, dogs, and men due to exercise, injection of strychnine, or faradic stimulation produces an occasional rise in the cystine content of the urine, whilst the cysteine and cystine+cysteine levels markedly increase. The role of SH-compounds in muscle metabolism is discussed. F. O. H.

Rôle of the endocrine glands in the resynthesis of muscle-glycogen after fatigue. R. DAMBROSI (Compt. rend. Soc. Biol., 1934, **115**, 344—345).—In the dog, insufficiency of thyroid, parathyroid, pituitary, or gonads does not affect the re-formation of muscle-glycogen after severe exercise. Thyroid administration inhibits resynthesis only when the dosage is very high. NUTR. ABS. (b)

Lactic acid, total carbon dioxide, and p_H of venous blood during recovery from severe exercise. E. P. LAUG (Amer. J. Physiol., 1934, **107**, 687—692).—The max. lactic acid and min. p_H vals. were found in man 3—6 min. after exercise. In two cases, during the first 10 min. of recovery the total CO_2 continued to decline, despite a fall in lactic acid and rise in p_H . NUTR. ABS. (b)

Lactic acid metabolism of muscles made non-irritable by sugar solutions. A. H. HEGNAUER (Amer. J. Physiol., 1934, **107**, 667—676).—Measurement of the lactic acid (I) content of muscles at intervals after immersion in isotonic glucose solution in O_2 and N_2 shows that not all the observed increase in O_2 consumption (II) can be accounted for by increased lactate content. Addition of NaCl or KCl causes decrease in (II) and increase in oxidative quotient. (I) is not the sole pace-maker for (II). NUTR. ABS. (m)

Blood-sugar in the light athletic sports. F. MEYTHALER and A. DROSTE (Klin. Woch., 1934, **13**, 439—443).—The blood-sugar of trained and untrained persons is raised slightly by short-distance races (100—200 m.) and considerably by medium-distance races (400—800 m.), after which the return to normal is delayed in the untrained. Long-distance races (10,000 m.) produce in the trained a slight rise, which declines immediately after the race. In the untrained, hyperglycemia, or in the case of exhaustion, hypoglycemia, was observed. NUTR. ABS. (b)

Carbohydrate metabolism of the kidney. A. HEMINGWAY and H. J. PHELPS (*J. Physiol.*, 1934, 80, 369—376).—The perfused kidney uses 0.014—0.99 mg. of glucose per g. per min., whilst the perfused isolated lung uses 0.014 mg. About one third of the O₂ used by the kidney is employed in carbohydrate metabolism. NUTR. ABS. (m)

Fate of absorbed carbohydrate in the organism. H. SCHUR, A. LOW, and A. KRČMA (*Wien. Arch. inn. Med.*, 1934, 24, 463—480).—Single high doses of carbohydrate (I) cause a marked increase in depôt fat of mice, to > double the original amount. The glycogen content of liver (II) increases tenfold, and the wt. of the (II) is doubled. More than two thirds of the absorbed (I) appears in the form of fat; the transformation probably occurs in the fat tissues. Part of the absorbed (I) enters directly into metabolic processes. This implies that absorbed (I) inhibits formation of (I) from fat in (II). NUTR. ABS. (b)

Intravenous administration of glucose to infants. M. ELLERMANN and K. TORNING (*Rev. franç. Pédiat.*, 1933, 9, 632—639).—Intravenous administration of glucose (10—20 g. according to age) is, after the initial rise, followed by a steady fall in blood-sugar to < the fasting level in < 2 hr. In diabetic children the fall is interrupted after about 1 hr., after which it is much slower. NUTR. ABS. (b)

Effect of glucose derivatives on animals (rabbits) following hepatectomy. D. R. DRURY and W. T. SALTER (*Amer. J. Physiol.*, 1934, 107, 406—413).—A no. of hexose and triose derivatives, tested for ability to prolong the life of the hepatectomised rabbit, did not approach glucose in efficiency, the best being fructose with a survival period of 11.9 hr., as against 20 hr. with glucose. The so-called carbohydrate intermediates are of doubtful importance in the normal exchange of carbohydrate between various tissues and organs. NUTR. ABS. (b)

Heat production in *Ascaris lumbricoides* during feeding with glucose, fructose, and galactose. R. HOFFMANN (*Z. Biol.*, 1934, 96, 390—400).—Compared with other sugar fermentation processes, the utilisation of glucose and fructose by *A. lumbricoides* results in abnormally high production of heat. A. G. P.

Fructose and lactic acid metabolism. E. STERKIN and F. M. VENGEROVA (*Biochem. Z.*, 1934, 272, 246—258).—Oral administration of glucose, maltose, or lactose has no effect on the blood-lactic acid (I) val., but that of fructose (II), sucrose (III), or invert sugar (IV) brings about a considerable hyperlactacidæmia lasting 2—3 hr. (II) and (IV) but not (III) when administered intravenously have the same effect if the initial (I) is low, but if high, the effect may be small or hypolactacidæmia may result.

P. W. C.

Effect of large storage of glycogen on respiration of the liver. B. WALTHARD (*Z. ges. exp. Med.*, 1934, 93, 242—245).—Storage of glycogen (I) or fat, but especially of (I), in the rat's liver reduces its respiratory activity, indicating regressive tissue changes. The reduction in O₂ consumption takes

place even when (I) is in solution, and cannot be interpreted as a direct effect of (I).

NUTR. ABS. (m)

Glycogen storage and fructose tolerance. P. F. MEYER (*J. Physiol.*, 1934, 80, 480—490).—In rats an excessive hyperglycæmia after fructose feeding is not associated with a low glycogen (I) store nor with inability of the liver to form and hold (I), but rather with little or no (I) formation in the muscles.

NUTR. ABS. (b)

Storage of glycogen in the reproductive organs of invertebrates before ovulation. M. CHAIGNE (*Compt. rend. Soc. Biol.*, 1934, 115, 174—176).—The variations in glycogen (I) reserves in *Asterias rubens*, *Paracentrotus lividus*, *Maja squinado*, *Sepia filliouxii*, and *Helix pomatia* indicate that (I) forms an important store available for the formation of reproductive cells.

NUTR. ABS. (m)

Occurrence of citric acid in urine and body-fluids. W. M. BOOTHBY and M. ADAMS (*Amer. J. Physiol.*, 1934, 107, 471—479).—Citric acid (I), which is widely distributed in the body-fluids, plays an important part in the intermediary metabolism, but is not necessarily derived from ingested (I) or carbohydrates. Urinary (I) is increased by administration of a physiologically strong base and decreased by that of a strong acid.

NUTR. ABS. (m)

Urinary excretion of citric acid. I. Effect of ingestion of large amounts of orange juice and grape juice. II. Effect of ingestion of citric acid, sodium citrate, and sodium hydrogen carbonate. C. SCHUCK (*J. Nutrition*, 1934, 7, 679—689, 691—700).—I. Addition of 1 litre of juice to a basal diet for women resulted in an increased p_H and decreased titratable acidity in the urine. The increase in citric acid (I) excretion produced by orange juice was slightly > that from grape juice (II), but the ratio of amount excreted to amount ingested was much higher in the case of (II). Indications of a metabolic source of (I) are recorded.

II. Urinary p_H was not appreciably affected by ingestion of (I), but was raised considerably by citrate (III). The titratable acidity was decreased slightly by (I) and considerably by (III). Total org. acid excretion was decreased by (I) and increased by (III). The amount of (I) excreted varied irregularly after ingestion of (I), but increased considerably after ingestion of (III). Feeding of NaHCO₃ caused a small increase in total org. acids and a considerable increase in the (I) excreted. A. G. P.

Blood-sugar curve after administration of fat. G. PAASCH and H. SCHONFELD (*Monatsschr. Kinderheilk.*, 1934, 59, 181—182).—Oral administration of 50 g. of olive oil to children suffering from various complaints, including diabetes, had no effect on blood-sugar.

NUTR. ABS. (o)

Nutritive value of food fats and oils. II. and sunflower oil. A. PICKAT, N. ZENIN, O. KUR-SINA, and P. ALEXIEVA (*Problems of Nutrition*, U.S.S.R., 1934, 3, No. 1, 107).—Compared with butter, sunflower oil (I) has high, and suet very low, nutritive val. when fed to young rats as 30% of the caloric val. of the ration. The high biological val. of (I)

attributed to its content of highly unsaturated fatty acids. When groups of rats which have received the three rations are subsequently starved, the (I) group survives longest. NUTR. ABS. (m)

Effect of the saturated fatty acid content of the diet on the composition of body-fat. A. D. BARBOUR (J. Biol. Chem., 1934, 106, 281—288).—The saturated (I) and unsaturated acid (II) content of the body-fat (III) of albino rats α the (I) and (II) content, respectively, of the fat fed (20% of diet), but the (I) content of (III) never exceeds 25—27%, any excess being excreted. Excretion of arachidic acid (of pea-nut oil) is nearly quant. R. S. C.

Changes of total lipin and iodine number of blood-fat in alimentary lipæmia. W. R. WILSON and J. P. HANNER (J. Biol. Chem., 1934, 106, 323—330).—Alimentary lipæmia is induced by feeding cream (I) (I val. 30—40) or cod-liver oil (II) (I val. 165) by mouth. The I val. of the increment was 39—60 for (I) and 118—135 for (II). The blood-fat is composed of the same fatty acids as those in the fat ingested. C. G. A.

Relation of depôt-fat to egg-yolk in laying hens. H. J. ALMQUIST, F. W. LORENZ, and B. R. BURMESTER (J. Biol. Chem., 1934, 106, 365—371).—Depot- and yolk-fats of hens fed on malvaceous plants exhibit the Halphen test. Depôt-fat is not utilised in the formation of yolk-fat. H. G. R.

Synthesis of fat in the mammary gland. D. M. MICHLIN and Z. N. ZAPRUDSKAJA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 573—576).—The negative results of previous workers on the *in-vitro* synthesis (I) of fats by mammary gland preps. (II) are due to incomplete knowledge of the activators and inhibitors involved and to unsuitable conditions (*e.g.*, dilution). With COM₆-dried (II), (I) is increased by 50—60% by activators such as CaCl₂ or bile. F. O. H.

Fat and calcium metabolism. Influence of tripalmitin and triolein on the faecal output of Ca in full-grown rats. A. WESTERLUND (Lantbr.-Hogsk. Ann., 1934, 1).—With animals on low or moderate Ca diets, receiving tripalmitin (I) and triolein (II) together in inversely varying amounts totalling up to 1.2 g. daily, (I), but not (II), adversely affects Ca metabolism by raising the faecal Ca output and may even bring the animals into negative Ca balance. NUTR. ABS. (b)

Biology of the meal-worm. III. Fat changes during metamorphosis. M. BECKER (Biochem. Z., 1934, 272, 227—234).—Analysis of the fat of *Tenebrio larvæ* shows that whereas the reserve fat gradually disappears, the organ fat is not utilised. P C

Changes in total nitrogen content during the life of the imago of the worker honey-bee. M. H. HAYDAK (J. Agric. Res., 1934, 49, 21—28).—The most rapid increase in the N content of various parts of the insect occurred during the first 5 days after emergence, changes being greatest in heads and least in thoraxes. The N in the alimentary tract corresponded closely with the amount of pollen in the rectum, reaching a max. val. after 8 days and subsequently declining. A. G. P.

4 E

Distribution of urinary components of nitrogen metabolism. VI. Starvation. G. BOY (Bull. Soc. Chim. biol., 1934, 16, 1009—1106).—In the rabbit, rat, dog, and pig, starvation (I), succeeding a period of carbohydrate dieting, causes in the total N excretion an immediate increase, lasting almost until death, which varies inversely with the size of the animal. The increase appears rapidly in the rabbit, reaching a val. six times the original, and slowly in the pig, where the val. is at most doubled. The vals. for the rat and the dog are intermediate, but nearer those of the pig. This increase takes place mainly in urea-, NH₃-, and NH₂-N; purine-N is present in small amount, creatinine is absent, creatine present. The increase in the coeffs. of protein and purine oxidation, particularly the former, from the beginning of (I) is marked, but whilst the excretion of NH₃-N (II) always increases, the ratio (II)/(I) urea-+NH₂-N is lowered in the case of the rabbit, and much increased in the case of the pig. A. L.

Proteolysis in regenerating tissues. Autolysis of normal and regenerating tissues. N. V. BROMLEY and V. N. ORECHOVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 44—50).—After section of the tail of *Pelobates fuscus* tadpoles, the non-protein-N contents of the regenerated tissue and of the stump are 74 and 77 mg. per 100 g. (normal 94 mg.). The corresponding vals. after 4 hr. of autolysis at *p*_H 6.4 are 61, 90, and 128, and after 12 hr. 170, 310, and 184. R. T.

Specific dynamic action of proteins in the rabbit. (a) Peptone. (b) Amino-acids; glycine, α -, -alanine. E. LE BRETON and G. SCHAEFFER (Compt. rend. Soc. Biol., 1934, 115, 854—857, 858—860).—Widely varying results were found for the sp. dynamic action (I) of proteins, the val. at times being zero. The view that (I) conforms to a thermochemical law valid for all species and all doses of protein is therefore rejected. NUTR. ABS. (b)

Oxidation of proline and alanine by certain tissues. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1934, 106, 79—86).—Proline (I) and alanine (II) are oxidised at different rates by broken cell suspensions of the liver and kidney of various animals. 0.05M-NaF accelerates and increases the O₂ uptake, except in the case of mouse-, rat-, and pigeon-liver and -kidney. This is partly a salt effect, and in many cases may be brought about by NaCl and KCl. Oxidation of (II) is accompanied by deamination, whereas that of (I) is not, except with guinea-pig-kidney and rat-liver. (I) and (II) act as catalysts of the reduction of methylene-blue by tissues. H. G. R.

Metabolism of amino-acids. VI. Rate of absorption of leucine, valine, and their isomerides from the gastro-intestinal tract of the white rat. B. W. CHASE and H. B. LEWIS (J. Biol. Chem., 1934, 106, 315—321).—In 3-hr. periods the absorption coeffs. of the Na salts in milliequiv. per 100 g. per hr. are for valine, 0.40; leucine, 0.34; isoleucine and norleucine, 0.27; isovaline, 0.14. There is no difference between the rate of absorption of the naturally occurring

isomeride and the *dl*-form. No glycogen was formed in the liver following absorption. C. G. A.

Non-essential nature of tyrosine [as dietary factor]. R. S. ALCOCK (Biochem. J., 1934, 28, 1174—1177).—Rats fed on a diet containing hydrolysed caseinogen, free from tyrosine (I), grew as well as controls on diet containing (I). H. D.

Diet deficient in cystine and tissue-glutathione. A. MARENZI and B. BRAIER (Compt. rend. Soc. Biol., 1934, 115, 337—338).—The total glutathione content (I) of organs in the rat falls 24—36% on a diet low in cystine. The decrease is most marked in liver and kidney. Diet high in cystine does not appreciably increase (I). NUTR. ABS. (m)

Synthesis of purines in the mammalian organism. R. KAPPELLER-ADLER, E. LAUDA, and K. VON MEGAY (Biochem. Z., 1934, 272, 153—154; cf. this vol., 684).—The results obtained by Terroine *et al.* confirm the view that purines are synthesised, probably from the proteins of food, in the mammalian organism (pig, dog, rabbit). W. McC.

Utilisation of homogenised milk in man. K. VON STEJSKAL and C. NEUBURGER (Wien. med. Woch., 1934, 84, 317—319).—Homogenised milk is very well utilised, the amount of fat in the faeces being only about a third of that found with untreated milk. Fat absorption is promoted by the nature of the curd formation. Absorption of protein is also improved, but to a smaller extent. NUTR. ABS. (m)

Nutritive properties of protein, vitamin-*B*₁ and -*B*₂, and the germ in rye. D. W. JOHNSON and L. S. PALMER (J. Agric. Res., 1934, 49, 169—181).—The favourable effects on rats of additions of liver to a rye ration are not due to improved biological val. of the protein mixture. Lysine is the primary limiting NH_2 -acid of the rye protein. Unsatisfactory results of feeding rye to pigs are not attributable to the germ. Vitamin deficiency under customary feeding conditions is improbable. A. G. P.

Nutritive value of green immature soya beans. C. D. MILLER and R. C. ROBBINS (J. Agric. Res., 1934, 49, 161—167).—Cooked immature soya beans contained considerably larger amounts of protein, fat, Ca, P, and Fe than do other vegetables. Vitamin-*A*, -*B*₁, and -*B*₂ are present in adequate proportions, but -*C* is deficient. A. G. P.

Physiological effects of continued use of food-stuffs grown with and without artificial fertilisers. A. SCHEUNERT (Z. Pflanz. Düng., 1934, B, 13, 337—338).—Foodstuffs grown with heavy applications of fertilisers prolonged the life period of rats and improved reproductivity as compared with similar foods produced on unmanured soils. A. G. P.

Protein-free diet and the state of oxidation of the body. F. GRAPENTIN (Z. ges. exp. Med., 1933, 90, 750—757; Chem. Zentr., 1934, i, 73).—“Dysoxidative carbonuria” is observed in the rat. A. A. E.

Fundamental food requirements for growth of the rat. VII. Inheritance as a factor influencing food utilisation in the rat. H. P.

MORRIS, L. S. PALMER, and C. KENNEDY (Minnesota Agric. Exp. Sta. Tech. Bull., 1933, No. 92, 56 pp.).—In female rats, food consumption per unit live-wt. increase is > in males, and carcass analyses show higher dry matter, ash, and fat, and lower N and fat-free dry matter contents. The efficiency of food utilisation is probably influenced by inheritable factors. A. G. P.

Dietary depigmentation of young rats. F. J. GORTER (Nature, 1934, 134, 382). L. S. T.

Growth: statistical interpretation. H. C. SHERMAN and H. L. CAMPBELL (Proc. Nat. Acad. Sci., 1934, 20, 413—416).—The growth data obtained from both male and female rats fed on three different diets approximate to a symmetrical frequency distribution. P. G. M.

Ageing of the organism retarded by inhalation of negatively ionised air. TCHLJEVSKY and VON NARD (Compt. rend., 1934, 199, 496).—Systematic inhalation of negatively ionised air causes, in animals, more rapid growth, increased wt., more robust progeny, greater resistance to disease, and obviously delayed ageing. Gaseous exchange and metabolism are increased, whereas positively-charged air produces the reverse effect. H. W.

Acid-base equilibrium of inhabitants of the tropics. IV. W. RADSMA, G. M. STREEF, and J. V. KLERKS (Arch. Neerland. Physiol., 1934, 19, 372—383).—On a rice diet $[\text{H}^+]$, NH_3 , and the acidity were increased, whereas the excretion of $\text{PO}_4^{'''}$ and fixed bases was less; the morning alkaliuria, which is observed with European diets, is absent. H. G. R.

Sodium chloride requirement and its relationship to mineral metabolism. II, III. H. GLATZEL (Z. ges. exp. Med., 1934, 92, 653—666; 93, 179—194).—II. High K and low Na intake leads to excessive output of Na with retention of K. A diet of rice with a K : N ratio just > 1 does not cause undue loss of Na or Cl, so that addition of NaCl to the diet is unnecessary. Diets (such as potatoes) with a high K : Na ratio and high K content, which cause excessive excretion of Na and Cl, require the addition of NaCl to make good the loss and to facilitate excretion of the retained K. Flesh foods require NaCl only if the blood, which contains more Na than K, is removed. The effect of the diet on the reaction of the urine has no influence on the NaCl requirements. Bunge's hypothesis is therefore confirmed.

III. With rice diet (low K) the urinary output of K is the same as the intake; addition of NaCl increases the output of K. With other diets (higher K) addition of NaCl increases K retention, although the urinary output may also be increased. In a cases retention of Na and Cl, originally negative, becomes markedly positive. When K intake is sufficiently great, addition of NaCl to the diet does not prevent K retention. K retention cannot be explained by renal inefficiency. Changes in excretion of substances other than K, Na, and Cl are not const. The principal effect of NaCl is to act as a buffer by the excretion of more Na or Cl as circumstances demand. NUTR. ABS. (m)

Effect of a low-calcium ration on reproduction in cattle. C. P. FITCH, W. L. BOYD, C. H. ECKLES, T. W. GULLICKSON, L. S. PALMER, and C. KENNEDY (Cornell Vet., 1932, 22, 156—172).—The ration-Ca (I) had no appreciable effect on blood-plasma-Ca; no changes in milk or fat production could be attributed to (I). CH. ABS.

Absorption of calcium. A. R. BLISS, jun., E. O. PRATHER, jun., and R. W. MORRISON (J. Amer. Pharm. Assoc., 1934, 23, 656—662).—When administered to mice by stomach-tube in aq. solution containing equiv. amounts of Ca (0.3 mg. per g. of body-wt.) the efficacy of the salts in preventing narcosis by MgSO_4 is in the order lactate, gluconate, CaCl_2 , inositol Ca_6 gluconate, $\text{Ca}_3(\text{PO}_4)_2$, glycerophosphate, indicating the relative ease of absorption. C. G. A.

Changes in blood-calcium and -phosphorus partition during the life cycle of the chicken. V. G. HELLER, H. PAUL, and R. B. THOMPSON (J. Biol. Chem., 1934, 106, 357—364).—The total P and total Ca rise during egg production and fall on moulting, the rises being due to lipin-P (I), adsorbable non-filterable Ca (II), and protein-Ca; inorg. and acid-sol. P remain approx. const., whilst adsorbable filterable Ca (III) falls slightly during the production period. In osteoporotic chickens (III) is > in normal, plasma-(I) and -(II) being lower. C. G. A.

Influence of calcium and phosphorus intake on bovine blood. J. E. GREAVES, E. J. MAYNARD, and W. REEDER (J. Agric. Res., 1934, 48, 1033—1041).—Use of cottonseed cake, steamed bone flour, or bran as P supplements increased the inorg. P (I) of blood (II) to varying extents, but had no appreciable effect on the (II)-Ca. A close relationship between the P intake and (I) of (II) is demonstrated. A. G. P.

Normal development of the leg bones of chickens with respect to their ash content. H. M. HARSHAW, J. C. FRITZ, and H. W. TITUS (J. Agric. Res., 1934, 48, 997—1008).—Serum-Ca of pullets increased considerably just before the laying period, but otherwise no definite changes were apparent with increasing age. Calcification of the epiphyses of bones of females began earlier than in those of males. Variations due to difference of breed were also apparent. The Ca:P ratio in the ash of tibiae was low immediately after hatching, but subsequently increased, in all cases, to approx. 2.0:1. C.

Chemical structure of the bone salts of healthy and rachitic animals. J. MAREK, O. WELLMANN, and L. URBANYI (Z. physiol. Chem., 1934, 226, 3—17).—The inorg. constituents of the bones of pigs on different diets vary widely with the mineral composition of the diet. The outer layers of the tubular bones contain the least ash. P increases towards the interior, whilst Ca, Mg, and CO_2 are highest in the middle zone. The Ca not bound by PO_4^{3-} is present as CaCO_3 . The main inorg. constituent is $\text{Ca}_3(\text{PO}_4)_2$. Contrary to the views of Gassmann (A., 1930, 1609) and Klement (A., 1929, 1328), the $\text{Ca}_3(\text{PO}_4)_2$ and CaCO_3 are present solely as a mixture and not as a complex. J. H. B.

Role of copper in carbohydrate metabolism. H. L. KELL and V. E. NELSON (J. Biol. Chem., 1934, 106, 343—349).—Oral administration of Cu to anæmic rats lowers the max. of the glucose (I)-tolerance curves, the hæmoglobin val. remaining unaltered. Fe alone does not improve (I) utilisation. An increase in hæmoglobin (administration of Fe+Cu) produces a proportional increase in (I) tolerance together with lower fasting blood-(I) level. Fasting blood-(I) in anæmic is > in normal rats. C. G. A.

Zinc in the nutrition of the rat. W. R. TODD, C. A. ELVEHJEM, and E. B. HART (Amer. J. Physiol., 1934, 107, 146—156).—Rats fed from weaning on a synthetic ration containing only 1.6 mg. of Zn per kg., but supplied with all the essential vitamins, show a lower growth rate than rats on the same ration to which 5.0 mg. of Zn (as ZnO or ZnCl_2) have been added per 100 g. of ration. Rats on low-Zn ration lose hair. NUTR. ABS. (m)

Distribution of zinc in the animal organism. A. KOGA (Keijo J. Med., 1934, 5, 97—105).—The Zn content (I) of various tissues of the ox, dog, goose, tortoise, toad, fish (*Ophicephalus argus*, Cantor), and oyster is given. For nearly all the species examined, (I) is highest in the liver and pancreas and lowest in the lungs, brain, and testes; in the muscles and blood, (I) varies considerably with different animals. Dried oyster has a high (I) of 0.041%. F. O. H.

Effect of varying levels of iodine intake on the thyroglobulin content of the thyroid gland. M. E. JONES (Amer. J. Physiol., 1934, 107, 513—517).—I as KI fed to dogs produced an increase of 147—249% in thyroid-I, 94—99% of which was precipitable by 95% EtOH, and therefore presumed to be in the form of thyroglobulin. KI in doses of 0.02 g. per kg. of body-wt. given daily for 4 weeks produced as great a storage of I as did doses of 0.1 g. per kg. daily for 6 weeks. NUTR. ABS. (b)

Somatic and biochemical changes in chronic alcoholics. III. Protein metabolism. B. F. GOJCHER, E. G. TSCHERNYSHEVA, and KRASNOVSKAJA (Acta Med. Scand., 1934, 81, 1—13).—In chronic alcoholics the total N of the urine is increased, but the NH_2 -acid and NH_3 excretion is normal. Urinary excretion of these substances after administration of 20 g. of peptone is subnormal. Retention of H_2O occurs. NUTR. ABS. (m)

Fixation of toxic substances by endocrine glands. I. Chloroform. II. Barbiturates. R. FABRE (J. Pharm. Chim., 1934, [viii], 20, 97—101, 101—103).—I. The amount of CHCl_3 fixed by the endocrine glands during anaesthesia of dogs runs parallel with their lipin content, being highest for the suprarenal cortex (I). The disappearance of CHCl_3 from (I) is much slower than from the blood, approx. 30% remaining after 24 hr.

II. Veronal is taken up by the adrenals and thyroid to a greater extent than by blood, brain, and liver. C. G. A.

Detoxicating properties of sodium thiosulphate in "avertin" intoxication. A. BOLLIGER (Med. J. Austral., 1932, 125—140).—Clinical data are

recorded. $\text{Na}_2\text{S}_2\text{O}_3$ is retained in the body longer than phenolsulphonaphthalein. CH. ABS.

Local anæsthetic of the phenoxyaminoalcohol group. E. HESSE and O. SWOBODA (Arch. exp. Path. Pharm., 1934, **175**, 509—517).—2-*n*-Butoxy-5-*iso*-propylphenyl γ -diethylamino- β -hydroxypropyl ether has a toxicity (partly or wholly inhibited by artificial respiration or pernocton narcosis) to rabbits approx. 2.5 times that of cocaine, but 25—30 times the local anæsthetic action; as a lumbar anæsthetic it equals pantocaine. F. O. H.

Analogy between histamine- and anaphylactic shock. I—IV. A. DZSINICH and M. PELY (Arch. exp. Path. Pharm., 1934, **175**, 359—371).—During the reactions (I) following injection of histamine (II) into man, the coagulation time of the blood is markedly increased, being almost doubled at the height of (I). The blistering and erythema due to intradermal injection of (II) are greatly diminished by prior administration of cholesterol (III). During (I) the blood-(III) rises (in some cases to supersaturation), whilst the (III)-saturation val. of the blood falls. Oral administration of (III) for 12 days markedly reduces the (I) due to (II), whilst the characteristic changes in the blood-(III) (actual and saturation vals.) and the rate of blood-coagulation are unchanged. The above phenomena afford evidence for the analogy between (II)- and anaphylactic shock. F. O. H.

Chemistry and pharmacology of fermented foodstuffs. I. W. KEIL and H. KRITTER (Arch. exp. Path. Pharm., 1934, **175**, 736—744).—From sauerkraut juice were isolated histamine (I) (up to 0.02%), acetylcholine, and putrescine, constituents which produce the stimulation (partly inhibited by atropine) of the isolated guinea-pig's uterus. Colour reactions and pharmacological tests indicate the presence of (I) in wine-vinegar, but only betaine could be isolated. Curdled milk contains choline, but neither choline esters nor (I). The regeneration of reineckates by means of AgOAc is described. F. O. H.

Penetration of gaseous pyridine, piperidine, and nicotine into the bodies of certain insects. C. H. RICHARDSON, L. H. GLOVER, and L. O. ELLISOR (Science, 1934, **80**, 76—77).—The gaseous bases pass directly through the cuticula of cockroaches, corn-ear worm larvæ, and grasshoppers. L. S. T.

Elimination of morphine and quinine in human milk. W. G. TERWILLIGER and R. A. HATCHER (Surg. Gynecol. Obstet., 1934, **58**, 823—826).—Although a child born to a morphine (I) addict exhibited signs of (I) addiction, (I) could not be detected in the milk. Traces of quinine can be detected after administration, but the amounts are too small to affect the nursing infant. CH. ABS.

Pharmacology of narcotine. N. COOPER and R. A. HATCHER (J. Pharm. Exp. Ther., 1934, **51**, 411—420).—Narcotine (I) intravenously administered to cats disappears from the blood-stream and becomes fixed in the lungs, liver, and kidneys, whilst only traces are eliminated in the urine following intramuscular injection of large doses. There is no

evidence that (I) exerts an effect on the action of equal doses of morphine. W. O. K.

(a) [Physiological action of] hydrastine, bicuculline, and adlumine. (b) Bicucine. A. D. WELCH and V. E. HENDERSON (J. Pharm. Exp. Ther., 1934, **51**, 482—491, 492—494).—(a) Hydrastine (I) and bicuculline (II) (cf. A., 1933, 617) are similar in their pharmacological action except that (II) is about 100 times as active a convulsant as (I), whilst the convulsant action of adlumine (cf. A., 1933, 841) is relatively weak and differs quantitatively from that of (I) and (II).

(b) The convulsant activity of bicucine (A., 1933, 841) is < that of (II) and is comparable with that of (I). W. O. K.

Diffusible and non-diffusible calcium in blood and cerebrospinal fluid of cats intoxicated with bulbocapnine and of human beings under bromide treatment. S. KATZENELBOGEN (J. Pharm. Exp. Ther., 1934, **51**, 435—439).—In normal cats and in man with low blood-Br', the Ca content of the cerebrospinal fluid (I) is approx. equal to the diffusible Ca content of the serum, but in cats, intoxicated with bulbocapnine, in which the (I)-Ca content remains approx. const., the diffusible Ca of the blood shows a marked fall. A similar result is obtained in man with high blood-Br'. W. O. K.

Comparative actions of sympathomimetic compounds. Bronchodilator actions in perfused guinea-pig lungs. M. L. TAINTER, J. R. PEDDEN, and M. JAMES (J. Pharm. Exp. Ther., 1934, **51**, 371—386).—Of various derivatives of phenylethylamine, the most active bronchodilator in perfused isolated guinea-pig's lungs was adrenaline, whilst the next three in order of activity were also pyrocatechol derivatives. A single nuclear OH-group likewise conduces to activity. There was no consistent relationship between vasopressor and bronchodilator activity, probably because of the variety of mechanisms involved. W. O. K.

Action of diuretic drugs. I. In normal persons. H. L. BLUMGART, D. R. GILLIGAN, R. C. LEVY, M. G. BROWN, and M. C. VOLK (Arch. Int. Med., 1934, **54**, 40—81).—There was an increased excretion of H_2O , Na, Cl', K, and Ca, due to a loss of extracellular body fluids, but no change in PO_4''' , SO_4 , NH_3 , or total N. On the cessation of diuresis a compensatory retention immediately set in. There was no change in sp. gr., Na, or Cl' of the blood-serum or in the rate of glomerular filtration, but the tubular reabsorption decreased in proportion to the diuretic effect. H. G. R.

New type of fever agent. H. G. BARBOUR (Science, 1934, **80**, 144—146).—*p*-Nitrophenylethylamine rapidly raises the body temp. of guinea-pigs and rabbits. L. S. T.

Decrease in alkali reserve and movement of chlorine in the blood during hyperthermy caused by short waves. L. BINET, M. LAUDAT, and J. AUCLAIR (Compt. rend., 1934, **199**, 442—444).—This hyperthermy decreases the alkali reserve and slightly increases the Cl in the blood-plasma of dogs. R. S. C.

Toxicity of lysolecithin. M. IWATA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 174—192).—The oral administration of an EtOH extract of rice polishings to pigeons or rats on polished rice diets often caused vomiting and the excretion of greenish faeces. This toxic effect, which is due to the lysolecithin (I) in the EtOH extract and is intensified by intravenous or intramuscular injection of (I), can be counteracted by the addition of 3% of brewer's yeast to the diet, i.e. by a sufficient quantity of vitamin-B₁.

P. G. M.

Physiologically active phosphatide. L. UTKIN and R. TOPSTEIN (Biochem. Z., 1934, 272, 36—41).—Hydrolysis of the phosphatide fraction of the lipins of adrenal glands or egg-yolk with HCl in MeOH results in separation of a phosphatide (I) which has a physiological action similar to that of choline. (I) is not choline, but may be the precursor of the substance obtained by Mafori *et al.* (this vol., 700).

W. McC.

Weight and chemical composition of the heart under normal and pathological conditions. E. BONG, P. JUNKERSDORF, and H. STEINBORN (Z. ges. exp. Med., 1934, 92, 573—597).—Injection of phloridzin into dogs causes no reduction of heart-glycogen (I) and may cause increase, whilst glycogenogenesis from fat occurs. Adrenaline (II) acts similarly, apparently having a sp. action favouring change of fat to carbohydrate (III). In the fasting dog injection of choline results in high glycogen and low fat vals. Thyroxine causes a reduction in (I) which is < that in liver-glycogen and does not occur in young dogs. Administration of insulin to dogs on high-(III) diet causes increase in (I), but if prolonged causes reduction of glycogen and increase of fat. Administration of guanidine or synthalin causes slight reduction of glycogen in well-nourished dogs, but increase in dogs with previous inanition because of increased secretion of (II). In depancreatised dogs there is a fall in the fat content and an increase in (I).

NUTR. ABS. (m)

Physiological action of vicioside. H. HERISSEY and J. CHEYMOL (Bull. Soc. Chim. biol., 1934, 16, 1176—1181).—Vicioside injected intravenously into mice and dogs has no toxic action, and is excreted unchanged.

A. L.

Pharmacology of Digitalis. H. WEESE (Arch. exp. Path. Pharm., 1934, 175, 754—758).—The min. lethal dose for cats of digitoxin (I) injected intra-arterially is 0.309 and, intravenously, 0.210 mg. per kg. Following injection of (I), only traces are detectable in the blood (cf. Haferkorn and Lendle, this vol., 804). The mechanism and site of (I)-fixation in the organism are discussed. F. O. H.

Accumulation and elimination of Digitalis alkaloids in poikilotherms. L. LENDLE (Arch. exp. Path. Pharm., 1934, 175, 719—726).—Frogs can daily eliminate 50—70% of the lethal dose (I) of digitoxin (II), the elimination coeff. being therefore approx. 0.083 mg. per kg. per hr. Thus detoxication is about 80 times as rapid as in warm-blooded animals. Injection of 0.003 mg. of (II) per g. is followed by excretion of 40—50% (mainly as glucoside) during the first 24 hr. and only of traces during the second 24

hr. This rapid excretion explains the low sensitivity, comparison of the (I) for the intact frog with that for the isolated heart indicating that only 3% of the administered alkaloid acts on the heart. F. O. H.

Effect of strophanthin on gaseous metabolism during cardiac insufficiency. A. RUHL and A. WIEHLER (Arch. exp. Path. Pharm., 1934, 175, 665—680).—With cardiac insufficiency (spontaneous or by histamine- or barbituric acid-damage) in heart-lung preps., strophanthin (I) increases the heart performance and decreases coronary circulation, whilst sub-normal O₂ consumption is increased and R.Q. decreased (this vol., 214), changes probably due to increased capillary diffusion of O₂ by (I). Respiration in O₂ does not remove the existing lack of O₂ owing to the relatively lower increase of arterial tension.

F. O. H.

Determination of benzene in toxicology. I. Colorimetric determination of *m*-dinitrobenzene. M. PERONNET (J. Pharm. Chim., 1934, [viii], 20, 145—149).—The optimum conditions for the colour reaction with fructose have been determined. E. H. S.

Evaluation of light-protecting materials. F. ELLINGER (Arch. exp. Path. Pharm., 1934, 175, 481—488).—Various physical and biological methods are discussed. An approx. evaluation is obtained by comparison of the degree of erythema produced by ultra-violet irradiation of the bare and protected human arm, the agent being used as an ointment or dissolved in EtOH or aq. glycerol media. F. O. H.

Laxative effect of a regenerated cellulose in the diet. Its influence on mineral retention. H. MORGAN (J. Amer. Med. Assoc., 1934, 102, 995—997).—In healthy persons receiving 20 g. of cellulose (free from N, P, and Ca) in the diet the faecal dry wt. increases 69%, whilst the H₂O content alters only slightly. The N, P, and Ca contents of the faeces increase 4.3, 6.6, and 12.9%, respectively.

NUTR. ABS. (m)

Changes in the acid-base equilibrium during progressive asphyxiation. D. CORDIER (Ann. physiol. physicochim. biol., 1934, 10, 301—330).—In dogs under chloralose anaesthesia, asphyxiation due to O₂ deficiency causes a progressive decrease in the blood-CO₂ (I), an initial rise and then a fall in *p_H*, and a progressive increase in lactic acid (II). In asphyxiation due to confinement, an initial increase in (I) is followed by a decrease, *p_H* falls, and (II) decreases and then increases. CH. ABS.

Action of calcium-precipitating acids and salts on serum-calcium and its forms (calcium quotient). S. HERMANN and M. ZENTNER (Arch. exp. Path. Pharm., 1934, 175, 500—508).—Oral or subcutaneous administration of toxic but non-lethal doses of Na₂C₂O₄ or H₂C₂O₄ increases the free Ca (I) (i.e., Ca not pptd. with the blood-proteins), whilst lethal doses decrease both (I) and the total Ca (II). Citric, tartaric, and phosphoric acids and their salts increase (II) and, to a greater extent, (I). CaCl₂ increases both (I) and (II), the Ca quotient (A., 1932, 81; 1933, 1182) being unchanged, whilst prior or subsequent subcutaneous or intravenous injection does not influence the effect of Na₂C₂O₄. F. O. H.

Decrease of the magnesium content of blood-serum *in vivo* by intravenous injection of substances which precipitate magnesium. L. SEEKLES and B. SJOLLEMA (Biochem. Z., 1934, 272, 222—226).—By intravenous injection of an $\text{NH}_3\text{--Na}_2\text{HPO}_4$ mixture into young calves, the serum-Mg can be reduced by 29% of its initial val., but there is no proportionality between the amount of decrease and of reagent injected. Usually the Ca content is also decreased. Intravenous injection of 8-hydroxyquinoline decreases the Mg content only occasionally.

P. W. C.

Behaviour of thiocyanate and sulphate in the organism on different diets. W. VON MORACZEWSKI and R. ŚLIWIŃSKI (Biochem. Z., 1934, 272, 269—276).—CNS' and SO_4^{--} injected subcutaneously or given by mouth to rabbit and man are excreted more rapidly the more alkaline is the urine, the effects being emphasised by acidification after administration of NH_4Cl or alkalinisation after NaHCO_3 . SO_4^{--} causes diuresis and is excreted more quickly than CNS', which causes H_2O retention.

P. W. C.

Physiological effect of trihydrol in liquid water. A. W. C. MENZIES (Science, 1934, 80, 72—73).—A discussion (cf. this vol., 806).

L. S. T.

Application of filtered ultra-violet rays in investigation of poisoning cases. F. W. MARTIN (Analyst, 1934, 59, 531—532; cf. A., 1926, 701; 1927, 1101).—The only fluorescent inorg. substance of medico-legal importance is HgCl_2 , which gives a brilliant salmon-pink luminescence.

E. C. S.

Enzymes, vitamins, and the zone of maximum colloidal. J. ALEXANDER (Science, 1934, 80, 79—80).—A discussion.

L. S. T.

Isolation of crystalline yellow respiratory enzyme: reversible hydrolysis of the enzyme. H. THEORELL (Biochem. Z., 1934, 272, 155—156).—Material (20—30 g. containing 4—5 mg. of the pigment) treated with CHCl_3 by the method of Warburg and Christian is freed from almost all polysaccharide and part of the contaminating protein by cataphoresis at p_H 4.2—4.5. Fractional pptn. with $(\text{NH}_4)_2\text{SO}_4$ at p_H 5.2 followed by dialysis against saturated aq. $(\text{NH}_4)_2\text{SO}_4$ (2 vols.) + acetate buffer (p_H 5.2, 1 vol.) gives cryst. enzyme (N 15.5%, $[\alpha]_{-30^\circ}$) in 60% yield. Hydrolysis into the two inactive components, pigment and protein, occurs when solutions of the enzyme are dialysed against dil. HCl. Activity and yellow colour are restored when cold, electrolyte-free solutions of the components are mixed.

W. McC.

Activation by co-enzyme of the alcoholdehydrogenase of yeast. J. LEHMANN (Biochem. Z., 1934, 272, 95—103; cf. Muller, this vol., 448).—Purified solutions of the dehydrogenase (I) are obtained from yeast by extraction with aq. Na_2HPO_4 . (I) is inactive until treated with co-enzyme (II) (adenosinetriphosphoric acid). The dehydrogenase of glycerophosphoric acid is activated by (II). Yeast cells contain a very active (I) which is activated by (II). O_2 cannot serve as H acceptor in the dehydrogenation of EtOH.

W. McC.

Purine metabolism enzymes of the mammary gland and of milk. D. MICHLIN and A. RYŻOWA (Fermentforsch., 1934, 14, 389—394).—Xanthine-oxidase (I) is much more loosely combined with glandular tissue than are other purine metabolism enzymes, and is therefore the only enzyme of this group found in milk. During incubation of minced mammary gland, considerable formation and later destruction of uric acid occur, enzymes of both nucleic and purine metabolism being present. (I) passes into solution in the cold and at the beginning of extraction, whereas guanase and adenase are set free much later at the beginning of autolysis.

P. W. C.

Peroxidase reaction. XLIV. Short-timed peroxidase reaction of blood-leucocytes; prolongation of reaction in avitaminosis-B. T. SUZUKI. XLV. Arakawa's reaction of human milk from the toxicological point of view. A. TAKAMATSU. XLVI. Arakawa reaction and chlorine content of human milk. J. NOAZKI (Tôhoku J. Exp. Med., 1934, 23, 23—45, 46—59, 69—69).

CH. ABS.

Irreversible inhibition of catalase. M. G. SEVAG and L. MAIWEG (Naturwiss., 1934, 22, 561—562).—Catalase action is reversibly inhibited by the presence of diacetyl-di-, and -mon-oxime, phenylglyoxime, acetoxime, and acetaldoxime in buffered solution if the oximes are dissolved in dil. HCl and neutralised with NaOH. The oximes are ineffective if not treated in this way.

H. D.

Carboxylase. F. AXMACHER and H. BERGSTERMANN (Biochem. Z., 1934, 272, 259—268).—A method for the prep. of carboxylase in powder form is described. Extraction with 0.1N-HCl or -NaOH does not give more active solutions than does extraction with NaCl. The activity of the dry prep. is powerfully inhibited by I, SbCl_3 , NaNO_2 , CH_3O , and to a smaller extent by CuCl_2 , FeCl_3 , Br, and BiCl_3 .

P. W. C.

Amylase from sweet potato (*Ipomoea Batatas*). K. V. GIRI (J. Indian Chem. Soc., 1934, 11, 339—350).—The amylase (mostly β -) is pptd. by EtOH from aq. extracts of sun-dried sweet potatoes (I) and can be further purified by dialysis. It is contained mostly in the inmost parts of (I). The optimum p_H and temp. are 5.5—6.0 and 50—55°. Inactivation by heat (rapid at 55°) is unimol. and min. at p_H 5.4—6.0.

R. S. C.

Digestibility of some varieties of starch by pancreas-amylase of the dog and the pig. J. ROOS and C. ROMIJN (Arch. Néerland. Physiol., 1934, 19, 392—402).—There is no digestion of raw starch. After boiling, potato starch is digested most quickly and then follow rice, wheat, sol., and commercial starch, all varieties being hydrolysed to the extent of 50—55%.

H. G. R.

Pancreatic, salivary, and *Aspergillus*-amylase as mixtures of two enzymes. G. GIESBERGER (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 336—342).—Breakdown of sol. starch by salivary amylase (I) and by taka-diastase (II) considerably exceeds the limit of 36—40% found for malt α -amyl-

ase. Diffusion experiments in gelatin indicate the existence of two forms of amylase in (I), (II), and pancreatic amylase. L. D. G.

Invertase. I. Purification by precipitation. N. TAKETOMI (J. Soc. Chem. Ind. Japan, 1934, 37, 361—362B).—EtOH, MeOH, and COMe₂ may be used to ppt. crude koji-invertase (I), but have an injurious effect on the activity of the purified material. Impurities may be removed by adding 1.2% Pb(OAc)₂. With (NH₄)₂SO₄ (I) is only partly pptd. A. L.

Invertase concentration of germinating rye with potassium or phosphate deficiency. I. G. VON DOBY and A. BODNAR. II. G. VON DOBY and J. MAKFALVI (Fermentforsch., 1934, 14, 250—255, 256—265).—I. The p_H optimum of the invertase (I) of rye shoots receiving either complete or K- or PO₄'''-deficient nutrition is always 4.6, but whereas the concn. of (I) is 1.5—3.5 times as great with K-deficient as with complete nutrition, it is little affected by PO₄''' deficiency. The concn. of (I) decreases with the age of the plants. The amount of (I) increases during autolysis at 38° and p_H 4.6 with shoots receiving complete, but not with shoots receiving K-deficient, nutrition.

II. The concn. of (I) is proportional or asymptotic to the amount of N of nutrition, different sources of N giving the same result; the p_H optimum is in all cases 4.5 and the temp. optimum 38°. The concn. of (I) decreases at night and with age. P. W. C.

Intermediate processes in the degradation of carbohydrates (lactic acid formation and alcoholic fermentation). O. MEYERHOF (Ann. Inst. Pasteur, 1934, 53, 221—242).—A lecture. P. G. M.

Glyoxalase. II. Distribution in tissues of normal and cancerous albino rats. M. E. PLATT and E. F. SCHROEDER (J. Biol. Chem., 1934, 106, 179—190; cf. this vol., 449).—The kinetic behaviour of glyoxalase (I) in aq. extracts of animal tissues (except the kidney and pancreas, which contain inhibitors) is identical with that in COMe₂-yeast suspension. The (I) content in aq. extracts of organs of normal and cancerous rats and mice is determined; no relation exists between this and glycolytic activity. R. S. C.

Hydrolysis of hardened oil by pancreatic lipase. F. TORTE (Biochem. Z., 1934, 272, 308—316).—The greater is the degree of hardening of whale (I) and soya-bean (II) oil, the less is the velocity (III) of hydrolysis by pancreatic lipase. The difference in (III) for two oils of different degree of hardening decreases with rising temp. Experiments with tripalmitin, tristearin, and a mixture of triolein and tristearin show that (III) is not determined directly by the I val. and only indirectly by its effect on the m.p. Samples of (I) and (II) of the same m.p. had approx. the same (III). I. W. C.

Enzyme action in *Merlangus vulgaris* and *Scyllium canicula*. M. VAN HAUWAERT (Natuurwetensch. Tijds., 1934, 16, 227—232).—The action of aq. glycerol extracts of macerated portions of the digestive organs of *M. vulgaris* (I) and *S. canicula* (II) on fibrin at varying p_H vals. was examined. With

(I), the stomach extract is active at $p_H > 6.6$, pyloric extract in alkaline and faintly acid solution, and the intestine extract, to a less degree, at $p_H > 6.8$. In the case of (II), the stomach extract is extremely active at $p_H < 2$, the intestine is less active, whilst the pancreas is without effect. Starch is hydrolysed by the stomach, but not by the intestine, of (I); in the case of (II), the diastatic activity falls in the order liver, intestine, pancreas, stomach. H. F. G.

Dilatometric studies in the proteoclastic degradation of proteins. II. Peptic hydrolysis. M. SREENIVASAYA and H. B. SREERANGACHAR (Biochem. J., 1934, 28, 1219—1221).—For caseinogen there is no linear relationship between dilatometric depression and liberated NH₂-N (Van Slyke), but for gelatin an approx. proportionality holds. The average depression per millimol. of NH₂-N in both cases is $>$ for tryptic hydrolysis, pointing to a different mode of attack. C. G. A.

Antitrypsin of egg-white. A. K. BALLS and T. L. SWENSON (J. Biol. Chem., 1934, 106, 409—419).—The antitrypsin (I) has been conc. from thin egg-white and is insol. in org. solvents and sol. in H₂O. It is destroyed by H₂O₂ and NaOH, and may possibly be an -S-S'-containing peptide. The action of (I) is the same on active and inactive trypsin, but the progress of activation is retarded, and there is a disappearance of CO₂H already present in the digestion mixture. H. G. R.

Defence enzymes of the polypeptidase group. R. ABDERHALDEN (Fermentforsch., 1934, 14, 370—388).—Polypeptidase (I) of blood does not attack polypeptides (II) in which the free NH₂ is substituted. Plasma-(I) and erepsin react similarly in their behaviour to (II) and to benzoyl- and 2-naphthalenesulpho-polypeptide. After parenteral administration of these substituted (II), defence enzymes of the carboxy-(I) type appear in the blood. P. W. C.

Comparative investigation of the relative and absolute specific defence enzyme reactions using substrates from smooth and striated muscle. E. BRUNER (Fermentforsch., 1934, 14, 345—356).—The defence enzyme reactions of peptone and protein preps. from skeletal, heart, intestine, and uterus musculature of rabbit, dog, and ox are recorded. P. W. C.

Change of blood- and organ-proteins on ageing as shown by defence enzyme reactions. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 357—366).—Using protein preps. from serum, kidney, lung, liver, brain, and muscle of rabbit and of man of various ages, differences with age are detected by defence enzyme reactions in the fine structure of the protein. P. W. C.

Dependence of the composition of the proteins of blood-serum and -plasma on the diet. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 333—344).—By means of the defence enzyme reaction, individual differences in the fine structure of serum-protein and differences due to changes of nutrition can be detected. P. W. C.

Influence of ultra-violet light on serum-proteins as shown by defence-enzyme reactions. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1934, 14, 295—310).—Irradiation of the proteins of blood-plasma or -serum leads to their more ready disintegration, both in the body by the defence-enzyme system and *in vitro* by gastric juice.

P. W. C.

Technique of the interferometric method of [carrying out] the Abderhalden reaction. J. WADEL (Fermentforsch., 1934, 14, 266—282).—The sources of error in carrying out this reaction are discussed and a description of the prep. of the organ-protein substrate, of the technique of the reaction, and of taking readings is given.

P. W. C.

Critique of the interferometric method. P. HIRSCH (Fermentforsch., 1934, 14, 311—317).

P. W. C.

Arginase and arcaine. E. BALDWIN (Biochem. J., 1934, 28, 1155—1156).—Arcaine is not attacked by arginase from guinea-pig liver.

H. D.

Tyrosinase in *Macrolepidoptera*. C. E. M. PUGH (Biochem. J., 1934, 28, 1198—1200).—Tyrosinase (I) is present in all 29 species tested. Peroxidase was absent from all and a feeble laccase found in some species. The difference in marking of spring and summer broods of *Pieris rapae* and *P. brassicae* is not due to difference in (I) content.

C. G. A.

Influence of vitamin-C on the action of tyrosinase. E. ABDERHALDEN (Fermentforsch., 1934, 14, 367—369).—After addition of 0.01—0.001 g. of ascorbic acid (I) to a solution containing adrenaline (0.01 g. in 20 c.c. of H_2O) the latter was not oxidised to the red pigment, and the solution gave a green $FeCl_3$ colour and the usual biological tests for adrenaline. Tyrosine, 3:4-dihydroxyphenylalanine, and *dl*-adrenaline in presence of tyrosinase were all similarly stabilised by (I).

P. W. C.

Phosphoglycerase in red blood-corpuscles. A. E. BRAUNSTEIN (Biochem. Z., 1934, 272, 21—23; cf. A., 1933, 1202).—Haemolysed (but not intact) erythrocytes (rabbit, pigeon) produce $AcCO_2H$ from added phosphoglyceric acid.

W. McC.

Influence of antiseptics on the autolytic enzymes of yeast with special reference to the elimination of phosphoric acid. H. HAEHN and H. LEOPOLD (Fermentforsch., 1934, 14, 318—332).—The formation of volatile acid and H_3PO_4 and the degradation of protein are followed during autolysis of yeast at 50—52° using $PhMe$, $CHCl_3$, and $EtOAc$ as antiseptics. The normal displacement of p_H to the acid side during autolysis without antiseptic is considerably inhibited by $PhMe$ and $CHCl_3$, whilst the phosphatases and proteolytic enzymes are inhibited by $CHCl_3$ and $EtOAc$.

P. W. C.

Micrometabolism of yeast cells. E. A. PRIBRAM and L. KOTLER (J. Bact., 1934, 27, 24).—*Saccharomyces cerevisiae* and *S. lactis* absorb more glucose than galactose or lactose. The presence of $CaCl_2$ decreases and of KCl or $FeCl_3$ increases the absorption of sugars by both organisms, the effect of KCl being > that of $FeCl_3$.

A. G. P.

Biochemical control of heat-resistance [of yeast]. N. A. CHLEBNIKOVA and G. V. BOLONDZ (Compt. rend. Acad. Sci. U.R.S.S., 1934, 2, 584—588).—With two strains of *Saccharomyces cerevisiae* cultivated for 10—15 years at 8° [bottom yeast (I)] and 20° [top yeast (II)], respectively, the growth in unhopped wort at various temp. \propto the increase in NH_2-N content. The optimum temp. for growth was 8—22° for (I), but approx. 40° for (II).

F. O. H.

Relationship between metabolic processes of micro-organisms and the oxido-reduction potential of the medium. II. A. J. KLUYVER and J. C. HOOGHEIDE (Biochem. Z., 1934, 272, 197—214).—By using a Au electrode within the fermentation flask of a Warburg manometric apparatus, the oxido-reduction potential of media containing living cells and the type of metabolism of the cells are determined. Using the apparatus with different kinds of yeast in a buffer medium of p_H 5.4 containing sugar, the potential was always about 90 mv. independently of the strain of yeast or the kind or concn. of the sugar. If air replaces N_2 in the Warburg apparatus, the potential is higher. The potential val. characterises the nature of the metabolic processes of the cell.

P. W. C.

Effect of oxidation-reduction character of the medium on initiation of yeast growth. J. J. REID and I. L. BALDWIN (J. Bact., 1934, 27, 29—30).—The ability of *Saccharomyces cerevisiae* to initiate growth is influenced by the oxidation-reduction potential of the medium.

A. G. P.

Increase of invertase content of bottom yeast. R. WEIDENHAGEN (Angew. Chem., 1934, 47, 581—582).—A max. increase ($\times 10$ —15) in the invertase content (I) of bottom yeast is obtained by fermentation in presence of min. concns. of sucrose (cf. A., 1925, i, 1214) and with increased aeration. Optimal conditions include a fermentation period of 8—10 hr., a temp. of 41°, and p_H 4.5—5.5. Sucrose and fructose give the highest vals. of various carbohydrates. The growth in yeast is not related to (I). The non-appearance of the increase in (I) when air is replaced by N_2 indicates that it is not due to agitation or to the removal of metabolic products.

F. O. H.

Effect of esters of *p*-hydroxybenzoic acid on alcoholic fermentation. R. CULTRERA (Annali Chim. Appl., 1934, 24, 282—288).—The effect of salicylic acid (I), nipagin-*M* ($p-OH \cdot C_6H_4 \cdot CO_2Me$) (II), nipasol (the Pr ester) (III), and nipakombin (Na salts of nipagin and nipasol) (IV) on the alcoholic fermentation of a solution containing glucose, KH_2PO_4 , NH_2Ac , $MgSO_4$, and $CaSO_4$ has been studied. At p_H 7, fermentation is stopped by > 2.6, 2.5, 1.2, and 2.5 parts per 1000 of (I), (II), (III), and (IV) respectively; at p_H 3.2: 1, 2.05, 1, and 1.45.

T. H. I.

Effects of carbohydrates on growth of *Euglena anabaena* var. *minor* in darkness. R. P. DAL (Arch. Protistenk., 1934, 82, 45—50).—Multiplication of the organism is favourably influenced by glucose and fructose and, to a smaller extent, by maltose, but by no other carbohydrate examined. No change in the of the media resulted.

A. G. P.

Cellulose digestion by ciliates in the ruminant stomach. E. WEINECK (Arch. Protistenk., 1934, 82, 169—202).—The mechanism of the process of digestion is examined. A. G. P.

Limits of p_H for some saprophytic flagellates. E. G. PRINGSHEIM (Naturwiss., 1934, 22, 510).—Limits of p_H in a buffered synthetic medium for multiplication of *Polytoma uvella*, *Polytomella agilis*, *Chilomonas paramecium*, *Chlorogonium euchlorum*, and *C. elongatum* are characteristic, and some conclusions as to their natural occurrence can be reached, subject to the fact that p_H limits alter with the composition of the medium. R. K. C.

Photogenic granules of *Watasenia scintillans* (Berry). Y. K. OKADA, S. TAKAGI, and H. SUGINO (Proc. Imp. Acad. Tokyo, 1934, 10, 431—434).—The size of the granules in the brachial organs is $2.5-5 \mu \times 1.0-3.0 \mu$. The granules are insol. in Et_2O and $CHCl_3$; they appear to be crystalloids of protein nature and give a positive biuret reaction, whereas those from the luminous bacteria obtained from the octopus give a negative reaction. They are not lipins, since they do not oxidise pyrogallol, $p-C_6H_4(NH_2)_2$, etc., as do the lipin constituents of mitochondria. P. G. M.

Chemical constituents of the mycelium of *Oospora aurantia* (Cooke), Sacc. et Vogl. H. NISHIKAWA (Proc. Imp. Acad. Tokyo, 1934, 10, 414—416).—By extraction of the dried mycelium with Et_2O , 3% of cryst. material is obtained. *Oosporin*, $C_{10}H_{14}O_2$, decomp. 176° , forms an *Ac* derivative. *Aurantin*, $C_{16}H_{22}O_3$, decomp. 183° , is more sol. in cold Et_2O than (I). Both compounds give a purplish-brown colour with $FeCl_3$. P. G. M.

Biochemical origin of citric and oxalic acids. I. Formation of citric from acetic acid. V. S. BUTKEVITSCH, E. V. MENZSCHINSKAJA, and E. I. TROFIMOVA (Biochem. Z., 1934, 272, 290—307).—Evidence is brought against the view that citric acid (I) is formed by moulds from sugar by way of $AcOH$ (II). The small amounts of (I) formed by moulds when grown on (II) arise from the mycelial substance and not directly from (II), and any apparent increase of production of (I) on addition of (II) is due to the strong inhibition which (II) exerts on the utilisation of (I). There is no direct relationship between the utilisation of (II) and the production of (I). P. W. C.

Salt intake of *Aspergillus niger*. E. RENNERFELT (Planta, 1934, 22, 221—239).—Normal development of the mould occurs in the absence of Ca and Mn. Spores contain larger proportions of cations than does mycelium. The intake of bases was in the order $K > Mg > Na$; Ca and Mg exhibited antagonism especially towards K. Salt absorption is influenced by the permeability factor, by the concn. of the ions in the medium, and by the ability of the cells to accumulate and store particular ions.

Citric fermentation by *Aspergillus niger*. W. SCHWARTZ and H. LANG (Arch. Mikrobiol., 1934, 5, 387—401).—Growth of *A. niger* in lemons lowers the capacity for citric acid (I) formation, but this is restored by culture on gelatin (II) media. The fermentative

capacity of the organism varies with the age of the conidia used. The yield of (I) is increased by addition of $CaCl_2$ or (II). In the latter case the growth of the mould is simultaneously accelerated. $CHCl_3$, As compounds, and KCN restrict the formation of (I). The last-named probably acts indirectly by retarding growth and delaying the initiation of fermentation. (II) also induces rapid decomp. of the (I) formed, but this action is minimised by addition of mineral acid to the culture. A. G. P.

Biochemistry of micro-organisms. XXXIX. Metabolic products of *Penicillium crateriforme*, Gilman and Abbot. A. E. OXFORD and H. RAISTRICK (Biochem. J., 1934, 28, 1321—1324).—Spiculisporic acid (A., 1931, 1092), succinic acid, and an unidentified complex polysaccharide have been isolated. H. G. R.

Ability of a mould or its metabolic products to inhibit bacterial growth. R. D. REID (J. Bact., 1934, 27, 28).—The inhibitory substance (I), produced by a mould strain closely resembling *Penicillium notatum*, is similar to but not identical with the pigment formed simultaneously. Its formation is accompanied by alkaline material, but once formed its activity is not affected by p_H . (I) is relatively thermostable, contains enzymes (notably amylase and catalase), and is adsorbed by activated C. A. G. P.

Stimulation of fungus spore germination by aqueous plant extracts. F. WILCOXON and S. E. A. McCALLAN (Phytopath., 1934, 24, 20).—Germination of a no. of spores was stimulated by addition of small amounts of fruit juice (orange, tomato, etc.), of aq. extracts of lily or gladiolus bulbs, or of potato or dahlia tubers. Vitamin-C and inositol with "bios II" were non-effective. The stimulatory factor is heat-stable and dialysable. A. G. P.

Attempted removal of staling substances of fungus cultures. J. C. CARTER (Phytopath., 1934, 24, 4).—In media staled with *Helminthosporium sativum* or with a certain bacterial culture, sterilisation did not inactivate the staling agent, which migrated to the negative pole of a Bradfield dialyser. A. G. P.

Fermentation of citron. C. R. FELLERS and E. G. SMITH (J. Bact., 1934, 27, 63).—Organisms concerned in the preliminary brine fermentation of citron are examined and their biochemical activities described. A. G. P.

Utilisation of slime-forming micro-organisms. J. R. SANBORN (J. Bact., 1934, 27, 61).—Under suitable conditions the activities of slime-forming organisms from pulp and paper may result in desirable products, e.g., sol. gum-like substances, insol. materials resembling cellulose, mucilaginous and gelatinous products possessing adhesive and cohesive properties. A. G. P.

Acidoproteolytes in gaseous associative fermentation in milk. C. GORINI (J. Bact., 1934, 27, 69—70).—This type of fermentation may occur in milk if only two types of saccharolytic bacteria are present, provided one of these is both saccharolytic and proteolytic, e.g., the group of *Acidoproteolytes*, Gorini. A. G. P.

Economical sugar fermentation [by bacteria]. H. J. CONN and M. A. DARROW (J. Bact., 1934, 27, 51—52).—The soil organism, *B. globiforme*, is capable of free growth with unusually small supplies of sugar. The only by-product is CO_2 , and approx. 40% of the C utilised is converted into cell substance.

A. G. P.

Synthesis of carotene by bacteria. M. A. INGRAHAM and C. A. BAUMANN (J. Bact., 1934, 27, 25—26).—Bacteria of varied types produced carotene (I), but in no case was this found in anaerobic organisms. The (I) content of a given species varied with age and cultural conditions, max. being reached shortly prior to the exhaustion of supplies of available carbonaceous matter. In *Mycobacterium phlei* variations in (I) content are paralleled by those of lipins. In media having $p_H > 8.3$ (I) formation was minimised.

A. G. P.

Production of lipins by bacteria. I. Total fat formation by *B. prodigiosus* on solid media. II. Total fat formation by *B. prodigiosus* in nutrient solutions. G. GORBACH and A. SABLATNOG (Arch. Mikrobiol., 1934, 5, 311—317, 318—327).—I. Lipin (I) formation varied with the age of the culture and the reaction of the medium, max. vals. being obtained in 8-day cultures at p_H 6.6. Addition of EtOH increased the production of (I), especially in alkaline media. Among C sources examined glycerol favoured (I) formation more than did glucose or sucrose.

II. Similar conditions prevailed in liquid media, but the actual amounts of (I) produced were considerably greater. An optimum concn. for (I) formation exists for each C source. In this respect NH_4 salts of org. acids (malic, lactic) were more suitable sources of N than caseinogen or peptone. The amounts of (I) obtained increased with the concn. of N supplied. The (I) contained 12.8% of unsaponifiable matter.

A. G. P.

Lipolytic activities of several bacteria causing bitter cream. J. T. McGRATH and J. A. ANDERSON (J. Bact., 1934, 27, 68—69).—Of the fatty acid glycerides occurring in butter, only those of low mol. wt. (except tripalmitin) are rapidly hydrolysed by the organisms, tributyrin being the most readily decomposed. Glycerides of solid and semi-solid fatty acids undergo little change in 25 days. Tripalmitin is hydrolysed slowly at first, but subsequently breaks down as rapidly as the simpler homologues. Taste, odour, and throat irritation associated with bitterness in cream may be produced by additions of small amounts of the simpler acids, *n*- and *iso*-hexoic acid being particularly active in this respect.

A. G. P.

Decomposition of alginic acid by micro-organisms. M. C. ALLEN (J. Bact., 1934, 27, 59—60).—Decomp. of alginic acid (I) by certain bacteria is probably an incomplete hydrolysis. The total uronic acid content suffers little loss. The medium shows rapid increase in p_H . None of the fungi examined attacked (I).

A. G. P.

Methane fermentation of organic acids and carbohydrates. D. TARVIN and A. M. BUSWELL (J. Amer. Chem. Soc., 1934, 56, 1751—1755).—The amounts of CO_2 and CH_4 produced during anaerobic

fermentation of various fatty, α -OH-, CO-, and NH_2 -acids, $\text{Ph}[\text{CH}_2]_n\text{CO}_2\text{H}$ (I), aromatic compounds, and carbohydrates were determined. (I) ($n=1-2$) and BzOH are completely destroyed; lower fatty acids appear to be intermediates. Lactic acid is first reduced to EtCO_2H , which is also produced by reduction (and subsequent decarboxylation) of malic and tartaric acids. AcCO_2H undergoes fission to AcOH and HCO_2H , whilst alanine and tyrosine (II) are deaminated. PhOH is produced from (II) and then undergoes further slow decomp. Decomp. of glucose, fructose, sucrose, and starch occurs in 2 stages: (i) production of volatile acids (and possibly some non-volatile substance), much CO_2 and H_2 , and little CH_4 ; (ii) decomp. of intermediate acids to much CH_4 , little CO_2 , and no H_2 . PhCHO, C_6H_6 , PhBr, PhMe, and NH_2Ph are not attacked.

H. B.

Fermentation of tobacco. J. JOHNSON (J. Agric. Res., 1934, 49, 137—160).—Heat generated during fermentation of tobacco \propto the H_2O present (min. 30%). Treatment with CHCl_3 , HgCl_2 , COMe_2 , PhMe, or β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ largely reduces thermogenesis by restricting bacterial activity (I) and inactivating, although not destroying, enzymes (II). AgNO_3 lowers heat production by approx. 50%, (I) being prevented but (II) remaining unaffected. Micro-organisms, notably fungi, are concerned in the processing of cigar leaf.

A. G. P.

Development of micro-organisms on fermenting tobacco. G. P. VOLGUNOV (State Inst. Tobacco Invest., U.S.S.R., 1933, No. 87, 52—72).—The influence of composition of medium, reaction, and O_2 tension is discussed. Small quantities of CH_2O stimulate the activity of the fungi, which do not grow in 75% CO_2 .

CH. ABS.

Strain variation of *Azotobacter* and the utilisation of carbon compounds. N. R. SMITH (J. Bact., 1934, 27, 54—55).—All strains examined utilised sucrose and glucose, but considerable differences were shown in ability to act on mannitol, glycerol, lactose, starch, and dextrin.

A. G. P.

Growth limits of *Azotobacter chroococcum* in the alkaline range. H. WENZL (Arch. Mikrobiol., 1934, 5, 358—365).—For strains isolated from arable soils the growth limit was p_H 9.1—9.2; for those from saline soils of high Na content vals. were 0.3—0.4 unit higher.

A. G. P.

Magnesium, calcium, and iron requirements for growth of *Azotobacter* in free and fixed nitrogen. C. K. HORNER and D. BURK (J. Agric. Res., 1934, 48, 981—995).—The concns. of nutrient elements required by the organism to produce half-max. growth were determined. Vals. for Ca approached zero in fixed N, and $2-5 \times 10^{-5}M$ in free N_2 . Vals. for Mg and Fe were independent of the nature of the N source. Mg is essential to the growth process and no other element examined can replace it.

A. G. P.

Accessory factor for legume nodule bacteria. Sources and activity. F. E. ALLISON and H. HOOVER (J. Bact., 1934, 27, 561—581).—The growth factor (a respiratory co-enzyme) occurs in considerable proportions in yeast, cane molasses, humic acid, and

commercial ovalbumin and may be obtained in moderate concn. by extraction of commercial sucrose or cane molasses with abs. EtOH. A. G. P.

Production of peroxidase by *Streptococci* and its possible significance. M. A. FARRELL (J. Bact., 1934, 27, 24—25).—The presence of peroxidase (I) was demonstrated in all strains examined. Colour tests for (I) are examined. The (I) of *Streptococci* withstands autoclaving at 120° for 15 min. The colour reactions are inhibited by respiratory poisons (KCN, H₂S, CH₂I-CO₂H, etc.). A. G. P.

Separation of some cellular constituents of the *Brucella* group of micro-organisms. R. C. HUSTON, I. F. HUDDLESTON, and A. D. HERSHEY (Michigan Agric. Exp. Sta. Tech. Bull., 1934, No. 137, 25 pp.).—From *B. abortus*, *B. melitensis* (I), and *B. suis* nucleoproteins, sol. proteins, lipins, and sol. polysaccharides, but no simple carbohydrate, have been isolated. Each species contains two biologically inactive polysaccharides and two lipins, the proportions of these being characteristic for the different species. (I) was peculiar in yielding a N-containing substance [S substance (II)] which seems to be neither a protein nor a carbohydrate. (II) reacts with *Brucella* anti-serum in a dilution of 1 in 10⁵. W. O. K.

Influence of concentration of soluble calcium on the precipitation of calcium carbonate by micro-organisms. F. T. WILLIAMS and E. B. FRED (J. Bact., 1934, 27, 58—59).—Organisms from lake muds pptd. cryst. calcite from artificial media containing 0.01—0.02% of CaCl₂. A. G. P.

Products of oxidation of thiosulphate by bacteria in mineral media. R. L. STARKEY (J. Bact., 1934, 27, 53—54).—The organism examined (probably *Thiobacillus thioparus*) converted 60% of S₂O₃"-S into SO₄" and 40% into free S. A second organism produced from Na₂S₂O₃ equimol. proportions of Na₂SO₄ and H₂SO₄. In the case of *T. trautweinii*, Na₂S₄O₆ is the initial product, although this subsequently breaks down to yield varied S products. The C assimilation of these bacteria is examined. A. G. P.

Oxygen consumption of luminous bacteria in water containing deuterium oxide. E. N. HARVEY and G. W. TAYLOR (J. Cell. Comp. Physiol., 1934, 4, 357—362).—Luminescence (I) and respiration (II) of a salt-H₂O bacterium were reduced by a heavy H₂O concn. of 86%. With fresh-H₂O organisms (II) was reduced without effect on (I). A. G. P.

Effect of narcotics on respiration and luminescence in bacteria with special reference to the relation between the two processes. G. W. TAYLOR (J. Cell. Comp. Physiol., 1934, 4, 329—355).—Respiration (I) and luminescence (II) vary with the amount of nutrient matter in the medium, the effect on (I) being > that on (II). Low concns. of narcotics stimulate and higher proportions cause a reversible narcosis of both processes, the threshold of susceptibility for (I) being > for (II). The relative effectiveness of homologous series of narcotics < the relative lipin solubilities and their ability to lower surface tension. (I) and (II) are probably independent pro-

cesses. Et urethane inactivates luciferase in *Cypridina* extracts. A. G. P.

Light intensity of luminous bacteria as a function of oxygen pressure. H. SHAPIRO (J. Cell. Comp. Physiol., 1934, 4, 313—327).—Light intensity (I) of *Vibrio phosphorescens* is not affected by O₂ pressures > 1.06 mm. Hg. At lower pressures (I) declines steadily and is not measurable by a photo-electric cell at 0.076 mm. A. G. P.

Lipins of tubercle bacilli. XXXIX. Tuberculo-stearic acid. M. A. SPEELMAN (J. Biol. Chem., 1934, 106, 87—96).—Tuberculo-stearic acid (Anderson, A., 1932, 1290), C₁₉H₃₈O₂, is oxidised by CrO₃ in AcOH to Me *n*-octyl ketone, azelaic and octoic acids. dl-*Methylstearic acid* was synthesised, m.p. 20—21° (amide, m.p. 76—77°; 2:4:6-tribromoanilide, m.p. 93—94°). It resembles (I) very closely, but identity is not established. H. D.

Antigenic properties of lipins of tubercle bacilli. II. Specificity. M. YATO (Manshu-igaku-zasshi, 1932, 17, No. 5).—A study of avian, bovine, and frog types of bacilli. CH. ABS.

Toxin of tubercle bacilli. I. Refining method for tuberculin and formol-tubercle bacilli. II. Specificity of toxin of tubercle bacilli. M. YATO (Manshu-igaku-zasshi, 1933, 18, No. 4).—Tuberculin free from albumin was obtained from culture filtrates by absorption with Al(OH)₃. Intracutaneous tests are described. CH. ABS.

Spectral analysis of purified tuberculin. M. SPIEGEL-ADOLF and F. B. SEIBERT (J. Biol. Chem., 1934, 106, 373—385).—When prepared by CCl₃-CO₂H pptn. human tuberculin contained thymus-nucleic acid (I). When fractionated with (NH₄)₂SO₄ (I) was absent, the P content lower, but the biological activity was not impaired. No trace of (I) could be found in preps. from non-pathogenic acid-fast bacteria, but from pathogenic acid-fast bacteria there was a definite correspondence between (I) and the potency. H. G. R.

Purification of vaccinia virus. M. SCHAEFFER and H. NALIBOW (Amer. J. Public Health, 1934, 24, 736—738).—Vaccinia virus is adsorbed on casein and other adsorbents, but best on a mixture of casein and Al(OH)₃ adjusted to *p*_H 4.9—5.5 by addition of KH₂PO₄. It is recovered in good yield by elution at *p*_H 8.0. W. O. K.

Re-alkalisation effect in virus species. G. PYL (Z. physiol. Chem., 1934, 226, 18—28).—The virus of stomatitis vesicularis is stable within the *p*_H range 3.5—11.5. It shows neither the double max. nor the min. given by the virus of foot-and-mouth disease and there is no "re-alkalisation effect" (cf. A., 1933, 984). J. H. B.

Artificial production of a lytic agent which behaves like bacteriophage. J. D. LE MAR and J. T. MYERS (J. Bact., 1934, 27, 49).—Optimum results were obtained by autoclaving a 48-hr. culture of *E. coli*, permitting autolysis for a further 48 hr., and subsequently oxidising (48 hr.) with 3% H₂O₂. Oxidation of living cultures or autolysis of killed cultures without oxidation failed to produce a lytic agent. A. G. P.

Bacteriological media. O. ACKLIN and R. G. VUILLEMIN (Mitt. Lebensm. Hyg., 1934, 25, 224—235).—Culture experiments with *B. coli*, *fluorescens*, and *putrificus* in various media are described. The following "universal medium" is suggested. 18 g. of agar, 5 g. of Liebig's meat extract, and 10 g. of peptone in 750 c.c. of H_2O are autoclaved at 104° for 15 min., 10 g. of commercial sol. starch are treated hot with 250 c.c. of H_2O + 2 c.c. of $N-NaOH$, and the two filtered solutions are mixed and adjusted to p_H 7.8—8.2 with $NaOH$; 10 g. of "eatan," 1 g. of glucose, and 10 c.c. of 0.2*M*-phosphate buffer (p_H 7.2) are added, the p_H of the final filtered medium being adjusted to 7.0—7.2 with HCl . "Eatan" contains $NaCl$ 18.36, total N 3.71, creatinine 0.40, and total acidity (as lactic acid) 1.91%.

J. C.

Metal tank for the preparation of mass cultures of anaerobic bacteria. C. WEISS and E. J. CZARNETZKY (Amer. J. Public Health, 1934, 24, 713—714).—A jar made from a cast Al pressure cooker suitable for the growth of anaerobic bacteria on a large scale is described.

W. O. K.

Cotton-blue as a mycological stain. C. G. C. CHESTERS (Ann. Bot., 1934, 48, 820—822).—Methods for staining permanent preps. of mycelium and for the direct examination of hyphae in woody tissue are described.

A. G. P.

Mercurochrome as a bacteriological stain. M. E. CONKLIN (J. Bact., 1934, 27, 30—31).—The use of mercurochrome in observations of changes in bacterial spores is described.

A. G. P.

Effect of certain triphenylmethane dyes on *Staphylococcus aureus* and *B. coli communis*. M. V. REED and E. F. GENUNG (J. Bact., 1934, 27, 29). Bacteriostatic effects of, and the "adaptability" of the organisms to, a no. of dyes are examined.

A. G. P.

Bacteriostatic azo-compounds.—See this vol., 1109.

Preparation and germicidal properties of some alkyl derivatives of hydroxydiphenyls.—See this vol., 999.

Bacterostatic effect of indole and skatole. L. A. SANDHOLZER and R. P. TITSLER (J. Bact., 1934, 27, 28—29).—The inhibitory action of indole (I) and skatole (II) on numerous organisms is examined. (II) is more active than (I), although there is a general parallelism in their effects in relation to concn.

A. G. P.

Determination of indole in bacterial cultures. F. C. HAPFOLD and L. HOYLE (Biochem. J., 1934, 28, 1171—1173).—Indole is determined in bacterial cultures by twice extracting with light petroleum or xylene, extracting the resultant solution with Ehrlich's reagent, and comparing the solution of rosindole with a standard.

H. D.

Pneumococcicidal powers of sodium oleate and sodium ricinoleate. L. A. BARNES and C. M. CLARKE (J. Bact., 1934, 27, 107—108).—Min. concns. of the soaps necessary to devitalise broth cultures of *Pneumococcus* were 0.0004% (oleate) and 0.004% (ricinoleate).

A. G. P.

Survivor curves exhibited by bacterial spores in chlorine disinfection. D. B. CHARLTON and M. LEVINE (J. Bact., 1934, 27, 37—38).—The nature of survivor curves indicates differences in the mechanism of disinfection by hypochlorites and by chloroamines.

A. G. P.

Germicidal efficiency of hypochlorite solutions in presence of chicken manure. E. C. McCULLOCH (J. Bact., 1934, 27, 37).—Hypochlorite solutions containing as little as 130 p.p.m. of available Cl killed *Salmonella pullorum* in the presence of a 5% suspension of chicken manure. The formation of a derivative of NH_2Cl by interaction with NH_3 from the manure is indicated.

A. G. P.

Oligodynamic action of metals and metallic salts. C. W. RAADSVELD (Chem. Weekblad, 1934, 31, 497—504).—A review.

H. F. G.

Practical applications of oligodynamic action. C. W. RAADSVELD (Chem. Weekblad, 1934, 31, 505—510).—A review.

H. F. G.

Effect of muscle extracts on blood-sugar. GOEBEL (Compt. rend. Soc. Biol., 1934, 115, 1135—1137). Rabbit muscle contains a substance (I) having a sp. effect on carbohydrate metabolism. The thyroid plays an important part in the production of (I).

NUTR. ABS. (m)

Hypoglycæmic action of duodenal extracts. J. LA BARRE and J. LEDRUT (Compt. rend. Soc. Biol., 1934, 115, 750—752).—Hydrolysis of secretin by pepsin or pancreatic juice activated by enterokinase yields a product having marked hypoglycæmic action, *per os* or intravenously, in normal and depancreatized dogs.

NUTR. ABS. (m)

Insulin content of the pancreas in cattle at various ages. A. M. FISHER and D. A. SCOTT (J. Biol. Chem., 1934, 106, 305—310).—The amount of insulin, in international units per g., obtainable from the pancreas by an improved technique (described) is: foetal calves, < 5 months old, 29.2—38.8, 5—7 months, 21.1—24.9; calves, 6—8 weeks (milk diet), 10.4—12.8; cattle, 2 years, 3.9—6.1; cows, > 9 years, 1.7—2.0, > 7 years (pregnant), 2.0—2.3.

R. S. C.

Action of phenylcarbimide on insulin. S. J. HOPKINS and A. WORMALL (Nature, 1934, 134, 290). The activity of insulin (I) is destroyed in 10 min. at $5-8^\circ$ by treatment with phenyl- or *p*-bromophenyl-carbimide. The carbimide reacts with all the free NH_2 of (I), which appears to contain free NH_2 in addition to that of the lysine mols. The basic groups of insulin appear, therefore, to be of importance in the physiological activity of (I).

L. S. T.

Peptic hydrolysis of insulin. A. M. FISHER and D. A. SCOTT (J. Biol. Chem., 1934, 106, 289—303).—A method for determining the N distribution in 0.1 g. of insulin (I) is described. Destruction of the potency of (I) by pepsin is accompanied by decrease in tyrosine, increase in lysine, but no change in cystine content. Slight deactivation changes the cryst. form of (I).

R. S. C.

Role of insulin in peripheral metabolism. N. B. LAUGHTON and A. B. MACALLUM (Nature, 1934, 134, 325).—The relative effects of Et urethane, cyan-

ides, NaF, and $\text{CH}_3\text{I}\cdot\text{CO}_2\text{H}$ on the action of insulin on rabbits have been examined. Results indicate that the insulin mechanism is largely concerned with the reaction between α -glycerophosphoric and pyruvic acids resulting in the formation of lactic acid.

L. S. T.

Dietetic factors influencing the glucose tolerance and the activity of insulin. H. P. HEMS-WORTH (J. Physiol., 1934, 81, 29—48).—Adult male rabbits on a fat-rich diet (soya bean and limited cabbage) become resistant towards insulin (I). The hyperglycæmia following intravenous injections of glucose is also more marked and, on repeated injections, slower in declining than in rabbits receiving excess of carbohydrates (oats, bran, and excess cabbage). Thus diet alters the susceptibility towards (I), rather than causes variations in the internal secretion of (I). (I) as secreted is probably inert, and becomes activated by a tissue-kinase the production of which depends on diet.

NUTR. ABS. (b)

Effect of insulin on ketonic substances. A. Löw and A. KRÖMA (Wien. Arch. inn. Med., 1934, 24, 455—462).—One hr. after injection of insulin into man or animals, an increase occurs in ketones of blood and urine, subsiding or disappearing when insulin response is greatest.

NUTR. ABS. (b)

Secretion of insulin during hyperamino-acidæmia. J. LA BARRE (Compt. rend. Soc. Biol., 1934, 115, 748—750).—Injection of large doses of glycine causes hypoglycæmia, which is due chiefly to increased secretion of insulin of adrenal origin.

NUTR. ABS. (m)

Mechanism of insulin secretion. IV. Dynamics. E. S. LONDON and N. P. KOTSCHNEFF (Pflüger's Arch., 1934, 234, 194—199).—The insulin (I) content of the blood of the pancreatico-duodenal vein and femoral artery of dogs was determined by its effect on the blood-sugar (II) of mice. Increase of (II) produced by injection of glucose or adrenaline led to an increase of (I) in the pancreatico-duodenal vein: the secretion of (I) was inhibited by blockage of the vagus nerve by atropine (III). When (III) was injected prior to the production of the hyperglycæmia the secretion of (I) was stimulated.

NUTR. ABS. (b)

Assay of insulin and the blood-sugar level. M. C. HRUBETZ (Amer. J. Physiol., 1934, 107, 284—292).—The blood-sugar (I) of rats falls progressively during the first 24 hr. of a fast, after which it approaches a const. level. No correlation between (I) and age, sex, or wt. was found. With doses of < 0.5 unit of insulin per kg. the % decrease in (I) is a logarithmic function of the dosage. This fact might be used for the assay of insulin.

NUTR. ABS. (b)

Effect of insulin on the glucose-chloride relationship and anhydræmia in the blood of rabbits.

A. S. CHAIKELIS (J. Biol. Chem., 1934, 105, 67—778).—A reciprocal relationship is brought about by the injection of small doses (1/32—1 unit per kg. of body-wt.) of insulin into rabbits, tending to keep the acid-base balance of the blood const. A moderate anhydræmia is also caused, together with changes in the hæmoglobin content and red blood-cell count

(unrelated to blood vol.), said to be the result of the intervention of the spleen.

C. G. A.

Blood-lipins in completely depancreatized dogs maintained with insulin. I. L. CHAIKOV and A. KAPLAN (J. Biol. Chem., 1934, 106, 267—279).—The lipins decrease under these conditions, particularly the cholesteryl ester (usually to zero).

R. S. C.

Effect of the central nervous system on the action of insulin and adrenaline. F. HÖGLER and F. ZELL (Klin. Woch., 1933, 12, 1719—1722; Chem. Zentr., 1934, i, 72).—Removal of the cerebrum, corpus striaticus, and mid brain (I) of rabbits has little effect on the action of insulin (II) or adrenaline (III). After removal of (I) the sensitivity towards (II) is reduced and towards (III) raised. A regulating mechanism must thus exist in (I), and must have an inhibitory action on the sympathetic part of the central blood-sugar regulation.

L. S. T.

Adrenals and glucose tolerance. H. BANERJI and C. REID (J. Physiol., 1934, 81, 93—101).—The fasting blood-sugar is subnormal and the rate of disappearance of intravenously injected glucose temporarily more rapid in rabbits which survive adrenalectomy (I) for only a short time. No differences in this respect are observed in rabbits surviving (I) indefinitely.

NUTR. ABS. (m)

Relationship between creatinuria and rise in blood-lactic acid after adrenaline in the rabbit. F. QUEROL and A. REUTER (Z. ges. exp. Med., 1934, 92, 598—602).—In healthy animals injection of adrenaline (I) is followed by rise in blood-sugar (II) and lactic acid (III). Conditions (inanition, injection of urethane, thyroxine, or sulfogel) which produce creatinuria (IV) prevent the post-(I) rise of (III), but do not interfere with the increase of (II). When the (IV) is prolonged, the rise of (III) after (I) reappears even when considerable amounts of creatine are present in the urine.

NUTR. ABS. (m)

Diurnal rhythm in adrenaline secretion and carbohydrate metabolism in the rabbit and hedgehog. U. S. VON EULER and A. G. HOLMQUIST (Pflüger's Arch., 1934, 234, 210—224).—In the hedgehog the adrenaline (I) content of the blood and adrenal glands is greater in the waking (II) than in the sleeping state (III). In the rabbit there is a rise in blood-sugar, liver-glycogen, and (I) of the blood and adrenal glands at 4—10 and 16—22 hr. The temp. rises at 16—22 hr., whilst serum-P is high at 4—16 hr. No regular differences between (III) and (II) are noticed, nor does muscular activity have a const. effect.

NUTR. ABS. (m)

Effect of drugs on induced cardiac standstill. Effect of adrenaline and related compounds. M. H. NATHANSON (Arch. Int. Med., 1934, 54, 111—130).—Adrenaline is the most active drug for the treatment of cardiac standstill, but ephedrine and phenylethanolamine are effective by the mouth. Digitalis prolonged the period of standstill.

H. G. R.

Formation of adrenaline in the adrenal gland. Role of lipins. J. E. ABELOUS and R. ARGAUD (Compt. rend., 1934, 199, 535—537).—Treatment of adrenaline (I)- and lipin-free powder preps. of adrenal

cortex (horse), or of the derived nucleoprotein, with ligroin extracts (II) of the cortical lipins in presence of 0.02*N*-NaOH at 22–24° for 4 hr. produces (I) due to its liberation (probably enzymic) from (I)-lipin complexes in (II). F. O. H.

Function of the adrenal cortex : general, carbohydrate, and circulatory theories. S. W. BRITTON and H. SILVETTE (*Amer. J. Physiol.*, 1934, 107, 190–206).—The following observations do not support a proposed circulatory theory of the function of the adrenal cortex, but favour the carbohydrate theory : (1) a shift in the H₂O balance in adrenalectomised animals occurred with the development of insufficiency symptoms; the liver and muscle showed increased hydration, whilst the blood became dehydrated, although the organism as a whole (rat) contained more H₂O than normal; (2) the blood vol. was usually reduced after adrenalectomy; (3) intraperitoneal or intracardial injections of NaCl restored the circulatory vol., but did not affect the general condition or survival period of the adrenalectomised animal; (4) liver-glycogen was practically depleted, blood-glucose reduced, and muscle-glycogen decreased in adrenalectomised guinea-pigs, cats, and marmots; in rats there was a reduction of liver-glycogen; (5) emotional excitement and adrenaline injection had practically no effect on blood-glucose of adrenalectomised cats; (6) Na lactate and glucose injections resulted in insignificant glycogen storage in adrenalectomised animals compared with normal controls.

NUTR. ABS. (b)

Effect of thyrotropic hormone on mineral metabolism. F. EGGS (*Deut. Z. Chirurg.*, 1934, 242, 321–327).—In guinea-pigs, injection of the hormone leads to a marked fall in the Na content of serum and liver accompanied by increased urinary output and deposition in the skin. Similar results are obtained with Ca, but practically no alteration in K, Cl, or urinary vol. is observed. There is no evidence of a shift of Na between cells and plasma.

NUTR. ABS. (m)

Myokinin. L. KARZOG (*Orvosi Hetilap*, 1933, 77, 508–509).—The uterus-active factor of blood-serum and cerebrospinal fluid is not oxytocin but *myokinin*, which was also separated from the radish.

CH. ABS.

Pituitrin-fixing substance in serum of pregnancy. F. G. DIETEL (*Klin. Woch.*, 1933, 12, 1683–1686; *Chem. Zentr.*, 1934, i, 71).—Injection into the frog of a mixture of 0.01 c.c. of pituitrin (II) with 1 c.c. of serum (especially serum of pregnancy) does not cause expansion of the melanophores. After deproteinisation with EtOH the hormone can be determined in the conc. serum. The substance concerned is inactivated by short heating at 60° or by heating for 30 min. at 55°, and is adsorbed by kaolin. Reactivation is rapidly accomplished by addition of a small quantity of the serum. Serum contains also another substance, not adsorbed by kaolin, which adsorbs the antidiuretic component of (I).

A. A. E.

Diuretic action of pituitary extracts and the responsible principle or constituent. K. I. MELVILLE and D. V. HOLMAN (*J. Pharm. Exp. Ther.*, 1934, 51, 459–470).—The diuretic action of oxytocic and

pressor preps. on urethanised rabbits is correlated with the quantity of vasopressin present and is probably due to the latter.

W. O. K.

Anti-diuretic fraction of posterior pituitary gland. R. L. STEHLE (*Arch. exp. Path. Pharm.*, 1934, 175, 471–480).—The action of various posterior pituitary preps. on diuresis (I) in dogs does not indicate the presence of a definite anti-diuretic principle, the action being due to the pressor substance. With certain preps., 1×10^{-5} mg. partly inhibits (I), indicating that the action of the hormone concerns the regulation of the H₂O balance more than the vasomotor system.

F. O. H.

Effect of pituitary preparations on fat metabolism. W. RAAB (*Klin. Woch.*, 1934, 13, 281–285).—The presence in the pituitary of lipoitrin and orophysin, their effect on blood-fat and -ketones and on liver-fat and -glycogen, and their functional importance are reviewed.

NUTR. ABS. (m)

Melanophore-enlarging action of pituitary extracts. R. L. STEHLE (*Arch. exp. Path. Pharm.*, 1934, 175, 466–470).—The oxytocic principle (I) (cf. this vol., 117) of the pituitary gland has no melanophore-enlarging action (II) in frogs. Pitressin, a pressor prep., has 25–50% of the (II) of pituitary gland powder and is 40 times as active as the purified pressor principle (III) (*ibid.*). Partial separation of the substance causing (II) from (I) and (III) occurs during treatment of gland preps. with EtOH etc. This substance, which is adsorbed by Fe(OH)₃, is therefore not identical with, but merely a contaminant of, (III).

F. O. H.

Mode of action of the contra-insulin hormone of the anterior pituitary lobe. I. Anterior pituitary lobe, thyroid gland, and carbohydrate metabolism. H. LUCKE, E. R. HEYDEMANN, and F. DUENSING (*Z. ges. exp. Med.*, 1933, 91, 106–113; *Chem. Zentr.*, 1934, i, 71–72).—Injection of thyrotropic hormone into the dog does not raise the blood-sugar. In the animal with injured anterior pituitary lobe thyroxine hyperglycæmia is more marked than normally; on injection of thyroxine and “praphyson” it is smaller than usual. After thyroidectomy reaction to “praphyson” alone or with thyroxine is normal. Contra-insulin and thyrotropic hormones are not identical.

A. A. E.

Mode of action of the pituitary growth-hormone. E. MARGITAY-BECHT and L. BINDER (*Arch. exp. Path. Pharm.*, 1934, 175, 353–358).—The increase in body-wt. due to injection of anterior pituitary preps. (I) into rats and the decrease when administration is discontinued are the same for both normal and thyroidectomised female rats. An increase in the basal metabolism parallel with that in body-wt. confirms the importance of the thyroid gland in the action of (I).

F.

Selective gametogenic effect of certain pituitary extracts. H. M. EVANS, R. I. PENCHARZ, and M. E. SIMPSON (*Science*, 1934, 80, 114).—Et extracts of desiccated anterior pituitary tissue, trypsin-crepsin digests of such extracts, which have a relatively greater influence on the germinal than

the internally secreting mechanism of the testis, have been prepared.

L. S. T.

Does the anterior pituitary substance from urine of pregnancy raise the blood-sugar level? E. DINGEMANSE and S. KOBER (Endocrinol., 1933, 17, 149—151).—The rise is not due to pituitary hormone.

CH. ABS.

Estrogenic substances from coal and associated minerals. R. POTONIE (Pharm. Ztg., 1934, 79, 878—879).—The origin, nature, and separation of estrogenic substances from coal, asphalt, bitumen, etc. are discussed.

F. O. H.

Action of folliculin on plants. III. W. SCHOELLER and H. GOEBEL (Biochem. Z., 1934, 272, 215—221; cf. this vol., 934).—The hormone alone did not, but after addition of a little NaOH (which converted it into the more readily absorbed alkali salt) did, increase the rate of development of the hyacinth. The optimum amount of hormone was 250 mouse units per week.

P. W. C.

Determination of small amounts of gonadotropic material. P. A. KATZMAN and E. A. DOISY (J. Biol. Chem., 1934, 106, 125—139).—Gonadotropic material (I) can be quantitatively removed by pptn. with tungstic acid and decomp. with Ba or brucine, or (better) by adsorption on BzOH. This is probably due to adsorption of the active material on a protein-like substance. Data are given for the daily excretion of (I) by men and women at various ages. Extracts from the urine of women after the menopause and of castrates produce less follicular stimulation and enlargement of the ovaries than extracts from urine of pregnancy and anterior lobe.

H. G. R.

Hormonal interruption of broodiness in hens. K. WODZICKI (Nature, 1934, 134, 383).—Administration of prolactin, pituitrin (I), and cattle thyroid gland had no effect on the interruption of broodiness in hens. (I) had no effect on health or laying.

L. S. T.

Physico-chemical studies of complex organic molecules. III. Surface properties of concentrates of vitamin-A. F. P. BOWDEN and L. H. BASTOW (Proc. Roy. Soc., 1934, B, 116, 27—37).—Vitamin-A forms an insol. film of the liquid expanded type, resembling that of a long-chain alcohol, slowly oxidising with a decrease in surface area. It is adsorbed on solid surfaces, not as strongly as carotene (I), and more readily from a non-polar than from a polar solvent, and can be recovered unchanged. It is taken up by freshly killed liver tissue from cyclohexane solution in contrast to (I).

H. G. R.

Colour reaction for vitamin-A. E. ROSENTHAL and J. ERDELYI (Biochem. Z., 1934, 271, 414—419).—The reaction for vitamin-A previously described (this vol., 225) using SbCl_3 and pyrocatechol is greatly improved by substituting guaiacol for the latter. The colour is more stable, and accurate determinations may be made by its use in the Leitz abs. colorimeter.

P. W. C.

Hydrogenation of vitamin-A fraction of the liver-oil of *Stereolepsis ischinagi* (Hilgendorf). Z. NAKAMIYA (Bull. Inst. Phys. Res. Japan, 1934, 13, 48—49).—The oil was hydrogenated at 70° using a

PtO_2 catalyst. Nonacosane was not obtained. Distillation in a high vac. gave five fractions; the lowest was a hydrocarbon, $\text{C}_{18}\text{H}_{38}$, b.p. 85—86°, whilst the highest was probably a polymerisation product of vitamin-A (mol. wt. 451). The vitamin-A of *S. ischinagi* is different from that of *Madara* or *Sukeo* oils.

P. G. M.

Carotenoids, their relation to other natural compounds and their biological importance. L. ZECHMEISTER (Bull. Soc. Chim. biol., 1934, 16, 993—1008).—A lecture.

Vitamin content of pituitary. E. VOGT (Med. Klin., 1933, 52, 1734—1735).—In man, hormone potency is connected with the vitamin-A (I) content of the pituitary (II). (I) is found in (II) as long as a malignant tumour (III) is growing, but becomes exhausted during the development of slow-growing tumours, so that in severe cancer cachexia it is present only in the liver in min. amounts. Hence the relatively slow growth of (III) after 60 years of age, for the (I) content of (II) declines with age.

NUTR. ABS. (m)

Vitamin content of African cereals. I. Vitamin-B complex. M. CAMIS (Atti R. Accad. Lincei, 1934, [vi], 19, 462—465).—*Eragrostis tef*, *Sorghum athiopicum*, and, to a smaller extent, *Pennisetum spicatum* and *Eleusine coracana* contain the vitamin-B complex.

T. H. P.

Vitamin-B growth-promoting factor for rats, found in whole wheat. N. HALLIDAY (J. Biol. Chem., 1934, 106, 29—40).—Although wheat germ is the richest source, the factor can be extracted from bran by dil. acids or dil. EtOH, but not by Et_2O . A cryst. concentrate closely resembling vitamin-B₄ has been prepared by the method of Peters (A., 1933, 541).

H. G. R.

Vitamin content of Philippine foods. II. Vitamin-C in various fruits and vegetables. A. J. HERMANO and G. SEPULVEDA, jun. (Philippine J. Sci., 1934, 53, 379—390).—Of 15 common fruits and vegetables, mangoes and mandarins have the highest content (determined biologically) of vitamin-C.

F. O. H.

Vitamin-C in the adrenal glands and the pituitary of the ox. B. WESTERGAARD (Biochem. J., 1934, 28, 1212—1213).—Ascorbic acid is demonstrated in the tissues by its reduction of AgNO_3 . The cytoplasm is stained but not the nucleus. Some Ag granules are found in the intercellular spaces and lymph vessels.

C. G. A.

Prune as an oxidation-reduction indicator. Its suitability for the titration of ascorbic acid. J. MELVILLE and G. M. RICHARDSON (Biochem. J., 1934, 28, 1565—1574).—The electrode equation for the oxazine dye, prune, is given for the range p_H 0—10. It is useful in the range between Lauth's violet and the indophenols. It is at the limit of weakness for oxidising agents for titrating ascorbic acid, but is not weak enough to eliminate other biological reducing agents from the titration.

C. G. A.

Variation in reducing power with concentration of vitamin-C and other reducing substances. N. BEZSSONOFF, A. DELIRE, and H. VAN

WIEN (Bull. Soc. Chim. biol., 1934, 16, 1133—1159).—Ascorbic acid (I), pyrocatechol, quinol, and tannin are characterised by the variations of their reducing powers (II) with concn., the determinations of (II) being made by solution potential measurements and by the decolorising action on dichlorophenol-indophenol. The technique for the identification of (I) in lemon juice is described. A. L.

Identification of vitamin-C. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1934, 16, 1107—1132).—A method for the identification and determination of ascorbic acid (I) in biological liquids is based on the determination of the dienol concn. by means of the colour reaction (II) with monomolybdic-phosphotungstic acid combined with a determination of the variation of the potential of solutions with the dienol concn. This differentiates between (I) and other substances such as pyrocatechol, quinol, and tannin which also give (II). A. L.

Identification and determination of vitamin-C in biological media. N. BEZSSONOFF and H. VAN WIEN (Bull. Soc. Chim. biol., 1934, 16, 1160—1175).—The direct determination of ascorbic acid (I) in fresh antiscorbutic juices gives results in agreement with those obtained using guinea-pigs, but in the case of a preserved vegetable (sauerkraut) the vals. are high. Human, guinea-pig, and horse urine from animals fed on antiscorbutic diet give the monomolybdic-phosphotungstic colour reaction, but in some cases the reduction curves do not correspond with (I). Summer milk had 38, winter milk, from the same source, 28 mg. of (I) per litre. Whilst the dichlorophenol-indophenol titration of cryst. extracts of animal origin indicates that (I) is the dienol present, the electrometric titration results are too low. A. L.

Antirachitic activity of salts of ergosteryl sulphate on irradiation in aqueous medium.—See this vol., 1099.

Effect of the administration of calciferol on the increased calcium excretion induced by thyroxine. L. I. PUGSLEY and E. ANDERSON (Biochem. J., 1934, 28, 1313—1315).—Administration of 5000 units of calciferol daily to rats decreases the faecal excretion of Ca and corrects the negative Ca balance. H. G. R.

Calcium and phosphorus metabolism in diseases of the thyro-parathyroid apparatus. II. Mode of action of vitamin-D. F. S. HANSMAN (Med. J. Austral., 1934, i, 81—95).—In two patients with combined hyperthyroidism and hypoparathyroidism (I) treated with large doses of vitamin-D (II), the symptoms of (I) cleared up rapidly with little or no change in the level of Ca or P in the blood and only a very slight improvement in the Ca and P balances. The beneficial effects could not be due to better absorption of Ca from the intestinal tract. (II) probably acts by making Ca available for tissue metabolism. NUTR. ABS. (m)

Relation of the parathyroid glands to the action of irradiated ergosterol. N. B. TAYLOR, C. B. WELD, and J. F. SYKES (Proc. Roy. Soc., 1934, B, 116, 10—26).—Dale's theory (A., 1932, 1176) is not

supported, the gastro-intestinal features of over-dosage of parathormone and irradiated ergosterol not being the result of the hypercalcaemia. Elevation of serum-Ca by other agents is no less in a parathyroidectomised than in a normal animal. H. G. R.

Absorption spectrum of vitamin-E. A. J. P. MARTIN, T. MOORE, M. SCHMIDT, and F. P. BOWDEN (Nature, 1934, 134, 214; cf. A., 1933, 987).—A sharp absorption band with a max. at 2940 Å. has been detected in a vitamin-E (wheat-germ oil) concentrate. L. S. T.

Improved vitamin-E-deficient diet for female rats. P. SCHOORL (Arch. Neerland. Physiol., 1934, 19, 403—407).—A diet is described in which sterility is reached in the first insemination of the first generation. H. G. R.

Carbon economy of greenhouse plants during winter in daylight alone and supplemented with electric lighting. E. K. GABRIELSEN (Planta, 1934, 22, 180—189).—The light intensity-C assimilation curves of plants artificially lighted in winter resembles that of shaded plants under normal conditions, but shows a higher max. Dry-matter production agreed with that calc. from amounts of CO₂ assimilated and respired. A. G. P.

Influence of temperature on the respiration and carbon dioxide assimilation of some green algæ. F. VAN DER PAAUW (Planta, 1934, 22, 396—403).—In *Stichococcus bacillaris*, respiration (I) and CO₂-assimilation (II) are similarly affected by changes in temp. In other cases (e.g., *Oocystis* sp.) (I) increases more rapidly than (II) with rising temp. > 22°. A. G. P.

Uspenski's iron hypothesis of the distribution of algæ. E. G. PRINGSHEIM (Planta, 1934, 22, 269—312).—The extent of the formation of complex Fe compounds (I) is indicated by the limiting p_H for max. colour formation by CNS reagents. The toxic action of Fe is reduced and its nutrient action improved by formation of (I). Numerous factors other than [Fe⁺⁺⁺] have an important influence on the distribution of algæ in waters. A. G. P.

Presence of cellulose and its distribution in the cell-walls of brown and red algæ. G. L. NAYLOR and B. RUSSELL-WELLS (Ann. Bot., 1934, 48, 635—641).—The cellulose (I) content of a no. of species varied from 2 to 15%. The distribution of (I) in the tissues is examined. A. G. P.

Alkaloids of *Dicentra oregana*, Eastwood. See this vol., 1117.

Non-infectious leaf-deforming principle from mosaic tomato plants. M. H. THORNTON and H. R. KRAYBILL (Phytopath., 1934, 24, 19). Juice from diseased plants, after autolysis and boiling, contained the non-infectious leaf-deforming principle. The activity of the juice was not diminished by ppn. of the proteins or by extraction with Et₂O. Infected plants had less reducing sugars, sucrose, starch, and hemicellulose and more total and NO₃-N than healthy plants. A. G.

Uric acid reagent.—See this vol., 1083.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1934.

General, Physical, and Inorganic Chemistry.

Interferometer patterns of the hydrogen isotopes. J. K. ROBERTSON (*Nature*, 1934, 134, 378).—Photographs of Fabry-Perot patterns of the red Balmer line of H_2 and of H_2 containing up to 75–80% of D_2 are reproduced. The method affords a means of estimating the relative amounts of the two isotopes in a mixture. L. S. T.

Stark effect in helium. B. KULLENBERG (*Z. Physik*, 1934, 90, 567–575). A. B. D. C.

Analysis of profiles of helium lines in spectra of B stars. J. S. FOSTER and A. V. DOUGLAS (*Nature*, 1934, 134, 417–418). L. S. T.

Relative intensities of bands in the N_2 α -system measured in the vacuum arc and afterglow of active nitrogen. Excitation function for nitrogen afterglow. F. CAVALLONI (*Z. Physik*, 1934, 90, 342–347). A. B. D. C.

Spectra of neon in the extreme ultra-violet. J. C. BOYCE (*Physical Rev.*, 1934, [ii], 46, 378–381).—Revised and extended data are tabulated, with classifications, of the lines of Ne I, Ne II, Ne III, and Ne IV, in the range λ 2000– λ 282. N. M. B.

Excitation of light by alkali ions. R. E. HOLZER (*Physical Rev.*, 1934, [ii], 46, 280–283).—Light emission was obtained in He, Ne, and A at the lowest ion accelerating potential for the particular alkali ion that lay nearest to the gas in the periodic table. Na ion beam in Ne produced light at lower accelerating potentials than those reported for Ne ions in Ne. N. M. B.

Displacement of high series lines of sodium and potassium by foreign gases; calculation of effective cross-sections of inert gases for very slow electrons. C. FUCHTBAUER, P. SCHULZ, and A. F. BRANDT (*Z. Physik*, 1934, 90, 403–415).—Displacements due to He, Ne, A, and N_2 , measured with a photo-electric photometer, show for high series lines a limiting val. characteristic only of the inert gas; from this val. is deduced the effective cross-section of the inert mol. for very slow electrons. A. B. D. C.

Spectra of singly and doubly ionised sulphur in the region $\lambda\lambda$ 3300–4900 Å. A. HUNTER (*Phil. Trans.*, 1934, A, 233, 303–326).—Full data and classifications are tabulated for approx. 350 lines. New lines are included and previous assignments corr. N. M. B.

New band spectrum of sulphur in the Schumann region. K. WIELAND, M. WEHRLI, and E. MIESCHER (*Helv. phys. Acta*, 1933, 6, 460; *Chem.*

Zentr., 1934, i, 1284).—The absorption of S at 0.5 and 9 mm. pressure and at 200° and 600° has been measured to 1500 Å. A new series of sharp bands at 1850–1600 Å. was observed in the hot vapour. H. J. E.

Lines of neutral sulphur in Procyon. F. E. ROACH (*Science*, 1934, 80, 73).—Six lines are identified with those of neutral S. L. S. T.

Singlet lines of Cl IV. I. S. BOWEN (*Physical Rev.*, 1934, [ii], 46, 377).—Ten singlet and inter-combination lines are classified and the singlet terms of the ground configuration located. N. M. B.

Zeeman effect of the configurations $3p^4 4p$ and $3p^5 5p$ of argon I. J. TERRIEN and H. DIJKSTRA (*J. Phys. Radium*, 1934, [vii], 5, 439–444).—Zeeman data are tabulated for the infra-red $1s$ – $2p$ and the violet $1s$ – $3p$ lines of A I. Vals. of g are discussed for A and Kr (cf. *Inglis, A.*, 1932, 2). N. M. B.

Electron configurations $p^2 s$, $p^4 s$. R. SCHLAPP (*Proc. Roy. Soc. Edinburgh*, 1934, 54, 109–114).—The secular equations for the energy levels of these configurations are deduced. For As the energy levels observed in the arc spectrum agree with theory. J. W. S.

Molecular spectrum of cadmium vapour. S. W. CRAM (*Physical Rev.*, 1934, [ii], 46, 205–209).—Observations of the fluorescence and discharge spectra in the range 1900–5000 Å. to include emission of bands between 2212 and 2288 Å. in both spectra, and the process of excitation of some of the fluorescence spectrum, were made under various conditions of excitation. Potential energy nuclear separation curves are deduced. N. M. B.

Nuclear spins and magnetic moments of the isotopes of antimony. S. TOLANSKY (*Proc. Roy. Soc.*, 1934, A, 146, 182–199).—The Sb II spectrum has been excited in an oxide-free Sb hollow cathode, and examined for fine structure in the region 6800–5000 Å. Structures were measured in 26 lines, and are explained by attributing a nuclear spin of $5/2$ to both Sb^{121} and Sb^{123} . The nuclear magnetic moment of the former, however, is 1.37 times that of the latter. L. L. B.

Polarisation of the ultra-violet band fluorescence of iodine vapour. S. MROZOWSKI (*Acta phys. polon.*, 1933, 2, 229–233; *Chem. Zentr.*, 1934, i, 1004–1005).—The effect of He (10 mm. pressure) on the fluorescence of I vapour, excited at room temp. by the Al spark, has been studied. H. J. E.

Hyperfine structure in the arc spectrum of xenon. E. G. JONES (Proc. Physical Soc., 1934, 46, 634—636).—The hyperfine structure of the 9045, 9799, and 9923 Å. lines of the Xe I spectrum has been investigated, and the separations of the $2p_9$ and $2p_{10}$ terms have been calc. The lines $1s_5-2p$ are readily self-reversed. J. W. S.

Band spectrum of caesium. F. W. LOOMIS and P. KUSCH (Physical Rev., 1934, [ii], 46, 292—301).—Data are tabulated for band systems, in absorption, in magnetic rotation, and in fluorescence, with max. at 6250, 7200, 7667, 4800, and 8950 Å. The first is highly complex, and the last two are new. Quantum assignments are made to 218 bands in the 7667 Å. system. The extrapolated dissociation energy of the ground state is 0.45 volt. N. M. B.

Molecular absorption of mercury vapour in Schumann's region. N. V. KREMENEVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 237—241).—The $\lambda\lambda$ of bands at 2110—2017 Å. (I) and 1754—1647 Å. in the absorption spectrum of Hg mixed with He at 180—360° are tabulated. The convergence limit of system (I) is < 1600 Å. J. G. A. G.

Quenching of mercury resonance radiation by hydrogen, carbon monoxide, and nitrogen. O. S. DUFFENDACK and J. S. OWENS (Physical Rev., 1934, [ii], 46, 417—424).—Dependence on temp. was investigated. Quenching by H_2 was independent of temp. from 473° to 973° abs., that by CO and by N_2 decreased with rise of temp. Quenching mechanisms are proposed and discussed. N. M. B.

Quenching of mercury resonance radiation by compounds containing deuterium. M. G. EVANS (J. Chem. Physics, 1934, 2, 445—451).—The quenching of Hg resonance radiation by H_2 , H_2O , NH_3 , $N(H^1, H^2)_3$, H_2O vapour, and H_2O vapour has been measured. The differences in quenching efficiencies have been referred to the changes in vibrational level of the mols. due to the introduction of H^2 atoms. If the higher vibrational level in $N(H^1, H^2)_3$ is responsible for the quenching, the quenching cross-section fits the general type of resonance curve. M. S. B.

Fluorescence of lead vapour. W. KŁOSKOWSKA (Acta phys. polon., 1933, 2, 239—244; Chem. Zentr., 1934, i, 1005).—Pb vapour at 900° shows 23 bands at 4059—5136 Å. and a series at 3200—4100 Å. On illuminating with a Zn spark, Pb lines at 3684, 4058 Å. were observed, attributed to optical dissociation of Pb_2 mols. H. J. E.

Absorption of saturated bismuth vapour. A. TROJECKA (Acta phys. polon., 1933, 2, 245—252; Chem. Zentr., 1934, i, 1006).—Absorption bands of saturated Bi vapour at 1050° were measured and classified. H. J. E.

Wave numbers of infra-red spectral lines beyond $\lambda 10,000$. H. D. BABCOCK (Physical Rev., 1934, [ii], 46, 382—383).—An application of Kayser's table is described. N. M. B.

Relative multiplet transition probabilities from spectroscopic stability. C. W. UFFORD and F. M. MILLER (Physical Rev., 1934, [ii], 46, 283—285; cf.

this vol., 3).—Relative transition probabilities of different multiplets in Russell-Saunders coupling are tabulated for the transitions d^3p-d^4 , dp^2-pd^2 , and $d^2p^2-d^3p$. N. M. B.

Generalisation of the Michelson experiment. L. BAUMGARDT (Z. Physik, 1934, 90, 327—330).—Theoretical. A. B. D. C.

Electric arcs with fused metals and salts as electrodes. M. PIERUCCI and L. B. SILVA (Nature, 1934, 134, 495—496; cf. A., 1932, 667).—The characteristics of the arcs formed between C and molten Na or its salts, molten Cu, porcelain, or Al are outlined. L. S. T.

Waller-Hartree theory of X-ray scattering applied to the diffuse scattering from crystals. G. G. HARVEY, P. S. WILLIAMS, and G. E. M. JAUNCEY (Physical Rev., 1934, [ii], 46, 365—367).—The inclusion of the extra term, calc. for Ne, in the incoherent part of the scattered radiation due to the operation of the Pauli exclusion principle gives better agreement with experimental results for NaF. N. M. B.

Polarisation of general X-radiation from thick targets. Y. F. CHENG (Physical Rev., 1934, [ii], 46, 243—247).—For bands of the X-ray spectrum between the K-absorption limits of Mo and Nb, of Pd and Rh, and of W and Ta, from targets of W, Cu, and Al, whilst the max. experimental val. of polarisation was < 60%, the polarisation at the quantum voltage of the band by extrapolation is nearly complete, and the polarisation for a given wave-length from targets of lower at. no. is > that from targets of higher at. no., except near the quantum voltage, where it approaches 100%. N. M. B.

Absorption of monochromatic X-rays of short wave-length. T. M. HAHN (Physical Rev., 1934, [ii], 46, 149—153).—The mass absorption coeffs. for the W $K\alpha_1$ line, 208.6 X, were measured for H, C, Al, Cu, Ag, Ta, W, and Pb, and, with a single- instead of a double-crystal spectrometer, measurements were extended to 138 X. Results lead to an expression for the at. absorption coeffs. in agreement with the Klein-Nishina formula. N. M. B.

Dependence of secondary structure in X-ray absorption on crystal form. V. P. BARTON and G. A. LINDSAY (Physical Rev., 1934, [ii], 46, 362—365).—Microphotometer curves of the Ca K absorption edge in the X-ray absorption spectra of calcite, aragonite, dolomite, anhydrite, ankerite, and ovskite, of Fe K in ankerite, Ti K in perovskite, Fe K and Cr K in chromite show, in agreement with Kronig's theory, that the secondary structure is not the same in different compounds, and differs also for two elements in the same crystal. N. M. B.

Scattering of X-rays by silver. A. A. RUSTERHOLZ (Helv. phys. Acta, 1933, 6, 565—569; C. em. Zentr., 1934, i, 1772).—Scattering of Cu K radiation by the (220) plane of Ag has been studied. The electrons of Ag do not contribute to the scattering.

Absorption of hard X-rays by lead. A. ALICHAN JAN and M. KOSMAN (Z. Physik, 1934, 90, 779—781).

—Absorption coeffs. are given for $\lambda\lambda$ between 80 and 24 X. A. B. D. C.

Determination of X-ray line shapes by a double-crystal spectrometer. L. P. SMITH (Physical Rev., 1934, [ii], 46, 343—351). N. M. B.

Natural widths of the K series of W (74). F. K. RICHTMYER and S. W. BARNES (Physical Rev., 1934, [ii], 46, 352—356).—The full widths at half max. in volts, determined by a double-crystal X-ray spectrometer, are: $K\alpha_2$ 43.3, α_1 43.0; β_3 50.0, 48.6; γ_2 37.0, γ_1 37.0; δ_2 34.0, 34 volts. N. M. B.

M series absorption spectrum of metallic bismuth. W. D. PHELPS (Physical Rev., 1934, [ii], 46, 357—362).—Data for the five M absorption edges are tabulated. N. M. B.

Photo-electrons expelled from elements by chromium K radiations. H. R. ROBINSON (Proc. Physical Soc., 1934, 46, 693—702).—The energies of photo-electrons ejected from targets of Au, Pt, W, Sm, La, Sn, Ag, and Cu by Cr K radiation have been measured and compared with the vals. calc. from X-ray data. J. W. S.

Emission of ions and electrons from heated sources. A. J. DEMPSTER (Physical Rev., 1934, [ii], 46, 165—166).—Electrons from an oxide-coated filament and Li ions from spodumene allowed pin-hole photographs to be made. In addition to general emission there are conc. point sources where the emission is especially intense. N. M. B.

Surface ionisation on glowing metals. A. I. ANSELM (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 329—334).—Theoretical. H. J. E.

Ionisation of alkali metal atoms at tungsten, molybdenum, and tungsten coated with thorium. L. DOBREZOV (Z. Physik, 1934, 90, 788—801).—Ionisation at different temp. follows the Langmuir-Saha formula. A. B. D. C.

Secondary electron emission and atomic number. P. L. COPELAND (Physical Rev., 1934, [ii], 46, 167—168).—The relative mean variation of the secondary emission from a given element, as a function of the energy of the primary electrons, is related to the at. no. of the elements bombarded by an equation of the form $R=k/E_p^s$, where R is the ratio total secondary current/incident current, E_p is the energy of the incident beam, and k and s are consts. N. M. B.

Ionisation of air by electrons liberated from "air-equivalent" solid substances by X-rays. E. MIEHLNICKEL (Ann. Physik, 1934, [v], 20, 737—772).—The mechanism of closed ionisation chambers was investigated. The ionisation current in such a chamber depends on the electron emission of the walls, which must be "air-equiv." if the chamber is to be used for the abs. measurement of X-rays. A. J. M.

Ionisation by positive ions in helium. J. S. TOWNSEND and G. D. YARNOLD (Phil. Mag., 1934, [vii], 18, 594—606).—In He ionisation can occur by single collisions with electrons and positive ions. The authors' theory of the conductivity of gases is supported. H. J. E.

Effect of adsorbed oxygen on the photo-electric emissivity of silver. A. K. BREWER (J. Amer. Chem. Soc., 1934, 56, 1909—1913).—Three effects are distinguished: (1) at room temp. the presence of O_2 slightly enhances the emissivity, the effect disappearing with removal of O_2 ; (2) after heating in O_2 , the Ag when heated in vac. shows a greatly enhanced emission; (3) heating in O_2 or exposure to O_3 destroys the emissivity. It is suggested that (1) and (2) are due to positive O ions and (3) to negative O ions. E. S. H.

Photo-electric thresholds of some turned metallic surfaces. J. S. HUNTER (Proc. Roy. Soc. Edinburgh, 1934, 54, 102—108).—The long-wave photo-electric thresholds for turned Cu, Ag, Sb, Bi, Sn, Pb, Ni, Fe, Zn, Al, brass, and cast steel, as measured with a valve electrometer, are 2985, 3200, 2996, 3075, 3000, 3060, 3125, 2980, 3225, 3740, 3025, and 2916 Å., respectively. These are approx. the vals. for the same metals in the partly outgassed state. It is concluded that a turned surface is partly denuded of occluded gases. J. W. S.

Activation energy on vaporisation and condensation. N. FUCHS (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 335—340).—The possibility of experimental verification of Miyamoto's hypothesis is discussed (cf. A., 1933, 787). The emission of an electron from a surface covered with a gas or an oxide film probably requires an activation energy. H. J. E.

Efficiencies of ionisation of helium and mercury by electron impact at high voltages. J. W. LISKA (Physical Rev., 1934, [ii], 46, 169—176; cf. Smith, A., 1931, 665).—An apparatus for measuring relative ionisation efficiencies at high voltages is described. Results for He and Hg vapour are given as a function of electron velocities up to 11 kv., and are compared with vals. based on classical and quantum mechanics. N. M. B.

Magnetic electrons. R. ZAIKOFF (J. Phys. Radium, 1934, [vii], 5, 431—435).—Mathematical. The Dirac equations and the Whittaker tensorial equations lead to the postulation of four different types of electrons of positive mass. N. M. B.

Fock's self-consistent field for electrons in metals. L. BRILLOUIN (J. Phys. Radium, 1934, [vii], 5, 413—418; cf. A., 1933, 1005).—Mathematical. Application of the equations due to Fock and the methods due to Hartree leads to the same general results. N. M. B.

Electron scattering by atomic electrons. A. L. HUGHES and R. C. HERGENROTHER (Physical Rev., 1934, [ii], 46, 180—186).—Velocity distribution curves are given for electrons scattered by He atoms in the angular range 10—60° and electron energies of 800, 1000, and 1200 volts. Narrow max. denote elastic scattering, and broad peaks represent inelastic scattering associated with collisions between incident electrons and at. electrons when the binding energy is small compared with energy transfers during the collision. Jauncey's theory of the breadth of the modified Compton line is discussed. N. M. B.

Polarisation of electrons in magnetic fields. E. RUPF (Z. Physik, 1934, 90, 166—176).

A. B. D. C.

Approximate wave functions for high-energy electrons in Coulomb fields. W. H. FURRY (Physical Rev., 1934, [ii], 46, 391—396).—Mathematical.

N. M. B.

Excitation of band systems by electron impact. G. O. LANGSTROTH (Proc. Roy. Soc., 1934, A, 146, 166—177).—A theory of direct excitation by electron impact for band systems of symmetric diat. mols. is developed, from which the complete relative intensities of bands of a system may be calc.

L. L. B.

Stopping of fast particles and the creation of electron pairs. H. BETHE and W. HEITLER (Proc. Roy. Soc., 1934, A, 146, 83—112).—The probability for the emission of radiation by fast electrons passing through an atom is calc. by Born's method. The quantum theory is invalid for electrons of energy $>137\text{ mc}^-$. The probability for the creation of a positive and a negative electron by a γ -ray is calc.

L. L. B.

Compton effect of bound electrons. W. FRANZ (Z. Physik, 1934, 90, 623—649).—Theoretical.

A. B. D. C.

Self energy of the electron. V. WEISSKOPF (Z. Physik, 1934, 90, 817—818).—A correction (cf. this vol., 711).

A. B. D. C.

Dirac's theory of the positron. W. HEISENBERG (Z. Physik, 1934, 90, 209—231).

A. B. D. C.

Emission of positive electrons by a radioactive source. A. I. ALICHANOV and M. S. KOSODAEV (Z. Physik, 1934, 90, 249—265).

A. B. D. C.

Theory of spontaneous positron disintegration. E. N. GAPON (Z. Physik, 1934, 90, 279—286).

A. B. D. C.

Range and absorption of natural H -rays. E. FRANK (Z. Physik, 1934, 90, 764—772).— H -Rays liberated from paraffin by Po α -rays show a group structure.

A. B. D. C.

Scattering of molecular rays in gases. II. F. KNAUER (Z. Physik, 1934, 90, 559—566; cf. A., 1933, 203).—He slow rays are scattered by Hg to a greater extent than fast rays. He and H rays were investigated to 0.9° , and at this angle fast rays are scattered to the greater extent.

A. B. D. C.

Scattering of lithium ions by a polycrystalline nickel surface. A. LONGACRE (Physical Rev., 1934, [ii], 46, 407—410).—The angle of max. scattering is independent of the incident energy and nearly so of the angle of incidence. The ratio of the most probable energy of the scattered ions to that of the incident ions decreases as the total angle of scattering increases and is independent of the energy or the angle of incidence.

N. M. B.

Scattering of hydrogen and helium beams in mercury vapour. R. M. ZABEL (Physical Rev., 1934, [ii], 46, 411—416).—Scattering curves are given for the angular range 5 — 65° at beam temp. 115° , 300° , and 590° abs. Results are compared with theory.

N. M. B.

Isotopic constitution and at. wts. of the rare-earth elements. F. W. ASTON (Proc. Roy. Soc., 1934, A, 146, 46—55).—A provisional survey of the isotopic constitution of the rare-earth elements has been made, using intense anode-ray beams and the mass spectrograph. Thirty new isotopes have been discovered, and the following at. wt. vals. are obtained from the mass spectra and % abundance: La 138.91 ± 0.05 , Ce 140.13 ± 0.05 , Pr 140.91 ± 0.05 , Nd 143.5 ± 0.2 , Sm 150.1 ± 0.2 , Eu 151.90 ± 0.03 , Gd 156.9 ± 0.2 , Tb 158.91 ± 0.05 , Dy 162.5 ± 0.2 , Ho 164.91 ± 0.05 , Er 167.15 ± 0.2 , Tm 168.91 ± 0.05 , Yb 173.2 ± 0.2 , Lu 174.91 ± 0.05 . Errors in the International Table of At. Wts. for 1934 are indicated.

L. L. B.

Measurements with a Geiger-Muller counter using polished electrodes. E. HENNING and R. SCHADE (Z. Physik, 1934, 90, 597—606).—A counter using electrodes free from films of foreign substances is described.

A. B. D. C.

Unknown radioactivity. A. V. GROSSE (J. Amer. Chem. Soc., 1934, 56, 1922—1924).—An α -activity, having a mean life of 1 year, detected in eudyalite, has not been traced to any known origin.

E. S. H.

Radioactivity of potassium. G. VON HEVESY, M. PAHL, and R. HOSEMANN (Nature, 1934, 134, 377).—A discussion of results.

L. S. T.

Radioactivity of neodymium and samarium. W. F. LIBBY (Physical Rev., 1934, [ii], 46, 196—204).—Methods are described for determining the abs. activity of an element, the penetrating power of its radiation, the deflectability in a magnetic field, and the sign of the charge of the radiation. Nd emits β -rays of max. $H\phi$ val. 355, and 2.4 mm. air-penetrating power. The half-life is slightly $< 1.5 \times 10^{12}$ years. The range of the Sm α -particle is 1.23 ± 0.05 cm. in air, and its half-life is 6.3×10^{11} years. Gd, Pr, Sn, I, and Be are inactive. If they emit particles of ranges > 1 cm. they cannot have half-lives $< 10^{14}$ years. The limit for Be is 10^{15} years.

N. M. B.

Radioactivity of samarium. G. ORTNER and J. SCHINTLMEISTER (Z. Physik, 1934, 90, 698—699).—Only a group of α -rays could be detected.

A. B. D. C.

Diffusion of radioactive recoil. (MILLE) C. CHAMIE (J. Phys. Radium, 1934, [vii], 5, 436—438; cf. this vol., 470).—Langevin's theory (cf. this vol., 470) is confirmed. When the distance between the receiver and the source is $<$ the recoil range the quantity of Th-C'' collected in absence of field was 8%, and with saturated field 27% of the total amount present in the source, showing the influence of re-absorption of the recoil by the source.

N. M. B.

Ionisation of air by α - and β -rays as a function of pressure. O. E. POLK (Physical Rev., 1934, [ii], 46, 405—406).—Ionisation by β -rays excited γ -rays increased at a decreasing rate with pressure. Ionisation by Po α -rays decreased rise of pressure; at 80 atm. the val. was approx. 0.10 of that at atm. pressure.

N. M.

Counting of α -particles by determination of the charge which they carry. R. GRÉGOIRE (A

Physique, 1934, [xi], 2, 161—196).—The method used is an improvement of that of Rutherford and Geiger, in which the α -particles fall on a plate, the charge of which is determined by an electrometer. A. J. M.

Theory of anomalous α -scattering. P. WENZEL (Z. Physik, 1934, 90, 754—763). A. B. D. C.

Scattering of α -rays by H nuclei. H. POSE and K. DIEBNER (Z. Physik, 1934, 90, 773—778). A. B. D. C.

Absorption coefficients of Ra-C' γ -radiation. H. KETELAAR, A. PICCARD, and E. STAHEL (J. Phys. Radium, 1934, [vii], 5, 385—388).—Absorption data are tabulated, and plotted as a function of filter thickness, for Al, Fe, Sn, Pb, and U. The observed and calc. coeffs. of absorption agree for Al and Fe, but for the other metals differences \propto (at. no.)³ are found. N. M. B.

Spectrography of γ -rays by diffraction at crystals. M. J. N. VALADARES (Ann. Physique, 1934, [xi], 2, 197—240).—The spectrum of the γ -rays from Ra-B and -C in the range 100—250 X has been investigated. All intense lines within this range are fluorescence lines. The X-ray spectrum (K series) for Ra has been studied. Certain lines attributed to radio-Th in the spectrum of the γ -radiation from the Th family are shown to be due to the transformation Th-B \rightarrow Th-C (cf. A., 1932, 556, 671, 791; 1933, 111). A. J. M.

Internal conversion of γ -rays. J. B. FISK and H. M. TAYLOR (Proc. Roy. Soc., 1934, A, 146, 178—181).—A nucleus may emit fields of radiation due to magnetic multipoles, besides those arising from electric multipoles. Such magnetic multipole radiations give rise to conversion coeffs. much $>$ the corresponding vals. for electric multiple radiation. On the assumption of a simple model nucleus, it is deduced that the amount of "magnetic" radiation present is too small to make any appreciable alteration in the conversion coeffs. as given by Hulme and by Taylor and Mott (A., 1933, 110, 111, 1224). L. L. B.

Scattering of short-wave γ -rays. L. MEITNER [with H. H. HUFFELD and H. KOSTERS] (Helv. phys. Acta, 1933, 6, 445—450; Chem. Zentr., 1933, ii, 3807—3808).—Results are recorded for the scattering of filtered γ -radiation from Th-C' and Ra-C. With decreasing λ the photo-effect becomes progressively smaller compared with scattering, and Compton scattering replaces classical scattering. H. J. E.

Excitation function of proton emission from aluminium nuclei by α -rays of high energy. O. HAXEL (Z. Physik, 1934, 90, 373—383). A. B. D. C.

Proton emission of boron and phosphorus under fast α -rays. R. F. PATON (Z. Physik, 1934, 90, 586—596). A. B. D. C.

Energy spectra of the neutrons from the disintegration of fluorine, boron, and beryllium by α -particles. T. W. BONNER and L. M. MOTT-SMITH (Physical Rev., 1934, [ii], 46, 258—267).—Using an expansion chamber filled with H₂ or CH₄ at 15 atm., range-distribution curves were obtained of the recoil protons from Po-F, Po-B, and Po-Be

neutrons. In the first and last cases disintegration schemes are proposed for the neutron groups found in the radiation from the sources. The anomalously low val. of the calc. mass of the neutron in the second case is discussed. N. M. B.

Detection of neutrons liberated from beryllium by γ -rays: new technique for inducing radioactivity. L. SZILARD and T. A. CHALMERS (Nature, 1934, 134, 494—495).—A radiation emitted from Be bombarded by γ -rays from Ra (from containers used in therapy) excites induced radioactivity (I) in I, and it is concluded that neutrons are thus liberated from Be. Using the method previously described (this vol., 1152), the AgI obtained after irradiation from EtI showed an activity with a half-period of 30 min. L. S. T.

Atomic disintegration measurements with metallic sodium. A. KÖNIG (Z. Physik, 1934, 90, 197—208; cf. this vol., 471). A. B. D. C.

Artificial radioactivity. C. D. ELLIS and W. J. HENDERSON (Proc. Roy. Soc., 1934, A, 146, 206—216).—The phenomenon of induced radioactivity discovered by Curie and Joliot (this vol., 714) has been studied, with special reference to the influence of the energy of the α -particle on the production of radio-P from Al. The relative magnitudes of the effects from B, N, and Mg have been measured. The energy of emission of the positrons from radio-P has been investigated, using both an absorption method and magnetic analysis. L. L. B.

Radioactivity artificially induced by neutron bombardment. M. S. LIVINGSTON, M. C. HENDERSON, and E. O. LAWRENCE (Proc. Nat. Acad. Sci., 1934, 20, 470—475).—Neutron-induced activity in CaF, Al, Ag, Si, Cu, and Zn was investigated. Ionisation due to the irradiated samples was plotted against time for Ag, Cu, and Al. For Ag there are two decay periods, probably connected with the two isotopes. The half-lives of the activity periods are 154 ± 10 and 26 ± 4 sec. for Ag, and 9.5 ± 0.5 , and 7 min. for Al and Cu, respectively. Abs. induced activities are estimated. N. M. B.

Possibility of decomposition of the ordinary elements by neutrons. H. HERSZFINKIEL and A. WRONBERG (Acta phys. polon., 1933, 2, 157—159; Chem. Zentr., 1934, i, 1939).—No neutron emission (I) was detected from KF, Bi(NO₃)₃, or KCl. For K the ionisation due to (I), if any, is $< 15\%$ of that due to γ -rays. H. J. E.

Inelastic collisions with changes of mass and the problem of nuclear disintegration with capture or non-capture of a neutron or another nuclear projectile. W. D. HARKINS and D. M. GANS (Physical Rev., 1934, [ii], 46, 397—404).—Relativity equations for cases in which the nuclear projectile is not captured in at. disintegrations, and for velocities not too close to that of light, are developed. Analysis of evidence indicates that there is no instance of any nucleus being disintegrated by bombardment of another nucleus without capture. N. M. B.

Possibility of disintegrating nuclei by neutrons with the emission of three heavy particles. L. MISOVSKI, I. KURTSCHATOV, N. DOLROTN, and I. GUREVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 230—232).—Two photographs of disintegration experiments with neutrons, one in the atm. of a Wilson chamber and the other in an emulsion, each show three non-coplanar tracks of common origin. The tracks are attributed to the emission of three heavy particles by a nucleus under neutron impact.

J. G. A. G.

Fermi effect in aluminium. B. KURTSCHATOV, I. KURTSCHATOV, G. SCHTSCHEPKIN, and A. VIBE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 226—229).—Two radioactive substances with half-life periods of 12 min. (I) and >12 hr. (II), respectively, are produced by neutron bombardment of Al. Radioactive Mg is formed and the changes corresponding with (I) are ${}_{13}\text{Al}^{27} + {}_0^1\text{n} \longrightarrow {}_{12}\text{Mg}^{27} + \beta + \gamma$. Radioactive Na is probably involved in change (II).

J. G. A. G.

Fermi effect in phosphorus. I. KURTSCHATOV, L. MISOVSKI, G. SCHTSCHEPKIN, and A. VIBE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 221—225; cf. this vol., 714, 826).—The bombardment of P by neutrons affords two products with half-life periods of approx. 3 hr. and 3 min., respectively. The changes suggested are: (1) ${}_{15}\text{P}^{31} + {}_0^1\text{n} = {}_{14}\text{Si}^{31} + {}_1^1\text{H}^1$ and (2), ${}_{15}\text{P}^{31} + {}_0^1\text{n} = {}_{13}\text{Al}^{28} + {}_2\text{He}^4$, ${}_{13}\text{Al}^{28} = {}_{14}\text{Si}^{28} + \epsilon$. The probabilities of reactions (1), (2), and ${}_{14}\text{Si}^{28} + {}_0^1\text{n} = {}_{13}\text{Al}^{28} + {}_1^1\text{H}^1$, ${}_{13}\text{Al}^{28} = {}_{14}\text{Si}^{28} + \epsilon$ are approx. 15 : 1 : 2.

J. G. A. G.

Chemical separation of the radioactive element from its bombarded isotope in the Fermi effect. L. SZILARD and T. A. CHALMERS (Nature, 1934, 134, 462).—A new principle is described for the separation of the radioactive isotope (I) of a bombarded element from the main bulk and applied to I. EtI has been irradiated and a trace of I added to protect (I). Reduction and pptn. as AgI gave a ppt. 10 times as active as the irradiated EtI (cf. this vol., 1151).

L. S. T.

The new elementary particles. E. N. DA C. ANDRADE (Nature, 1934, 134, 345—347).—A summary.

L. S. T.

Nuclear spin of radioactive elements. G. GAMOW (Proc. Roy. Soc., 1934, A, 146, 217—222).—The possible effect of nuclear angular momenta on β -ray spectra is considered.

L. L. B.

Nuclear magnetic moments and the properties of the neutron. I. TAMM (Nature, 1934, 134, 380).—A criticism (cf. this vol., 827).

L. S. T.

Pauli's principle in nuclei. W. M. ELSASSER (J. Phys. Radium, 1934, [vii], 5, 389—397; cf. this vol., 6).—A simple nuclear potential scheme, the same for neutrons and protons, is proposed for the succession of quantum nos. Direct relation between periodic nuclear properties and the "envelopes" of the neutrons is found, and the existence of sub-groups is considered. There are indications that the neutrons and protons are arranged in layers.

N. M. B.

Structure of heavy nuclei. A. SCHIDLÖF (Helv. phys. Acta, 1933, 6, 581—596; Chem. Zentr., 1934, i, 1279).—The heavy nuclei contain, in addition to α -particles, a stable unit composed of a proton and 3 neutrons.

H. J. E.

Annihilation radiation from paraffin bombarded with neutrons. H. J. WÄLKE (Nature, 1934, 134, 495).—A discussion.

L. S. T.

Spectroscopic stability. O. HALPERN and E. WASSER (Physical Rev., 1934, [ii], 46, 177—180).—A direct test of the spectroscopic stability required by quantum mechanics shows that the atoms of saturated TI vapour exhibit no double refraction due to spatial quantisation in a magnetic field up to 1200 gauss, establishing a constancy of at. refractivity of 1 part in 10^4 .

N. M. B.

Origin of the cosmic corpuscles. L. G. H. HUXLEY (Nature, 1934, 134, 418—419).

L. S. T.

Analysis of cosmic-ray data. L. V. KING (Physical Rev., 1934, [ii], 46, 154—156).

N. M. B.

Determination of the ultra-radiation in the upper atmosphere by means of the counter tube. E. REGENER and G. PFOTZER (Physikal. Z., 1934, 35, 779—784).—The apparatus used for the investigation of ultra-radiation up to heights of 28 km. is described. The curve of intensity of radiation against height is approx. the same as that obtained with the ionisation chamber.

A. J. M.

Further determinations of the ultra-radiation in the upper atmosphere with open ionisation chambers. E. REGENER and R. AUER (Physikal. Z., 1934, 35, 784—788).—Experiments made with open ionisation chambers lined with paraffin or celluloid indicated that the primary radiation is not composed of neutrons.

A. J. M.

Determination of ultra-radiation on mountains in different latitudes. H. HOERLIN (Physikal. Z., 1934, 35, 793—795).—The ultra-radiation in European latitudes has a different intensity and composition from that at the Equator. There is a considerable increase in the latitude effect with the height, which is to be expected, since there is a greater proportion of "soft" radiation at great heights, which is markedly affected by the earth's magnetic field.

A. J. M.

Binding energies of the neutron and the proton. L. STRUM (Nature, 1934, 134, 497—498).—Theoretical.

L. S. T.

Heights of nuclear potential barriers. V. A. KRAVTSOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 233—237).—The extrapolation, to heavy elements exhibiting radioactivity, of the rectilinear relation between the at. no. of light elements and the height of the nuclear potential barrier (A., 1933, 205, 443) is considered. The val. for Sm (*ibid.*, 442) agrees well, and the max. deviation amongst the heavy radioactive elements is $\pm 20\%$. The data for B and B¹¹ show that the isotope with odd at. wt. has the higher potential barrier. The effective radius of the nucleus increases < 1.6-fold through the periodic table as compared with the factor 2.5—3 required by Gamow's cube-root hypothesis. The *d* of radioactive nuclei must be 4 times > that of N.

J. G. A.

Spin and statistics of the deuteron from thermal data. F. PATAT and H. HOCH (Monatsh., 1934, 64, 229—235).—The variation of rotation heat with temp. is compared for H_2 , H_2^2 , H^2H^2 , and the ortho- and para-modifications of H_2 and H_2^2 , and the equilibrium consts. of the change $\text{H}_2 + \text{H}_2^2 \rightleftharpoons 2\text{H}^2\text{H}^2$ are calc. for different temp. The use of these data for the calculation of the spin and statistics of the deuteron is discussed. A. J. M.

Magnetic moment of (I) the proton, (II) the deuteron. I. I. RABI, J. M. B. KELLOGG, and J. R. ZACHARIAS (Physical Rev., 1934, [ii], 46, 157—163, 163—165).—I. The val. $3.25 \pm 10\%$ was obtained by a method depending on the deflexion of a beam of neutral H atoms in weak non-homogeneous magnetic fields, the nuclear spin being partly decoupled from the electron spin. A special method of producing the field is described.

II. Using a method similar to the above, the val. 0.75 ± 0.2 nuclear unit was obtained for H^2 . In each case the method does not distinguish the sign of the nuclear moment. N. M. B.

Vibrational isotope effects in three-particle systems. II. A. ADEL (Physical Rev., 1934, [ii], 46, 222—225; cf. this vol., 232).—Mathematical. A quantum-mechanical analysis of the general potential energy function of the linear unsymmetrical triat. mol. XYZ is developed in terms of the infra-red spectrum of the mol. N. M. B.

Hartree fields of carbon. C. C. TORRANCE (Physical Rev., 1934, [ii], 46, 388—390).—A new integration method is described, and the wave functions for the ground state and first excited state of C are tabulated. N. M. B.

Absorption spectrum of oxygen at high pressures and the existence of O_4 molecules. H. SALOW and W. STEINER (Nature, 1934, 134, 463).

Photographs of the ultra-violet solar spectrum in the stratosphere, and the vertical distribution of ozone. E. REGENER and V. H. REGENER (Physikal. Z., 1934, 35, 788—793).—A spectrograph was sent up to a height of 30 km., photographs of the ultra-violet spectrum being taken automatically at definite intervals. The thickness of the O_3 layer above the apparatus was determined, assuming it to be 0.24 cm. at 10 km. The max. $[\text{O}_3]$ was found at about 24 km. A. J. M.

Absorption spectrum of nitrous oxide and energy of dissociation of nitrogen. L. HENRY (Nature, 1934, 134, 498—499).—The limit of continuous absorption of N_2O moves towards the long wave-length with rising temp. The limit of absorption extrapolated for $T_{\text{abs}} = 0^\circ$ is $2140 \pm 130 \text{ \AA}$. corresponding with the energy $D_{\text{N}_2\text{O}} = 132,000 \pm 8000 \text{ g.-cal}$. The absorption spectrum after photochemical decomp. of N_2O by radiations of a Cd spark filtered through AcOH shows the presence of increasing amounts of NO, indicating the reaction $\text{N}_2\text{O} = \text{NO} + \text{N}$. The photochemical decomp. of N_2O is explained as $\text{N}_2\text{O}(^1\Sigma) = \text{NO}(^2\Pi) + \text{N}(^2D) - 132,000 \text{ g.-cal}$. This gives $(D)_{\text{N}_2}(^1\Sigma) \longrightarrow \text{N}_2(^4S) = 6.9 \pm 0.2 \text{ volts or } 158,000 \pm 8000 \text{ g.-cal}$. L. S. T.

Band spectrum of NaK. F. W. LOOMIS and M. J. ARVIN (Physical Rev., 1934, [ii], 46, 286—291).—Full data are tabulated for the visible and infra-red of the NaK spectrum in absorption and magnetic rotation. The dissociation energies of the four states of the mol. are 0.62, 0.24, 0.14, and 0.74 volt. Two new band systems, in the green and infra-red, probably due to perturbations, have been found and analysed. N. M. B.

Abnormal rotation of molecules. O. OLDENBERG (Physical Rev., 1934, [ii], 46, 210—215; cf. A., 1931, 404).—Explanations of abnormal rotation are tested by investigation of the OH bands. Strongly abnormal rotation is observed in emission and normal rotation in absorption. In the former case rotation is reduced to its normal val. by addition of He, and there is no appreciable persistence of rotation in collisions. General rules for the determination of the temp. from band spectra are proposed. N. M. B.

Proton spin and hyperfine structure in band spectra. S. MROZOWSKI (Acta phys. polon., 1933, 2, 235—237; Chem. Zentr., 1934, i, 1004).—No effect attributable to proton spin was observed in the band lines of the OH band at 3064 \AA . The effect observed with the HgH band (Hulthén, A., 1932, 104) was probably due to an isotope effect. H. J. E.

Absorption of light by sodium chloride crystals under electron bombardment. L. REVERDATTO (Z. Physik, 1934, 90, 512—520).—An absorption max. appears at $472 \text{ m}\mu$. A. B. D. C.

Band systems of BaCl. A. E. PARKER (Physical Rev., 1934, [ii], 46, 301—307).—Data and analyses are given for a green system, $\lambda\lambda 5047\text{—}5322$, $^2\Pi\text{—}^2\Sigma$ transition, and two ultra-violet systems with (0,0) bands at $\lambda 3922$ and $\lambda 3692$, respectively, $^2\Sigma\text{—}^2\Sigma$ transitions. The isotope effect of Cl^{35} and Cl^{37} was observed. N. M. B.

Band spectra of aluminium hydride and deuteride. W. HOLST and E. HULTHÉN (Z. Physik, 1934, 90, 712—727).—Comparison of these two spectra indicates the interaction of electronic and nuclear motion. A. B. D. C.

New band spectrum of aluminium hydride. W. HOLST (Z. Physik, 1934, 90, 728—734). A. B. D. C.

New $^1\Sigma^{*}\text{—}^1\Pi$ system of aluminium hydride.** W. HOLST (Z. Physik, 1934, 90, 735—741). A. B. D. C.

Activated states in the spectrum of copper hydride. A. HEIMER and T. HEIMER (Nature, 1934, 134, 462). L. S. T.

Band spectrum and structure of the CP molecule. H. BARWALD, G. HERZBERG, and L. HERZBERG (Ann. Physik, 1934, [v], 20, 569—593; cf. A., 1930, 1074).—The complete vibrational and rotational analysis of the band spectrum of the CP mol. from 5000 to 2900 \AA . is given. The band system from 4400 to 5000 \AA . is weak. Vals. are given for the moment of inertia, internuclear distance, and other mol. consts. for the $^2\Sigma^*$ and $^2\Sigma$ states. There is great similarity between the CP mol. and SiN, CN, and N_2^+ . A. J. M.

Absorption spectrum of tin sulphide vapour. K. BUTKOV and W. TSCHASSOVENNI (*Z. Physik*, 1934, 90, 815—816).—Absorption of SnS was investigated from 3800 to 2530 Å., and ground state vibrational levels are deduced. A. B. D. C.

Absorption spectrum of mercuric sulphide. P. K. SEN-GUPTA (*Nature*, 1934, 134, 498).—A reply to criticism (this vol., 828). L. S. T.

Absorption spectra of the vapours of trivalent bismuth and antimony halide compounds. K. BUTKOV (*Z. Physik*, 1934, 90, 810—814).—Absorption of BiI₃, BiBr₃, and SbI₃ was investigated from 7000 to 2000 Å. and the corresponding photo-dissociation is discussed. A. B. D. C.

Absorption spectra of cobalt compounds. V. Cobalt ethylenediamine halogen complexes. M. L. ERNSBERGER and W. R. BRODE (*J. Amer. Chem. Soc.*, 1934, 56, 1842—1843).—A study of absorption spectra of compounds of the type (Co en₂X₂)X (X=halogen) has shown a regular decrease in mean frequency difference corresponding with increase in the wt. of substituents. The prep. of the compound (Co en₂I₂)I is described. E. S. H.

Absorption spectra of the samarium ion in solids. IV. Absorption of Sm(EtSO₄)₃·9H₂O and partial energy level diagrams for the Sm⁺⁺⁺ ion as it exists in hydrated crystalline samarium ethyl sulphate, samarium iodide, and samarium perchlorate. F. H. SPEDDING and R. S. BEAR (*Physical Rev.*, 1934, [ii], 46, 308—315; cf. A., 1933, 997).—Complete data for the hexagonal Et sulphate in the temp. range 20—295° abs., and a summary for the iodide and perchlorate, are tabulated. N. M. B.

Absorption spectra of some organic molecules in the vapour state. R. A. REHMAN, R. SAMUEL, and SHARF-UD-DIN (*Indian J. Physics*, 1934, 8, 537—545).—The absorption limits and max. have been measured for Pr^δI, Pr^αI, Bu^δI, and *n*-hexyl iodide and [CH₂Br]₂, Pr^δBr, Bu^δBr, and octyl bromide. The absorption spectra are almost independent of the nature of the alkyl radical. AcCl and CH₂Cl·COCl show band systems with points of pre-dissociation and continuous absorption bands with two max., but CCl₃·COCl, CCl₃·CHO, and CBr₃·CHO have a continuous spectrum in place of the band spectrum. J. W. S.

Absorption and fluorescence spectrum of decacyclene and tribenzyldecacyclene. B. KLARNER and S. WOSZCZEROWICZ (*Acta phys. polon.*, 1933, 2, 1—5; *Chem. Zentr.*, 1934, i, 1780).—Each substance in C₆H₆ solution gave 8 absorption bands and a continuum commencing below 3125 Å. Two of the bands correspond with absorption bands of C₁₀H₈ at 3235, 3130 Å. Green fluorescence was observed. H. J. E.

Absorption spectra of cyanidin and delphinidin derivatives.—See this vol., 1226.

Absorption spectrum of vitamin-E.—See this vol., 1146.

Spectrum of chlorophyll. J. A. PRINS (*Nature*, 1934, 134, 457—458).—Absorption measurements for alcoholic solutions of chlorophyll-*a* and -*b* are recorded graphically and discussed. L. S. T.

Infra-red absorption spectrum of water containing deuterium. J. W. ELLIS and B. W. SORGE (*J. Chem. Physics*, 1934, 2, 559—564).—The absorption in the region 1—10 μ has been determined for H₂O containing 60% H² and 99.5% H², respectively. The fundamental frequencies, as indicated by the max., are in good agreement with those obtained by an isotopic shift calculation from the data for H₂O. This does not necessarily indicate a similarity between vapour and liquid mols. of H₂O, H¹H²O, and H₂O. The degree of polymerisation of H₂O appears to be greater than that of H₂O. M. S. B.

Analysis of the pure rotation spectrum of the water molecule. M. ELJASCHWITSCH (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 3, 248—252).—20 of the 32 frequencies observed by Wright and Randall (A., 1933, 1102) have been identified with transitions and frequencies deduced from vibration-rotation spectrum data. J. G. A. G.

Absorption of carbon dioxide in the neighbourhood of the band λ=2.7 μ, between 300° and 1100° abs. C. TINGWALDT (*Physikal. Z.*, 1934, 35, 715—720).—The effect of temp. and thickness of layer on the absorption of CO₂ in the region of 2.7 μ was investigated. From the results, the emissivity was calc. (cf. Schack, *Z. tech. Physik*, 1924, 5, 267). A. J. M.

Infra-red absorption of solutions of hydroxides and hydrolysing salts. E. K. PLYLER and W. GORDY (*J. Chem. Physics*, 1934, 2, 470—473).—Aq. NaOH, KOH, and LiOH have absorption bands at 3.65 and 5.2 μ, even in concn. as low as 0.1N. Aq. ZnCl₂, ZnBr₂, NH₄OAc, Na₂CO₃, NaOAc, Na₂B₄O₇, Na₂SiO₃, and Al₂(SO₄)₃ have bands at approx. 3.45, 4.5, 5.2, and 5.6 μ. When the solution is acid in reaction the more intense bands are at 3.45 and 5.2 μ, whilst basic solutions give a strong band at 5.6 μ. The former are probably due to undissociated hydroxide mols. attached to H₂O mols. and the 5.6 μ band is due to undissociated, weak, hydrated acid mols. The intensity of these bands is a measure of the hydration. M. S. B.

Infra-red absorption of alcoholic solutions of hydroxides. E. K. PLYLER and F. D. WILLIAMS (*J. Chem. Physics*, 1934, 2, 565—566).—11 bands have been observed between 0.76 μ and 5.20 μ, and they are the same for both NaOH and KOH in EtOH. If those at 3.80 μ and 5.20 μ are fundamental, the remaining bands may be classed as harmonics. There is apparently very little difference between the behaviour in H₂O and EtOH, indicating that the energy levels between solvent and solute are the same in each. M. S. B.

Transmission measurements in the spectral region between 50 and 240 μ. C. H. CARTWRIGHT (*Z. Physik*, 1934, 90, 480—488).—Transmission measurements are given for paraffin wax, colophony, cellophane, bakelite, rhombic S, hard rubber, black tissue paper, white filter-paper, black photo-paper, camphor black, Welsbach mantle material, lampblack, glass, and of paraffin with NaCl, KCl, glass, TiCl, TiBr, CaF₂, CsCl, NH₄Cl, TlI, KI, and

Structure and polarisation of Raman bands of water. I. R. RAO (Z. Physik, 1934, 90, 658—662).—Structure and polarisation of these bands are largely due to spectrographic errors with quartz instruments.

A. B. D. C.

Raman spectrum of heavy water vapour. D. H. RANK, K. D. LARSEN, and E. R. BORDNER (J. Chem. Physics, 1934, 2, 464—467).—Heavy H_2O of d_{20}^{25} 1.073 was used and the v.p. in the scattering tube was 2 atm. A line $\Delta\nu$ 2666 cm^{-1} was found for H_2O and $\Delta\nu$ 2718 cm^{-1} for $\text{H}^1\text{H}^2\text{O}$. The line $\Delta\nu$ 3650 cm^{-1} of H_2O was resolved into 3646.1 and 3653.9 cm^{-1} . The Raman spectrum of H_2O is discussed on the basis of Mecke's infra-red absorption of H_2O . M. S. B.

Molecular scattering of light by binary gaseous mixtures. R. ANANTHAKRISHNAN (Indian J. Physics, 1934, 8, 555—579).—From thermodynamic grounds a formula is derived for the extinction coeffs. of binary gaseous mixtures at high pressures which is in agreement with Zernike's formula derived from statistical grounds (Diss., Amsterdam, 1915); for perfect mixtures it reduces to the Lorentz formula. The intensity of the light scattering by mixtures of CO_2 and H_2 and of CO_2 and O_2 is calc. At pressures much < the plait point pressure, the density scattering and the composition scattering both diminish with rising temp., but the former is much > the latter. At higher pressures the latter increases rapidly and finally predominates. Both attain a max. at the plait point. J. W. S.

Raman frequencies of sodium nitrate in different states. I. R. RAO (Z. Physik, 1934, 90, 650—657).—The cryst. frequencies at 726, 1071, 1389, and 1670 cm^{-1} become 721, 1049, 1361, and 1683 cm^{-1} in solution; the inactive frequency in the melt is 1053 cm^{-1} . A. B. D. C.

New frequencies in the Raman spectrum of ethyl alcohol. G. BOLLA (Z. Physik, 1934, 90, 607—622).—56 displacements are tabulated, and those at 3632, 3359, 3240, 1618, 814, and 257 cm^{-1} are given as new fundamental frequencies. A. B. D. C.

Raman effect of molecule type XY_6 . O. REDLICH, T. KURZ, and P. ROSENFELD (J. Chem. Physics, 1934, 2, 619).—There is no essential difference between the authors' interpretation (A., 1933, 113) of the Raman frequencies of the type XY_6 and that given by Yost, Steffens, and Gross (this vol., 830). The calculations of the latter go further, but are uncertain. M. B.

Raman spectra of some isomeric octanes. J. W. MURRAY (J. Chem. Physics, 1934, 2, 618). The Raman spectra of $\gamma\delta$ - (I) and $\beta\epsilon$ -dimethylhexane (II) have been determined. (II) has lower frequencies than (I) in agreement with the fact that the Me groups in (II) are nearer the ends of the vibrating hydrocarbon chain.

Raman effect in organic esters. G. R. PARANJPE and K. S. SAVANUR (Indian J. Physics, 1934, 8, 503—520).—Data are given for Me, Et, Pr, Bu, and isoamyl formates and acetates, and for Me and Et propionates and butyrates, and are compared with the infra-red absorption data. The Raman frequencies of about

630 and 1730 cm^{-1} are attributed to the C:O linking and that at 1030 cm^{-1} to the C-O linking. The elastic stretching forces of these linkings are calc., and the effect of homology and isomerism on Raman spectra is discussed. J. W. S.

Raman effect of organic substances. III. α -Mono-derivatives of furan. K. MATSUNO and K. HAN (Bull. Chem. Soc. Japan, 1934, 9, 327—344; cf. this vol., 473).—Raman lines 888, 925, 1020, 1081, 1153, 1232, 1390, 3122, and 3153 cm^{-1} are characteristic of α -mono-derivatives of furan. Frequencies 1507 and 1605 are attributed to $\text{C}_4\text{H}_3\text{O}\cdot\text{CH}_2\cdot$, 1477 and 1572 to $\text{C}_4\text{H}_3\text{O}\cdot\text{C}\llcorner$, 1641 to $\cdot\text{CH}\cdot\text{CH}\cdot$ in the side-chain; frequencies 1460, 1463, 1476, and 1507 are due to the ring, and not to $\cdot\text{CH}_2\cdot$. It is inferred from the appearance of frequencies 1563, 1572, and 1607, that the furan ring contains double linkings.

R. S. B.

Raman spectrum of fluorobenzene. F. W. CRAWFORD and J. R. NIELSEN (J. Chem. Physics, 1934, 2, 567—571).—The Raman spectrum of PhF has been studied, and relative intensities have been determined. There are not yet sufficient data to determine whether the C_6H_5 mol. has a 3-fold or a 6-fold symmetry axis. M. S. B.

Fine structure of Rayleigh radiation of liquids. W. RAMM (Physikal. Z., 1934, 35, 756—773).—The light scattered by various org. liquids (CCl_4 , C_6H_6 , PhMe, PhCHO, CS_2) and H_2O was investigated to determine the fine structure in the immediate neighbourhood of the irradiating frequency. Using the Zn line 4680 Å., and a scattering angle of 180° , it was found that besides the primary frequency, two lines of equal intensity were present on the red and blue sides, respectively. The distance from the primary line is in good agreement with the Brillouin theory of scattering. The triplet is on a continuous background, the intensity of which \propto the anisotropy of the scattering mols. Further discrete lines were not found. A. J. M.

Ultra-violet fluorescence of X-irradiated rock-salt crystals. V. KUDRJAVEVA (Z. Physik, 1934, 90, 489—503).—Ultra-violet fluorescence excited by visible light was investigated with a photon counter, and the results are fitted to an electron level scheme for crystals. A. B. D. C.

Simple phosphorescence emission from crystals of alkali halides. W. ROOS (Ann. Physik, 1934, [v], 20, 783—792).—The phosphorescence spectrum emitted by alkali halides which show "U-bands" consists of equidistant double bands. The width of each band is $> 1 \text{ m}\mu$. The effect of temp. on the phosphorescence was also investigated. The phosphorescence spectrum varies with the method of prep. of the crystal. A. J. M.

Catalytic influences on the chemiluminescence of phosphorus. F. SCHACHERL (Atti Cong. naz. Chim., 1933, 4, 599—608; Chem. Zentr., 1934, i, 1290).—The chain theory is supported. POCl_3 is a positive catalyst, and forms new active centres.

H. J. E.

Polarisation of the fluorescence of some dye solutions for excitation in different absorption

regions. L. GRISEBACH (Naturwiss., 1934, 22, 633—634).—The degree of polarisation and the absorption coeff. of the light emitted from glycerol solutions of various dyes between 4537 Å. and the characteristic emission of the dye were compared, and the regularities discovered by Frohlich confirmed. Eosin, fluorescein, rhodamine-B, and aesculin behave alike.

A. J. M.

Ionisation of carbon disulphide by electron impact. H. D. SMYTH and J. P. BLEWETT (Physical Rev., 1934, [ii], 46, 276—277).— CS_2^+ , CS^+ , S^+ , and C^+ ions are produced at 10.4 ± 0.2 , 14.7 ± 0.5 , 14.0 ± 0.5 , and 21.5 ± 1.0 volts, respectively. The absence of S_2^+ ions and the high appearance potential of C^+ indicate a linear mol. By raising the filament temp. free CS and S_2 are produced, and their ionisation potentials are 10.6 ± 0.3 and 10.7 ± 0.3 volts.

N. M. B.

Ionisation of arginine and histidine. T. H. JUKES and G. E. K. BRANCH (Science, 1934, 80, 228).—Certain anomalies in the behaviour of arginine and histidine are explained by the resonance theory.

L. S. T.

Photo-electric conduction and electron energy levels in crystals. P. TARTAKOVSKY (Z. Physik, 1934, 90, 504—511).—A level scheme is given for NaCl.

A. B. D. C.

Photo-effect of the thinnest layers of organic molecules at the interface water/air. H. CASSEL and E. TOHMEER (Z. Physik, 1934, 90, 427—431).—Dependence of the photo-effect for NH_2Ph , NHPh_2 , and NPh_3 on layer thickness and time of exposure gives the initial photo-current and the mol. condition of the surface.

A. B. D. C.

Spectral distribution of the photo-electric effect in cuprous oxide. (MME.) A. JOFFE and A. JOFFE (Compt. rend., 1934, 199, 569—571).—The sp. curve of the photo-electric effect of Cu_2O depends on the thickness of the layer, the λ of the max. becoming shorter the thinner is the layer. With a specimen having a stopping layer, the behaviour is such as would be expected from a layer 10^{-5} cm. thick (cf. A., 1933, 999). The difference between the $\lambda\lambda$ of the max. for photo-conductivity and photo-electric effect is attributed to differences in the thicknesses of the layers concerned.

J. W. S.

Temperature variation of the contact potential of cuprous oxide. G. MONCH (Z. Physik, 1934, 90, 576—585).— Cu_2O in contact with a metal in vac. gives a potential increasing by -0.15 volt per 100° rise in temp., and this increase occurs at the Cu_2O -vac. interface.

A. B. D. C.

Determination of dipole moments in solution. F. FAIRBROTHER (Nature, 1934, 134, 458—459).—Measurements of the polarisation of PhNO_2 in decane and in *p*-xylene at concns. up to nearly 28 wt.-% and at 20° intervals between 20° and 120° give vals. of P_2 at each temp. which when plotted against $(\epsilon-1)/(\epsilon+2)$ are straight lines meeting at the point $(\epsilon-1)/(\epsilon+2)=2$. The average val. obtained for the dipole moment is 4.25×10^{-18} e.s.u. in agreement with 4.23 (this vol., 944) for the vapour.

L. S. T.

Dipole moment and cohesion. A. E. VAN ARKEL (Trans. Faraday Soc., 1934, 30, 698—705).—The b.p. of halogen derivatives of CH_4 and C_2H_6 has been calc. using a formula neglecting dipole effects. Calc. and observed vals. agree. In mols. containing dipoles the dipole energy (I) may be calc. When the distance between the centres of the dipoles is $>$ twice the smallest distance of the dipole from the surface of the mol., the val. of (I) is independent of the dipole orientation. If this distance is < 0.25 of the smallest distance to the surface, the dipoles behave as the resultant dipole. The order of the b.p. of C_6H_6 derivatives and groups of isomerides is predicted, in agreement with observed vals.

H. J. E.

Atomic polarisation. S. SUGDEN (Trans. Faraday Soc., 1934, 30, 734—739).—Methods of determining the at. polarisation, P_A , are discussed. No definite relationship can be traced between dipole moments (I) and P_A , nor can P_A vals. be assigned to groups. P_A does not increase as the mol. size increases: for most org. mols. it is < 10 c.c., and is usually < 5 c.c. It is approx. correct to take P_A as 10% of P_E when (I) is > 1 Debye unit.

H. J. E.

Dipole induction effect and the moments of individual linkings. C. P. SMYTH (Trans. Faraday Soc., 1934, 30, 752—758).—A crit. review and discussion.

H. J. E.

Dipole moment and ionic binding. W. H. RODEBUSH (Trans. Faraday Soc., 1934, 30, 778—786).—A discussion of types of linking, the significance of ionic and at. radii, and the relation of these to dipole moments.

H. J. E.

Electric dipole moments and resonance in molecules. L. E. SUTTON (Trans. Faraday Soc., 1934, 30, 789—801).—The effects of resonance in a mol. on valency angles, on the freedom of rotation of one part of a mol. relative to another, and on electron distribution are discussed. The effect of resonance on the dipole moments of some conjugated mols. and on certain heterocyclic mols. is considered. The existence of resonance in a mol. may be decided from dipole moment data.

H. J. E.

Determination of intra-molecular forces from measurements of dipole moments. J. E. LENNARD-JONES and H. H. M. PIKE (Trans. Faraday Soc., 1934, 30, 830—851).—Theoretical.

H. J. E.

Temperature variation of the dielectric constant of ionic crystals. E. BRETSCHER (Trans. Faraday Soc., 1934, 30, 684—687).—The temp. coeff. of the dielectric const. of NaCl and CaF_2 has been measured, Au films being evaporated in vac. on to the appropriate cryst. surface to form a condenser. Discrepancies between the experimental and theoretical vals. are discussed.

H. J.

Dielectric constant of magnesium platinocyanide crystals and the possibility of molecular rotation in solids. J. ERRERA and A. SACK (Trans. Faraday Soc., 1934, 30, 687—691, A., 1933, 663).—Measurements at -160° to 50° dependence of the dielectric const. on the water content of the crystal, and on the direction of the

with respect to the axes. Pronounced dispersion phenomena are observed, similar to those in ice.

H. J. E.

Stereochemistry of mercury and the moment of the Hg-C linking. G. C. HAMPSON (Trans. Faraday Soc., 1934, 30, 877—883).—The dipole moments of HgPh_2 in C_6H_6 and decalin (I) at 25° , and of HgPh_2 , $\text{Hg}(\text{C}_6\text{H}_4\text{R}-p)$ ($\text{R}=\text{Me}, \text{Cl}, \text{Br}, \text{and F}$) in (I) at 142.4° have been measured. The vals. are all small, and follow the order $\text{R}=\text{Cl} > \text{Br} > \text{F} > \text{Me}$. The moment of the $\text{Ph}\cdot\text{Hg}$ linking is probably about $0.5D$, with the negative pole towards the Hg. The small moments observed may be due to flexibility in mols. of the HgPh_2 type.

H. J. E.

Dipole association in pure liquids. P. GIRARD (Trans. Faraday Soc., 1934, 30, 763—772).—*tert.*-Alcohols are shown, from the temp. variation of the dielectric const. (I), to form non-polar association complexes. Polyhydric alcohols form polar association complexes, shown by discontinuities in the dispersion and absorption curves, tending to disappear with rise of temp. For long $\lambda\lambda$ the polyhydric alcohols all have approx. the same val. of (I) as glycerol at the same temp. In these alcohols the dipole moment where is the elementary moment of each alcoholic group in the mol. and n is the no. of such groups.

H. J. E.

Free rotation and the electric moment of organic molecules. C. T. ZAHN (Trans. Faraday Soc., 1934, 30, 804—820).—A discussion of the free rotation in the CO_2H group, $\text{HCO}\cdot\text{NH}_2$, HCO_2H , CH_2Ac , Ac_2O , $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$, and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ on the basis of Eucken and Meyer's method of calculating electric moments (A., 1929, 980) and on the conception of quantum resonance.

H. J. E.

Electric moment measurements of cyclohexane derivatives and their relationship to conclusions reached from X-ray crystallographic work. O. HASSEL (Trans. Faraday Soc., 1934, 30, 874—876).—A discussion. The compounds 1:4-dibromo- and -di-iodo-cyclohexane have zero moment at room temp., and are symmetrical. Such mols. should show a moment if examined at a sufficiently high temp. for conversion of the mols. into the "pliable" form to occur. In 1:3-di-iodocyclohexane (m.p. 67.5°) the angle between the two C-I directions is approx. 105° .

H. J. E.

Polarisation of chloro-derivatives of diphenyl and naphthalene. Dipole moment and structure of organic compounds. XIII. A. WEISSBERGER, R. SANGEWALD, and G. C. HAMPSON (Trans. Faraday Soc., 1934, 30, 884—891; cf. A., 1933, 339).—The dipole moments of 1:2-, 1:3-, 1:4-, 1:5-, 1:8-, 2:6-, and 2:7- $\text{C}_{10}\text{H}_6\text{Cl}_2$ have been measured and are compared with calc. vals. The 2:6-derivative has zero moment, showing the system to be planar. In the 1:3- and 1:4-derivatives the observed val. differs from that calc., due to a shift of electrons in the mol., as in 3- $\text{C}_6\text{H}_4\text{PhCl}$.

H. J. E.

Dipole moments of methyl and ethyl halides. C. P. SMYTH and K. B. McALPINE (J. Chem. Physics, 1934, 2, 499—502).—Dielectric consts. have been determined for vapour of MeF , MeBr , MeI , EtF ,

EtBr , and EtI . There is an increase in dipole moment from Me to Et halide due to inductive effect, but the increase in Me—Et difference with increase in size of halogen involved indicates the existence of some additive factor. The change in moment observed has been compared with the change in Raman frequency associated with the C-halogen linking.

M. S. B.

Electric moments of fatty acids. C. J. WILSON and H. H. WENZKE (J. Chem. Physics, 1934, 2, 546—547).—The moments of HCO_2H (I), AcOH (II), EtCO_2H (III), and stearic acid in solution in dioxan have been measured. For (II) and (III) the vals. are practically identical with those obtained for the acids in the vapour state. For (I) there is a considerable discrepancy between the two vals. The higher electric moment of (I) appears to be related to the higher ionisation const. The O·H linking may be more polar in (I) than in the higher fatty acids.

M. S. B.

Constancy of polarisation of non-polar molecules. C. P. SMYTH and K. B. McALPINE (J. Chem. Physics, 1934, 2, 571—573).—The dielectric consts. of $n\text{-C}_6\text{H}_{14}$ and $n\text{-C}_7\text{H}_{16}$ in the vapour state have been determined for a temp. range of approx. $330\text{--}560^\circ$ abs. The polarisation is practically const. This confirms the view that the mols. of non-polar substances have no detectable dipole moments.

M. S. B.

Valency angles of oxygen and sulphur. G. M. BENNETT (Trans. Faraday Soc., 1934, 30, 853—858).—The valency angle of O, calc. from the dipole moments (I) of ethylene oxide and Me_2O , is $115^\circ \pm 7^\circ$. In substituted aromatic ethers this angle cannot be accurately calc. from (I) of the constituent groups, as additional moments arise within the mol. From the val. of (I) for thianthrene the valency angle of S is $< 120^\circ$.

H. J. E.

Structure of the organic azides. N. V. SIDGWICK (Trans. Faraday Soc., 1934, 30, 801—804).—The org. azides consist probably of a mixture of the two chain forms $\text{R}\cdot\text{N}:\text{N} \rightleftharpoons \text{N}$ and $\text{R}\cdot\text{N} \leftarrow \text{N}:\text{N}$ in resonance. This agrees with thermochemical data and with the very small dipole moments of such azides. The ring structure is excluded by the heat of formation. N_2O may likewise consist of the two linear structures $\text{N} \leftarrow \text{N}:\text{O}$ and $\text{N}:\text{N} \rightarrow \text{O}$ in resonance. It also has a small dipole moment.

H. J. E.

Oxidation of sulphurous acid. II. Molal volume of sulphur dioxide, oxygen, and sulphur trioxide in dilute aqueous solution. R. C. HOATHER and C. F. GOODEVE (Trans. Faraday Soc., 1934, 30, 630—635; cf. this vol., 1086).—The equiv. vols. of SO_2 , O_2 , and SO_3 at 30° and 35° have been determined in aq. solution $< 0.006N$. In the range of concn. used the contraction for oxidation of aq. SO_2 \propto the amount of reaction. The molal vols. of H_2SO_3 , $\text{H}^+ + \text{HSO}_3^-$, and H_2SO_4 are approx. 57.5, 36, and 16—22 c.c., respectively.

R. S. B.

Refractive index of an ionised medium. C. G. DARWIN (Proc. Roy. Soc., 1934, A, 146, 17—46).—It is confirmed that a gas of electrons neutralised by a continuum of positive electricity will obey the Sellmeyer formula, $S = \mu^2 - 1$, whilst a set of self-con-

tained atoms will obey the Lorentz formula, $L = 3(\mu^2 - 1)/(\mu^2 + 2)$. The conditions for the S formula are fulfilled in the ionosphere and in metals. L. L. B.

Optical constants of alkali halide crystals. A. KUBLITZKY (Ann. Physik, 1934, [v], 20, 793—808).—The n of crystals of NaF, KF, RbBr, and RbI were determined for various λ . Abs. vals. for the absorption const. for the first ultra-violet absorption bands of RbBr and RbI are given. A. J. M.

Dispersion measurements with sodium and potassium chloride in the long-wave infra-red. II. C. H. CARTWRIGHT and M. CZERNY (Z. Physik, 1934, 90, 457—467; cf. A., 1933, 1104).—Refractive index and extinction coeff. were measured between 120 and 240 μ . The optical coeffs. of NaCl and KCl vary analogously. A. B. D. C.

Rotatory dispersion in the carbohydrate group.—See this vol., 1092.

Magnetic anisotropy of the fatty acids. A. PIEKARA (Compt. rend., 1934, 199, 527—529).—The magnetic birefringence of EtCO_2H at 5780 and 4360 Å. is $>$ that of AcOH , $\text{Pr}^n\text{CO}_2\text{H}$, $\text{Pr}^i\text{CO}_2\text{H}$, and Ac_2O . Assuming that the acids exist entirely in the dimeric form, the magnetic anisotropy has been calc. J. W. S.

Magnetic double refraction in liquids. H. A. BOORSE (Physical Rev., 1934, [ii], 46, 187—195).—An improved instrument of high sensitivity is described. Data are given for MeOH , EtOH , Pr^nOH , Bu^nOH , n -heptane, HCO_2Et , MeOAc , EtOAc , Pr^nOAc , Bu^nOAc , n -amyl acetate, Et_2O , Bu_2O , and H_2O . Certain discrepancies in available data are discussed. N. M. B.

Magnetic rotatory power of arsine and phosphine. R. DE MALLEMANN and P. GABIANO (Compt. rend., 1934, 199, 600—601).—For AsH_3 , the Verdet const. at 0° and 760 mm. is 68×10^{-6} min. and the mol. rotation is 44×10^{-5} radians ($\lambda = 578 \text{ m}\mu$). For PH_3 , the corresponding vals. are 57×10^{-6} and 36.5×10^{-6} . D. R. D.

Valencies of polonium. M. HAISSINSKY and M. GUILLOT (J. Phys. Radium, 1934, [ii], 5, 419—425).—The addition of increasing quantities of electrolytes (Na salts) to acid solutions of Po causes a progressive displacement to the negative of the crit. potential of the cathode deposit. Similar displacement is found in presence of traces of reducing agents. The phenomenon is distinct from electrolytic effect, and, in conjunction with evidence from the isomorphism of Po compounds, is attributed to a reduction of Po^{IV} to Po^{III} . N. M. B.

Chemistry of metallic substances in relationship to classical chemistry. U. DEHLINGER (Angew. Chem., 1934, 47, 621—624).—A theoretical treatment of the type of main and subsidiary valency linking and the law of multiple proportions and of affinity and osmotic pressure in compounds and mixed crystals. H. W.

Nature of the chemical linking. V. L. PAULING and G. W. WHEELAND (J. Chem. Physics, 1934, 2, 482).—Errors in a previous paper (this vol., 15) are corr. M. S. B.

Theory of the stability of the benzene ring and related compounds. W. G. PENNEY (Proc. Roy. Soc., 1934, A, 146, 223—238).—The resonance between the p_A electrons does not select C_6H_6 as the most stable of the single-ring structures $(\text{CH})_n$, but the binding energy of the other three linkings on each C nucleus does. The energy of the ring $(\text{CH})_n$ is evaluated in terms of n and certain exchange integrals. The fact that $n=6$ is the most stable plane ring over wide ranges in the relative magnitudes of the exchange integrals indicates that any or all of the H atoms in C_6H_6 can be replaced by other univalent atoms or groups with little change in the form and stability of the ring. The ring nearest in stability to C_6H_6 is C_3H_3 . The analysis indicates that it is slightly buckled out of a plane and should hydrogenate with ease, as is the case. The calculations are extended to the ring structures $(\text{CH})_n$. L. L. B.

Structure of H_2O_2 and N_2H_4 with particular reference to electric moments and free rotation. W. G. PENNEY and G. B. B. M. SUTHERLAND (Trans. Faraday Soc., 1934, 30, 898—902).—The large dielectric moments of H_2O_2 and N_2H_4 are due to an unsymmetrical mol. form, and not to free rotation. This accords with the Raman spectra and with wave-mechanical considerations. H. J. E.

Theory of the structure of hydrogen peroxide and hydrazine. W. G. PENNEY and G. B. B. M. SUTHERLAND (J. Chem. Physics, 1934, 2, 492—498).—The most stable configuration for the atoms of the mols. $\text{HO}\cdot\text{OH}$ and $\text{H}_2\text{N}\cdot\text{NH}_2$ has been determined by the method of electron pairs. Free rotation cannot occur at ordinary temp. and the only stable forms for both mols. are those in which the azimuth of half the mol. with respect to the other is approx. 90° . M. S. B.

Structure of the pseudo-halogens and of their compounds. I. Thallium thiocyanates. M. STRADA (Gazzetta, 1934, 64, 526).—A comment on the paper of Büssem, Gunter, and Tubin (this vol., 243) O. J. W.

Determination of the magnetic susceptibility of the free radical $\text{C}_{11}\text{H}_{14}\text{O}_3\text{N}$ and comparison with van Vleck's theory. F. GALAVICS (Helv. phys. Acta, 1933, 6, 555—564; Chem. Zentr., 1934, 1, 1950).—Measurements at 19 — 50° in COMe_3 gave a val. of χ corresponding with one unpaired electron in the radical. H. J. E.

Magnetic susceptibility of some hydrates of magnesium sulphate and some compound salts of magnesium. E. DUCHEMIN (Compt. rend., 1934, 199, 571—573).—The magnetic susceptibilities, χ , of $\text{MgSO}_4\cdot\text{H}_2\text{O}$, $\text{MgSO}_4\cdot 2\text{H}_2\text{O}$, and $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ are $<$ calc. from the vals. for MgSO_4 and H_2O . χ for $\text{MgSO}_4\cdot\text{K}_2\text{SO}_4$ is also $<$ the theoretical val., but for $\text{MgSO}_4\cdot\text{K}_2\text{SO}_4\cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}$ is in approx. agreement with theory. The low vals. observed are attributed to complex formation in the solid. J. W. S.

Magnetic susceptibility of metal ketals. R. DOESCHER and G. W. WHEELAND (J. Amer. Chem. Soc., 1934, 56, 2011—2012).—Data are given for

three Na compounds. The % dissociation in C_6H_6 or dioxan solution has been calc. E. S. H.

Magnetic anisotropy in cobaltamine crystals. L. W. STROCK (Z. Krist., 1934, 88, 238—247).—A summary of the diamagnetic behaviour of several cobaltamine compounds, mostly of known optical and crystallographic properties. B. W. R.

Atomic diamagnetic susceptibility of hydrogens. S. S. BHATNAGAR, N. G. MITRA, and G. D. TULI (Phil. Mag., 1934, [vii], 18, 449—456).—From measurements of the magnetic susceptibilities of homologous series of org. compounds, the mean val. for CH_n is calc. as -11.36 and -11.35 ($\times 10^{-6}$) for aliphatic and aromatic compounds, respectively. Combining this with Pascal's val. for C, the at. diamagnetic susceptibility of H is -2.68 and -2.675 ($\times 10^{-6}$), respectively, in good agreement with theory. J. W. S.

Anomalous diamagnetism of selenium. S. S. DHARMATTI (Nature, 1934, 134, 497).—As the particle size of Se is increased the diamagnetism decreases until the Se becomes paramagnetic; the paramagnetism (I) then increases. Colloidal is more paramagnetic than powdered Se. (I) persists after removal of possible oxides by EtOH. L. S. T.

Paramagnetic behaviour of Cr^{++} ions. E. LIPS (Helv. phys. Acta, 1933, 6, 482—483; Chem. Zentr., 1934, i, 1950).—The susceptibility of $CrCl_2$ and $CrSO_4 \cdot 6H_2O$ has been measured from 55° to 400° abs. The moments are 4.97 and 4.78 Bohr magnetons, respectively. H. J. E.

Quantum mechanics of unsaturated and aromatic molecules. Comparison of two methods of treatment. G. W. WHELAND (J. Chem. Physics, 1934, 2, 474—481).—The two methods of quantum-mechanical treatment of problems connected with the mol. structure of unsaturated and aromatic compounds, viz., the Keiller-London-Slater-Pauling and the Hund-Mulliken-Hückel methods, have been compared. The former method is, on the whole, the more trustworthy, but cannot be used so widely. M. S. B.

Wave-mechanical treatment of the naphthalene molecule. J. SHERMAN (J. Chem. Physics, 1934, 2, 488—491).—The secular equation corresponding with the 42 canonical structures of $C_{10}H_8$ has been set up and solved with certain assumptions and the coeffs. of the structures in the wave function have been determined. Of the three unexcited structures the symmetrical one makes a 50% greater contribution to the wave function than either of the two unsymmetrical structures. M. S. B.

Heat of dissociation of CO and the electron affinity of O. W. W. LOZIER (Physical Rev., 1934, [iii], 46, 268—276; cf. A., 1933, 1237).—Dissociation produced by primary electron impact in CO and O_2 was studied for the processes $O_2^- \rightarrow O^- + O$ at 2.9 and 12.0 ± 0.2 volts, giving for the electron affinity of the O atom the val. 2.2 ± 0.2 volts, and $CO \rightarrow C + O^-$ at 9.5, $CO \rightarrow C^+ + O^-$ at 20.9, and $CO^+ \rightarrow C^+ + O$ at 22.8 ± 0.1 volts. The heat of dissociation of CO may be 9.6 or 11.6 ± 0.1 volts. N. M. B.

Measurements of mean inner potential. J. R. TILLMAN (Phil. Mag., 1934, [vii], 18, 656—675).—Data are recorded for single crystals of rock-salt, galena, pyrites, stibnite, calcite, fluor spar, gypsum, and Zn blende. Approx. the same vals. were obtained with 4-kv. or 30-kv. electrons. H. J. E.

Lattice energies of ferrous halides and the nature of the radical $Fe^{II}(CO)_4$. W. HIEBER and E. LEVY (Z. Elektrochem., 1934, 40, 608).—A correction (cf. this vol., 734). E. S. H.

Lattice energy due to lattice distortion of cold-worked copper. W. A. WOOD (Phil. Mag., 1934, [vii], 18, 495—505).—By X-ray methods it is shown that cold-working produces an irregular expansion of the Cu lattice. The equiv. heat energy required to produce a similar state is calc., and the conception of a latent energy of lattice distortion advanced. J. W. S.

Ionic distances in crystals of complex salts with fluorite structure. G. BØDTKER-NÆSS and O. HASSEL (Skr. Norske Vidensk.-Akad. Oslo, I. Mat. Nat. Kl., 1933, No. 7, 1—10; Chem. Zentr., 1934, i, 1274).—Interionic distances have been measured in crystals of $[Mg(NH_3)_6](BF_4)_2$ and $[Mg(NH_3)_6](SO_3F)_2$, and the corresponding Mn, Fe, Co, Ni, and Cd salts. All gave a fluorite structure. The ionic radii of BF_4^- and SO_3F^- were 2.28 and 2.37 Å., respectively. The lattice consts. of K_2PtCl_6 , $(NH_4)_2PtCl_6$, Rb_2PtCl_6 , and Cs_2PtCl_6 were measured. H. J. E.

Vibration frequency and nuclear separation for some simple non-hydride diatomic molecules. C. H. D. CLARK (Phil. Mag., 1934, [vii], 18, 459—470).—Modifications of Morse's rule (A., 1929, 975) which are capable of relating these two magnitudes are suggested. J. W. S.

Influence of crystal forces on the vibration of a complex ion. M. BLACKMAN (Phil. Mag., 1934, [vii], 18, 425—433).—Theoretical. J. W. S.

Normal vibrations of molecules having tetrahedral symmetry. N. S. N. NATH (Indian J. Physics, 1934, 8, 581—592).—Theoretical. J. W. S.

Electron energy levels in a finite crystal lattice. A. SOKOLOV (Z. Physik, 1934, 90, 520—541).—Levels are determined for a one-dimensional crystal. A. B. D. C.

Theory of liquids. T. S. WHEELER (Indian J. Physics, 1934, 8, 521—536).—Assuming that at temp. of low v.p. the diameters of the mol. of a liquid increase with rise of temp. so that on an average they continue to touch, Edser's calculations (Brit. Assoc. Rept. on Colloid Chem., 1922, 40) are extended to thermodynamic properties for which a knowledge of the effect of temp. on the liquid is necessary. It is concluded that the mols. of non-associated org. liquids appear to attract one another with a force approx. $\propto (\text{distance})^{10}$. The general parachor law, surface tension $\propto 1/\text{mol. vol.}$, follows from the theory. J. W. S.

Surface tension determinations of some barbiturates. J. H. GRAHAM (Amer. J. Pharm., 1934, 106, 295—298).—Vals. at $28-29^\circ$ of 12 derivatives in solution are given. E. H. S.

Parachor of thallium in amalgams. L. BELLA-DEN (*Gazzetta*, 1934, **64**, 461—465).—*d* and surface tension data have been obtained for amalgams containing 2—28.95 wt.-% of Tl. The mean val. of the parachor calc. for Tl is 85.9, which is $21.9 >$ the val. for at. Tl. This indicates that in the amalgams the Tl is not present in the at. state, but combined either with Hg or with other Tl atoms. O. J. W.

Appearance of atoms as determined by X-ray scattering. E. O. WOLLAN and A. H. COMPTON (*J. Opt. Soc. Amer.*, 1934, **24**, 229—233).—A template of white paper is cut of a shape so calc. that it will scatter light in the same proportion as the corresponding atom scatters X-rays. Photographs of the template, rotated about its centre, are the images of atoms, illustrated for He, Ne, and A, as obtained by X-ray diffraction, magnified about 2×10^8 times. The *K* and *L* electrons in Ne and the *M* electrons in A are distinguishable. N. M. B.

Determination of the inner-electric field of Rochelle salt by means of X-rays. H. STAUB (*Physikal. Z.*, 1934, **35**, 720—725).—Determinations of the effect of temp. on the intensity of X-ray interference in Na K tartrate show that a considerable increase in intensity takes place between the two Curie points. This is due to an increase in the quasi-elastic bindings of the lattice constituents, through alteration in the inner-electric field. The moment of the dipole (3.7×10^{-18} e.s.u.) and its length (0.4 Å.) calc. from the observed intensities agree with vals. obtained by other methods. A. J. M.

Polarisation energy of the cubic lattice. T. NEUGEBAUER (*Z. Physik*, 1934, **90**, 693—697).—Polarisation energy due to penetration of electron clouds is deduced theoretically. A. B. D. C.

New law of slipping and friction. B. DERJUGIN (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 93—96).—Theoretical. The law is applied to slipping in single crystals. H. J. E.

Test of lattice optics for active crystals. G. SZIVESSY and C. MÜNSTER (*Ann. Physik*, 1934, [v], **20**, 703—736).—The laws given by the Ewald-Born lattice optics for non-absorbing active crystals were confirmed experimentally for α -quartz. A. J. M.

Interpretation of X-ray diffraction patterns of a fluid at various densities. N. S. GINGRICH and B. E. WARREN (*Physical Rev.*, 1934, [ii], **46**, 248—251).—Calc. intensities of X-rays diffracted by a fluid of various densities can be applied only over a small range of densities in the absence of detailed knowledge of the density distribution of atoms about any one atom. On the basis of assumed approximations a set of intensity-angle curves are drawn for several densities, and are compared with experimental curves for Et₂O. N. M. B.

Fourier integral analysis of X-ray powder patterns. B. E. WARREN and N. S. GINGRICH (*Physical Rev.*, 1934, [ii], **46**, 368—372).—Mathematical. A radial distribution function is obtained giving the no. of atoms at any distance from a given atom. For rhombic S each atom has two neighbours

at about 2.3 Å. distance, agreeing with an S₈ ring mol. N. M. B.

Fourier series method for the determination of the components of interatomic distances in crystals. A. L. PATTERSON (*Physical Rev.*, 1934, [ii], **46**, 372—376; cf. preceding abstract).—The method developed is illustrated for KH₂PO₄ and C₆Cl₆. N. M. B.

Crystal cleavage induced by impurity. H. E. BUCKLEY (*Z. Krist.*, 1934, **88**, 122—127).—K₂SO₄ normally shows very poor cleavage, and none at all on (100) face. When it is grown in presence of 0.1% alizarin-yellow 5G, very perfect (100) cleavage appears in any portion of crystal which has passed through a growing (100) face. B. W. R.

Oriented inclusion of impurities in crystals. H. E. BUCKLEY (*Z. Krist.*, 1934, **88**, 248—255).—A discussion of the growth of crystals in the presence of impurity (chiefly K₂SO₄ with added dyes). The impurity may alter the rate of growth of a face, whilst itself being collected on some quite different face. B. W. R.

Molecular configuration and its relation to modification of crystal-growth. H. E. BUCKLEY (*Z. Krist.*, 1934, **88**, 381—411).—A comprehensive discussion of the effect of dyes on crystallisation of KClO₃ and K₂SO₄. For about 100 dyes a crit. concn. was found, able, e.g., to make (011) planes as prominent as (001) for KClO₃; this was quite definite and served as a basis of comparison from one dye to another. Results are complex; the SO₃Na is the most important group in the dyes. Substituent effects are examined, also inhibiting effects, e.g., of phenols on otherwise active dyes. A foreign mol. perhaps affects the crystal growth in some way other than as an obstruction. B. W. R.

X-Ray diffraction study of carbon black. B. E. WARREN (*J. Chem. Physics*, 1934, **2**, 551—555).—X-Ray diffraction data for C black indicates definitely the existence of single graphite layers. C black probably consists of a continuous series extending from the mesomorphic state to graphite crystals several layers thick. The intense small angle scattering is due to the difference between grain *d* and average *d*, caused by the loose packing of extremely small grains. M. S. B.

Powder figures of magnetised single iron crystals. II. S. KAYA (*Z. Physik*, 1934, **90**, 551—558; cf. this vol., 1059).—Figures are given for dodecahedral and octahedral faces. The figures indicate elementary groups in the magnetised state.

X-Ray study of red monoclinic selenium. Proof of the existence of two red monoclinic varieties of selenium. H. P. KLUG (*Z. Krist.*, 1934, **88**, 128—135).—Muthmann's α and β forms of red monoclinic Se have both definite X-ray identities, the consts. are: α , *a*₀ 8.992, *b*₀ 8.973, *c*₀ 11.02, β 91° 34', space-group probably C_{2h}; and β , *a*₀ 8.992, *b*₀ 8.04, *c*₀ 9.25 Å., β 93° 4', space-group probably C_{2h}. B. W. R.

X-Ray investigation of calcium at higher temperatures. L. GRAF (*Metallwirt.*, 1933, **12**,

653; Chem. Zentr., 1934, i, 1002).—The discontinuity in the cooling, dilatometer, and temp.-resistance curves of Ca at 450° is shown by X-ray measurements to be due to a change from a cubic face-centred lattice to a cubic body-centred lattice (a at 480° 4.43 Å.). The high resistance of Ca wires pressed at 300° (Schulze, this vol., 949) is due to lattice distortion. H. J. E.

Intensity measurements on deformed crystals and mixed crystals. J. HENGSTENBERG [with H. MARK and WASSERMANN] (Ergebn. techn. Röntgenkunde, 1931, 2, 139—150; Chem. Zentr., 1934, i, 1001—1002).—The change in intensity of X-ray reflexion for deformed crystals of Ta, W, Mo, or KCl or the degree of deformation. In mixed crystals of Ag-Au (4, 8, and 10 wt.-% Au) an increase in the diffuse scattered radiation was observed, the Laue intensity distribution being confirmed. Duralumin showed characteristic effects for both mixed and deformed crystals. H. J. E.

Hydrides of the rare earths. I. X-Ray investigation of the product of hydrogenation of lanthanum. A. ROSSI (Atti Cong. naz. Chim., 1933, 4, 593—594; Chem. Zentr., 1934, i, 1178).—The product of heating La for 3 hr. at 230—240° in H₂ gave an X-ray diagram different from that of pure La. H. J. E.

Comparison of X-ray diffraction curves of water and deuterium oxide at 25°. A. W. STEWART (J. Chem. Physics, 1934, 2, 558—559).—The peaks in the H₂O curve are slightly sharper than in the D₂O curve, and the differences are definitely > can be ascribed to experimental error. M. S. B.

Crystal lattice of boric acid, H₃BO₃. W. H. ZACHARIASEN (Z. Krist., 1934, 88, 150—161).—The cell is triclinic, with a_0 7.04, b_0 7.04, c_0 6.56 Å., α 92° 30', β 101° 10', γ 120°, 4 mols. in cell, space-group C_2^1 . B and O atoms are positioned from estimated intensities, H atoms from general considerations. The structure has strongly marked layers 3.18 Å. apart, agreeing with cleavage and softness. B

Crystal lattice of telluric acid, H₆TeO₆. B. GOSSNER and O. KRAUS (Z. Krist., 1934, 88, 298—303).—H₆TeO₆ has two modifications; one cubic, a_0 7.83 Å., 4 mols. to unit cell, space-group O_h^2 ; the other monoclinic, a_0 5.54, b_0 9.30, c_0 9.74 Å., β 104° 30', 4 mols. to cell, space-group probably C_{2h}^2 . The relation between the two forms is discussed. B. W. R.

Crystal structures of some alkali hydrosulphides and monosulphides. C. D. WEST (Z. Krist., 1934, 88, 97—115).—Structures of CsSH, NH₄SH, NaSH, KSH, RbSH, K₂S, Li₂Se, and Li₂Te are discussed from powder and oscillation photographs, at room temp. Also above 90° NaSH and above 170° KSH have cubic modifications (RbSH similarly). Anisotropic expansions of KSH, NaN₃, and NaNCO are observed. B. W. R.

Crystallographic and X-ray researches on potassium lead chloride. M. MEHMEI and W. NESPITAL (Z. Krist., 1934, 88, 345—355).—The compound (KPbCl₃)₃.H₂O is prepared and found to be

triclinic, nearly monoclinic, with a_0 14.35, b_0 9.05, c_0 14.5 Å., α and γ nearly 90°, β 113°; 4 mols. in cell, space-group C^1 . The formation of mixed crystals with KCl is discussed. B. W. R.

Regular and hexagonal silver iodide. N. H. KOLKMEIJER and J. W. A. VAN HENGEL (Z. Krist., 1934, 88, 317—322).—AgI pptd. from a solution containing excess of KI is hexagonal (wurtzite B₄ type), whilst from excess of AgNO₃ it is cubic (Zn blende B₃ type). d (X-ray) 5.69₆ and 5.71₃, respectively. The parameters for the hexagonal form are evaluated in detail. B. W. R.

Cæsium nitrate and the perovskite structure. L. WALDBAUER and D. C. MCCANN (J. Chem. Physics, 1934, 2, 615—617).—The crystal structure of dysanallyte has been confirmed. The crystal structure of CsNO₃ has been determined and shown to be hexagonal. No inversion takes place at 161°. The term "perovskite structure" has been wrongly applied to KIO₃. It can be applied only to perovskite which is most probably orthorhombic, although it has been used as a type of cubic symmetry on the basis of a similarity of powder pattern. M. S. B.

Structure and colour of anhydrous cobalt chloride, CoCl₂, at room and very low temperatures. H. GRIME and J. A. SANTOS (Z. Krist., 1934, 88, 136—141).—There is evidence that the colour of Co^{II} compounds depends on the no. of groups surrounding the Co atom; four gives blue and six gives red compounds. Anhyd. CoCl₂ is blue; the cell is rhombohedral with a_0 6.16 Å., α 33° 26'. Structure is of layer type and has six-co-ordinated Co atoms; CoCl₂ is thus an exception to the rule. At liquid air temp. it turns pink, with no apparent change of X-ray reflexions. B. W. R.

Crystal structure of tetramminopalladous chloride, Pd(NH₃)₄Cl₂.H₂O. B. N. DICKINSON (Z. Krist., 1934, 88, 281—297).—The structure is tetragonal, 2 mols. in unit cell, a_0 10.30, c_0 4.34 Å., space-group probably D_{2h}^2 . A detailed analysis of at. co-ordinates is made, and satisfactory vals. are obtained; Werner's contention, that Pd^{II} is surrounded by four coplanar groups, is verified. B. W. R.

Crystal structures of some hydrated compounds. C. D. WEST (Z. Krist., 1934, 88, 198—204).—Optical and X-ray examination of LiClO₄.3H₂O, LiI.3H₂O, and Ba(ClO₄)₂.3H₂O gives the following for hexagonal cell sides and probable space-groups, respectively: a_0 7.71, c_0 5.42 Å., C_{6v}^1 ; 7.45, 5.45, C_{6v}^2 ; and 7.28, 9.64, C_6^2 or C_{6h}^2 . B. W. R.

Crystallographic researches on double cyanides. IV. Barium nickel cyanide. H. BRASSEUR, A. DE RASSENFOSSE, and J. PIÉREARD (Z. Krist., 1934, 88, 210—222).—This compound is BaNi(CN)₄.4H₂O, and is isomorphous with BaPt(CN)₄.4H₂O. It is monoclinic, with a_0 11.71, b_0 13.48, c_0 6.63 Å., β 104° 50', space-group C_{2h}^2 . At. positions based on intensities are given for Ba and Ni. B. W. R.

Crystal lattice of ammonium silicofluoride, (NH₄)₂SiF₆. B. GOSSNER and O. KRAUS (Z. Krist., 1934, 88, 223—225).—The hexagonal modification

has a_0 5.76, c_0 4.77 Å., space-group D_{3d}^4 . Comparison is made with the cubic modification. B. W. R.

Crystal structure of ammonium beryllium fluoride, $(\text{NH}_4)_2\text{BeF}_4$. R. HULTGREN (Z. Krist., 1934, 88, 233—237).— $(\text{NH}_4)_2\text{BeF}_4$ is orthorhombic, a_0 5.8, b_0 10.2, c_0 7.5 Å. Space-group V_h^{16} . The at. positions seem to agree with those of K_2SO_4 , confirming that the BeF_4^{2-} is of about the same dimensions as the SO_4^{2-} group. B. W. R.

Crystal structure of the fluoberyllates. P. L. MUKHERJEE (Current Sci., 1934, 3, 66—67).—Crystallographic data, obtained by optical and X-ray measurements, for the fluoberyllates (I) of K, Rb, NH_4 , and Tl are given and compared with corresponding vals. for the sulphates. The space-groups of (I) are V_h^{16} . L. S. T.

Crystal structure of ilmenite. T. F. W. BARTH and E. POSNJAK (Z. Krist., 1934, 88, 265—270).—At. positions are given for ilmenite, FeTiO_3 , and reasons discussed for allotting it to space-group C_{2v}^2 , instead of to the plausible D_3^+ . B. W. R.

Structures of the ilmenite type. E. POSNJAK and T. F. W. BARTH (Z. Krist., 1934, 88, 271—280).—The system Fe_2O_3 – Ti_2O_3 forms a complete range of solid solutions between the compositions Fe_2O_3 (hæmatite) and FeTiO_3 (ilmenite; cf. preceding abstract). CdTiO_3 is dimorphous (ilmenite type below 1000°, perovskite type above this temp., not reversible). The structures of NiTiO_3 , CoTiO_3 , MnTiO_3 , MgTiO_3 , and low-temp. CdTiO_3 are very similar. B. W. R.

Crystal structures of talc and pyrophyllite. J. W. GRUNER (Z. Krist., 1934, 88, 412—419).—From powder measurements the following data are found: talc, monoclinic, a_0 5.26, b_0 9.10, c_0 18.81 Å., β 100°, space-group C_{2h}^2 , 4 mols. of $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ in cell; pyrophyllite, same space-group, a_0 5.14, b_0 8.90, c_0 18.55 Å., β 99° 55', 4 mols. of $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ in cell. B. W. R.

Crystal structure of the chlorite minerals. R. C. MCMURCHY (Z. Krist., 1934, 88, 420—432).—Analysis of six chlorites confirms Pauling's proposal of alternating mica and brucite sheets. Space-group is C_{2h}^2 , perhaps C_{2h}^3 ; cell contains 4 mols. approx. $\text{Al}_2\text{Mg}_5\text{Si}_3\text{O}_{10}(\text{OH})_8$. Cell sizes for the specimens examined vary as follows: a_0 5.30—5.35, b_0 9.19—9.27, c_0 28.31—28.58 Å. The variation is ascribed to isomorphous replacement of Mg by Fe^{II} . B. W. R.

Structure of epididymite, $\text{HNaBeSi}_3\text{O}_8$. T. ITO (Z. Krist., 1934, 88, 142—149).—The cell is rhombic, with a_0 12.63, b_0 7.32, c_0 13.58 Å., containing 8 mols. of $\text{HNaBeSi}_3\text{O}_8$, space-group V_h^{16} . Structure is essentially one of Si_3O_8 chains parallel to b -axis. B. W. R.

Crystal structure of the silver nitrate-carbamide additive compound. I. Space-group and molecular association. G. L. CLARK and C. O. WERNER (Z. Krist., 1934, 88, 162—172).—The compound $\text{AgNO}_3 \cdot \text{CO}(\text{NH}_2)_2$ is monoclinic, 8 mols. per unit cell, a_0 10.23, b_0 16.84, c_0 6.25 Å., β 77°. Space-group probably C_{2h}^2 . B. W. R.

Crystal structure of hexamethylethane and of cubic hexachloroethane. C. D. WEST (Z. Krist., 1934, 88, 195—197).— C_2Me_6 (above -125°) and C_2Cl_6 (above 71°) are cubic, a_0 7.69 and 7.43 Å., respectively. B. W. R.

Determination of the structure of p -azoxy-anisole. F. WURSTLIN (Z. Krist., 1934, 88, 185—194).—The crystals are monoclinic, a_0 16.0, b_0 8.08, c_0 20.5 Å., β 107° 30', 8 mols. in cell, space-group C_{2h}^2 , disagreeing with results of Bernal and Crowfoot (A., 1933, 1107). The suggested structure links two C_6 rings by a "kinked" azoxy-group. B. W. R.

X-Ray analysis of the structure of chrysene. J. IBALL (Proc. Roy. Soc., 1934, A, 146, 140—153).—Chrysene has a 8.34, b 6.18, c 25.0 Å., β 115.8°; space-group C_{2h}^2 ($I2/c$) or C_2^2 (Ic); 1.27, giving 4 mols. of $\text{C}_{18}\text{H}_{12}$ per unit cell. The mol. is planar and consists of regular hexagons, the interat. distance being 1.41 Å. L. L. B.

Crystallography of some sugar derivatives and of γ -benzoylmethylaminobutyric acid. R. NOVAČEK (Z. Krist., 1934, 88, 82—89).—Crystallographic data are given. B. W. R.

X-Ray investigations on some sugars and derivatives. H. BRÆKKEN, C. J. KOREN, and N. A. SORESENSEN (Z. Krist., 1934, 88, 205—209).—Cell consts. from X-ray and crystallographic measurements are given for *cis*- α -methylxyloside, *trans*- β -1-methyl-arabinoside, *cis*- α -1-methylarabinoside, *trans*- β - α -galactose (stable form), and *cis*- α -1-methylrhamnoside. B. W. R.

X-Ray examination of the acetates of glucose, cellobiose, and cellotriose. G. L. LEUCK and H. MARK (J. Amer. Chem. Soc., 1934, 56, 1959—1962).—A method by which crystals of the materials may be obtained is described. The crystals are orthorhombic. Space-lattice data have been obtained. E. S. H.

Structure of the water layer of the starch micelle. N. H. KOLKMEIJER and J. C. L. FAVEJEE (Z. Krist., 1934, 88, 226—232).—According to present ideas, the micelles of emulsoid sols are surrounded by a layer of H_2O . Debye-Scherrer photographs were taken of gradually dehydrated starch, to observe any "cryst." structure which this layer might possess. Distinct evidence of such a structure (*i.e.*, lines corresponding with normal ice powder lines) was

Theory of anisotropic liquids. XVIII. Structure of cholesterol nematic substances. A. Temperature dependence of anisotropy in presence of external forces. C. W. OSEEN (Ark. f. Astron. Fysik, 1933, A, 23, Nos. 24, 25; Zentr., 1933, ii, 3653—3654).—XVIII. Cholesterol nematic substances exist in two modifications at same temp. The mol. arrangements are discussed.

XIX. Above a definite temp. the mol. orient follows a law of the Maxwell-Boltzmann type. At this temp. another state is stable in which there preferred orientation, determined by the force. Over a certain temp. range either state can be produced. At lower temp. a third state can

in which the mols. have all approx. the same orientation. H. J. E.

Electron diffraction in carbon tetrachloride vapour. V. E. COSSLETT (Trans. Faraday Soc., 1934, 30, 981—991).—An improved method for determining electron diffraction is described. A val. 2.85 ± 0.03 Å. has been obtained for the Cl—Cl separation in CCl_4 vapour and 1.74 ± 0.02 Å. for the C—Cl separation. The electron scattering is also considered theoretically. M. S. B.

Scattering of slow electrons by organic molecules. I. Acetylene, ethylene, and ethane. E. C. CHILDS and A. H. WOODCOCK (Proc. Roy. Soc., 1934, A, 146, 199—205).—The angular distributions of 4, 6, 8, 10, 12, 15, 20, 25, 30, and 40 volt electrons scattered elastically in C_2H_2 , C_2H_4 , and C_2H_6 have been measured. The results are discussed with reference to the shapes of the mol. field contours and the symmetry of the at. configurations. L. L. B.

Inverse piezoelectric properties of Rochelle salt. C. I. VIGNESS (Physical Rev., 1934, [ii], 46, 255—257).—The relation between the change of lattice spacing of the (021) planes as a function of the change in voltage applied along the a -axis of the crystal was determined by X-ray methods for the temp. range 10 — 30° . There is correspondence between change of lattice const. as measured by X-rays and by measurements of strain set up by change of voltage applied along the a -axis. The piezoelectric modulus determined from the inverse effect is $>$ that determined from the piezoelectric effect. N. M. B.

Thermal resistivity and the Wiedemann-Franz ratio of single-crystal zinc. C. A. CINNAMON (Physical Rev., 1934, [ii], 46, 215—221).—Thermal resistivities at 57° of 13 large, strain-free, single crystals of Zn obey the Voigt-Thomson symmetry relation. The agreement of the ratio at 0° and 90° orientations with the corresponding ratio for electrical resistivities shows that the Wiedemann-Franz ratio is the same for all orientations of the crystal, and has the val. 7.15×10^{-6} watt ohm/ 1° at 57° . The two principal thermal conductivities are $\lambda_0 = 1.009$ and $\lambda_{90} = 1.068$ at 57° . N. M. B.

Thermal and electrical conductivities of metals and alloys. I. Iron from 0° to 800° . R. W. POWELL (Proc. Physical Soc., 1934, 46, 659—679).—The thermal conductivity, κ , of a Ni-plated rod of Armco Fe (99.92% Fe) has been determined at 30 — 800° by a longitudinal flow method; after allowance for the plating κ of Fe at 0° is 0.177 c.g.s. unit. A purer specimen of Fe gave 0.194 unit. It is concluded that the lower results previously obtained have been due to impurity. κ of Armco Fe decreases with rise of temp., becoming 0.071 c.g.s. unit at 800° . From the measured electrical conductivity of this sample, the Lorenz function is calc. and found to increase from 0.62×10^{-8} at 0° to 0.74×10^{-8} at 400° , remaining almost const. from 400° to 700° . J. W. S.

Conductivity of metals. N. F. MOTT (Proc. Physical Soc., 1934, 46, 680—692).—The resistances of pure metals, measured for the same amplitude of thermal oscillation of the atoms, exhibit a periodic behaviour. This observation is discussed on the

basis of wave mechanics, and it is suggested that the greater conductivity of univalent over bivalent metals is due to the smaller effective no. of free electrons in the latter. This is confirmed by the optical consts. of metals and the increase of resistance due to foreign metals in solid solution. The change in resistance of metals under pressure is discussed. J. W. S.

Surface conductivity of metals. A. W. MAUE (Naturwiss., 1934, 22, 648; cf. A., 1932, 902).—The contribution of surface electron waves to electrical conductivity is discussed. On collision with the crystal lattice a surface electron may pass either into another surface state or into a space state. J. W. S.

Theory of superconductivity. H. BETHE (Z. Physik, 1934, 90, 674—679).—A criticism of Schachenmeier's theory (cf. A., 1932, 453). A. B. D. C.

Theory of superconductivity. R. SCHACHENMEIER (Z. Physik, 1934, 90, 680—692).—A reply to Bethe (preceding abstract). A. B. D. C.

Properties of tin. E. S. HEDGES and C. E. HOMER (Tech. Pub. Internat. Tin Res. Council, 1934, B, No. 1, 1—45).—A comprehensive compilation of the at., crystallographic, mechanical, thermal, electrical, magnetic, and optical properties of Sn. E. S. H.

Structure sensitivity of low-temperature ionic conductivity of rock-salt. M. KASSEL (Z. Physik, 1934, 90, 287—311).—Low-temp. ionic conducting power was determined for crystals of different origin between 20° and 500° , and at various deformations; the solution energy of Na ions for this effect corresponds with 7400° abs. A. B. D. C.

Relation between lattice parameter and ferromagnetism. W. KOSTER and W. SCHMIDT (Arch. Eisenhüttenw., 1934—1935, 8, 25—27).—The lattice parameter (a) of Fe has been measured at 0 — 1550° ; the a - T graph consists of three straight lines for α -, β -, and γ -Fe, the line for δ -Fe being a continuation of the β -line. The γ -line is steeper than and below the β -line, which is appreciably steeper than the α -line, showing that the sp. vol. in the ferromagnetic state is $>$ that in the paramagnetic state. For Fe this difference is 1.6% , for Ni 1% , and for Co 2.3% . Similar differences are observed for the different magnetic states of Co-Mn, Fe-Co-Mn, and Ni-Mo alloys. A. R. P.

Magnetic effects in iron crystals. A. G. HILL (Phil. Mag., 1934, [vii], 18, 539—545).—Magnetisation curves were measured at -190° to 312° for fields near saturation, and show no discontinuities when magnetisation is summed in all directions in a face plane of a Fe crystal. The effect of self-demagnetisation was studied. H. J. E.

Transverse thermomagnetic effect: a method of measurement. G. S. NIELSEN (Phil. Mag., 1934, [vii], 18, 575—579).—A temp. gradient is maintained between the inside and outside of a Ni tube, the p.d. between its ends being measured for different magnetic forces. H. J. E.

Temperature variation of isothermal tensile strength and tearing strength of synthetic rock-salt crystals. D. MAHNKE (Z. Physik, 1934, 90,

177—188).—The tensile strength for infinitely slow extension normal to the cubic plane was determined between -190° and 765° , and agrees with the temp. variation of statical tearing strength up to 600° . The temp. variation of plastic properties of these crystals is similar to that of metals. A. B. D. C.

Strength properties of wetted rock-salt crystals. VI. Dependence on direction of stretch limit of uniformly wetted rods of rock-salt. (FRL.) S. DOMMERICH (Z. Physik, 1934, 90, 189—196).—Plastic deformation at room temp. is due to slip along either rhombic dodecahedral or along cubic planes. A. B. D. C.

Rendering visible ultra-sonic waves in transparent solids. I. Optical investigation of a piezo-quartz. E. HEIDEMANN, H. R. ASBACH, and K. H. HOESCH (Z. Physik, 1934, 90, 322—326). A. B. D. C.

Supersonic dispersion in gases. E. G. RICHARDSON (Proc. Roy. Soc., 1934, A, 146, 56—71).—The propagation through O_2 , CO_2 , N_2O , SO_2 , and A of supersonic radiation has been examined, and a theory is advanced to explain the anomalous dispersion and absorption. L. L. B.

Temperature variation of the thermo-electric properties and the specific heat of nickel-chromium alloys. A. W. FOSTER (Phil. Mag., 1934, [vii], 18, 470—488).—From measurements of the thermo-electric power, it is shown that Ni alloys containing 1% and 2% Cr exhibit respectively only 30% and 10% of the change in the Thomson coeff. at the Curie point found with pure Ni. The sp. heats of the alloys, measured by an improved method, show respectively 55% and 30% of the fall in the sp. heat at the Curie point measured for Ni. J. W. S.

Thermoelectric electromotive force in the magnetisation of nickel. T. KOUSMINE (Helv. phys. Acta, 1933, 6, 474—476; Chem. Zentr., 1934, i, 1949).—Measurements were made of the change of thermo-e.m.f. in a thermoelement containing Ni, due to an applied magnetic field. H. J. E.

Internal [and total] latent heats of vaporisation of liquids. II. N. A. DE KOLOSOVSKI and A. ALIMOV (Bull. Soc. chim., 1934, [v], 1, 877—880). The data refer to 13 org. compounds and to CS_2 . Interpolation formulæ for mol. latent heats and v.p. between 0° and the b.p. are given for $COMe_2$, $COMeEt$, MeI , NH_4Et_2 , Et_2CO_3 , CCl_4 , cyclohexane, $CHCl_3$, and CS_2 . J. G. A. G.

Influence of the method of testing on the results obtained for the heat content of iron. H. ESSER and W. BUNGARDT (Arch. Eisenhüttenw., 1934—1935, 8, 37—38).—Determinations of the heat content (C_H) of Fe with the H_2O - or ice-calorimeter give low results for the heat effect (H) at the α - γ transformation, probably due to partial suppression of the A2 transformation. Measurements of the true sp. heat in which the temp. of the specimen is changed only slightly show that the temp.- C_H curve is convex to the temp. axis at $<$ the A2 point, and concave thereto between the A2 and A3 points; from this curve H = about 3.6 g.-cal. per g. A. R. P.

Disposition of work energy applied to crystals. C. G. MAIER and C. T. ANDERSON (J. Chem. Physics, 1934, 2, 513—527).—Heats of dissolution of finely-divided and coarse calcite have been determined, and also sp. heats at low temp. of similar samples and of samples of finely-drawn Cu and Al wires in both the annealed and cold-worked state. The work and heat of the drawing process have also been compared for Cu and Al. No evidence has been obtained for any increase of intrinsic energy of calcite due to comminution to 0.5μ size. Differences previously observed appear to be due to impurities, chiefly $Ca(OH)_2$ and H_2O , introduced on grinding. Single crystals of hard-drawn and annealed Cu and Al do not show measurable differences of entropy at 298° abs. Only when carefully annealed samples of Cu and Al are used can a discrepancy between work and heat be shown to exist. This discrepancy for a given degree of cold-working is directly \propto the mass of metal, but not to the degree of cold working. M. S. B.

Anomaly in the specific heat of ferrous chloride at the Curie point. O. N. TRAPEZNIKOWA and L. W. SHUBNIKOW (Nature, 1934, 134, 378—379).—The sp. heat of $FeCl_2$ increases to a sharp max. at 23.5° abs. It is concluded that the anomaly in the sp. heat and in the susceptibility is connected with the appearance of a mol. field at a well-defined temp., the Curie point. Preliminary determinations of the sp. heat of $NiCl_2$ between 20° and 80° abs. show no such anomaly. L. S. T.

Kinetic energy of polyatomic molecules. C. ECKART (Physical Rev., 1934, [ii], 46, 383—387).—Mathematical. N. M. B.

Equation of state for gases. II. K. JABECZYNSKI (Physikal. Z., 1934, 35, 731—737; cf. A., 1932, 906).—Theoretical. A modification of van der Waals equation is considered. A. J. M.

Vapour pressures and derived thermal properties of hydrogen and deuterium. R. B. SCOTT, F. G. BRICKWEDDE, H. C. UREY, and M. H. WAHL (J. Chem. Physics, 1934, 2, 454—464).—Determinations of the v.p. of H_2 and D_2 have been made at 13.9 — 20.40° abs. The triple point of H_2 is thus found to be 18.58° abs. and the b.p. 23.5° abs. Comparison of the rates of ortho-para conversion in the two gases, by comparison of the rate of change of v.p., shows that the rate for H_2 is only $1/40$ of that for D_2 . Latent heats and heat capacities of H_2 have been calc. $C_p - C_v$ for solid H_2 is much $>$ for solid D_2 , indicating that H_2 has a larger coeff. of expansion. This is in accordance with the greater zero-point energy of H_2 . The heat capacity under saturation pressure of liquid H_2 is much $<$ that of D_2 . S. B.

Vapour pressure of high-boiling metals. II. Determinations by Ruff's spring-balance method. J. FISCHER (Z. anorg. Chem., 1934, 219, 367—370). The v.-p. curves obtained by Ruff's spring-balance method have been studied theoretically. The method has been perfected and tested by measurements of the v.p. of Zn and Cd, which are found to be in agreement with the values obtained by other methods. Errors in earlier measurements were due to the use

of porous crucibles. V.-p. measurements of Ag have been made at temp. up to 2300° abs. and the v.-p. const. is deduced. M. S. B.

Vapour pressure of ZnF_2 , CdF_2 , MgF_2 , CaF_2 , SrF_2 , BaF_2 , and AlF_3 . O. RUFF and L. LE BOUCHER (Z. anorg. Chem., 1934, 219, 376—381).—V.-p. measurements of fluorides have been made by the spring-balance method (cf. preceding abstract) and b.p. and heats of vaporisation deduced. Except for AlF_3 , which sublimes, the results are in good agreement with the formula $\lambda_s/T_s = 21/(1 - 10^{-4}T_s)$, where λ_s is the mol. heat of vaporisation at b.p. T_s . M. S. B.

Physical constants of anabasine. O. A. NELSON (J. Amer. Chem. Soc., 1934, 56, 1989—1990).—The v.-p. of anabasine, b.p. 280.9°/760 mm., $[\alpha]_D^{20} = -59.66^\circ$ (lit. -82.2°), is determined at different temp. H. B.

Properties of sublimed calcium. P. BASTIEN (Compt. rend., 1934, 199, 577—579).—The coeff. of cubic expansion of Ca (99.3%), prepared by sublimation and subsequent fusion in A, is 25.2×10^{-6} over the range 20—100°, and $d^{20} = 1.542 \pm 0.0005$. J. W. S.

Thermal expansion of some compounds and its evaluation according to the Grüneisen rule. O. HÜLSMANN and W. BILTZ (Z. anorg. Chem., 1934, 219, 357—366).—Determinations of d for a large no. of salts have been made at room temp. and approx. -75° and -195° , and the expansion coeffs. calc. In most cases the results conform to a modification of Grüneisen's law, viz., $100(v_R - v_0)/v_0 - 8.290/T_M$, where v_R and v_0 are the vols. at room temp. and 0° abs., respectively, and T is the m.p. M. S. B.

Thermodynamic functions of a diatomic gas the molecules of which have a multiplet normal electronic state belonging to Hund's case (a). E. E. WITMER (J. Chem. Physics, 1934, 2, 618—619).—Theoretical. M. S. B.

Calculation of the outer work of removal, W_a , from compressibility. H. BOMKE (Z. Physik, 1934, 90, 542—550).—An equation is deduced that gives W_a in terms of compressibility; it divides metals into two classes, and reduces to the usual formula for univalent metals. A. B. D. C.

Comparison of liquid viscosity data. (MISS) M. D. WALLER (Phil. Mag., 1934, [vii], 18, 505—516).—The intrinsic viscosities of liquids may be compared by taking the m.p. and b.p. as comparison temp. For the halogens the order is $\text{I} > \text{Br} > \text{Cl}_2$, and if the crit. temp. be taken as a second reference temp. for the vapour state, the order is the same for the vapours. The ratios of the viscosities of liquids at the m.p. and b.p. are about 1.6—3 for metals, halogens, and C_6H_6 , but > 9 for paraffins, alkyl bromides, and Et_2O . J. W. S.

Influence of molecular structure on the variation of viscosity between the m.p. and b.p. (MISS) M. D. WALLER (Phil. Mag., 1934, [vii], 18, 579—594; cf. preceding abstract).—Data are recorded for viscosities at the m.p. and b.p. of many compounds. The ratio (r) of these two quantities is < 4 for highly

symmetrical mols., and is much higher for elongated mols. For C_6H_6 and its homologues r varies from 2.2 to 24 according to the symmetry. In paraffins with an odd no. of C atoms r is $>$ in mols. with an even no. In paraffins and the alcohol series r varies periodically as the no. of C atoms increases by 6, indicating flexibility in the hydrocarbon chains. The use of this criterion in determining structure is discussed. Diat. mols. of fused salts with an ionic linking have high vals. of r . H. J. E.

Diffusion of very dilute gases. J. ROTBLAT (Acta phys. polon., 1933, 2, 143—145; Chem. Zentr., 1934, i, 1936).—The diffusion of Hg vapour in presence of H_2 , O_2 , A, Kr, and Xe at very low pressures have been studied. H. J. E.

Thermal diffusion of gases near a hot metal surface. J. CHIPMAN and M. G. FONTANA (J. Amer. Chem. Soc., 1934, 56, 2011).—In passing a mixture of steam and H_2 over Fe at 1600° a partial thermal separation of the cool gases near the hot metal surface seems to occur. E. S. H.

Van der Waals' equation for gaseous mixtures. E. NEUSSER (Physikal. Z., 1934, 35, 738—739; cf. A., 1931, 31; 1932, 220).—The co-vol. (b) of a mixture is additively compounded of the co-vols. of its constituents. b vals. for mixtures of N_2 and H_2 , and air are given. An expression connecting the a val. for a mixture with the a vals. of the constituents is given. A. J. M.

Thermal properties of benzene-air and methyl alcohol-air mixtures. J. SMALL (Phil. Mag., 1934, [vii], 18, 554—560; cf. B., 1933, 1042).—Total heat and partial pressure data are tabulated and represented on charts. H. J. E.

Parameter values of copper-nickel alloys. E. A. OWEN and L. PICKUP (Z. Krist., 1934, 88, 116—121).—Accurate measurements on Cu-Ni alloys disprove Vegard's law, and show a max. density at about 34 at.-% Ni, corresponding with a lattice contraction of 0.11%. B. W. R.

Crystal structure of a complex copper-silicon compound. F. R. MORRAL and A. WESTGREN (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 37, 6 pp.).—The alloy containing 21.2% Si, d 7.77, is stable at $< 600^\circ$ and the length of the edge of the unit cube is 9.694 Å. This corresponds with 76 atoms in the cube and the formula $\text{Cu}_{15}\text{Si}_4$, which is confirmed by X-ray data. A. G.

Binary systems iron-copper and iron-antimony. R. VOGEL and W. DANNOHL (Arch. Eisenhüttenw., 1934—1935, 8, 39—40).—Various points in these systems have been redetermined by microscopic examination of quenched alloys. The solubility of Cu in γ -Fe falls from 8.5% at 1094° to 8% at 1477° (solidus). The field of immiscibility in the liquid state does not touch the liquidus line; the min. temp. is 1480° at 50% Cu. In the Sb-Fe system there is a region of solid solutions between 55 and 65% Sb with a max. in the m.-p. curve at $1018 \pm 3^\circ$ (63.5% Sb) corresponding with the compound Fe_3Sb_4 . The max. solubility of Sb in γ -Fe is 2%. A. R. P.

X-Ray investigation of zinc-nickel alloys. V. CAGLIOTI (Atti Congr. naz. Chim., 1933, 4, 431—441; Chem. Zentr., 1934, i, 1283).—The system (up to 53% Ni) shows an ill-defined ϵ -phase (5% Ni), a homogeneous γ -phase (15—22 at.-% Ni, cubic body-centred, probably $\text{Ni}_5\text{Zn}_{21}$), a β -phase (46% Ni, tetragonal, $c:a$ 0.83, composition NiZn), and a cubic α -phase (53% Ni).
H. J. E.

Constitution of iron-rich Fe-Al-C alloys. F. R. MORRAL (Iron and Steel Inst., Sept., 1934, Advance copy, 10 pp.).—The system has been examined by microscopical and X-ray methods up to about 5% C and 18% Al. The phases found are α -Fe solid solution, austenite containing up to 1.5% C (at 1000°) and 6% Al, and a hard and brittle magnetic phase (ϵ) in which the metal atoms form a cubic lattice with 4 atoms in the unit cell, with Fe at the centres of the faces and Al at the corners; space-group O_1 ; it corresponds with Fe_3Al containing 4% C. The lattice spacing of the austenite phase is 3.60—3.68 Å., the increase being partly accounted for by the entry of Al atoms into the lattice. A tentative phase diagram is given.
H. F. G.

System iron-copper-antimony. R. VOGEL and W. DANNOHL (Arch. Eisenhüttenw., 1934—1935, 8, 83—92).—Thermal and micrographic data show that two ternary compounds exist: (i) FeCuSb formed at 780° by the reaction: liquid (low in Fe) + α -Fe (saturated with Cu and Sb) + ($\text{FeSb} + n\text{Fe}$) \rightarrow FeCuSb ; and (ii) FeCu_4Sb_2 formed at 758° by reaction between liquid (low in Fe), saturated α -Fe, and FeCuSb . Both compounds decompose on melting and only (i) is stable at room temp. On solidification of liquid containing > 5% Fe the primary crystallites consist of ternary solid solutions of α - or γ -Fe or of the ($\text{FeSb} + n\text{Fe}$) phase (ρ), α and γ being primary with ρ , and ρ with γ , 53% Sb. The miscibility gap in the liquid phase of Fe-Cu alloys is displaced to higher temp. on addition of quite small amounts of Sb, and no separation into layers occurs in the ternary system on solidification. The space model shows primary surfaces (P) corresponding with the separation of ternary α , ternary γ , ρ , FeSb_2 , Sb, ϵ (Cu saturated with Sb and Fe), ternary ν (Cu_5Sb_2 saturated with FeCu_4Sb_2), ternary μ (Cu_5Sb_2 saturated with FeCuSb), and Cu_2Sb . Separation of a second solid phase occurs when the composition of the liquid corresponds with a point on one of 13 curves forming the boundaries of P ; 7 of the points of intersection of these curves correspond with non-variant four-phase equilibria, one of the phases in all cases being the liquid. The two three-phase equilibria in the Fe-Cu system liquid + $\alpha \rightleftharpoons \gamma$ and $\gamma \rightleftharpoons \alpha + \epsilon$ intersect in the ternary system in a point of four-phase equilibrium: liquid + $\gamma \rightleftharpoons \alpha + \epsilon$. The two ternary compounds form no solid solution with one another, the miscibility gap extending to the composition corresponding with Cu_5Sb_2 , thus providing an example of three curves of univariant equilibrium in a ternary system merging at a temp. max. of a curve of equilibrium of one of the component binary systems. In the solid state there are 17 curves of three-phase, and 4 points of four-phase, equilibria.
A. R. P.

Influence of diffusing elements on the α - γ inversion of iron. W. D. JONES (Iron and Steel Inst., Sept., 1934, Advance copy, 9 pp.).—Elements which diffuse into Fe at 1000—1300° are classified according to whether they inhibit or extend the γ -modification, i.e., do or do not produce a diffusion boundary. The heats of oxidation of the elements in the first group are >, and of those in the second group <, that of Fe; B is exceptional. At 1150° the limits of the γ -loop in binary systems containing As, Sb, Zn, and Sn lie at 3.75, 4.25, 17.5, and 2.25%, respectively, of the added element.
H. F. G.

Theory of transformation of metallic mixed phases. U. DEHLINGER (Ann. Physik, 1934, [v], 20, 646—649).—Polemical against Borelius (this vol., 724).
A. J. M.

Theory of transformation of metallic mixed phases. II. G. BORELIUS (Ann. Physik, 1934, [v], 20, 650—652).—A reply to Dehlinger (preceding abstract).
A. J. M.

Condition of sodium dissolved in fused sodium hydroxide. F. HALLA and H. TOMPA (Z. anorg. Chem., 1934, 219, 321—331).—Na reacts with fused NaOH giving Na_2O and NaH. The system has been investigated by thermal and X-ray analysis. The m.p. of pure NaOH is $327.6 \pm 0.9^\circ$, which is > any val. previously recorded. The transition point is $295.3 \pm 1.3^\circ$. Formulæ showing the dependence of the m.p. on the H_2O and Na_2CO_3 content are given. The X-ray diagram of the solidified product indicates a mean extension of the lattice dimensions of about 1.5%, probably due to a solid solution of NaH in NaOH.
M. S. B.

"Apparent mixed crystals." H. G. GRIMM and G. WAGNER (Z. anorg. Chem., 1934, 220, 31—32).—Benrath and Schackmann's results under the above title (this vol., 725) do not contradict the authors work. The latter have shown the existence of true mixed crystals of KMnO_4 and BaSO_4 by X-ray methods.
S.

Viscosity of solutions of menthol. A. CASTIGLIONI (Gazzetta, 1934, 64, 469—473).—Data are recorded for solutions of menthol in C_6H_6 , CHCl_3 , EtOH , Et_2O , vaseline oil, olive oil, sesame oil, and oleic acid. In the first four solvents η increases and in the others decreases with increasing concn. of menthol.
O. J. W.

Viscosity in the systems (a) arsenic trichloride-benzene. M. P. SCHULGINA. (b) Phosphorus trichloride-benzene and -nitrobenzene. S. SCHATMOVA. (c) Arsenic trichloride-nitrobenzene. (d) Arsenic trichloride-pyridine. B. KONDRAATENKO (J. Gen. Chem. Russ., 1934, 4, 226, 240—243, 244—245, 246—247).—(a) The η -concn. curves at 0—60° indicate $\text{C}_6\text{H}_6 \cdot 2\text{AsCl}_3$. (b) The curves at 0—30° are not indicative of compound formation. Contrary to Kahlenberg (Lincoln A., 1899, ii, 397), the systems do not conduct electricity.

curves at 0—50° indicate $2\text{PhNO}_2 \cdot \text{AsCl}_3$.
(d) The curves at 50—100° indicate $\text{C}_5\text{H}_5\text{N} \cdot \text{AsCl}_3$.
T.

Electrochemistry of ethereal solutions. XII. Conductivity in the system sulphuric acid-ethyl ether. M. USANOVITSCH. XIII. Viscosity in the system arsenic trichloride-anisole. M. P. SCHULGINA. XIV. Viscosity in the system anisole-sulphuric acid. R. A. ZAVARICHINA. XV. System antimony tribromide-ethyl ether. M. USANOVITSCH and V. SEREBRENNIKOV. XVI. Conductivity and viscosity in the system monochloromethyl ether-arsenic trichloride. F. I. TERPUGOV (J. Gen. Chem. Russ., 1934, 4, 215—221, 222—224, 227—228, 229—234, 235—239).—XII. The temp. coeff.-concn. curves indicate $\text{H}_2\text{SO}_4\cdot\text{Et}_2\text{O}$ and $\text{H}_2\text{SO}_4\cdot 2\text{Et}_2\text{O}$.

XIII. The η -concn. curves at 0—80° indicate $\text{AsCl}_3\cdot\text{PhOMe}$. The solutions are non-conducting.

XIV. Max. η corresponds with formation of $\text{PhOMe}\cdot 2\text{H}_2\text{SO}_4$, isolated as a cryst. salt.

XV. Measurements of κ and its temp. coeff. indicate $2\text{SbBr}_3\cdot\text{Et}_2\text{O}$.

XVI. Measurements of κ and its temp. coeff., and of η indicate $\text{AsCl}_3\cdot\text{CH}_2\text{Cl}\cdot\text{OMe}$. R. T.

Distillation. I, II. Methyl alcohol-water mixtures. S. UCHIDA and H. KATO (J. Soc. Chem. Ind. Japan, 1934, 37, 525—530B).—Sp. gr. of $\text{MeOH}\cdot\text{H}_2\text{O}$ mixtures at 15°, 20°, and 30°, and the composition of the liquid and vapour phases in equilibrium at the b.p. have been determined.

R. S. C.

Calculation of the composition of the vapour phase over ternary mixtures. I. KRITSCHESKI and J. KASARNOVSKI (Z. anorg. Chem., 1934, 220, 67—72).—A formula has been deduced and confirmed by comparison of the calc. partial v.p. with the experimental data for a no. of systems consisting of H_2O , EtOH , and a third non-volatile, non-ionised substance. M. S. B.

Alumina glasses. G. KEPPELER and R. SCHOLLE (Glastech. Ber., 1933, 11, 357—365, 392—397; Chem. Zentr., 1934, i, 2021).—Replacement of SiO_2 by Al_2O_3 in the system $\text{Na}_2\text{O}\cdot\text{CaO}\cdot\text{SiO}_2$ produces a progressive lowering of the fusion temp. up to a limiting concn. of Al_2O_3 . This limit is higher the greater is the amount of CaO in the glass. Al_2O_3 increases the viscosity and the alkali-resistance is improved, but the thermal expansion shows little change.

H. J. E.

System lime-water and the determination of calcium. H. BASSETT (J.C.S., 1934, 1270—1275).—Uncertainty in the determination of the solubility of $\text{Ca}(\text{OH})_2$, due to the high solubility of fine particles, may be overcome by high temp. and vigorous shaking. Solubilities at temp. 0—100° are given. There are no indications of the existence of a hydrate of $\text{Ca}(\text{OH})_2$ or of $>$ one cryst. form. Errors in the determination of CaC_2O_4 , due to solubility in H_2O or aq. NH_3 , can be obviated by washing CaC_2O_4 ppts. with cold saturated aq. CaC_2O_4 ; the volumetric determination with KMnO_4 then becomes very accurate. Pure pptd. CaCO_3 can be used as a standard in acidimetry and by calcining a weighed amount, adding H_2O , and titrating with the acid to be standardised with Me-red or Me-orange as indicator. M. S. B.

Solubility of iodine in sodium sulphate solutions. K. SANDVED (Kong. Norske Vidensk. Selsk. Forhandl., 1933, 6, No. 37, 1—3; Chem. Zentr., 1934, i, 1177).—Measurements at 15° in presence of K_2SO_4 and H_2SO_4 are recorded. The solubility is reduced by the electrolytes. H. J. E.

Solubility of the alkali salts of arachidic acid. A. CALO' (Atti Congr. naz. Chim., 1933, 4, 681—686; Chem. Zentr., 1934, i, 2057).—Solubility data in H_2O and EtOH from 15° to 50° are recorded for the Li, Na, and K salts. H. J. E.

Basic salts. IV. Solubility of hydroxides in solutions of their salts. E. HAYEK (Z. anorg. Chem., 1934, 219, 296—300).—The solubilities of various bivalent metallic hydroxides in 7—16N solutions of the corresponding chlorides have been determined. Solubility is apparently not related to the acidity of the solution, but is governed by the degree to which the hydroxide is amphoteric. The strongly polar, undissociated hydroxide attaches to the cation in the solution. Sn, Zn, etc. salts dissolve most hydroxide in conc. solution, but with Be and Pb salts dil. solutions are the more active, since the stronger bases exist as undissociated hydroxide only in conc. salt solutions. The nature of the anion is of importance; large univalent ions favour in general the production of complex cations, but the ease of polarisation has considerable influence. H. F. G.

Solubility of bismuth phosphate in hydrochloric acid. K. A. JENSEN (Z. anorg. Chem., 1934, 219, 238—242).—Measurements of the solubility of BiPO_4 in solutions of various $[\text{Cl}']$, $[\text{H}']$, and $[\text{H}_3\text{PO}_4]$ show the reaction to be mainly $\text{BiPO}_4 + 2\text{H}^+ + 3\text{Cl}^- \rightleftharpoons [\text{BiCl}_3\text{H}_2\text{PO}_4]'$. H. F. G.

Solubilities of metal and ammonium salts of various organic acids in methyl alcohol and acetone. H. HENSTOCK (J.C.S., 1934, 1340—1343).—The solubilities of a no. of salts of org. acids have been determined in COMe_2 and C_6H_6 at 15° and in MeOH at 15° and b.p. A few only are sol. in C_6H_6 . Some can be recryst. from MeOH forming crystals containing MeOH . Salts of di- and tri-basic acids are practically insol. in MeOH , although salicylates are more sol. than benzoates. In general, the higher the at. wt. of the metal the less is the solubility of its salts in MeOH . NH_4 salicylate in COMe_2 forms, at 25—35°, an orange-red compound less sol. than the original salt. KEtSO_4 is sol. in MeOH , but not in COMe_2 , but by adding COMe_2 up to 30% to the MeOH solution, the solubility is increased. Further additions decrease it. M. S. B.

Solubility of diphenyl in non-polar solvents. J. C. WARNER, R. C. SCHEIB, and W. J. SVIRBELY (J. Chem. Physics, 1934, 2, 590—594).—Solubility data are given for Ph_2 in C_6H_6 , CS_2 , CCl_4 , C_7H_{16} , dioxan, and $p\text{-C}_6\text{H}_4\text{Cl}_2$. In all cases the vals. are lower than the ideal. The f.-p. curve for mixtures of Ph_2 and $p\text{-C}_6\text{H}_4\text{Cl}_2$ shows a simple eutectic at 42.5 mol.-% Ph_2 and 27.7°, which are fairly close to the vals. calc. for ideal solutions and const. heats of fusion. The application of Hildebrand's equations to the results is dis-

cussed, and it appears that "regular solution" behaviour requires that the mols. of the constituents should not only be non-polar, but should also possess spherical symmetry. M. S. B.

Solubility relations of guanine in the region of its isoelectric point. R. W. MARTIN (Z. physiol. Chem., 1934, 226, 53—57).—The p_H -velocity of pptn. curve of guanine (I) has been determined by measuring the NH_3 liberated by guanase from (I) in solution. The isoelectric point is at p_H 7—8. J. H. B.

Physico-chemical properties of lactose. I. Spontaneous crystallisation of supersaturated solutions of lactose. B. L. HERRINGTON (J. Dairy Sci., 1934, 17, 501—518).—The degree of supercooling necessary for crystallisation in non-agitated solutions of lactose (I) decreases with rising concn. Max. vals. for rates of nuclei formation and of cryst. growth have been found. Solid solutions of (I) are supersaturated with respect to α -hydrate and β -anhydride, but are stable at room temp. α -(I) is more rapidly pptd. from solution by EtOH than is β -(I). Ppts. so obtained are not equilibrium mixtures of the two forms.

A. G. P.

Influence of cations on the crystal growth of alkali metal chlorides. T. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1108—1138).—The influence of cations on the max. velocity at which clear crystals of alkali chlorides can be grown, their relative effects on the development of different crystal planes, and the amount of the foreign cation passing into the crystal phase have been investigated. The most effective ions in this respect are those with electron configurations not of the rare-gas type, so their influence is attributed to the physico-chemical effect of the force-field of these ions on the crystallising ions. The development of planes other than the 100 plane is explained by adsorption of cations on these planes.

J. W. S.

Occlusion and diffusion of hydrogen in metals. Metallographic study of palladium-hydrogen. D. P. SMITH and G. J. DERGE (Trans. Electrochem. Soc., 1934, 66, 25—42).—The effects of mechanical and thermal treatment and of absorption of H, brought about either by exposure to H_2 under various conditions or by cathodic treatment in aq. H_2SO_4 , on the micro-structure of the surface of Pd foil and on its susceptibility to the action of etching agents have been studied. It appears that the diffusion of H through Pd does not depend primarily on occlusion in the lattice and hence on the differing absorptive velocities of various crystal faces or the differing rates of diffusion in various directions through the lattice, but much more on the presence and character of intergranular crevices. Metallographic evidence indicates that the surface intersections of the dodecahedral and octahedral planes are regions of especially marked and probably determinative activity in occlusion and evolution of H. Since susceptibility to attack by etching agents varies in parallel with avidity of absorption of H, this and other chemical and electrochemical properties of Pd are probably also determined by intergranular fissures.

H. J. T. E.

State of solution of hydrogen in palladium and hydrogenation catalysis. J. FRANCK (Nachr. Ges. Wiss. Gottingen, Math.-phys. Kl., 1933, 293—29 Chem. Zentr., 1933, ii, 3656).—The energy set free when a free proton is taken up by Pd is 10.7 ± 0.5 e.v. H_2 in Pd is almost completely decomposed into protons and electrons. The heat of adsorption (I) of H_2 in Pd is positive. When (I) is feebly negative (e.g., for Pt, Fe, or Ni) adsorption occurs at higher temp.

H. J. E.

Rate of adsorption of ethylene by silica and nickel. E. W. R. STEACIE and H. V. STÖVEL (J. Chem. Physics, 1934, 2, 581—584).—Adsorption of C_2H_4 by SiO_2 at 20—300° is practically instantaneous, giving typical adsorption isotherms and showing no indication of any slow adsorption process. In the adsorption of C_2H_4 by reduced Ni at -80° to 150° , however, slow adsorption effects and adsorption hysteresis with change of temp. are observed, and for certain temp. ranges the adsorption increases with rise of temp. This appears to represent the first system in which the phenomena of activated adsorption may be observed without any complicating factor due to solubility of the gas in the adsorbent. M. S. B.

Chemistry of solid surfaces. I. Adsorption of gases on pseudomorphous and amorphous ferric oxide. H. W. KOHLSCHÜTTER (Z. physikal. Chem., 1934, 170, 20—32; cf. A., 1933, 1019).—The van der Waals adsorption of CO_2 and N_2 at -77° has been studied. The adsorptive power, A , of pseudomorphous $Fe_2O_3 \cdot xH_2O$ formed topochemically by action of aq. NH_3 on anhyd. $Fe_2(SO_4)_3$ is reduced by powdering. If it is heated in vac. at T before A is measured, A is increased, due to loss of H_2O , if T is not above 132° , but above 180° A falls rapidly; above 200° the X-ray interferences of α - Fe_2O_3 are detectable. Amorphous $Fe(OH)_3$ formed by pptn. behaves similarly to the above, but the reduction in A caused by pulverising is smaller. For Fe_2O_3 recryst. by heating in O_2 , A is increased by powdering. The differences between the powdered and intact pseudomorphous forms are also revealed by heats of adsorption.

R. C.

Reversible sorption of gases by alkali benzenesulphonates. W. LANGE (Z. anorg. Chem., 1934, 219, 305—312).—Rb and Cs benzenesulphonates resemble the K salt in that they adsorb gases and vapours reversibly, the effect being similarly dependent on pressure and temp. and resulting, at the saturation point, in a simple integral relation between the no. of mols. of gas adsorbed per mol. of adsorbent. The Li, Na, and NH_4 salts appear to possess a different structure, since they exhibit no adsorptive properties. The stoicheometric relation (usually 4 or 5:1) is ascribed to the presence in the crystals of a definite no. of spaces, each of which is capable of accommodating a given no. of mols. of adsorbed gas. The K salt adsorbs A, although to a smaller extent than the other gases, but not Hg vapour. In the case of CO_2 , the isotherms are not smooth but stepped, as has been found for this gas with other adsorbents. H. F.

Adsorption by charcoal of binary mixtures in aqueous solution. R. AMOT (Compt. rend., 19 ,

199, 636—638; cf. A., 1933, 899).—Data are given for aq. solutions of PhOH (I) and sucrose (II). The adsorption of (I) is scarcely influenced by the presence of (II), but that of (II) is reduced by (I). R. S.

Sorption of methyl and ethyl alcohol by silica gels. A. G. FOSTER (Proc. Roy. Soc., 1934, A, 146, 129—140).—Sorption isothermals have been determined for two samples of SiO_2 gel at 25° . These are similar at low pressures, and show a linear range at intermediate pressures. The gel with the higher capacity shows a hysteresis area at higher pressures, which is reproducible and is not altered by flushing out or by evacuation at 350° . The different behaviour of the two types of gel is attributed to a difference in capillary structure. L. L. B.

Absorption of dyes by cellulose. V. Effect of various electrolytes on the absorption. S. M. NEALE and A. M. PATEL (Trans. Faraday Soc., 1934, 30, 905—914).—Methods for the purification of benzopurpurin 4B and sky-blue FF, and for their determination colorimetrically or by absorption on cellulose, are described. The absorption of the dyes by viscose sheet from boiling aq. electrolytes has been measured colorimetrically. It increases with time in accordance with the diffusion equation (cf. this vol., 594) and the amount of absorption at equilibrium increases with the concn. of electrolyte. When this is low the absorption increases with the valency of the cation if there are no disturbing effects such as pptn. of the dye by the electrolyte. The influence of the electrolytes studied decreases in the order: $\text{BaCl}_2 > \text{CaCl}_2 > \text{ZnSO}_4 > \text{MgCl}_2 > \text{NH}_4\text{Cl} > \text{NaCl} > \text{KH}_2\text{PO}_4 > \text{Na}_2\text{HPO}_4$. The apparent diffusion coeff. through cellulose rises to a max. and then decreases with increasing salt concn. The action of electrolytes on absorption is analogous to their destabilising action on colloids. M. S. B.

Role of aluminium in the reactions of clays. H. PAYER and C. E. MARSHALL (Chem. and Ind., 1934, 750—760).—The cations of LaCl_3 , FeCl_3 , and $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ react with unsaturated clays of the montmorillonite and beidellite types by normal exchange, but AlCl_3 does not react with H-clays in this way. The liberation of Al^{+++} from unsaturated clays by neutral salt solutions is due to direct exchange. The Al^{+++} freed is only approx. equiv. to the total acidity; in all cases H^+ is exchanged simultaneously. The reduction in base-exchange capacity caused by treating clays with Al salts is due to pptn. of $\text{Al}(\text{OH})_3$ within the clay micelles. The results are discussed on the assumption that unsaturated clays are to be regarded as mixed Al-H-clays rather than as H-clays. E. S. H.

Surface tensions of aqueous solutions of some thickeners and wetting agents. F. KRONBERGS (Latvian Univ. Raksti, 1934, 2, 385—400). Measurements are recorded of the surface tensions of aq. solutions of many wetting agents and thickeners used in printing. The sharpness of the design depends on the colloidal structure of the thickener as well as on the surface tension and viscosity. A. G.

Boundary surface tensions of mixtures of organic liquids. A. G. NASINI and C. ROSSI (Atti

Congr. naz. Chim., 1933, 4, 524—536; Chem. Zentr., 1934, i, 1296).—The interfacial tension, σ , of C_6H_6 -PhMe mixtures relative to H_2O changes linearly with the composition of the mixture. Deviations from linearity, attributed to adsorption of the component with the higher σ , occur in C_6H_6 -amyl acetate, PhMe-amyl acetate, and PhNO_2 - CCl_4 mixtures. The linear relationship holds for very insol. liquids.

H. J. E.

Duration of liquid drops on the surface of the same liquid. L. D. MAHAJAN (Kolloid-Z., 1934, 69, 16—21; cf. A., 1933, 1002, 1113).—The duration of the drops depends on the oscillation of the liquid surface, the relative motion of surface and drop, the viscosity and surface tension of the liquid, the presence of its saturated vapour and the presence of impurities.

E. S. H.

Movement of a borax bead on platinum wire. J. L. CULBERTSON (J. Amer. Chem. Soc., 1934, 56, 1921—1922).—The forces involved are analysed.

E. S. H.

Firmness of oil films. J. TAUSZ and P. SZEKELY (Erdöl u. Teer, 1933, 9, 331—333; Chem. Zentr., 1933, ii, 3944).—The change in thickness of an oil film on Hg is measured by partly immersing a steel ball in the Hg. Change in thickness of the film under these conditions is recorded as a change in capacity of the condenser formed by the steel and Hg. Thin, resistant films could not be obtained with oils having an aromatic base.

H. J. E.

Structure of monolayers of myristic acid. N. W. H. ADDINK (J. Chem. Physics, 1934, 2, 574—577).—A re-examination of force-area and surface potential-area curves has been made for areas $< 40 \text{ \AA}^2$ in order to determine whether a true hysteresis or a collapse phenomenon takes place when an expanded film of myristic acid on H_2O is condensed. It is found that a metastable expanded film is obtained on compression, and this forms a stable film after several hr. The time of stabilisation can be reduced by the presence of tannic acid without causing any change in the surface potentials. During the time necessary to obtain stable films no further change in force occurs after 25—30 min., whilst a slow change in the phase boundary potential continues for several hr. The probable changes occurring in the hydration and orientation of the mols. are discussed.

M. S. B.

Small-scale structure of surfaces. G. P. THOMSON (Phil. Mag., 1934, [vii], 18, 640—656).—A discussion of surface structure, based on electron diffraction experiments.

H. J. E.

Complex nature of the surface of wood charcoal. A. KING and C. G. LAWSON (Kolloid-Z., 1934, 56, 21—30).—Mainly a crit. review of published work. Experiments on the extraction of $\text{H}_2\text{C}_2\text{O}_4$ from wood charcoal, after activation in O_2 , are described.

E. S. H.

Friction at mica surfaces. B. DERJAGUIN and V. LAZAREV (Kolloid-Z., 1934, 69, 11—16).—The coeff. of friction, μ , between fresh surfaces of mica is approx. 1.0; with repetition of the test on the same specimens μ falls to 0.4—0.5. In presence of

H₂O $\mu=0.2$, whilst for aq. 0.18% NaOH $\mu=0.18$. Liquids which are usually good lubricants are less effective than H₂O in lowering μ (e.g., with oleic acid $\mu=0.35$, with isoamyl alcohol $\mu=0.75$). The bearing of these phenomena on the role of H₂O in the plasticity of clay is discussed. E. S. H.

Diffusion of magnesium and cadmium sulphates. L. W. ÖHOLM (Finska Kem. Medd., 1934, 43, 55—66).—The optical method of Davies (A., 1933, 347) gives vals. for the coeff. of diffusion of MgSO₄ and CdSO₄ which do not agree with those obtained by other methods or with the relations shown by other physico-chemical properties of these salts. H. W.

Physico-chemical investigations of aqueous potassium permanganate solutions. A. SINGH (Arch. Phys. biol. Chim.-Phys., 1933, 10, No. 5, 1—95; Chem. Zentr., 1934, i, 1793).—The position of the absorption bands of aq. KMnO₄ depends on the p_H of the solution for bands in the visible spectrum. In the ultra-violet this effect is not observed. This is correlated with potentiometric observations. H. J. E.

Vapour-pressure measurements with aqueous solutions of alkali halides. A. LANNUNG (Z. physikal. Chem., 1934, 170, 134—144).—By means of a hot-wire manometer of the Knudsen type the v.p. of aq. solutions of all the alkali halides, except LiF and NaF, at concns. from about M to saturation and the v.p. of their stable hydrates have been measured at 18°. The solubilities in air-free H₂O under reduced pressure at 18° are recorded. R. C.

Theory of Brownian movement. J. A. KRUTKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 87—93).—Mathematical. H. J. E.

Law of fall of ultramicroscopic selenium particles. A. BERKOWITSCH (Helv. phys. Acta, 1933, 6, 259—261; Chem. Zentr., 1933, ii, 3669).—With velocities of fall up to 20 cm. per sec. the velocity of fall of a charged Se particle in a field, and its dependence on pressure, followed the same laws as for an uncharged particle falling under gravity alone. H. J. E.

Sedimentation equilibrium of inorganic salts in the ultra-centrifuge. K. O. PEDERSEN (Z. physikal. Chem., 1934, 170, 41—61).—The formula for sedimentation equilibrium in solutions of electrolytes and non-electrolytes has been derived thermodynamically. It affords a new means of determining activity coeffs. from the variation in concn. of a solute in sedimentation equilibrium. Measurements of the sedimentation equilibrium of CsCl, CsI, KIO₃, LiIO₃, TiNO₃, HgCl₂, and CdI₂ in the ultra-centrifuge in a centrifugal field of about 2×10^5 times gravity gave mol. wts. agreeing, except for CdI₂ and CsCl, with the true mol. wts. to within about 10%. R. C.

Determination of intensity of the Tyndall light in the ultra-violet spectral region, and the intensity of the Tyndall light of gold hydrosols prepared by the nuclear method. H. RINDE (Kolloid-Z., 1934, 69, 1—11).—Apparatus and technique are described. With Au sols prepared by the nuclear method the Tyndall light is weak between

$\lambda\lambda$ 440 and 330 m μ , but passes through a max. between 300 and 270 m μ . The intensity is very small for highly disperse sols, but increases rapidly with increasing particle size; at const. [Au] the greatest intensity is observed when the particle radius is 40—50 m μ . E. S. H.

Chromatic disperse two-phase glasses. E. KNUDSEN (Kolloid-Z., 1934, 69, 35—43).—The optical properties of the system Na₂O—PbO—SiO₂—Ca₃(PO₄)₂ are described. The change of chromatic dispersion brought about by adding different amounts of CaO, PbO, TiO, TiO₂, and SiO₂ is discussed. E. S. H.

Preparation of colloidal iron sulphide. T. PINTER (Farm. Vjesnik, 1933, No. 22, 1—6; Chem. Zentr., 1934, i, 1169).—H₂S was passed into a dialysed colloidal solution of electronegative basic Fe arsenite (I). Alternatively the (I) solution was poured into aq. (NH₄)₂S_x. The resulting solutions contain Na⁺, NH₄⁺, and AsS₃[—]. Colloidal FeS solution is also formed by the reaction in sunlight of aq. K₄Fe(CN)₆ with (NH₄)₂S_x or of K₄Fe(CN)₆ with NH₄HS and S in aq. solution. H. J. E.

Action of carbon monoxide on chloroplatinic acid solution. I. SANO (Bull. Chem. Soc. Japan, 1934, 9, 320—326).—The red negatively-charged colloidal Pt prepared by passing CO into aq. H₂PtCl₆ at room temp. is more stable than the black sol. O₂, H₂O₂, alcohols, and COMe₂, also evacuation and heating, turn the red sol black. It is inferred from these results and from the action of aq. Br, and the change in electrical conductivity on formation, that the red sol contains Pt carbonyl. R. S. B.

Colloidal hydrous beryllium oxide. W. H. MADSON (Trans. Illinois State Acad. Sci., 1933, 25, 171—172).—BeCl₂ solution was evaporated almost to dryness and the residue plunged into boiling H₂O. The sols thus obtained were dialysed through collodion membranes; the p_H rose to approx. 7, and the [Cl[—]] was very small. The stabilisation of the sols is discussed. CH. ABS.

Similarity of aluminium salt solutions and aluminium hydrosols. T. H. WHITEHEAD and J. P. CLAY (J. Amer. Chem. Soc., 1934, 56, 1844—1846).—The effect of several anions on the p_H of Al⁺⁺⁺, Al(OH)⁺⁺, and Al(OH)₂⁺ solutions, and Al(OH)₃ sols shows that there is no abrupt transition throughout the series. E. S. H.

Solutions of titanium dioxide in sulphuric acid and the properties of the products obtained from them by hydrolysis and dialysis. N. PARRAVANO and V. CAGLIOTI (Gazzetta, 1934, 64, 429—450).—Solutions of TiO₂ in H₂SO₄ contain an equilibrium mixture of Ti⁺⁺⁺⁺ and SO₄[—] ions and colloidal complexes of TiO₂ and H₂SO₄. The proportions of these constituents depend on the age and concn. of the solution and the temp. to which it has been heated. On boiling the solutions, metatitanic acid is formed by hydrolysis, but the kinetics of the process depend on the acidity and TiO₂ content of the solution. When the product of hydrolysis is calcined, X-ray investigation shows that the resulting TiO₂ may have the structure of either anatase or rutile, depending on the concn. of the original solution. Similarly two

types of gel are obtained by dialysis of TiO_2 solutions in H_2SO_4 . These are also characterised by their different behaviour on calcination. O. J. W.

Peptisation of titanium hydroxide and properties of the resulting solutions. N. PARRAVANO and V. CAGLIOTI (*Gazzetta*, 1934, 64, 450—460).—Various colloidal solutions of TiO_2 have been prepared by peptising the products of hydrolysis and dialysis of TiO_2 solutions in H_2SO_4 and HCl . The particles of TiO_2 have a weak positive charge which can be reversed by suitable agents such as alkalis and Na_3PO_4 . The solutions are thixotropic. For the univalent ions the flocculating power decreases in the order $\text{Br} > \text{CNS} > \text{I} > \text{Cl} > \text{NO}_3 > \text{ClO}_3$. Viscosity measurements have also been made. O. J. W.

Viscosimetric investigations of the structure formation of vanadium pentoxide sols. I. Factors of structure viscosity. A. RABINERSON (*Kolloid-Z.*, 1934, 69, 66—73).—Viscosity measurements in presence and in absence of electrolytes indicate that the main factors are the rod-like shape of the particles, their mode of aggregation, and the degree of orientation of the coagulation structures. E. S. H.

Setting and structure viscosity of benzopurpurin and chrysophenin sols. T. P. PAPKOVA-KVITZEL (*Kolloid-Z.*, 1934, 69, 57—65).—Benzopurpurin (I) sols ($< 1\%$) and chrysophenin (II) sols set to thixotropic gels. Structure viscosity observed in (I) is due to the rod-like shape of the particles, but the structural effect is lost after adding electrolytes. The behaviour of sols of (II) resembles that of (I) in the presence of electrolytes. E. S. H.

[Validity of the Clausius-Mosotti law for emulsions.] W. S. URBANSKI (*Acta phys. polon.*, 1932, 1, 411—412; *Chem. Zentr.*, 1934, i, 1019; cf. Piekara, A., 1933, 123).—Polemical. H. J. E.

Adherence and coalescence in emulsions. W. C. M. LEWIS (*Trans. Faraday Soc.*, 1934, 30, 958—967).—If the crit. potential is the limiting condition for adherence between emulsion droplets which possess the average kinetic energy of translation, the min. area of adherence is of the order of 10^{-13} sq. cm. The estimate of 30 mv. by Powis for the crit. potential is probably too high. The decrease of interfacial surface energy in the change from adherence to coalescence is probably sufficient to account for the removal of the H_2O mols. separating two adhering oil droplets. M. S. B.

Reversal of emulsion type. C. L. WILSON (*J.C.S.*, 1934, 1360—1361).—Na oleate which is hydrolysed in H_2O is not a simple emulsifier, and, by varying the relative amounts of its hydrolytic products in the system $\text{C}_6\text{H}_5-\text{H}_2\text{O}$, a reversal of the type of emulsion may be obtained. The behaviour is complex and a double reversal can be observed, but it is not electrolytic in origin. M. S. B.

Coagulation of colloids. VIII. Viscosity changes in colloidal arsenious sulphide when coagulated by binary mixtures of potassium halides in the slow region. IX. Effect of stirring on the time variation of viscosity of colloidal

arsenic and antimony sulphides when coagulated by simple electrolytes in the slow region. S. S. JOSHI and T. R. G. IYENGAR (*J. Indian Chem. Soc.*, 1934, 11, 555—571, 573—577; cf. this vol., 597).—VIII. Using KCl , KBr , KI , KF , and their mixtures as coagulants, the viscosity (η) of the coagulating sol shows discontinuities in the η -time curve. There is usually a fall in η in the initial stages of coagulation. These two effects disappear with rapid coagulation.

IX. The above effects persist when the sol is stirred during coagulation. H. J. E.

Sensitising action of sera on the coagulation of ferric hydroxide. A. BOUTARIC and F. MORIZOT (*Arch. Phys. biol.*, 1933, 10, 81—90; *Chem. Zentr.*, 1934, i, 1085).—Human and horse serum both reduced the time needed for coagulation of $\text{Fe}(\text{OH})_3$ sol (0.6 g. per litre) by 0.349N- KNO_3 . The activity of the sera is reduced by warming. Protein separated from the sera by Piëtre's COMe_2 method had approx. the same activity. H. J. E.

Rhythmic precipitation of silver chromate in Cellophane. J. RATELADE (*Compt. rend.*, 1934, 199, 555—557). J. L. D.

Dispersion of argillaceous colloids of the soil and sediments. A. DEMOLON and E. BASTISSE (*Compt. rend.*, 1934, 199, 675—677; cf. A., 1933, 24).—On adding alkali to a clay suspension, the cation tends to produce flocculation, and OH^- to produce dispersion. The max. stability is obtained with NaOH , LiOH , aq. NH_3 , and KOH at p_H 8.7, 8.6, 9.0, and 7.7, respectively. Other anions also stabilise the suspension, the citrate anion being the most effective. Results of soil analyses are recorded. H. J. E.

Fractional dissolution of cellulose dextrin acetate and of fibre-forming cellulose triacetate. M. TANIGUCHI and I. SAKURADA (*J. Soc. Chem. Ind. Japan*, 1934, 37, 485B).—Cellulose dextrin acetate (I), prepared according to Hess and Friese, and cellulose triacetate can be fractionated by extracting with more and more conc. solutions of COMe_2 in C_6H_6 . The viscosity in CHCl_3 and the optical rotation of (I) increase with decreasing solubility, whilst the OAc content and the I val. of (I) vary only slightly. A. G.

Viscosimetric investigation of solutions of cellulose dextrin acetate and of cellulose triacetate. M. TANIGUCHI and I. SAKURADA (*J. Soc. Chem. Ind. Japan*, 1934, 37, 486B).—Data are recorded for the viscosities in CHCl_3 of fractions of cellulose dextrin acetate (I) and of cellulose triacetate (II) of graded solubility in $\text{COMe}_2-\text{C}_6\text{H}_6$. The vals. of the sp. vol. v and of the form and charge factor a , calc. from $c/\eta_{sp} = 100/av - (1/a)c$, where c is the concn., increase with decreasing solubility. The vals. of a do not differ greatly from that (2.5) for a sphere. A. G.

Comparison of the viscosities of cellulose triacetate and of acetone-soluble cellulose acetate. M. TANIGUCHI and I. SAKURADA (*J. Soc. Chem. Ind., Japan*, 1934, 37, 487—488B).—The vals. of the sp. vol. and of the form and charge factor, calc. from the viscosities of mixtures of COMe_2 and sol. cellulose

acetate, vary considerably with the solvent, and decrease with rising temp.; cellulose triacetate is not markedly different. A. G.

State of cellulose compounds in solution. II. Rotatory dispersion of cellulose nitrate and degradation products of cellulose acetate. (MME.) A. DOLRY and J. DUCLAUX (Bull. Soc. chim., 1934, 1, [v], 967—970).—Vals. of $[\alpha]$ at 6520—4700 Å. in 12 solvents favour the view that the mols. of cellulose nitrate, cellobiose octa-acetate, and *d*-glucose α - and β -penta-acetate are deformed by the solvents and that the effects differ in magnitude only and not in kind. For each substance in the several solvents the lines representing the relation between $[\alpha]$ and λ are concurrent (cf. A., 1933, 1243). J. G. A. G.

Characteristics of aqueous starch solutions. Measurements by Svedberg's ultra-centrifuge. O. LAMM (Kolloid-Z., 1934, 69, 44—56).—Measurements of sedimentation velocity and equilibrium in the ultra-centrifuge provide a means of characterising aq. starch sols, prepared by different methods. Vals. of mean mol. wt. are given. Two components in acid-treated starch solutions have been identified with amylose and amylopectin, respectively. Both components are complex (especially amylopectin) and are influenced by the previous treatment of the starch and the mode of prep. of the solution. E. S. H.

Lyophilic colloids. III. Solvation of different fractions of gelatin. S. M. LIEPATOV and J. PUTILOVA (Kolloid-Z., 1934, 69, 73—79; cf. this vol., 1069).—The osmotic pressure, viscosity, and heats of swelling and dissolution of different fractions of gelatin in H_2O have been determined. The heat changes have identical vals. The less sol. fractions are more highly hydrated than the more sol. fractions. The high temp. coeffs. of viscosity and osmotic pressure are not due to hydration changes, but to changes in the size of particles; at about 60° the different fractions behave similarly. E. S. H.

Surface tension measurements of glue and gelatin solutions. T. ACKERMANN (Kolloid-Z., 1934, 69, 87—93).—The bubble-pressure method has been used. The results do not distinguish between hide- and bone-glue, and do not show any simple relation with viscosity, although solutions having a high temp. coeff. of viscosity have a high temp. coeff. of surface tension (I). The (I) of gelatin solutions is at a max. about p_H 3.0. (I) decreases when the gelatin solution is boiled, but is raised by hydrolysis with acid. (I) has also been measured for a no. of NH_2 -acids. E. S. H.

Mordanting and dyeing processes. XVIII. Theory of mineral tanning. Experiments with complex compounds of chromium. E. ELOD and T. SCHACHOWSKOY (Kolloid-Z., 1934, 69, 79—87; cf. B., 1934, 72).—The effect of several Fe^{III} and Cr^{III} compounds on gelatin has been examined by noting the change of solubility, and with Cr^{III} compounds by measuring the absorption spectrum. As with Co^{III} compounds the tanning effect depends on hydrolysis. E. S. H.

Predominating significance of the cation in compounds of neutral salts and isoelectric gelatin. A. SCALA (Ann. Igiene, 42, 313—326; Chem. Zentr., 1934, i, 1824).—The adsorption of $NaCl$, $CaCl_2$, $BaCl_2$, $Al_2(SO_4)_3$, and $CuSO_4$ by swollen isoelectric gelatin at 0° has been measured. H. J. E.

Qualitative chemical observations in gelatin layers. (MLLE.) S. VEIL (Compt. rend., 1934, 199, 611—613).—Diffusion figures in gelatin (this vol., 961) differentiate the ppts. formed by interaction of Na_2CrO_4 with sol. Zn , Tl , Pb , Ba , Sr , and Cd salts, and of KI with Hg^{II} , Tl , Pb , and Ag salts. J. W. B.

Colloidal behaviour of sericin. IV. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 344—352; cf. this vol., 1069).—Colour reactions of sericin (I) have been studied. The Au no. of (I) is nearly equal to that of gelatin, and depends on the concn., the p_H , temp., and age of the solution. The emulsifying properties of (I) have been studied and it is found that (I) protects pyrogallol from oxidation by complex Co salts, and H_2O_2 from decomp. by Pt sol. R. S. B.

Tyrosine-binding power of ovalbumin. J. GRÖH and Z. KERESZTES (Z. physiol. Chem., 1934, 226, 139—145).—When the tyrosine (I) bound by ovalbumin (II) in aq. solution at varying p_H is plotted against (I) concn. the curves show discontinuities (III). These correspond, at p_H 4.7, 3.8, and 8.2, with the fixation of 0.21, 0.21, and 0.27, and at p_H 9.8 [which shows 3 (III)] with 0.43, 1.05, and 2.06 mol. of (I) per mol. of (II), respectively, i.e., approx. simple multiples which suggest mol. compounds. The fixation of (I) is reversible. J. H. B.

Swelling of protein fibres. III. Horsehair. (Miss) D. J. LLOYD and R. H. MARRIOTT (Trans. Faraday Soc., 1934, 30, 944—958).—Keratin fibres, in the form of horsehair, absorb H_2O to the extent of 28% of their dry wt. The amount is increased by preliminary treatment with dil. $NaOH$, which also causes the appearance of regions of max. swelling under both acid and alkaline conditions; the effect is attributable to the establishment of a Donnan equilibrium. The latter is not produced by preliminary treatment with 4*N*- HCl . In acid solutions the birefringence of hair and wool varies slightly up to a concn. of 5*N*, but above this there is a rapid fall. In alkalis the fall is rapid and continuous, the hair becoming isotropic at about *N*- $NaOH$. In neither case is birefringence restored by washing. Oxidising and reducing agents cause swelling and other effects. No treatment, however, produces a fundamental change in the X-ray diagram. Hydrating salts, such as $NaCl$, $NaNO_3$, and LiI , and also $CO(NH_2)_2$ and $CS(NH_2)_2$, cause slightly swelling, but do not affect birefringence appreciably. Keratin appears to have a crystalline structure. The nature of the chemical taking place in the fibre is discussed. M. S. B.

Thermal decomposition of deuterium iodide. D. RITTENBERG and H. C. UREY (J. Amer. Chem. Soc., 1934, 56, 1885—1889).—The observed % of thermal dissociation of mixtures of H^1I and H^2I at 398° and 468° agrees satisfactorily with theoretical predictions. E. S.

Equilibrium between nitric oxide, bromine, and nitrosyl bromide. C. M. BLAIR, jun., P. D. BRASS, and D. M. YOST (J. Amer. Chem. Soc., 1934, 56, 1916—1918).—The equilibrium in the gaseous phase has been measured at 273.1—520° abs., yielding the following results: $\Delta H^\circ = -8780 - 13.41T + 0.0186T^2 - 11.6 \times 10^{-6}T^3$, $\Delta F^\circ = -8780 + 30.88T \log_{10} T - 51.26T - 0.0186T^2 + 5.8 \times 10^{-6}T^3$. The free energy of formation of NOBr at 25° is 19,260 g.-cal. and the virtual entropy at 25° and 1 atm. 65.2 ± 0.3 g.-cal. per degree. E. S. H.

Electrolytic dissociation of heavy water. E. ABEL, E. BRATU, and O. REDLICH (Z. physikal. Chem., 1934, 170, 153).—E.m.f. measurements with cells containing solutions in heavy H₂O indicate that the product of the (total) H⁺ and OH⁻ concns. for H₂O containing 60 mol.-% H₂O is about 0.4 times the val. for ordinary H₂O. R. C.

Ionic product of heavy water. B. TOPLEY and W. F. K. WYNNE-JONES (Nature, 1934, 134, 574).—A preliminary determination gives a val. for K_w which is about one third that for H₂O at the same total ionic strength (0.1 and 0.05). L. S. T.

Ionisation of weak electrolytes in heavy water. G. N. LEWIS and P. W. SCHUTZ (J. Amer. Chem. Soc., 1934, 56, 1913—1915).—The conductivities of AcOH², CH₂Cl-CO₂H², and NH₃OH² in H₂O at 25° have been determined. The derived ionisation consts. are considerably < those for the corresponding H¹ compounds in ordinary H₂O. The theoretical implications are discussed. E. S. H.

Distribution of ions in electrolytic solutions. R. M. FUOSS (Trans. Faraday Soc., 1934, 30, 967—980).—Mathematical. A definition of ion pairs is given. The distribution curve for such pairs has two peaks, one corresponding with short-range pairs and the other with pairs in which the distance apart of the partners approximates to that between the uncharged solute particles. The two groups are considered separately. M. S. B.

Thermodynamic dissociation constant of benzoic acid at 25°. A. I. VOGEL and G. H. JEFFERY (Chem. and Ind., 1934, 779).—The val. 6.373×10^{-5} has been obtained (cf. this vol., 963). E. S. H.

Ionisation constants of benzoic acid and of the three monochlorobenzoic acids at 25°, from conductance measurements. B. SANTON and H. F. MEIER (J. Amer. Chem. Soc., 1934, 56, 1918—1921).—The vals. of K obtained are: BzOH 6.295×10^{-5} , *o*-1.197 $\times 10^{-3}$, *m*-1.506 $\times 10^{-4}$, and *p*-C₆H₄Cl-CO₂H 1.04×10^{-4} . E. S. H.

Relative strengths of hydrocarbon derivatives of boric acid. D. L. YABROFF, G. E. K. BRANCH, and B. BETTMAN (J. Amer. Chem. Soc., 1934, 56, 1850—1857).—The measured dissociation consts. are discussed on the basis of the resonances and negativities of the various groups involved. The prep. of the following compounds is described: β -phenylethylboric acid, m.p. 88°, *n*-butylboric acid, m.p. 93—94°, *o*-, m.p. 195°, *m*-, m.p. 207—208°, and *p*-diphenylboric acid, m.p. 232—234°. E. S. H.

Dissociation constants of organic boric acids. B. BETTMAN, G. E. K. BRANCH, and D. L. YABROFF (J. Amer. Chem. Soc., 1934, 56, 1865—1870).—Data obtained for phenylboric acid derivatives are discussed on the basis of resonance and negativity. The true resonance order for the halogens is F > Cl > Br. *o*-Nitrophenylboric acid is weaker than the *m*- and *p*-isomerides. The prep. of *m*-, m.p. 220—221°, and *p*-fluorophenylboric acids, m.p. 289—290°, *m*-bromophenylboric acid, m.p. 170°, and *p*-phenoxyphenylboric acid, m.p. 123—124°, is described. E. S. H.

Application of colorimetry in the ultra-violet to the determination of the strength of acids and bases. L. P. HAMMETT, A. DINGWALL, and L. FLEXSER (J. Amer. Chem. Soc., 1934, 56, 2010).—In many very weak org. acids and bases ionisation is accompanied by a marked change in the ultra-violet absorption spectrum. A method of deducing the strength of the acid or base from such data is outlined. E. S. H.

Determination of the activity coefficient of hydrochloric acid at high concentrations from solubility measurements. G. ÅKERLOF and H. E. TUREK (J. Amer. Chem. Soc., 1934, 56, 1875—1878).—In the system HCl-NaCl-H₂O at 25° there is reasonably good agreement between the vals. for the activity coeff. of HCl derived from measurements of v.p. and solubility, respectively. E. S. H.

F.-p. measurements. III. Activity coefficients and dissociation of iodic acid. E. ABEL, O. REDLICH, and P. HERSCH (Z. physikal. Chem., 1934, 170, 112—122; cf. A., 1933, 675).—Methods for the derivation of the thermodynamic dissociation const. of an electrolyte of medium strength from f.-p. and from conductivity data have been developed. From f.-p. measurements with aq. HIO₃ solutions containing 0.1—1 g.-mol. HIO₃ per 1000 g. H₂O the dissociation const. at 0° is found to be 0.26₂, whilst from available conductivity data the val. 0.19 is obtained for 18°. Activity coeffs. of HIO₃ are recorded. The validity of the Debye-Huckel theory for HIO₃ has been demonstrated. R. C.

Activity coefficients of the alkali chlorides and of lithium iodide in aqueous solution from vapour-pressure measurements. R. A. ROBINSON and D. A. SINCLAIR (J. Amer. Chem. Soc., 1934, 56, 1830—1835).—V.p. of solutions of sucrose, LiCl, NaCl, RbCl, CsCl, and LiI relative to those of aq. KCl have been determined by an isopiestic method. From the results the activity coeffs. of the halides have been derived. E. S. H.

Equilibrium constants in terms of activities (cryoscopic). IV. Dissociation of *p*-toluidine *o*-tolylxide in benzene and in *p*-dichlorobenzene. H. M. GLASS and W. M. MADGIN (J.C.S., 1934, 1292—1296).—At the f.p. of the solvents, 277.4° and 324.7° abs., respectively, the true equilibrium const. for the dissociation of the solute in C₆H₆ is 31.64 and in *p*-C₆H₄Cl₂ is 6.42. The calc. val. of the heat of formation is -6000 g.-cal. This is < for *o*-chlorophenoxides (cf. this vol., 490) and the difference is attributed to the phenolic H in *o*-C₆H₄Cl-OH being

more positive than in *o*-cresol. The heat of formation of a covalent as compared with that of a coordinate linking is discussed. M. S. B.

Amphoteric oxide hydrates, solutions of their hydrolysable salts, and their complex compounds. XXV. G. JANDER and K. F. JAHR (Z. anorg. Chem., 1934, 219, 263—270).—Recent unpublished work on the absorption spectra of aq. solutions of H_3PO_4 , H_3AsO_4 , and H_2TeO_4 , which indicates the existence of two forms in each case, is discussed in relation to corresponding results with silicic acid and with HNO_3 . It is probable that the existence of two forms is a general property of the oxy-acids. Theories of the structure of the complex acids are discussed, and it is pointed out that attention must be given to the nature of the simple component acids, as well as of the isopoly-acids, when considering the heteropoly-acids. H. F. G.

Two co-existent phases. A. K. VLČEK (Chem. Listy, 1933, 27, 412—415; 1934, 28, 60—63, 73—74).—Theoretical. R. T.

Affinity of metals for oxygen. II. Equilibrium between iron and water vapour. E. V. BRITZKE, A. F. KAPUSTINSKI, and T. I. SCHASCHKINA (Z. anorg. Chem., 1934, 219, 287—295).—Sources of error in previous work on the system are summarised. In the method described, equilibrium is assured by maintaining conditions const. for a long period (24 hr.), and the system is examined by physical methods which obviate removal of samples and consequent disturbance of the system, the partial pressures of the H_2O and H_2 being measured directly and independently, and errors due to inert gases eliminated by preliminary high vac. heat treatment of the apparatus. A vessel containing the Fe and FeO is connected to one side of a differential manometer, and a Pd bulb sealed within the vessel to the other, and the reading thus results from the H_2O v.p. alone. Vals. of K_p between 850° and 1225° are recorded. For the reaction $2\text{Fe} + \text{O}_2 \rightleftharpoons 2\text{FeO}$, $\log K_p = -29078/T + 3.5 \log T - 0.00165(T - 600^\circ) - 1.68$; the equilibrium O_2 pressure rises from 15.7×10^{-18} atm. at 850° to 1.72×10^{-12} atm. at 1200°. H. F. G.

Activation of metals. III. R. SCHENK and F. KURZEN (Z. anorg. Chem., 1934, 220, 97—106).—Measurements of the pressure of O_2 over PdO, alone, and also adsorbed on SiO_2 gel or Al_2O_3 , indicate that the adsorbed PdO is more stable than the former. The smaller is the amount adsorbed the greater is the stability. Al_2O_3 is more effective than SiO_2 . By long heating and sintering part of the reduced Pd passes into the normal form. The remainder is much more readily oxidisable, apparently because adsorption on the SiO_2 gel prevents it from forming the normal Pd lattice. Adsorption thus increases the activity of the metal while stabilising the oxide. M. S. B.

Ease of reduction of the oxides of the alkaline-earth metals, including Be. W. KROLL (Z. anorg. Chem., 1934, 219, 301—304).—Heat of formation is not the sole criterion. In addition to temp. and pressure it is necessary to take into account the formation of salts (e.g., aluminates) and of intermetallic

compounds. Reduction of BeO by alkaline-earth metals is appreciable only when a substance is present which lowers the v.p. of the Ca etc. Al does not react appreciably with BeO within 1 hr. at 1600°. H. F. G.

Boric acid and alkali borates. VIII. System $\text{B}_2\text{O}_3\text{--H}_2\text{O}$. H. MENZEL, H. SCHULZ, and H. DECKERT (Z. anorg. Chem., 1934, 220, 49—66).—The system has been studied by thermal dehydration, by X-ray analysis, and tensimetrically. H_3BO_3 exists as a triclinic modification only, other apparent modifications being merely altered growth forms. HBO_2 and H_3BO_3 are the only hydrates. M. S. B.

Binary systems: water-sodium azide and water-potassium azide. J. WOHLGEMUTH (Compt. rend., 1934, 199, 601—603).—The complete binary diagrams, from the eutectic to the b.p., are given. NaN_3 forms a trihydrate, $\text{NaN}_3 \cdot 3\text{H}_2\text{O}$, at low temp. (decomp. -2.1°). KN_3 forms no hydrates. D. R. D.

Hydrazine: transition points and dissociation pressures of hydrated hydrazonium salts. B. E. CHRISTENSEN and E. C. GILBERT (J. Amer. Chem. Soc., 1934, 56, 1897—1899).—The prep. of $\text{N}_2\text{H}_4 \cdot 2\text{HBr} \cdot 2\text{H}_2\text{O}$ (I) is described. Dissociation pressures have been determined for (I), $\text{N}_2\text{H}_4 \cdot \text{HClO}_4 \cdot 0.5\text{H}_2\text{O}$ (II), $\text{N}_2\text{H}_4 \cdot \text{C}_6\text{H}_5(\text{NO}_2)_3\text{OH} \cdot 0.5\text{H}_2\text{O}$, and $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ over a range of temp. (I) has a transition point at $60.5 \pm 0.05^\circ$ and (II) at $61.5 \pm 0.05^\circ$. E. S. H.

Physico-chemical properties of lactose. III. Aqueous vapour tension of α -hydrate-anhydride systems. Preparation of α -anhydride. B. L. HERRINGTON (J. Dairy Sci., 1934, 17, 595—605).—The rate of loss of H_2O of crystallisation (I) of lactose (II) at 80° is controlled by the size of the crystals. The latter does not affect the rate of uptake of H_2O by the anhydride. Prolonged heating of (II) produces changes other than loss of (I). A. G. P.

Thermal analysis and its application to the dinitrobenzenes. F. E. POUNDER and I. MASSON (J.C.S., 1934, 1357—1360).—The setting point and ordinary m.-p. methods for the thermal analysis of binary or ternary mixtures are discussed, and a simple and accurate method is described and applied to the study of mixtures of *o*-, *m*-, and *p*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$. The method is applicable to any other ideal ternary system. The vals. found for the m.p. of the pure isomerides are 117.4°, 90.4°, and 174.2°, respectively. M. S. B.

Caustification of sodium carbonate by ferric oxide. XVII. Dissociation pressure of sodium carbonate in the presence of ferric oxide. M. MATSUI, K. BITO, and G. TANABE (J. Soc. Chem. Ind. Japan, 1934, 37, 515—517B).—The dissociation pressure curve of Na_2CO_3 in the presence of Fe_2O_3 shows discontinuities at 610—640°, 730—740°, and 780—800°, the last of which corresponds with the thermal change of ferrite. A.

Caustification of sodium carbonate by ferric oxide. XVIII. Heat of formation of sodium ferrite. M. MATSUI and K. KINJO (J. Soc. Chem. Ind. Japan, 1934, 37, 517—522B).—From data for

the heat of dissolution of $\text{Na}_2\text{Fe}_2\text{O}_4$ in HCl its heat of formation is $-42,695.6 \pm 35.2$ g.-cal., and hence the heat of dissociation of Na_2CO_3 in the presence of Fe_2O_3 is $-34,357$ g.-cal.: the mean val. calc. from the dissociation pressure is $34,574$ g.-cal. A. G.

Calcium cyanamide. V. Cyanide-melt process and its inversion. (Preparation of calcium cyanamide from sodium cyanide.) H. H. FRANCK and W. BURC (Z. Elektrochem., 1934, 40, 686—692; cf. this vol., 148).—The inversion of the reaction $\text{CaCN}_2 + \text{C} + 2\text{NaCl} = \text{CaCl}_2 + 2\text{NaCN}$ has been studied at 900° , 1000° , and 1100° . The formation of CaCN_2 is favoured by lowering the temp. E. S. H.

Reaction $\text{Ba}(\text{CN})_2 \rightleftharpoons \text{BaCN}_2 + \text{C}$ in the temperature region $500\text{--}1000^\circ$. H. H. FRANCK and R. NEUBNER (Z. Elektrochem., 1934, 40, 693—698).—Investigations on 97% BaCN_2 and 99% $\text{Ba}(\text{CN})_2$ show that with rising temp. the equilibrium shifts in the direction of increasing $\text{Ba}(\text{CN})_2$. This result is discussed from the viewpoint of the phase rule. E. S. H.

Thermochemical data of reaction in the system $\text{Me}^{\text{U}}\text{CN}_2 + \text{C} = \text{Me}^{\text{II}}(\text{CN})_2$ determined with alkaline earths. H. H. FRANCK and H. BANK (Z. Elektrochem., 1934, 40, 699—702).—The following heats of formation or reaction are given (kg.-cal.): BaCN_2 , 65.5, $\text{Ba}(\text{CN})_2$, 49.0, $\text{BaCN}_2 + \text{C} \rightarrow \text{Ba}(\text{CN})_2$, -16.6 , $\text{Ca}(\text{CN})_2$, 45.5, $\text{CaCN}_2 + \text{C} \rightarrow \text{Ca}(\text{CN})_2$, -38.5 . E. S. H.

(a) **Equilibria in the system $\text{MgCl}_2\text{--NH}_4\text{Cl--H}_2\text{O}$.**
(b) **Tensimetric study of ammonium carnallite.** N. K. VOSKRESENSKAJA (J. Gen. Chem. Russ., 1934, 4, 153—167, 173—175).—(a) The solid phases over the range -34.6° to 115° are $\text{MgCl}_2 \cdot 4, 6, 8$, and $12\text{H}_2\text{O}$, NH_4Cl , $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (I), and ice; solid solutions are not formed. The solubility of NH_4Cl in saturated aq. MgCl_2 is $< 1\%$, except in the vicinity of the transition point, at which it rises to 2.8% .

(b) The dissociation pressure of (I) is 0.5 mm. at 25° , the products being NH_4Cl and $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, which loses H_2O only over P_2O_5 . R. T.

Active oxides. LXXVIII. Active states during the conversion of mixtures of alkaline-earth carbonates and ferric oxide into spinel. G. F. HUTTIG and H. KITTEL (Z. anorg. Chem., 1934, 219, 256—262).—The colour, bulk density, and magnetic susceptibility, χ , of 1:1 mixtures of $\text{Ca}(\text{Sr}, \text{Ba})\text{CO}_3$ and Fe_2O_3 heated for 6 hr. at temp. up to 1000° are recorded, together with the vol. of CO_2 evolved during the heating. The decomp. temp. of the carbonate is lowered considerably for Ba, to a smaller extent for Sr, and inappreciably for Ca. The change of χ indicates that "nascent" CaO is more reactive than is ordinary CaO . Ferromagnetic properties appear when only a little spinel has been formed; for mixtures containing no ferromagnetic material, $\chi \propto$ the quantity of carbonate which has decomposed. H. F. G.

Equilibria between iron, oxygen, and silicon, calcium, or phosphorus. F. KANZ, E. SCHEIL, and E. H. SCHULZ (Arch. Eisenhüttenw., 1934—1935, 8, 67—74).—The phases stable at room temp. in ternary systems of Fe and O with Si, Ca, and P have been

determined at the Fe corner by micrographic examination. In the Fe-O-Si system there are three two-phase fields: $\alpha + \text{FeO}$, $\alpha + \text{Fe}_2\text{SiO}_4$, and $\alpha + \text{SiO}_2$; and two three-phase fields: $\alpha + \text{FeO} + \text{Fe}_2\text{SiO}_4$, and $\alpha + \text{Fe}_2\text{SiO}_4 + \text{SiO}_2$, from which it follows that the systems Fe- Fe_2SiO_4 and Fe- SiO_2 are quasibinary. Saturated α solid solution in equilibrium with FeO contains 0.6% Si, and in equilibrium with Fe_2SiO_4 2.5% Si. A silicate corresponding with grünerite cannot be prepared by fusion. In the ternary system Fe-Ca-O regions of three-phase equilibrium with Fe are: $\alpha + \text{FeO} + 2\text{CaO} \cdot \text{Fe}_2\text{O}_3$; $\alpha + 2\text{CaO} \cdot \text{Fe}_2\text{O}_3 + \text{CaO}$; and $\alpha + \text{CaO} + \text{Ca}$. In the Fe-O-P system $\text{Fe}_2\text{P}_2\text{O}_7$ (I) forms quasibinary systems with Fe, FeO, Fe_3O_4 , Fe_3P , and FePO_4 , and three-phase fields with $\alpha + \text{FeO}$, $\alpha + \text{Fe}_3\text{P}$, $\text{FeO} + \text{Fe}_3\text{O}_4$, and $\text{Fe}_3\text{O}_4 + \text{FePO}_4$. In the presence of (I) decomp. of FeO is strongly accelerated. The results indicate that the usual slag inclusions in steel may consist of FeO, Fe_2SiO_4 , SiO_2 , $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$, CaO, or (I). A. R. P.

Glass. XI. Some thermodynamic relations of glassy and α -crystalline glucose. G. S. PARKS, L. J. SNYDER, and F. R. CATTOIR (J. Chem. Physics, 1934, 2, 595—598).—The difference in heat content between the glassy form and α -crystals has been determined calorimetrically at 20° , and the corresponding differences in entropy and free energy have been calc. 1670 g. cal.-per mol. ΔF_{298}° determined experimentally from the difference in solubility of the two forms in MeOH, EtOH, and Pr^nOH , respectively, is in good agreement with this val. The results indicate that fairly satisfactory thermodynamic data may be obtained for well-annealed glasses, especially near the softening temp. The thermodynamic potential of glucose glass is only slightly $>$ that of either α - or β -crystals. M. S. B.

New thermodynamical principle. B. BRUŽS (Latvian Univ. Raksti, 1934, 2, 341—356).—To the fundamental laws of energy, of potential, and of capacity it is proposed to add the relation that the force acting in statistical processes on a mole of a mobile substance is equal to the gradient of the latent energy, $dTS/dx = (\partial TS/\partial \psi) \times (\partial \psi/\partial x)$, where ψ is potential, of this substance. This is in accord with the fundamental observation that energy changes at the walls of stationary systems take place without change in free energy. The new principle may be expressed by the statement that free energy, considered as a function of an arbitrary variable, cannot change discontinuously. A. G.

Heat of formation of hydrogen chloride and its dilute solutions. W. A. ROTH and H. RICHTER (Z. physikal. Chem., 1934, 170, 123—133).—Redetermination of the heat of formation of HCl from its elements has led to the adoption of $+21.89 \pm 0.02$ kg.-cal. at 22° as the most probable val. Determination of heats of dissolution of HCl in H_2O at concns., m , of $0.0058\text{--}0.095$ g.-mol. per 1000 g. H_2O has given results representable by $Q = (17.78 - 0.4514m^{\frac{1}{2}})$ kg.-cal. R. C.

Thermochemistry of solutions. II. Heats of dissolution of electrolytes in non-aqueous solvents. F. A. ASKEW, E. BULLOCK, H. T. SMITH,

R. K. TINKLER, O. GATTY, and J. H. WOLFENDEN. **III. Heats of dilution of electrolytes in non-aqueous solvents.** N. S. JACKSON, A. E. C. SMITH, O. GATTY, and J. H. WOLFENDEN (J.C.S., 1934, 1368—1376, 1376—1379).—II. The heats of dissolution of 17 uni-univalent salts have been determined at 20°, and at a concn. of approx. 0.01*N*, in one or more of the solvents H₂O, MeOH, EtOH, MeNO₂, PhNO₂, and COMe₂. The results do not confirm the Born-Bjerrum equation for the heat of solvation of ions and they indicate that the term involving solvent properties is at fault. Further, the equation does not correctly relate ionic size to the magnitude of heat of transfer. There appear to be characteristic differences between the heats of solvation of cations and of anions.

III. The heats of dilution of 11 salts in one or more of the solvents H₂O, MeOH, EtOH, MeNO₂, and PhNO₂ have been measured. Negative heats of dilution are less frequently observed in non-aq. solvents than in H₂O. A correlation between negative heats of dilution on the one hand, and negative heats of dissociation, together with low heats of ionic solvation, on the other, is indicated. Even when allowance is made for incomplete dissociation the results cannot be explained on the basis of the Debye-Bjerrum theory of heats of dilution. M. S. B.

Ionic hydration. J. BABOROVSKY (Chem. Listy, 1934, 28, 242—244).—Polemical against Ulich.

R. T.
Relation of ionic mobility to viscosity of medium. G. ANGEL (Z. physikal. Chem., 1934, 170, 81—96).—Theoretical. The variation with temp., *t*, of the fluidity, ϕ , of H₂O may be accurately represented by the empirical equation $\phi_t - \phi_{18} [1 + a(t-18) + a'(t-18)^2]$ over the temp. range of validity of Kohlrausch's formula for the variation with temp. of ionic mobility, *l*, at infinite dilution, $l_t = l_{18} [1 + c(t-18) + c'(t-18)^2]$. Combining these, $(l/l_t)(dl/dt) = m(1/\phi_t)(d\phi/dt)$, where $m = c/a$. This equation agrees approx. for H⁺ and OH⁻, and exactly for the other ions, with Kohlrausch's experimental data at 0—35°, and is equiv. to Johnston's formula where *k* and *m* are consts. (A., 1909, ii, 854). The above fluidity equation is valid also for the electrolytes themselves, being in approx. agreement with Kohlrausch's data for acids and bases and in exact agreement with the data for neutral salts. Hence for the equiv. conductivity of an electrolyte $\Lambda_t - \Lambda_{18} f_t^{n_e} = u_{18} f_t^{m_u} + v_{18} f_t^{m_v}$, where $\Lambda_{18} m_u - u_{18} m_u + v_{18} m_v$ and f_t is the fluidity of H₂O at *t*, relative to that at 18°. R. C.

Deviations from Ohm's law in weak electrolytes. L. ONSAGER (J. Chem. Physics, 1934, 2, 599—615).—Theoretical. The effect of an external electric field on electrolytic dissociation is calc. from the equations for Brownian motion in the combined Coulomb and external fields. The theory is confirmed quantitatively by the deviations from Ohm's law observed for solutions of weak electrolytes in H₂O and C₆H₆. For solutions of salts in COMe₂, and for solid electrolytes such as glass, mica, and celluloid, the observed increments of conductance are smaller than those expected from theory, but of the same

order. The kinetic consts. of dissociation and recombination can be calc. separately, assuming that recombination is regarded as the mutual approach of two ions due to the Coulomb attraction. It may be slower than this owing to the necessity for a chemical rearrangement of ion pairs. The most general scheme is ions pairs \rightleftharpoons mols. Dissociation alone depends on the field, and there may be a time lag if a large field is applied suddenly. The saturation phenomena in dielectrics are discussed in relation to the field effect. M. S. B.

Conductivity of isomeric organo-magnesium compounds in ethereal solution. N. V. KONDIRIEV and A. I. SHELVIS (J. Gen. Chem. Russ., 1934, 4, 203—208).—MgPr^aBr and MgPr^bBr give conductivity-concn. curves of the same type, and are equally good electrolytes. The temp. coeff. is positive in higher, and negative in lower, concn. R. T.

Properties of electrolytic solutions. XII. Influence of temperature on the conductance of electrolytes in anisole. G. S. BIEN [with C. A. KRAUS and R. M. FUOSS] (J. Amer. Chem. Soc., 1934, 56, 1860—1865).—The conductance of NBu₄ nitrate and picrate in anisole has been determined over the range 0.00001—0.01*N* and -33° to 95.1°. The significance of the results is discussed.

E. S. H.
Properties of electrolytic solutions. XI. Temperature coefficient of conductance. R. M. FUOSS (J. Amer. Chem. Soc., 1934, 56, 1857—1859; cf. A., 1933, 1120).—A theoretical derivation for the case of solvents of low dielectric const. The terms involved are viscosity and two terms arising from the shift of the simpler ionic equilibria with temp. The dependence of the coeff. on temp. and concn. is discussed. E. S. H.

Constitution of the quinquivalent vanadium ion in acid solution. J. E. CARPENTER (J. Amer. Chem. Soc., 1934, 56, 1847—1850).—Determinations of the e.m.f. of the cells Pt|VO₂⁺, VO²⁺, H⁺, ClO₄⁻|H, ClO₄⁻|H₂|Pt at different concns. show that the V^V ion in acid solution is VO₂⁺. Recalculation of the data of Coryell and Yost (A., 1933, 675) shows their results to be in agreement and leads to the val. 0.9996 volt for the standard electrode potential for the reaction VO₂ + 2H⁺ + e = VO²⁺ + H₂O. E. S. H.

Normal potential of beryllium. F. H. GETMAN (Trans. Electrochem. Soc., 1934, 66, 93—102). Measurements have been made of conductivity and μ_{H} of aq. Be(ClO₄)₂ solutions and of the electrode potential of Be|Be(ClO₄)₂ solutions, over a wide concn. range up to 0.215*N*. For $\Lambda_{\infty} = 75.5$, vals. of Λ for dil. solutions conform to Onsager's equation. The electrode potential $\propto \log [\text{Be}(\text{ClO}_4)_2]$. Calculations of normal electrode potential (e_0) assuming equilibrium with Be are claimed to give greater constancy than for Be equilibrium, and e_0 for Be|Be⁺ is given as -1.13 volt on the H scale. H. J. T. E.

Tungsten electrode and its temperature coefficient. Z. A. JOFA and B. I. PETROV (Zavod. Lab., 1934, 3, 728—731).—The potential of the W electrode (I) over the range μ_{H} 4—10 is given by $E - A + \mu_{\text{H}}$

where A and b are consts. characteristic of (I) and of the temp., respectively; the p_H is given by $p_H = [E - A + (t^\circ - 18)]/[50.3 + 0.24(t^\circ - 18)]$. R. T.

Hydrolysis of ferric ion. Standard potential of the ferric-ferrous electrode at 25°. Equilibrium $\text{Fe}^{+++} + \text{Cl}^- = \text{FeCl}^{++}$. W. C. BRAY and A. V. HERSHEY (J. Amer. Chem. Soc., 1934, 56, 1889—1893).—The following data have been calc. from published measurements at 25°: $\text{Fe}^{+++} + e = \text{Fe}^{++}$, $E^\circ = 0.772 \pm 0.001$ volt; $\text{Fe}^{+++} + \text{H}_2\text{O} = \text{FeOH}^{++} + \text{H}^+$, $K^\circ = (60 \pm 5) \times 10^{-4}$; $2\text{Fe}^{+++} + 2\text{Hg} = 2\text{Fe}^{++} + \text{Hg}_2^{++}$, $K^\circ = 0.137 \pm 0.010$, $E^\circ = -0.026 \pm 0.001$; $\text{Fe}^{+++} + \text{Ag} = \text{Fe}^{++} + \text{Ag}^+$, $K^\circ = 0.363 \pm 0.015$, $E^\circ = -0.026 \pm 0.001$; $\text{Fe}^{+++} + \text{Cl}^- = \text{FeCl}^{++}$, $K^\circ = 20 \pm 5$. E. S. H.

Potential measurements in stannic chloride solution. (Miss) M. PRYTZ (Z. anorg. Chem., 1934, 219, 89—96).—E.m.f. measurements in aq. $\text{Sn}(\text{ClO}_4)_4$ give ϵ_0 0.158 volt for $\text{Sn}|\text{Sn}^{++++}$ at 25°. In aq. SnCl_4 the change of e.m.f. with increasing $[\text{SnCl}_4]$ at const. $[\text{Cl}^-]$ is in accordance with Nernst's formula. With increasing f_{Cl^-} const. $[\text{SnCl}_4]$ there is a strong diminution in $f_{\text{Sn}^{++++}}$. KCl appears to depress $[\text{Sn}^{++++}]$ more strongly than HCl, indicating greater complex formation in the former case. M. S. B.

Polarographic studies with the dropping mercury cathode. XLII. Salt action in the electro-reduction of nitrates. M. TOKUOKA and J. RUŽIČKA (Coll. Czech. Chem. Comm., 1934, 6, 339—353).—The reduction potentials, r , of NO_3^- in 0.1-N-chloride solutions, with respect to the $N\text{-Hg}_2\text{Cl}_2$ electrode are $\text{La}^{++} -1.22$, $\text{Ce}^{+++} -1.23$, $\text{Mg}^{++} -1.74$, $\text{Ca}^{++} -1.78$, $\text{Sr}^{++} -1.79$, $\text{NMe}_4^+ -2.15$, and $\text{Li}^+ -2.17$ volts. In alkali nitrate solutions 0.001M- LaCl_3 changes r from -2.0 to -1.2 volts. Ions deposited at more negative potentials than r assist the reduction of NO_3^- and NO_2^- , and ions (e.g., Zn, Cu, Tl, Pb, and BrO_3^-) reduced at more positive potentials than r lower the limiting current of the anion. Halide ions, OH^- , OAc^- , and HCO_2^- have little effect, but SO_4^{--} , $\text{C}_2\text{O}_4^{--}$, and PO_4^{---} depress the limiting current and make r more negative. At high concn. of salts, r tends to -1.5 volts. The results are interpreted in terms of electrokinetic potential effects and the formation of ion-pairs and complexes. J. G. A. G.

p_H measurements in diluted hydrogen carbonate solutions at various pressures of carbon dioxide. J. CARLBERG (Suomen Chem., 1934, 7, [B], 91—92).—The val. obtained for the first thermodynamic dissociation const. of H_2CO_3 is 3.50×10^{-7} at 25°, in disagreement with the results of MacInnes and Belcher (cf. A., 1933, 904); a similar experimental method was used. R. S. B.

Potentiometric investigation of electrolytic dissociation. II. Copper and cadmium carb-ox-yl-ic salts. (Miss) E. FERRELL, J. M. RIDGION, and H. L. RILEY. **III. Copper halides.** H. L. RILEY and H. C. SMITH (J.C.S., 1934, 1440—1447, 1448—1449).—II. By the potentiometric method previously described (A., 1932, 343), the electrolytic behaviour of many Cu and Cd salts of org. acids has been investigated. The results provide information on the structure of several org. anions and also on their catio-

philic properties. A method of distinguishing between *cis*- and *trans*-isomerides is indicated.

III. Potentiometric measurements have been made on Cu halides. Contrary to the generally accepted view, these and the earlier results show that Cu^{++} is more aniphilic than Cd^{++} , i.e., has a greater tendency to form complex ions. M. S. B.

Electrode potential of palladium-black in buffer solutions. P. NYLEN (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 32, 6 pp.).—The electrode first acquires a const. potential slightly positive to the H_2 electrode (at the same p_H), and after some hr. rises rapidly to a second more positive steady val. The first potential varies with the H^+ activity in the same way as the H_2 electrode, and can be used for electrometric titration. It corresponds with a H_2 electrode at 4 mm. partial pressure of H_2 . The potential is unaffected by redox systems at low concns., unless the redox potential is $<$ the first const. potential, when the Pd electrode gives more reproducible redox potentials than the Pt electrode. It is suggested that Pd contains a small amount of H_2 not readily removed by O_2 and other oxidising agents. R. P. B.

Reduction potential of hypophosphite. P. NYLEN (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 29, 6 pp.).—An electrode coated with Pd-black in a solution of hypophosphite and phosphite acquires a strongly negative potential which $\propto \log$. of the hypophosphite concn., is independent of the phosphite concn., and varies with p_H in the same way as the H_2 electrode. Small quantities of Cu and Fe have no effect. The primary oxidation product appears to be transformed irreversibly into $\text{P}(\text{OH})_3$ or $\text{HPO}(\text{OH})_2$. R. P. B.

Cell with hydrogen and mercurous sulphate electrodes. F. ISHIKAWA and H. HAGISAWA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1019—1026).—From the e.m.f. and the temp. coeff. of the cell $\text{H}_2|\text{H}_2\text{SO}_4|\text{Hg}_2\text{SO}_4|\text{Hg}$, the calc. differences between the heats of formation of H_2SO_4 and Hg_2SO_4 or PbSO_4 are $\Delta H_{\text{H}_2\text{SO}_4(l)} - \Delta H_{\text{Hg}_2\text{SO}_4} = -25,291$ g.-cal., and $\Delta H_{\text{PbSO}_4} - \Delta H_{\text{H}_2\text{SO}_4(l)} = -16,874$ g.-cal., respectively. J. W. S.

Piezochemical studies. XXXI. Effect of pressure on affinity. IV. E. COHEN and K. PIEPENBROEK (Z. physikal. Chem., 1934, 170, 145—148; cf. this vol., 365).—The pressure coeff. of the e.m.f. of the cell $\text{Ti}(\text{Hg})|\text{TICNS-KCNS}|\text{KCl-TiCl}|\text{Ti}(\text{Hg})$ under 1—1500 atm., and thus the effect of pressure on the affinity of $\text{TiCl}_{\text{solid}} + \text{CNS}^- \rightarrow \text{TICNS}_{\text{solid}} + \text{Cl}^-$ agree with the Gibbs-Duhem equation $-(\partial E/\partial p)_{T,e} = (\sigma V/\partial e)_{T,p}$. R. C.

Relation between the electromotive force of the lead accumulator and the heat of cell reaction. F. ISHIKAWA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1027—1033).—Improved agreement between the heat of reaction calc. from E and dE/dT and that measured thermochemically is obtained by taking the differential heat of dissolution of H_2SO_4 at infinite dilution as 20,900 g.-cal. per mol. The agreement between the former val. and that calc. independently from the heats of formation of PbSO_4 and H_2SO_4 (cf.

this vol., 1077) indicates that the double sulphate theory is correct within limits of experimental error.

J. W. S.

Eutectic galvanic elements. V. PLOTNIKOV, M. FORTUNATOV, and E. GORENBEIN (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1934, 1, 29—33).—In the cells $\text{Cd|aq. CdCl}_2\text{|Bi-Sn-Pb or Bi, Al|aq. AlCl}_3\text{|NaCl|Cu}$, and $\text{Zn|aq. ZnSO}_4\text{|Cu}$, the baser metal is deposited on the nobler, and the current ceases when the composition of the electrode is identical with that of the given eutectic alloy.

R. T.

Over-potentials in the electrodeposition of metals on indifferent electrodes. A. G. SAMARTZEV and K. S. EVSTROPIEV (Bull. Acad. Sci. U.R.S.S., 1934, 603—613).—Deposition of metals (Cd, Ag) begins at a higher potential than that attained after a few min.; this phenomenon is not due to growth of the crystals, but to the passage of the metal through a state intermediate between the ionic and the metallic.

R. T.

Cathode processes in electrolysis of copper salts. O. KUDRA (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1934, 1, 81—102).—The deposition on the cathode of a spongy black deposit of Cu at high c.d. (σ) does not take place immediately, but after an interval of time τ . The concn. C of Cu^{II} of a given solution is given by $x = \alpha \log \sigma + \beta \log \tau + \gamma$, where $x = \log C$ for CuCl_2 and $\text{Cu(NO}_3)_2$, $x = C$ for CuSO_4 , and α , β , and γ are consts.

R. T.

Anodic behaviour of metallic iron. W. J. MULLER (Korros. u. Metallschutz, 1934, 10, 1—5; Chem. Zentr., 1934, i, 1786).—A crit. review.

H. J. E.

Anodic passivation of gold. W. J. SHUTT and A. WALTON (Trans. Faraday Soc., 1934, 30, 914—926).—Oscillograms of potential variations at an anodically polarised Au electrode have been obtained. The max. limiting c.d., c_0 , for the anodic dissolution of Au and the time of passivation, T , have been measured in aq. solutions of Cl^- , Br^- , and SO_4^{2-} at 25° and in $N\text{-HCl}$ at 15—65°. If c is the c.d. actually applied, $(c - c_0)T = K$ (i.e., coulombs required for passivation) for a given electrolyte. Both c_0 and K approx. \propto halogen-ion concn. in acid, neutral, or slightly alkaline solution. In a pure SO_4^{2-} solution K corresponds approx. with the amount of electricity necessary to form a unimol. layer of oxide on the Au surface. The observed relations hold only if a uniform concn. of electrolyte is maintained by vigorous stirring. To explain the results it is assumed that anions are adsorbed on the electrode surface before anodic action can take place, the rate of adsorption depending on the nature of the ions and their relative concns. in solution. Anodic passivation finally takes place through the discharge of OH^- and formation of a surface layer of Au peroxide which is continuous with the crystal lattice of the metal.

M. S. B.

Attempts to find a substitute for platinum as anode material in electrolytic oxidation processes. II. Lead peroxide anodes. G. ANGEL and H. MELLQUIST (Z. Elektrochem., 1934, 40, 702—707; cf. this vol., 1078).—The properties of electrodes, made by depositing anodically a hard,

dense coating of $\text{PbO}_2 \cdot \text{H}_2\text{O}$ from alkaline Pb tartrate solution on to foils of Fe, steel, or Cu, are described. At such an anode ClO_3^- may be oxidised to ClO_4^- .

E. S. H.

Electrolysis of water under high pressure. I. V. IPATIEV, V. SCHISCHKIN, and S. JURIEV (Z. Elektrochem., 1934, 40, 713—724).—Apparatus and technique for electrolysing H_2O at 200 atm. are described. The results show that with increasing pressure the polarisation does not change in accordance with the thermodynamical formula for the e.m.f. of gas cells. The greater part of the change in p.d. is due to change in the transfer resistance at the electrode surface, and to changes in the resistance of the electrolyte due to the relative amount of gas bubbles.

E. S. H.

Theoretical foundation of the experimentally observed dependence of bath potential on pressure in the electrolysis of water. II. V. SCHISCHKIN and I. DUBKOF (Z. Elektrochem., 1934, 40, 724—728; cf. preceding abstract).—Published work is discussed. The observed fall of p.d. with increasing pressure is attributed to the influence of pressure on the gas bubbles in the liquid.

E. S. H.

Electrolysis of aqueous solutions of hydrogen fluoride and certain alkaline fluorides. H. D. CROCKFORD and J. C. LORTIN (Trans. Electrochem. Soc., 1934, 66, 109—112).—At 0° and 25° electrolysis of aq. solutions of fluorides of H, Li, Na, and K with step-wise increase of applied voltage across rotating smooth Pt electrodes furnishes current-voltage curves with an initial break at 1.62 volts and a second break at a voltage dependent on the cation and the temp. H₂ and O₂ are the only products of electrolysis.

H. J. T. E.

Electrochemistry of the system aluminium bromide-potassium bromide-ethyl bromide. V. PLOTNIKOV and S. JAKUBSON (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1934, 1, 43—47).—During electrolysis Al is liberated at the cathode, and Br at the anode.

Concept of critical increment and radiation hypothesis. W. V. BHAGWAT (J. Indian Chem. Soc., 1934, 11, 507—509).—The radiation frequency deduced from the temp. coeff. of a reaction should accelerate a reaction only when the active state and the state of energy retention for a mol. are identical.

H. J.

Lower explosion limit of mixtures of heavy hydrogen and air. K. CLUSIUS and H. GUTSCHMIDT (Naturwiss., 1934, 22, 693).—The concns. of H₂ and H₂ in mixtures of these gases with air, necessary for the ignition of the mixture in vertical tubes, when fired from below, are 4.10% H₂ and 5.65% H₂, when fired from above, 9.6% H₂ and 11.0% H₂. Differences can be explained by considering different mol. velocities.

Extinction of flames.—See B., 1934, 815.

Ignition temperatures of gases. "tube" experiments of (the late) H. B. H. F. COWARD (J.C.S., 1934, 1382—1406).—The min. temp. of ignition (I) of combustible gases issuing as a jet into 0.06—11 atm. of air, O₂, or N₂O at equal temp

are recorded for lags, t , of 0.5–15 sec. between the time of turning on the jet and ignition occurring. In all cases (I) diminishes with increasing t , and, in general, the pressure–(I) curve is of the same form for all vals. of t . (I) of H_2 burning in dry air has max. vals. at 1–2 atm., and is raised, particularly at low pressure, by H_2O . (I) in O_2 and N_2O is slightly < in air. Ignition of CO in air and in O_2 is preceded by a marked blue phosphorescent beam (II) extending upwards from the orifice of the central tube. The flame appeared in (II). The (I) of CO in air passes through min. with 5–6% of H_2O , and for any % H_2O , (I) has max. at pressures which increase as t is increased. At < 1 atm., H_2 lowers (I) of dry CO in air > does H_2O , but at 1000 mm. the magnitude of the effects is reversed. A mixture of H_2O and H_2 did not diminish (I) to < the val. for the more effective reagent acting alone. The (I) of CH_4 in air is raised by CO_2 and N_2 and max. vals. occur at < 150 mm., whereas with O_2 , the max. are at 200 mm. (I) is slightly diminished by < 25% of H_2 . The (I) of C_2H_6 in O_2 is < in air and only with t < 3 sec. are max. found at 100–760 mm. A luminous beam precedes the ignition of C_5H_{12} , and in air (I), which decreases with increasing pressure, is > in O_2 . (I) of C_2H_4 in air has max. at 400 mm. and is slightly > in O_2 or N_2O . The vals. of (I) for C_3H_6 are < for C_2H_4 . C_2H_2 in air affords max. vals. of (I) at 100 mm. The (I) of Et_2O in air decreases > 400° when the pressure is raised from 75 mm. to 2.5 atm., and with O_2 , (I) is approx. 350° < with air at 400–760 mm. The (I) with N_2O is > with O_2 . Optimum $[NO_2]$ between 0.5 and 1.1% lowered the (I) of H_2 , CO, C_2H_4 , and CH_4 in air 80–170°, but the (I) of H_2 and CH_4 were raised approx. 100° by optimum [I] between 0.01 and 0.15%, and the (I) of CO was raised to 928° by 0.062% of I. The (I) of CH_4 in air is increased by EtI , CHI_3 , $C_2H_4Br_2$, iso-amyl bromide, and $PhBr$, the efficiency of Br being I compounds and twice as great as for $POCl_3$ and $PbEt_4$. Linear relationships were found between log pressure and $1/(I)$ of CO and H_2 , thus correlating the data with those of Semenov and others.

J. G. A. G.

Kinetics of the oxidation of mixtures of ethylene and acetaldehyde. E. W. R. STEACIE and A. C. PLEWES (Proc. Roy. Soc., 1934, A, 146, 72–82).—In general, the oxidation of C_2H_4 is not influenced by the presence of $MeCHO$, from which it is concluded that $MeCHO$ and its products of oxidation are unimportant in chain propagation in C_2H_4 – O_2 mixtures. The oxidation of unsaturated is different in character from that of saturated hydrocarbons. L. L. B.

Polymerisation of olefines. Kinetics of the thermal polymerisation of propylene, isobutylene, and amylene. M. V. KRAUZE, M. S. NEMTZOV, and E. A. SOSKINA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 262–267; cf. this vol., 736).—With initial concn. between 1.6 and 5.1 g.-mol. per litre at 370°, the reactions are homogeneous and afford second-order velocity coeffs. given by $\log K = B - E/RT$, where, for C_3H_6 , $CMe:CMe$, $CH_2:CMe_2$, and mixed amylenes, respectively, B is 10.2, 10.0, 12.3, and 9.8 and energies of activation, E , are 38,000, 38,000,

43,000, and 38,000 g.-cal. With the normal chain compounds, K decreases with increasing mol. wt. owing to steric effects, but the activation energy of the double linking is not affected. J. G. A. G.

Influence of pressure on the spontaneous ignition of inflammable gas-air mixtures. III. Hexane- and isobutane-air mixtures. D. T. A. TOWNEND, L. L. COHEN, and M. R. MANDLEKAR (Proc. Roy. Soc., 1934, A, 146, 113–129; cf. A., 1933, 1016).—Previous investigations have been extended to include the effect of pressure on the spontaneous ignition of C_6H_{14} - and *iso*- C_4H_{10} -air mixtures. As with *n*- C_4H_{10} - and C_5H_{12} -air mixtures, the ignition points lie in two temp. ranges, location in the higher range occurring at low pressures, and in the lower range at high pressures. The results support the view that the lower group of ignition points is due to the survival and further rapid oxidation of certain intermediate compounds, whereas the higher group results from ignitions mainly of the products of their thermal decomp. which are favoured by low pressure. The bearing of the results on the problem of knock is discussed. L. L. B.

Theory of flame propagation. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1934, 2, 537–546).—A new theory of flame propagation, which supplies a knowledge of the structure of the flame front during slow inflammation, is developed on the assumption that the highly energised atoms or radicals formed in the flame front play a more important part than heat conductivity in making the unburned gas reactive. A small no. of these energised atoms diffuse over into the unburnt phase and initiate chemical reaction. It is suggested that the sum of the thermal and chemical energy per unit mass of gas in all layers from the burnt to the unburnt phase is const. A formula is given for flame speed, and the theory has been applied to explosions of mixtures of O_3 and O_2 , the observed and calc. velocities being in satisfactory agreement. The differences between the present and previous theories are discussed. M. S. B.

Kinetics of the homogeneous thermal decomposition of ethyl ether at pressures up to 200 atmospheres. E. W. R. STEACIE and E. SOLOMON (J. Chem. Physics, 1934, 2, 503–512).—A simple apparatus for the measurements is described, and has been used to follow the decomp. of gaseous Et_2O at 426° for pressures of 2000–14,500 cm. The rate of reaction increases rapidly with pressure up to 10,000 cm. and then more slowly. At 14,500 cm. it is approx. 50 times the val. previously assumed for infinite pressure. The results can be explained on the assumption that the no. of degrees of freedom involved \propto the time between mol. collisions.

M. S. B.

Homogeneous first-order gas reactions. V. Decomposition of paracetaldehyde at high pressures. A. L. GEDDES and C. C. COFFIN (Canad. J. Res., 1934, 11, 180–189; cf. A., 1932, 1094).—The homogeneous first-order decomp. of paracetaldehyde has been studied from 230° to 254° up to pressures causing appearance of the liquid phase. Over-all velocity coeffs. have been determined from this point

to the crit. point. In the gaseous state increase of pressure diminishes the reaction velocity, which is five times as great in the liquid state. The peculiarities at the crit. point are discussed and preliminary observations on the termol. reverse reaction described.

H. N. R.

Velocity of reactions in solution. A. E. BRADFIELD (Nature, 1934, 134, 421—422).—Williams and Hinshelwood's conclusion (this vol., 971) supports the authors' previous work (A., 1932, 26). The bromination of ethers in 50 and 75% AcOH indicates that change in the medium or reagent is accompanied by a change in the activation energy such that $E_1 - mE_2$, where m is a const. independent of the constitution of the ether.

L. S. T.

Kinetics of esterification. Reaction between acetic acid and methyl alcohol. A. C. ROLFE and C. N. HINSHELWOOD (Trans. Faraday Soc., 1934, 30, 935—944).—The reaction takes place in buffer solutions according to the equation $-d[\text{AcOH}]/dt = [\text{MeOH}](k_0[\text{AcOH}][\text{H}^+] + k_1[\text{AcOH}][\text{AcOH}] + k_2[\text{AcOH}][\text{X}])$, where X, a basic constituent of the buffer, $\propto 1/[\text{AcOH}]$. The k_0 term is important in absence of a buffer. In presence of a buffer the k_1 term preponderates in *N*-AcOH, but below 0.05*N* the k_2 term outweighs it. Measurements have been made at temp. up to 151.4°. The energy of activation is 13,000 g.-cal. In anisole solution the rate of esterification has been determined at temp. up to 237° and is given approx. by $-d[\text{AcOH}]/dt = k[\text{MeOH}][\text{AcOH}]^{1.5}$. From the initial rate of reaction the energy of activation is 10,800 g.-cal. and from the rate after 40 min. 11,300 g.-cal. The mol. statistics of the reaction are discussed. The reaction is of the "slow" type between uncharged mols.

M. S. B.

Determination of the velocity of esterification and the viscosity in ethyl-alcoholic hydrochloric acid, with and without addition of neutral salts and of benzophenone. A. KAILAN and V. KIRCHNER (Monatsh., 1934, 64, 191—212; cf. A., 1931, 45).—The relative η of EtOH-H₂O mixtures and of dry (I) and H₂O-containing (II) (*w* mol. H₂O per litre) HCl (concn. *c*)-EtOH mixtures with and without addition of BzOH, and with addition of various concns. of LiCl, CaCl₂, HgCl₂, and CPh₂, and the corresponding velocities of esterification (*v*), have been determined at 25°. The decrease (LiCl > HgCl₂ > CaCl₂) in *v* with (I), and the increase (CaCl₂ >> LiCl > HgCl₂; HgCl₂ causes an increase only in concn. > 0.333*N*) in *v* with (II), approx. \propto the concn. of added salt. In (I) the decrease in *v* results from increased η , to which it is approx. proportional, whereas in (II) such decrease is outweighed by the increase in *v* resultant on the removal of H₂O by solvation of the salt ions. In agreement with this view, CPh₂, which cannot combine with H₂O, causes a slight decrease in *v* (except for *c*=0.667, *w*=1.333) in both (I) and (II), corresponding with a similar slight increase in η . The results are fully discussed on this basis.

J. W. B.

Velocity of esterification of substituted fatty acids. A. KAILAN and L. JUNGERMANN (Monatsh., 1934, 64, 213—228).—The velocity coeffs. (*k*) of the HCl (concn. *c*)-catalysed esterification of

OPh·CH₂·CO₂H, CN·CH₂·CO₂H, and CH₂Br·CO₂H (I) (also at 15°, *k* increases 1.97 times from 15° to 25°) in H₂O-free (II) and aq. (III) EtOH, and of CH₂I·CO₂H, CHMeBr·CO₂H (IV), CH₂Cl·CO₂H (V), CH₂Br·CH₂·CO₂H (VI), α -bromo-butyric (VII), -valeric (VIII), and -isovaleric (IX) acids, in (II) at 25°, have been determined. The decrease in *k* caused by α -substituents in AcOH is Cl < Br < OPh < Ph < I < CN, the vals. of *k/c* in EtOH containing 0.030 mol. H₂O per litre being, respectively, 0.630, 0.568, 0.542, 0.401, 0.355, and 0.077, relative to AcOH=1. Differentiation between Cl and Br is much less in the β - than in the α -position, *k/c* for (V) and (VI) being 3.08 and 3.35, respectively. The retarding action of an α -Br is the greater the longer is the C-chain, the *k/c* vals. for (I), (IV), (VII), (VIII), and (IX) being, respectively, 56.8, 18.1, 12.2, 12.9, and 9.5% of those for the unsubstituted parents.

J. W. B.

Velocity of hydrolysis of stereoisomeric hydrazones and oximes. R. W. JOHNSON and J. STIEGLITZ (J. Amer. Chem. Soc., 1934, 56, 1904—1908).—The velocities of hydrolysis of the hydrazones and oximes of CPh₂ and the stereoisomeric α - and β -methoxybenzophenone have been determined. A considerable difference occurs in the stereoisomeric oximes, but not in the stereoisomeric hydrazones. In all cases the reactions are pseudo-unimol. In the hydrolysis of hydrazones a side reaction occurs, producing a ketazine, [$\text{N}:\text{CRR}'$]₂.

E. S. H.

Semicarbazone formation in 60% methyl cellosolve [glycol monomethyl ether]. F. H. WESTHEIMER (J. Amer. Chem. Soc., 1934, 56, 1962—1965).—The [H^+] of buffer solutions in aq. 60% OH·CH₂·CH₂·OMe (I) have been determined, using the Sb electrode. The rates of condensation of semicarbazide with several aldehydes and ketones in buffered solutions of (I) have been measured and compared with results obtained in H₂O.

E. S. H.

Action of dilute alkali on tetramethylglucose. J. H. SIMONS and H. C. STRUCK (J. Amer. Chem. Soc., 1934, 56, 1947—1958).—The reaction has been studied kinetically by measuring the absorption of I by titration, and the fate of OH' by means of the glass electrode. On adding the sugar, [OH'] falls to a low val.; the destruction of the sugar by the alkali [Ca(OH)₂ or Ba(OH)₂] increases with time and increasing concn. of the alkali. The initial rate of reaction approx. \propto [OH']. The decrease of optical rotation with time is the more rapid the more conc. is the alkali. A mechanism of the reaction is proposed.

E. S. H.

Dependence of velocity of inversion of sucrose on the heavy water content of water. P. GROSS, H. SUESS, and H. STEINER (Naturwiss., 1934, 22, 662).—The inversion of sucrose in acidified H₂O containing different proportions of H₂O is more rapid than in H₂O. The variation of the velocity coeff. *a* 25° with the composition of the H₂O is not linear. The dissociation const. of H₂O must be > the *a* of H₂O.

A. J. M.

Rate of oxidation of graphite by steam. M. A. MAYERS (J. Amer. Chem. Soc., 1934, 56, 1879—1881).—Eliminating the effect of diffusion as the rate

determining process, at 745 mm. v.p. the rate of gasification of C in micromol. per sq. cm. per sec. at 1000—1160° is given by $\log G_1 = 6.20 - (35,130/4.575T)$, and at 850—1000° by $\log G_2 = 8.42 - (49,720/4.575T)$.

E. S. H.

Difference effect. P. FISCHER (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1934, 1, 103—110).—The velocity of dissolution of Al and its alloys with Sb, Ag, Zn, and Pb is increased in aq. HCl and diminished in aq. NaOH on establishing connexion with a Pt electrode.

R. T.

Action of dilute silver solutions on mineral sulphides. S. A. KAMENEZKI (Z. anorg. Chem., 1934, 219, 335—340).—The rate of pptn. of Ag as metal or Ag_2S from dil. aq. $AgNO_3$ has been determined for different mineral sulphides and for different surface areas of the minerals exposed to the action. The nature of the action in different cases is discussed.

M. S. B.

Velocity of corrosion from the electrochemical viewpoint. III. U. R. EVANS and R. B. MEARS (Proc. Roy. Soc., 1934, A, 146, 153—165; cf. A., 1932, 1003).—Bengough's film distribution theory of corrosion is in part accepted. Criticisms of the differential aeration theory based on Bengough's linear corrosion-time curves are considered to be invalid; if rust is prevented from falling over the edges of the specimens the curves soon cease to be straight. Measurements of O_2 advance through columns of KCl solution show that all the corrosion products tested offer obstruction to O_2 transport. With Fe vertically immersed in aq. KCl below O_2 - N_2 mixtures, the velocity of corrosion increases, but the area affected diminishes, with O_2 concn. A statistical study of drops of KCl on Fe below O_2 - N_2 mixtures shows that the probability of attack decreases and the conditional velocity increases with O_2 concn.

L. L. B.

Corrosion of tin and its alloys.—See B., 1934, 890.

Action of complex copper salts on the decomposition of hydrogen peroxide. M. BOBELSKY and B. KIRSON (Compt. rend., 1934, 199, 573—575).—The decomp. of H_2O_2 is not catalysed by conc. solutions of NH_4Cl , $(NH_4)_2SO_4$, or NH_4NO_3 , and not very appreciably so by conc. $CuSO_4$ or $Cu(NO_3)_2$, but is accelerated considerably by $CuCl_2$. The rate of decomp. $\propto [CuCl_2]$ and $[H_2O_2]$, and the catalysis is attributed to a complex $CuCl_2'$ ion. $Cu(CN)_2'$ has no influence on the decomp., but $Cu(NH_3)_n$ acts vigorously, being most active at about $n=5$; hence it is suggested that only loose Cu complexes are effective, and the fact that excess of NH_3 renders the ion less active is attributed to its stabilising action on the complex.

J. W. S.

Decrease in the quantity of hydrogen peroxide present in various solutions on boiling. J. TAKAGI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1078—1090).—About 4% of the initial quantity of H_2O_2 disappears from H_2O in 1 hr. after the liquid has begun to boil. HCl accelerates the decomp. even when in very dil. solution. HNO_3 and H_3PO_4 also accelerate the decomp. when their concn. exceeds a

certain limit. When the aq. H_2O_2 contains a trace of H_2SO_4 or H_3PO_4 the decomp. is < with pure H_2O . The stability of H_2O_2 on boiling with dil. acid and a salt of that acid depends on the cation, Na^+ being a fairly effective decomp. catalyst, Mn^{++} much more effective, and Fe^{+++} exceedingly effective. J. W. S.

Catalyses by means of radon, and its visibility [when exposed] to Wood's light. L. FRANCESCONI and R. BRUNO (Gazzetta, 1934, 64, 485—497).—Rn dissolved in H_2O can act as a positive or negative catalyst in many reactions involving iodides or I in solution. Those reactions which are catalysed by light are retarded by Rn. H_2O containing Rn, when exposed to Wood's light (filtered ultra-violet radiation) shows a green fluorescence.

O. J. W.

Velocities of adsorption of hydrogen and deuterium on hydrogenation catalysts. J. PACE and H. S. TAYLOR (J. Chem. Physics, 1934, 2, 578—580).—The rates of adsorption of H_2 and D_2 on the hydrogenation catalysts Cr_2O_3 , $ZnO-Cr_2O_3$, and a supported Ni catalyst, at 110°, 132°, and 184°, are the same for the two gases, which indicates that the rate-determining process cannot depend on the zero-point energy of the gas, the frequency of collision of the mols. with the adsorbing surface, or the velocity of diffusion. The bearing of these observation on the problems of chemical kinetics is indicated.

M. S. B.

Effect of ammonia on the thermal hydrogen-oxygen reaction. A. T. WILLIAMSON and N. J. T. PICKLES (Trans. Faraday Soc., 1934, 30, 926—935).—The thermal reaction between H_2 and O_2 at 500° and 300 mm. is very slow, but is sensitised by 2—3 mm. of NH_3 . After an induction period the rate becomes faster and ends in explosion. The effect of varying conditions on the time of induction (I) and the amount of H_2O formed during the induction period (II) have been studied. By increasing the concn. of NH_3 , (I) and (II) are decreased, but above a certain crit. pressure no explosion takes place. Added NO acts as a simple independent catalyst, having no influence on the NH_3 process. The phenomena observed can be explained as due to a reaction between NH_3 and the chain carriers present in H_2 - O_2 mixtures at this temp. An unknown substance X is formed and acts as a sensitiser in initiating more H_2 - O_2 chains. An explosion occurs when X reaches its crit. concn. X does not appear to be NO_2 . Other possibilities are discussed. $(CN)_2$ influences the H_2 - O_2 reaction similarly to NH_3 , but the results are not reproducible and vary chiefly with the time of contact of $(CN)_2$ and H_2 .

M. S. B.

Decomposition of hydrogen peroxide by the catalytic action of ferric hydroxide. O. T. ROTINI and F. SNASSEL (Magyar chem. Fol., 1933, 39, 65—72; Chem. Zentr., 1933, ii, 3803—3804).—The catalytic effect is unaltered in presence of an acetate buffer solution, but is reduced by 5% with a phosphate or citrate buffer, due probably to reaction with the $Fe(OH)_3$. The buffer solution has no effect on the inner reaction mechanism. Fe_2O_3 has no catalytic action.

H. J. E.

Reduction of iron oxides by means of mixtures of carbon monoxide and hydrogen. C. PADOVANI

and S. BAYAN (*Annali Chim. Appl.*, 1934, 24, 394—409).—The course of the reaction between a gas of the approx. composition $2\text{H}_2 + \text{CO}$, obtained by the incomplete catalytic oxidation of natural CH_4 (A., 1933, 1253), and crude Fe oxide obtained by the calcination of siderite has been followed by analysis of the emergent gas, using a streaming method. At 830—880°, the reaction ceases suddenly when about 45% of the O in the Fe oxide has been removed. If air is then passed over the solid product at the same temp. re-oxidation occurs and the Fe oxide is obtained almost unchanged. D. R. D.

Catalytic and electrical properties of metallic surfaces. I. Silver surface catalysing the combustion of carbon monoxide. B. W. BRADFORD (*J.C.S.*, 1934, 1276—1283).—The methods previously described (this vol., 608) were applied in the range 335—575°. The catalytic properties of Ag, unlike those of Au, are mobile and depend on the previous history of the surface, which adjusts itself only slowly to new temp. conditions and at the same time undergoes a sintering process. The reaction is not retarded by CO_2 , and neither CO nor O_2 is strongly adsorbed, either gas in excess displacing the other. Pretreatment with CO or O_2 catalyses the reaction in the dry system, but retards in presence of H_2O . H_2O accelerates the combination at low partial pressures of CO or O_2 , but retards at high vals., probably owing to displacement of these gases from the surface. At approx. 500°, there is a large and abrupt increase of reaction velocity which is not due to propagation of reaction chains into the gas phase, but is attributed to vitrification of the Ag surface. The surface potentials, in general, indicated the composition of the film adsorbed on the metal, whilst rates of charging chiefly reflected changes in the general activity of the catalytic surface. J. G. A. G.

Decomposition of nitrous oxide on the surface of platinum. I. Retarding effect of oxygen. E. W. R. STEACIE and J. W. MCCUBBIN (*J. Chem. Physics*, 1934, 2, 585—589).—In the investigation of the decomp. of N_2O on a spongy Pt surface at 485—570° the results obtained are in agreement with the data of other investigators for filament catalysts. O_2 formed in the reaction has a much greater retarding effect than added O_2 , probably due to adsorption of the former in the at., and of the latter in the mol., condition. Added gases also retard the reaction by hindering the diffusion of the reactant to the catalyst. The order of admission of the gases is therefore important. M. S. B.

Limitation of catalytic activity of hydrogenating catalysts. II. Poisoning of catalyst and catalytic activity. K. YOSHIKAWA (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, 13, 1042—1044; cf. A., 1932, 918).—Addition of NiSO_4 to Ni catalyst used in the hydrogenation of PhNO_2 abolishes only the power of hydrogenating the C_6H_5 nucleus, leaving intact the reduction of the side-chain. Using catalyst prepared from $\text{Ni}(\text{NO}_3)_2$ containing 1.5—2% of NiSO_4 the space-time yield of NH_2Ph is so good that the method is of practical val. It is concluded that progressive poisoning may be explained by the existence

of active centres the component parts of which have variable activity. J. W. S.

Contact oxidation of methyl alcohol to formaldehyde. Z. B. GUREVICH (*Trans. Centr. Inst. Sci. Res. Forest Chem., U.S.S.R.*, 1933, 1, 79—100).—Thomas' results for Cu (A., 1920, i, 473) are confirmed. Ag and Ag-Cu catalysts gave promising results. CH. ABS.

X-Ray examination of copper methyl alcohol catalysts. K. IVANOV (*Mem. Inst. Chem. All-Ukrain. Acad. Sci.*, 1934, 1, 49—59).—Activation of CO and H. mols. by Cu-ZnO- Cr_2O_3 catalysts (I) is due to active Cu and CuO mols., the dispersion of which is increased by the ZnO. Cr_2O_3 acts as a promoter, forming solid solutions with CO. Inactivation of (I) is due to diminution in the dispersion of Cu, to reduction of active CuO, and to increase in the parameters of the Cu lattice consequent on conversion into α -brass. R. T.

Enrichment of hydrogen by the heavy isotopes. S. E. FRISCH and V. I. TSCHERNIAEV (*Compt. rend. Acad. Sci. U.R.S.S.*, 1934, 3, 245—247).—With the electrolytic apparatus described, 2 litres of H_2O afford 0.5 c.c. of H_2O containing $\text{H}^2 : \text{H}^1 = 3 : 100$. The $[\text{H}^2]$ is increased to 5% by allowing the gas liberated by Na to diffuse through hot Pd. J. G. A. G.

Fluorine from caesium acid fluoride. F. C. MATHERS and P. T. STROUP (*Trans. Electrochem. Soc.*, 1934, 66, 113—119).—Following a survey of F compounds of low m.p. which might be suitable as electrolytes for production of F_2 , a system approximating to $\text{CsF} \cdot 2\text{HF}$ (m.p. 19°) was electrolysed in a Mg cell of the Mathers type. During anodic liberation of F_2 crystals separate and the temp. has to be raised progressively to about 100°, when the bath is regenerated by a simple process. If CuF_2 be added at intervals, continuous production of F_2 is possible, Cu being deposited on the cathode. H. J. T. E.

Electrolysis of rare-earth metal salts in non-aqueous solvents. B. S. HOPKINS and L. F. AUDRIETH (*Trans. Electrochem. Soc.*, 1934, 66, 139—146).—Solubilities of anhyd. rare-earth chlorides prepared by heating the oxides with NH_4Cl were measured in alcohols and other org. solvents at 20°. Attempts to electrodeposit the metals from such solutions were unsuccessful, but amalgams of La, Ce, Nd, Sm, and Y were obtained as pasty masses containing 0.5—3% of metal by electrolysis of saturated solutions of the chlorides in EtOH with a stirred Hg cathode. The current efficiency was $> 12.5\%$. H. J. T. E.

Co-deposition of tungsten and iron from aqueous solutions. M. L. HOLT (*Trans. Electrochem. Soc.*, 1934, 66, 147—152).—Successive electrolyses of W plating baths of the phosphate and citrate types for 20 min. periods at 5 amp. per sq. dm. yield progressively diminishing wts. of cathode deposit. This is due to progressive removal of traces of Fe which are always present in ordinary H_2WO_4 used for making up the bath and appear to be necessary for W deposition. So-called W deposits claimed to be obtained from solutions are always alloys, often containing up to 1% Fe. Baths made up with specially prepared p

H_2WO_4 yield practically no deposits, and ordinary baths which have ceased to give deposits can be caused to do so by a small addition of Fe salt. H. J. T. E.

Electrolytic production of tungsten metal from a fused phosphate bath. S. T. LEO and T. N. SHEN (Trans. Electrochem. Soc., 1934, 66, 129—137).—Using a graphite crucible as cathode and graphite rod anode, the highest current efficiency (88%) was obtained from an electrolyte of the composition $4\text{WO}_3 \cdot 3\text{NaPO}_3 \cdot 7\text{Na}_4\text{P}_2\text{O}_7$ as recommended by Hartmann (A., 1931, 805), but at a higher temp. (900°) and c.d. (35 amp. per sq. dm.). The highest energy efficiency (470 g. per kw.-hr.) was attained by addition of 15 g.-mol. of NaCl to the bath. The product averaged 99.7% W. H. J. T. E.

Sulphur tetroxide. R. SCHWARZ and H. ACHENBRACH (Z. anorg. Chem., 1934, 219, 271—277).— SO_4 results from the action of the glow discharge on a mixture of SO_2 and O_2 (1 : 10) at 0.5 mm. pressure, as a white solid of m.p. 3° (decomp.). Decomp. in dil. H_2SO_4 solution at 0° is complete in about 60 hr., but no H_2SO_5 appears to be formed. The reaction with HI at 0° is correspondingly slow. SO_4 oxidises NH_4Ph to PhNO_2 , Mn^{++} to Mn^{VII} , and Cu^{++} to Cu^{+++} . H. F. G.

Preparation of free hydroxyl. E. M. STODDART (Phil. Mag., 1934, [vii], 18, 409—421).—Contrary to Lavin and Stewart (A., 1929, 520), free OH is not removable from a discharge through H_2O vapour. The formation of OH can be observed when O_2 afterglow is quenched with H_2O vapour, H, or H_2 . Since its apparent life period is the same as that of the afterglow, whereas the real life period is very short, it is concluded that the OH is formed during a secondary change brought about by O atoms.

N S

Decomposition of lead tetraethyl in the glow discharge. N. A. PRILESHAeva (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 252—255).—The emission spectrum contains radiation due to CH, C_2 , H_2 , and H. Spark lines of Pb are absent and the Pb arc spectrum is emitted at the decomp. of PbEt_4 . It appears that the decomp. is due to slow electrons.

J. G. A. G.

Reduction of oxygen to hydrogen peroxide by irradiation of its aqueous solution with X-rays. H. FRICKE (J. Chem. Physics, 1934, 2, 556—557).—X-Rays have no action on air-free H_2O . In the presence of O_2 , H_2O_2 is formed. The initial production of H_2O_2 is independent of the pressure from 4 to 70 cm. Hg, but is dependent on p_{H} between 1.5 and 11.5, falling with increasing p_{H} . Two reactions appear to take place, one independent of p_{H} and only slightly inhibited by H_2O_2 , and the other inhibited by H_2O_2 and depending on p_{H} .

Photochemical decomposition of sulphur dioxide. G. KORNFIELD and M. McCaIG (Trans. Faraday Soc., 1934, 30, 991—994).—Although SO is produced photochemically (cf. Franck *et al.*, A., 1932, 896), no new bands have been found in the absorption spectrum of SO_2 between 3100 and 2500 Å. on irradiation by the Al spark. Its reaction must, therefore, be very rapid. Possible reactions are discussed.

M. S. B.

Influence of foreign substances on the photochemical equilibrium $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$. M. TRAUTZ and F. HELFRICH (Z. wiss. Phot., 1934, 33, 111—116; cf. this vol., 975).—The introduction of A or N, has no effect on the val. or constancy of the equilibrium const. At the temp. of the reaction vessel (300°) no O_3 is formed from O_2 by ultra-violet radiation. When completely dried (contact with tap-grease must be excluded), SO_2 does not react with O_2 , nor is SO_2 alone decomposed to S and SO_3 , by exposure to ultra-violet light. The formation of O_3 from O_2 (which occurs in a cool vessel) is unaffected by drying. The light causing O_3 formation is completely absorbed by a filter of SO_2 gas 3 mm. thick.

J. L.

Explanation of the validity of the mass action law for the photochemical equilibrium $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$. M. TRAUTZ and F. HELFRICH (Z. wiss. Phot., 1934, 33, 117—122; cf. preceding abstract).—The conditions necessary for the applicability of the mass action law are discussed; it is shown that the validity of the law is in agreement with theory, for a homogeneously irradiated mixture of gases in equilibrium.

J. L.

Three manifestations of a new catalytic reaction. W. HILLER (Z. anorg. Chem., 1934, 219, 313—320).—Whereas $\text{Na}_4\text{Ag}_6(\text{S}_2\text{O}_3)_3$ solution begins to darken only after about 30 hr. when exposed to light and air, a mixture with KI becomes dark when exposed for 2—5 min., Ag_2S being formed. The reaction is one of oxidation, since H_2O_2 , but not Na_2SO_3 , produces the same result. If benzidine is present it becomes blue within 30 sec. A solution containing starch, AgNO_3 , and an excess of KI becomes blue rapidly on exposure to light, but this does not occur in absence of Ag^+ or with an excess of Ag^+ . The I liberated must therefore be derived from KI adsorbed on AgI, the latter exerting an enormous accelerating influence on the oxidation of the former. This type of reaction is regarded as of importance in many directions; in particular, it is closely connected with photographic solarisation.

H. F. G.

Deuterium as an indicator of mechanism in the photo-decomposition of ammonia. H. S. TAYLOR and J. C. JUNGERS (J. Chem. Physics, 1934, 2, 452—453).—By illuminating mixtures of NH_3 and H^+ with light of λ suitable for the photo-decomp. of NH_3 , an equilibrium mixture of $\text{N}(\text{H}^1\text{H}^2)_3$ has been obtained. The displacement of H^1 by H^2 did not occur in the absence of light. This indicates that, in the photo-decomp. of NH_3 , the reverse reaction $\text{NH}_2 + \text{H} = \text{NH}_3$ takes place and is one reason for the low quantum yield of approx. 0.25 for the dissociation at room temp. The results also show that at. H does not readily react with NH_3 .

M. S. B.

Formation of hyponitrous acid as an intermediate compound in the biological or photochemical oxidation of ammonia to nitrous acid. I. Chemical reactions. A. S. CORBER (Biochem. J., 1934, 28, 1575—1582).— $(\text{HNO})_2$ is an intermediate in both the bacterial and photochemical conversion of NH_3 into HNO_2 . $(\text{HNO})_2$ with resorcinol and KIO_4 gives an orange to cherry-red colour

which becomes fluorescent on keeping. Similar colours are given by NH_2OH , borates, and NaHCO_3 .

C. G. A.

Solarisation. VII. Dependence of solarisation on the time of development. H. ARENS (Z. wiss. Phot., 1934, 33, 105—110; cf. A., 1933, 577).—By increasing the time of development the solarisation effect is progressively removed, until normal max. density is again reached. All emulsions show this effect, but differences in the intermediate stages occur between large-grain and fine-grain emulsions. It is postulated that, whilst solarisation renders the outside of the AgBr grain undevelopable, by long development active nuclei in the middle of the grains may be reached, whereupon normal development is possible.

J. L.

Quantum theory of the latent photographic image. T. H. JAMES and J. J. COLEMAN (J. Chem. Physics, 1934, 2, 483—487).—The relation between the amount of photolytic action in latent image formation and the amount of light producing it is discussed, and a method given for deducing the no. of effective quanta per grain necessary to cause development. 3—4 quanta are necessary for slow emulsions and 1—2 for fast, varying to some extent with the developer. Equations are given showing the relation between the amount of photolytic product and no. of developable grains, and characteristic curves are plotted.

M. S. B.

Photographic desensitisers and oxygen. N. BLAU and H. WAMBACHER (Nature, 1934, 134, 538).—The rows of Ag particles marking the tracks of protons set in motion by neutrons appear after development only when the plate has been treated with pinacryptol-yellow (I), densitol, induline-scarlet (II), phenosafranine, a mixture of (I) and (II), antilumin, and pinacryptol, but not pinaflavol, and when the exposure to the particles is made in air at reduced pressure or in N_2 . The dye plays only an auxiliary part, probably that of catalyst, in the desensitisation process, the main part being played by the O_2 of the air.

L. S. T.

Spectral sensitivity of the silver salts of some organic dyes. G. UNGAR (Z. wiss. Phot., 1934, 33, 123—128).—Pure compounds of Ag with eosin, benzogreen, alizarin-pure-blue, anthracene-yellow, and anthracene-blue, have been prepared, free from AgCl and AgNO_3 , and their absorption spectra (measured by the transparencies) compared with their chemical (photographic) spectral sensitivities. Contrary to the usual absorption and quantum laws, the point of max. absorption is not the same as the position of max. sensitivity, the latter being about 50 m μ nearer the red. These Ag compounds may be increased in red sensitivity by bathing with other dyes, e.g., pinacyanol. The theoretical implications are briefly discussed.

J. L.

Primary photochemical reactions. V. Spectroscopy and photochemical decomposition of acetone. R. G. W. NORRISH, H. G. CRONE, and (MISS) O. D. SALTmarsh (J.C.S., 1934, 1456—1464).—The absorption spectrum of COMe_2 vapour (I) consists of a continuous band (II) between about 3000 and

2200 Å. with a few faint max. (ν , 1100 cm^{-1}) and a region of discrete absorption between 3340 and about 2950 Å. (III), slightly overlapping (II). Light absorbed in both regions causes decomp., but the greenish fluorescence (IV) is evoked only by light in region (III) and consists of three structureless bands at 5034—6203 Å. The inferred levels of the mol. are confirmed by the absorption found at 7200—10,000 Å. (IV) increases with increasing pressure of (I), is unaffected by added N_2 , and the sp. effect of O_2 (A., 1933, 792) is attributed to removal of O_2 by excited (I) and the formation of a second transient fluorescent substance. The photo-decomp. of (I) at 3150 Å. ($\gamma=0.2$) and 2650 Å. ($\gamma=0.4$) accords with the net reaction $\text{COMe}_2=\text{C}_2\text{H}_6+\text{CO}$, but CO and free Me are first formed (cf. this vol., 852). The full Hg arc gives, in addition, < 10% CH_4 , probably derived from a photo-reaction in the liquid (I) present (cf. *loc. cit.*). The light absorbed by mols. which do not decompose is degraded as heat by the process of "internal stabilisation" detailed, or partly as (IV) when light in region (III) is used. The characteristics of (IV) argue against a bimol. decomp. involving excited mols.

J. G. A. G.

Chain decomposition of dimethyl ether photo-sensitised by acetone. J. A. LEERMAKERS (J. Amer. Chem. Soc., 1934, 56, 1899—1904).—Studies of the high-temp. decomp. of COMe_2 show that Me radicals do not initiate a chain decomp. of COMe_2 at < 400°. The rate of photo-decomp. of Me_2O , sensitised by COMe_2 , $\propto [\text{Me}_2\text{O}]$, the square root of the absorbed light, and $1/[\text{COMe}_2]^{\frac{1}{2}}$. The rate coeff. is $10^4 e^{-16,000/RT}$ mol.¹ einsteins⁻¹ sec.⁻¹. Chain lengths of the Me_2O decomp. were as great as 230 mols. decomposed per quantum of light absorbed. Mechanisms of the reactions are discussed.

E. S. H.

Dark reaction between sodium formate and iodine. A. VON KISS and A. URMANCZY (Z. anorg. Chem., 1934, 219, 348—356).—The dark reaction between HCO_2Na and I in H_2O and in aq. KCl, KBr, and KI has been investigated at 15°, 25°, 35°, and 45° and the mechanism previously suggested for HCO_2H (A., 1933, 1017) has been confirmed. The salts delay the reaction due to the formation of the less reactive ions $\text{I}_2\text{Cl}'$, $\text{I}_2\text{Br}'$, and I_3' , respectively. The temp. coeff. of the reaction is > normal, but diminishes with rise of temp. The activation work of the reaction between 15° and 45° is 23,480 g.-cal. The results of Doosay and Bhagwat (this vol., 265) are criticised.

Autoxidation of decalin. A. CASTIGLIONI (Gazzetta, 1934, 64, 465—469).—Light, especially ultra-violet, accelerates the autoxidation of $\text{C}_{10}\text{H}_{18}$. The acidity of the hydrocarbon affords a measure of the degree of oxidation.

O. J. n.

Photo-synthesis of amino-acids in vitro.—this vol., 1208.

Photolysis of β -caryophyllene nitrosite. HOFFMAN (J. Amer. Chem. Soc., 1934, 56, 1897, 1897).—No reaction occurs at room temp. dark. The gaseous product contains N_2 86 and N_2O 14%. The quantum yield for N_2 liberated is

mol. per quantum. The mechanism of the reaction is discussed. E. S. H.

Potential and Becquerel effect in photochemical processes. Irradiation of extracts of visual purple.—See this vol., 1245.

Mechanism of ionogenic reactions. R. A. OGG, jun., and M. POLANYI (Mem. Manchester Phil. Soc., 1933—1934, 78, 41—45).—Qual. principles are outlined for a theory (not detailed) of the mechanism of ionogenic reactions (those involving formation of an ion by rupture of a co-valent linking). R. S. C.

Optical inversion by negative substitution. R. A. OGG, M. POLANYI, and L. WERNER (Chem. and Ind., 1934, 614—615).—In confirmation of previous theories (preceding abstract) that inversion accompanies interchange of negative groups, $\text{CHPhMe}\cdot\text{OH}$ is racemised by 0.01*N*-NaOH in 60% EtOH at 72° (unimol. reaction; $k=2.5\times 10^{-4}$). $l\text{-Bu}^{\beta}\text{OH}$ is unchanged by 0.1*N*-NaOH at 135°, thus showing the expected effect of Ph on the C·O linking. R. S. C.

Isotope separation. Purification of heavy hydrogen by diffusion. H. HARSEN, G. HERTZ, and W. SCHÜTZE (Z. Physik, 1934, 90, 703—711; cf. A., 1933, 658).—The no. of diffusion elements was doubled, and gave practically pure Ne^{22} . A sample of H_2 containing 1% of H_2^3 gave pure H_2^3 within 8 hr. A. B. D. C.

Heavy water and water of crystallisation. J. N. FRIEND (Nature, 1934, 134, 463).—Using Na_2SO_4 , H_2O cannot be conc. by repeated crystallisation, dehydration, and re-dissolution of the dehydrated crystals in the mother-liquor (cf. this vol., 1080). L. S. T.

Possibility of separating heavy water by fractional freezing. G. BRUNI (J. Amer. Chem. Soc., 1934, 56, 2013—2014).—The attempts were unsuccessful. E. S. H.

Is water isotopically fractionated on partial condensation of the vapour? M. DOLE (J. Chem. Physics, 1934, 2, 548—549; cf. this vol., 853).—The production of H_2O of $d > \text{normal}$ by burning C_6H_6 , previously observed, appears to have been due to fractional condensation of H_2O vapour and not to a natural separation of the isotopes of H in C_6H_6 . Cholesterol from the spinal fluid of cattle has also a normal H^2 content. M. S. B.

Action of potassium halides on mercurous chloride. J. FIALKOV and N. TSCHOVNIK (Z. anorg. Chem., 1934, 219, 382—388).—By the action of KCN, KCNS, KI, KBr, and KCl on Hg_2Cl_2 there is some decomp. with the formation of Hg and a complex Hg^{II} salt. The nature of the final products appears to depend partly, but not entirely, on the dissociation const. of the complex ion $\text{Hg}(\text{CN})_4^{--}$, $\text{Hg}(\text{CNS})_4$, HgI_4^{--} , HgBr_4^{--} , or HgCl_4^{--} . Another important factor is the stability of the corresponding Hg_2^{II} salt. M. S. B.

Ammoniates of sodium and calcium cyanides and chlorides. B. B. VASSILIEV, J. L. ETTINGER, and M. P. GOLOVKOV (Z. anorg. Chem., 1934, 219, 341—347).—The optical consts. of the above four cryst. ammoniates have been measured. In accord-

ance with Biltz's rule the sol. ammoniates of NaCl and NaCN are less stable than the insol. ammoniates of CaCl_2 and $\text{Ca}(\text{CN})_2$. The solubility of NaCl and NaCN in liquid NH_3 has been determined and the system NaCN-NaCl-NH_3 has been partly investigated between -19° and 35°. The two salts separate out from NH_3 solution as mixed crystals of the same form as from the fused salts. M. S. B.

Reduction of inorganic halides by magnesium in presence of ether. H. RHEINBOLDT and K. SCHWENZER [with, in part, R. BUNGE] (J. pr. Chem., 1934, [ii], 140, 273—290).—Anhyd. inorg. halides which are reduced by Mg at a high temp. generally react spontaneously and with evolution of heat with the metal in presence of anhyd. Et_2O . Reaction also occurs in presence of C_6H_6 , PhMe, CHCl_3 , CCl_4 , and CS_2 , but not in presence of amyl ether, dioxan, COMe_2 , or EtOAc . Among chlorides, bromides, and iodides, reaction is usually most vigorous when the solubility of the halides and their etherates is greatest. The quant. course of the change depends on the concn. of the inorg. halide, a min. concn. being observed below which such change does not occur. When intermediate stages are possible the yield depends somewhat on the initial temp. of the solution. For preparative purposes, excess of Mg is employed. The product is exhaustively extracted with an org. solvent, usually Et_2O , and, if necessary, placed under 1—2 mm. pressure. Excess of Mg is removed by AcOH or NH_4Cl . Be, Zn, Ca, Hg, Al, C, Ge, Sn, P, As, Sb, Br, S, Se, and Te are obtained from their halides. With halides of Hg^{II} , Ti^{IV} , Sn^{IV} , Se^{IV} , and Fe^{III} intermediate substances are produced. The bromides are best suited to reduction. H. W.

Mechanism of the oxidation of magnesium and calcium alloys at high temperatures. R. DELAVALT (Compt. rend., 1934, 199, 580—582; cf. this vol., 853).—The oxidation phenomenon described previously can be observed with Mg-Al alloys containing >40% Al, and with Ca containing 10 mol.-% of Ag. Cu, Cd, Zn, and Al also show analogous results. A qual. explanation is offered. J. W. S.

Hydrochloric acid metathesis of barium perchlorate to form perchloric acid. G. F. SMITH and B. S. FREIDMAN (J.S.C.I., 1934, 53, 299—300T).—The metathesis of anhyd. $\text{Ba}(\text{ClO}_4)_2$ (I) by 37% aq. HCl (II) is incomplete owing to deposition of BaCl_2 on (I). The optimum yield of HClO_4 (98.75% of theory) is obtained by adding 15 ml. of (II) to 10 g. of (I) in 10 ml. of H_2O , and the resulting aq. HClO_4 contains <1.15% of (I). J. G. A. G.

Existence of mercury permanganate. A. OLIVIERO (Atti Congr. naz. Chim., 1933, 4, 552—556; Chem. Zentr., 1934, i, 1298; cf. Rend. Sem. Fac. Sci. Cagliari, 1932, 2, 81—86).— HgOAc with KMnO_4 gave a cryst. ppt. containing acetate, decomposing explosively on shock or heating. HMnO_4 with HgO or AgMnO_4 with HgCl_2 gave basic Hg permanganates. The bands in the absorption spectrum of aq. Hg "permanganate" were more widely spaced than in aq. KMnO_4 . H. J. E.

"Mineral" and "vegetable" hydrates of aluminium oxide. F. DRIESSEN (Bull. Soc. Ind. Mulhouse, 1934, 100, 472—474).—The term "vege-

table" hydrate of Al_2O_3 is suggested for the form produced from Al in contact with Hg. It differs from $\text{Al}(\text{OH})_3$ obtained by pptn. in being partly sol. in H_2O , from which solution it is strongly adsorbed by cellulose and forms a strong positive mordant. It is suggested that it contains a hydrated cation $[\text{Al}_2(\text{H}_2\text{O})_3]^{+++}$, the hydration accounting for the solubility. It is considered probable that Al-containing plants contain sol. $\text{Al}(\text{OH})_3$, and that the fastness of oriental dyes may be partly due to the sol. form of the mordants. J. W. S.

[Aluminium hydroxides.] C. SUNDER (Bull. Soc. Ind. Mulhouse, 1934, 100, 475—480; cf. preceding abstract).—Oxidation of Al in contact with Hg leads to the production of $\text{Al}(\text{OH})_3$ gel containing a little positive sol, the latter being Driessen's sol. hydrate. This sol can also be obtained by passing a current between an Al cathode and a C anode in H_2O , but by passing the current in the reverse direction an unstable and non-mordanting negative sol is obtained. J. W. S.

Structure of ultramarines. IV. Significance of silver salts for elucidating the structure and nature of ultramarines. M. DOMINKIEWICZ (Arch. Chem. Farm., 1934, 1, 252—268).—The Ag salts are prepared by boiling 10 g. of ultramarine (I) with 100 c.c. of 20% AgNO_3 for 48 hr., or by heating at 120—130° for 10 hr. Under these conditions $\approx 1.5\%$ of the (I) undergoes decomp. with elimination of S. The application of the above reaction to the analysis of commercial (I) is described and illustrated. R. T.

Oxidation of graphite. V. SIHVONEN (Ann. Acad. Sci. Fennicae, 1934, A, 41, No. 3, 1—80).—A summary of work previously published (cf. this vol., 742). F. L. U.

Compounds of zirconyl iodide with alkali iodides. E. CHAUVENET and (Mlle.) J. BOULANGER (Compt. rend., 1934, 199, 575—577).—By measurement of the heats of mixing of conc. solutions of ZrOI_2 and alkali iodides, evidence has been obtained for the existence of the following complexes: $\text{ZrOI}_2\cdot\text{KI}_2$, $2\text{ZrOI}_2\cdot\text{RbI}$, $2\text{ZrOI}_2\cdot\text{CsI}$, and $2\text{ZrOI}_2\cdot\text{NH}_4\text{I}$. By slow evaporation of a cold solution corresponding with the mixture $2\text{ZrOI}_2+\text{CsI}$, kept saturated with HI, crystals of the composition $2\text{ZrOI}_2\cdot\text{CsI}\cdot 20.7\text{H}_2\text{O}$ are deposited. The compounds with the other iodides could not be isolated. J. W. S.

Preparation of cerium silicide and lanthanum silicide by igneous electrolysis. M. DODERO (Compt. rend., 1934, 199, 566—568).—After electrolysis for 2 hr. of a melt containing $\text{CaO}\cdot\text{SiO}_2$ (1 mol.), CaF_2 (2 mols.), CaCl_2 (0.33 mol.), and CeO_2 (0.1 mol.), 6—8-mm. metallic globules can be detached from the cathode consisting of alloys containing free Si and CeSi_2 . Under similar conditions with La_2O_3 in place of CeO_2 the melt yields Si and La silicide, LaSi_3 . The latter forms steel-grey grains which turn yellow on oxidation. It is unattacked by conc. HNO_3 , but attacked by dil. HNO_3 , HCl , and H_2SO_4 . Aq. alkali has little effect on it, but with molten alkali it reacts vigorously. J. W. S.

Lead periodates. H. H. WILLARD and J. J. THOMPSON (J. Amer. Chem. Soc., 1934, 56, 1828—

1830).—The ppt. formed under different conditions of concn., temp., and acidity is $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$, although its appearance varies with the conditions. H_2O is retained up to 130° and is not taken up by the anhyd. salt. When heated at 275°, the salt is converted into $\text{Pb}_3(\text{IO}_5)_2$. The existence of other Pb periodates has not been confirmed. E. S. H.

Absorption of oxygen by phosphorus. H. R. AMBLER (Analyst, 1934, 59, 593—606).—P used as an absorbent for O_2 may leave unabsorbed quantities of the order of 0.2%. If this residual O_2 is determined, O_2 - N_2 mixtures and O_2 in presence of N_2O may be accurately determined. Appreciable decomp. of N_2O may take place, but this does not interfere. When gases containing O_2 and H_2 are treated with P, up to 0.5% of H_2 may be oxidised. The effect is greatest when the amount of O_2 originally present is small. CO is oxidised to a rather greater extent. CO_2 greatly decreases the max. $[\text{O}_2]$ above which absorption is inhibited. N_2O has a similar, but much smaller, effect. The mechanism of the absorption of O_2 by P is discussed. E. C. S.

Influence of sulphur dioxide and of hydrogen sulphide on the glow of phosphorus. A. BLÁHA and F. SCHACHERL (Coll. Czech. Chem. Comm., 1934, 6, 287—301; cf. A., 1932, 445).—The upper limiting pressure, p_x , of O_2 at which P glows in SO_2 - O_2 (I) and H_2S - O_2 (II) mixtures is given by $p_x=k/(a+x)$, where $x=[\text{SO}_2]/[\text{O}_2]$ or $[\text{H}_2\text{S}]/[\text{O}_2]$ and k and a are sp. const. depending on the temp. The data refer to the complete range of partial pressures for (I) at 15—25° and for (II) at 0—10°. The inhibiting effect of H_2S approx. equals that of N_2 and is $<$ that of SO_2 . The inhibition probably proceeds by removal of O atoms, thus: $\text{SO}_2+\text{O}\longrightarrow\text{SO}_3$ and $\text{H}_2\text{S}+\text{O}\longrightarrow\text{S}+\text{H}_2\text{O}$. J. G. A. G.

Technical production of protoactinium. G. GRAUE and H. KADING (Angew. Chem., 1934, 47, 650—653).—Residues from pitchblende (5.5 tons containing 950 mg. of Pa) are fused with NaOH, treated with Zr, and the double phosphate pptd. from acid solution. After removal of Fe, Pb, and SiO_2 by NaOH and HCl, Zr is separated as ZrOCl_2 . From the residue containing Ta, Zr, and Pa, Pa can be separated as the double K Pa fluoride, the final stages being dependent on the response of Pa to reactions for Zr and Ta (yield 0.7 g., of which 0.5 g. is pure). Pa has a basic character $<$ that of Ta. F. O. H.

Action of sulphur on chlorates. F. TARADOIRE (Compt. rend., 1934, 199, 603—605).—S reacts slowly and quietly with KClO_3 in presence of H_2O , forming K_2SO_4 and S_2Cl_2 . A paste of S, $\text{M}(\text{ClO}_3)_2$, and H_2O ($\text{M}=\text{Ba}$ or Pb) ignites spontaneously on evaporation of the H_2O . S_2Cl_2 , MCl_2 , MSO_4 , HClO_3 , and its decomp. products, viz., Cl_2 , ClO_2 , and HClO_4 , are formed. The reaction appears to be $2\text{H}_2\text{O}+2\text{S}+\text{M}(\text{ClO}_3)_2=2\text{H}_2\text{SO}_4+\text{MCl}_2$; $\text{H}_2\text{SO}_4+\text{M}(\text{ClO}_3)_2=\text{MSO}_4+2\text{HClO}_3$. When $[\text{HClO}_3]$ becomes sufficiently high, spontaneous ignition occurs. When conc. HClO_3 is dropped on to a mixture of S and $\text{M}(\text{ClO}_3)_2$, the mixture inflames immediately. The presence of org. matter is not necessary and the ignition is not due to the action of ClO_2 (cf. this vol., 616). D. R. D.

Properties of the chlorides of sulphur. VIII. Reaction of sulphur monochloride with chlorine. A. H. SPONG (J.C.S., 1934, 1283—1292; cf. this vol., 605).—Traces of H_2O strongly retard the reaction $\text{S}_2\text{Cl}_2 + \text{Cl}_2 \rightleftharpoons 2\text{SCl}_2$, which has been investigated in mixtures containing 54—71.2 at.-% Cl by the methods previously described. S_3Cl_4 in an ionic form appears to be the only autocatalyst and the mechanism is: (1) S_2Cl_2 (Y-shaped) + $\text{Cl}^- \longrightarrow \text{SCl}_2 + \text{SCl}^-$, (2) $\text{S}_3\text{Cl}_3^+ + \text{SCl}^- \longrightarrow \text{SCl}_2 + \text{S}_3\text{Cl}_2$, (3) $\text{S}_3\text{Cl}_2 + \text{Cl}_2 \longrightarrow \text{S}_3\text{Cl}_3^+ + \text{Cl}^-$, where (1) is the rate-controlling step. When allowance for the change of free space with change of temp. is made in calculating the velocity coeff., the energy of activation is of the same order as the electrostatic energy of the semipolar double linking which is ruptured in stage (1). The results are consistent with only a small fraction of the S_nCl_n being in the Y-form.

J. G. A. G.

Preparation and properties of disulphur decafluoride. K. G. DENBIGH and R. WHYTLAW-GRAY (J.C.S., 1934, 1346—1352).— F_2 prepared by electrolysis at a C anode contains C fluorides, but apart from CF_4 , these are eliminated by condensation in a liquid O_2 trap. The fractionation of the products of interaction of such purified F_2 with S affords pure SF_6 , a substance, probably S_2F_{12} , b.p. about -50° , absorbed by aq. KOH, and *disulphur decafluoride* (I), m.p. $-92^\circ \pm 1$, which is not absorbed by aq. KOH, but reacts with many metals at elevated temp. and is less inert than SF_6 . The v.p. of (I) is given by $\log_{10} p = -1530/T + 7.95$, from which the b.p. is $29 \pm 1^\circ$, the mol. latent heat 7000 g.-cal., and Trouton's const. 23.0. α° is 2.08 ± 0.3 and γ° 13.9 dynes per cm., from which the parachor is 236 ± 4 in accord with a sexavalent structure.

J. G. A. G.

Alkali-free syntheses of minerals of the salt deposits. J. LEONHARDT and H. IDE (Naturwiss., 1934, 22, 634).—The prep. of double sulphates by direct combination of the components in the powdered state has been carried out, the products being identified by X-ray and polarisation methods. Such reactions may occur even below 100° , e.g., the formation of langbeinite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$) at 90° , and polyhalite ($2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) at 80° . Compression of the mixture favours reaction. On the basis of these experiments it is possible to explain the metamorphosis of salts in the German deposits without introducing alkalis.

A. J. M.

Fluorine. III. Stability of oxygen fluoride. F. ISHIKAWA and H. SATO. **IV. Reactions between oxygen fluoride and the aqueous solutions of some inorganic salts.** F. ISHIKAWA and I. TAKAI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1053—1057, 1058—1064; cf. A., 1933, 1251).—III. The decrease in $[\text{OF}_2]$ is very slight over periods > 150 days at 20° . No effect of H_2O vapour on the stability could be detected. It is concluded that OF_2 can be stored if not in contact with liquid H_2O .

IV. Aq. solutions of SnCl_2 are oxidised very rapidly by OF_2 . Oxidation of NaAsO_2 by OF_2 in presence of O_2 induces reaction between the AsO_2' and O_2 . Oxidation of FeSO_4 and K_2SO_3 solutions has also been

studied. In all cases oxidation occurs through the O atoms liberated: $\text{OF}_2 + \text{H}_2\text{O} = 2\text{HF} + 2\text{O}$. J. W. S.

Frequent type of complex iodide in organic solution. A. CHRETIEN and P. LAURENT (Compt. rend., 1934, 199, 639—641).—The existence of a compound $(\text{C}_5\text{H}_5\text{N})_2\text{I}_2$ in mixtures of I and $\text{C}_5\text{H}_5\text{N}$ in CS_2 or cyclohexane is shown by measurements of sp. inductive capacity. Similar compounds are formed with quinoline, NH_2Ph , *n*-toluidine, NHPh , and $\text{N}(\text{CH}_2\text{Ph})_3$.

R. S.

Iodine mononitrate. M. I. USCHAKOV (J. Gen. Chem. Russ., 1934, 4, 194—196).—I is added to AgNO_3 suspended in MeOH, the suspension is filtered, and more I is added to the filtrate; the reactions taking place are: $2\text{I}_2 + 3\text{AgNO}_3 \longrightarrow 3\text{AgI} + \text{I}(\text{NO}_3)_3$ (I); $(\text{I}) + \text{I}_2 \rightleftharpoons 3\text{INO}_3$; $\text{INO}_3 + \text{MeOH} \rightleftharpoons \text{MeOI} + \text{HNO}_3$. The presence of MeOI in the solution is established by identifying the products of reaction with various substances; thus C_2H_4 at 10° yields $\text{CH}_2\text{I} \cdot \text{CH}_2 \cdot \text{OMe}$, cyclohexene yields 1-iodo-2-methoxycyclohexane, *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ yields 2-iodo-4-nitroaniline at -15° , and PhOH at 0° yields *o*- and *p*- $\text{C}_6\text{H}_4\text{I} \cdot \text{OH}$. AgOAc suspended in CHCl_3 on addition of Br yields AcOBr , which with C_6H_4 gives $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{OAc}$.

R. T.

Studies on chemical reactions by the potentiometric method. I. Reactions between potassium ferrocyanide and zinc sulphate in solution. S. SAITO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 226—229).—Reaction between $\text{K}_4\text{Fe}(\text{CN})_6$ and ZnSO_4 gives rise first to $\text{Zn}_2\text{Fe}(\text{CN})_6$ (I), a reaction which is soon complete and is succeeded by the formation of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (II). (I) is stable only in AcOH solutions, but (II) is stable, especially in presence of HCl and H_2SO_4 . Conditions under which titration of $\text{K}_4\text{Fe}(\text{CN})_6$ and ZnSO_4 may be made accurately are described.

J. W. S.

Behaviour of cobaltous oxide on heating. M. PRASAD, S. M. MEHTA, and T. S. SURATKAR (J. Indian Chem. Soc., 1934, 11, 513—516).—Pure CoO is formed by heating CoCO_3 in vac. at 900° . Samples of CoO prepared at lower temp. (900 — 500°) were less dense and more sol. in $0.1N \cdot \text{H}_2\text{SO}_4$, were more active in the catalytic decomp. of H_2O_2 in neutral or alkaline solution, and had a lower electrical resistance. H. J. E.

Hydrates of cobaltous sulphate. R. ROHMER (Compt. rend., 1934, 199, 641—643).—The hydrates $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (I), $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (II), $\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$ (III), $\text{CoSO}_4 \cdot 2\text{H}_2\text{O}$ (IV), $\text{CoSO}_4 \cdot \text{H}_2\text{O}$ (V) have been established by solubility measurements. At 20° (V) is metastable yielding (I) or (II). (III) and (IV) exist above 64.2° forming metastable equilibria with (II). The b.p. of the saturated solution of (II) falls from 104.5° to 103.5° , 102.3° , and 101.2° with time, corresponding with the changes $(\text{II}) \longrightarrow (\text{III}) \longrightarrow (\text{IV}) \longrightarrow (\text{V})$.

R. S.

Complex chemical behaviour of the ethanolamines. II. W. HIEBER and E. LEVY [with E. A. EHMANN, K. HEINTZ, and G. BADER] (Z. anorg. Chem., 1934, 219, 225—237; cf. A., 1933, 150).—The following compounds are described [X, Y, and

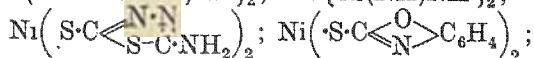
Z=mono-, di-, and tri-(hydroxyethyl)amine, respectively]: $\text{Co}(\text{NO}_3)_3 \cdot 3\text{X}$; $\text{Co}(\text{NO}_3)_3 \cdot \text{Y} \cdot 2\text{MeOH}$ (and 2EtOH); $\text{Co}(\text{NO}_3)_2 \cdot 2\text{Z}$; $\text{CoSO}_4 \cdot 2\text{Z}$; $\text{NiSO}_4 \cdot 3\text{X}$; $\text{Ni}(\text{NO}_3)_3 \cdot 3\text{X}$; $\text{NiCl}_2 \cdot 3\text{X}$; $\text{NiCl}_2 \cdot 2\text{X}$; $\text{NiBr}_2 \cdot 3\text{X}$; $\text{NiBr}_2 \cdot 2\text{X}$; $\text{NiI}_2 \cdot 2\text{X} \cdot \text{H}_2\text{O}$; $\text{NiI}_2 \cdot 3\text{X}$; $\text{NiI}_2 \cdot 4\text{X}$; $\text{Ni}_2\text{Cl}_3 \cdot 3\text{Y} \cdot \text{H}_2\text{O}$; $\text{NiCl}_2 \cdot 2\text{Y} \cdot \text{H}_2\text{O}$; $\text{NiCl}_2 \cdot \text{Y} \cdot \text{H}_2\text{O}$; $\text{NiBr}_2 \cdot \text{Y}$; $\text{NiI}_2 \cdot 2\text{Y}$; $\text{NiCl}_2 \cdot 2\text{Z}$; $\text{NiBr}_2 \cdot 2\text{Z}$; $\text{CuSO}_4 \cdot 3\text{X}$; $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{X}$; $\text{CuCl}_2 \cdot \text{X}$; $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{Y} \cdot \text{EtOH}$; $\text{CuCl}_2 \cdot 2\text{Y}$; $\text{CuBr}_2 \cdot 2\text{Y}$; $\text{ZnSO}_4 \cdot 3\text{X}$; $\text{ZnCl}_2 \cdot 2\text{X}$; $\text{ZnBr}_2 \cdot 2\text{X}$; $\text{ZnCl} \cdot \text{C}_4\text{H}_{10}\text{O}_2\text{N}$ (from Y) (also bromide and iodide), $\text{ZnCl} \cdot \text{C}_6\text{H}_{14}\text{O}_3\text{N}$ (from Z) (also bromide and iodide). Co halides do not form analogous complexes. Ni exhibits a smaller affinity for hydroxyl O than does Co. Certain of the Ni complexes are exceptional in that they contain OH groups not coordinatively bound to the metal atom. Cu and Ni salts react in similar manner with the hydroxyethylamines, but Zn differs in yielding only internal complexes with $\text{NH}(\text{C}_2\text{H}_4 \cdot \text{OH})_2$ and $\text{N}(\text{C}_2\text{H}_4 \cdot \text{OH})_3$; in those with $\text{N}(\text{C}_2\text{H}_4 \cdot \text{OH})_3$ 2 Zn atoms are linked by halogen or O atoms. The results confirm that the complexes are formed by alcoholic action.

H. F. G.

Hexamminecobaltic salts containing molybdenum and tungsten. E. NEUSSER (Z. anorg. Chem., 1934, 219, 278—286).—The following compounds are described: $\text{Co}(\text{NH}_3)_6\text{WO}_4\text{Br} \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NH}_3)_6\text{MoO}_4\text{Br} \cdot 3\text{H}_2\text{O}$ and $\text{Co}(\text{NH}_3)_6\text{MoO}_4\text{NO}_2 \cdot 3\text{H}_2\text{O}$ (rhombic); $\text{Co}(\text{NH}_3)_6\text{WO}_4\text{NO}$ and (probably) $\text{Co}(\text{NH}_3)_6\text{MoO}_4\text{CNS}$ (cubic); $\text{Co}(\text{NH}_3)_6\text{MoO}_4\text{NO}_2 \cdot \text{H}_2\text{O}$; $\text{Co}(\text{NH}_3)_6\text{MoO}_4\text{ClO}_3 \cdot 2\text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_6]_2\text{Mo}_7\text{O}_{24} \cdot 12\text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_6]_2\text{Mo}_4\text{O}_{14} \cdot \text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_6]_2(\text{WO}_4)_2\text{W}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$; $[\text{Co}(\text{NH}_3)_6]_2\text{Mo}_3\text{O}_{10}(\text{ClO}_3)_4 \cdot 6\text{H}_2\text{O}$. The red compound described by Hassel and Naess (A., 1928, 974) as a normal luteomolybdate is an aquopentammine salt. Two pentammine salts have been isolated, viz., $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{MoO}_4\text{I}$ and $[\text{Co}(\text{NH}_3)_5\text{MoO}_4]\text{I}$.

H. F. G.

Complex compounds of thiosemicarbazide. K. A. JENSEN and E. RANCKE-MADSEN (Z. anorg. Chem., 1934, 219, 243—255).—The following compounds are described (X=thiosemicarbazide): $[\text{NiX}_3]\text{SO}_4$ (also nitrate and chloride), $[\text{NiX}_3]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$, $[\text{NiX}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$, $[\text{NiX}_2](\text{C}_{10}\text{H}_{14}\text{OBrSO}_3)_2 \cdot \text{H}_2\text{O}$, $[\text{Ni}(\text{CSN}_3\text{H}_4)_2]$, $[\text{CoX}_2]\text{SO}_4$, $[\text{CoX}_3](\text{SO}_4)_3$, $[\text{CuX}_2]\text{SO}_4$ (and chloride and nitrate), $\text{Cu}(\text{CSN}_3\text{H}_4)_2$; $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NHMe}\}_3](\text{NO}_3)_2$; $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NHet}\}_3](\text{NO}_3)_2$ (also sulphate and Pr derivative), $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NHPr}\}_3]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (and Ph derivative); $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NHMe}\}_2]\text{SO}_4$ (and chloride), $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NHet}\}_2](\text{NO}_3)_2$ (and sulphate and chloride), $[\text{Ni}\{\text{CS}(\text{NMe} \cdot \text{NH}_2)\text{NHPr}\}_2](\text{NO}_3)_2$ (also sulphate and chloride); $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NHPh}\}_2]\text{SO}_4$, $[\text{Ni}\{\text{CS}(\text{NPh} \cdot \text{NH}_2)\text{NHPh}\}_2]\text{NO}_3$; $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NMe}\}_2]$ (and Pr derivative); $[\text{Ni}\{\text{CS}(\text{NMe} \cdot \text{NH}_2)\text{NPr}\}_2]$; $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{N} \cdot \text{CHPh})\text{NH}\}_2]$; $[\text{Ni}\{\text{CS}(\text{NH} \cdot \text{NH}_2)\text{NH}\}_2]$;



$\text{Ni}\left(\text{S} \cdot \text{C} \begin{array}{c} \text{S} \\ \text{N} \end{array} \text{C} \cdot \text{H}_4\right)_2; \text{Ni}\left(\text{S} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{CMe} \\ \text{N} \cdot \text{CMe} \end{array} \text{CH}\right)_2$ The Ni compounds of the type $[\text{NiX}_3]\text{C}_2$ (C=anion) are blue, and those of the type $[\text{NiX}_2]\text{C}_2$ red; the Ni atom is probably linked to the S atom and to a N

atom. Compounds in which a H atom of the X is replaced by Ni are obtained from alkaline solutions.

H. F. G.

Microanalysis of gases. III. Hydrogen, carbon monoxide, hydrogen chloride, and ammonia. F. E. BLACET and G. D. MACDONALD (Ind. Eng. Chem. [Anal.], 1934, 6, 334—336; cf. A., 1933, 930).— H_2 is determined by heating the gas sample in presence of a bead consisting of a fused mixture of CuO and KOH. By the same method CO may be oxidised selectively in presence of CH_4 and other paraffins. Known methods are recommended for HCl and NH_3 .

E. S. H.

Acidimetric titrations in presence of managanous salts. V. MACRI (Boll. chim. farm., 1934, 73, 640).—A criticism (cf. Marangoni, this vol., 858).

O. J. W.

Anhydrous sodium carbonate for standardisation. L. WALDBAUER, D. C. McCANN, and L. F. TULEEN (Ind. Eng. Chem. [Anal.], 1934, 6, 336—337).—Anhyd. Na_2CO_3 does not decompose below 450° . Na_2CO_3 is satisfactory as a volumetric standard after washing with EtOH and drying at 110° .

E. S. H.

Titration of chloride and bromide with mercurous nitrate using bromophenol-blue as adsorption indicator. I. M. KOLTHOFF and W. D. LARSON (J. Amer. Chem. Soc., 1934, 56, 1881—1884).—The titration is accurate for $>0.04N\text{-Cl}^-$ or $>0.01N\text{-Br}^-$ and may be reversed for the titration of Hg_2^{++} . Small amounts of HNO_3 or SO_4^{--} , or large amounts of Ca^{++} , K^+ , Na^+ , Ba^{++} , Al^{+++} , or Fe^{+++} , have no effect, but moderate amounts of Cu^{++} , Zn^{++} , or Cd^{++} interfere. Freshly pptd. Hg_2Cl_2 ages rapidly, with considerable decrease of surface. The indicator action is attributed to an exchange reaction.

E. S. H.

Detection and determination of small quantities of bromine by the Deniges-Chelle reaction. J. FREZOULS (Ann. Falsif., 1934, 27, 351—357).—Br is liberated from its compounds present in small quantities (e.g., sea- H_2O) by Caro's acid instead of by the more tedious method involving $\text{H}_2\text{SO}_4\text{-H}_2\text{CrO}_4$ mixtures. It is then absorbed in a layer of CHCl_3 and determined by the coloration produced with the sulpho-fuchsin reagent of Deniges and Chelle. The determination may be made in the presence of large amounts of Cl^- .

E. B. H.

Determination of bromides and iodides in mixtures. R. L. RAIGORODSKAJA and E. S. BINOVA (Pharm. Zentr., 1934, 75, 609—611).—Total $\text{Br}^- + \text{I}^-$ is determined by Volhard's method. I is liberated by addition of FeCl_3 . After 10 min., the solution is diluted and H_3PO_4 added. A further quantity of KI is added, and the free I titrated with $\text{Na}_2\text{S}_2\text{O}_3$.

J. S. A.

Colorimetric determination of iodine by the starch-iodine reaction. H. G. WOODARD (Ind. Eng. Chem. [Anal.], 1934, 6, 331—333).—The influence of concn. of starch and KI, and of added acids and salts, has been examined. The most important source of error is the dissociation of the starch-compound. Correction factors are given for the concn. range 0.5—7.0 mg. I per 100 c.c.

E. S. H.

Iodometry. II. Micro-determination of iodine by a quantity-increasing process. F. RAPPAFORT and H. ENGELBERG (*Mikrochem.*, 1934, 16, 1—12).—The I is converted into I' and its solution acidified (Me-red) with dil. H_3PO_4 . It is then oxidised with Br in glacial AcOH and the excess of Br removed by gentle heating in vac. CdI_2 and KHSO_4 are then added to convert the IO_3' formed into I, the amount produced being 6 times the I content of the original solution. This is distilled off in H_2O vapour and absorbed in Na_2SO_3 . The process is repeated until the quantity formed is sufficient for ordinary determination. J. W. S.

Qualitative tests for periodate and iodate in presence of each other. H. H. WILLARD and J. J. THOMPSON (*J. Amer. Chem. Soc.*, 1934, 56, 1827—1828).—0.6 mg. of IO_4' can be detected in presence of 5 g. IO_3' in 100 c.c. of solution by removing most of the IO_3' with $\text{Ba}(\text{NO}_3)_2$ and pptg. IO_4' by $\text{Bi}(\text{NO}_3)_3$. 1.5 mg. of IO_3' can be detected in presence of 5 g. of IO_4' in 25 c.c. of solution by removing excess of IO_4' as KIO_4 and pptg. IO_3' with AgNO_3 . E. S. H.

Spectral determination of fluorine in water. A. W. PETREY (*Ind. Eng. Chem. [Anal.]*, 1934, 6, 343—345).—Using electrodes impregnated with CaCl_2 , examination of the band with head at λ 5291 furnishes a means of determining F' in the mineral residue of H_2O . The accuracy is greatest when F' is 0.05—1.5% of the residue. E. S. H.

Detection of small amounts of fluorine. S. K. HAGEN (*Mikrochem.*, 1934, 15, 313—314).— H_2SO_4 is heated in a test-tube with a very little $\text{K}_2\text{Cr}_2\text{O}_7$, completely removing grease. Addition of material containing F then gives a distinct "oiliness" with 5×10^{-7} g. of F. SiO_3'' and BO_2' reduce the sensitivity. J. S. A.

Determination of elemental sulphur. H. R. FLECK and A. M. WARD (*Quart. J. Pharm.*, 1934, 7, 179—181).—The material is boiled with aq. Na_2SO_3 , excess of Na_2SO_3 is destroyed by the addition of aq. CH_2O and AcOH, and the $\text{Na}_2\text{S}_2\text{O}_3$ formed titrated iodometrically. A. L.

Colour reactions between nitroprussides and sulphides (Gmelin reaction) and between nitroprussides and sulphites (Bodeker reaction). G. SCAGLIARINI (*Atti Congr. naz. Chim.*, 1933, 4, 597—599; *Chem. Zentr.*, 1934, i, 1178).—The reaction product from $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ and alkali sulphides was isolated as violet crystals by its insolubility in MeOH, the reactants being sol. The Bodeker reaction between $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ and SO_3'' depends on the formation of the coloured ion $[\text{O}:\text{N}(\text{SO}_3) \dots \text{Fe}'' \dots (\text{CN})_5]'''$, the Cd salt of which, combined with $(\text{CH}_2)_6\text{N}_4$, may be isolated as the compound $\text{Cd}[\text{Fe}(\text{CN})_5\text{NOSO}_3], 12\text{H}_2\text{O}, 2(\text{CH}_2)_6\text{N}_4$. H. J. E.

Rapid determination of sulphate ion by a coupled precipitation. J. E. ORLOV (*Z. anal. Chem.*, 1934, 98, 326—329).—The BaSO_4 ppt. is coagulated by co-pptn. of $\text{Al}(\text{OH})_3$. A known amount of AlCl_3 (10 mg. of Al_2O_3 suffice) is added to the SO_4'' solution. As soon as turbidity due to BaSO_4

appears, Al is pptd. by neutralising with aq. NH_3 (Me-red). Coagulation, filtration, and washing are then rapid. J. S. A.

Rapid determination of sulphates in technical hydrochloric acid.—See B., 1934, 831.

Colorimetric determination of sulphuric acid in drinking water.—See B., 1934, 862.

Simplified nephelometric method of determining sulphate in acid extracts. L. V. VLADIMIROV, L. LOBANOV, and S. S. BORISOVA (*Zavod. Lab.*, 1934, 3, 707—710).—10—20 c.c. of 10% HCl and H_2O to 250 c.c. are added to 10 c.c. of extract, 5 c.c. of the solution are diluted to 200 c.c., to 5 c.c. of which 1 c.c. of BaCl_2 solution (20 c.c. of 10% BaCl_2 , 0.25 g. of sol. starch, 0.75 c.c. of conc. HCl, and H_2O to 100 c.c.) is added, and BaSO_4 is determined nephelometrically. R. T.

Determination of SO_4'' in presence of chromates. G. V. RABOVSKI and G. V. RASKATOVA (*Zavod. Lab.*, 1934, 3, 592—593).—50 ml. of solution are boiled during 15 min. with 30 ml. of AcOH and 30 ml. of aq. CH_2O , the solution is diluted to 400 c.c., and 30—40 ml. of 1% BaCl_2 are added, followed by 10 ml. of 10% BaCl_2 . 16 hr. later the ppt. of BaSO_4 is collected, washed, dried, and weighed. A more rapid but less accurate method consists in adding 2% $\text{Ba}(\text{OH})_2$ to 25 ml. of boiling solution to decolorisation of the supernatant fluid, cooling, diluting to 200 ml., and filtering. Standard aq. Na_2CO_3 is added to 100 ml. of filtrate to complete pptn. of BaCO_3 , the solution is boiled, diluted to 200 ml., and filtered. 100 ml. of filtrate are titrated with 0.1N-HCl, CrO_3 is determined manganometrically in 25 ml. of filtrate, and SO_4'' is calc. by difference. R. T.

Potentiometric determination of selenocyanogen in presence of chlorine and bromine. G. SPACU and P. SPACU (*Z. anal. Chem.*, 1934, 98, 248—254).— SeCN' may be titrated potentiometrically in presence of Cl' and Br' . Attainment of a steady potential near the equivalence point is retarded by adsorption effects, but is assisted by addition of MgSO_4 or $\text{Ba}(\text{NO}_3)_2$. J. S. A.

Colour reaction for ammonia. L. LAPIN and W. HEIN (*Z. anal. Chem.*, 1934, 98, 236—240).— NH_4' gives with NaOBr and phenols intense blue colorations, turning red on acidification. That from thymol (I) may be extracted with org. solvents, and separates as a red pigment from C_6H_6 . 5 c.c. of solution containing 5×10^{-4} mg. NH_4' , treated with 1 c.c. of 25% (I) in EtOH and 12 c.c. of fresh 2N- NaOBr , give a distinct violet colour when extracted with 5 c.c. of Et_2O . Other cations, and org. bases (except NH_2Ph), do not interfere. J. S. A.

Use of formaldehyde to expel ammonium salts in qualitative and quantitative analysis. I. A. HEMMELER (*Annali Chim. Appl.*, 1934, 24, 364—369).—It seems possible that removal of NH_4 salts from solution by evaporation and calcination may be avoidable by converting them into $(\text{CH}_2)_6\text{N}_4$ with CH_2O . T. H. P.

Determination of nitrates. Modification of the Devarda method. J. DAVIDSON and A. KRASNITZ (Ind. Eng. Chem. [Anal.], 1934, 6, 315—316).—MgO is substituted for NaOH, allowing NH_3 and NO_3^- to be determined in the same solution. E. S. H.

Validity of the Dusart-Blondlot test for phosphorus. J. H. KŘEPELKA and J. CHMELÁŘ (Coll. Czech. Chem. Comm., 1934, 6, 307—324).— H_3PO_2 (I) and H_3PO_3 (II) were reduced very slowly and at different rates in the presence of Zn and 30% H_2SO_4 . After 48 hr., < 17% of the (I) and < 8% of the (II) in the solution were reduced to PH_3 , and hence shorter periods of reduction are inadequate. Serious loss of P occurs if the ppt. of $\text{Ag}_3\text{P} \cdot 3\text{AgNO}_3$ is washed, but with the modified Dusart-Blondlot test (III) described 7×10^{-4} mg. of P can be detected. In all instances, animal material containing organically combined P after rotting for 1—2 weeks afforded a blue H_2 flame in the (III) owing to volatile P and S compounds. Vegetable matter, after rotting for 4 months, gave a similar flame, which, after 0.5 min., became emerald-green. Hence, when the material under examination contains organically bound P, the positive (III) is not trustworthy evidence of P poisoning (cf. A., 1901, ii, 343). J. G. A. G.

Selenium as reduction-oxidation indicator in the volumetric determination of arsenite with potassium bromate. L. SZECELLÉDY and K. SCHICK (Magyar gyógys. Társaság Értes., 1933, 9, 449—454; Chem. Zentr., 1934, i, 1082).—Arsenite may be determined by Gyory's method with KBrO_3 in daylight. In artificial light an indicator is necessary. Colloidal red Se is used as a reversible reduction-oxidation indicator in place of Me-orange. 5 g. of KBr are dissolved in the arsenite solution, the vol. is made up to 35 c.c., and 25 c.c. of conc. HCl are added. The solution is warmed to 55—60°, 1 c.c. of aq. H_2SeO_3 (1 mol. per litre) is added, and the red solution is titrated with 0.1N-KBrO₃ until colourless. H. J. E.

Detection of boric acid by a fluorescence reaction. L. SZECELLÉDY and H. GAAL (Z. anal. Chem., 1934, 98, 255—258).—Cochineal tincture gives with H_3BO_3 between 5.8 and 6.9 (best in presence of an equimol. Na_2HPO_4 - KH_2PO_4 buffer) a solution fluorescing orange-yellow by ultra-violet light. Other anions, except CO_3^{2-} , do not interfere; most heavy metals do so. Al, Mg, Zr, Ti, Ta, Nb, and Mo show characteristic fluorescence colours. J. S. A.

Spectroscopic determination of carbon monoxide. S. L. KAGAN and A. V. PAMFILOV (Zavod. Lab., 1934, 3, 756—757).—Nieloux's micro-method does not give trustworthy results. R. T.

Determination of small quantities of CO_3^{2-} . N. K. TOPTSCHIEVA (Zavod. Lab., 1934, 2, 702—705). CO_3^{2-} can be determined in concn. $\leq 0.01N$ by titration with standard aq. $\text{Pb}(\text{NO}_3)_2$ at 100° (phenol-red), and in concn. of $\leq 0.001N$ nephelometrically, stabilising the suspension of PbCO_3 with gelatin. R. T.

Determination of carbon dioxide content of an atmosphere in a closed system. E. M. SMYTH (Science, 1934, 80, 294; cf. this vol., 47).—Two

methods depending on the colorimetric determination of the p_{H} of a standard NaHCO_3 solution and suitable for use in closed systems are described. L. S. T.

Determination of carbon dioxide in cyanides.—See B., 1934, 831.

Determination of phosgene by the soda method. Effect of fire-extinguisher chlorinated hydrocarbons. M. P. MATUSZAK (Ind. Eng. Chem. [Anal.], 1934, 6, 374—375).—The presence of CCl_4 or CHCl_3 introduces no error in the determination of COCl_2 . For absorption aq. N-NaOH is preferred to alcoholic NaOH. E. S. H.

Determination of radioactive precipitates with the help of the point-counter and the counter tube. A. KREBS (Physikal. Z., 1934, 35, 796—800).—The use of the above apparatus in the determination of Rn in air is described. A. J. M.

Determination of potassium in presence of other elements. K. L. MALJAROV and V. B. MATZKEVITSCH (Zavod. Lab., 1934, 3, 705—706).—2 c.c. of saturated aq. NaOAc, 0.2 c.c. of EtOH, and 0.2 c.c. of 77% AcOH are added to 20 c.c. of the neutral solution under examination, followed by 4 c.c. of aq. $\text{Co}(\text{NO}_2)_2$. The ppt. of $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ is collected 12 hr. later, washed with 20% EtOH, and heated at 100° for 30 min. with 25 c.c. of 0.01N- $\text{K}_2\text{Cr}_2\text{O}_7$ (I) and 5 c.c. of 50% H_2SO_4 , after which excess of (I) is determined iodometrically. R. T.

Occlusion of water by potassium and sodium chlorides. Influence on indirect determination of sodium. G. F. SMITH, F. M. STUBBLEFIELD, and E. B. MIDDLETON (Ind. Eng. Chem. [Anal.], 1934, 6, 314).—The amount of H_2O retained after drying at 550° is about 0.08%. Weighing after fusion, with precautions to prevent volatilisation, is preferred. E. S. H.

Visual spectral method for quantitative analysis of solutions. A. K. RUSSANOV (Z. anal. Chem., 1934, 98, 335—342).—The solution (3—4 c.c.) is injected by a Lundegardh atomiser into a C_2H_2 flame, air and C_2H_2 pressure being controlled. Variable light absorption is provided by a wedge-shaped filter cell containing aq. CuSO_4 or KMnO_4 . The concn. of Li, Na, K, Ca, Sr, Ba, and Tl is determined, from calibration curves, from the cell thickness at which the visible lines vanish. The presence of small amounts of other cations can introduce error; comparison must be made with similar solutions. J. S. A.

Reaction for distinguishing calcite and aragonite. H. LEITMEIER and F. FEIGL (Tsch. Min. Petr. Mitt., 1934, 45, 447—456).—A slightly alkaline solution of MnSO_4 and Ag_2SO_4 produces a black colour ($\text{MnO}_2 + \text{Ag}$) on powdered aragonite in a few sec., but on calcite only after several min. The same reagent can be used on micro-sections, but is here rather slower. Strontianite and witherite behave like aragonite, and dolomite like calcite. This reaction has the advantage over that of Meigen (1902) in that it can be used in the cold. L. J. S.

Direct titration of barium salts with potassium chromate, with rosolic acid as indicator. A. v.

VINOGRADOV and A. E. SOLOVEVA (Zavod. Lab., 1933, No. 10, 17—19).— K_2CrO_4 may be added to $BaCl_2$ or the reverse. Sulphates can be determined by adding excess of $BaCl_2$ and titrating without filtering. Much Fe interferes; small quantities may be removed by adding $CaCO_3$ in the cold. Hydrolysis of NH_4 salts prevents the colour change. Acetates, H_3PO_4 , and $H_2C_2O_4$ interfere. CH. ABS.

Microchemical determination of magnesium. A. QUARTAROLI (Annali Chim. Appl., 1934, 24, 383—390).—The negative catalytic effect of Mg^{++} on the blackening of $Cu(OH)_2$ (this vol., 731) provides a means for its determination. To 1 c.c. of aq. $CaCl_2$ (prepared by dissolving 10 g. of $CaCO_3$ in HCl and diluting to 250 c.c., taking 20 c.c. of this solution, and diluting again to 250 c.c.) is added a known vol., V , of the solution to be analysed, and H_2O (twice distilled) added to bring the vol. to 15 c.c. 0.75 c.c. of 2% aq. $CuSO_4$ is added and the mixture shaken and left in a bath at 50° for 10 min. 0.75 c.c. of 20% aq. NaOH is then added and the tube left in the bath for 30 min. with shaking. If $>11 \times 10^{-6}$ g. of Mg is present, no change occurs; if less, the $Cu(OH)_2$ darkens visibly. By varying V , the vol. containing 11×10^{-6} g. can be estimated to an accuracy of 10%. Alternatively, the vol. of the ppt. after 1 hr. may be observed. The application of the method to the analysis of H_2O , salt, chalk, biological fluids, soil, Mg alloys, lime, cement, etc. is described. D. R. D.

Rapid volumetric determination of magnesium in duralumin.—See B., 1934, 890.

Detection of small amounts of zinc and cadmium. N. A. TANANAEV (Z. anal. Chem., 1934, 98, 330—331).—Heavy metals are pptd. by boiling with aq. NH_3 , and adding KI and H_2O_2 to ppt. Ag and Mn. To the filtrate, excess of KCN is added, and then aq. Na_2S . Cd if present is pptd. as CdS . NH_3 in a second portion is removed by adding NaOH and CH_3O , and pptg. Cu, Ni, and Cd. Addition of Na_2S then ppt. ZnS. J. S. A.

Volumetric determination of cadmium in presence of zinc and copper. J. FLALKOV and V. GORODISSKI (Mem. Inst. Chem. All-Ukrain. Acad. Sci., 1934, 1, 61—69).—Saturated aq. $(NH_4)_2CO_3$ (I) is added to the solution in amount sufficient to dissolve the $CuCO_3$ and $ZnCO_3$ at first pptd., the ppt. of $CdCO_3$ is washed with (I) and then with H_2O , and dissolved in standard acid, excess of which is titrated. The experimental error is ± 0.2 — 0.3% . R. T.

Use of potassium mercuriselenocyanate as reagent in qualitative micro-analysis. A. A. BENEDETTI-PICHELLE and W. F. SPIES, jun. (Mikrochem., 1934, 15, 271—287).— $K_2Hg(CNSe)_4$ (prep. described) gives characteristic cryst. ppts. with Cd, Zn, Co, Cu, Ni, Fe, and Mn. The sensitivity is somewhat $>$ with $K_2Hg(CNS)_4$. Traces of Cu, Fe, or Ni (yellowish spherulitic ppts.) may thus be readily detected in Co (bluish-green needles). The compounds $XHg(CNSe)_4$ ($X=K$, Zn, Cd) were prepared. J. S. A.

Dithizone in qualitative and quantitative micro-analysis. H. FISCHER (Angew. Chem., 1934, 47, 685—692).—In part a review of the analytical use of

dithizone (I). Cd may be detected in presence of Cu by pptg. Cu with H_3PO_4 ; Bi, in a NH_4Cl buffered KCN solution in the absence of Pb, Sn^{II} , and Tl; Au, in dil. acid solution, Ag being removed with NH_4Cl and Hg with KI. Pd forms preferentially a flocculent ppt. in acid solution. A group separation may be effected with (I), utilising the varying solubility of the ppts. in solutions of controlled acidity. Metallic Pb, Zn, and Cu react with (I) and may be so detected in metals and alloys; solid salts also react. Zn may be determined colorimetrically as for Pb (A., 1933, 923), reaction being carried out in NaOAc-buffered acid solution. Au may also be determined colorimetrically, using the change in colour of a CCl_4 solution of the Ag-(I) complex when shaken with Au. By extraction-titration with (I), 0.5 — 100×10^{-6} g. of Ag may be determined in acid solution in presence of all other metals except Au, Hg, and Pd; also Cd and Zn in neutral solution. Zn, Pb, and Bi may be titrated indirectly, proceeding as for the colorimetric determination, but determining the liberated (I) by addition of excess Ag, then titrating back. Alternatively, a measured excess of (I) may be added to the acid solution, followed by excess of Ag and back titration. 10 — 100×10^{-6} g. of Cl, Br, I, and S may also be determined by adding excess of Ag, then titrating with (I). J. S. A.

Detection of mercury. N. A. TANANAEV and N. V. JUNTZKAJA (Z. anal. Chem., 1934, 98, 334—335).—When shaken with a suspension of Ag_2S , Hg^+ and Hg^{++} yield HgS , which remains undissolved on warming with 50% HNO_3 . J. S. A.

Detection of small amounts of mercury. N. A. TANANAEV (Z. anal. Chem., 1934, 98, 331—333).—The solution is treated with Br to oxidise Fe^{++} and Sb, and then added to aq. NaOH containing 10% of KI. Reducible metals except Hg are pptd., and Hg is detected in the filtrate by addition of $SnCl_2$. J. S. A.

Determination of mercury in air, and absorption of mercury vapour by gold. V. MAJER (Chem. Listy, 1934, 28, 228, 244—247).—The air should be filtered before passage over Au, as in presence of solid particles absorption of Hg is incomplete. 10^{-6} g. of Hg per cu.m. can be determined by passing the air through U-tubes cooled in liquid air, and converting the condensed Hg into $HgCl_2$, determined by the usual methods. R. T.

Prussian-blue as a mercurimetric indicator. R. UZEL (Coll. Czech. Chem. Comm., 1934, 6, 302—306).— 0.005 — $0.1N$ - Hg_2^{++} is titrated with Cl^- or Br^- in presence of $K_4Fe(CN)_6$ and Fe^{III} alum. The yellow solution affords a blue coloration, chiefly on the ppt., immediately excess of halide has been added. The results accord with those obtained potentiometrically. The end-point of the inverse titration is unsatisfactory, but Cl^- and Br^- are determined by back titration. Hg^{++} requires more Br^- than is indicated by theory, and the method is unsatisfactory for determining Ag^+ . J. G. A. G.

Reaction for cerium with pyrogallol, and the reaction of thorium, lanthanum, and elements of the third analytical group with pyrogallol. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1934, 4, 248—252).

—A few drops of solution are added to 10 c.c. of 1% pyrogallol, followed by a few drops of 10% aq. NH_3 , when a blue ppt. indicates $< 1.4 \times 10^{-6}$ g. of Ce^{III} or Ce^{IV} . La and Th do not interfere with this reaction. Under similar conditions Fe^{III} , Ti^{III} , Zn, Al, Ni^{II} , and Co^{II} give a brown coloration, Cr^{III} a ppt. of $\text{Cr}(\text{OH})_3$, and Mn^{II} a dark brown ppt. R. T.

Separation and determination of gallium. IV. Separation of gallium from indium, thallium, and iron, and the determination of all these elements. S. ATO (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1934, 24, 270—282; cf. A., 1931, 927).—Ga can be separated from In by pptn. of the latter with 5% Na_2CO_3 , and then pptg. the Ga from the filtrate with camphoric acid (I), both elements being determined gravimetrically. Ga and Tl can be separated by conversion into sulphates, reduction of Tl^{III} to Tl^{I} with SO_2 or H_2O_2 , and pptn. of Ga with (I) and Tl from the filtrate with K_2CrO_4 ; or by reducing Tl^{III} with $\text{Na}_2\text{S}_2\text{O}_3$ and pptg. Ga with (I). Ga and Fe are separable by pptg. Fe with 1.5N-KOH or by reducing Fe^{III} to Fe^{II} with $\text{Na}_2\text{S}_2\text{O}_3$, Ga being pptd. in each case with (I). J. W. S.

Rapid micro-determination of manganese. I. M. KORENMAN (Zavod. Lab., 1934, 3, 699—702, and Mikrochem., 1934, 15, 289—294).—1 c.c. of 10% $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.5 c.c. of 3N- HNO_3 , 1 c.c. of 0.1N- AgNO_3 , and H_2O to 5 c.c. are added to 1—2 c.c. of the solution, which is then heated at 100° for 5 min. 0.01—0.015N- KMnO_4 (I) is added to 5 c.c. of H_2O in a similar test-tube until the intensity of coloration matches that of the test, when the vol. of (I) taken corresponds with the Mn content of the solution examined. Fe^{II} , Fe^{III} , Ni, Co, Zn, Al, and Cu do not interfere, but Cr should be absent. In presence of a very great excess of Fe^{III} , H_3PO_4 should be added. An alternative method consists in titrating the MnO_4^- formed with 0.01N- H_3AsO_3 , applying an empirical correction of -0.04 to the burette reading. In presence of Co, $\text{Co}(\text{NO}_3)_2$ may be added to the comparison solution also. Pb is pptd. as PbSO_4 . In presence of Cl⁻, excess of Ag must be added. R. T.

Polarographic studies with the dropping mercury cathode. XLI. Micro-determination of manganese in biological material. E. HAMAMOTO (Coll. Czech. Chem. Comm., 1934, 6, 325—338).—As little as 0.02×10^{-6} g. of Mn in 1—2 g. of biological material is determined by removing the Fe and Zn from the ash and electrolysing the neutral MnCl_2 solution at the dropping Hg cathode. The ash in HCl solution is nearly neutralised with Na_2CO_3 , excess of NaOAc is added, and the Fe is pptd. by boiling; under the conditions Mn is not lost by adsorption on the ppt. The Mn pptd. from the filtrate by boiling with NaOH and a little KClO_3 is ashed, dissolved in HCl, excess of the latter being removed by evaporation, and finally dissolved in 0.01M-LiCl. The magnitudes of the saturation currents are recorded for polarograms obtained with 0.02 — 11×10^{-6} g. of Mn. J. G. A. G.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXVII. Observations on manganese, and analysis of tantalite. W. R. SCHOELLER and H. W. WEBB (Analyst,

1934, 59, 667—671; cf. A., 1933, 139, 479; this vol., 933).—Ammoniacal tartrate solutions (I) of pure Mn^{II} salt were readily pptd. by NH_4 sulphide, but (I) obtained in the analysis of manganotantalite, when so treated, were incompletely pptd., in some cases scarcely at all. Almost quant. pptn. of MnS resulted after previous evaporation to a very small vol. Mn is almost quantitatively pptd. from tartrate solution by tannin and excess of aq. NH_3 . A new process for the analysis of tantalite is described. E. C. S.

Use of potassium mercurithiocyanate as a microchemical reagent. A. A. BENEDETTI-PICHLER and W. F. SPIKES, jun. (Mikrochem., 1934, 15, 288).— $\text{K}_2\text{Hg}(\text{CNS})_4$ gives with conc. Fe^{III} solutions a blood-red cryst. ppt. Fe^{II} if present may give a ppt. similar to that given by Cu. J. S. A.

Rapid micro-determination of iron. I. M. KORENMAN (Mikrochem., 1934, 15, 315—318).—To 2—3 c.c. of solution are added 0.5 c.c. of 10% aq. sulphosalicylic acid and 1.5 c.c. of 10% aq. NH_3 , and the vol. is made up to 5 c.c. The colour is matched against that produced by a measured vol. of standard Fe solution in the same total vol. J. S. A.

Enhancement of sensitivity of microchemical reactions for Co^{II} and Cu^{II} , and an induced reaction for Fe^{II} , Fe^{III} , and Ni^{II} . I. M. KORENMAN (Zavod. Lab., 1934, 3, 713—714).—Aq. $(\text{NH}_4)_2\text{Hg}(\text{CNS})_4$ (I) gives a dark blue cryst. ppt. in presence of $< 0.5 \times 10^{-6}$ g. of Co^{II} , and a greenish-yellow ppt. in presence of $< 0.25 \times 10^{-6}$ g. of Cu^{II} . The white ppt. of $\text{ZnHg}(\text{CNS})_4$ obtained by adding (I) to aq. Zn salts is coloured blue by $< 0.02 \times 10^{-6}$ g. of Co^{II} , violet by $< 0.015 \times 10^{-6}$ g. of Cu^{II} , yellow by $< 0.14 \times 10^{-6}$ g. of Fe^{II} , violet, brown, or rose by $< 0.02 \times 10^{-6}$ g. of Fe^{III} , and greyish-green by $< 3.3 \times 10^{-5}$ g. of Ni^{II} . R. T.

Organic reagents in qualitative analysis. II. Analysis of the common metals of the ammonium sulphide group. L. LEHRMAN, H. WEISBERG, and E. A. KABAT (J. Amer. Chem. Soc., 1934, 56, 1836—1838; cf. A., 1933, 1133).—By the following scheme of analysis 1 mg. of each metal can be detected in presence of 500 mg. of any other or combination of others. Fe^{III} is removed with cupferron, and Ni, Co^{II} , and Zn^{II} are pptd. in NaOAc-AcOH solution by H_2S . The HCl extract of the ppt. is treated with dimethylglyoxime to ppt. Ni^{II} , a brown filtrate indicating Co^{II} , whilst Zn^{II} is detected by 8-hydroxyquinoline. $\text{Al}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ are pptd. by $(\text{CH}_2)_6\text{N}_4$, and after dissolution Al^{III} is identified by 8-hydroxyquinoline and Cr^{III} by oxidation to Cr_2O_7 followed by adding H_2O_2 or diphenylcarbazide. MnO_2 is pptd. by NaOH and Na_2O_2 and is identified by a bead test or by Na bismuthate in HNO_3 . E. S. H.

Iodometric determination of chromate ion. F. L. HAHN (Z. anal. Chem., 1934, 98, 225—227).—Polemical against Friedrich and Bauer (this vol., 982). J. S. A.

Determination of dichromates in presence of chromates. A. SCONZO and L. MARSENGO (L. In. Chimica, 1934, 9, 1163—1167).—The solution is treated with excess of 0.1N-NaOH and then ¹

just enough 0.1*N*-BaCl₂ to ppt. the CrO₄^{''} (=2/3 of the vol. of 0.1*N*-Na₂S₂O₃ required to titrate the original solution). The BaCrO₄ is filtered off and washed, and the filtrate is titrated with 0.1*N*-HCl in presence of Me-orange to determine the excess of NaOH added beyond that required to convert Cr₂O₇^{''} into CrO₄^{''}. This gives the Cr₂O₇^{''}; the CrO₄^{''} is then calc. from the result of the Na₂S₂O₃ titration.

T. H. P.

Determination of chromium in presence of iron, aluminium, and phosphoric acid, with perchloric acid as oxidising agent. J. HASLAM and W. MURRAY (Analyst, 1934, 59, 609—613).—In presence of Fe, Jarvinen's method (A., 1928, 1206), using NaOBr, gives low results, but a modification of Lichtin's (B., 1930, 417), using HClO₄, is satisfactory. Cl⁻ and Mn should, however, be excluded.

E. C. S.

Oxidimetric determination of tin. S. FERJANIČ (Z. anal. Chem., 1934, 98, 246—248).—To the boiled-out HCl solution of SnCl₂, are added NaHCO₃ to eliminate atm. oxidation, and 10 c.c. of 0.1*N*-KI. A slight excess of 0.1*N*-KBrO₃ is run in rapidly, and liberated I titrated back with Na₂S₂O₃. J. S. A.

Determination of vanadium by means of 8-hydroxyquinoline. S. L. TZINBERG (Zavod. Lab., 1933, No. 1, 18—20).—V is pptd. as V₂O₃(C₉H₆ON)₄, dried at 120°, and weighed. The method is applied to steels. MoO₂(C₉H₆ON)₄ is insol. in dil. AcOH. The org. complex can also be determined by titration with Br in alkali or KBrO₃ in acid. CH. ABS.

Detection of bismuth with sulphur-containing organic reagents. III. J. V. DUBSKY, A. OKAČ, B. OKAČ, and J. TRTILEK (Z. anal. Chem., 1934, 98, 184—193).—In feebly acid Bi solutions 5-thiol-2-thion-*o*- and -*p*-tolyl-1 : 3 : 4-thiodiazole produce red ppts. (sensitivity 1.5 × 10⁻⁶ g. at a dilution of 1 : 25,000), whereas the *m*-compound gives a yellowish-red ppt. (1.0 × 10⁻⁶ g.; 1 : 38,000). Ethylenethiocarbamide reacts with Bi solutions similarly to CS(NH₂)₂. Chrysean gives an orange-yellow solution from which small red crystals of BiCl₃·2C₄H₅N₃S₂·2H₂O slowly separate; in the presence of KI a red ppt. forms immediately, but it is sol. in excess of KI and in acids. Reactions of Bi with some other complex org. compounds containing S are discussed; none is characteristic. A. R. P.

Rubianic acid as micro-reagent for elements of the platinum group. H. WOLBLING and B. STEIGER (Mikrochem., 1934, 15, 295—301).—Rubianic acid, (NH₂·CS⁻)₂ (I), as 0.2% solution in AcOH gives a strictly sp. blue coloration with neutral or slightly acid solutions of Ru salts, slowly at room temp., rapidly at 100°; limit 2 × 10⁻⁷ g. Ru. PdCl₂ with (I) in EtOH gives in 12 hr. a quant. red cryst. ppt. of C₂S₂N₂H₂Pd(NH₂·CS⁻)₂, insol. in dil. HCl. The ppt., dried at 110°, may be used for the determination of Pd. H₂PtCl₆ and other Pt solutions with excess of (I) give a quant. ppt. of Pt(C₂S₂N₂H₂)₂(NH₂·CS⁻)₂. J. S. A.

Analytical uses of isopropyl alcohol. G. W. FERNER and M. G. MELLON (Ind. Eng. Chem. [Anal.],

1934, 6, 345—348).—Pr³OH may serve as a substitute for EtOH as a solvent for analytical reagents, for the separation of inorg. compounds, and as a washing medium for ppts. E. S. H.

M.-p. apparatus for minute samples. S. GRANICK (Science, 1934, 80, 272—273). L. S. T.

Micro-m.-p. apparatus with thermometer calibrated on the apparatus. L. KOFER (Mikrochem., 1934, 15, 242—246).—Descriptive. An ungraduated Hg thermometer may conveniently be calibrated *in situ*. J. S. A.

Approximate determination of the specific heat of liquids. G. E. SEAVOY (Chem. Met. Eng., 1934, 41, 473).—Some of the liquid is evaporated under vac. The fall in temp. of the liquid and wt. of condensate are determined and the sp. heat is calc. D. K. M.

Thermochemistry of solutions. I. Calorimeter for use with non-aqueous solvents. F. A. ASKEW, N. S. JACKSON, O. GATTY, and J. H. WOLFENDEN (J.C.S., 1934, 1362—1368).—Details are given of the construction and operation of a sealed adiabatic rotating calorimeter adapted from that already described (A., 1927, 954). A special percussion valve enables heats of dissolution of hygroscopic substances to be determined. The heat of dilution of NaClO₄ in MeOH is 316 g.-cal. per mol., and the magnitude of the errors involved is considered. J. G. A. G.

Visual spectrophotometry. K. S. GIBSON (J. Opt. Soc. Amer., 1934, 24, 234—249).—A general survey of instruments, methods, and factors affecting the trustworthiness of data. N. M. B.

Effect of treatment of the surfaces of calcite crystals on the resolving power of the two-crystal spectrometer. K. V. MANNING (Rev. Sci. Instr., 1934, [ii], 5, 316—320).—Cleavage faces after grinding and etching with 0.7*N*-HCl give, as determined by the widths of rocking curves in the (1, -1) position, higher resolving power than the original faces, the improvement being greater at the shorter wavelengths. N. M. B.

Burner to give a brilliant monochromatic flame. A. I. SCHATTENSTEIN (Z. anal. Chem., 1934, 98, 235—236).—A pencil of NaCl+NaBr, made into a cement with MgO and Na₂SiO₃, is fed into a flat O₂-coal gas flame. J. S. A.

Ultra-violet microscope illuminator. Use with rayons. T. H. DAUGHERTY and E. V. HJORT (Ind. Eng. Chem. [Anal.], 1934, 6, 370—371).—The apparatus is described. Preliminary observations on the fluorescence of rayons have been made. E. S. H.

Cell for refractivity measurements on minute crystals. F. I. G. RAWLINS and C. W. HAWKSLEY (J. Sci. Instr., 1934, 11, 282—284).—The crystal is mounted on a holder which is inserted into the cell containing the comparison liquid, and examined through a polarising microscope. C. W. G.

Grating interferometer. B. P. RAMSAY (J. Opt. Soc. Amer., 1934, 24, 253—258).—The construction and action of a modified Michelson interferometer, in

which reflecting mirrors are replaced by gratings to produce wave fronts giving rise to fringes, are described. N. M. B.

New interferential device. Q. MAJORANA (Compt. rend., 1934, 199, 552—554).—A simple apparatus is described, and some of its applications are indicated. J. L. D.

Determination of small differences in X-ray wave-lengths by the powder method. A. H. JAY (Proc. Physical Soc., 1934, 46, 713—720).—Using a microphotometer it is possible to determine accurately the positions of lines at high angles of reflexion on a powder photograph. From such a photograph of quartz, the val. of the λ difference for the $\text{Cu } K\alpha$ doublet is calc. as 3.833 X. J. W. S.

Five-kilowatt X-ray generator with a spinning target. R. E. CLAY (Proc. Physical Soc., 1934, 46, 703—712).—A generator in which the power input is increased by utilising a water-cooled rotating disc as target is described. J. W. S.

Optical lever and furnace for thermal expansion measurements using small specimens. H. G. JONES (J. Sci. Instr., 1934, 11, 325—326).—Two legs of a tripod carrying a mirror rest on a standard specimen, and the other on the specimen under test. C. W. G.

Effect of scattering of different types of sensitometer wedge on their reproducing properties. E. SPILLER (Physikal. Z., 1934, 35, 753—756).—With two wedges of equal blackening, but different structure, a different blackening of the copy was obtained, due to a difference in the spectral transmission of the wedges in the ultra-violet. Such difference was, however, within the tolerance allowed by the DIN process. A. J. M.

Use of photo-elements in colorimetry. A. L. DAVIDOV and V. F. STEFANOVSKI (Zavod. Lab., 1934, 3, 640—645).—Greater accuracy is obtainable using photo-elements than by visual comparison. Cr in C steels can be determined photocolometrically with an error of $\pm 1\%$. R. T.

Colorimetric standards for silica. H. W. SWANK and M. G. MELLON (Ind. Eng. Chem. [Anal.], 1934, 6, 348—350).—Spectrophotometric observations of the yellow coloration formed with SiO_3^{2-} and NH_4 molybdate in presence of acid shows that solutions of picric acid or unbuffered K_2CrO_4 are not satisfactory, permanent reference standards. Aq. K_2CrO_4 , buffered with $\text{Na}_2\text{B}_4\text{O}_7$, is preferred as a standard. E. S. H.

Electrographic methods. R. JIRKOVSKY (Mikrochem., 1934, 15, 331—342).—A review.

Angular distribution of particles inside Wilson's chamber. N. A. DOBROTIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 241—244; cf. this vol., 470).—Mathematical. The angular distribution function is obtained from the projection of the tracks on one plane. J. G. A. G.

[New method for] p_H measurement. H. A. FREYE (Chem.-Ztg., 1934, 58, 783).—In place of agar jelly in the bridge for connecting the standard elec-

trode, a core of porous material (unspecified) is formed in a glass tube and moistened with a suitable solution. D. R. D.

Apparatus for colorimetric oxidation-reduction studies. H. P. LUNDGREN (Science, 1934, 80, 209). L. S. T.

Cuprous oxide solid photo-electric cells. C. G. FINK and M. E. FOGLE (Trans. Electrochem. Soc., 1934, 66, 43—91).—Relations between cell voltage, V , current, I , and internal resistance, R_i , of photo-electric cells with a Cu_2O film formed under standardised conditions and a pressed-on anode were determined for various intensities of illumination, L (controlled by a special lamp voltage regulator), external resistances, R_e , and temp. Contrary to previous conclusions, total I is not independent of L at given L , but varies with V ; and R_i is independent of L , but does vary with I and with temp. V , I , and R_i decrease with rise of temp. Variation of V with anode distance at various temp. and of R_i with anode width indicate that the layer of the Cu_2O film adjacent to the Cu base is of higher resistance than the rest. Generation of current and voltage by photo-electric emission is suppressed when V reaches a certain val. which is independent of L . The output of a cell at normal incidence can be increased by 10—25% by coating it with an inert transparent solid or liquid which decreases losses due to reflexion of light from the surface. Marked differences in the behaviour of Cu_2O photo-electric and photo-voltaic cells are discussed in relation to their fundamental differences in mechanism. H. J. T. E.

Electron counter and the physical demonstration of the Gurwitsch radiation. R. RUYSSSEN (Natuurwetensch. Tijds., 1934, 16, 221—227).—A small quartz cell fitted with an Al, Cd, or Zn etc. cathode and an Fe wire oxidised on the surface by means of HNO_3 is described; it has the advantage of producing \approx about 7 spontaneous impacts per min. with a cathode area of 10 sq. cm. Details are given of a complete four-valve counter, the sensitivity of which rises rapidly to 65 quanta at 2200 Å. with decrease of λ . H. F. G.

Production of spectrally pure carbon electrodes. A. K. RUSSANOV (Z. anorg. Chem., 1934, 219, 332—334).—The impurities Fe, Si, Al, Ti, and V are volatilised from C by heating below 2480° for a length of time up to 3 min. At about 2700° 10 20 sec. only are necessary, and since the time is short it is possible to carry out the purification in air. Cu lines disappear after 35 sec. at the higher temp. an very faint lines only of Ca, Mg, and B remain. M. S. B.

Plastometric investigations of substances of high consistency. I. Construction of plastometer. G. UNGAR (Kolloid-Z., 1934, 69, 30—35). The instrument described may be used over the range 10—10⁸ poises. E. S. H.

Laboratory stirrers. K. B. HUMPHREY (Science, 1934, 80, 273—274). L. S. I.

Aluminium desiccator plates. H. W. PUTNAM (Cereal Chem., 1934, 11, 566).—The advantages of Al

desiccator plates for ash and H_2O determinations are indicated. E. A. F.

Laboratory production of sintered glassware. H. V. A. BRISCOE and A. R. LOWE (J.C.S., 1934, 1379—1380).—A sintered-glass filter plate is made by compressing with a plunger in a brass tube on a porous plate the appropriate quantity of specially cleaned Pyrex powder graded between 60- and 80-mesh sieves and treated, while wet, with the min. quantity of aq. commercial Na_2SiO_3 . The moist disc is sintered on a charcoal block with a hand blow-pipe and is sealed into a tube after the Na_2SiO_3 has been washed out. J. G. A. G.

Suction device. L. COHEN (Ind. Eng. Chem. [Anal.], 1934, 6, 322).—The apparatus facilitates filtration. E. S. H.

Preparation of samples for determination of arsenic. Oxygen-bomb combustion method. F. P. CAREY, G. BLODGETT, and H. S. SATTERLEE (Ind. Eng. Chem. [Anal.], 1934, 6, 327—330).—The combustion bomb described includes a cloud-pptn. apparatus, which minimises loss of As through formation of fume. E. S. H.

Microscope cold stage with temperature control. C. W. MASON and T. G. ROCHOW (Ind. Eng. Chem. [Anal.], 1934, 6, 367—369).—The apparatus is designed for use at temp. $\leq -25^\circ$, with control to 0.1° . E. S. H.

Constant-temperature high-pressure laboratory autoclave. F. J. DYKSTRA and G. CALINGAERT (Ind. Eng. Chem. [Anal.], 1934, 6, 383—384).—The reaction tube is surrounded by a jacket filled with a liquid, kept at the b.p. It is suitable for work up to 280° and 218 atm. E. S. H.

Rubber stopper remoulding for reduced pressure filtration. G. F. SMITH and J. L. GRING (Ind. Eng. Chem. [Anal.], 1934, 6, 385—386).—The advantages of a modified form of rubber stopper are enumerated. E. S. H.

Apparatus and methods of micro-sublimation. R. FISCHER (Mikrochem., 1934, 15, 247—270).—A sublimation block, for use with the Fischer micro-p. apparatus (see this vol., 1193), permits continuous observation and temp. control. J. S. A.

Simple automatic pump. J. PALMER (Science, 1934, 80, 229—230). L. S. T.

Use of automatic extractors. L. E. WARREN (J. Assoc. Off. Agric. Chem., 1934, 17, 516—522).—The automatic extractor is not satisfactory for mixtures of solvents unless their b.p. is similar. It is most useful in difficult separations, particularly those readily producing emulsions. Its application to the assay of pharmaceutical materials is discussed. E. C. S.

Direct-indicating radium meter. G. HERZOG (Helv. phys. Acta, 1933, 6, 237—239; Chem. Zentr., 1933, ii, 3886).—Intensity measurements on Ra preps. are based on measurements of the γ -ray ionisation current, using a valve method. H. J. E.

Clock device for teaching soil texture. J. E. CHAPMAN (Science, 1934, 80, 166—167).—A clock

device is used to show limiting % of sand, silt, and clay in a given soil texture. L. S. T.

Etching process for metallographic investigation of alloys of the platinum metals. F. BECK (Metallwirt., 1933, 12, 636—637; Chem. Zentr., 1934, i, 113).—The usual processes have no etching effect on alloys of the systems Re-Pt, Re-Rh, and Re-Ir. Alloys with 50 at.-% Pt, and with $> 50\%$ at.-% Rh or Ir give no useful etching figure with a melt of equal parts of Na_2O_2 and NaOH at 500 — 600° or with $KHSO_4$ at a red heat. Electrolytic etching with Cl at 860° is successful. L. S. T.

Vacuum tap-grease of the piceine type. I. D. GONTCHAROV (Zavod. Lab., 1934, 3, 758).—The grease contains rubber 100, colophony 50, pine pitch 170, and soot 20 parts. R. T.

Simple hair hygrometer. K. V. TSCHMUTOV and A. F. MARKINA (Zavod. Lab., 1934, 3, 757).—Apparatus is described. R. T.

Self-recording coagulometer. S. B. STOKER (J. Sci. Instr., 1934, 11, 315—319).—A wire plunger is dipped into blood at 0.5 min. intervals by a clockwork mechanism, and its movement is recorded by a pointer touching a smoked drum. C. W. G.

Two designs of flow-meter, and a method of calibration. G. BARR (J. Sci. Instr., 1934, 11, 321—324).—(i) Compactness is attained by placing the capillary tube inside one arm of the manometer. (ii) A pulsing meter is described. (iii) The gas passing through is collected in a graduated tube closed by a soap film, which is sufficiently strong and mobile to enable the vol. to be measured at atm. pressure. C. W. G.

Absolute method of determining the co-efficients of viscosity in liquids. A. D. SOKOLSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 341—347).—A twisting wire viscosimeter is described. Measurements for glycerol at 15 — 30° are recorded. H. J. E.

Calibration of Ostwald viscosimeters. C. R. BURY (J.C.S., 1934, 1380—1382).—The disadvantages of earlier methods of testing and calibrating viscosimeters are discussed. In the method proposed, the characteristics of the instrument are calc. from the plot of h' against $1/t$, where the times of flow, t , for a no. of external pressures, h_e , have been determined and $h' = h_e t / (t_0 - t)$; $t - t_0$ when $h_e = 0$. It is essential to calibrate with a range of velocities $>$ that for which the instrument is to be used. J. G. A. G.

Low-temperature semi-micro-still. C. L. BERNIER (Science, 1934, 80, 249). L. S. T.

Apparatus for production of double-distilled water. F. RAPPAPORT (Mikrochem., 1934, 15, 302—304). J. S. A.

Differential pressure control mechanism for vacuum distillation. S. PALKIN and O. A. NELSON (Ind. Eng. Chem. [Anal.], 1934, 6, 386—387).—In the apparatus described, a dual pressure system is maintained with a difference of about 4—30 mm. One vessel is in continuous communication with the distillation system, and the other is in continuous commun-

ation with the pump, but in intermittent communication with the first vessel. E. S. H.

Preventing bumping in vacuum distillations. A. A. MORTON (Ind. Eng. Chem. [Anal.], 1934, 6, 384).—Ground glass is fused into the interior of the flask. E. S. H.

Still head for rapid concentration in a vacuum. H. B. VICKERY and G. W. PUCHER (Ind. Eng. Chem. [Anal.], 1934, 6, 372). E. S. H.

Self-filling pipette for hot caustic solutions. C. J. B. THOR (Ind. Eng. Chem. [Anal.], 1934, 6, 326). E. S. H.

Absorption pipette. E. A. MEANES and E. L. NEWMAN (Ind. Eng. Chem. [Anal.], 1934, 6, 387).—An absorption tube for CO₂ is described. E. S. H.

Agitator for lamp-method sulphur titrations. L. DOLAN (Ind. Eng. Chem. [Anal.], 1934, 6, 388). E. S. H.

Divided titration flask. J. W. YOUNG (Ind. Eng. Chem., 1934, 6, 388).—The reagent is added to the flask through a side tube fitted with a capillary, thus obviating the risk of adding excess. E. S. H.

Modification of Kjeldahl apparatus for nitrogen determination. G. COLOMBO (Boll. Uff. Staz. sperim. Seta, 1933, 3, 85—87; Chem. Zentr., 1934, i, 1083).—The amount of acid needed is reduced by using a flask with a special convex bottom. Aq. NaOH is added, and the NH₃ distilled from the same flask. H. J. E.

Air-damping attachment for analytical balances. F. SARTORIUS (Chem.-Ztg., 1934, 58, 742).—Two hollow Al cylinders are suspended from the pan suspensions. C. W. G.

Apparatus for the titrimetric determination of oxygen and hydrogen sulphide in gases.—See B., 1924, 818.

Use of activated carbon for removing traces of arsenic from pure hydrochloric acid.—See B., 1934, 831.

Magnetic analysis. N. S. AKULOV (Zavod. Lab., 1934, 3, 715—718).—Known methods are described. R. T.

Semi-automatic measurement of liquids in the laboratory. E. BUTTGEBACH (Chem.-Ztg., 1934, 58, 833).—A tap-funnel is filled through the top by gravity from a reservoir; the whole apparatus is a closed system except for the air inlet to the reservoir, and an exit in the top of the funnel which is a capillary tube, the height and diameter of which determine the vol. of liquid delivered when the tap of the funnel is opened. J. G.

Determination of the volume of solids.—See B., 1934, 911.

Absorption of nitrogen oxides. C. TONIOLO and G. GIAMMARCO (Atti Congr. naz. Chim., 1933, 4, 828—843; Chem. Zentr., 1934, i, 1442).—Nomograms are given for determining the time necessary for a given amount of oxidation in the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ in relation to the composition of the initial gas mixture (I), and for the absorption of NO-NO₂ mixtures in HNO₃ in relation to their concn., the composition of (I), and the temp. 10°, 25°, 50°, and 75°. L. S. T.

Positivistic chemistry. M. DELACRE (Bull. Acad. roy. Belg., 1934, [v], 20, 659—673).—Philosophical considerations. N. M. B.

Geochemistry.

Ultra-violet solar spectrum in the stratosphere and vertical distribution of ozone.—See this vol., 1153.

Boron content of natural waters. N. V. TAGEEVA, S. G. TSEITLIN, and A. I. MOROZOVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 360—366).—Analytical data for samples from petroleum (I), salt lakes, and thermal springs are recorded. B is a normal constituent in each case, and may be technically valuable in (I). H. J. E.

Chemical and physical examination of the hot springs of Fordongianus. E. PUXEDDU, A. RATTU, and P. OPPO (Annali Chim. Appl., 1934, 24, 409—426).—The physical properties (temp., *d*, *f.p.*, radioactivity, etc.) and chemical composition of the H₂O are recorded in detail. The H₂O is alkaline (*p_H* 8.01) and contains approx. 0.05% of NaCl and small quantities of the following (in order of decreasing concn.): SO₄²⁻, HCO₃⁻, SiO₂, Ca²⁺, Mg²⁺, CO₂, Li⁺, Fe²⁺, and HPO₄²⁻. D. R. D.

Geochemical distribution of the elements. I. NODDACK and W. NODDACK (Svensk Kem. Tidskr., 1934, 46, 173—201).—A lecture.

Exploration of the mineral world by X-rays. W. L. BRAGG (Nature, 1934, 134, 401—404).—A lecture to the British Association. L. S. T.

Thirteenth list of new mineral names. L. J. SPENCER (Min. Mag., 1934, 23, 624—640).—A dictionary list of 113 names collected from the lit. of the past three years. Chemical formulæ are given for each mineral, and a systematic chemical classification is appended. L. J. S.

Geochemistry and tectonics of the gold quartz veins of the Soviet mine in the North Yeniseysky Taiga. N. N. GORNOSTAEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 376—382). H. J. E.

Presence of rubidium, beryllium, gallium, and strontium in nephelines. J. M. TOLMATSCHEV and A. N. FILIPPOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 366—369).—Spectroscopic analyses for various samples are recorded. The richest contained Ga 0, Be 0.01, and Rb 0.04%. H. J. E.

Beryllium minerals (euclase and phenakite) from Africa. L. J. SPENCER (Min. Mag., 1934, 23, 616—623).—Apart from beryl, there are very few recorded occurrences of Be minerals in the whole

Africa. A large crystal of euclase from the Morogoro district in Tanganyika Territory, and small crystals of phenakite from Klein Spitzkopje in South-West Africa, are described. L. J. S.

Hydrocalumite, a new mineral from Co. Antrim. C. E. TILLEY [with MISS H. D. MEGAW and M. H. HEY] (Min. Mag., 1934, 23, 607—615).—This occurs as small, colourless to pale green, irregular fragments in the larnite-rock of the contact-zone between chalk and dolerite at Scawt Hill. It is pseudo-hexagonal with perfect basal cleavage. Analysis, CaO 41.5, Al_2O_3 18.8, H_2O 38.5, CO_2 1.8, corresponds with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$; d 2.15, n_a 1.535, n_β 1.553, n_γ 1.557. The crystal structure suggests $13\text{H}_2\text{O}$ with 4 mols. in the monoclinic unit cell of dimensions a 9.6, b 11.4, c 16.84 Å., β 69°. L. J. S.

Lusakite, a cobalt-bearing silicate from Northern Rhodesia. A. C. SKERL and F. A. BANNISTER [with A. W. GROVES] (Min. Mag., 1934, 23, 598—606).—This new mineral, a cobaltiferous variety of staurolite, occurs in a quartz-magnetite-kyanite rock about 80 miles E. of Lusaka. It is black in hand specimens, but in micro-section shows a deep cobalt-blue colour with strong pleochroism. Analysis (SiO_2 27.23, TiO_2 0.50, Al_2O_3 50.72, Fe_2O_3 4.96, FeO 3.42, NiO 0.89, CoO 8.48, MnO 0.08, MgO 2.56, H_2O 1.19) corresponds with $\text{H}_2\text{O} \cdot 2(\text{Co}, \text{Ni})\text{O} \cdot \text{FeO} \cdot \text{MgO} \cdot 9(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 8\text{SiO}_2$, analogous to that of staurolite ($\text{H}_2\text{O} \cdot 4\text{FeO} \cdot 9\text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$). The X-ray data are also very near to those for staurolite. The orthorhombic unit cell a 7.86, b 16.62, c 5.65 Å. contains $8[\text{RO} \cdot \text{Al}_2\text{SiO}_5]$. Hardness 7½, d 3.767, n about 1.74. The mineral is only slightly attacked by $\text{HF} + \text{H}_2\text{SO}_4$, and only slowly by fused Na_2CO_3 . L. J. S.

Crystal structure and optical properties of matlockite. F. A. BANNISTER [with M. H. HEY] (Min. Mag., 1934, 23, 587—597).—The conclusion of Nieuwenkamp (this vol., 54) that matlockite is PbFCl , and not Pb_2OCl_2 as long supposed, is confirmed and a complete analysis (Pb 79.55, F 7.11, Cl 13.44%) is given of the mineral, d 7.05, ω_{Na} 2.145, ϵ_{Na} 2.006. The unit cell, a 4.09, c 7.21 Å., contains 2 mols., and the structure is the same as for BiOCl . L. J. S.

Form relations of the lead oxychlorides, laurionite, paralaurionite, and fiedlerite. C. PALACHE (Min. Mag., 1934, 23, 573—586).—Detailed crystallographic descriptions are given. The dimorphism of $\text{PbCl}_2 \cdot \text{Pb}(\text{OH})_2$, as orthorhombic laurionite and monoclinic paralaurionite, is confirmed. Fiedlerite, $2\text{PbCl}_2 \cdot \text{Pb}(\text{OH})_2$, is monoclinic. L. J. S.

Geochemistry of titanium and vanadium in Western Siberia. The Azhinsk Gabbro complex of Oirotia. P. I. LEBEDEV and A. P. LEBEDEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 294—300).—The associated minerals described contain 0.2—0.6% MnO . The pyroxenite ores (TiO_2 4, V_2O_5 0.1%) contain approx. 42% of Ti-augite, and the associated ilmenite gabbro (I), constituting 7% of the minerals, contains approx. TiO_2 5%, V_2O_5 0.1%. Separation of (I) affords a Ti-augite with 9% TiO_2 and a magnetic fraction containing 21% TiO_2 and 0.42% V_2O_5 , showing that V enters almost wholly into the ilmenite mol. J. G. A. G.

Composition of black concretions in Onondaga limestone. F. W. SCHWARTZ and R. L. MATHIASSEN (Science, 1934, 80, 232).—Analyses are recorded. The black colour of the black limestone is due to finely-divided C. L. S. T.

Minerals. G. CESARO (Bull. Acad. roy. Belg., 1934, [v], 20, 674—685).—The following new faces, with data, are reported: (145) in pyrites, (421) in aragonite, cubic faces in melanite, and (17.1.17) in barytine. Analyses are given and formulae proposed for bityite and palmyerite. N. M. B.

Zeolites. J. WYART (Bull. Soc. franç. Min., 1933, 56, 81—187; Chem. Zentr., 1934, i, 681—682).—Chabazite has a rhombohedral lattice (a 13.75, c 14.95 Å.; space-group D_{3d}^5). The unit cell always contains 24 O atoms, but the no. of electropositive atoms is variable; 1 mol. of $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$ is generally present, but partial replacements of SiNa for AlCa or Na_2 for Ca or AlNa_3 for SiCa can occur. The arrangement of the atoms and the dehydration curve are discussed. Dehydration has also been followed by means of X-rays. Thermal analysis shows that 6 mols. of H_2O are removed at 120°, the more strongly combined mols. at 300°, and at 700° the zeolitic character is lost. 1 mol. of H_2O can be replaced by 1 atom of Hg. Heulandite is monoclinic (a 7.45, b 17.80, c 15.85 Å.; space-group C_{2h}^3). It always contains 36 O atoms and 2 mols. of $\text{CaAl}_2\text{Si}_2\text{O}_{18} \cdot 6\text{H}_2\text{O}$ in the unit cell; isomorphous replacements are Al_2Ca for Si_2 , AlNa for Si, AlNa_3 for SiCa, and Na_2 for Ca. Dehydration data are given and the X-radiograms at 210°, where 7 mols. of H_2O per cell are lost, and of the original material are the same. β -Heulandite has a 7.26, b 16.60, c 15.20 Å. Thomsonite is orthorhombic with a 13.02±0.05, b 13.14±0.05, c 13.22±0.05 Å.; the unit cell contains 1 mol. of $\text{Ca}_{10}\text{Al}_{20}\text{Si}_{20}\text{O}_{80} \cdot 24\text{H}_2\text{O}$ with the replacements SiNa for AlCa and Na_2 for Ca; probable space-group C_{2v}^{10} . Mesotype, orthorhombic, has a 18.25±0.05, b 18.50±0.05, c 6.57±0.02 Å.; space-group C_{2v}^{19} . The unit cell contains 2 mols. of $\text{Na}_4\text{Al}_4\text{Si}_6\text{O}_{20} \cdot 4\text{H}_2\text{O}$, where K_2O and CaO can replace Na_2O . Skolezite, monoclinic, has a 18.44, b 18.90, c 6.53 Å. The unit cell contains 1 mol. of $\text{Ca}_4\text{Al}_8\text{Si}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O}$ with the replacement of Na_2 for Ca. L. S. T.

Thermo-luminescent feldspars occurring in the vicinity of Naegi. S. IMORI, J. YOSHIMURA, and S. HATA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1091—1093).—These feldspars, found as constituents of pegmatite in certain localities, are all microcline perthites, containing Fe_2O_3 0.11—0.25, CaO 0.10—0.26, MgO 0.07—0.90, rare earths 0.01—0.05%, and a trace of Mn as minor constituents. On heating they exhibit an intense thermo-luminescence nearly comparable with that of fluorites. No change could be observed in either perthitic or characteristic microcline structure of the crystal after removal of this property by heating. J. W. S.

Acid clay derived from perthite. S. IMORI, J. YOSHIMURA, and S. HATA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1094—1097; cf. preceding abstract).—A clay from the same district as, and probably derived from the weathering of, the thermo-luminescent feldspar has a mol. $\text{SiO}_2 : \text{Al}_2\text{O}_3$ ratio 7.8, and also contains

0.037% of rare earths, which are readily extracted by warming with dil. HCl. J. W. S.

Constancy of the protoactinium-uranium ratio in radioactive minerals. CHENG DA-CHANG (Ann. Chim., 1934, [xi], 2, 186—223).—Fusion and dissolution methods, with the help of Ta_2O_5 , for the quant. extraction of Pa are described. Five minerals were analysed, and the ratio constancy, irrespective of the age of the mineral, is established. By fusion with $KHSO_4$ in presence of Ta_2O_5 , followed by hydrolysis, the Pa is completely pptd. with the Ta_2O_5 , and is easily sol. in dil. HF, from which pptn. by aq. NH_3 is incomplete. From other mineral acids pptn. by aq. NH_3 is quant. Pa on Ta_2O_5 is insol. in aqua regia. The HF solution can be evaporated to dryness and heated without loss only in presence of H_2SO_4 . From the HF- H_2SO_4 solution, Ba, Th, and Se can be pptd. without bringing down the Pa. N. M. B.

Geochemistry of helium. V. G. CHLOPIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 369—376).—The quantities of He in natural gas are consistent with a radioactive origin, its liberation from rocks being facilitated by hydrocarbons. H. J. E.

Origin of asphalts, oil, natural gas, and bituminous coal. E. BERL (Science, 1934, 80, 227—228).—A discussion. L. S. T.

Development of heavy clay pans in soils. G. D. SMITH (Missouri Agric. Exp. Sta. Res. Bull., 1934, No. 210, 31 pp.).—Clay suspensions pass through sand beds without pan formation (I) unless flocculated by electrolytes or oppositely-charged colloids. Rates of (I) increase with the valency of the flocculating ion.

Humus retards pan formation only to the extent that it retards flocculation. Building up of alternate layers of positive Fe sols and negative clay sols around the soil grains may lead to (I). A. G. P.

Soil profile studies. VI. Distribution of titanium in soils with special reference to podzols. J. S. JOFFE and A. J. PUGH (Soil Sci., 1934, 38, 245—257; cf. B., 1933, 482).—The distribution of TiO_2 in soils resembles that of the sesquioxides. In laterites TiO_2 accumulates in the surface horizon and in podzols in the B- and A_2 -horizons. Data from numerous profiles are examined in relation to the isoelectric pptn. of TiO_2 , and to the general classification of soil types. A. G. P.

Ironstone soils of north Auckland. L. I. GRANGE (New Zealand J. Sci. Tech., 1934, 16, 9—18).—The soils described have $SiO_2 : Al_2O_3$ ratio 0.7—1.9 and profiles resemble those of laterites. Active (toxic) Al occurs and Fe and Ti compounds present are such as to render small dressings of PO_4''' inoperative. A. G. P.

Soil formation and soil series in Switzerland. H. PALLMANN (Ernähr. Pflanze, 1934, 30, 225—234).—The weathering process is discussed and typical soil profiles are described. A. G. P.

Weathering and soil formation in extreme climates. E. BLANCK (Ernähr. Pflanze, 1934, 30, 234—237).—In both frigid and torrid zones, weathering by chemical action is very pronounced. The hydrolytic action of H_2O is more intense with high temp. and low rainfall than under arctic conditions where liberal supplies of H_2O occur intermittently. A. G. P.

Organic Chemistry.

Determination of the activity of hydrogen of organic compounds by measurement of the e.m.f. of their reaction with sodium. B. V. TRONOV and L. P. KULEV (J. Gen. Chem. Russ., 1934, 4, 197—202).—The activity (I) of H atoms of org. compounds \propto the e.m.f. obtained on immersing Pt and Na electrodes in the compound or in its C_6H_6 solution. The (I) of the OH group of alcohols diminishes periodically with increasing mol. wt.; the vals. of (I) for *n*-, *sec*-, and *tert*-alcohols are as 20—30 : 5—7 : 1. For ω -Ph-substituted alcohols, (I) is considerably < for purely aliphatic alcohols, but similarly diminishes with increasing length of side-chain. (I) is greater for unsaturated than for saturated alcohols; in the latter case, ring-closure does not affect (I). The (I) of phenols differs little from that of the *n*-alcohols with the same no. of C atoms. The (I) of cresols increases in the order *o*-<*p*-<*m*-cresol. No regular relationships were found between the (I) of aldehydes and ketones and their structure; thus for $PrOH$ (I) is 0.005 that of $EtCHO$, for CH_2Ph-OH (I) is $\frac{1}{2}$ that of $PhCHO$, and for *cyclohexanol* (I) is $\frac{1}{3}$ that of *cyclohexanone*, whilst Pr^sOH and $COMe_2$ have equal (I). Only aromatic amines possess active H atoms in C_6H_6 solution. For NO_2 -derivatives (I) is > for amines. Nitriles give a very

high e.m.f., due not to replacement of H, but to combination of Na with the N atom. R. T.

Deuterium content of natural butane. R. D. SNOW and H. L. JOHNSTON (Science, 1934, 80, 210—211).—Natural C_4H_{10} from the Burbank, Oklahoma, oil field contains approx. 30% more H_2^3 than corresponds with the H_2^3 content of ordinary H_2 . L. S. T.

[Preparation of ethylene.] P. K. SAKMIN (Ber., 1934, 67, [B], 1605; cf. this vol. 508).—A reply to Ipatiev (this vol., 864). H. W.

Reaction of propylene and Δ^{α} - and Δ^{β} -pentenes with sulphuric acid. B. T. BROOKS (J. Amer. Chem. Soc., 1934, 56, 1998—2000).— Pr^sOH and <0.2% of δ -methylpentan- β -ol (formed from δ -methyl- Δ^{α} -pentene, which arises by polymerisation of C_3H_6) are obtained from C_3H_6 and 90—92% in presence of a solvent (oil) and subsequent steam-distillation; Pr^sOH is not produced. Δ^{α} -Pentene and 85% H_2SO_4 containing H_2O_2 (1%) and Bz_2O_2 give (after hydrolysis) pentan- β -ol (I). Δ^{β} -Pentene and 80% H_2SO_4 afford a mixture of (I) (about 10%) and pentan- γ -ol (about 30%).

Polymerisation under high pressure. H. W. STARKWEATHER (J. Amer. Chem. Soc., 1934, 56, 1998—2000).

1870—1874).—A large no. of org. compounds have been polymerised, using pressures up to 900 atm. With one exception in each case, all the compounds containing conjugated double linkings underwent polymerisation under pressure, and all those containing adjacent double linkings, but no conjugated double linkings, were unchanged by pressure.

E. S. H.

Action of carbonyl chloride on α -monochlorohydrin. A. CONTARDI and A. ERCOLI (Gazzetta, 1934, 64, 522—526).—Glycerol or $\alpha\gamma$ -dichlorohydrin is inert towards COCl_2 at room temp., but α -monochlorohydrin reacts to give a product from which are separated α -monochlorohydrin carbonate, b.p. 156—157°/10—12 mm., and a fraction b.p. 130—156°/10 mm., containing γ -chloropropane- $\alpha\beta$ -diol dichloroformate, converted by aq. NH_3 into the dicarbamate, m.p. 157—157.5°.

R. K. C.

Catalytic syntheses with carbon monoxide and hydrogen under pressure. R. TAYLOR (J.C.S., 1934, 1429—1431).—Mn—Cr—Rb gives a large amount, Mn—Cu—CoS (I) < 10%, of branched chain alcohols, whilst Zn—Mn—K—Co gives an intermediate amount. Of the catalysts tried (I) at 400°/200 atm. gave the max. yield of EtOH (22%) with MeOH (17), higher alcohols (11), and CH_4 (47%).

R. S. C.

Decomposition of ethyl alcohol over some polycomponent catalysts. E. H. BOOMER and H. E. MORRIS (Canad. J. Res., 1934, 10, 743—758; cf. A., 1930, 1268; 1932, 819).—Data have been obtained of the gaseous and liquid products formed in the decomp. of EtOH, EtOH and H_2O , and EtOH and CO_2 over numerous polycomponent catalysts at temp. up to 500°. Of the gases CH_4 , C_2H_6 , and CO_2 , which have been chiefly studied, CH_4 can be produced by decomp. of MeCHO or C_2H_4 and the hydrogenation of CO and CO_2 , and C_2H_6 by the autoxidation and reduction of EtOH or the secondary hydrogenation of C_2H_4 . CO_2 is formed in most cases as a result of the water-gas reaction and the decomp. of CO.

H. S. P.

Action of ethylene oxide on acetylenic magnesium compounds; preparation of substituted δ -hydroxy- Δ^2 -butinenes. L. FAUCONNAU (Compt. rend., 1934, 199, 605—607; cf. A., 1903, i, 552).— $\text{CR}:\text{CH}$ (Mg derivative) (1 mol.) with $(\text{CH}_2)_2\text{O}$ (1.5 mol.) in dry Et_2O at room temp. affords the following: δ -hydroxy- α -amyl-, b.p. 103—130.5°/19 mm., α -hexyl-, b.p. 130—131°/22 mm., and α -phenyl- Δ^2 -butinene, b.p. 147°/16 mm. (phenylurethane, m.p. 88°; Bz derivative, m.p. 41°; is converted by SOCl_2 into a Cl-compound, b.p. 134—135°/22 mm.; Br_2 -derivative, m.p. 78°). The Raman spectra show a line between 2200 and 2300 cm^{-1} in each case (cf. A., 1933, 553).

J. L. D.

Pinacol-pinacolone molecular rearrangement. J. STIEGLITZ, R. B. COOPER, and G. W. AYERS, jun. (Trans. Illinois State Acad. Sci., 1933, 25, 173). The instability of the mol. leading to rearrangement is attributed to electronic strain in the group of the pinacol containing the two partly oxidised C atoms. Acids form oxonium salts with pinacols, which on dehydration leaves a + charge on one C atom; a Me then

moves to this position. This view is supported by velocity measurements.

CH. ABS.

Mannitol. III. Anhydrides of mannitol. P. BRIGL and H. GRUNER (Ber., 1934, 67, [B], 1572—1589; cf. this vol., 169).—The loss of H_2O from mannitol $\alpha\zeta$ -dibenzoate in boiling $\text{C}_2\text{H}_2\text{Cl}_4$ is greatly influenced by unknown catalysts present in very varying amount in the technical product. Uniform results are obtained by use of $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, whereas HCl is without influence. The dianhydride (I) and monoanhydride A (II) are thus obtained, whilst, particularly in the absence of powerful catalysts, a monoanhydride B (III), m.p. 141—142°, $[\alpha]_D -10.4^\circ$ in $\text{C}_5\text{H}_5\text{N}$, is also prepared. (I) is $\beta\delta\gamma\epsilon$ -dianhydromannitol $\alpha\zeta$ -dibenzoate (IV), since it is hydrolysed by cold $\text{NH}_3\text{-MeOH}$ to non-cryst. $\beta\delta\gamma\epsilon$ -dianhydromannitol [from which (IV) is regenerated by BzCl in $\text{C}_6\text{H}_5\text{N}$], which yields $\beta\delta\gamma\epsilon$ -dianhydromannitol $\alpha\zeta$ -di-*p*-toluenesulphonate, m.p. 89—90°, $[\alpha]_D +98.5^\circ$ in CHCl_3 , in which the position of the acyl groups is established by the formation of $\alpha\zeta$ -di-iodo- $\beta\delta\gamma\epsilon$ -dianhydromannitol, m.p. 69—70°, $[\alpha]_D +101.4^\circ$ in CHCl_3 . The absence of an ethylene oxide ring in (IV) has been demonstrated previously. (II) is $\beta\epsilon$ -anhydromannitol $\alpha\zeta$ -dibenzoate, since it is oxidised by KMnO_4 in COMe_2 to $\text{OBz}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ and non-cryst. $\alpha\alpha'$ -oxido- $\beta\beta'$ -dibenzyloxydipropionic acid $[\text{OBz}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})]_2\text{O}$ [Cu (+ H_2O) and Ag salts; anhydride, m.p. 131—132°]. The failure of (II) to react with $\text{Pb}(\text{OAc})_4$ is due to the *trans*-position of the OH groups. (III) is $\beta\delta$ -anhydromannitol $\alpha\zeta$ -dibenzoate, since it is converted by PhCHO and anhyd. ZnCl_2 into $\gamma\epsilon$ -benzylidene- $\beta\delta$ -anhydromannitol $\alpha\zeta$ -dibenzoate, m.p. 162°, $[\alpha]_D +33.6^\circ$ in CHCl_3 , does not react with COMe_2 and anhyd. CuSO_4 , and, with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$ in boiling $\text{C}_2\text{H}_2\text{Cl}_4$, affords (I). Hydrolysis of (I) with $\text{Ba}(\text{OH})_2\text{-MeOH}$ leads to $\beta\delta$ -anhydromannitol, m.p. 146°, $[\alpha]_D -24.2^\circ$ in H_2O , transformed by short benzylation into (III). More drastic treatment results in $\beta\delta$ -anhydromannitol $\alpha\zeta$ -tribenzoate, m.p. 128°, $[\alpha]_D -61.7^\circ$ in CHCl_3 , also obtained from mannitol $\alpha\zeta$ -tribenzoate in boiling $\text{C}_2\text{H}_2\text{Cl}_4$ containing $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$. (III) yields an *Ac* derivative, m.p. 89°, $[\alpha]_D -49.5^\circ$ in CHCl_3 .

H. W.

Production of diisopropyl ether from isopropyl alcohol. A. N. BRIK (Trans. Centr. Inst. Sci. Res. Forest Chem., U.S.S.R., 1933, 1, 148—161).— Pr^iOH (100 pts.) and 100% H_2SO_4 (37.5 pts.) gave Pr^i_2O in 43.5% yield. Complete separation from the distillation product was effected by washing thrice with 2 vols. of H_2O .

CH. ABS.

Magnesium tribromoethyl sulphate. E. MONESS and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 904—906).—The salt $(\text{CBr}_3\cdot\text{CH}_2\cdot\text{SO}_4)_2\text{Mg}$, obtained by treatment of $\text{CBr}_3\cdot\text{CH}_2\cdot\text{OH}$ (I) with fuming cold H_2SO_4 followed by MgSO_4 , is H_2O - and EtOH-sol., but is only $\frac{1}{3}$ as active as (I) as a rectal anaesthetic.

C. G. A.

Reactivity of the thiol group.—See this vol., 1073.

Selenium derivatives. I, II. R. POGGI and G. SPERONI. III. G. SPERONI and G. MANNELLI (Gazzetta, 1934, 64, 497—500, 501—505, 506—

509).—I. $\beta\beta'$ -Dihydroxydiethyl selenide is prepared by interaction of $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$ and Na_2Se . Treatment with conc. HCl yields the Cl_2 -compound; attempts to employ PCl_3 were unsuccessful.

II. Interaction of Se in Na_2S_2 and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CH}_2\text{Cl}$ yields *di-p-chlorobenzyl diselenide* (I), m.p. $76.5\text{--}77^\circ$. Treatment with NaOEt and CH_3PhCl successively yields *benzyl p-chlorobenzyl selenide*, an oil. *Di-p-bromobenzyl diselenide* (II), m.p. $101.5\text{--}102.5^\circ$, *di-p-bromobenzyl selenide* (III), m.p. 54° , and *di-p-chlorobenzyl selenide* (IV), m.p. 57.5° , are obtained similarly. Oxidation of (I) and (II) by conc. HNO_3 yields, respectively, *p-chlorobenzyl-*, m.p. 120.5° (decomp.), and *p-bromobenzyl-*, m.p. 128.5° (decomp.), *-selenious acid*. Attempts to prepare (III) and (IV) from the benzyl chlorides and Na_2Se gave mixtures of selenides and diselenides.

III. *Di-p-nitrobenzyl diselenide* (I), m.p. 107.5° , is oxidised to *p-nitrobenzylselenious acid*, m.p. 132° (decomp.). *Di-p-nitrobenzyl selenide*, m.p. 146° , is not obtainable from (I) by the usual method, but is prepared by interaction of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Cl}$ with Na_2Se in hot COMe_2 . R. K. C.

Electronic versus ionic mechanisms for intramolecular rearrangements. F. C. WHITMORE and G. H. FLEMING (J.C.S., 1934, 1269).—*tert.*-Amyl acetate and mainly $\text{CHMe}\cdot\text{CMe}_2$ are produced by heating AgOAc with $\text{CH}_2\text{Bu}^t\text{I}$ in conductivity AcOH at 60° for 36 hr. The absence of $\text{CH}_2\text{Bu}^t\text{OAc}$ from the products shows that the C atom of the transient CH_2Bu^t radical does not complete its octet by union with OAc , but by (i) intramol. transfer of electrons and Me to constitute *tert.*-amyl, which unites with OAc , and (ii) intramol. transfer of an electron pair affording a proton, $\text{CHMe}\cdot\text{CMe}_2$, and β -methyl- Δ^2 -butene.

J. G. A. G.

Interaction of carbon monoxide and alcohols.

I. **Synthesis of acetic acid.** D. V. N. HARDY (J.C.S., 1934, 1335—1340).—Thermal considerations indicate that formation of AcOH from MeOH and CO is feasible. At $320\text{--}340^\circ/150$ atm. in presence of H_3PO_4 there are obtained a pale yellow oil (I) (7%), AcOH (1%), MeOAc (7%), Me_2O (5%), MeOH (34%), and H_2O . (I), b.p. $< 240^\circ$ (C 87.8 ; H 10.4%), contains C_6Me_8 . Addition of $\text{Cu}_3(\text{PO}_4)_2$ (2% or more) prevents formation of (I) and gives AcOH 5.8, MeOAc 13.5, Me_2O 1.3, and MeOH 33%. Reaction probably proceeds thus: (a) $2\text{MeOH} \rightarrow \text{Me}_2\text{O} \rightarrow 2\text{CH}_2\cdot$, (b) $\text{CH}_2\cdot + \text{CO} \rightarrow \text{CH}_2\cdot\text{CO}$, (c) $\text{CH}_2\cdot\text{CO} + \text{H}_2\text{O} \rightarrow \text{AcOH}$, (d) $\text{CH}_2\cdot\text{CO} + \text{MeOH} \rightarrow \text{MeOAc}$. If (I) is formed from $\text{CH}_2\cdot$, the assumption that Cu catalyses reaction (b) explains the above results. Systematic variation of the conditions shows that conversion of MeOH into AcOH is favoured by increase in pressure, rate of gas circulation, and amount of catalyst. Using the optimum conditions for the apparatus (described), viz., $330^\circ/200$ atm., 700 g. of 87% H_3PO_4 and 14 g. of $\text{Cu}_3(\text{PO}_4)_2$, 40 litres of compressed gas circulated per hr., utilisation of MeOH in 14 hr. was: AcOH 44.9, Me_2O 9.5, C 4.8, unchanged 35.8, loss 5.0%, 1.6 kg. of AcOH being collected in this time. The reaction certainly proceeds by way of Me_2O , since the amount of the latter decreases and that of AcOH increases with time. R. S. C.

Reactions with liquefied hydrogen chloride. E. GEBAUER-FUELNEGG and E. MOFFETT (J. Amer. Chem. Soc., 1934, 56, 2009).—Vinyl acetate and liquid HCl (I) at atm. pressure give 50—70% of α -chloroethyl acetate; allyl alcohol affords diallyl ether; MeCHO yields $\alpha\alpha'$ -dichloroethyl ether (70% yield); $(\text{CH}_2)_2\text{O}$ furnishes $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{OH}$; $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ does not react. Pr^tOAc (1 mol.) and Bu^tOH (1 mol.) with (I) give some Pr^tOH and Bu^tOAc . H. B.

isoValeric acid. G. A. KIRKHOFF, O. I. KORZINA, and R. Y. ASTROVA (Khim. Farm. Prom., 1933, 279—280).—*iso*- $\text{C}_5\text{H}_{11}\cdot\text{OH}$ (I) is oxidised with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 at $25\text{--}30^\circ$; after 1 hr. the mixture is steamed to separate (I) from the aq. layer, which contains 1% of *isovaleric acid*. The operation is repeated, the esterified acid being hydrolysed and fractionated. CH. ABS.

Addition of hydrogen bromide to double linkings. Ethyl undecenoate, undecenol, and undecenyl acetate. R. ASHTON and J. C. SMITH (J.C.S., 1934, 1308—1310).— κ -Bromoundecenoic acid (modified prep.), m.p. 51° (52° , if rapidly heated; softens at 49.5°) when pure, with NaI in hot COMe , gives κ -iodoundecenoic acid, m.p. 66° [f.p. and m.p. 65.6° (Beckmann)]. The ι -Br-acid with $\text{KOAc}\cdot\text{AcOH}$ and subsequent hydrolysis gives the ι -OH-acid, m.p. $49\text{--}49.5^\circ$ (softens at 47°), metastable form, m.p. about 34° . Et undecenoate in C_6H_6 or ligroin in air with a peroxide catalyst (I) and HBr gives Et κ -bromoundecenoate, but with H_2 and NHPh_2 in both solvents gives the ι -Br-ester. Undecenol gives only the ι -Br-alcohol under all conditions, but the acetate gives the κ -Br-ester if air and (I) are present. $\alpha\lambda$ -Dibromoundecane (from the glycol and dry HBr) yields $\alpha\lambda$ -di-iodoundecane, m.p. 31° (lit. an oil). R. S. C.

Tuberculostearic acid.—See this vol., 1141.

[Chlorinated fatty acid soap.] T. MAZUME and K. KINO (J. Soc. Chem. Ind. Japan, 1934, 37, 539B; cf. Tanaka *et al.*, this vol., 847).—A chlorinated fatty acid and alkali may give an unsaturated and not a OH-acid. R. S. C.

[Chlorinated fatty acid soap.] R. KOBAYASHI (J. Soc. Chem. Ind. Japan, 1934, 37, 540B).—The contention (preceding abstract) may be correct, but calculation of k is still justified if dehydration is much faster than replacement of Cl by H. R. S. C.

Autoxidation of linolenic acid and its esters. S. GOLDSCHMIDT and K. FREUDENBERG (Ber., 1934, 67, [B], 1589—1594).—Agitation of linolenic acid (I) or its Me ester (II) at room temp. with O_2 in presence of a Co catalyst with periodic determinations of O absorbed and I val. (Wijs) prove that a double linking disappears for each mol. of O_2 . Simultaneous polymerisation of (I) or (II) does not therefore occur, and enlargement of the mol. of (I) can take place only by the union of several mols. through $\cdot\text{O}\cdot\text{O}\cdot$. Autoxidation of (II) is not accompanied by the development of acidic groups, and Zerevitinov's method gives no indication of the formation of OH, so that the main products of autoxidation appear to be peroxides formed directly. This view is confirmed by deter-

mination of I liberated by the action of HI in warm AcOH, addition of halogen occurring so slowly under these conditions that it can be neglected. Since the peroxide val. remains const. during many days, the peroxides are very stable. After addition of about 2O₂ to 1 mol of (I) free (I) is no longer present; otherwise there is no simple relationship between absorption of O₂ and disappearance of (I). H. W.

Crystalline derivatives of oleic and elaidic acid dibromide. Synthesis of dibromo-derivatives of *p*-substituted phenacyl esters of oleic and elaidic acids. W. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 474B; cf. this vol., 639).—Bromination of *p*-substituted phenacyl esters of oleic and elaidic acids or esterification of the dibromides of oleic and elaidic acids with *p*-substituted ω -bromoacetophenones gives *p*-phenyl-, m.p. 53.5°, and *p*-bromo-, and *p*-chloro-phenacyl oleo- θ -dibromostearate, *p*-phenyl-, m.p. 74°, and *p*-iodo-, m.p. 74°, *p*-bromo-, m.p. 58°, and *p*-chloro-phenacyl elaido- θ -dibromostearate, m.p. 47°. F. S. H. H.

p-Substituted phenacyl esters of acetylenic acids of the stearolic acid series. W. KIMURA (J. Soc. Chem. Ind. Japan, 1934, 37, 476B).—Treatment of θ -dibromostearic, $\mu\nu$ -dibromobehenic, and $\kappa\lambda$ -dibromobehenic acid, m.p. 42°, with NaOH or KOH in BuOH or amyl alcohol at 120–125° gives stearolic acid, m.p. 48.5°, behenolic acid, m.p. 59.5°, and cet-stearolic acid, m.p. 59°, respectively. The following are described: *p*-chloro-, m.p. 48.5°, *p*-bromo-, m.p. 57°, *p*-iodo-, m.p. 69°, and *p*-phenyl-phenacyl stearolate, m.p. 58.5°; *p*-chloro-, m.p. 61.5°, *p*-bromo-, m.p. 66.5°, *p*-iodo-, m.p. 77°, and *p*-phenyl-phenacyl behenolate, m.p. 69.5°; *p*-chloro-, m.p. 61.5°, and *p*-phenyl-phenacyl cetstearolate, m.p. 68°. F. S. H. H.

Polymerisation of methyl esters of higher unsaturated fatty acids. XIV. Structure of the intramolecular reaction products of methyl clupanodionate. K. KINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 218–225).—The intramol. reaction product (I) (cf. A., 1933, 807) affords with O₃ a monocarboxylic acid, succinic acid, C₁₀H₁₇·CO₂H, C₉H₁₄(CO₂H)₂, and [C₈H₁₁(CO₂H)]₂ (?). Clupanodonic acid with BuOH containing HCl at 100° gives the Bu ester, b.p. 230–246°/7 mm., which is rearranged by H₂ during 0.5 hr. at 290–300°. The product affords CO₂H·C₈H₁₄·CO₂Bu with O₃, which orients the ester grouping with respect to one double linking. The other products of ozonisation of (I) are explained by the new formula for Me clupanodionate which is proposed. J. L. D.

Negative catalysts of hydrogenation of oil. X. Inhibiting influence of dyes at a lower temperature. S. UENO (J. Soc. Chem. Ind. Japan, 1934, 37, 497B–505B; cf. B., 1932, 313).—Inhibition of hydrogenation (Ni) of soya-bean oil by dyes (1%) is less at a low than at high temp. Basic and S dyes are most effective. NH₂- or NO₂-groups, but not both together, confer anticatalytic properties. R. S. C.

Preparation of ethyl lactate. G. A. KIRKGOFF and K. I. ZNAEVA (Khim. Farm. Prom., 1933, 280–281).—Ca lactate (308 g.) is dissolved in hot H₂O

(600 c.c.); CuSO₄ (250 g.) in boiling H₂O (300 c.c.) is added, and the Cu lactate (I) collected and crystallised. (I) (556 g.) is heated with 96% EtOH (360 g.) and 27% oleum (1.84 g.) for 6–8 hr., the CuSO₄ filtered off, and the solution fractionated at 40 mm. Yield 64%. CH. ABS.

Polymembered heterocyclic compounds. IV. Approximately quantitative lactonisation of ν -hydroxytetradecane- and ω -hydroxypentadecane-carboxylic acid. M. STOLL and A. ROUVE. V. Ring closure during the formation of polymembered lactones. M. STOLL, A. ROUVE, and G. STOLL-COMTE (Helv. Chim. Acta, 1934, 17, 1283–1288, 1289–1308).—IV. Gradual addition of a solution of ω -hydroxypentadecanecarboxylic acid (I) in C₆H₆ to a boiling solution of PhSO₃H in C₆H₆ in such a manner that the concn. of (I) in the mixture is always very low gives the corresponding lactone in 74% yield with a small amount of dimeric lactone, m.p. 108–109°. ν -Hydroxytetradecanecarboxylolactone, b.p. 111–112°/0.06 mm., m.p. 30–31°, is similarly obtained in 87% yield.

V. Examination of the kinetics of the lactonisation of ν -hydroxytetradecanecarboxylic acid in C₆H₆ in presence of PhSO₃H shows that the degree of cyclisation (relationship of the unimol. to the polymeric cyclic compounds) directly \propto the cyclisation const. and inversely \propto the concn. The cyclisation const. (relationship of the const. of uni- and bi-mol. reaction) is a measure of the ease of ring formation under definite conditions. The rate of cyclisation is inversely \propto the degree of cyclisation. The measured reaction const. cannot be "pure," and may only be used with caution for calculating the Arrhenius const. Nevertheless, it is established that the no. of mols. in the ring position in C₆H₆ is about 100 times as great with the heterocyclic 6-ring as with the corresponding 16-ring. The reaction consts. alone are useless for the determination of degree of cyclisation. Under identical conditions ring closure occurs at least 46 times as rapidly with the 16-ring as with the 12-ring. H. W.

isoButyrylformic acid phenylhydrazone. L. C. CRAIG (J. Amer. Chem. Soc., 1934, 56, 2008–2009).—The phenylhydrazone of Pr^oCO·CO₂H [prepared essentially by Tschelinev and Schmidt's method (A., 1929, 1272)] has m.p. 152° (lit. 128° and 143°) (cf. this vol., 538). H. B.

Compounds of bivalent carbon. VIII. Derivatives of diethoxyacetic acid and their adaptability to carbon monoxide-acetal fission. H. SCHEIBLER, W. BEISER, H. COBLER, and A. SCHMIDT (Ber., 1934, 67, [B], 1507–1514; cf. A., 1933, 491).—Diethoxyacetic dimethylamide, b.p. 105°/12 mm., obtained in 50.5% yield by heating (OEt)₂CH·CO₂Et with anhyd. NHMe₂ at 100° in presence of CaCl₂, and converted by NMe₂·MgBr and subsequent distillation under diminished pressure into a substance, m.p. 134°, which does not contain OEt, gives NH₃ when heated with NaOH, and is therefore probably glyoxylamide trihydrate; this conception is supported by the detection of Et₂O in the distillate. Diethoxyacetic dibenzylamide, b.p. 168–170°/1 mm., could not be prepared

similarly, but is obtained from $(\text{OEt})_2\text{CH}\cdot\text{CO}_2\text{Et}$ and $\text{MgBr}\cdot\text{N}(\text{CH}_2\text{Ph})_2$. It is transformed by $\text{MgBr}\cdot\text{N}(\text{CH}_2\text{Ph})_2$ and subsequent distillation into $\text{NH}_2\cdot\text{CH}_2\text{Ph}$ and $\text{N}(\text{CH}_2\text{Ph})_3$. *Ph diethoxyacetate*, b.p. 150—152°/13 mm., cannot readily be purified when made by the successive action of SOCl_2 and PhOH on $(\text{OEt})_2\text{CH}\cdot\text{CO}_2\text{H}$ in $\text{Et}_2\text{O}-\text{C}_5\text{H}_5\text{N}$, but is obtained in 61.1% yield from ClSO_2Ph and the acid in $\text{Et}_2\text{O}-\text{C}_5\text{H}_5\text{N}$: $(\text{OEt})_2\text{CH}\cdot\text{CO}_2\text{H} + \text{ClSO}_2\text{Ph} + \text{C}_5\text{H}_5\text{N} \rightarrow (\text{OEt})_2\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{SO}_2\text{Ph} + \text{C}_5\text{H}_5\text{N}\cdot\text{HCl}$ and $(\text{OEt})_2\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{SO}_2\text{Ph} \rightarrow \text{SO}_2 + (\text{OEt})_2\text{CH}\cdot\text{CO}_2\text{Ph}$. It is transformed by $\text{Net}_2\cdot\text{MgBr}$ mainly into a non-volatile mass, probably formed by union of PhOH with a polymerisation product of $\text{C}(\text{OEt})_2$; in the volatile portion of the product, which consists chiefly of NHEt_2 , monomeric $\text{C}(\text{OEt})_2$ is detected by the production of HCO_2H during hydrolysis. $(\text{OEt})_2\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ and P_4O_{10} in quinoline afford *diethoxyacetoneitrile*, b.p. 55—56°/12 mm., which gives AgCN when acted on by Ag_2O and evolves NH_3 when treated with NaNH_2 in Et_2O . H. W.

Reduction of ethyl diketobutyrate. P. KARRER and E. B. HERSBERG (Helv. Chim. Acta, 1934, 17, 1014—1025).— $\text{COMe}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$, b.p. 64—65°/9 mm., in anhyd. CHCl_3 is converted by $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ in abs. EtOH into the α - (I), m.p. 122—123°, and by the reagent in dil. EtOH into β - (II), m.p. 171—172°, p -nitrophenylhydrazone. With excess of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$ in dil. EtOH containing a trace of HCl , the ester and (I) or (II) give the *di-p-nitrophenylhydrazones* (III), m.p. 294° (decomp.) after becoming yellow at 200° and softening at 220—230°, transformed by boiling AcOH into 4-*p-nitrobenzeneazo*-1-*p-nitrophenyl*-3-methylpyrazol-5-one, m.p. 297—298°. (I) and $\text{NHPh}\cdot\text{NH}_2$ in boiling AcOH afford 4-*p-nitrobenzeneazo*-1-phenyl-3-methylpyrazol-5-one, m.p. 198—199°, whereas 4-benzeneazo-1-*p-nitrophenyl*-3-methylpyrazol-5-one, m.p. 242—243°, results similarly from (II). Reduction of $\text{COMe}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ by Al-Hg leads to a liquid (IV), b.p. 78—83°/9 mm., possibly $\text{OH}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$, and a solid (V), m.p. 140—141°, probably $\text{OH}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$. Neither substance reduces $\text{Cu}(\text{OAc})_2$, but both are readily dehydrogenated by $\text{NHPh}\cdot\text{NH}_2$ or $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}_2$, whereby (IV) gives (II) and (III) in good yield, whereas (V) affords (III) and an unstable, orange-yellow substance, m.p. 103—104°. A substance, probably $\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{Et}$ or $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$, which strongly reduces cold $\text{Cu}(\text{OAc})_2$ and warm aq. AgNO_3 and absorbs I, is present in certain fractions. H. W.

Conversion of glyceric and phosphoglyceric acid into pyruvic acid. C. NEUBERG and M. KOBEL (Biochem. Z., 1934, 272, 459—460).— Ca glycerate (I) and Ba phosphoglycerate (II) heated at 220° for 2½ hr. with $\text{K}_2\text{S}_2\text{O}_7$ yield AcCO_2H , the yield from (I) being > that from (II). When H_3BO_3 replaces $\text{K}_2\text{S}_2\text{O}_7$, neither (I) nor (II) yields AcCO_2H and when P_2O_5 replaces it (I) yields no AcCO_2H , (II) very little. W. McC.

Salts of phosphoglyceric acid. C. NEUBERG and M. KOBEL (Biochem. Z., 1934, 272, 461—464).—The prep. of the cryst. salt, $\text{C}_3\text{H}_5\text{O}_7\cdot\text{PCd}\cdot\text{H}_2\text{O}$ (by the action of the acid on excess of CdCO_3) and cryst.

benzidine salt $\text{C}_3\text{H}_7\text{O}_7\cdot\text{P}(\text{C}_{12}\text{H}_{12}\text{N}_2)_2\cdot\text{H}_2\text{O}$ (from the Na salt) is described. The Zn, Mn, Co, Fe^{II} , and uranyl salts sometimes form jellies. The Sr and Ca salts are more sol. in cold than in hot H_2O . Salts of Pb, Sn^{IV} , Bi, Ce, Y, La are insol., those of Li, Na, Ni, Cu, Cr, Fe^{III} , Al, Hg^{II} , Be, Th, and V sol., in H_2O . W. McC.

Complex cobaltic salts with acid esters.—See this vol., 1083.

Racemisation of *l*-bromosuccinic acid by bromide ion in non-aqueous solvents. Mechanism of organic reactions. A. R. OLSON and H. H. VOGEL (J. Amer. Chem. Soc., 1934, 56, 1690—1693).—The heat of activation of the reaction *l*-bromosuccinic acid + $\text{Br}^- = d$ -bromosuccinic acid + Br^- has been determined in the solvents MeOH , COMe_2 , AcOH , and aq. COMe_2 . The vals. are almost independent of the dielectric const. or other physical properties of the solvent, but vary by as much as 5000 g.-cal. with change in the chemical properties. In absence of large resonance effects any reaction mechanism which involves the primary breaking of strong linkings at room temp. is probably erroneous. E. S. H.

Walden inversion of type I. H. N. K. RORDAM (Ber., 1934, 67, [B], 1595—1601; cf. A., 1933, 145).—Refinements of experimental technique allow the transformation of bromo- into xantho- (I) -succinic acid to be followed to concns. $\geq 0.0004M$. A continuous transition is observed from strongly (+) (I) formed at high concn. to strong (−) (I) at concn. $\geq 0.006M$. At higher dilutions the rise in −rotation is followed by a decline. The existence of a min. is clearly defined. The results support the author's oscillation hypothesis (A., 1930, 1407). H. W.

Chloralides from α -hydroxycarboxylic acids and their reduction products. N. M. SHAH and R. L. ALIMCHANDANI (J. Indian Chem. Soc., 1934, 11, 545—550).—*r*-Malic acid, $\text{CCl}_3\cdot\text{CHO}$, and H_2SO_4 give *r*-malic acid chloralide, m.p. 180—181°, reduced by Zn dust and AcOH to r - β' -*dichloroethoxysuccinic acid*, m.p. 130—131°. *d*-Tartaric acid affords two chloralides, m.p. 161—162°, and m.p. 170°, respectively, each of which is reduced to $\alpha\beta$ -*di- β' -dichloroethylsuccinic acid*, (+ H_2O), m.p. 216—217° (decomp.). Citric acid chloralide, m.p. 164°, is reduced to the substance, $\text{C}_8\text{H}_8\text{O}_7\cdot\text{Cl}_2$, m.p. 208° (*Ba* salt). *r*-Mandelic acid and $\text{CCl}_3\cdot\text{CHO}$ at 120—125° yield *mandelic acid chloralide*, m.p. 70—71°, reduced to $\beta\beta$ -*dichloroethoxyphenylacetic acid*, m.p. 114—115°. *Benzilic acid chloralide*, which is remarkably stable towards NaOH , gives $\beta\beta$ -*dichloroethoxydiphenylacetic acid*, m.p. 102—104°. H. W.

Formation of enolates from α -lactonic esters. A. MICHAEL and N. WEINER (J. Amer. Chem. Soc., 1934, 56, 2012—2013).—The Na-derivative of α -carbethoxy- γ -butyrolactone (Traube and Lehmann, A., 1901, i, 501) has the enolate structure, since it is formed from the lactone and NaOEt , with MeI gives the α -Me derivative, and with I affords a mixture of two stereoisomeric lactonic esters. The Na enolate of δ -chloro- α -carbethoxy- γ -valerolactone (*loc. cit.*) heated with EtOH gives (as the result of an intramol.

CH_2 C-alkylation) the ester $\text{CH} \begin{array}{c} \diagup \text{O} \cdot \text{CO} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \diagdown \text{CH}_2 \end{array}$, con-

verted by hot HCl into the dilactone of $\beta\gamma$ -dihydroxypropylmalonic acid (Leuchs, A., 1907, i, 176). The views of Tschelincev (this vol., 868) are criticised.

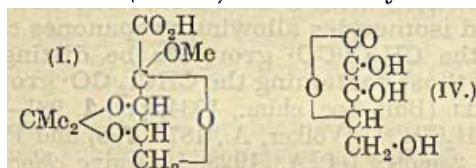
H. B.

Di(hydroxymethyl)malonic acid and its ester. H. GAULT and A. ROESCH (Compt. rend., 1934, 199, 613—615).—Condensation of $\text{CH}_2(\text{CO}_2\text{Et})_2$ with 35% aq. CH_2O in presence of K_2CO_3 gives a 65—70% yield of cryst. Et di(hydroxymethyl)malonate (Ac_2 , b.p. $172.5^\circ/12\text{ mm.}$, and Bz_2 , m.p. 98° , derivatives), hydrolysed by 10% aq. EtOH-KOH at 45° to the corresponding acid, m.p. 185° (decomp.) (*Na* and *Ag* salts).

J. W. B.

Large-scale preparation of ascorbic acid from Hungarian pepper (*Capsicum annuum*).—See this vol., 1270.

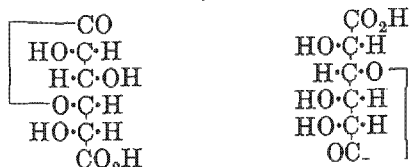
Derivatives of α -keto-*l*-ribonic acid and their transformation into β -keto-*l*-pentonolactone, a C_5 compound resembling ascorbic acid. T. REICHSTEIN (Helv. Chim. Acta, 1934, 17, 1003—1008).—*iso*Propylenemethyl-*l*-adonose (probably a mixture of α - and β -forms) is oxidised by KMnO_4 to



a mixture of α -keto- $\beta\gamma$ -isopropylidene-*l*-ribonomethyl-lactolides, one of which is readily isolated as the cryst. hydrate (I), m.p. $80\text{--}83^\circ$ (in open capillary), $[\alpha]_D^{25} +121^\circ$ to $+111^\circ$ in H_2O , whereas the other (II) remains liquid. Treatment of (I) or (II) with H_2O or dil. acids affords β -keto-*l*-pentonolactone (IV), m.p. $159\text{--}161^\circ$ (corr.), the possible intermediate phase being passed much more quickly than in the C_6 series. (IV) shows the reactions characteristic of ascorbic acid. The possibility that (IV) is a δ -lactone is not excluded.

H. W.

Synthesis of hexuronic acids. VII. Synthesis of *l*-glycuronic acid and the resolution of *dl*-galacturonic acid. C. NIEMANN and K. P. LINK (J. Biol. Chem., 1934, 106, 773—781).—Reduction of *l*-saccharic acid (I) by the authors' usual method gives the *Ba* salt, $[\alpha]_D^{25} -8.5^\circ$ in H_2O , of *l*-glycuronic acid (II), which yields *l*-glycurone, sinters at 165° , m.p. $169\text{--}172^\circ$ (decomp.), $[\alpha]_D^{25} -18.5$ in H_2O (properties in accord with those of *d*-glycurone), together with γ -*d*-gulonolactone, m.p. $183\text{--}184^\circ$, formed by over-reduction of the uronic acid. *l*-Saccharolactone may exist in two isomeric forms, which on partial reduction



should give (II) and *d*-guluronic acid, but the latter has not as yet been isolated from the reduction product of (I). Recrystallisation of the brucine salt of *dl*-galacturonic acid (III), $+\text{H}_2\text{O}$, sinters at 110° , m.p. $156\text{--}158^\circ$ (decomp.) (modified prep.), gives the brucine salt, m.p. $180\text{--}181^\circ$ (decomp.), of *d*-galact-

uronic acid $+\text{H}_2\text{O}$, sinters at 110° , m.p. $157\text{--}159^\circ$ (decomp.), $[\alpha]_D^{25} +50.0^\circ$ in H_2O , and fractionation of the mixture of partly resolved acids derived from the mother-liquors affords *l*-galacturonic acid (IV), m.p. $156\text{--}158^\circ$ (decomp.), $[\alpha]_D^{25} -52.0^\circ$ in H_2O . (III) and (IV) with HCl-MeOH give methyl α -methyl-*dl*-, m.p. $126\text{--}128^\circ$, and methyl α -methyl-*l*-galacturonate, m.p. $130\text{--}135^\circ$.

F. S. H. H.

Reactions of nitrosulphonyl chlorides. III. Identification and characterisation of aldehydes and ketones as nitrobenzenesulphonylhydrazones. J. M. L. CAMERON and F. R. STORRIE (J.C.S., 1934, 1330—1332; cf. A., 1931, 610).—Nitrobenzenesulphonylhydrazones of the following are described, the figures quoted being m.p. in the order *o*-, *m*-, *p*-, all with decomp. except those marked * : MeCHO , (*p*-) $121\text{--}122^\circ$; COMeEt , (*o*-) $143\text{--}144^\circ$, (*p*-) $155\text{--}156^\circ$; furfuraldehyde, $118\text{--}120^\circ$, $156\text{--}157^\circ$, 152° ; *iso*-valeraldehyde, (*p*-) $132\text{--}133^\circ$; COMePr^n , (*m*-) 115° ; COMePr^n , $113\text{--}114^\circ$, $129\text{--}130^\circ$, $160\text{--}161^\circ$; COEt_2 , (*o*-) $99\text{--}101^\circ$; mesityl oxide, $139\text{--}140^\circ$, $128\text{--}130^\circ$, $127\text{--}128^\circ$; cyclohexanone, $135\text{--}136^\circ$, $152\text{--}153^\circ$, 162° ; COMeBu^n , $73\text{--}74^\circ$, * 102° , $155\text{--}156^\circ$; glucose, (*m*-) $149\text{--}150^\circ$; *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{CHO}$, (*m*-) $175\text{--}176^\circ$, (*p*-) $186\text{--}187^\circ$; *o*-, $190\text{--}192^\circ$, $179\text{--}180^\circ$, $199\text{--}200^\circ$; *m*-, $185\text{--}186^\circ$, $182\text{--}183^\circ$, $195\text{--}196^\circ$, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, $194\text{--}196^\circ$, $162\text{--}163^\circ$, $197\text{--}198^\circ$; PhCHO , (*o*-) $170\text{--}171^\circ$; *o*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, $195\text{--}196^\circ$, $167\text{--}168^\circ$, 192° (lit. $178\text{--}179^\circ$); bromopiperonal (I), (*o*-) $169\text{--}171^\circ$, (*p*-) 197° ; COPhMe , $138\text{--}140^\circ$, 175° , 192° ; *o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, $116\text{--}118^\circ$, $130\text{--}131^\circ$, * 160° ; vanillin, $168\text{--}169^\circ$, $159\text{--}160^\circ$, $166\text{--}167^\circ$; $\text{CHPh}\cdot\text{CH}\cdot\text{CHO}$, (*o*-) $153\text{--}155^\circ$; veratraldehyde, (*m*-) $181\text{--}182^\circ$, (*p*-) $188\text{--}189^\circ$; $\text{CHPh}\cdot\text{CH}\cdot\text{COMe}$, (*m*-) $176\text{--}177^\circ$, (*p*-) $173\text{--}174^\circ$; $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, $95\text{--}96^\circ$, $131\text{--}132^\circ$, $153\text{--}154^\circ$; COPh_2 , (*o*-) $138\text{--}140^\circ$, (*m*-) $146\text{--}147^\circ$; *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COPh}$, (*o*-) $128\text{--}130^\circ$; benzoin, (*m*-) $159\text{--}160^\circ$; benzil (*dihydrazone*), (*m*-) $166\text{--}167^\circ$. 2:4-Dinitrobenzenesulphonylhydrazones (m.p. with decomp.) of the following are prepared at $<-10^\circ$: COMe_2 , m.p. 148° ; PhCHO , m.p. 188° ; (I), m.p. 177° ; COPhMe , m.p. $172\text{--}173^\circ$; COPh_2 , m.p. $132\text{--}133^\circ$. Acetone- and benzaldehyde-2-chloro-5-nitrotoluene-4-sulphonylhydrazones have m.p. $156\text{--}157^\circ$ and $158\text{--}160^\circ$, respectively. Acetone-*p*-nitrobenzenesulphonylhydrazone is dimorphic, m.p. $169\text{--}171^\circ$ (from COMe_2) and $183\text{--}184^\circ$ (stable; from EtOH).

R. S. C.

Interchangeability of hydrogen atoms in organic compounds with the hydrogen atoms of water.—See this vol., 1080.

Condensation of formaldehyde and arylsulphonamides. E. HUG (Bull. Soc. chim., 1934, [v], 1, 990—1004).—*p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{NH}_2$ (I) (1 mol.) and aq. CH_2O (1 mol.) at p_H 7—9 give almost entirely *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{NH}\cdot\text{CH}_2\cdot\text{OH}$ (II), m.p. 137° , which is hydrolysed (aq. NaOH) to (I) and converted by dil. aq. NH_3 into (I) and $(\text{CH}_2)_6\text{N}_4$. Attempted condensation of (II) with various phenols (usually in acid media) affords (I) and CH_2O (which then reacts further). Thus, *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ gives 3:3'-di-nitro-4:4'-dihydroxydiphenylmethane (*diacetate*, m.p. 185°); β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ affords dinaphthoxanthan

and di-2-hydroxy- α -naphthylmethane; 2:3-OH-C₁₀H₆·CO·NHPh (in C₆H₅N) yields methylenedi-2-hydroxynaphthalene-3-carboxylanilide, m.p. 260°, and a substance, m.p. 260° (cf. Brass and Sommer, A., 1928, 755). (II) heated with C₆H₆ gives *methylenedi-p-toluenesulphonamide*, m.p. 154° (Na₂ derivative), and a little *di-p-toluenesulphonyldimethylenedi-imide* (III), m.p. 165°. (III) is prepared by the method of Magnus-Lévy (A., 1893, i, 714) [a little 1:3:5-tri-*p*-toluenesulphonylhexahydro-1:3:5-triazine (IV), m.p. 236° (decomp.) (cf. this vol., 1232) is produced also] or, better, from (I) (1 mol.) and 37.5% CH₂O (1 mol.) in cold AcOH-conc. H₂SO₄. (III) is also obtained from (II) and conc. H₂SO₄ in MeOH, EtOH, or BuⁿOH. Prolonged action of boiling Ac₂O or AcOH on (IV) gives *p*-C₆H₄Me·SO₂·NHAc, m.p. 139°. PhSO₂·NH·CH₂·OH heated with C₆H₆ affords *methylenedibenzenesulphonamide*, m.p. 133–134° (Na₂ derivative), also prepared from PhSO₂·NH₂ (0.1 mol.) and 37.5% CH₂O (0.2 mol.) in aq. K₂CO₃ (0.01 mol.) at 80°. 1:3:5-Tribenzenesulphonylhexahydro-1:3:5-triazine has m.p. 228° (lit. 218°). *o*-C₆H₄Me·SO₂·NH₂ and CH₂O in dil. aq. K₂CO₃ give *methylenedi-o-toluenesulphonamide*, m.p. 162° (Na₂ derivative). *Di-o-toluenesulphonyldimethylenedi-imide* and 1:3:5-tri-*o*-toluenesulphonylhexahydro-1:3:5-triazine, prepared by the method of Magnus-Lévy (*loc. cit.*), have m.p. 166° and 222°, respectively (cf. McMaster, this vol., 307). *Methylenedi-p-toluenesulphon-methylamide*, m.p. 115°, and *-anilide*, m.p. 210°, are obtained from *p*-C₆H₄Me·SO₂·NHR and CH₂O (excess) in dil. HCl at 100°. The resinous product obtained from (I) and CH₂O in an acid medium is considered to be [N(SO₂·C₆H₄)·CH₂·N(SO₂·C₆H₄)·CH₂·N(SO₂·C₆H₄)·CH₂]_n. *p*-Toluenesulphon-*o*-, *-m*-, and *-p*-nitro-anilide, *-o*-toluidide, and *-m*-4-xylylide do not react with CH₂O. Polymeric products are obtained from β -C₁₀H₇·SO₂·NH₂, 4-nitro- and 4-amino-*o*-toluenesulphonamides, and 2:4:6-C₆H₂Cl₃·SO₂·NH₂.

H. B.

Manufacture of acraldehyde. T. HANYU and T. YANAGIBASHI (J. Soc. Chem. Ind. Japan, 1934, 37, 538B).—FePO₄ (optimum yield 51%) and Japanese acid clay (optimum yield 37%) are less effective than KHSO₄–K₂SO₄ for dehydration of glycerol.

R. S. C.

Constitution of the aldehyde of violet leaves. E. SPATH and F. KESZTLER (Ber., 1934, 67, [B], 1496–1500).—Distillation of the oil of violet leaves affords a fraction, b.p. 87–100°/12 mm., which gives a semicarbazone (I), C₁₀H₁₁ON₃, m.p. 158–159° (cf. Walbaum *et al.*, A., 1930, 966). Treatment of (I) with HCl regenerates the odoriferous principle. Hydrogenation of (I) (Pd–C at 20°) leads to *n*-non-aldehydesemicarbazone, m.p. 95–96° (comparative experiments with heptaldehyde- and citral-semicarbazone show that the aliphatic double linking is rapidly saturated at 20° without appreciably affecting the semicarbazone double linking, whereas at 50° the latter is rather more rapidly affected). Oxidation of (I) with KMnO₄ in COMe₂ yields H₂C₂O₄ and [CH₂·CO₂H]₂, whilst ozonisation in EtCl gives EtCHO, thus establishing the presence of CHEt. Partial hydrogenation of (I) followed by oxidation of

the product with KMnO₄ leads to *n*-heptoic acid (phenylhydrazide, m.p. 98–99.5°). The aldehyde is therefore *n*-Δ^α-nonadien- α -al.

H. W.

Thoria aerogel catalyst: aliphatic esters to ketones. S. SWANN, jun., E. G. APPEL, and S. S. KISTLER (Ind. Eng. Chem., 1934, 26, 1014).—Aliphatic ketones of high mol. wt. may be prepared in good yield by distilling the Et esters of the corresponding acids over ThO₂ aerogel. Examples given are laurone prepared in 90% yield over a catalyst at 360° and undecylenone, CO[(CH₂)₈·CH·CH₂]_n, m.p. 43°.

C. I.

Convenient keten generator. R. M. HERRIOTT (J. Gen. Physiol., 1934, 18, 69–70).—A simple apparatus for production of CH₂:CO from COMe₂ vapour by a hot filament is described.

C. G. A.

Action of carbonyl chloride on acetone. M. P. MATUSZAK (J. Amer. Chem. Soc., 1934, 56, 2007).—COMe₂ and liquid COCl₂ at room temp. give (probably) some *isopropenyl chloroformate*, b.p. 93° (corr.)/746 mm.

H. B.

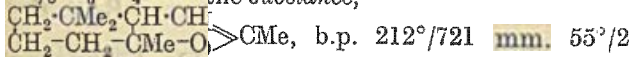
Reactions with *s*-dichloroacetone and its so-called isomerides allowing propanones containing the CH₂Cl·CO· group to be distinguished from those containing the CHCl₂·CO· group. G. FAVREL (Bull. Soc. chim., 1934, [v], 1, 981–990).—CO(CH₂Cl)₂ (I) (Volker, A., 1878, 780) and PhN₂·OH (1 or 2 mols.) (cf. A., 1928, 166) give *chloropyruvyl chloride phenylhydrazone* (II), CH₂Cl·CO·CCl₂·N·NHPh, m.p. 156–157°; the corresponding *o*-, m.p. 85–86°, and *p*-, m.p. 192.5°, *-tolylhydrazones* are similarly prepared using C₆H₄Me·N₂·OH. The same hydrazones are similarly obtained from the so-called ψ -dichloroacetone (III) of Cloez (A., 1887, 1091) and the polymeric CO(CH₂Cl)₂ (IV) of Barbaglia (A., 1874, 789; cf. Cloez, *loc. cit.*). Further proof of the identity of (I), (III), and (IV) is established by the prep. (from each) of the same NaHSO₃-compound, the same CO(CH₂Cl)₂ (by the action of AgI), and the same cyanohydrin. Mol. wt. determinations also show that (IV) is really (I). Impure (IV) contains some CH₂Cl·CO·CHCl₂ (V), since treatment with PhN₂·OH gives (II) and *dichloropyruvyl chloride phenylhydrazone* (VI), CHCl₂·CO·CCl₂·N·NHPh, m.p. 115–116° [also prepared from (V) and from (II) and SO₂Cl₂ in CCl₄]. The production of (VI) from (V) shows that the mobility of the H atoms of the CH₂Cl group is > that of the H of the CHCl₂ group or that of the ·CO·CH₂Cl group (non-production of CH₂Cl·CO₂H). CHCl₂·COMe [or CO(CHCl₂)₂] and the appropriate ArN₂·OH give the compounds CCl₂(N·NPh)₂, m.p. 81–82°, and CCl₂(N·N·C₆H₄Me-*p*)₂, m.p. 159–160°. Propanones containing ·CO·CHCl₂ are thus distinguished from those containing ·CO·CH₂Cl. The reaction with ArN₂·OH is sp. for propanones; CH₂Cl·COEt and CH₂Cl·COPrⁿ do not react, but CH₂Cl·COPh gives COPh·CCl₂·N·NHPh, m.p. 136–137°.

H. B.

Catalytic transformation of mesityl oxide into acetone. Action of Al₂O₃, ThO₂, pumice, silica gel. A. ZANGIROLAMI (Annali Chim. Appl., 24, 347–352).—When CMe₂·CHAc vapour, mixed with steam, is passed over SiO₂ gel at 200–300° under atm. pressure, 19–32% is hydrolysed to COMe₂; at 300 °C.

is also formed, and the reaction products are partly decomposed. Al_2O_3 and ThO_2 also catalyse the reaction, but give lower yields of COMe_2 . T. H. P.

Methyl geranyl ketone. H. BARBIER (Helv. Chim. Acta, 1934, 17, 1026—1030).—Citral and $\text{CHMeCl}\cdot\text{CO}_2\text{Et}$ in presence of $\text{NaOEt}\cdot\text{EtOH}$ afford *Et* $\alpha\beta$ -oxido- $\alpha\delta\theta$ -trimethyl- Δ^7 -decadienoate, b.p. $135^\circ/2$ mm. The corresponding acid (*K* and *Na* salts) is transformed by distillation in vac. into *Me geranyl ketone* (I), b.p. $238^\circ/721$ mm., $94^\circ/2$ mm. (semicarbazone, m.p. 126°). (I) is converted by 60% H_2SO_4 or 80% H_3PO_4 into the substance,



mm., α -, $\text{CH}_2\cdot\text{C}(\text{CH}_2\cdot\text{CMe}_2)\cdot\text{CH}_2\cdot\text{CH}_2\text{Ac}$, b.p. $237^\circ/721$ mm., $72^\circ/2$ mm. (semicarbazone, m.p. 166°), and β -, $\text{CH}_2\cdot\text{C}(\text{CH}_2\cdot\text{CMe}_2)=\text{CH}\cdot\text{CH}_2\text{Ac}$, b.p. $78^\circ/2$ mm. (semicarbazone, m.p. 175°), -cyclogeranyl *Me ketone*. Condensation of (I) with MeCHO in presence of solid KOH gives Δ^2 -propenyl geranyl ketone, b.p. $104^\circ/2$ mm. (semicarbazone, m.p. 89°). Analogously, citronellal yields *Et* $\alpha\beta$ -oxido- $\alpha\delta\theta$ -trimethyl- Δ^7 -decenoate, b.p. $123^\circ/2$ mm., whence *Me citronellal ketone*, b.p. $241^\circ/733$ mm., $83^\circ/2$ mm. H. W.

Raman effect and problems of constitution. VI. Keto-enolic tautomerism among β -diketones and β -ketonic esters. K. W. F. KOHLRAUSCH and A. PONGRATZ (Ber., 1934, 67, [B], 1465—1477; cf. this vol., 869).—Comparison of the Raman spectra of CMe_2Ac_2 (I) and *Me tert.*-amyl ketone shows the absence of detectable enolisation in (I). Similar comparison of CHMeAc_2 (II) with $\text{COMe}\cdot\text{sec}\cdot\text{Bu}$ indicates the possibility of structures $\text{OH}\cdot\text{CMe}\cdot\text{CMeAc}$ and $\text{OH}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{CH}_2$ for (II), the second of which is excluded by the absence of 2 C:C frequencies. The non-observation of a C:O frequency at $1650\text{--}1670$ leads to the hypothesis that C:O is not present, or exists in a linking devoid of or possessing a quite distinct proper frequency, or that the no. of enolised mols. is insufficient for the appearance of the C:O line. CH_2Ac_2 , compared with COMePr_2 , appears to contain the 2CO symmetrically arranged and in the β position, and to be enolised to the form $\text{OH}\cdot\text{CMe}\cdot\text{CHAc}$, but the small intensity of the C:C line indicates some other variety. The spectrum of $\text{CH}_2\text{Bz}\cdot\text{CO}_2\text{Et}$ is completely in accord with the presence of ketonic and enolic forms, but those of CH_2Bz_2 and CH_2AcBz are more difficult to interpret. In the spectra of $\text{CO}(\text{CH}_2\text{Ph})_2$ and $[\text{CH}_2\text{Ac}]_2$ lines occur in the expected regions for C:C (aromatic) and C:O, together with those undoubtedly due to C:C. H. W.

l-Adonose (*l*-erythro-2-ketopentose). T. REICHSTEIN (Helv. Chim. Acta, 1934, 17, 996—1002).—Oxidative fermentation of adonitol leads to non-cryst. *l*-adonose (I), $[\alpha]_D^{25}$ about $+16$ in H_2O , best purified through its *o*-nitrophenylhydrazone, m.p. $168\text{--}169$ (corr.; slow decomp.), $[\alpha]_D^{25} +41.5$ in MeOH [*p*-nitrophenylhydrazone, m.p. $121\text{--}123^\circ$, $[\alpha]_D^{25} -48.7^\circ$ to -53.2° in (I) $\text{MeOH}\cdot\text{C}_6\text{H}_5\text{N}$ (1:1)], which is readily decomposed by PhCHO . The constitution of (I) is

established by its conversion by $\text{NHPh}\cdot\text{NH}_2$ into *l*-arabinosazone and its isomerisation to *l*-arabinose by $\text{C}_6\text{H}_5\text{N}$ or alkali (this effect is noticed if animal C with the frequent small proportion of alkali is used). (I) is transformed by COMe_2 containing anhyd. CuSO_4 and conc. H_2SO_4 into diisopropylidene-*l*-adonose (II), b.p. $76\text{--}78^\circ/0.3$ mm., m.p. 5° , $[\alpha]_D^{25} +107^\circ$ in COMe_2 , and a substance, (?) $\text{C}_{16}\text{H}_{24}\text{O}_8$, m.p. $120.5\text{--}121.5^\circ$, $[\alpha]_D^{25} +221^\circ$ in COMe_2 . Acetonisation of crude methyladonoside affords (II) and non-cryst. isopropylidene-methyladonoside, b.p. $88\text{--}90^\circ/0.3$ mm., $[\alpha]_D^{25} +113.2^\circ$ in MeOH , separated from one another by distribution between H_2O and C_6H_{12} . H. W.

Monoacetone [isopropylidene-]*d*-xyloketose. P. A. LEVENE and R. S. TIESON (J. Biol. Chem., 1934, 106, 603—604).—Condensation of *d*-xyloketose (this vol., 173) and COMe_2 with H_2SO_4 and CuSO_4 gives isopropylidene-*d*-xyloketose (I), b.p. $130\text{--}140^\circ$ (bath temp.)/0.1 mm., m.p. $50\text{--}52^\circ$ after softening at 45° , $[\alpha]_D^{25} -2.6^\circ$ in H_2O . (I) does not exhibit mutarotation and is presumably α - or β -1:2-(or 2:3)-isopropylidene-*d*-xyloketose. F. S. H. H.

Determination of reducing sugars. P. GUARNIERI (Atti Congr. naz. Chim., 1933, 4, 727—728; Chem. Zentr., 1934, i, 2010).—The sugar solution (50 c.c.) is cleared by successive additions of 2 c.c. of 25% aq. ZnSO_4 and 3 c.c. of 15% aq. $\text{K}_4\text{Fe}(\text{CN})_6$. Sugar is determined volumetrically by means of Fehling's solution [with $\text{K}_4\text{Fe}(\text{CN})_6$] using methylene-blue as indicator. Test solutions should contain approx. 1% of sugar. A. G. P.

Transformation of carbohydrates into ethoxy-methylfurfuraldehyde and ethyl lævulate. R. WEIDENHAGEN and B. KOROTKYJ (Z. Ver. deut. Zucker-Ind., 1934, 84, 470—493).—The known conversion of sugars into hydroxymethylfurfuraldehyde and lævulic acid can be combined with esterification of the products by use of $\text{EtOH}\cdot\text{HCl}$, and high yields obtained. Fructose or inulin, heated at $105\text{--}110^\circ$ for several hr. with a 1% solution of HCl in EtOH , yielded up to 48—49%, and sucrose up to 24%, of the mixed esters, as an oil sol. in Et_2O and volatile in vac. The relative proportions of the two esters varied rather widely about 1:1, *Et* lævulate preponderating when the conditions were made more severe. A similar transformation of aldoses requires higher concn. of acid and higher temp. With 2.5% HCl at $150\text{--}165^\circ$ glucose yielded up to 25% and sucrose up to 34% of the mixed esters, consisting chiefly of *Et* lævulate. With 6.8% HCl at the same temp. starch yielded up to 28%. J. H. L.

Resinification of sugars by acids and its bearing on the determination of lignin. R. S. HILPERT and E. LITTMANN (Ber., 1934, 67, [B], 1551—1556).—In equal intervals of time, equal quantities of black substances are invariably produced from sugars under the influence of H_2SO_4 or HCl . Among hexoses galactose is least sensitive, glucose and mannose give yellow solutions but only slight ppts., whereas fructose (I) rapidly separates black masses which, under the conditions of the lignin determination, attain 25% of its wt. Polyoses containing (I) give ppts. according to the amount of (I) obtainable by hydrolysis.

Fructose lignin (II) contains less H than wood lignin, in which, however, its presence cannot be established by elementary analysis. The main difference lies in the OMe content. Methylation of (II) yields a product with about 12% of OMe. Xylose (III) and arabinose give lignins differing from (II) in their complete insolubility in alkali and great resistance to methylation, but resembling wood lignins in composition. The "sugar lignins" are rapidly attacked by Cl_2 with evolution of HCl, giving yellow products closely resembling the chlorolignins. Treatment of straw, (I), and (III) with extractants, such as PhOH , AcOH , or dioxan, in presence of "catalysts" (HCl , ZnCl_2) follows exactly similar lines. The fundamental action is the formation of a strong acid from catalyst and solvent which causes hydrolysis and passage of deeply coloured products into the solution. The "black boil" of the bisulphite process is attributed to the resinification of sensitive sugars.

H. W.

Hydrogenation of saccharides. K. YOSHIKAWA Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1045—1052).—Aq. solutions of *D*-glucose, *D*-fructose, *D*-galactose, maltose, sucrose, dextrin, and starch hydrogenated (Ni and Ni-Fe) under 40—150 atm. pressure yield hexitols at 130—200°, and if further heated to 250—300° glycerol and propylene glycol. Ni-Fe is a better catalyst for the second reaction than is Ni.

J. W. S.

Oxidation of glucose by air in presence of iron pyrophosphate.—See this vol., 1077.

Condensation of α -methylgalactoside with benzaldehyde. G. J. ROBERTSON and R. A. LAMB (J.C.S., 1934, 1321—1322).—Condensation of α -methylgalactoside (modified prep.; 54% yield), m.p. 110—111°, $[\alpha]_D^{25} +178.5^\circ$ in H_2O , with PhCHO by Irvine and Scott's or Freudenberg's method yields 4:6-benzylidene- α -methylgalactoside (I), m.p. 170—172°, $[\alpha]_D^{25} +166.5^\circ$ in CHCl_3 , the 2:3-*Me*₂ ether, m.p. 123—124°, $[\alpha]_D^{25} +173.7^\circ$ in CHCl_3 , of which by regulated hydrolysis affords 2:3-dimethyl- α -methylgalactoside (II), an oil, $[\alpha]_D^{25} +173.7^\circ$ in CHCl_3 [4:6-dinitrate, m.p. 88—90°, $[\alpha]_D^{25} +100.3^\circ$ in CHCl_3 , also obtained from (I)], and thence 2:3-dimethylgalactose, a resin, $[\alpha]_D^{25} +11.3^\circ$ in CHCl_3 (anilide, m.p. 130—131°, $[\alpha]_D^{25} +119.4^\circ$ in EtOH), which with $\text{NH}_3 \cdot \text{NHPh}$ gives 3-methylgalactosazone, m.p. 176—179°, and with cold 0.3% dry HCl - MeOH gives a laevorotatory solution. The structure of (I) is thus proved.

R. S. C.

Sugar anhydride, anhydromannose. F. VALENTIN (Coll. Czech. Chem. Comm., 1934, 6, 354—370).— α -Methylmannoside (improved prep.) with CPh_3Cl in dry $\text{C}_5\text{H}_5\text{N}$ and subsequent addition of Ac_2O affords 6-triphenylmethyl- α -methylmannoside 2:3:4-triacetate, m.p. 131—132°, $[\alpha]_D^{25} +58.6^\circ$ in C_6H_6 , converted by PBr_5 in CCl_4 into the corresponding 6-*Br*-derivative, m.p. 78—81°, $[\alpha]_D^{25} +57.6^\circ$ in MeOH , deacetylated by $\text{NH}_3 \cdot \text{MeOH}$ to α -methylmannosidyl 6-bromide, m.p. 97—99°, $[\alpha]_D^{25} +52^\circ$, converted by boiling aq. Ba(OH)_2 into 3:6-anhydro- α -methylmannopyranoside (I), m.p. 130—132°, $[\alpha]_D^{25} +97.1^\circ$ in H_2O (cryst. and optical data). Hydrolysis of (I) with boiling 6% H_2SO_4 causes conversion into the stable dicyclic system of the furanose form to give 3:6-anhydromannofuranose,

sinters at 100°, m.p. 102—103°, decomp. 197°, $[\alpha]_D^{25} +95.92^\circ$ in H_2O (benzylphenylhydrazone, m.p. 144—145°, $[\alpha]_D^{25} +43.59^\circ$ in MeOH ; gives the same phenyl-osazone, m.p. 188—189°, as does 3:6-anhydroglucose), converted by MeOH-HCl into 3:6-anhydro- α -methylmannofuranoside, m.p. 85°, $[\alpha]_D^{25} +157^\circ$ in H_2O , different from (I).

J. W. B.

Identification of common glucosides. K. E. JACKSON and W. M. DEHU (Ind. Eng. Chem. [Anal.], 1934, 6, 382).—Tests (mostly colour tests) are described for differentiation of 14 glucosides and picrotoxin.

R. S. C.

Heart glucosides. VII. Double linkings of scillaridin-A. A. STOLL, A. HOFMANN, and W. KREIS (Helv. Chim. Acta, 1934, 17, 1334—1354; cf. this vol., 635).—Homogeneous Br or I additive compounds of scillaridin-A (I) or anhydrosillaridin-A (II) could not be obtained. By use of excess of Br and back titration it is shown that (I) absorbs 4 and (II) absorbs 6 atoms of Br, whereas in MeOH-CHCl_3 either absorbs only 2 atoms of I. (I) rapidly absorbs 6 and finally 8, (II) quickly adds 7 and ultimately 8, atoms of Br vapour [modified method of Rossmann (A., 1933, 142)], indicating that (I) loses $1\text{H}_2\text{O}$ during the process. Exhaustive hydrogenation of (II) (PtO_2 in AcOH) leads to decahydroanhydrosillaridin-A, $\text{C}_{25}\text{H}_{40}\text{O}_2$, m.p. 170—175° (corr.), which titrates as a lactone and is free from OH (Zerevitinov), and decahydrodeoxyanhydrosillaridic acid-A (scillanic acid), m.p. 154°, $[\alpha]_D^{25} +25.0^\circ$ in dioxan, which is fully saturated, does not contain OH, and is titrated as a monobasic acid. Similarly, (I) yields octahydrodeoxyanhydrosillaridin-A, m.p. 183°, and octahydrodeoxyanhydrosillaridic acid-A (hydroxyscillanic acid), m.p. (indef.) 117—120°; distillation of the non-cryst. acidic products leads to anhydro-octahydrodeoxyanhydrosillaridic acid-A, m.p. 130—135°. The prep. of homogeneous reduction products permits the conclusion that (I) and (II) contain 4 and 5 double linkings, respectively. The further consumption of 1H_2 is due to reductive scission of the lactone ring, in which respect the *Scilla* aglucones differ from strophanthidin and the aglucones of the *Digitalis* glucosides. Fresh evidences in favour of the view that (II) is derived from (I) by loss of $1\text{H}_2\text{O}$ and production of a double linking is found in the absorption of the extra mol. of H_2 . Hydrogenation of isoscillaridic acid-A and its Me ester indicates that these compounds contain 4 double linkings, and that further consumption of H is due to the opening of the oxide ring characteristic of the *iso*-compounds. Me anhydrosillaridate absorbs about 5H_2 , indicating the presence of 5 double linkings. The presence of 4 and 5 double linkings, respectively, in (I) and (II) in conjunction with the established empirical formulae prove the presence of 4 C rings in the fundamental skeleton of the *Scilla* aglucone. In this respect (I) resembles strophanthidin and the aglucones of other heart glucosides, from which it is distinguished by markedly more unsaturated character. Apparently only 3 double linkings exist in the *Scilla* glucosides, the fourth double linking in (I) being due to loss of H_2O during hydrolysis. Attention is directed to the similarity of scillanic and cholanolic acids.

H.

Primula saponins. I. J. LINDNER [with N. FIGALA and J. HAGER] (Ber., 1934, 67, [B], 1641—1652).—Extraction of the dried roots of *P. veris* with 70% EtOH (apparatus described) and treatment of the extracted matter with EtOH or MeOH followed by electrodialysis leads to the isolation of a cryst. saponin (I), (3) $C_{52}H_{84}O_{22}$, m.p. 225° (decomp.) after becoming brown at 220°, and an amorphous saponin (C 58.44, H 7.93%). The aglucone (C 77.15, H 10.46%) from (I) has m.p. >155° (gradual decomp.) after becoming yellow at 150° and softening at 154—155°. H. W.

Synthesis of theophylline-5-methylrhamnofuranoside. P. A. LEVENE and I. E. MUSKAT (J. Biol. Chem., 1934, 106, 761—771).—Rhamnose with pure $COMe_2$, H_2SO_4 , and $CuSO_4$ gives 2 : 3-isopropylidenerhamnofuranose (I) (A., 1926, 601), b.p. 115°/0.2 mm., m.p. 90°, $[\alpha]_D^{25} +6.4^\circ$ in H_2O (on addition of $NH_3 \rightarrow +17.7^\circ$), but in presence of MeOH a mixture of α - and β -methylisopropylidenerhamnofuranosides (II), a syrup, b.p. 100—105°/0.7 mm., results. By Purdie's method (I) gives 71% of methyl-2 : 3-isopropylidene-5-methylrhamnofuranoside (III), b.p. 65°/1 mm., $[\alpha]_D^{25} -53.7^\circ$ in MeOH. The *K* salt of (II) with MeI (this vol., 512) gives 92% of (III), $[\alpha]_D^{25} -54.5^\circ$ in MeOH. (II) with $p\text{-}C_6H_4Me\cdot SO_2Cl$ and C_5H_5N gives a $Me\cdot SO_2$ derivative, m.p. 80°, $[\alpha]_D^{25} -12.2^\circ$ in MeOH, which is not converted into an iodide by heating with NaI and $COMe_2$ in a sealed tube. Hydrolysis of (III) with dil. H_2SO_4 gives 5-methylrhamnofuranose (IV), which with Ac_2O and C_5H_5N yields a syrup, b.p. 128—131°/2 mm., consisting of α -, m.p. 114°, $[\alpha]_D^{25} -66.2^\circ$ in MeOH, and β -5-methylrhamnofuranose triacetate, which is converted (HBr-AcOH) into bromo-5-methylrhamnofuranose 2 : 3-diacetate (VII), m.p. 100.5°, $[\alpha]_D^{25} -176.2^\circ$ in $CHCl_3$. Condensation of the Ag salt of theophylline with (VII) in xylene gives theophylline 5-methylrhamnofuranoside diacetate (IX), shrinks at about 62°, m.p. about 83°, $[\alpha]_D^{25} -23.2^\circ$ in MeOH, which does not reduce boiling Fehling's solution prior to hydrolysis. (VII) with MeOH and quinoline yields 1 : 2-methylorthoacetyl-3-acetyl-5-methylrhamnofuranose in admixture with the glucoside.

F. S. H. H.

Analysis of γ -methylfructoside mixtures by means of invertase. III. Behaviour of crystalline γ -methylfructoside in methyl alcohol containing hydrogen chloride. C. B. PURVES. IV. Behaviour of sucrose in methyl alcohol containing hydrogen chloride. C. B. PURVES and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 1969—1973, 1973—1977).—III. γ -Methylfructoside (I), $[\alpha]_D^{25} +93^\circ$ in H_2O (this vol., 513), is rapidly converted by HCl in anhyd. MeOH into an equilibrium mixture of approx. equal amounts of (I) and the invertase-hydrolysable methylfructoside (II), $[\alpha]_D^{25} -52 \pm 2^\circ$ in H_2O (*loc. cit.*); the reaction is unimol. Reaction is slower with MeOH-HCl containing 1% of H_2O ; about 5% of fructose is also formed. Hydrolysis of (I) with aq. 0.2*N*-HCl is unimol. and the velocity coeff. is 8.1 times that similarly determined for sucrose; the partly hydrolysed material is unaffected by invertase, indicating the absence of side-reactions leading to (II).

IV. Sucrose (III) is rapidly converted by MeOH-HCl into glucose (isolation described) (which is then slowly transformed into a non-reducing mixture of γ -methylglucosides) and (II) [which then gives a mixture of (I) and (II)]. Details are given for the isolation of (I) from the reaction mixture. H. B.

Chemistry of starch. M. PRINGSHEIM (Chim. et Ind., 1934, 31, Spec. No., 996—999).—A brief survey of some present views on the nature of starch and amylases. J. H. L.

Chemistry of starch and other polysaccharides. K. FREUDENBERG (Angew. Chem., 1934, 47, 675—677).—A lecture. S. C.

Hydrolysis of starch by acid.—See this vol., 1074.

Thermal degradation of glycogen. E. BERNER and O. G. DAHL (Kong. Norske Vidensk. Selsk. Forhandl., 1933, 6, No. 34, 1—4; Chem. Zentr., 1934, i, 1187).—The degradation of glycogen occurs in 76 hr. in glycerol at 160°/20 mm. In $[CH_2\cdot OH]_6$ the reaction is less complete. With small amounts of H_3PO_4 reaction occurs at 130°. The degradation resembles that of lichenin, inulin, and sucrose, a mixture of α - and β -glycerylglucosides being formed. H. J. E.

Constitution of cellulose. H. STAUDINGER (Z. Elektrochem., 1934, 40, 729).—Polemical.

E. S. H.

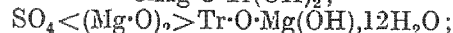
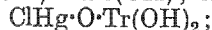
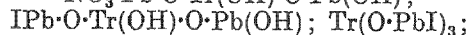
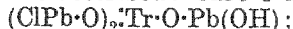
$\beta\beta'$ -Diaminodiethylamine. D. H. PEACOCK and U. C. DUTTA (J.C.S., 1934, 1303—1305).—Dry $p\text{-}C_6H_4Me\cdot SO_2\cdot NHNa$ and $CH_2Cl\cdot CH_2\cdot OH$ at 120° give $p\text{-}C_6H_4Me\cdot SO_2\cdot NH\cdot CH_2\cdot CH_2\cdot OH$ (I), an oil, which with $SOCl_2$ gives *p*-toluenesulphon- β -chloroethylamide, m.p. 99°, whence by $NaOPh\text{-}EtOH$ was obtained the β -OPh-amide, and by $6N\text{-}NH_3\text{-}EtOH$ at 100—120° *p*-toluenesulphon- β -aminoethylamide, m.p. 124° (lit. 121°) [*Bz* derivative, m.p. 135°; with $p\text{-}C_6H_4Me\cdot SO_2Cl$ gives *di-p*-toluenesulphonylethylenediamine, m.p. 155°, also obtained from $(\text{-}CH_2\cdot NH_2)_2$], $\beta\beta'$ -di-*p*-toluenesulphonamidodiethylamine (II) [*hydrochloride* (III), m.p. 163°; *H* sulphate, m.p. 228°; corresponding $(p\text{-}C_6H_4\cdot SO_2)_3$ derivative, m.p. 173°; *Bz* derivative, m.p. 167°], and a substance, m.p. 104°. (I) and HBr afford *p*-toluenesulphon- β -bromoethylamide, m.p. 88—90°. (III) and conc. HCl at 160° give $\beta\beta'$ -diaminodiethylamine trihydrochloride (IV), m.p. 215—220°. The Na derivative of (I) with $CH_2Cl\cdot CH_2\cdot OH$ at 110—120° yields *p*-toluenesulphon-di- β -hydroxyethylamide, m.p. 101° [$O\text{-}(p\text{-}C_6H_4Me\cdot SO_2)_2$ derivative, m.p. 65—67° (clear at 75°)], and with CH_3ClPh at 120—140° *p*-toluenesulphonbenzyl- β -hydroxyethylamide, $p\text{-}C_6H_4Me\cdot SO_2\cdot N(CH_2Ph)\cdot CH_2\cdot CH_2\cdot OH$, m.p. 107°. Phthal- β -hydroxyethylimide (IV), m.p. 126.5—127.5° (lit. 88—89°), with $p\text{-}C_6H_4Me\cdot SO_2Cl$ at 100—120° gives the *O-p*- $C_6H_4Me\cdot SO_2$ derivative, m.p. 142°, which with $NH_3\text{-}EtOH$ forms (IV), phthalimide, and NN' -diphtalyl-diethylenediamine. $n\text{-}C_6H_{13}Me\cdot SO_2\cdot NH_2$ (or its Na derivative), $p\text{-}C_6H_4Me\cdot SO_2\cdot CH_2\cdot CH_2Cl$, and aq. NaOH at 100° give only 1 : 4-di-*p*-toluenesulphonylpiperazine, m.p. 268°. $NH(CH_2\cdot CH_2\cdot Br)_2\cdot HBr$ [best obtained from $NH(CH_2\cdot CH_2\cdot OH)_2$ and HBr at 120—130°], m.p. 210°, does not give a $p\text{-}C_6H_4Me\cdot SO_2$ derivative, but affords an Ac, m.p. 107°, unstable, and *Bz* derivative (*hydro*-

chloride, m.p. 165°; hydrobromide, m.p. 135°), from which (IV) could not be obtained. R. S. C.

Synthesis of δ -diethylaminobutylamine. I. T. STRUKOV (Khim. Farm. Prom., 1933, 332—333).— γ -Chlorobutyronitrile (I) (65 g.) is prepared by heating for 5 hr. a mixture of 62 g. of NaCN, 500 c.c. of EtOH, and 200 g. of trimethylene chloride bromide. γ -Diethylaminobutyronitrile (II) is prepared by refluxing NHET_2 with (I) for 8—10 hr., extracting with Et_2O , and distilling in vac. (II) (100 g.) is mixed with abs. EtOH (1500 c.c.), slowly treated with Na (8—10 g.), saturated with dry HCl, filtered, and fractionated in vac. The residue is treated with 50% NaOH, extracted with C_6H_6 , dried, and distilled in vac. The yield is 59%; d_{20}^{20} 0.8429. CH. ABS.

Complex compounds of thiosemicarbazide.—See this vol., 1188.

Alcoholysed compounds formed from tris-(β -hydroxyethyl)amine and bivalent metallic salts. F. GARELLI and A. TETTAMANZI (Gazzetta, 1934, 64, 474—485; cf. A., 1933, 1280).—In certain cases $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, $[\text{—Tr}(\text{OH})_3]$ reacts with salts with replacement of the acid radical by $\cdot\text{O}\cdot\text{Tr}(\text{OH})_2$ ("alcoholysis"). Certain differences from results of other workers (cf. A., 1933, 150, 151) are ascribed to the influence of experimental conditions. The following compounds are described: $\text{ClPb}\cdot\text{O}\cdot\text{Tr}(\text{OH})_2\cdot 4\text{H}_2\text{O}$;



R. K. C.

Complex chemical behaviour of the ethanolamines. II.—See this vol., 1187.

Photosynthesis of amino-acids *in vitro*. N. R. DHAR and S. K. MUKHERJEE (Nature, 1934, 134, 499).— NH_2 -acids (I) are synthesised when solutions of $[\text{CH}_2\cdot\text{OH}]_2$ or glucose (II) and NH_4 , Na, or K nitrate are exposed to sunlight for 6—8 hr. in presence of TiO_2 . (I) reaches a max. with an increase in exposure and then decreases; it increases with an increase in concn. of (II). No photosynthesis occurs when aq. NH_3 or an NH_4 salt is substituted for the nitrate. Tartaric acid, glycerol, and carbohydrates can replace (II). Glycine is mainly formed with glycol and KNO_3 , and arginine with (II) and KNO_3 . Small amounts of (I) are also formed when (II) and nitrates are exposed with NH_4 U carbonate as photocatalyst. L. S. T.

[Preparation of] urethane. G. A. KIRKHOFF and O. P. ALBITZKAYA (Khim. Farm. Prom., 1933, 282).— ClCO_2Et (217 g.) is slowly mixed with 25% aq. NH_3 (136 c.c.) and 26.6% NaOH (300 c.c.) at 40°. When the oily layer disappears, urethane (67.4%) crystallises on cooling, and is recryst. from PhMe. CH. ABS.

Preparation of glycine. A. CONTARDI and C. RAVAZZONI (R. Ist. lombardo Sci., 1933, [2], 66, 786—790; Chem. Zentr., 1934, i, 1186).— $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ is treated with 24% aq. NH_3 and the mixture evaporated to dryness in vac. The residue of NH_4Cl and $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ is dissolved in H_2O and treated with Ac_2O . The Ac derivative is less sol. than NH_4Cl and

separates. It is refluxed with aq. $\text{Ba}(\text{OH})_2$, and after removing excess of $\text{Ba}(\text{OH})_2$ with H_2SO_4 or $(\text{NH}_4)_2\text{CO}_3$, pure glycine is obtained. H. J. E.

Synthesis of the phosphoric esters of hydroxy-amino-acids. III. Resolution of *dl*-serinephosphoric acid and synthesis of *l*-hydroxyprolinephosphoric acid. P. A. LEVENE and A. SCHOR-MULLER (J. Biol. Chem., 1934, 106, 595—602).—*dl*-Serine (modified prep.) is converted into *dl*-serine- β -phosphoric acid (this vol., 876), which is resolved by recrystallisation of the dibrucine salt to give the dibrucine salt, sinters at 100°, decomp. about 130° of *d*-serine- β -phosphoric acid (I), $[\alpha]_D^{25} +16.3^\circ$ in aq. BaCl_2 , isolated as the Ba salt (α almost identical with that of the naturally occurring substance; A., 1932, 1269). HNO_3 readily converts (I) into the Ba salt, $[\alpha]_D^{25} -6.2^\circ$, changing after addition of HBr to $+2.4^\circ$, of *l*-phosphoglyceric acid. Natural *l*-4-hydroxyproline with P_2O_5 and H_3PO_4 gives the Ba salt (anhyd. and $+1\text{H}_2\text{O}$) of *l*-4-hydroxyproline-O-phosphoric acid, $[\alpha]_D^{25} -21.9^\circ$ in aq. BaCl_2 , dibrucine salt (anhyd. and $+5\text{H}_2\text{O}$), m.p. (anhyd.) 180—183° (indef.). The method fails with hydroxy-aspartic and -glutamic acids. Hydrogenation (Ni) of $\text{OH}\cdot\text{N}:\text{C}(\text{CO}_2\text{Et})_2$ in EtOH gives $\text{NH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{HCl}$, m.p. 170°, and the Et_2 ester, m.p. 124°, of 2 : 3-dicarbethoxydihydropyrazine-3 : 6-diacetic acid (converted into 3 : 6-dimethylpyrazine picrate, m.p. 157°) can be obtained by a similar reduction of Et_2 [α -oximino?] acetonedicarboxylate. F. S. H. H.

Chemical reactivity of cystine and its derivatives. J. S. FRUTON and H. T. CLARKE (J. Biol. Chem., 1934, 106, 667—691).—The following are described: *di*formyl- (I), m.p. 187—188°, $[\alpha]_D^{25} -162.1^\circ$, diacetyl- (II) (modified prep.), $[\alpha]_D -71.1^\circ$ in H_2O (Et ester, m.p. 122°), di(chloroacetyl)-, m.p. 136—138°, $[\alpha]_{548} -115.4^\circ$, diglycyl-, m.p. 197—199° (decomp.), $[\alpha]_{546}^{24} -87.7^\circ$, di- α -bromopropionyl-, m.p. 145—146.5°, $[\alpha]_{546}^{24} -93.4^\circ$, dialanyl-, m.p. 206°, $[\alpha]_{546}^{24} -180.2^\circ$, di(trichloroacetyl)-, m.p. 79—81° (decomp.), $[\alpha]_{546}^{24} -15.2^\circ$, dibenzenesulphonyl- (III), m.p. 213—214°, $[\alpha]_{546}^{24} +88.2^\circ$, *NN'*-dimethyldibenzenesulphonyl- (IV), an oil, from (III) with Me_2SO_4 and NaOH, and *NN'*-dibenzylidibenzenesulphonyl-cystine (V), from (III) with CH_2PhCl and NaOH, cystine phenylhydantoin (VI), m.p. 117—118°, cystine phenylhydantoic acid, m.p. 148—149°, $[\alpha]_{546}^{25} -54.1^\circ$, and $(\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S})_2\cdot 2\text{HCl}$ (VII), m.p. 214° (all $[\alpha]$ in *N*-NaOH). On reduction (II) gives acetyl-, m.p. 104.5°, (I) ($\text{Zn} + \text{HCO}_2\text{H}$) gives formyl-, m.p. 87—89° (effervesces), and (III) NaOH gives benzenesulphonyl-cysteine, m.p. 136—138°. *N*-Acyl substituents increase the lability of α during alkaline decomp. of cystine and cysteine derivatives (A., 1931, 76) in the order carbobenzyloxy $< \text{CO}\cdot\text{CCl}_3 < \text{glycyl}$, alanyl, phenylhydantoic acid $< \cdot\text{CO}\cdot\text{CHMeBr}$, $\cdot\text{CO}\cdot\text{CH}_2\text{Cl} < \text{Ac}$, $\cdot\text{CHO}$, and in general accelerate the formation of the aminoacrylic acid derivative formed as primary decomp. product. There is an induction period for the accumulation of AcU (VIII), and since an *N*-acyl substituent is present neither (VIII) nor $\text{NH}_2\cdot\text{OMe}$ affects the course of the reaction. Ring structures as in (VI) greatly increase the instability of the mol. (III) is relatively stable to alkali, but (IV), (V), and dibenzylidenecystine are less

so; $(\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot)$, (VII), and homocystine are very slowly decomposed. The effect of *N*-acyl substituents on the rate of autoxidation of cysteine derivatives is qualitatively similar to that on the alkaline decomp. of corresponding derivatives of cystine. Oxidation-reduction studies (this vol., 602) show that the $\cdot\text{SH}\cdot\text{S}\cdot\text{S}\cdot$ system behaves reversibly at p_{H} 7 and higher. In all cases examined potentials of about 0.23 volt at p_{H} 7 were observed. F. S. H. H.

Interaction of an acid amide with glycerol and ethylene glycol. R. ODA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 211—217).—Lauramide (I) and $[\text{CH}_2\cdot\text{OH}]_2$ (II) in equimol. amounts at 190° afford a monolauric ester as a result of a second-order reaction. With (I) and (II) in the ratio of 2:1, a mono-ester is first formed, followed by the di-ester. Glycerol reacts similarly. J. L. D.

Condensation of chloral and bromal hydrates with amides. A. N. MELDRUM and G. W. DEODHAR (J. Indian Chem. Soc., 1934, 11, 529—533).—Chloral- and bromal-amides are obtained by heating an equimol. mixture of $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ or $\text{CBr}_3\cdot\text{CH}(\text{OH})_2$ and amides until a solid is obtained. The corresponding anhydrides conform to the type, $(\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}\cdot\text{CCl}_3)_2\text{O}$, except in the case of chloral-salicylamide. Ac derivatives are obtained by dissolving the amides in $\text{C}_5\text{H}_5\text{N}$ and adding AcCl or by the action of Ac_2O containing H_2SO_4 and the Me ethers by the action of Me_2SO_4 and dil. NaOH . Reduction products are formed by use of AcOH and Zn dust, $\text{OH}\cdot\text{CH}\cdot\text{CCl}_3$ becoming $\cdot\text{CH}\cdot\text{CCl}_2$ and $(\text{OH})\text{CH}\cdot\text{CBr}_3$ being changed to $\cdot\text{CH}\cdot\text{CBr}_2$ or $\cdot\text{CH}\cdot\text{CHBr}$. The following -amides are described: *dichloral-malon*, m.p. 171°; *dichloral-succin*, m.p. 172°; *benzoylchloralacet*, m.p. 101—102°; *acetylchloral-n-butyr*, m.p. 84—86°; *benzoylchloral-n-butyr*, m.p. 126—127°; *methylchloral-n-butyr*, m.p. 94—95°; *anhydrochloral-n-butyr*, m.p. 173—174°; *acetylchloralbenz*, m.p. 153—154°; *chloral-p-tolu*, m.p. 152°; *dichloroethylene-p-tolu*, m.p. 101°; *acetylchloralphenylacet*, m.p. 152°; *benzoylchloralphenylacet*, m.p. 164°; *diacetylchloral-salicyl*, m.p. 134°; *anhydrochloral-salicyl*, m.p. 174—175°; *acetyl-anhydrochloral-salicyl*, m.p. 53—55°; *acetyl-bromalacet*, m.p. 120°; *bromal-n-butyr*, m.p. 145°; *bromalbenz*, m.p. 148°; *acetyl-bromalbenz*, m.p. 142°; *benzoyl-bromalbenz*, m.p. 164—165°; *methyl-bromalbenz*, m.p. 140—141°; *anhydrobromalbenz*, m.p. 199° (decomp.); β -*bromoethylenebenz*, m.p. 122—123°; *bromal-p-tolu*, m.p. 151°; β -*bromoethylene-p-tolu*, m.p. 128—129°; *bromalphenylacet*, m.p. 146°; *acetyl-bromalphenylacet*, m.p. 151°; *benzoyl-bromalphenylacet*, m.p. 143°; *methyl-bromalphenylacet*, m.p. 127—128°; *anhydrobromalphenylacet*, m.p. 150°; β -*bromoethylene-phenylacet*, m.p. 115—116°; *bromal-salicyl*, m.p. 161°; β -*dibromoethylenesalicyl*, m.p. 177°; *bromal-o-methoxybenz*, m.p. 141—142°; *acetyl-bromal-o-methoxybenz*, m.p. 115—117°; *methyl-bromal-o-methoxybenz*, m.p. 103—104°; *anhydrobromal-o-methoxybenz*, m.p. 185—186°; β -*bromoethylene-o-methoxybenz*, m.p. 128°. H. W.

Carbamide from diphenyl carbonate and aqueous ammonia. G. A. KIRKGOFF and R. Y. ASTROVA (Khim. Farm. Prom., 1933, 281).—Dry

Ph_2CO_3 (224 g.) is heated with 22% aq. NH_3 (160 g.) until the homogeneous mixture gives no ppt. of Ph_2CO_3 with H_2O (2 hr.). $\text{CO}(\text{NH}_2)_2$ is extracted with H_2O ; yield 70%. PhOH is regenerated.

CH. ABS.

Organic compounds of thallium. I. Pseudo-metallic character of the residue TlR_2 . II. Cyclic organo-thallium compounds. W. VON PLATZ (Helv. Chim. Acta, 1934, 17, 1073—1076).—The salts of TlR_2 ($\text{R}=\text{Me}$, Et , or Ph) do not resemble those of Ag , Hg^{I} , or Hg^{II} or the alkali metals, but are similar to those of Tl^{I} (cf. Erlenmeyer, A., 1933, 557; Perret *et al.*, *ibid.*, 815). Attempts to prepare compounds with Tl in the ring were unsuccessful. Thus the Grignard compound from Mg and $\text{Br}[\text{CH}_2]_5\text{Br}$ gives Tl , TiCl , and a resin with TiCl_3 and TiPh_2Cl , m.p. > 300°, and a resin with TiPhCl_2 . H. W.

Complex compounds of iridium. III. Compounds with ammonia and ethylamine. P. C. RAY and N. ADHIKARI (J. Indian Chem. Soc., 1934, 11, 517—520).—When heated with 50% $\text{NH}_2\text{Et}\cdot\text{EtOH}$ at 140—145°, $\text{IrCl}_3\cdot 3\text{Et}_2\text{S}$ affords the compounds $\text{IrCl}_3\cdot 3\text{NH}_2\text{Et}$, m.p. 220° (decomp.), $\text{IrCl}_3\cdot 4\text{NH}_2\text{Et}$, m.p. 281—282° (decomp.), and $\text{IrCl}_3\cdot 5\text{NH}_2\text{Et}$. The substances, $\text{IrCl}_3\cdot \text{Et}_2\text{S}\cdot 2\text{NH}_3$ and $\text{IrCl}_3\cdot 5\text{NH}_3$, are derived from $\text{IrCl}_3\cdot 3\text{Et}_2\text{S}$ and $\text{NH}_3\cdot\text{H}_2\text{O}$ at 135—145°. H. W.

Characteristic transformation of cyclohexane under the influence of contact with nickel catalyst. N. D. ZELINSKI and N. I. SCHUIKIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 255—258).—*cycloHexane* is converted at 300—350° in a H_2 atm. ($\text{Ni}\cdot\text{Al}_2\text{O}_3$ catalyst) into CH_4 , C_6H_6 , PhMe , xylene, methyl- and dimethyl-*cyclohexane*. The formation of free CH_2 is inferred. R. T.

Theory of the stability of the benzene ring and related compounds.—See this vol., 1158.

Action of aluminium chloride on benzene and cyclohexane. V. N. IPATIEV and V. I. KOMAREWSKY (J. Amer. Chem. Soc., 1934, 56, 1926—1928).— C_6H_6 (saturated with HCl) with 10% (wt.) of AlCl_3 in N_2 at 125° for 24 hr. gives 1.7% (on C_6H_6 used) of PhEt (isolated from the upper layer) and 0.84% of Ph_2 and a little unsaturated ethylenic polymeride (both isolated from the lower layer after decomp. with ice). The following changes probably occur: (i) $2\text{C}_6\text{H}_6 \rightarrow \text{Ph}_2 + \text{H}_2$; (ii) decomp. of the C_6H_6 and hydrogenation of the fragments to C_2H_4 ; ethylation by C_2H_4 (the whole process is termed “destructive alkylation”). Phenols and other O-containing compounds are not produced, indicating that the results of Wertyporoch and Sagel (A., 1933, 1152) are due to the presence of O_2 and H_2O in the reaction mixture. *cycloHexane* similarly gives (at 150°) methylcyclopentane, 1:3-dimethylcyclohexane (6.5%) (formed by isomerisation of ethylcyclohexane, which arises by destructive alkylation), 12.1% of a mixture of dicyclohexyl (25%) and dimethyldicyclopentyl (75%), and 0.7—0.8% of gas (containing 61% of isobutane, formed by destructive hydrogenation). H. B.

Mode of studying nitration. II. Isomeric ratios in dinitrobenzene. F. E. POUNDER and I. MASSON (J.C.S., 1934, 1352—1357; cf. A., 1933, 267).

—By thermal analysis (confirmed by chemical analysis of the *m*-isomeride) it is shown that PhNO_2 with varying ratios of H_2SO_4 , HNO_3 , and H_2O at 35° gives 89.6—91% of *m*-, 7.3—9.0% of *o*-, and 1.1—2.1% of *p*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$ (I). Increase in the concn. of H_2SO_4 increases the *m*/(*o*+*p*) ratio (0.2—0.25 for a 10% increase), decreases the amount of *o*- (9.0% in pure HNO_3), and increases the amount of *p*-isomeride. A mixture of H_2SO_4 50, HNO_3 29.6, and H_2O 20.4 mols.-% at 0° , 35° , and 60° gives 93.7, 90.15, and 87.3% of *m*-, 5.8, 8.1, and 11.5% of *o*-, and 0.5, 1.75, and 1.2% of *p*-(I), respectively (cf. lit.). The yield of crude (I) at 35° is 96.8%, loss being partly (2%) due to solubility of (I) in H_2O and to formation of nitrophenols from *m*-(I) and the acids. The previous hypothesis that *m*-nitration is due to formation of $\text{PhNO}_2\cdot\text{H}^+$ is confirmed and it is concluded that H_2SO_4 is most effective in formation of this ion. No dinitration occurs at 35° with AcOH 52, HNO_3 39, and H_2O 9 mols.-%. R. S. C.

Structure of a *p*-xylylene. (MLLE.) S. ALLARD (Compt. rend., 1934, 199, 423—424).—Triphenyl- α -naphthyl-*p*-xylylene, m.p. 238—239°, and the chloride from which it is prepared, are highly paramagnetic and thus contain two C^{III} atoms. The paramagnetism of $\text{CPh}_2\cdot\text{C}_{10}\text{H}_7\cdot\alpha$ is confirmed. R. S. C.

Phenyl tolyl and ditolyl sulphoxides. C. COURTOT and J. FRENKIEL (Compt. rend., 1934, 199, 557—559; cf. A., 1932, 506).— $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{SOCl}$ with C_6H_6 containing AlCl_3 affords *Ph o-tolyl sulphoxide*, m.p. 42° . Similarly were prepared *Ph m-tolyl*, b.p. $215^\circ/12$ mm. (*sulphone*, m.p. 109°), and *o-tolyl p-tolyl sulphoxide*, b.p. $210^\circ/9$ mm. [*sulphone*, m.p. 60° ; *o-tolyl di-p-tolylsulphonium chloride*, m.p. 128° (cf. this vol., 177)]. *o*-Tolyl *m*-tolyl sulphide (cf. A., 1906, i, 948) with H_2O_2 gives first the *sulphoxide*, b.p. $213^\circ/9$ mm., and then the *sulphone*, m.p. 82° . Similarly prepared, *m*-tolyl *p*-tolyl *sulphoxide* has m.p. 72° . *Di-o-tolyl* and *di-p-tolyl sulphoxide*, m.p. 121° and b.p. $215^\circ/15$ mm., respectively, are prepared by the method of Strecker (A., 1910, i, 532). J. L. D.

Diphenyl series. III. Cain's supposed 4'' : 4'''-disubstituted tetranitrobenzerythrenes. H. H. HODGSON and P. F. HOLT (J.C.S., 1934, 1431—1433; cf. A., 1926, 1133).—The supposed tetranitrobenzerythrene derivatives of Cain *et al.* (J.C.S., 1913, 103, 274) are really impure 3 : 3'-dinitrobenzidine, m.p. 200° , and its 4 : 4'- Cl_2 - (I), m.p. 237° , $-\text{Br}_2$ -, m.p. 259° , $-(\text{CN})_2$ -, m.p. 280° , and $-(\text{CNS})_2$ -, m.p. 307° , derivatives. (I) with Fe-AcOH affords 4 : 4'-*dichloro-3 : 3'-diaminodiphenyl*, m.p. 133.5° (*dihydrochloride*, m.p. 267° ; Ac_2 , m.p. 254° , and Bz_2 , m.p. 260° , derivatives), whence $[\text{p-C}_6\text{H}_4\text{Cl}]_2$ was obtained. R. S. C.

Absorption spectra of some carotenoid pigments at liquid-air temperatures.—See this vol., 1275.

Cracking of polycyclic compounds. S. YAMAGUCHI (Bull. Chem. Soc. Japan, 1934, 9, 303—319).—When C_{10}H_8 is heated with H_2 ($450\text{--}500^\circ/80$ atm.) in presence of CaCl_2 for 5 hr. at 500° , 60% is converted into the following lower hydrocarbons, the molar yields being given in parentheses: C_6H_6 (0.08), PhMe (0.20), *o*-xylene (0.22), CH_4 (0.40), C_2H_6 (0.46). Anthracene

is converted into 20% of gaseous hydrocarbons [CH_4 (0.401), C_2H_6 (0.967)], 37.6% of C_{10}H_8 homologues [C_{10}H_8 (0.220), $\text{C}_{10}\text{H}_8\text{Me}_2$ (0.357)], 21.6% of benzenoid hydrocarbons [C_6H_6 (0.146), PhMe (0.295), *o*-xylene (0.113)] and 8% of dianthracene at 450° . Quinoline undergoes 90% conversion into NH_2Ph (0.04), $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ (0.18), $\text{o-C}_6\text{H}_4\text{Et}\cdot\text{NH}_2$ (0.06), $\text{o-C}_6\text{H}_4\text{Pr}\cdot\text{NH}_2$ (0.03), $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NHMe}$ (0.02), $\text{o-C}_6\text{H}_4\text{Me}\cdot\text{NHEt}$ (0.03), methylindole, (0.16), C_6H_{12} (0.03), $\text{C}_6\text{H}_{11}\text{Me}$ (0.03), $\text{C}_6\text{H}_{11}\text{Et}$ (0.03), $\text{C}_6\text{H}_{11}\text{Pr}$ (0.04), PhMe (0.007), PhEt (0.006), PhPr (0.004), CH_4 (0.44), C_2H_6 (0.26), NH_3 (0.21), but no trace of $\text{C}_6\text{H}_5\text{N}$ (I), and isoquinoline gives (I) (0.03), $\text{C}_6\text{H}_4\text{MeN}$ (0.03), $\text{C}_6\text{H}_3\text{Me}_2\text{N}$ (0.03), PhMe (0.06), *o*-xylene (0.15), indane (0.20), dimethylantracene (0.01), CH_4 (0.43), C_2H_6 (0.18), and NH_3 (0.65). S. C.

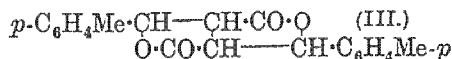
Sensitivity of aromatic nitro-compounds to light. V and VI. *peri*-Derivatives of 1-nitronaphthalene. R. E. STEIGER (Helv. Chim. Acta, 1934, 17, 1142—1157, 1354—1360).—V. Nitration of 5-methylnaphthalene-8-sulphonyl chloride with HNO_3 (*d* 1.475) at -5° to 0° leads to a mixture of isomerides from which 5-nitro-1-methylnaphthalene-4-sulphonyl chloride (I), decomp. about 170° (corr.), varying greatly with mode of heating, is separated by C_6H_6 and COMe_2 . From (I) are prepared the corresponding -sulphonamide, m.p. about 228° (corr.) when placed in bath at 224° , -sulphonmethylamide, m.p. $243\text{--}244^\circ$ (corr., slight decomp.) when placed in a bath at 239° , -sulphondimethylamide, m.p. $171.5\text{--}172.0^\circ$ (corr.); -sulphonethylamide, m.p. $185.5\text{--}186.0^\circ$ (corr.); -sulphonanilide, m.p. 256° (corr., slight decomp.); -sulphonmethylanilide, m.p. $244\text{--}245^\circ$ (corr.) when introduced into a bath at 240° (corr.); -sulphonethylanilide, m.p. $156\text{--}157^\circ$ (corr.). *Me*, m.p. $138\text{--}139^\circ$ (corr.) after softening, *Et*, m.p. $107.5\text{--}108.5^\circ$ (corr.), *Ph*, m.p. $175.5\text{--}176.5^\circ$ (corr.), and NH_3Ph , decomp. $244^\circ\pm 1^\circ$ according to mode of heating, 5-nitro-1-methylnaphthalene-4-sulphonate are described. 1-Methylnaphthalene-4-sulphonmethylamide has m.p. $165\text{--}166^\circ$ (corr.).

VI. Exposure of derivatives (I) of 1-nitronaphthalene-8-sulphonic acid, $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\text{R}$, and those (II) of its 5-Me derivative, $\text{NO}_2\cdot\text{C}_{10}\text{H}_5\text{Me}\cdot\text{SO}_3\text{R}$, to light in the solid state produces discoloration, which is always more rapidly obvious with (II) than with (I). In the case of (II) the photosensitiveness diminishes in the sequence, $\text{R}'=\text{NHMe}$, NMe_2 , OEt , NH_2 , OMe , NHEt , NPhMe , NHPh , OPh ; with (I) the corresponding sequence is $\text{R}=\text{NHEt}$, NEt_2 , NPhEt , NPhEt , NHMe , OEt . In solution (usually in C_6H_6 or $\text{C}_5\text{H}_5\text{N}$), the photosensitiveness of (II) is $> \text{OEt}$. It increases when NH is transformed into NPh , when Ph is replaced by Me or Me by Et in mono- or *ci*-substituted amides or in esters, when NHR is replaced by OR , and when OR passes into NHPh . H. W.

Syntheses of 2-phenylnaphthalenes. F. S. SPRING (J.C.S., 1934, 1332—1335).—Deoxybenzoin and $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ (acetoacetic acid) $\beta\gamma$ -diphenylbutyrate, m.p. $57\text{--}58^\circ$ [corresponding (I), m.p. 120°], giving with hot Ac_2O and subsequent hydrolysis 20% of β -benzylcinnamic acid, *re u* by Na-Hg to $\beta\gamma$ -diphenylbutyric acid (II), *ab* from (I) P and HT (II affords

with 80% H_2SO_4 at 100° 1-keto-3-phenyl-1:2:3:4-tetrahydronaphthaleno [semicarbazone, m.p. 211° (lit. 208°)], which by reduction (Clemmensen) and dehydrogenation yields 2- $\text{C}_{10}\text{H}_7\text{Ph}$. α -Phenylpropio-phenone by similar reactions leads to β -hydroxy- β - γ -diphenylvaleric acid, m.p. 178° (unchanged by Ac_2O), β - γ -diphenylvaleric acid, m.p. 132° (by red P and HI), 4-keto-2-phenyl-1-methyl-1:2:3:4-tetrahydronaphthalene, m.p. 68° (semicarbazone, m.p. 221°), and 2-phenyl-1-methylnaphthalene, m.p. 84° (semipicrate, m.p. 83° , decomposed by crystallisation). R. S. C.

Homologues of naphthacene. I. 2:6-Dimethylnaphthacene. E. A. COULSON (J.C.S., 1934, 1406—1412).— p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}_2\text{H}$ (best obtained from p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$ and NaOBr) and PBr_3 give p -toluoyl bromide, b.p. $173^\circ/113$ mm., which by condensation with $\text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et}$ and treatment with cold aq. $\text{NH}_4\text{Cl}\cdot\text{NH}_3$ affords Et p -toluoylacetate, b.p. $133^\circ/2$ mm. (42%), and thence (NaOEt; I) Et₂ di- p -toluoyl-succinate, β - (I), m.p. 145° , and γ -forms, m.p. 82 — 83° . Both isomerides with hot NaOH-EtOH afford $\alpha\beta$ -di- p -toluoylthane, m.p. 161° (lit. 159°) (rapidly converted by a little hot, conc. HCl into 2:5-di- p -tolylfuran, m.p. 166°), and both at 320° give rapidly 9:10:11:12-tetraketo-2:6-dimethyl-9:10:11:12:15:16-hexahydronaphthacene (II), m.p. 320° , and Et₂ 2:5-di- p -tolylfuran-3:4-dicarboxylate, m.p. 118° [corresponding acid, m.p. 264° (decomp.)]. (II) is not vatted by Zn dust and aq. NH_3 , is unaffected by Clemmensen reduction, with Zn-Hg in AcOH-HCl gives resins, and sublimes from Se at $>280^\circ$. With 50% aq. NaOH (II) rapidly gives a gummy acid (not isoethinedipthalide). The Na derivative of (I) with I in Et₂O gives the dilactone (III), m.p. 228 — 229° , of $\alpha\delta$ -dihydroxy- $\alpha\delta$ -di- p -tolylbutane- $\beta\gamma$ -dicarboxylic acid. Fumaryl chloride,



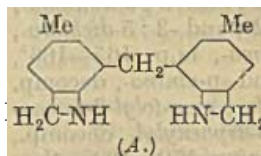
b.p. 157 — 162° (obtained by PCl_5 , but not by SOCl_2), with m -xylene and AlCl_3 in CS_2 affords trans- $\alpha\beta$ -bis-2:4-dimethylbenzoylthylene (IV), yellow, m.p. 129 — 130° [previously (A., 1923, i, 1098) called erroneously di-(2:4-xylyl)ethylene] [$\alpha\beta$ -dibromide, m.p. 146° (decomp.)], reduced by Zn dust in AcOH to $\alpha\beta$ -bis-2:4-dimethylbenzoylthane (V), m.p. 131 — 132° , which with hot HCl-AcOH gives 2:5-di-4'- m -xylylfuran (VI), m.p. 95 — 96° . (IV) in sunlight or with hot HCl-AcOH or KOH-EtOH gives the unstable, colourless cis-isomeride, cryst., low m.p. (IV) at 315° gives 2:4-dimethylbenzoic acid (V), 2:4-dimethylacetophenone, (VI), and a little 2:6-dimethylnaphthacene (VII), m.p. 365° (350 — 360° after darkening, if slowly heated) [9:10-quinone, m.p. 249° (decomp.)]. 3:7-Dimethyl- β -naphthylamine [best obtained from the naphthol, $(\text{NH}_4)_2\text{SO}_3$, and aq. NH_3 at 200°], m.p. 129° [hydrochloride, m.p. 275° (decomp. from 200°); Ac derivative, dimorphic, m.p. 231°], gives (Sandmeyer) the 2-nitrile, m.p. 160° , hydrolysed (KOH) to 3:7-dimethyl-2-naphthoic acid, m.p. 228° (anilide, m.p. 238°) (also obtained in poor yield from the Na 2-sulphonate and KCN), the chloride, m.p. 79° , b.p. 182 — $185/6$ mm., of which yields (AlCl_3 , PhMe, 40 — 50) 3- p -toluoyl-2:6-dimethylnaphthalene, m.p. 168° . At 400° this gives slowly a little (VII) and much 2:6-dimethyl-

9:10-dihydronaphthacene, m.p. 217° , dehydrogenated (Se; 230°) to (VII).

R. S. C.

β -isoPropylnaphthacene. J. W. COOK (J.C.S., 1934, 1412).—2:3- $\text{C}_{10}\text{H}_8(\text{CO})_2\text{O}$ and AlCl_3 in cold cumene give 2-cuminyol-3-naphthoic acid, m.p. 218 — 219° , reduced (Zn-KOH) to 2-isopropylbenzyl-3-naphthoic acid, m.p. 183° , which with ZnCl_2 at 185 — 190° affords 6-isopropyl-2:3-benz-10-anthrone, m.p. 180° , oxidised (CrO_3) to the quinone, m.p. 131 — 132° , and reduced (Zn-NaOH-aq. EtOH) to 6-isopropyl-2:3-benzanthracene (β -isopropylnaphthacene), m.p. 273 — 274° , non-carcinogenic. R. S. C.

Condensation of aromatic amines with formaldehyde in media containing acid. I. p -Toluidine. A. EISNER and E. C. WAGNER. **II. Formation of diarylmethane bases.** E. C. WAGNER (J. Amer. Chem. Soc., 1934, 56, 1938—1943, 1944—1946).—I. Prolonged interaction of p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$ (I), 37% CH_2O (1.1 equivs.), and an excess of 3- N -HCl at or $<$ room temp. gives a base $\text{C}_{24}\text{H}_{27}\text{ON}_3$ (II) [described by Lepetit *et al.* (A., 1928, 284) as $\text{C}_{17}\text{H}_{18}\text{ON}_2$], m.p. 139 — 140° (corr.) [hydrochloride, m.p. 246° ; picrate, m.p. 203° (corr.)], the base $\text{C}_{17}\text{H}_{18}\text{N}_2$ (III), m.p. 135° (corr.) (Troeger, A., 1888, 286; cf. *loc. cit.*) [hydrochloride, m.p. 215° ; picrate, m.p. 172.6° (corr.) (lit. 186°); (NO_2)-derivative, m.p. 253° (corr.) (lit. 260 — 264°)], 3- p -tolyl-6-methyl-3:4-dihydroquinazoline (IV), m.p. 162.5° (corr.) (cf. Maffei, A., 1928, 775) [dihydrochloride, m.p. about 212° ; picrate, m.p. 210° (corr.)], small amounts of p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NHMe}$ (V) and p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NMe}_2$ (VI), and resinous material. The base $\text{C}_{17}\text{H}_{20}\text{ON}_2$ of Lepetit *et al.* (*loc. cit.*) was not found. Reduction (Zn dust, 3- N - H_2SO_4) of (II) gives small amounts of (I) and (V); with Sn and EtOH-conc. HCl, (I) and a little m -4-xylylidine (VII) result. (II) is considered to be 2-hydroxy-3- p -tolyl-6-methyl-1- p -toluidinomethyl-1:2:3:4-tetrahydroquinazoline and is probably formed from (I) and (VIII) (below) with subsequent ring closure by HCO_2H (which is produced during the condensation). (III) could not be reduced (Zn dust, 6- N - H_2SO_4); the constitution (A) is assigned. Reduction (Sn, HCl) of (IV) affords (I) and (VII). o -Amino- m -xylyl- p -toluidine [p -tolyl-(2-amino-5-



methylbenzyl)amine] (VIII), m.p. 88° (corr.), obtained by prolonged interaction of (p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$)₂ CH_2 (I), and p - $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{HCl}$ in PhNO_2 at 20° , is reduced (cf. A., 1933, 387) to (I) and (VII). (VIII) and 37% CH_2O in EtOH-KOH give 3- p -tolyl-6-methyl-1:2:3:4-tetrahydroquinazoline, m.p. 141° (lit. 138°), also obtained by reduction (Na, EtOH) of (IV). (IV) is also prepared from (VIII) and HCO_2H (cf. von Walther and Bamberg, A., 1906, i, 385). (VI) is the sole volatile product obtained when < 2 mols. of CH_2O per mol. of (I) are used in the above condensation. Werner's mechanism (J.C.S., 1917, 111, 844) of methylation by CH_2O is preferred to that of Maffei (*loc. cit.*).

II. Dialkyldiaminodiphenylmethanes (accompanied by higher condensation products) are obtained in 46—62% yield from NHPhAlk , 37% CH_2O (slightly < 0.5 equiv.), and 6- N -HCl (1.1—2.5 equivs.) (cf. von

Braun, A., 1908, i, 684); the following are described: dimethyldiamino-, b.p. 261—262°/9 mm. (Ac_2 derivative, m.p. 121°), diethyldiamino-, b.p. 265—267°/9 mm., *di-n-propyldiamino*-, b.p. 275—276°/9 mm. [$(NO)_2$ -derivative, m.p. 49·5°], *di-n-butyldiamino*-, b.p. 292°/9 mm. (Bz_2 derivative, m.p. 95°), and *diisooamyl-diamino*-, b.p. 301—303°/9 mm., *-diphenylmethanes*. $o-C_6H_4Me \cdot NH_2$ similarly gives 70% of 4:4'-diamino-3:3'-dimethyldiphenylmethane, m.p. 158° (*picrate*, m.p. 192—193°; Ac_2 , m.p. 224°, Ac_4 , m.p. 119°, and Bz_2 , m.p. 214·5°, derivatives), whilst $m-C_6H_4Me \cdot NH_2$ affords 70% of 4:4'-diamino-2:2'-dimethyldiphenylmethane, m.p. 123° [*hydrochloride*, (+ H_2O), m.p. 258° (decomp.); *picrate*, m.p. 216·5° (decomp.); Ac_2 derivative, m.p. 228°]. 4:4'-Diaminodiphenylmethane (*picrate*, blackens at 225°; Ac_4 derivative, m.p. 170—171°), similarly prepared in 41% yield, is best obtained by Rivier and Farine's method (A., 1929, 1437). 2:2'-Diamino-5:5'-dimethyldiphenylmethane, m.p. 96° [*picrate*, m.p. 198·7° (decomp.); Ac_2 m.p. 226·5°, and Ac_4 , m.p. 152°, derivatives], could not be similarly obtained from $p-C_6H_4Me \cdot NH_2$; it is best prepared (cf. Eberhardt and Welter, A., 1894, i, 451) from (VIII) (above), $p-C_6H_4Me \cdot NH_2$, and $p-C_6H_4Me \cdot NH_2 \cdot HCl$ at 120—130°. H. B.

Reaction of certain primary amines with phenyl- and *o*-tolyl-thiocarbimide. M. F. GOERING and M. E. POTTEBAUM (Amer. J. Pharm., 1934, 106, 344—346).—From $PhSCN$ and the appropriate arylamine are prepared *as-phenyl-2:4-dibromo*-, m.p. 171°, *4-chloro-2-bromo*-, m.p. 171°, *-2-chloro-4-bromo*-, m.p. 170·5°, *-2:5*-, m.p. 172°, and *-3:5-dibromo*-, m.p. 163°, *-2:5*-, m.p. 165—166°, and *-3:5-dichloro*-, m.p. 155°, and *-3:5-dinitro*-, m.p. 190—191°, *-phenylthiocarbamide*; *as-phenyl-3-bromo*-, m.p. 157—158°, and *-3:5-dibromo-*o*-tolyl*-, m.p. 169°, *-2-bromo-4-methoxy-*m*-tolyl*-, m.p. 150—151°, *-*p*-anisyl*-, m.p. 146°, and *-*p*-diphenyl*-, m.p. indef., *-thiocarbamide*. Similarly from $o-C_6H_4Me \cdot SCN$ are obtained *as-*o*-tolyl-2:4*-, m.p. 164°, *-2:5*-, m.p. 179—180°, and *-3:5-dibromo*-, m.p. 162°, *-2:5*-, m.p. 161—162°, and *-3:5-dichloro*-, m.p. 153—154°, *-4-chloro-2-bromo*-, m.p. 165—166°, *-2-chloro-4-bromo*-, m.p. 162°, and *-*p*-amino*-, decomp. about 210°, *-phenylthiocarbamide*; *as-*o*-tolyl-2-bromo-4-methoxy-*m*-tolyl*-, m.p. 159°, *-*p*-diphenyl*-, decomp., and *-4'-amino-*o*-diphenyl*-, decomp. 170—190°, *-thiocarbamide*. J. W. B.

Reaction between aromatic carbimides and organic acids. I. Theory and application of the reaction to the preparation of acid anhydrides. C. NAEGELI and A. TYABJI (Helv. Chim. Acta, 1934, 17, 931—957).—The following scheme is suggested in explanation of the course of the reaction between aromatic carbimides and org. acids: $NR_2C \cdot O + R' \cdot CO_2H \rightarrow NR_2C(OH) \cdot O \cdot COR' \rightarrow R \cdot NH \cdot CO \cdot O \cdot COR' (I) \rightarrow (R' \cdot CO)_2O + (R \cdot NH \cdot CO)_2O \rightarrow CO(NHR)_2; (I) \rightarrow R \cdot NH \cdot COR' + CO_2$. Detailed study has been made of the anhydriding action of $PhNCO$, its 2-, 3-, and 4- NO_2 -, 3:5-(NO_2)₂-, and 3-benzeneazo-derivatives on $AcOH$, stearic acid, $CH_2Ph \cdot CO_2H$, $CH_2Ph \cdot CH_2 \cdot CO_2H$, $BzOH$, $CHPh \cdot CH \cdot CO_2H$, $CCl_3 \cdot CO_2H$, sebacic acid, $CN \cdot CH_2 \cdot CO_2H$, isovaleric, pivalic, and crotonic acids. Reaction is generally effected in C_6H_6 or, preferably,

in $PhMe$. The rate of reaction diminishes very rapidly with increasing dilution of the reactants, but the direction of decomp. of the mixed anhydrides is almost independent of the concn. of the initial materials. Disproportionation of the mixed anhydrides is favoured by high temp., whereas at lower temp. the change swings in the direction of acyl derivatives. Anhydridation of carboxylic acids is best effected in conc. carbimide solution in presence of the calc. amount of acid, and, if possible, at raised temp. Dil. carbimide solutions necessitate either the use of an excess of acid or very prolonged experiment. $NPh \cdot CO$ is inferior to its nitrated derivatives in rate of reaction, in that it gives marked amounts of acylated amines at low temp., and because $CO(NHPh)_2$ in boiling C_6H_6 or to a greater degree in boiling $PhMe$ is converted into 2 mols. of acylated NH_2Ph by equiv. amounts of acid anhydride or even by excess of acid. H. W.

Manufacture of 4-amino-3-alkoxydiphenylamine derivatives.—See B., 1934, 825.

Chlorination of *o*-toluidine, *p*-xylydine, cresidine, and other arylamines.—See B., 1934, 874.

Manufacture of *as*-thiocarbamides.—See B., 1934, 874.

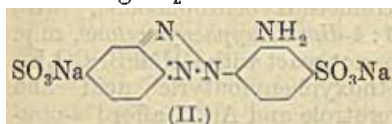
Use of dielectric constant in the study of reactions in organic solvents. P. LAURENT (Compt. rend., 1934, 199, 582—584).—By observation of the changes in ϵ on mixing C_6H_6 solutions of the reacting compounds, evidence has been obtained for the existence of the following compounds: $NPh \cdot NPh + 1$ and $2o-C_6H_4(OH) \cdot NO_2$ [or $2:4-C_6H_3(NO_2)_2 \cdot OH$]; $NHPh \cdot NPh + 1$ and $2o-C_6H_4(NO_2)_2$; $PhCN, o-C_6H_4(OH) \cdot NO_2$; $CHPh_3, C_5H_5N$; $o-C_6H_4(NH_2) \cdot NO_2, C_5H_5N$; $m-C_6H_4(NH_2) \cdot NO_2, 2:4-C_6H_3(NO_2)_2 \cdot OH$; $NHPh_2, C_5H_5N$; $NHPh_2, o-C_6H_4(NO_2) \cdot OH$, diphenylguanidine, C_5H_5N and diphenylguanidine, $o-C_6H_4(OH) \cdot NO_2$. J. W. S.

Preparation of acetophenetidide from *p*-aminoacetanilide. H. L. HALLER and G. L. KEENAN (J. Assoc. Off. Agric. Chem., 1934, 17, 512—516).— $p-NH_2 \cdot C_6H_4 \cdot NHAc$ is diazotised and treated with HBf_4 . The *p*-acetamidobenzenediazonium borofluoride, m.p. 135° (decomp.), is heated with Ac_2O , giving *p*-acetoxycetanilide, m.p. 151·5—152·5°, which when treated with EtI and $NaOEt$ gives acetophenetidide. E. C. S.

Electrochemical preparation of aromatic hydrazine compounds. F. FICHTER and E. WILLI (Helv. Chim. Acta, 1934, 17, 1416—1420).—Sulphobenzene-, benzene-, 4-chlorobenzene-, 4-bromobenzene-, α - and β -naphthalene-isodiazonium hydroxide smoothly pass into the corresponding hydrazines by indirect electrochemical reduction at a Hg cathode in alkaline solution with intermediate formation of $Na-Hg$. In the case of sulphanilic acid reduction of the normal diazonium hydroxide can be effected in alkaline solution or of the free acid in H_2SO_4 containing Na_2SO_4 , but the yields are inferior.

Azo-dyes and their intermediates. XV. *o*-Bisazo- and *oo'*-trisazo-dyes. III. and M. HINOKER (Helv. Chim. Acta, 1934, 17, 1

992; cf. A., 1932, 264; this vol., 520).—2:2'-Dinitroazobenzene-4:4'-disulphonic acid is reduced by Na-Hg to 2:2'-diaminoazobenzene-4:4'-disulphonic acid (I) (*Ac* and *Bz* derivatives), which after diazotisation with amyl nitrite couples slowly with 6- $C_{10}H_7\cdot OH$ and with 3-chloro- β -naphthol slowly yields the compound $C_{32}H_{18}O_8N_6Cl_2S_2Na_2$ in a sufficiently pure condition to establish that double coupling has occurred. Reduction of (I) with Zn dust and NH_4Cl in boiling H_2O leads to a mixture of *o*-amino-



phenylbenzotriazole-disulphonic acid (II) (*Ac* derivative) and 1:2:4- $C_6H_3(NH_2)_2\cdot SO_3H$

(corresponding phenanthrazine $C_{20}H_{11}O_3N_2SNa$). Diazotisation of (II) and coupling with 6-bromo- β -naphthol leads to the dye, $C_{22}H_{13}O_7N_5S_2BrNa_2$. Coupling of 3:3'-dihydroxyazobenzene (III) with 2 mols. of diazotised NH_2Ph in alkaline solution yields a dye which is difficult to purify, but is reduced by $SnCl_2$ and HCl or $Na_2S_2O_4$ in presence of $COMe_2$ and $EtOH$ to much resin, 3:4-diaminophenol (*Bz*₃ derivative, m.p. 225°), and NH_2Ph . The incidence of double coupling is established by the isolation of the substance $C_{24}H_{16}O_2N_6Br_2$, m.p. 155° (decomp.) [reduced to diaminophenol and $p\text{-}C_6H_4Br\cdot NH_2$ and decomposed by hot $NaOH$ into (III), N_2 , and resin], from (III) and diazotised $p\text{-}C_6H_4Br\cdot NH_2$. From (III) and diazotised $p\text{-}NO_2\text{-}C_6H_4\cdot NH_2$ an (impure) dye, $C_{24}H_{16}O_6N_8$, m.p. 183°, is derived. (III) and diazotised $p\text{-}NH_2\text{-}C_6H_4\cdot SO_3H$ give a non-homogeneous product, whereas diazotised naphthionic acid gives the expected compound, $C_{32}H_{20}O_8N_6S_2Na_2$ (*Bz*₂ derivative), reduced to naphthionic acid and diaminophenol. 3:3'-Diaminoazobenzene (IV) reacts very slowly with diazo-components, apparently giving diazoamino-compounds. (IV) and $PhNO$ give 3:3'-trisazobenzene, m.p. 165°. H. W.

Azotriphenylmethane and azopyrnone dyes (ortho-series). R. N. SEN and S. N. ROY (J. Indian Chem. Soc., 1934, 11, 521—528).— $m\text{-}OH\text{-}C_6H_4\cdot CHO$ can be coupled with diazotised NH_2Ph with minimal evolution of N_2 if reaction occurs at -6° to -8° and $NaOH$ is replaced by Na_2CO_3 in presence of $NaOAc$. Evolution of N_2 occurs also with other diazotised amines, but is not observed if NO_2 , Br , SO_3H , or CO_2H is present in the amine. The following -azo-*m*-hydroxybenzaldehydes are described: benzene- (I), m.p. 127° (semicarbazone, m.p. 250°); 1-naphthalene- (II), m.p. 167—168° (semicarbazone, m.p. 251°); *p*-toluene- (III), m.p. 130° (semicarbazone, m.p. 251°); *o*-nitrobenzene- (IV), m.p. 150—151° (semicarbazone, m.p. 250°); *p*-nitrobenzene- (V), m.p. 175° (semicarbazone, m.p. 246°); *m*-nitrobenzene- (VI), m.p. 130° (semicarbazone, m.p. 243°); *p*-bromobenzene-, m.p. 130°; *o*-carboxybenzene-, m.p. 162°; *p*-sulphobenzene-. Condensation of the requisite azoaldehyde with $NPhMe_2$ and HCl at 100—115° leads to the following -azo-4-hydroxytetramethyldiaminotriphenylmethanes, which are oxidised to the corresponding carbinols by PbO_2 in cold $AcOH\text{-}HCl$: benzene-, m.p. 95—100° (decomp.); naphthalene-, m.p. 95—100° (decomp.); *p*-toluene-, m.p. 120—125° (decomp.); *o*-nitrobenzene-, m.p. 100—110° (decomp.); *m*-nitro-

benzene-, m.p. 100—110° (decomp.); *p*-nitrobenzene-, m.p. 100—110° (decomp.). With *o*-cresotic acid the following -azotrihydroxydimethyltriphenylmethanedicarboxylic acids are produced: benzene-, m.p. 208°; naphthalene-, m.p. 200°; *p*-toluene-, m.p. 210°; *o*-nitrobenzene-, m.p. 213°; *m*-nitrobenzene-, m.p. 212°; *p*-nitrobenzene-, m.p. 212°. (I), (II), (III), (IV), (V), and (VI) yield condensation products with $m\text{-}C_6H_4(OH)_2$ and pyrogallol, all of m.p. < 300°. The properties of the corresponding dyes are described.

H. W.

Preparation of alkylphenols. R. W. STOUGH-TON, R. BALTZLY, and A. BASS (J. Amer. Chem. Soc., 1934, 56, 2007—2008).—2-Butyryl-4-, b.p. 112—113°/1 mm., and -6-ethyl-, b.p. 170—175°/1 mm., m.p. 91—92°, 2-propionyl-4-, b.p. 115—118°/3 mm. (phenylhydrazones, m.p. 96°), and -6-propyl-, b.p. 164°/3 mm., m.p. 78—79°, 2-butyryl-4:5-, m.p. 40—41°, and -4:6-dimethyl-, b.p. 121°/2 mm. (phenylhydrazones, m.p. 168—170°), and 4-butyryl-2:5-dimethyl-, m.p. 131—132°, -phenols are prepared from the requisite aryl esters by Rosenmund and Schnurr's method (A., 1928, 1010). 4:4'-Dihydroxy-3:3'-diacetyl-, m.p. 219—219.5°, and -3:3'-dipropionyl-, m.p. 140—141°, -diphenyl, 2-valerylquinol, b.p. 174—176°/2 mm., and 4-hexoylpyrocatechol, m.p. 93—94°, are obtained essentially by Rosenmund and Lohfert's method (A., 1929, 188). The above acylphenols are reduced to the corresponding alkylphenols by the method of Coulthard *et al.* (A., 1930, 468); the following are described: 4-, b.p. 112—118°/5 mm., and 6-, b.p. 108—112°/2 mm., -ethyl-2-butyl-, 2:4-, b.p. 125—126°/10 mm., and 2:6-, b.p. 114—116°/5 mm., -dipropyl-, 4:5-, b.p. 135—140°/8 mm., m.p. 43—45°, and 4:6-, b.p. 106—108°/3 mm., -dimethyl-2-butyl-, and 2:5-dimethyl-4-butyl-, b.p. 130—132°/4 mm., -phenol; 4:4'-dihydroxy-3:3'-diethyl-, m.p. 119—120°, and -3:3'-dipropyl-, m.p. 113—114°, -diphenyl; 4-hexylpyrocatechol, b.p. 169°/4.5 mm., m.p. 25—26°; 2-amylquinol, b.p. 176—180°/3 mm., m.p. 85—86° (quinol and *Et* valerate are also produced during the reduction). H. B.

Reactions between hexamethylenetetramine and phenolic compounds. II. Formation of phenolic aldehydes. Distinctive behaviour of *p*-nitrophenol. J. C. DUFF and E. J. BILLS (J.C.S., 1934, 1305—1308; cf. A., 1932, 946).— $\beta\text{-}C_{10}H_7\cdot OH$ heated with $(CH_2)_6N_4$ in $AcOH$ affords 2:2'-dihydroxy-1-naphthylidene-1'-naphthylmethylamine (hydrochloride), readily hydrolysed by boiling $EtOH\text{-}HCl$ to 2-hydroxy-1-naphthylmethylamine and 2-hydroxy-1-naphthaldehyde. Contrary to Marotta *et al.* (A., 1932, 266) $\alpha\text{-}C_{10}H_7\cdot OH$ and $(CH_2)_6N_4$ in $AcOH$ give *s*-di- α -naphthoxydimethylamine (hydrochloride). $p\text{-}C_6H_4(NO_2)\cdot OH$ with $(CH_2)_6N_4$ in aq. $EtOH$ at 15° gives the additive compound $C_6H_4N_4\cdot 2C_6H_4(NO_2)\cdot OH$, but in H_2O at 100° is obtained bis-5-nitro-2-hydroxybenzyl-N-hydroxymethylamine, $OH\cdot CH_2\cdot N[CH_2\cdot C_6H_3(NO_2)\cdot OH]_2$, m.p. 255° (decomp.) ($Na_2\cdot 3H_2O$ salt; hydrochloride, sulphate, phosphate; *Bz*₂ derivative, m.p. 181°), oxidised by $KMnO_4\text{-}KOH$ to 5-nitrosalicylic acid and NH_3 , and reduced by $Sn\text{-}conc. HCl$ to the hydrochloride of bis-5-amino-2-hydroxybenzylamine. J. W. B.

Reaction of cerium [etc.] with pyrogallol.—See this vol., 1191.

Direct nitration of 5-chloro-3-hydroxy- and -3-nitro-anisole. H. H. HODGSON and W. E. BATTY (J.C.S., 1934, 1433—1435).—With NaNO_3 - H_2SO_4 5-chloro-3-hydroxyanisole (I) affords successively its 4- NO_2 - (II) and 4:6-(NO_2)₂-derivative (III), m.p. 126°, and with hot HNO_3 (*d* 1.47) the 2:4:6-(NO_2)₃-derivative, m.p. 147°, is obtained. 5-Chlororesorcinol Me_2 ether, m.p. 38° [from (I) and Me_2SO_4 - NaOH], with HNO_3 - Ac_2O gives successively its 4- NO_2 - and 4:6-(NO_2)₂-derivative (IV), m.p. 216° [identical with a specimen prepared from (III) and CH_2N_2]. With Ac_2O - HNO_3 (*d* 1.5) at 50° 5-chloro-2-nitroresorcinol Me_2 ether (V), m.p. 184° (A., 1928, 408 gives m.p. 171°), gives its 2:4-(NO_2)₂-derivative, m.p. 110°, and 5-chloro-3-nitroanisole with HNO_3 (*d* 1.4)- H_2SO_4 gives its 3:4:6-(NO_2)₃-derivative (VI), m.p. 128°. With boiling NaOMe - MeOH 2:4:6- $\text{C}_6\text{H}_2\text{Cl}_3$ - NO_2 affords 3:5-dichloro-2-nitroanisole (VII); at 120° some (V) is also obtained, and at 150°, nitrophloroglucinol Me_2 ether, m.p. 153° [converted by Ac_2O - HNO_3 into the known (NO_2)₂-derivative (VIII)], is formed. Cold NaOMe - MeOH converts 1:3:5:2:4- $\text{C}_6\text{HCl}_2(\text{NO}_2)_2$ in C_6H_6 into (VIII) and (IV). With warm NaOMe - MeOH (VI) gives (IV). With 20% KOH - EtOH at 130° (VII) gives 5-chloro-2-nitro-3-hydroxyanisole, m.p. 88° [depressed by (II)].

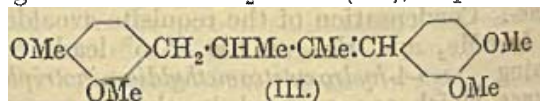
J. W. B.

Unsymmetrical aryl sulphides. N. E. FOSS, F. DUNNING, and G. L. JENKINS (J. Amer. Chem. Soc., 1934, 56, 1978—1980).— p - NO_2 - C_6H_4 - SCl (I) [from (p - NO_2 - C_6H_4)₂ S and Cl_2 in cold CHCl_3] and PhOH in Et_2O - CHCl_3 give about 20% of p -nitrophenyl hydroxyphenyl sulphide, m.p. 150—151° (acetate, m.p. 80.5—81.5°; Br_2 -derivative, m.p. 155—156°), reduced (Adams) to p -aminophenyl hydroxyphenyl sulphide, m.p. 151—152° [ON- Ac_2 derivative, m.p. 158.5—159°; azo-dye, $\text{C}_{22}\text{H}_{17}\text{O}_8\text{N}_2\text{S}_3$, by coupling with β -naphthol-3:6-disulphonic acid (II) in acid solution], which with KNCO in cold 50% AcOH affords p -carbamidophenyl hydroxyphenyl sulphide, m.p. 223—229°. (I) and m - $\text{C}_6\text{H}_4(\text{OH})_2$ similarly give 80—90% of p -nitrophenyl dihydroxyphenyl sulphide, m.p. 184—185° (cf. A., 1915, i, 398) (diacetate, m.p. 110—111°; Br_2 -derivative, m.p. 179—180°), converted (as above) into p -aminophenyl, m.p. 151—152° [ON- Ac_2 derivative, m.p. 158—158.5°; azo-dye, $\text{C}_{22}\text{H}_{17}\text{O}_8\text{N}_2\text{S}_3$, with (II)], and p -carbamidophenyl, m.p. 178—178.5°, dihydroxyphenyl sulphides. m -Cresol and (I) afford 80—90% of p -nitrophenyl hydroxytolyl sulphide, m.p. 193—193.5° (acetate, m.p. 98—99°; Br_2 -derivative, m.p. 204—205°), converted into p -aminophenyl, m.p. 149.5—150° [ON- Ac_2 derivative, m.p. 128—128.5°; azo-dye, $\text{C}_{23}\text{H}_{19}\text{O}_8\text{N}_2\text{S}_3$, with (II)], and p -carbamidophenyl, m.p. 201—201.5°, hydroxytolyl sulphides. Thymol and (I) give about 20% of p -nitrophenyl hydroxymethylisopropylphenyl sulphide, m.p. 116—117° (acetate, m.p. 77—78°; Br -derivative, m.p. 126—127°), converted into p -aminophenyl, m.p. 112.5—113° [ON- Ac_2 derivative, m.p. 90—91°; azo-dye, $\text{C}_{26}\text{H}_{25}\text{O}_8\text{N}_2\text{S}_3$, with (II)], and p -carbamidophenyl (III), m.p. 177—177.5°, hydroxymethylisopropylphenyl sulphides. Pharmacological data for the

carbamides are reported; only (III) possesses germicidal activity. H. B.

Constituents of guaiacum resin. II. Synthesis of *dl*-guaiaretic acid dimethyl ether. R. D. HAWORTH, C. R. MAVIN, and G. SHELDRIK (J.C.S., 1934, 1423—1429).— α -Bis-3:4-dimethoxyphenyl- Δ^a -propylene, b.p. 200—205°/0.3 mm., m.p. 78—79°, obtained together with *triveratrylmethane* (?), b.p. 220—270°/0.3 mm., m.p. 154—155°, from MgEtI and 3:4:3':4'-tetramethoxybenzophenone, with BzO_2H gives *as-bis*-3:4-dimethoxyphenylacetone, m.p. 123—124°, which does not react with $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$. 2-Bromo-4:5-dimethoxyphenylbutyric acid and OCl_2 , followed by veratrole and AlCl_3 , afford α -veratroyl- γ -(2-bromo-4:5-dimethoxyphenyl)propane, m.p. 82—84° (semicarbazone, m.p. 172—173°), reduced (Zn-Hg) to 2-bromo- α -bis-3:4-dimethoxyphenylbutane, m.p. 89—90°, which is further reduced (Pd-H_2) to α -bis-3:5-dimethoxyphenylbutane, m.p. 90—91° (2- Br -, m.p. 116—117°, and 2- NO_2 -derivatives, m.p. 184—185°). Attempts to condense γ -(2-bromo-4:5-dimethoxyphenyl)- α - β -dimethylbutyryl chloride, m.p. 104—105°, with veratrole gave 1-keto-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene. α -Cyano- α - δ -diphenylbutan- β -one, b.p. 190—200°/0.4 mm., m.p. 76—78°, obtained from $\text{CH}_2\text{Ph}\cdot\text{CN}$ and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, forms β -keto- α - δ -diphenylvaleramide, m.p. 128°, converted (HCl) into α - δ -diphenylbutan- β -one, b.p. 146—150°/0.2 mm., m.p. 43—44°, which with MgMeI yields α - δ -diphenyl- β -methyl- Δ^a -butene (dibromide, m.p. 91—92°). 2-Bromo-4:5-dimethylphenylacetone nitrile has m.p. 90—91° [azlactone of 2-bromo-4:5-dimethoxybenzaldehyde, m.p. 206°; 2-bromo-4:5-dimethoxyphenylpyruvic acid, m.p. 222—224°, and its oxime, m.p. 172—173° (decomp.)]. β -3:4-Dimethoxyphenyl- α -methylcrotonic acid (*Et* ester, b.p. 198—200°/15 mm., m.p. 97—98°) is reduced (Na-Hg) to the γ -propionic acid [*Me* ester (I), b.p. 153—154°/0.4 mm.], which gives the β -2-bromo-4:5-dimethoxy-acid, m.p. 94—95° (*Me* ester, b.p. 162—164°/0.2 mm.).

(I) and 3:4-dimethoxyphenylacetone nitrile give a nitrile, converted into β -keto- α - δ -3:4-dimethoxyphenyl- γ -methylvaleramide (II), m.p. 130—131°, which with HCl yields 3':4':5:6-tetramethoxy-3-benzyl-2-methylindene, m.p. 115—117°, reduced catalytically to a *H*-derivative, m.p. 102—103°. α -Cyano- α - δ -bis-bromo-4:5-dimethoxyphenyl- γ -methylbutan- β -one, m.p. 130—131°, is hydrolysed to β -keto- α - δ -bis-2-bromo-4:5-dimethoxyphenyl- γ -methylvaleramide, m.p. 174—175°, which forms α - δ -bis-2-bromo-4:5-dimethoxyphenyl- γ -methylbutan- β -one, m.p. 105—106°. (II) with NaOH forms α - δ -bis-3:4-dimethoxyphenyl- γ -methylbutan- β -one, b.p. 226—228°/0.2 mm., characterised by the (NO_2)₂-compound, m.p. 175—176°, and with MgMeI followed by dehydration with KHSO_4 , *dl*-guaiaretic acid Me_2 ether (III), m.p. 112°.



(III) is reduced to the *dl*- H_2 -derivative (IV) and prep. of derivatives indicates the identity with natural specimen, confirming the structure assigned by Schroeter *et al.* (A., 1919, i, 84). Hübl's I solution

converts (III) into dehydroguaiaretic Me₂ ether, but no (IV) accompanies it.

F. R. S.

Experiments with acetylenylcyclohexanol and related compounds. C. D. HURD and R. N. JONES (J. Amer. Chem. Soc., 1934, 56, 1924—1926).—1-Acetylenylcyclohexan-1-ol (I) (modified prep.; cf. Rupe *et al.*, A., 1928, 640) and SOCl₂ in C₅H₅N at 50—60° give 1- α -chlorovinyl- Δ^1 -cyclohexene, b.p. 89—92°/21 mm. (cf. Carothers and Coffman, A., 1932, 1232), and some 1-acetylenyl- Δ^1 -cyclohexene (II). (I), 48% HBr, and H₂SO₄ afford a mixture, b.p. 49—50°/30 mm., of (II) and 1- α -bromovinyl- Δ^1 -cyclohexene. 1-Chloro-1-ethylcyclohexane, b.p. 90—93°/50 mm. (from the carbinol and SOCl₂ in C₅H₅N), and conc. EtOH-KOH at 100° give (probably) ethylcyclohexene, b.p. 135—139°. 1-Phenylcyclohexan-1-ol (III) reacts slowly with PCl₅ in Et₂O; the resultant mixture of (III) and chloride is completely hydrolysed (EtOH-KOH) to (III). 1-Phenylacetylenylcyclohexan-1-ol (cf. A., 1931, 618) is largely dehydrated by PCl₅ in cold Et₂O or SOCl₂ in C₅H₅N to impure 1-phenylacetylenyl- Δ^1 -cyclohexene, b.p. 167—170°/16 mm. 1-Chloroacetylenylcyclohexan-1-ol and SOCl₂ in C₅H₅N at 70—80° give a mixture of 1-chloroacetylenyl- and 1-dichlorovinyl- Δ^1 -cyclohexene; 1-bromoacetylenylcyclohexan-1-ol similarly affords a mixture of 1-bromoacetylenyl- and 1-chlorobromovinyl- Δ^1 -cyclohexene. H. B.

Reduction of *o*-nitrobenzaldehyde to *o*-nitrobenzyl alcohol. F. SCHENCK (Ber., 1934, 67, [B], 1571).—*o*-NO₂·C₆H₄·CHO is heated with Al(OPrⁱ)₃ in PrⁱOH under a Widmer column until about half the liquid has distilled; this is replaced by fresh PrⁱOH and distillation is repeated as before, after which no more COMe₂ passes over. *o*-NO₂·C₆H₄·CH₂·OH, m.p. 74°, is obtained in 90% yield. Under these conditions PhNO₂ remains unchanged. H. W.

Reaction between $\alpha\beta$ -oxides and dibenzylamine. G. GABEL (Bull. Soc. chim., 1934, [v], 1, 1006—1010).—NH(CH₂Ph)₂ (1 mol.), (CH₂)₂O (1 mol.), and H₂O (1 mol.) at 100° (sealed tube) give 25% of β -dibenzylaminoethyl alcohol, m.p. 45.5—47° (hydrochloride, m.p. 173°; benzoate hydrochloride, m.p. 168—169°). Dibenzylaminotert.-butyl alcohol, b.p. 202—206°/23 mm. [hydrochloride, m.p. 248° (decomp.); benzoate hydrochloride, m.p. 165—166°], is similarly obtained from isobutene oxide. H. B.

Smooth synthesis of diphenylstyrylcarbinol. A. LUTTRINGHAUS, jun. (Ber., 1934, 67, [B], 1601—1603).—Diphenylstyrylcarbinol, m.p. 108—111°, is obtained in 89% yield by addition of CHPh·CHBz to LiPh in Et₂O, thus affording a striking example of the difference of the action of LiPh and MgPhBr. H. W.

Preparation of inositol from salts of inositol-phosphoric acid. K. LINDENFELD (Biochem. Z., 1934, 272, 284—289).—A method for the prep. of inositol (I) from phytin depending on HCO₂H hydrolysis at high temp. and pressure is described and is used for the approx. determination of (I). The yield of (I) represents 91% of the real content.

P. W. C.

Polyterpenes and polyterpenoids. XCI. Preparation of coprosterol, epicoprosterol, and epi-

dihydrocholesterol. Spatial position of the hydroxyl groups of sterols. L. RUZICKA, H. BRUNGER, E. EICHENBERGER, and J. MEYER (Helv. Chim. Acta, 1934, 17, 1407—1416).—In the prep. of epidihydrocholesteryl acetate (cf. Vavon *et al.*, A., 1933, 1047) reduction of cholestanone is best effected by H₂ in presence of PtO₂ and HBr. Hydrogenation of allocholesterol (Pt-black or PtO₂ in Bu₂O or Et₂O-AcOH) gives mixtures of dihydrocholesterol and coprosterol (I). In Et₂O-EtOH, cholestenone (II) is reduced (PtO₂) to a mixture which, after isomerisation by Na amyloxyde, affords about 80% of epicoprosterol, further purification of which from (I) requires the use of digitonin. Better results are obtained by reducing (II) to coprostanone (III) (Pd sponge-Et₂O; cf. Grasshof, this vol., 655), which is hydrogenated (PtO₂ in AcOH-HBr) to (I) in 95% yield. The hydrogenation of (II) + (III) to epicoprosterol is described. Consideration of the results indicates for the sterols the constitutions corresponding with (I)—(IV) of Ruzicka *et al.* (this vol., 1221). H. W.

Hydrogenation of ergosterol and of 22-dihydroergosterol. S. VON REICHEL (Z. physiol. Chem., 1934, 226, 146—148).—The production of dihydroergosterol with Na and EtOH or catalytically from ergosterol, and of γ -ergosterol with Na and PrOH from 22-dihydroergosterol, is confirmed.

J. H. B.

Non-basic constituents of the leaves and roots of *Adlumia fungosa*, Greene.—See this vol., 1276.

Decomposition of acetyl benzoyl peroxide by ultra-violet light. F. FICHTER and E. WILLI (Helv. Chim. Acta, 1934, 17, 1173—1176).—Decomp. of AcO₂Bz leads to CO₂, PhMe, MeOBz (AcO₂Bz = MeOBz + CO₂), CH₄, PhOBz, and complex materials (I) of acidic and neutral character. Possibly hydrolysis occurs, 2AcO₂Bz + H₂O = Bz₂O₂ + AcO₂H + AcOH, the H₂O being liberated in the formation of (I). H. W.

Occurrence of free radicals in chemical reactions. VII. Thermal fission of acyl peroxides. H. WIELAND, S. SCHAPIRO, and H. METZGER (Annalen, 1934, 513, 93—106; cf. A., 1930, 911).—Slow decomp. of β -phenylpropionyl peroxide (I), m.p. 38° (decomp.) (prepared by alternate additions of 4N-KOH and CH₂Ph·CH₂·COCl to cold 10% H₂O₂), in presence of sand at 60—100° gives CO₂ (1.45 mols.), CH₂Ph·CH₂·CO₂H (II), CH₂Ph·CH₂·CO₂·CH₂·CH₂Ph (III), $\alpha\delta$ -diphenylbutane (IV), PhEt, and higher hydrocarbon, b.p. 253°/12 mm. (cf. below). The following reactions are considered to occur: (i) (main) (CH₂Ph·CH₂·CO·O)₂ \rightarrow 2CO₂ + 2CH₂Ph·CH₂·[\rightarrow (IV)]; (ii) (CH₂Ph·CH₂·CO·O)₂ \rightarrow CO₂ + CH₂Ph·CH₂·[CH₂Ph·CH₂·CO₂·[+H \rightarrow (II)]]; (CH₂Ph·CH₂·CO·O)₂ \rightarrow CO₂ + CH₂Ph·CH₂·CO₂·CH₂·CH₂Ph. The following subsidiary reactions between (I) and (IV) probably occur also: PhEt + CH₂Ph·CH₂·CO₂·C₄H₉·Ph₂ \rightarrow (I) + (IV) \rightarrow CH₂Ph·CH₂·CO₂H + CH₂Ph·CH₂·C₄H₉·Ph₂. Similar decomp. of benzoyl β -phenylpropionyl peroxide, m.p. 46°, at 80—100° affords CO₂ (60%), BzOH, esters of BzOH, and (probably) PhEt and styrene. Benzoyl hexahydrobenzoyl peroxide, m.p. 56° (decomp.), gives

CO_2 (about 50%), BzOH , *cyclohexyl benzoate* (main product), and *cyclohexene* (formed thus: $\text{C}_6\text{H}_{11}\cdot\text{CO}\cdot\text{O}\cdot\text{OBz} \longrightarrow \text{CO}_2 + \text{BzOH} + \text{C}_6\text{H}_{10}$). *Benzoyl o-chlorobenzoyl peroxide*, m.p. 49–50°, affords CO_2 (40%) and (probably) chlorodiphenyl and a mixture of acids containing 2 C_6H_5 nuclei; Ph_2 could not be detected. Thermal decomp. of Bz_2O_2 in a high vac. does not give C_6H_6 , indicating that Ph radicals are not produced (cf. *loc. cit.*). *o*- and *p*- $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NO}_2$ are formed by decomp. of Bz_2O_2 in PhNO_2 at 74° and finally at 100°: $\text{Bz}_2\text{O}_2 + \text{PhNO}_2 \longrightarrow \text{CO}_2 + \text{BzOH} + \text{C}_6\text{H}_4\text{Ph}\cdot\text{NO}_2$. Decomp. of (I) in boiling C_6H_6 gives CO_2 , (IV), and small amounts of (II) and (III). The above $\text{R}\cdot\text{CO}\cdot\text{O}\cdot\text{OBz}$ are prepared from $\text{NaO}\cdot\text{Bz}$ and $\text{R}\cdot\text{COCl}$ in COMe_s . H. B.

Preparation of some fluoro-aromatic acids. J. F. J. DIPPY and F. R. WILLIAMS (J.C.S., 1934, 1466).—Using the diazonium borofluoride method *o*- and *m*- (but not *p*- $\text{C}_6\text{H}_4(\text{NH}_2)\cdot\text{CO}_2\text{H}$) are converted into *o*- and *m*-fluorobenzoic acid, respectively. *p*-Fluorophenylacetic acid, m.p. 86°, cannot be similarly obtained, but is prepared from $\text{p}\text{-C}_6\text{H}_4\text{F}\cdot\text{CH}_2\text{Cl}$ and $\text{EtOH}\cdot\text{NaCN}$ and hydrolysis of the nitrile with 10% HCl . J. W. B.

Action of nitrosyl chloride on aromatic nitriles. R. PERROT (Compt. rend., 1934, 199, 585–587).— $\text{CH}_2\text{Ph}\cdot\text{CN}$ with NOCl in CHCl_3 at 60–80° affords α -oximinophenylacetonitrile (I) (*p*-nitrobenzoyl derivative, m.p. 175°; benzene- and *p*-toluene-sulphonates, m.p. 132° and 134.5°, respectively). The following are prepared similarly: α -oximino-*o*-tolyl-, an oil; *o*-chlorophenyl- (benzene- and *p*-toluene-sulphonates, m.p. 91° and 104°, respectively); *o*-nitrophenyl-, m.p. (*syn*-form) 80°, (*anti*-form) 142° (*p*-toluenesulphonate, m.p. 150°); *p*-nitrophenyl- (*p*-toluenesulphonate, m.p. 152°); β -naphthyl-, m.p. 145°, and benzoyl-acetonitrile (benzene- and *p*-toluene-sulphonates, m.p. 112° and 117°, respectively). The *Bz* derivatives of the above have m.p. 82°, 104°, 156°, 156°, 172°, and 117°, respectively, whilst the *p*-nitrobenzoyl derivatives have m.p. 175°, 149.5°, 203°, 237°, 226°, 224°, and 180°, respectively. (I) (*Na* derivative) with $\text{COCl}\cdot\text{CO}_2\text{Et}$ affords an ester, m.p. 93°, and with CNBr gives α -cyano-oximinophenylacetonitrile, m.p. 243°. When CN is in the aromatic nucleus, reaction with NOCl proceeds as described in this vol., 641. J. L. D.

Oxygen a factor in bromination of cinnamic acid. W. H. BAUER and F. DANIELS (J. Amer. Chem. Soc., 1934, 56, 2014; cf. this vol., 374).—Addition of Br_2 to $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ in CCl_4 in the dark at room temp. is inhibited by dissolved O_2 . H. B.

Steric hindrance and geometrical isomerism. P. R. AYYAR (Nature, 1934, 134, 535).—*cis*- α - β -Dibromocinnamic acid is esterified to an extent of only 6% in 1 hr. and 33% in 16 hr. by the Fischer-Speier method, whilst the *trans*-acid is esterified completely in 1 hr. *cis*-*o*-Nitro- α -bromocinnamic acid, m.p. 159°, is obtained in yellow rhombic tablets by crystallising from C_6H_6 the unesterified portion of the acid produced by direct nitration of *cis*- α -bromocinnamic acid. It is also prepared by the action of $\text{KOH}\cdot\text{EtOH}$ and $\text{C}_6\text{H}_5\text{N}$ on *o*-nitrocinnamic acid dibromide. Exposure to direct sunlight in 10% CHCl_3 solution

containing a trace of free Br transforms it in a few min. into insol., needle-shaped crystals of the *trans*-isomeride, which can be completely esterified in 1 hr. L. S. T.

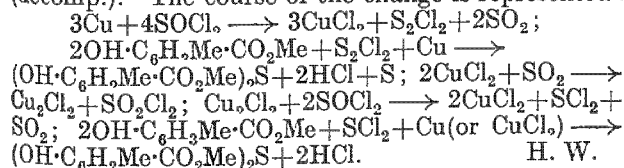
Amino-acids. VII. Synthesis of *N*-methylated aromatic amino-acids. V. DEULOFEU (Ber., 1934, 67, [B], 1542–1545).— PhCHO , benzoylsarcosine (I), Ac_2O , and NaOAc at 130–135° afford α -benzoylmethylamino- β -phenylacrylic acid (II), m.p. 110–111° after softening at 105° (possible mixture of isomerides) in 40% yield. (II) is reduced by $\text{Na}\cdot\text{Hg}$ and H_2O to α -benzoylmethylamino- β -phenylpropionic acid, m.p. 121°, and converted by HI (*d* 1.7) and red P in boiling Ac_2O into phenylmethylalanine, sublimes 254–256°. (I) and $\text{p}\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ similarly yield α -benzoylmethylamino- β -*p*-anisylacrylic acid, m.p. 183–184° (yield 59%), whence α -benzoylmethylamino- β -*p*-anisylpropionic acid, m.p. 146°, and methyltyrosine. α -Benzoylmethylamino- β -piperonylacrylic acid (yield 48%) has m.p. 199°. H. W.

Synthesis of hydroxyphenyl- and hydroxytolyl-dihydrochaulmoogric acids. J. B. NIEDERL and B. WHITMAN (J. Amer. Chem. Soc., 1934, 56, 1966–1968).—Prolonged interaction of chaulmoogric acid (1 mol.) and PhOH (1.1 mols.) in cold AcOH -conc. H_2SO_4 gives hydroxyphenyldihydrochaulmoogric acid [probably μ -2-*p*-hydroxyphenylcyclopentyltridecoic acid], m.p. 80–81° (*Me* ester, b.p. 255–261°/3 mm., m.p. 56–57°; *Na*₂ salt). Hydroxy-*o*-, m.p. 56–61° (*Me* ester, b.p. 245–255°/2 mm., m.p. 40–41°; *Na*₂ salt), *m*-, m.p. 50–52° (*Me* ester, b.p. 230–237°/2 mm.; *Na*₂ salt), and *p*-tolyl-dihydrochaulmoogric acid, m.p. 49–50° (*Me* ester, b.p. 240–250°/3 mm., m.p. 62–63°), are similarly prepared from *o*-, *m*-, and *p*-cresol, respectively. The acids are purified through the *Me* esters. The *Na* salts all show antiseptic activity towards *S. aureus*. The *Me* ester, b.p. 245–265°/4–5 mm., of *p*-tolylxydydihydrochaulmoogric acid, m.p. 62–64.5° (*Na* salt), is prepared from *Me* bromodihydrochaulmoograte.

Derivatives of hydroxybenzoic acids. N. HURRY and (the late) A. N. MELDRUM (J. Indian Chem. Soc., 1934, 11, 535–540).—*o*- $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is converted by $\text{CCl}_3\cdot\text{CHO}$ and H_2SO_4 at room temp. into 2-methoxy-5- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzoic acid (I), m.p. 216° [*K*, *Ba* (+1 H_2O), and *Ca* (+6 H_2O) salts; *Ac* derivative, m.p. 143°; *Me*, m.p. 145°, and *Et*, m.p. 157°, esters; *amide*, m.p. 241°]. Treatment of (I) with SOCl_2 and subsequent hydrolysis leads to 2-methoxy-5- $\alpha\beta\beta\beta$ -tetrachloroethylbenzoic acid, m.p. 132° (*anilide*, m.p. 154°; *p*-toluidide, m.p. 184°). (I) is oxidised by KMnO_4 to 4-methoxysophthalic acid, m.p. 265° [*Ca* (+2 H_2O) salt]. Hydrolysis of (I) with $\text{KOH}\cdot\text{H}_2\text{O}$ at 100° gives 4-methoxy-3-carboxyphenylglycollic acid, m.p. 263°, in poor yield. (I) is reduced by Zn dust and AcOH to 2-methoxy-5- $\beta\beta$ -dichloroethylbenzoic acid (II), m.p. 127° (*Me* ester, m.p. 57°; *amiae*, m.p. 147°; *anilide*, m.p. 105°; *p*-toluidide, m.p. 115°). (II) is transformed by HI at 125° into 2-hydroxy-5- $\beta\beta$ -dichloroethylbenzoic acid, m.p. 166°, by NaOH at 165° into 4-methoxy-3-carboxyphenylacetaldehyde, m.p. 165° [*K* (+1.5 H_2O) salt], and by fuming HNO_3 at 100° into 5-methoxysophthalic acid, m.p. 265°. Reduc-

tion of 5-hydroxytrichloromethylphthalide (from $m\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{CCl}_3\cdot\text{CHO}$) affords 3-hydroxy-6- $\beta\beta$ -dichloroethylbenzoic acid, m.p. 194°. Similarly, 5-methoxytrichloromethylphthalide (from $m\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and $\text{CCl}_3\cdot\text{CHO}$) yields 3-methoxy-6- $\beta\beta$ -dichloroethylbenzoic acid, m.p. 165° (Na salt, Me, m.p. 88°, and Et, m.p. 64°, esters; anilide, m.p. 118°), reduced by Na-Hg to 3-methoxy-6-ethylbenzoic acid, m.p. 87°. $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, $\text{CCl}_3\cdot\text{CHO}$, and H_2SO_4 afford 4-methoxy-3- $\beta\beta\beta$ -trichloro- α -hydroxyethylbenzoic acid, m.p. 275° after shrinking at 161°, reduced by Zn dust and AcOH to 4-methoxy-3- $\beta\beta$ -dichloroethylbenzoic acid, m.p. 221° after shrinking at 210°. H. W.

Derivatives of salicylic acid. VIII. Interaction of thionyl chloride with esters of hydroxy-aromatic acids in presence of finely-divided copper. III. Synthesis and constitution of 3:3'-dicarbomethoxy-4:4'-dihydroxy-5:5'-dimethyldiphenyl sulphide and its 6:6'-dimethyl analogue. N. W. HIRVE, G. V. JADHAV, and Y. CHAKRADEO (J. Indian Chem. Soc., 1934, 11, 551—554).—Addition of Cu powder to a mixture of Me 4-methylsalicylate and SOCl_2 leads to 3:3'-dicarbomethoxy-4:4'-dihydroxy-6:6'-dimethyldiphenyl sulphide (I), m.p. 162° [Ac_2 , m.p. 132°, and Bz_2 , m.p. 140°, derivatives; corresponding diamide, m.p. 280° (decomp.)]. (I) is hydrolysed to 3:3'-dicarboxy-4:4'-dihydroxy-6:6'-dimethyldiphenyl sulphide (II), m.p. 260° (decomp.) (Ac_2 , m.p. 199°, Bz_2 , m.p. 188°, and Me_2 , m.p. 232°, derivatives), converted by Br in AcOH into 3:3'-dicarboxy-4:4'-dihydroxy-6:6'-dibromomethyldiphenyl sulphide, m.p. 267° (decomp.). (II) is oxidised by dil. HNO_3 to 5-nitro-4-methylsalicylic acid, m.p. 219°, and by conc. HNO_3 to 2:4:6-trinitro-*m*-cresol, m.p. 108°. 3:3'-Dicarbomethoxy-4:4'-dihydroxy-5:5'-dimethyldiphenyl sulphide, m.p. 161° (from Me 3-methylsalicylate, SOCl_2 , and Cu powder), is hydrolysed to 3:3'-dicarboxy-4:4'-dihydroxy-5:5'-dimethyldiphenyl sulphide, m.p. 279° (decomp.). The course of the change is represented:



H. W.

Reactions of γ -ketonic acids. III. Ketonic β -lactones. E. P. KOHLER, W. D. PETERSON, and C. L. BICKEL (J. Amer. Chem. Soc., 1934, 56, 2000—2006; cf. this vol., 523).— β -Benzoyl- α -phenylpropionic acid [obtained by hydrolysis ($\text{MeOH}\text{--}\text{NaOH}$) of the Me ester] and Br in boiling CHCl_3 give about 0.66 and 0.24 mol., respectively, of the two β -Br-acids, m.p. 208° (I) and 185° (II) (which contains 1Et₂O). 0.03 mol. of *cis*- β -bromo- β -benzoyl- α -phenylacrylic acid (III), m.p. 195° (Me ester, m.p. 98°), and polymeric material. (III) and $\text{Ac}_2\text{O}\text{--}\text{AcOH}$ give β -bromo- γ -acetoxy- $\alpha\gamma$ -diphenyl- γ -crotonolactone, m.p. 98°, hydrolysed (HCl) to (III). (I) and (II) are converted by $\text{Ac}_2\text{O}\text{--}\text{conc. H}_2\text{SO}_4$ into β -bromo- γ -acetoxy- $\alpha\gamma$ -diphenyl- γ -butyrolactones, m.p. 145° (IV) and 110° (V), respectively. (V) heated with NaOAc in $\text{Ac}_2\text{O}\text{--}\text{AcOH}$ gives (IV), which with NaOAc in AcOH at

100° affords (mainly) γ -acetoxy- $\alpha\gamma$ -diphenyl- γ -crotonolactone (VI), m.p. 95° [oxidised (KMnO_4 in aq. COMe_2 at 0°) to $\alpha\beta$ -dihydroxy- β -benzoyl- α -phenylpropionic acid, m.p. 165° (about 10%), BzOH , and BzCO_2H], and some β -bromo- $\alpha\gamma$ -diphenyl- γ -crotonolactone, m.p. 149° [oxidised (KMnO_4) to an isomeric $\alpha\beta$ -dihydroxy- β -benzoyl- α -phenylpropionic acid, m.p. 154—155°, BzOH , and BzCO_2H]. Dil. aq. solutions of the Na salt of (II) deposit slowly β -benzoyl- α -phenyl- β -propiolactone (VII), m.p. 148°, which, like its isomeride (VIII), m.p. 95° (*loc. cit.*), is converted by aq. bases into the corresponding OH-acid and finally into phenylacetylphenylcarbinol. (VIII) and NaOAc in $\text{AcOH}\text{--}\text{Ac}_2\text{O}$ give *trans*- β -benzoyl- α -phenylacrylic acid (IX), m.p. 128°, similarly obtained together with (VI) and Ph styryl ketone from (I). (II) and (VII) similarly afford a little (IX). (IX) is converted into the *cis*-form [also obtained from (VII) or (VIII) and $\text{C}_5\text{H}_5\text{N}$ at 100°] by prolonged heating with $\text{AcOH}\text{--}\text{HCl}$ or short treatment with hot aq. NaOH. (I) and $\text{MeOH}\text{--}\text{NaOMe}$ give β -hydroxy- $\alpha\gamma$ -diphenyl- γ -crotonolactone, m.p. 209° [previously described (A., 1928, 309) as (IX)] [*Me ether* (CH_2N_2), m.p. 105°], the acetate, m.p. 85°, of which is reduced (H_2 , PtO₂, Ac_2O , AcOH) to β -acetoxy- $\alpha\gamma$ -diphenyl- γ -butyrolactone, m.p. 165°, which with conc. HCl in AcOH affords $\alpha\gamma$ -diphenyl- γ -crotonolactone. H. B.

cis-trans-Isomerism in hydrindene derivatives, and its relation to the Walden inversion.

I. D. H. PEACOCK and B. K. MENON (J.C.S., 1934, 1296—1302).—Condensation of 2-bromo-1-hydroxyhydrindene (I) with $\text{CH}_2(\text{CO}_2\text{Et})_2$ and NaOEt in boiling xylene and subsequent hydrolysis affords *trans*-1-hydroxyhydrindene-2-malonic acid, m.p. 118°, decarboxylated at 120—130° to the *trans*-2-acetic acid (II) [also by conc. aq. KOH hydrolysis of the condensation product of (I) with $\text{CHNaAc}\cdot\text{CO}_2\text{Et}$]. With $\text{HBr}\text{--}\text{AcOH}$ (II) affords the lactone (III), m.p. 73°, of *cis*-1-hydroxyhydrindene-2-acetic acid (IV), but with aq. HBr (saturated at 0°) at 100° a mixture of (III) and *indene*-2-acetic acid, m.p. 150—160°, is obtained. (III) is also formed by the action of PBr_5 or SOCl_2 on the Me ester of (II). With cold saturated $\text{NH}_3\text{--}\text{EtOH}$ Et bromohydrindene-2-acetate [by dry $\text{HBr}\text{--}\text{EtOH}$ on (II)] affords (III) and the NH_4 salt of (IV) [gives only (III) on acidification]. Similarly from (I) and $\text{CH}_2\text{Ph}\cdot\text{CNaAc}\cdot\text{CO}_2\text{Et}$ (V) and hydrolysis (in H_2) of the product is obtained *trans*- β -phenyl- α -1-hydroxyhydrindene-2-propionic acid (A form) (VI), converted by either HBr (*d* 1.78) at 100°, $\text{HBr}\text{--}\text{AcOH}$, or PBr_5 in Et_2O , into the *cis*-lactone (A form) (VII), m.p. 84°, converted by boiling 2*N*-KOH- EtOH into (IX) (below), but unchanged by $\text{HBr}\text{--}\text{EtOH}$. The 1-*p*-toluenesulphonyl derivative (VIII) (not purified) of the Et ester of (VI) with $\text{NH}_3\text{--}\text{EtOH}$ (saturated at 0°) at 100°, gives the B-form (IX), m.p. 102° of the *cis*-lactone [also by hydrolysis of (VIII) with 2*N*-NaOH]. The crude Br-ester obtained from (VI) and $\text{HBr}\text{--}\text{EtOH}$, with either 6*N*- $\text{NH}_3\text{--}\text{EtOH}$ at 100°, $\text{C}_6\text{H}_4(\text{CO})_2\text{NK}$, or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NHNa}$, also gives (IX). Condensation of 2-bromo- α -hydrindone with (V) or $\text{CH}_2\text{Ph}\cdot\text{CNa}(\text{CO}_2\text{Et})_2$, and hydrolysis, affords only bromohydrindonylhydrindone (Kipping *et al.*, J.C.S., 1897, 71. 243). The mother-liquor from

the crystallisation of (VI) with boiling Ac_2O affords the *B*-form, m.p. 121° , of the *Ac* derivative of (VI) [converted by $\text{HBr}-\text{AcOH}$ into (IX)], whereas (VI) itself similarly gives the *A*-form, m.p. 147° , of the *Ac* derivative [gives (VII) with $\text{HBr}-\text{AcOH}$], both hydrolysed to (VI). Thus derivatives of all four possible forms of β -phenyl- α -1-hydroxyhydrindene-2-propionic acid have been obtained, *A* and *B* forms relating to the configuration around the α -C. By similar methods are obtained (small yields) *trans*- α -1-hydroxyhydrindene-2-propionic, m.p. 131° (cis-lactone, m.p. 102°), and -2-*n*-hexoic acid, m.p. 122° (cis-lactone, m.p. 105°). J. W. B.

Effect of substituents on inversion at the α -carbon atom. D. H. PEACOCK and B. K. MENON (Chem. and Ind., 1934, 762).— α -2-Hydroxy-1-hydrindyl- γ -phenylbutyric and α -2-hydroxy-1-hydrindyl- β -4-bromophenylpropionic acids give lactones, isomerised by alkalis to stereoisomeric forms due to inversion at the α -C-atom. Na 4-bromobenzyl-benzylacetate is rapidly racemised in aq. solution at 100° , whilst the benzyl- and 4-bromobenzyl-butylacetates racemise slowly. S. C.

Electrolyses of methyl hydrogen hexahydrophthalate. F. FICHTER and C. SIMON (Helv. Chim. Acta, 1934, 17, 1218—1226).— $\text{o-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ is reduced at a Hg cathode to Δ^2 -tetrahydro-*o*-phthalic acid, m.p. 215° (anhydride, m.p. $78-79^\circ$), which, with saturated HBr at $115-120^\circ$, yields 1-bromocyclohexane-1:2-dicarboxylic acid, m.p. $183-188^\circ$ when rapidly heated, transformed by Na-Hg in alkaline solution into *trans*-hexahydrophthalic acid, whence the anhydride and Me H *trans*-hexahydrophthalate (I), m.p. $96-97^\circ$. Electrolysis of (I) at a Pt anode in presence of $\text{KHCO}_3-\text{H}_2\text{O}$ leads to CO_2 and the following substances: *Me cyclohexenecarboxylate*, b.p. $43-46^\circ/0.5$ mm., transformed by Br into *Me tribromohexahydrobenzoate*, b.p. $146-148^\circ/17$ mm., $82^\circ/0.05$ mm.; *Me cyclohexan-2-one-1-carboxylate*, b.p. $55^\circ/0.2$ mm., transformed by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ into 3:4-tetramethylenopyrazolone, m.p. $280-283.5^\circ$; Me_2 hexahydrophthalate, b.p. $60^\circ/1$ mm.; *Me cyclohexan-2-ol-1-carboxylate*, b.p. $68-69^\circ/0.5$ mm. (whence hexahydrosalicylic acid, m.p. $110-111^\circ$), and the corresponding ether

$(\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{Me})\text{CH}_2)_n\text{O}$, b.p. $126^\circ/0.5$ mm.; a substance, $\text{C}_8\text{H}_{14}\text{O}_2$, probably a reduction product of (I), 1:1'-*di*hydroxydicyclohexyl-2:2'-dicarboxylic acid, b.p. $95^\circ/0.5$ mm., m.p. $96-97^\circ$. The course of electrolysis is therefore similar to that observed with hexahydrobenzoic acid. H. W.

Influence of the double linking in $\alpha\beta$ -unsaturated fatty-aromatic dicarboxylic acids on the rate of hydrolysis of their esters. H. POHL (J. pr. Chem., 1934, [ii], 141, 44—60).—Conditions are described for the conversion of *p*-xylene into $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$ (I), $\text{CH}_2\text{Br}-\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br}$ (II), and $\text{C}_6\text{H}_4(\text{CHBr})_2$ (III). Homogeneous products are not obtained from (II) and $\text{CH}_2(\text{CO}_2\text{Et})_2$. *p*- $\text{C}_6\text{H}_4(\text{CHO})_2$ (IV) is obtained from (I) with H_2O containing $\text{Pb}(\text{NO}_3)_2$, or dil. HNO_3 by which it is extensively oxidised further; it is best prepared from (III) and conc. H_2SO_4 at $120-140^\circ$,

whereby further oxidation, attributed to the liberated HBr , causes admixture with *p*- $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and *p*- $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. Application of Perkin's reaction to (IV) leads essentially to *p*-formylcinnamic acid, m.p. 239° , hydrogenated (colloidal Pd) to β -*p*-formylphenylpropionic acid, m.p. 139° [*phenylhydrazone*, m.p. 245° (decomp.)]. Under more drastic conditions (IV) affords *p*-phenylenediacrylic acid, $\text{C}_6\text{H}_4(\text{CH}:\text{CH}\cdot\text{CO}_2\text{H})_2$, m.p. about 340° (decomp.) [*Et*₂ ester (V), m.p. 73°], hydrogenated (Pd) to *p*-phenylene- $\beta\beta'$ -dipropionic acid, m.p. 223° [*Et*₂ ester (VI), m.p. 69°]. *Et* β -*p*-formylphenylpropionate is transformed by Perkin's reaction or Claisen's synthesis into *Et*₂ *p*-phenylene- β -acrylate- β' -propionate (VII), m.p. 73° [corresponding acid, m.p. about 340° (decomp.)]. The first stage of the alkaline hydrolysis of (V) and (VI) is much more rapid than the second stage, as shown by a more or less marked break in the alkali-consumption curve. This is completely blurred in the case of (VII) owing to the four concurrent bimol. changes. H. W.

Derivatives of naphthalene-2:3-dicarboxylic acid. W. BAKER (J.C.S., 1934, 1413—1414).—With HNO_3 (*d* 1.42) at 100° 2:3- $\text{C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ gives its 5- NO_2 -derivative (I), m.p. 238° (anhydride, m.p. 208° ; imide, m.p. 300° ; anil, m.p. 232° ; *p*-nitroanil, m.p. 254°), but with HNO_3 (*d* 1.42)- H_2SO_4 it affords a (? 5:6- or 1:5-) dinitronaphthalene-2:3-dicarboxylic acid, m.p. 254° (*Et* H ester, + EtOH and solvent-free, m.p. 229°). Reduction of (I) with FeSO_4 -aq. NH_3 affords 5-aminonaphthalene-2:3-dicarboxylic acid (II), + AcOH , m.p. $> 360^\circ$ (8-*p*-sulphobenzenazo-derivative; anhydride of *Ac* derivative, m.p. 290°). This couples with PhN_2Cl to give an aminoazo-compound, reduced by $\text{SnCl}_2\cdot\text{HCl}-\text{EtOH}$ to 5:8-diaminonaphthalene-2:3-dicarboxylic acid, decomp. at high temp. without melting. The constitution of (II) follows from the observation that the aminoazo-compound obtained by coupling (II) with diazotised β -naphthylamine-6:8-disulphonic acid, can be further diazotised and coupled with β -naphthol- and 1-amino-8-naphthol-3:6-disulphonic acid to give bisazo-dyes. The *p*-nitroanil, m.p. 253° , and *p*-acetamidoanil, m.p. 295° (decomp.), of 4-nitrophthalic acid are prepared. J. W. B.

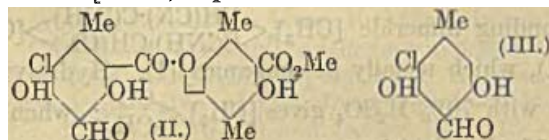
Occurrence of free radicals in isomerisations. G. WITTIG and H. PETRI (Annalen, 1934, 513, 26—43).—Isomerisation of tetraphenylsuccinonitrile (I) to *p*- α -cyanobenzyltriphenylacetoneitrile (II) occurs in CHCl_3 containing NEt_3 at $40-55^\circ$ (cf. A., 1932, 117). The unimol. velocity coeff. (k_m), calc. from the rate of disappearance of (I) (as determined by redue to with TiCl_4 in boiling $\text{AcOH}-\text{HCl}$ and CO_2 titration with FeCl_3), using 0.306*M*- $\text{CHCl}_3\text{-NEt}_3$ is 0.0026 at 40° and 0.00835 at 54° ; the activation energy is 16.9 kg.-cal. The val. of k_m does not appreciably with 0.306—3.535*M* solutions at 5, with small concns. (0.002—0.061) a pronounced increase occurs. Measurements with 0.002—0.0031*M* solutions of NEt_3 and NPhMe_2 , respectively, at 40° and 54° show that the reaction is now 1st ol. These results are explained by the dissociation into cyanodiphenylmethyl (cf. *loc. cit.*), which passes (slowly with small concns. and very rapidly with high concns. of the amine) into (II). The

velocity coeff. directly \propto the concn. (0.00153—0.00612*M*) of *NPhMe*, at 54°. The function of the catalyst (base) is discussed.

CHPh_2Cl and $\text{Hg}(\text{CN})_2$ in boiling MeCN in absence of moisture give $\text{CHPh}_2\cdot\text{CN}$, oxidised (method; Meyer and Auwers, A., 1889, 883) to (I). *Phenyldiphenylmethyl chloride*, m.p. 62.5° (from the carbinol, HCl , and SOCl_2 in CHCl_3), similarly affords *phenyldiphenylacetone nitrile*, m.p. 130—131.5°, oxidised (Et_2O —I in dioxan and EtOH — NaOEt) to $\alpha\alpha'$ -diphenyl- $\alpha\alpha'$ -di-(diphenyl)succinonitrile, decomp. 193—199° (becoming red). *Di- α -naphthylacetone nitrile*, m.p. 170—172°, is similarly oxidised to *tetra- α -naphthylsuccinonitrile*, decomp. slowly $> 200^\circ$, which dissolves in C_6H_6 or CHCl_3 to a deep violet solution. H. B.

Thermal decomposition of the silver salts of carboxylic acids. S. I. KANEVSKAJA, M. M. SCHEMJAKIN, and E. M. BANDASS-SCHEMJAKINA (Ber., 1934, 67, [B], 1518—1522).—Thermal decomp. of Ag opianate affords veratraldehyde (I) (about 30%), hemipinic anhydride (II) (40%), and veratric acid (10%), the ratios being independent of the amount of material employed. It is suggested that the initial action is the formation of opianic anhydride (III) and Ag_2O , which oxidises 1 CHO of (II), forming Ag and the mixed anhydride of opianic and hemipinic acid, which decomposes into (I) and (II). H. W.

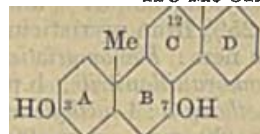
Components of lichens. IV. Chloroatranorin. A. S. PFAU (Helv. Chim. Acta, 1934, 17, 1319—1328).—The presence of Cl in certain samples of atranorin (I) is shown not to be due to CHCl_3 used in its purification, but to the presence of *chloroatranorin* (II), the occurrence of which appears somewhat uncertain. (I) containing Cl is converted by boiling 10% KOH in H_2 followed by decarboxylation of the acid so produced into *chloroatranol* (III), m.p. 141.5—142° [*oxime*, m.p. 172.5—173°; *semicarbazone*,



m.p. 306—308° (block, decomp.)). (III) is also obtained from (I) containing Cl by hydrolysis to the aldehyde mixture, which is treated with NaOH and Ac_2O ; fractional crystallisation of the product from 70% EtOH leads to the Ac_1 derivative, m.p. 121.5°, of (III), whence (III). More simply, repeated partial extraction of the aldehyde mixture with boiling H_2O leaves a residue from which pure (III) is isolated by crystallisation from much boiling H_2O or 50% AcOH . The isolation of (II) from *Evernia prunastri* (L.), Ach., is described in detail. $\text{Et } 2:4$ -dihydroxy-3-aldehyde-6-methylbenzoate is converted by Cl_2 in AcOH into *Et 5-chloro-2:4-dihydroxy-3-aldehyde-6-methylbenzoate*, m.p. 100—101°; the corresponding acid, m.p. 179.5—180.5° (block, decomp.), passes at 170° into (III). Atranol (IV) and (III) cannot be separated from one another by crystallisation; treatment of the mixture with boiling 50% KOH causes the more rapid decomp. of (III), thus leading to the isolation of homogeneous (IV), m.p. (anhyd.) 124°, m.p. (hydrated) 118—119°. The diverse m.p. observed for (IV) are due to its

hygroscopicity. The *Ac* derivative, m.p. 75—75.5°, and *oxime*, m.p. 194.5—195° (decomp.), of (IV) are described. H. W.

Toad-bile. II. Trihydroxybufosterocholenic acid $\text{C}_{28}\text{H}_{46}\text{O}_5$ from winter bile. T. SHIMIZU and T. ODA (Z. physiol. Chem., 1934, 227, 74—83; cf. Makino, A., 1933, 1166).—*Trihydroxybufosterocholenic acid* (I), $+\text{H}_2\text{O}$, m.p. 160°, $+\text{MeOH}$, decomp. 120—130°, $[\alpha]_D^{25} -13.42^\circ$ in MeOH (*bromolactone*, $\text{C}_{28}\text{H}_{45}\text{O}_5\text{Br}$, m.p. 225°), was isolated from purified winter bile of toads by treatment with CH_2N_2 as the *Me* ester, m.p. 171—172°. An isomeric *Me* ester, m.p. 192—193°, was also obtained. With CrO_3 — AcOH , (I) affords *triketobufosterocholenic acid* (II), m.p. 268—269°, $[\alpha]_D^{25} -27.14^\circ$ in EtOH (*Me*, m.p. 181—182°, *Et*, m.p. 164—165°, esters; *Et* ester *trioxime*, m.p. 238°). Clemmensen reduction of (II) affords *bufosterocholenic acid*, $\text{C}_{28}\text{H}_{46}\text{O}_2$, m.p. 142—144° (*Me* ester, m.p. 103—104°), and *diketobufosterocholenic acid*, m.p. 267—268°. Hydrogenation (PtO_2) of (I) *Me* ester yields as *Me* ester, m.p. 172°, *trihydroxysterobufocholenic acid* (III), $\text{C}_{28}\text{H}_{48}\text{O}_5$, sinters 60°, decomp. 100°, m.p. 200°. Oxidation of (III) with CrO_3 — AcOH gives *triketobufosterocholenic acid* (IV), m.p. 260°, $[\alpha]_D^{25} +15.8^\circ$ in EtOH (*Me* ester, m.p. 181—182°), also obtained by hydrogenation of (II). Hydrogenation (Pt-black) of (IV) affords *hydroxydiketobufosterocholenic acid*, m.p. 217—218° (*dioxime*, m.p. 266—267°). Clemmensen reduction of (IV) yields *bufosterocholenic acid*, m.p. 161—162°, and *diketobufosterocholenic acid*, m.p. 253°. The suggested constitution for (I) is:



The positive Hammarsten reaction of (I) makes it probable that the 3 sec.-OH groups are in positions C_3 , C_7 , and C_{12} . J. H. B.

Synthesis of substances analogous to bile-acid degradation products. II. J. W. BAKER (J.C.S., 1934, 1467).—A correction. $\text{C}_5\text{H}_5\text{N}$ and $\text{CO}_2\text{Me} \cdot \text{CHMe} \cdot \text{CBr}(\text{CO}_2\text{Me})_2$ afford not the $\Delta\alpha$ - but the $\Delta\beta$ -propene ester, converted by HBr — AcOH into *Me γ -bromopropane- $\alpha\alpha\beta$ -tricarboxylate*, m.p. 68°, and not into the β -Br-ester (A., 1933, 935). J. W. B.

Humic acids. II. Identification and determination of the oxygenated functional groups. I. UBALDINI and C. SINIRAMEO (Annali Chim. Appl., 1934, 24, 370—382; cf. this vol., 295).—Determinations of the carbonyl O in the humic acids from lignite and peat by means of $p\text{-C}_6\text{H}_4\text{Br} \cdot \text{NH} \cdot \text{NH}_2$ indicate the presence of two CO groups to the mol. of wt. 1600—1700. The *Me* derivative obtained from the acids by treatment with AcCHO in presence of HCl is not a decomp. product of oxygenated heterocyclic nuclei (cf. Fuchs and Horn, B., 1931, 833), but an acetal of the type $\text{R} \cdot \text{C}(\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OMe})_2$, where R is the humic acid residue originally attached to the CO group. Acetylation of the acids with Ac_2O and $\text{C}_5\text{H}_5\text{N}$ confirms the phenolic OH content previously found and excludes the presence of alcoholic OH.

The approx. formula $C_{78}H_{52}O_5(CO_2H)_8(OH)_7(CO)_2$ for the acids is suggested. When the acids are heated with KOH under pressure, acids with fewer CO_2H and phenolic groups are obtained. T. H. P.

Mol. wt. of lignin. P. B. SARKAR (Current Sci., 1934, 3, 64—65).—A val. of 830 has now been obtained, deduced from CH_2O determination. Freudenberg's formula (A., 1933, 176) needs modification. L. S. T.

Resinification of sugars by acids and its bearing on the determination of lignin.—See this vol., 1205.

[Separation of the components of lignin.] H. PAULY (Ber., 1934, 67, [B], 1658; cf. this vol., 893).—Various corrections of analytical data are recorded. H. W.

β -Hydroxyphenylethylamines and their transformations. II. Synthesis of amines and of the corresponding hydroxyphenylacetic acid from natural allyl compounds. G. HAHN and O. SCHALES (Ber., 1934, 67, [B], 1486—1493; cf. this vol., 647).—The allyl compounds are treated with (usually) 1% ozonised O_2 and the ozonides are transformed into the corresponding hydroxyphenylacetaldehydes by catalytic hydrogenation ($Pd-CaCO_3$); these are converted through the $NaHSO_3$ derivatives into the oximes. Treatment of the latter with Ac_2O affords the nitriles, which are hydrolysed by KOH to the acids or catalytically reduced to the amines. The yields of acid and amine are 60% and 59% from safrole, 54% and 50% from methyleugenol, 47% and — from eugenol, and 27% and 25% from myristicin, respectively. The following are new: *homomyristic-aldoxime*, m.p. 80°; *4-acetylhomovanillonitrile*, b.p. 204°/16 mm., m.p. 52°; *5-methoxy-3:4-methylene-dioxyphenylacetoneitrile*, b.p. 198°/20 mm., m.p. 90° (corresponding acid, m.p. 108°). H. W.

Carbon rings. XXVIII. Preparation of 2-methyl-, 3-methyl-, and 7-methyl-cyclopentadecan-1-one. Synthesis of *dl*-muscone. L. RUZICKA and M. STOLL [with H. SCHINZ and H. A. BOEKENOOGEN] (Helv. Chim. Acta, 1934, 17, 1308—1318).—Oxidation of *cyclopentadecene* with CrO_3 in $AcOH$ and treatment of the product with $NH_2CO-NH-NH_2, AcOH$, gives a product, $C_{17}H_{34}O_3N_6$, m.p. (indef.) 210—220°, and a substance, m.p. about 190°. Similar treatment of 1-methyl- Δ^1 -cyclopentadecene (I) leads to a *semicarbazone*, m.p. 220—225°, whereas oxidation in Ac_2O-CCl_4 followed by hydrolysis, treatment with $o-C_6H_4(CO)_2O$, and hydrolysis affords *methylcyclopentadecanol*, b.p. 150—151°/1 mm., in very small yield. Treatment of (I) with SeO_2 in boiling abs. $MeOH$ and hydrogenation ($Ni-EtOH$) of the product gives 2-methylcyclopentadecan-1-one (*semicarbazone*, m.p. 148.5—149.5°). *cyclopentadecanone* and Br in $CHCl_3$ yield 2-bromocyclopentadecan-1-one, b.p. 126—134°/0.06 mm., transformed ($BaCl_2$ at 300°/0.1 mm.) into Δ^2 -cyclopentadecan-1-one (II), b.p. 113—118°/0.04 mm. Addition of $CHNa(CO_2Et)_2$ to (II) affords *Et*, 3-ketocyclopentadecyl-1-malonate, b.p. 190—200°/0.1 mm.; the corresponding acid, m.p. 140—141°, is decarboxylated to

3-ketocyclopentadecyl-1-acetic acid, m.p. 89—90°, electrolysis of which leads to $\alpha\beta$ -di-3-ketocyclopentadecylethane, m.p. 104°, and liquid products which are hydrogenated (Ni) to a mixture of saturated ketones, giving *semicarbazones*, m.p. 170—171°, and m.p. 143—144°, respectively. α -Methyltetradecane- $\alpha\zeta$ -dicarboxylic acid is transformed successively into the chloride, *diamide*, m.p. 151—154°, *dinitrile*, b.p. 248—249°/2 mm., and *dl*-muscone, the *semicarbazone* and *phenylsemicarbazone* of which have m.p. 136—137° and 170—171°, respectively. The *phenylsemicarbazone* of natural muscone has m.p. 158—160°. (The method of mixed m.p. appears untrustworthy with these compounds.) δ -Methyloctane- $\alpha\theta$ -diol, b.p. 128—133°/2.5 mm., is transformed into $\alpha\theta$ -dibromo- δ -methyloctane, b.p. 122—123°/2 mm., whence successively *Me*, ϵ -methyldecan- $\alpha\kappa$ -dicarboxylate, b.p. 180—187°/10 mm., ζ -methyldecan- $\alpha\mu$ -diol, b.p. 185—193°/12 mm., $\alpha\mu$ -dibromo- ζ -methyldecan- $\alpha\epsilon$ -dicarboxylate, b.p. 187—193°/1 mm., and η -methyltetradecane- $\alpha\zeta$ -dicarboxylic acid (III), m.p. 77—78°. Decomp. of the Ce salt of (III) gives 7-methylcyclopentadecanone, b.p. 182—183°/20 mm. (*semicarbazone*, m.p. 181—182°). H. W.

Poly-membered ring systems. V. Tendency of formation of cyclic compounds. K. ZIEGLER and R. AURNHAMMER (Annalen, 1934, 513, 43—64).—

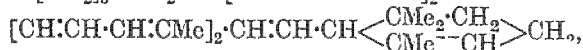
The yields of $[CH_2]_n \begin{smallmatrix} C:NH \\ \diagup \quad \diagdown \\ CH:CN \end{smallmatrix}$ (I) obtained from $CN \cdot [CH_2]_n \cdot CH \cdot CN$ and 0.67N-Et.O-NaPhAlk (cf. A., 1933, 951) are: $n=3-6$ (90—95%); 7 (about 1%); 8 (trace); 9 (about 0.5%); 10 (8%); 11 (15%); 12—13 (60%); 14 (77%); 15 (70%); 16 (83%); 17 (73%); 18 (79.4%). The difficulty in formation of 9—11-membered rings is probably concerned with the high demand on the energy of activation. When $n=7-9$, the main product of the condensation is the corresponding dimeride $[CH_2]_n \begin{smallmatrix} CH(CN)C(NH) \\ \diagup \quad \diagdown \\ C(NH)CH(CN) \end{smallmatrix} [CH_2]_n$ (II), which usually accompanies (I). Hydrolysis of (I) with 70% H_2SO_4 gives $[CH_2]_n \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CH \end{smallmatrix}$; when n is < 12 , the yield is very poor and the use of more dil. acid is necessary. (II) are similarly hydrolysed to $[CH_2]_n \begin{smallmatrix} CH_2CO \\ \diagup \quad \diagdown \\ COCH_2 \end{smallmatrix} [CH_2]_n$. The following are described (cf. loc. cit.): 2-cyanocycloheptanoneimine, m.p. 97—98°; 2-cyanocyclooctanoneimine, m.p. 106—107°; 2-cyanocyclotetradecanoneimine, m.p. 147—148°; 1:10-di-imino-2:11-dicyanocyclooctadecane, m.p. 245° (sinters from 240°); 1:11-di-imino-2:12-dicyanocycloicosane, m.p. 182°; 1:12-di-imino-2:13-dicyanocyclodocosane, m.p. 194°. *cycloNonanone* (III) [*semicarbazone*, m.p. 184—185° (lit. 178—179°)] has m.p. 28° (lit. 10°), whilst *cycloundecanone* (IV) could not be obtained solid; the vals. of for (III) and (IV) are somewhat $>$ those determined by Ruzicka et al. (A., 1926, 727). The mol. depressions of the f.p. of several *cycloalkanones* are determined essentially by Pirsch's method (cf. A., 1932, 713, 925). Contrary to the previous statement (A., 1933, 951), 2-cyanocycloheptanone (V) is not hydrolysed by aq. $NaOH$; the Na salt (+ H_2O) of the enolic form of (V) is produced.

cis- and *trans*-Chlorohydrins of 1-methyl- Δ^1 -cyclohexene. P. D. BARTLETT and R. H. ROSENWALD (J. Amer. Chem. Soc., 1934, 56, 1990—1994).—2-Chlorocyclohexanone (I) and MgMeBr in cold Et₂O give (cf. Tiffeneau and Tchoubar, this vol., 654) 55—82% of 2-chloro-1-methylcyclohexanol (II), b.p. 73—75°/15 mm. (the 2-Br-analogue has b.p. 83°/7 mm.), which is unaffected by cold aq. NaOH or powdered NaOH in dry Et₂O, is converted by boiling 33% NaOH into cyclopentyl Me ketone, and when heated with quinoline affords 1-methyl- $\Delta^{1:5}$ -cyclohexadiene. A ketone, b.p. 42—46°/14 mm. (semicarbazones, m.p. 144—145° and 188—189·5°), is obtained from (II) and H₂O at 200° (sealed tube). Addition of HOCl to 1-methyl- Δ^1 -cyclohexene gives a 2-chloro-1-methylcyclohexanol (III), b.p. 90—95°/28 mm., converted by cold dil. NaOH into 1:2-oxido-1-methylcyclohexane (which is unaffected by hot 33% NaOH), and hydrolysed (hot dil. NaOH) to impure *trans*-1-methylcyclohexane-1:2-diol (the *cis*-form is prepared from 2-hydroxycyclohexanone and MgMeBr). (II) and (III) appear to be geometrical isomerides. 2-Methylcyclohexanone is obtained from (I) and MgMeBr in boiling C₆H₆. H. B.

Preparation of cyclic $\alpha\beta$ -unsaturated ketones and ketonic acids. II. H. BERGS [with C. WITTFIELD and H. FRANK] (Ber., 1934, 67, [B], 1617—1623; cf. this vol., 409).—Mg cyclohexyl bromide (chloride) and CH₂Ph·CHO afford benzylcyclohexylcarbinol, b.p. 178—182°/16—17 mm., 173—174°/12 mm., smoothly oxidised by CrO₃ to cyclohexyl CH₂Ph ketone, b.p. 166—167°/19 mm. [NaHSO₃ compound; oxime (I), m.p. 117·5°; semicarbazone, m.p. 138—139°]. (I) is reduced by Na and boiling EtOH to β -phenyl- α -cyclohexylethylamine (II), b.p. 160—165°/12—13 mm. (picrate, m.p. 203·5°; hydrochloride, m.p. 216°). Since (II) is also obtained by the reduction of the oxime of 1-phenylacetyl- Δ^1 -cyclohexene (*loc. cit.*), the constitution of the latter substance is confirmed. CH₂Ph·CH₂·COCl and cyclohexene in presence of SnCl₄ and CS₂ or CH₂Ph·CH₂·MgCl and Δ^1 -tetrahydrobenzonitrile give 1-phenylpropionyl- Δ^1 -cyclohexene, b.p. 175—180°/10—11 mm. (oxime, m.p. 115—116°; semicarbazone, m.p. 163°). CHPh·CH·COCl, SnCl₄, and cyclohexene in CS₂ yield cinnamyl cyclohexenyl ketone, m.p. 174·5—175° (semicarbazone, m.p. 213°). cycloHexenyl α -phenyl-n-propyl ketone, m.p. 75°, from α -phenyl-n-butyryl chloride, b.p. 104°/12 mm., does not yield an oxime or semicarbazone. δ -Carbethoxy-n-valeryl chloride, b.p. 128°/17 mm., from Et H adipate and SOCl₂, and cyclohexene, SnCl₄, and CS₂ give Δ^1 -cyclohexenyl δ -carbethoxybutyl ketone, b.p. 182—185°/14 mm. (semicarbazone, m.p. 100—101°; non-cryst. oxime); the corresponding acid has b.p. 116—118°/12—13 mm., m.p. 73—74°. H. W.

Condensation of aminoguanidine with fluorenone and 2-nitrofluorenone. A. C. DE DEGIORGI (Anal. Asoc. Quím. Argentina, 1934, 22, 41—44).—Aminoguanidine (I) as sulphate condenses with fluorenone in EtOH to fluorenoneaminoguanidine, m.p. 205—206° [sulphate, m.p. 237—239° (decomp.)], whilst 2-nitrofluorenone with (I) in AcOH gives 2-nitrofluorenoneaminoguanidine, m.p. 265—268° (decomp.) phate, m.p. 300° (decomp.)]. R. C.

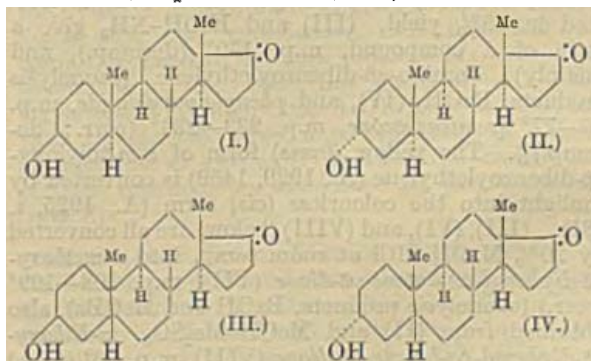
Products of the oxidation of α -carotene. Relationships between constitution and vitamin-A action. P. KARRER, H. VON EULER, and U. SOLMSSEN (Helv. Chim. Acta, 1934, 17, 1169—1172).—Oxidation of α -carotene with CrO₃ in C₆H₆-AcOH (course of the change is irregular) leads to α -carotone (I), α -hydroxycarotene (II), and α -semicarotenone, COMe·[CH₂]₃·CMe₂·CO·[CH·CH·CMe·CH]₂·



m.p. 135°, the absorption spectrum of which resembles closely that of (I). (II) is probably C₄₀H₅₈O₂. Provitamin-A properties are not shown by α -carotene derivatives which contain only the intact α -ionone ring. H. W.

Sexual hormones. I. Preparation of 3-chloro- and 3-hydroxy- α -tioallocholan-17-one. Synthesis of a compound with the properties of the testicular hormone. L. RUZICKA, M. W. GOLDBERG, and H. BRUNGER. II. Synthesis of the testicular hormone (androsterone) and stereoisomerides thereof by degradation of hydrogenated sterols. L. RUZICKA, M. W. GOLDBERG, J. MEYER, H. BRUNGER, and E. EICHENBERGER (Helv. Chim. Acta, 1934, 17, 1389—1394, 1395—1406).—I. β -Cholestyl chloride (I), m.p. 105° (corr.) (improved prep.), is converted by excess of CrO₃ in AcOH into acid materials, including chlorocholanic acid, m.p. 186—188° (corr.), and neutral compounds including unchanged (I) and 3-chloro- α -tioallocholan-17-one (possibly the *epi*-compound), m.p. 128—128·5° (corr.) [semicarbazone, m.p. 268—269° (corr.)]. Similarly, dihydrocholesteryl acetate affords 3-acetoxy- α -tioallocholan-17-one, the semicarbazone, m.p. 261—262° (corr.), of which is transformed by HCl-AcOH into 3-hydroxy- α -tioallocholan-17-one, m.p. 174—174·5° (corr.), [α]_D +87·5° in MeOH, closely similar to the testicular hormone.

II. The prep. of 3-hydroxy- α -tioallocholan-17-one (I), m.p. 174—175°, is somewhat modified; its acetate, m.p. 96—97°, or m.p. about 96—115° after sublimation in vac., and oxime, needles, m.p. 185—186° (corr.), or leaflets, m.p. 182—183° (corr.), are described.



Oxidation of epidihydrocholesteryl acetate leads to 3-epihydroxy- α -tioallocholan-17-one (II), m.p. 182—183° (corr.), [α]_D +94·6° in abs. EtOH, +103·5° in MeOH, chemically and physiologically identical with androsterone. (II) gives a semicarbazone, m.p. 272—273° (corr.), normal oxalate, m.p. 248·5—249·5° (corr.), oxime, leaflets, m.p. 207—209° (corr.), or

needles, m.p. 214—215° becoming transparent at 217—218°, *acetate*, m.p. 164.5—165.5° (corr.), and its *oxime*, decomp. about 215°, and *propionate*, m.p. 151—152° (corr.). Similarly, *epicoprosteryl acetate* affords 3-*epihydroxyetiocholan-17-one* (IV), m.p. 150—151° (corr.) [*semicarbazone*, m.p. 254—255° (corr.)]. 3-*Hydroxyetiocholan-17-one* (III), m.p. 151—152° (corr.) [*semicarbazone*, m.p. 244—245° (corr.)], is derived from coprosteryl acetate. H. W.

Benzoin-benzil change. K. M. PANDALAI (J. Indian Chem. Soc., 1934, 11, 511—512).—When heated with NH_2Ph and $\text{NH}_2\text{Ph}\cdot\text{HCl}$ at 100°, benzoin affords benzil and Ph, thus: $\text{OH}\cdot\text{CHPh}\cdot\text{COPh} \rightarrow \text{OH}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{OH} \rightarrow \text{Ph}_2+(\text{COPh})_2+\text{NH}_4\text{Cl}+\text{NH}_3$. Similar results are not obtained with cumuinoin, anisoin, furoin, or piperoin. H. W.

Tautomerism of $\alpha\delta$ -diphenylbutane- $\alpha\beta\delta$ -trione enol. R. E. LUTZ, F. N. WILDER, and C. I. PARRISH (J. Amer. Chem. Soc., 1934, 56, 1980—1987).— $\alpha\beta$ -Dibromo- $\alpha\beta$ -dibenzoylthane and dibenzoylacetylene are converted by $\text{MeOH}\cdot\text{NaOH}$ at 60° into α -hydroxy- $\alpha\beta$ -dibenzoylthylene (I) [*Na* (II) and *Cu* salts], which exists in colourless (probably *cis*) (Ia), m.p. 88—89° (corr.), and yellow (probably *trans*) (Ib), m.p. 68° (corr.), forms; at room temp. or 40°, α -methoxy- $\alpha\beta$ -dibenzoylthylene (III), also obtained in 50—65% yield by methylation (CH_3N_2) of (Ia) or (Ib), results. (III) is hydrolysed ($\text{MeOH}\cdot\text{NaOH}$ at 60°) to (I). When (Ia) is fused and the melt cooled (Ib) is obtained; (Ib) is converted into (Ia) by the action of direct or diffused light on the solid. Dissolution of either form in EtOH gives an equilibrium mixture; subsequent crystallisation gives (Ia). In CHCl_3 , (Ib) predominates; rapid evaporation in the cold or addition of light petroleum affords (Ib) only. (I) is hydrolysed [aq. $\text{Ba}(\text{OH})_2$] to COPhMe and BzCO_2H (IV). Ozonolysis of (I) in CHCl_3 [*i.e.* (Ib)] gives BzOH , (IV), and a little BzCHO (V); (III) similarly affords BzOH , BzCO_2Me , and a little (IV); $(\text{CHBz})_2$ yields BzOH and small amounts of (IV) and (V) (the yield of which is higher in 94% AcOH). Alcoholysis of (III) occurs when it is treated with $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{ONa}$ in EtOH; α -ethoxy- $\alpha\beta$ -dibenzoylthylene (VI) is isolated in 15% yield. (III) and $\text{EtOH}\cdot\text{NH}_3$ give a little of a compound, m.p. 170° (decomp.), and (mainly) α -amino- $\alpha\beta$ -dibenzoylthylene {ozonolysis products, BzOH , (IV), and *phenylglyoxylamide*, m.p. 76—77° [*semicarbazone*, m.p. 233—234° (corr.; decomp.)]}. The yellow (*trans*) form of α -*m*-tolyl- $\alpha\beta$ -dibenzoylthylene (A., 1929, 1459) is converted by sunlight into the colourless (*cis*) form (A., 1925, i, 681). (III), (VI), and (VIII) (below) are all converted by 20% $\text{MeOH}\cdot\text{HCl}$ at room temp. into α -methoxy- $\alpha\delta$ -diphenyl- Δ^a -butene- $\gamma\delta$ -dione (VII), m.p. 108—109° (corr.) (ozonolysis products, BzOH and MeOBz), also obtained from (II) and $\text{MeOH}\cdot\text{Me}_2\text{SO}_4$. α -Ethoxy- $\alpha\delta$ -diphenyl- Δ^a -butene- $\gamma\delta$ -dione (VIII), m.p. 96° (corr.) (ozonolysis products, BzOH and EtOBz), is prepared by the action of abs. $\text{EtOH}\cdot\text{HCl}$ on (I), (III), (VI), (VII), $\alpha\beta$ -dibenzoylthylene oxide and chlorohydrin, dibenzoylacetylene, and *cis*- and *trans*- α -chloro- $\alpha\beta$ -dibenzoylthylene (cf. this vol., 778), and also from (II) and Et_2SO_4 . (VII) and (VIII) are both hydrolysed ($\text{MeOH}\cdot\text{NaOMe}$) to (I). (I) or (III) with Ac_2O —

conc. H_2SO_4 gives 3:4-diacetoxy-2:5-diphenylfuran (IX), m.p. 139—139.5° (corr.), converted [as is (I)] by $\text{AcCl}\cdot\text{H}_2\text{SO}_4$ into 3-chloro-4-acetoxy-2:5-diphenylfuran (X), m.p. 132° (corr.). (IX) or (X) with $\text{MeOH}\cdot\text{NaOMe}$ and $\text{MeOH}\cdot\text{HCl}$ affords (I) and (VII), respectively. 3:4-Dichloro-2:5-diphenyl- and 3:4-dibromo-2:5-di-*p*-bromophenyl-furan are obtained from (VIII) and PCl_5 and PBr_5 , respectively. α -Hydroxy- $\alpha\beta$ -di-*p*-chlorobenzoyl-, m.p. 154°, and -di- β -bromobenzoyl- (XI), m.p. 171°, -ethylene are prepared from the $\alpha\beta$ -dibromo- $\alpha\beta$ -diaroylthane and $\text{MeOH}\cdot\text{NaOH}$; the previously described (A., 1927, 59) (XI) is a complex mixture. H. B.

Dibenzoylthylene oxide and chlorohydrin. R. E. LUTZ and F. N. WILDER (J. Amer. Chem. Soc., 1934, 56, 1987—1989).— $(\text{CHBz})_2$ and 20% H_2O_2 in EtOH give $\alpha\beta$ -dibenzoylthylene oxide (I), m.p. 128—129° (corr.), which is stable to AcCl , $\text{Ac}_2\text{O}\cdot\text{H}_2\text{SO}_4$, and PCl_5 and SOCl_2 at 25°; with PCl_5 at 100° or boiling SOCl_2 , 3:4-dichloro-2:5-diphenylfuran (II) is formed. Prolonged interaction of (I) and HCl in 80% EtOH affords β -chloro- $\alpha\beta$ -dibenzoylthyl alcohol (III), m.p. 102° (corr.) [*acetate*, m.p. 71.5° (corr.)], prepared by the action of cold AcCl , converted by $\text{MeOH}\cdot\text{NaOMe}$ into (I) and by $\text{AcCl}\cdot\text{H}_2\text{SO}_4$ into (II). (III) heated at 125—130° gives α -hydroxy- $\alpha\beta$ -dibenzoylthylene (IV). (I), (III), or (IV) with $\text{Et}_2\text{O}\cdot\text{HCl}$ affords an unstable chlorohydrin (V), m.p. 75—80° (isolated by evaporation of the solution at room temp.), which readily loses HCl (when warmed alone or in solvents) to give (IV). (V) heated with MeOH and EtOH affords α -methoxy- and α -ethoxy- $\alpha\delta$ -diphenyl- Δ^a -butene- $\gamma\delta$ -dione, respectively (cf. preceding abstract). *dl*- (VI) and *meso*- (VII) - $\alpha\beta$ -Dichloro- $\alpha\beta$ -dibenzoylthanes are unaffected by PCl_5 (alone or in presence of POCl_3 and HCl) at 100° or SOCl_2 (treated at the b.p. with SO_2 and HCl); (VI) is converted by AcCl -conc. H_2SO_4 into (II), whilst (VII) is similarly unaffected. H. B.

Quinic acid and its derivatives. IV. Degradation of quinic to citric acid. V. Constitution of shikimic acid. H. O. L. FISCHER and G. DANGSCHAT (Helv. Chim. Acta, 1934, 17, 1196—1200, 1200—1207; cf. A., 1932, 850).—IV. Oxidation of anhydroisopropylidenequinamide with HIO_4 affords the anhydroisopropylideneamide of citridialdehyde (I), $\text{NH}\cdot\text{CO} > \text{C}(\text{CH}_2\cdot\text{CHO})_2$, m.p. 138°, or (+2 H_2O), m.p. 115°, and HCO_2H . (I) gives a *di-p*-nitro-, m.p. 226° (decomp.), and *di-2*:4-dinitro-, m.p. about 200° after darkening at 190°, -phenylhydrazone, but with $\text{NH}_2\text{OH}\cdot\text{HCl}$ gives the compound $\text{C}_9\text{H}_9\text{O}_3\text{N}_2$, decomp. about 290°. Oxidation of (I) with $\text{Br}\cdot\text{H}_2\text{O}$ followed by hydrolysis gives citric acid.

V. Shikimic acid (I) is converted by $\text{HCl}\cdot\text{MeOCH}_2\text{N}_2$ into *Me shikimate* (I), m.p. 113—114°, by generated ($\text{Pd}\cdot\text{BaSO}_4$ in 50% EtOH) to non-cryst. *di dihydroshikimate* (III), whence *dihydroshikimic*, m.p. 176—178°. (III), COMe_2 , and CuSO_4 afford *di isopropylidenedihydroshikimate*, b.p. 145—150° (0.2 mm., (Bz derivative, m.p. 121°). Hydrogenation of (II) in abs. EtOH or, better, AcOH in presence of Pd apparently leads to a *Me dihydrocyclo carboxylate*, b.p. 145—150° (bath)/0.2 mm.,

yields an isopropylidene derivative, b.p. 120—125° (bath)/0.1 mm., and is hydrolysed to a lactone. Oxidation of (III) with HIO_4 gives γ -carbomethoxy-pentanedioldi-p-nitrophenylhydrazide, m.p. 155—160°, oxidised by $\text{Br}-\text{H}_2\text{O}$ and then hydrolysed to tricarballic acid. (III) is transformed by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in boiling EtOH into dihydroshikimhydrazide, m.p. 200—202°, whence the corresponding urethane, $\text{C}_7\text{H}_{11}\text{O}_4\text{N}\cdot\text{H}_2\text{O}$, m.p. 234° (decomp.) [Ac_2 , m.p. 253° (slight decomp.), and formyl, m.p. 181—181°, derivatives], hydrolysed to 3:4:5-trihydroxycyclohexylamine (IV), m.p. 129—130° (hydrochloride, m.p. 176—177°; sulphate; Ac_4 derivative, m.p. 150°, $[\alpha]_D^{25} -9.9^\circ$ in MeOH). Treatment of (IV) with NO_2^+ followed by decomp. and acetylation of the product appears to lead to an acetylated cyclohexenetriol, b.p. 130—140° (bath)/high vac., and an oxidocyclohexanediyl diacetate, b.p. 170—180° (bath)/high vac. (I) is therefore 3:4:5-trihydroxy- Δ^1 -cyclohexenecarboxylic acid.

H. W.

Lichen materials. Y. ASAHINA (Acta Phytochim., 1934, 8, 33—45).—A group classification of lichen products on the basis of their chemical structures.

J. W. B.

[Pterasantalin, a crystalline dye from red sandalwood.] H. RAUDNITZ (Ber., 1934, 67, [B], 1603—1604; cf. this vol., 900).—In reply to Leonhardt *et al.* (this vol., 1007), it is maintained that "pterasantalin" is identical with (impure) santalin and the name should be deleted.

H. W.

Crystalline pigments of species in the Aspergillus glaucus series.—See this vol., 1263.

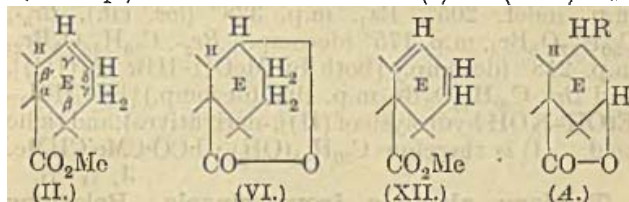
Preparation of l-abietic acid and properties of its salts. S. PALKIN and T. H. HARRIS (J. Amer. Chem. Soc., 1934, 56, 1935—1937).—l-Abietic acid (I), m.p. 172—177°, $[\alpha]_D -104^\circ$ (all rotations are in EtOH) (cf. Schulz, A., 1917, i, 649), is readily purified through the diamylamine (mixture of *n*- and *iso*-) salt, m.p. 139—141°, $[\alpha]_D -57^\circ$. Purification can also be effected through the compound, $\text{C}_{20}\text{H}_{29}\text{O}_2\text{Na}\cdot 3\text{C}_{20}\text{H}_{30}\text{O}_2$, m.p. 205—208°, $[\alpha]_D -97^\circ$ (cf. Dupont *et al.*, A., 1926, 611). The following salts of (I) are described: NH_2Bu^a , m.p. 164—169° (decomp.), $[\alpha]_D -72.7^\circ$; $(\text{NH}_2\text{Pr}^a)_2$, m.p. 160—162°, $[\alpha]_D -63.5^\circ$; $(\text{NH}_2\text{Bu}^a)_2$, m.p. 158—161°, $[\alpha]_D -69.3^\circ$; di-*n*-, m.p. 141—142°, $[\alpha]_D -74.5^\circ$, and *iso*-, m.p. 139—141°, $[\alpha]_D -62.4^\circ$ (lit. 133° and -17.1° , respectively), -amylamine; quinine, m.p. 185—187° (lit. 180°), $[\alpha]_D -140.3^\circ$. Crystallographic data for (I) and most of the salts are given.

H. B.

Constitution of hederagenin and oleanolic acid.

VI. Z. KITASATO (Acta Phytochim., 1934, 8, 1—18; cf. this vol., 412; A., 1933, 612).—Clemmensen reduction of ketodiacylhederagenin Me ester (I) and subsequent methylation gives an ester, $\text{C}_{31}\text{H}_{50}\text{O}_4$, m.p. 250—255° ($\text{CO} \rightarrow \text{CH}_2$ in ring E), not identical with hederagenin Me ester (II), or with (IV) or the dehydro-compound (below). With boiling AcOH-HCl diacylhederagenin Me ester (III) affords the isomeric epihederagenin Me ester (IV), m.p. 225—227° [Ac_2 derivative (V), m.p. 185°, not identical with (III)], and a lactone the Ac_2 derivative of which is identical with the A-form (VI) of diacylhederagenin lactone.

With AcOH-HCl, Me acetyloleanolate (VII) gives an anhydro-compound, $\text{C}_{31}\text{H}_{48}\text{O}_2$ or $\text{C}_{30}\text{H}_{46}\text{O}_2$, m.p. about 240°. With HBr-AcOH and subsequent hydrolysis (MeOH-KOH) (I) affords ϕ -ketoederagenin (geometrical isomeride), m.p. > 300° [Me ester, m.p. 245° [Ac_2 derivative (VIII), m.p. 226°, not identical with (I)]]; similarly Meketoacetyloleanolate (IX) affords the isomeric Ac derivative, m.p. 287° [Me ester (X), m.p. 310°], of ϕ -ketoacetyloleanolic acid, m.p. 267—271° (decomp.). Reduction of either (I) or (VIII) with

(IV.) (double linking at $\beta'\gamma'$).

5% Na-Hg in 90% EtOH and reacylation affords the Ac_2 derivative (XI), m.p. 198° [together with a substance, m.p. 155°, only from (I)], of dehydroederagenin Me ester (XII), m.p. 219—220°. Similarly (X) affords Me dehydroacetyloleanolate (XIII), m.p. 225°, whereas (IX) gives (VII). With HBr-AcOH either (III) or (V) gives (VI), thus proving the relative positions of the double linkings in (II) and (IV). By similar HBr-AcOH treatment (VII) affords acetyloleanolic acid lactone (XIV), m.p. > 340°; hedragone Me ester affords hedragone lactone, m.p. > 300° [B-derivative (in ring A), m.p. 282° (decomp.)]; the Me_2 ester of hedragenonediacyl gives hedragenonediacyl Me_1 ester monolactone (XV), m.p. 205°; (XI) gives bromodiacylhederagenin lactone (A; R-Br), m.p. 236° (decomp.), reduced by Zn-AcOH to the Ac_2 derivative, m.p. 245° [not identical with (VI)], of the B-form (A; R=H), m.p. 308—310°, of hederagenin lactone; (XIII) gives bromoacetyloleanolic acid lactone, m.p. 228° (decomp.), reduced to an acetyloleanolic acid lactone, m.p. 315°, not identical with (XIV) (allocation of A and B structures not established); Me dehydrohedragenonediester (by Na-Hg-AcOH-EtOH reduction of the keto-compound), after re-methylation of the product, gives bromohedragenonediacyl Me_1 ester monolactone, m.p. 218—220° (decomp.), reduced to hedragenonediacyl Me_1 ester monolactone, m.p. 198—200°, not identical with (XV). Oxidation of (V) with CrO_3 -AcOH gives an ester, m.p. 235°, the Ac derivative, m.p. 240—242°, of which is not identical with either (I) or (IV). The mechanisms of these reactions are elucidated by partial formulæ (ring E).

J. W. B.

Resin acid from Manila elemi resin. II. Oxidation product and oxime from γ -elemic acid. M. MLADENOVIC (Monatsh., 1934, 64, 173—176).—Oxidation of the OH-acid, γ -elemic acid (I) (previously termed γ -elemic acid, A., 1931, 961), with CrO_3 -AcOH at 60° affords the keto-acid, γ -elemic acid, $\text{C}_{30}\text{H}_{48}\text{O}_3$, m.p. 295° [oxime, m.p. 273°, regenerating (I) with warm NaNO_2 -AcOH].

J. W. B.

Constitution of jegosapogenin. I. C. SONE (Acta Phytochim., 1934, 8, 23—31).—Jegosapogenin, $\text{C}_{35}\text{H}_{56}\text{O}_6$ (I) (2 double linkings) (prep. by method of

Asahina *et al.*, A., 1914, i, 856, who gave $C_{37}H_{58}O_7$, with boiling $Ac_2O-NaOAc$ gives an Ac_4 derivative, m.p. 250—254° (decomp.), but with $AcCl-C_5H_5N$ only an Ac_3 derivative, m.p. 278°, a corresponding Bz_3 derivative, m.p. 296—299°, also being obtained. With $MeOH-Br$ at 0° (I) gives a Br_4 -derivative, $C_{35}H_{54}O_6Br_4$, m.p. 235° (decomp.), whereas in $CHCl_3-MeOH$ a Br_3 -derivative, $C_{35}H_{55}O_6Br_3$ (II), m.p. 246°, is obtained. Hydrolysis of (I) with $KOH-EtOH$ gives iegasapogenol, $C_{30}H_{50}O_5$ (III) (1 double linking) [Ac_4 , m.p. indef. 205°, Bz_4 , m.p. 328° (*loc. cit.*), Br_3 , $C_{30}H_{47}O_5Br_3$, m.p. 175° (decomp.), Br_2 , $C_{30}H_{48}O_5Br_2$, m.p. 218° (decomp.) [both by $MeOH-HBr$ on (III)], and Br , $C_{30}H_{49}O_5Br$, m.p. 193° (decomp.) [by $CHCl_3-EtOH-KOH$ hydrolysis of (II)], -derivatives, and tiglic acid. (I) is therefore $C_{30}H_{45}(OH)_4 \cdot O \cdot CO \cdot CMe \cdot CHMe$.

J. W. B.

Tertiary alcohols from cineole. Relations between the cineole and camphane nuclei. A. GANDINI (Gazzetta, 1934, 64, 594—606).—Keto-cineole and $MgMeI$ yield two isomeric 2-hydroxy-2-methylcineoles (I), one m.p. 67°, and the other an oil. Dehydration of (I) at the b.p. (214—217°) yields a product which is converted by $KMnO_4$ into cineolic acid, and is therefore the Δ^2 -compound. Dehydration with H_2SO_4 yields $\Delta^{2:6:8(9)}$ -2-methylmenthatriene (?), converted by $AcOH-HCl$ into methylcumene, which yields tetrabromo-*o*-xylene. Oxidation of (I) by alkaline $KMnO_4$ yields terebinic acid, with the intermediate formation of the Me ketone of homoterpenilic acid. 2-Hydroxy-1-ethylcineole, two isomerides, m.p. 74° and 100°, and 2-hydroxy-2-phenylcineole, two isomerides, m.p. 84° and 119°, are obtained by analogous methods and have similar properties.

R. K. C.

Action of primary bases on camphorquinone and formation of methylaminoepicamphor. H. RUPE and H. MARTIN (Helv. Chim. Acta, 1934, 17, 1207—1218).—Aminocamphor (I) is converted by $p-C_6H_4Me \cdot SO_2Cl$ and KOH into p -toluenesulphonamidocamphor, m.p. 107°, the *Na* salt of which is transformed by MeI in $MeOH$ into the *Me* derivative, m.p. 89°, hydrolysed by 80% H_2SO_4 , H_2SO_4-AcOH , or conc. HCl to resinous products and a little camphorquinone (II). 2-Naphthalenesulphonamidocamphor has m.p. 127°. Treatment of (I) with CH_3N_2 does not yield a *sec.*-base. (I) and CH_3O at 130° afford (II), [$\cdot CH_2 \cdot NMe_2$] $_2$, and (?) anhydroadiaminocamphor, m.p. 116°. (II) and $NH_2Me-MeOH$, alone or in presence of $NaOAc$ at 120—130°, yield methyliminoepicamphor, b.p. 126—130°/13 mm. (perchlorate, m.p. 264°), reduced (Ni in 60% $EtOH$, but not by Zn dust and $AcOH$) to methylaminoepicamphor (perchlorate, m.p. 254—255°), also prepared, b.p. 103—103.5°/9 mm., m.p. 18°, [α] $_D^{25} +13.99^\circ$ (perchlorate, m.p. 255°), from aminoepicamphor and MeI in $EtOH$ and purified through the NO -derivative. Me bornyl-enecarboxylate has b.p. 102°/11 mm., $\alpha_D +125.2^\circ$ ($l=1$). Acetyl- p -phenylenediamine and (II) afford a compound, m.p. 109° after softening at 95°, reduced (Zn dust and $NaOH$) to p -acetamidocamphor, m.p. 166°. The action of 1:2:4- $C_6H_3Cl(NO_2)_2$ on α -aminocamphor leads to 2:4-dinitroanilinoepicamphor, needles, m.p. 177°, or coarse prisms, m.p. 173.6°,

hydrogenated (Ni, $H_2O-EtOH$) to a substance (hydrochloride, $C_{16}H_{22}N_3Cl$). H. W.

Betaines and amino-acids of camphor. H. RUPE and H. MARTIN (Helv. Chim. Acta, 1934, 17, 1263—1282; cf. A., 1931, 1300).—Chloroacetamidocamphor (I) and NH_2Me yield methyldiacetylcamphoramine, $NMe(CH_2 \cdot CO \cdot NHR)_2$ [$R = \cdot CH < \begin{smallmatrix} C_{18}H_{14} \\ CO \end{smallmatrix}$] m.p. 134°, [α] $_D +25.14^\circ$ in C_6H_6 [perchlorate, m.p. (indef.) 175—180° after softening at 125°; methiodide, m.p. 197—198° after softening at 194°]. (I) and aminocamphor in boiling $MeOH$ afford camphorylaminoacetcamphorylamide (II), $NHR \cdot CO \cdot CH_2 \cdot NHR$, m.p. 131°, [α] $_D +3.22^\circ$ in C_6H_6 , $+1.81^\circ$ in C_5H_5N [perchlorate, m.p. 249—250°; hydrobromide, m.p. (indef.) 204°; hydrochloride, m.p. 191°; Bz , m.p. 228°, and NO , m.p. 171°, or (+ $EtOH$) m.p. 118°, -derivatives; corresponding phenylthiocarbamide, $C_9H_{30}O_3N_3S$, m.p. 184.5°]. (II) and $CH_2Cl \cdot COCl$ in C_6H_6 give chloroacetylcamphorylaminoacetcamphorylamide (III), $NHR \cdot CO \cdot CH_2 \cdot NR \cdot CO \cdot CH_2Cl$, m.p. 209°, transformed by $NHMe_2$ in $EtOH$ into dimethylaminoacetylcamphorylaminoacetcamphorylamide (IV), $NHR \cdot CO \cdot CH_2 \cdot NR \cdot CO \cdot CH_2 \cdot NMe_2$, m.p. 119°, [α] $_D +3.67^\circ$ in C_6H_6 (hydrochloride). Addition of $CH_2Br \cdot CO_2Et$ to (IV) in C_6H_6 leads to the bromide, $NHR \cdot CO \cdot CH_2 \cdot NR \cdot CO \cdot CH_2 \cdot NMe_2Br \cdot CH_2 \cdot CO_2Et$, m.p. 184—186°, [α] $_D +56.21^\circ$ in H_2O , which with Ag_2O affords the betaine,

$NHR \cdot CO \cdot CH_2 \cdot NR \cdot CO \cdot CH_2 \cdot NMe_2 \cdot CH_2 \cdot CO_2$, m.p. 189°, [α] $_D +65.39^\circ$ in H_2O , which does not exhibit anomalous dispersion (cf. *loc. cit.*). (Dicamphorylmethyl)amine and (I) in abs. $EtOH$ do not yield the expected *tert.*-base (V), hydrolysis occurring with formation of camphylcarbinol and camphorylmethylaminoacetcamphorylamide, $CH_2R \cdot NH \cdot CH_2 \cdot CO \cdot NHR$, m.p. 137° (hydrochloride, m.p. 173°); evidence of the intermediate production of (V) is obtained by isolation of the methiodide $(CH_2R)_2N \cdot CH_2 \cdot CO \cdot NHR$, MeI , m.p. 196° after softening at 178°, when reaction is effected in dioxan. Camphorylmethyl bromide and NH_2Me give methylenecamphor and methylcamphorylmethylamine, $NHMe \cdot CH_2R$, b.p. 126—127°/0.5 mm., [α] $_D +59.78^\circ$, transformed by (I) into methylcamphorylmethylaminoacetcamphorylamide, $CH_2R \cdot NMe \cdot CH_2 \cdot CO \cdot NHR$, m.p. 127—130° after softening at 103° (perchlorate). (I) and dimethylaminocamphor yield, after treatment with $HClO_4$, methylcamphorylaminoacetcamphorylamide methoperchlorate, m.p. 209°, and trimethylcamphorylammonium perchlorate, m.p. 233°. The action of NMe_3 on (III) in $EtOH$ at 40—45° leads to camphoryltrimethylaminoacetamidocamphorylamide (hydrochloride, $NHR \cdot CO \cdot CH_2 \cdot NR \cdot CO \cdot CH_2 \cdot NMe_3Cl$, m.p. 212—213° (decomp.) (corresponding base, [α] $_D +30.6^\circ$ in H_2O , and iodide, decomp. 204°). (III) and aminocamphor in C_6H_6 afford camphorylaminoacetcamphorylamidoacetcamphorylamide, $NHR \cdot CH_2 \cdot CO \cdot NR \cdot CH_2 \cdot CO \cdot NHR$, m.p. 210°, [α] $_D +53.06^\circ$ in C_5H_5N , and a substance, m.p. 222°. (I) passes in boiling C_5H_5N into (?) diketodiamphorylpiperazine, $NR < \begin{smallmatrix} CO \cdot CH_2 \\ CH \cdot CO \end{smallmatrix} > NR$, m.p. 214° (decomp.) after softening at 205°. H. W.

Manufacture of 2-hydroxy-2-keto- β -pericyclo-camphane from 2:5-diketocamphane.—See B., 1934, 908.

Products of the degradation of cyclocamphanone and diketocamphane in the animal organism. F. REINARTZ, W. ZANKE, and K. FAUST (Ber., 1934, 67, [B], 1536—1542).—Biological oxidation of cyclocamphanone leads essentially to a mixture of the corresponding π -alcohols, oxidised by CrO_3 and finally by KMnO_4 to the corresponding stereoisomeric acids, one of which, m.p. 249—250° (*Ag* salt), is obtained homogeneous. Its constitution is established by its conversion by the successive action of HBr-AcOH and Zn dust-AcOH into isoketopinic acid. In addition, 5(?)-hydroxycyclocamphanone, m.p. 221—222.5°, stable towards CrO_3 and KMnO_4 (*p*-nitrobenzoate, m.p. 147.5—153.5°; semicarbazone), is produced, apparently with minor quantities of the 3-OH-derivative. Oxidation of *p*-diketocamphane, like that of *epicamphor*, occurs at C_4 , and the 4-hydro-diketocamphane is isolated after oxidation with CrO_3 as the *p*-nitrobenzoate, $\text{C}_{17}\text{H}_{17}\text{O}_6\text{N}$, m.p. 118.5—120°. Oxidation appears to produce cyclocamphanone- α -carboxylic acid, m.p. 248—250°, stable to warm KMnO_4 (disemicarbazone, m.p. 268—280°, according to the rate of heating). H. W.

Camphorsulphonic acid and some camphor-sulphonates. F. GIRAULT (J. Pharm. Chim., 1934, [viii], 20, 207—217).—The prep., properties, and determination of *d*-camphor-10-sulphonic acid and its cryst. *novocaine*, m.p. 138—139°, $\alpha_D^{25} +15^\circ 36'$, *quinine*, m.p. 210°, $\alpha_D^{25} -107^\circ 18'$, and *strychnine*, decomp. 250°, $[\alpha]_D -18^\circ$, salts are given.

E. H. S.

Synthesis of santene and its derivatives. L. M. MOHUNTA and J. N. RAY (J.C.S., 1934, 1328—1329).— $\text{Et } \alpha\alpha'$ -diacetyladi-pate, Na , PhMe , and CH_2I_2 give $\text{Et}_2 1:3$ -diacetylcyclopentane-1:3-dicarboxylate, b.p. 125—130°/10 mm., and a dicyclic ketone, b.p. 100—101°/9 mm., $n_D^{25} 1.5038$ (semicarbazidosemicarbazone, m.p. 205°). The ester is hydrolysed to 1:3-diacetylcyclopentane, reduced (Al-Hg) to santene glycol.

F. R. S.

Small-plant-scale liquid-phase hydrogenation under high pressure. Hydrogenation of furfuraldehyde. G. CALINGAERT and G. EDGAR (Ind. Eng. Chem., 1934, 26, 878—880).—Pure furfuryl alcohol is prepared by hydrogenating furfuraldehyde in a vertical, cylindrical, jacketed autoclave at a controlled temp. about 175°, and an initial pressure of 100—120 atm., in presence of Cu chromite and dry slaked CaO . Under optimum conditions, hydrogenation is complete in < 30 min. The catalyst is prepared by roasting pptd. basic Cu NH_4 chromate in an electrically heated rotary tube-furnace (cf. A., 1931, 598). C. C.

Furylmalonic acid and its derivatives. T. REICHSTEIN and H. J. MORSMAN (Helv. Chim. Acta, 1934, 17, 1119—1129).—Furan-2-carboxylic acid is converted by PCl_5 into the corresponding chloride, b.p. 58°/12 mm., thence by anhyd. HCN in Et_2O - $\text{C}_6\text{H}_5\text{N}$ into 2-furoylformonitrile, b.p. 67.71°/0.7 mm., which is reduced (NaOMe and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) to furyl-

2-acetic acid (I), b.p. 102—104°/0.4 mm., m.p. about 65°. Treatment of (I) with HCl and MeOH or EtOH at room temp. gives *Me* (II), b.p. 74—75°/11 mm., and *Et*, b.p. 81—82°/11 mm., 2-furylacetae. Condensation of (II) with $\text{Me}_2\text{C}_2\text{O}_4$ and KOMe followed by distillation of the product in vac. leads to (?) *Me* 2-furylpyruvate, needles, m.p. 99—99.5° (corr.), or granules, m.p. 101.5—102.5°, and *Me* 2-furylmalonate (I), b.p. 130—132°/9 mm., which, unlike $\text{CHPh}(\text{CO}_2\text{Et})_2$, is smoothly sol. in dil. alkali. Hydrolysis of (I) with $2N\text{-NaOH}$ at room temp. gives 2-furylmalonic acid, m.p. 106—107° (corr., decomp.) greatly dependent on rate of heating [*diamide* (II), m.p. 185—186° (corr.)]. Condensation of (I) with EtI and NaOMe affords *Me* 2-furylethylmalonate (III), b.p. 130—132°/9 mm., insol. in aq. alkali and hydrolysed by NaOH-MeOH to α -2-furyl-*n*-butyric acid, m.p. 50°. (III), $\text{CO}(\text{NH}_2)_2$, and NaOMe-MeOH at 105° yield α -2-furyl-*n*-butyramide, m.p. 97—98.5°, furylethylbarbituric acid (IV), m.p. 187.5—189° (corr.), and $\text{NH}_2\cdot\text{CO}_2\text{Me}$. (IV) could not be obtained from (II) with Ph_2CO_3 at 200—210° or $(\text{COCl})_2$ in boiling C_6H_6 , whereas $\text{CHPh}(\text{CO}\cdot\text{NH}_2)_2$ and $(\text{COCl})_2$ give phenylbarbituric acid. Furan-2-carboxyl bromide, b.p. 78°/11 mm., and $\text{CHN}_2\cdot\text{CO}_2\text{Me}$ afford *Me* 2-furoyl-diazoacetate, m.p. 108° (corr.), transformed in MeOH containing Pb at 140—150° into (I). H. W.

β -Santonin. G. R. CLEMO (J.C.S., 1934, 1343—1346).— β -Santonin (I), m.p. 216—218°, $[\alpha]_D^{25} -137.2^\circ$ in CHCl_3 (*oxime*, m.p. 224°), has been isolated from samples of *Artemisia*. Reduction (Pd-H_2) of (I) affords tetrahydro- β -santonin-a, m.p. 207—208°, and -b, m.p. 125—126°, each reduced (Zn-Hg) to deoxy-tetrahydro- β -santonin, m.p. 75—76°, dehydrogenated (Se) to 1-methyl-7-ethylnaphthalene. (I) with H_2SO_4 yields 1-desmotropo- β -santonin (II), m.p. 253°, $[\alpha]_D^{25} -101.7^\circ$ in EtOAc (*Ac* derivative, m.p. 156—157°), which with KOH leads to 1-isodesmotropo- β -santonin (III), m.p. 194°, $[\alpha]_D^{25} -136.8^\circ$ in EtOAc . (II) is reduced (Zn-AcOH) to *d*- β -santonous acid, m.p. 174°, $[\alpha]_D^{25} +54.9^\circ$ in EtOH , converted by heating with $\text{Ba}(\text{OH})_2$ into an acid, m.p. 152°, $[\alpha]_D^{25} +60.9^\circ$. (III) on reduction gives *d*-santonous acid. (I) is a stereoisomeride of santonin. F. R. S.

Hydropyran ring. I. α -Hydroxyvaleraldehyde and its derivatives. R. PAUL (Bull. Soc. chim., 1934, [v], 1, 971—980).—Largely a more detailed account of work previously reviewed (this vol., 281). The following is new. δ -Hydroxyvaleraldehyde (I) [*oxime*, m.p. 92—93° (Maquenne block)] is reduced (Al-Hg , H_2O) to pentane- $\alpha\alpha$ -diol [*di*(phenylcarbamate)], m.p. 176°. (I) and tetrahydrofurfuryl alcohol- HCl (trace) give the cyclic hemiacetal 2-(tetrahydrofurfuryloxy)tetrahydropyran, b.p. 97°/6 mm. The ether, $(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_2$, b.p. 106—110°/12 mm., is a by-product in the prep. (*loc. cit.*) of (I); it arises either by elimination of H_2O from 2 mols. of (I) or by addition of (I) to 2:3-dihydropyran. H. B.

Preparation of 7-ethoxy-4-methylcoumarin.—See B., 1934, 874.

Studies in the pyrone series. I. Alkyl benzo- γ -pyrones and α -naphtha- γ -pyrones. I. M. HEIL-

BRON, D. H. HEY, and A. LOWE (J.C.S., 1934, 1311—1315).—2-Propionoacetylphenol, m.p. 60°, obtained from *o*-hydroxyacetophenone, PrOEt , and Na , gives (AcOH-HCl) 2-ethylchromone, m.p. 18°, which with piperonal and NaOEt yields 3':4'-methylenedioxy-2- α -methylstyrylchromone, m.p. 147°. The following are similarly prepared: 5-methoxy-2-propionoacetylphenol, m.p. 101°, 7-methoxy-2-ethylchromone, m.p. 81° (3':4'-methylenedioxy-styryl derivative, m.p. 130°), 2-propionoacetyl- α -naphthol, m.p. 75—76°, 2-ethyl- α -naphthyl- γ -pyrone, m.p. 111° (3':4'-methylenedioxy-styryl derivative, m.p. 209°), 5-methoxy-2-butyroacetylphenol [5(3?)'-2'-hydroxy-4'-methoxyphenyl-3(5?)'-propylpyrazole-1-carbamide, m.p. 215°], and 7-methoxy-2-propylchromone, m.p. 83°. 2:4-Dimethoxyacetophenone (I), Na , and PrOEt give ω -propiono-3:4-dimethoxyacetophenone, m.p. 72°, the Na salt of which is methylated (MeI) to α -propiono-2:4-dimethoxypropionophenone, m.p. 80°, converted (AcOH-HBr) into 7-methoxy-3-methyl-2-ethylchromone (7-methoxy-3':4'-methylenedioxy-2- α -methylstyryl-3-methylchromone, m.p. 144—145°). (I), Na , and BuOEt afford ω -butyro-2:4-dimethoxyacetophenone [5(3?)'-2':4'-dimethoxyphenyl-3(5?)'-propylpyrazole-1-carbamide, m.p. 189—190°], which is methylated to α -butyro-2:4-dimethoxypropionophenone [5(3?)'-2':4'-dimethoxyphenyl-4-methyl-3(5?)'-propylpyrazole-1-carbamide, m.p. 226—227°], converted (AcOH-HBr) into 7-methoxy-3-methyl-2-propylchromone, m.p. 79°. 1-Methoxy-2-naphthyl Me ketone (semicarbazone, m.p. 191°) yields 2-propionoacetyl-1-naphthyl Me ether [5(3?)'-1'-methoxy-2'-naphthyl-3(5?)'-ethylpyrazole-1-carbamide, m.p. 174—175°], the Na salt of which is methylated (MeI) to 2-(α -propionopropionyl)-1-naphthyl Me ether [5(3?)'-1'-methoxy-2'-naphthyl-4-methyl-3(5?)'-ethylpyrazole-1-carbamide, m.p. 191°], converted into 3-methyl-2-ethyl- α -naphthyl- γ -pyrone (3':4'-methylenedioxy-2- α -methylstyryl derivative, m.p. 171—172°). 1-Methoxy-2-naphthyl Et ketone, m.p. 42—43°, forms a semicarbazone, m.p. 192°, and an oxime, m.p. 112—113°. *o*-Hydroxyaryl Me ketones give a coumarin in the Kostanecki reaction with NaOPr and Pr_2O , whilst the Et ketone gives a chromone. F. R. S.

New synthesis of benzopyrylium salts by condensation of reactive phenols with unsaturated aldehydes or ketones in the presence of a strong acid and an oxidising agent. I. Typical cases with resorcinol as phenolic compound. R. ROBINSON and J. WALKER (J.C.S., 1934, 1435—1440).—Oxidative condensation of benzylideneacetophenone and resorcinol (I) with EtOH-HCl and chloranil gives the monohydrate of 7-hydroxy-2:4-diphenylbenzopyrylium chloride. Similarly anisylideneacetophenone and (I) yield 7-hydroxy-2-phenyl-4-anisylbenzopyrylium chloride ($+\text{H}_2\text{O}$) (II), hydrolysed (KOH) to (I), COPhMe , and $p\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$. The salts described have been obtained by the condensation of the appropriate ketone: 7-hydroxy-4-phenyl-2-anisyl- (III), -2:4-dianisyl- ($+\text{H}_2\text{O}$), -4-phenyl-2-styryl-, ($+\text{2H}_2\text{O}$), and -4-phenyl-1'-benzylidene-2:3-cyclopenteno-(2':3')-benzopyrylium chloride ($+\text{H}_2\text{O}$); and 6-hydroxy-9-phenyl-1:2-dihydro-3:4-benzo- and 6-hydroxy-9-veratryl-4-veratrylidene-1:2:3:4-tetrahydroxanthylum chloride. The constitution of (II) and

(III) are proved, since 7-hydroxyflavone and Mg anisyl bromide give (II) and 7-hydroxy-4'-methoxyflavone and MgPhBr form (III). F. R. S.

Spectrographic investigations of benzopyrylium dyes. III. Absorption spectra of cyanidin and delphinidin derivatives. K. HAYASHI (Acta Phytochim., 1934, 8, 65—105; cf. this vol., 416).—Absorption spectra have been plotted for the following flavylum chlorides, prepared by usual methods (Robinson): 3:5:7-trihydroxy-, $+\text{H}_2\text{O}$ (lit. $+\text{2H}_2\text{O}$) ($\omega\text{-Bz}$ derivative, decomp. 222°); 3:5:7:3'-tetrahydroxy- ($\omega\text{-Bz}$ derivative, decomp. 180—181°); 3:3':4'-trihydroxy-5:7-dimethoxy-, decomp. 208°; 3:5:7:3':4'-pentahydroxy- (cyanidin chloride) and its 5- Bz derivative; 3-hydroxy-5:7:3':4'-tetramethoxy-, $+\text{2.5H}_2\text{O}$, sinters $> 135^\circ$, decomp. 202° (reactions differ from those of specimen prepared from natural cyanin, Karer *et al.*, A., 1927, 1197); 3:5:7-trihydroxy-3':4'-dimethoxy-, m.p. $> 250^\circ$ (5- Bz derivative, decomp. 232—233°); 3-hydroxy-5:7:3':4':5'-pentamethoxy-, $+\text{1.5H}_2\text{O}$, decomp. 203—204°; 3:5:7-trihydroxy-3':4':5'-trimethoxy-, 3:4'-dihydroxy-5:7:3':5'-tetramethoxy-, $+\text{1.25H}_2\text{O}$, sinters 207°, decomp. 235—239°; 3:5:7:4'-tetrahydroxy-3':5'-dimethoxy- (malvidin chloride), and 3:5:7:3':4':5'-hexahydroxy- (delphinidin chloride), and their 5- Bz derivatives. The effects of substitution on the absorption spectra are discussed, substitution of the 3-OH exerting a strongly bathochromic displacement on the first band ($1/\lambda=1800\text{--}2000$) and rendering the band in the ultra-violet very indistinct. Improved preps. for various intermediates are given; the following seem to be new: ω :3-diacetoxyacetophenone, b.p. 189—197°/14 mm. (from *m*-acetoxybenzoyl chloride, b.p. 138—139°, through the ω -diazo-compound); ω -acetoxy-, m.p. 85—86°, by EtOH-KOAc on ω -bromo-3:4:5-trimethoxyacetophenone, m.p. 64° (by direct bromination), and also by the action of AcOH on the ω -diazo-compound, decomp. 103° (from CH_2N_2 and trimethylgallic acid chloride at -10°). J. W. B.

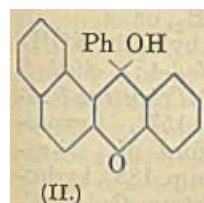
Synthesis of flavanols. J. ALGAR and J. P. FLYNN (Proc. Roy. Irish Acad., 1934, 42B, 1—8).—Flavanone with CH_2O in boiling EtOH-HCl during 10 hr. affords a product which is oxidised by H_2O_2 in NaOH-EtOH to flavanol (cf. A., 1930, 349). *o*-Hydroxyphenyl styryl ketone with H_2O_2 in hot EtOH -excess of KOH (cf. A., 1932, 859) affords flavanol, m.p. 171—172° (lit., 169—170°), in good yield. The following are prepared similarly: 4'-methoxy-, m.p. 235° (lit., 225°), 3':4'-methylenedioxy-, m.p. 218—219°, 3':4'-dimethoxy-, m.p. 203° (lit., 199—200°), 7-methoxy-3':4'-methylenedioxy-, m.p. 210°, and 4':7:8-trimethoxy-flavanol, m.p. 202° (lit., 198°). J.

Synthesis of diflavones. J. ALGAR and K. J. HANWAY (Proc. Roy. Irish Acad., 1934, 42B, 9—15). The Br_4 -derivative of 4:6-dibenzylidenediacetoresorcinol Me_2 ether with boiling MeOH-NaOMe during 3 hr., followed by boiling HCl , affords dibenzoylacetoresorcinol Me_2 ether (cf. A., 1915, i, 707; 190, 102), demethylated to diflavone. Similarly, tetrabromides of 4:6-dianisylidene-, 4:6-dipiperonylidene-, and 4:6-di-*m*-methoxybenzylidene-diacetoresorcinol Me_2 ether, m.p. 181—182°, 175° (decomp.),

and 186° (decomp.), respectively, are converted into dianisoylaceto-, *di*-(3:4-methylenedioxybenzoylaceto)-, and *di*-*m*-methoxybenzoylaceto-resorcinol Me_2 ether, m.p. 232—234°, 210—212°, and 175—176°, respectively, which are demethylated to 4':7-dihydroxy-, m.p. > 300°, and 3':4':7-trihydroxy-6-acetylflavone, m.p. > 360° (Ac_2 derivative, m.p. 293—295°), and 3':3''-dihydroxydiflavone, m.p. > 360° [Ac_2 derivative, m.p. 286—288°, identical with the Ac_2 derivative corresponding with the 3':3''-dimethoxydicoumaranone of Ryan and Ryan (A., 1931, 96)], respectively.

J. L. D.

Pyrenium salts. XXIII. Constitution of phenylbenzoxanthenols and β -benzoxanthone. W. DILTHEY, F. QUINT, and F. DAHM (J. pr. Chem., 1934, [ii], 141, 65—76).— β - $\text{C}_{10}\text{H}_7\cdot\text{OPh}$, BzCl , and AlCl_3 in CS_2 give *Ph* 2-phenoxy- α -naphthyl ketone, m.p. 111—112° (also obtained from 1:2- $\text{C}_{10}\text{H}_6\text{Bz}\cdot\text{OK}$, PhBr , and Cu -bronze at 200°), which when treated successively with AcOH -conc. H_2SO_4 and HClO_4 affords phenylbenzoxanthenium perchlorate (I), m.p.

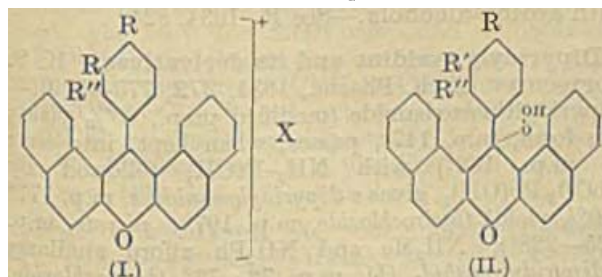


(II.)

270°. (I) is also formed when the product from p - $\text{C}_{10}\text{H}_7\cdot\text{ONa}$, o - $\text{C}_6\text{H}_4\text{Br}\cdot\text{COPh}$, and Cu -bronze at 240° is treated with HClO_4 in Ac_2O . Dissolution of (I) in COMe_2 and addition of H_2O gives phenylbenzoxanthene (II), m.p. 172—173° (*Me* ether, m.p. 150°). β - $\text{C}_{10}\text{H}_7\cdot\text{OMe}$, o - $\text{C}_6\text{H}_4\text{I}\cdot\text{COCl}$, and AlCl_3 in CS_2 afford 1-*o*-iodobenzoyl- β -naphthol, m.p. 149°, converted by MeOH - KOH into 1:2-benzoxanthone (III), m.p. 142°, which with MgPhBr gives (II). The benzoxanthone prepared by von Kostanecki (A., 1892, 1098) is (III), and the phenylbenzoxanthene of Gomberg and Schoepfle (A., 1917, i, 551) is, therefore, (II). Contrary to Rospendovsky (A., 1886, 625), bromination of 1- $\text{C}_{10}\text{H}_7\cdot\text{COPh}$ does not give 2:1- $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{COPh}$, since treatment of this with KOPh affords a compound, m.p. 127°. In agreement with Fierz-David and Jaccard (A., 1929, 70; cf. Fieser, A., 1931, 1292) and contrary to Pieroni (*ibid.*, 703), 1-benzoyl- β -naphthol heated with AlCl_3 gives 4-hydroxybenzanthrone (also prepared from 4-chlorobenzanthrone and MeOH - NaOMe or $-\text{KOH}$).

H. B.

Pyrenium compounds. XXII. Phenylbenzoxanthenyl hydrogen peroxides. W. DILTHEY and F. DAHM (J. pr. Chem., 1934, [ii], 141, 61—64; cf. A., 1933, 1303).—The following 1:2:7:8-dibenzoxanthenyl *H* peroxides are obtained by treatment of the corresponding xanthenium perchlorates, suspended or dissolved in AcOH , with H_2O_2 until the colour is dis-



charged. All liberate I from $\text{KI}\cdot\text{COMe}_2$. meso-*m*-Nitrophenyl- (II; $\text{R}=\text{R}'=\text{H}$, $\text{R}'=\text{NO}_2$), decomp.

4 L

250°; meso-*o*-chlorophenyl- (II; $\text{R}=\text{R}'=\text{H}$, $\text{R}'=\text{Cl}$), decomp. 194°; meso-*p*-diphenyl- (II; $\text{R}'=\text{R}''=\text{H}$, $\text{R}=\text{Ph}$), decomp. 175—177°; meso-*p*-methoxyphenyl- (II; $\text{R}'=\text{R}''=\text{H}$, $\text{R}=\text{OMe}$), decomp. 185—186°; meso-*p*-nitrophenyl (II; $\text{R}'=\text{R}''=\text{H}$, $\text{R}=\text{NO}_2$), decomp. 273—274°. meso-*p*-Diphenyl-1:2:7:8-dibenzoxanthene (cf. I; $\text{R}'=\text{R}''=\text{H}$, $\text{R}=\text{Ph}$), m.p. 270° [perchlorate, m.p. 278—280°; corresponding carbinol, m.p. 245° (decomp.)], is obtained from p - $\text{C}_6\text{H}_4\text{Ph}\cdot\text{CHO}$ and β - $\text{C}_{10}\text{H}_7\cdot\text{OH}$ in presence of AcOH and H_2SO_4 . meso-*p*-Methoxyphenyl-1:2:7:8-dibenzoxanthene is oxidised by PbO_2 in AcOH to the corresponding carbinol, m.p. 275°. H. W.

Survey of the anthocyanins. IV. G. M. ROBINSON and R. ROBINSON (Biochem. J., 1934, 28, 1712—1720).—Most of the delphinidin diglycosides are delphinidin 3:5-dimonosides. The effect of copigments on the distribution nos. (I) of anthocyanins may be very large. There is correlation between the colour change and effect on (I) brought about by addition of papaverine hydrochloride to solutions of chrysanthemin and cœnin chlorides. C. G. A.

Curtius degradation in the pyrrole series. II. H. FISCHER and A. WAIBEL (Annalen, 1934, 512, 195—217; cf. A., 1930, 1189).—Et 3-acetyl-2:4-dimethylpyrrole-5-carboxylate is converted by $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 130° into the hydrazone (I) of 3-acetyl-2:4-dimethylpyrrole-5-carboxyhydrazide, m.p. 185° (decomp.) (*CHPh* derivative, m.p. 174°), transformed by HCl in boiling EtOH into 3-acetyl-2:4-dimethylpyrrole-5-carboxyhydrazide hydrochloride, m.p. 262° (decomp.). (I) passes when treated with HCl and NaNO_2 into 3-acetyl-2:4-dimethylpyrrole-5-carboxylazide (II), m.p. 134° (decomp.), transformed by Br in AcOH into 3-bromo-2:4-dimethylpyrrole-5-carboxylazide, m.p. 146° (decomp.). (II) and NH_2Ph at 140° afford the phenylpyrrolylcarbamide, decomp. 248°. In boiling $\text{COMe}_2\cdot\text{H}_2\text{O}$ (II) passes into di-(3-acetyl-2:4-dimethyl-5-pyrrolyl)carbamide (III), m.p. 331° (decomp.). With 2:4-dimethylpyrrole and cryptopyrrole, respectively, (II) gives the compounds $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$, m.p. 242° (decomp.), and $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2$, m.p. 239° (decomp.). In boiling AcOH or $\text{C}_6\text{H}_5\text{N}$ (II) passes into (III). Treatment of (II) with boiling xylene leads to the carbimide, $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2$, m.p. 301° (decomp.), transformed by cryptopyrrole at 130° into (IV). Boiling EtOH converts (II) into the compound $\text{C}_{11}\text{H}_{16}\text{O}_3\text{N}_2$ or m.p. 143°, whereas $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 130° transforms it into (I). With Zn and AcOH at 70° (II) yields 3-acetyl-2:4-dimethylpyrrole-5-carboxylamide, m.p. 266°. Gradual addition of (II) to a boiling mixture of $\text{CH}_2\text{Ph}\cdot\text{OH}$ and xylene leads to 3-acetyl-2:4-dimethylpyrrole-*o*-benzylurethane, m.p. 163°, converted by H_2 (Pd sponge- AcOH - MeOH) into 5-amino-3-acetyl-2:4-dimethylpyrrole, m.p. 235° (decomp.). 2:4-Dimethylpyrrole-5-carboxyhydrazide is transformed by successive treatment with NaNO_2 and Br in AcOH into 3-bromo-2:4-dimethylpyrrole-5-carboxylazide (V), m.p. 146° (decomp.), which affords 3-bromo-4-methyl-2-dichloromethylpyrrole-5-carboxylazide (VI), m.p. 144° (decomp.), with 2 mols. of SO_2Cl_2 in Et_2O and the unstable Cl_3 -compound (VI) with 3 mols. of SO_2Cl_2 . (VI) and MeOH at $\pm 50^\circ$ afford 3-bromo-2-carbo-

methoxy-4-methylpyrrole-5-carboxylazide, m.p. 142° (decomp.), whence the corresponding *phenylcarbamide*, m.p. 253° (decomp.), compound $C_{14}H_{16}O_3N_3Br$, m.p. 210° (decomp.), with 2:4-dimethylpyrrole, carbimide, decomp. > 260°, *ethyl-*, m.p. 165° (decomp.), *isomyl-*, m.p. 129°, and *benzyl-*, m.p. 201° (decomp.), *-urethane*. (V) and $MeOH-H_2O$ at 50° give 3-bromo-2-aldehydo-4-methylpyrrole-5-carboxylazide, m.p. 133° (decomp.), whence 3-bromo-2-aldehydo-4-methylpyrrole-5-ethylurethane, m.p. 208° (decomp.), and the corresponding aldazine $C_{18}H_{22}O_4N_6Br_2$, m.p. 239° (decomp.). 2:4-Dimethylpyrrole-5-carboxylazide is converted by anhyd. HCN in Et_2O and subsequently by H_2O into 3-aldehydo-2:4-dimethylpyrrole-5-carboxylazide (VII), transformed by Br in AcOH or HCO_2H into 3-bromo-2:4-dimethylpyrrole-5-carboxylazide, m.p. 146°, by boiling AcOH into the carbamide $C_{15}H_{18}O_3N_4$, m.p. 297° (decomp.), and by boiling EtOH into the urethane (VIII), $C_{10}H_{14}O_3N_2$, m.p. 202°. Attempts to convert (VIII) into the corresponding amine were unsuccessful. Treatment of (VII) with boiling CH_2Ph-OH -xylene leads to the benzylurethane $C_{15}H_{16}O_3N_2$, m.p. 178°, transformed by H_2 (Pd sponge-AcOH-EtOH) into 5-amino-2:4-dimethyl-3-hydroxymethylpyrrole, decomp. > 200°. $N_2H_4.H_2O$ in boiling EtOH converts Et_2 2:4-dimethylpyrrole-3:5-dicarboxylate (IX) into the monohydrazide $C_{10}H_{15}O_3N_3$, m.p. 205° (decomp.) [*hydrochloride* (X), m.p. 249° (*CHPh* derivative, m.p. 189°)]; (X) and $NaNO_2$ in H_2O yield the azide, $C_{10}H_{12}O_3N_4$, decomp. 145°. 2:4-Dimethylpyrrole-3:5-dicarboxyldihydrazide, m.p. 262° (decomp.), from (IX) and $N_2H_4.H_2O$ at 130°, affords 2:4-dimethylpyrrole-3:5-dicarboxydiazide, decomp. 119°, whence 2:4-dimethylpyrrole-3:5-dibenzylidurethane, m.p. 177°. 5-Carbethoxy-2:4-dimethylpyrrole-3-carboxylic acid and $N_2H_4.H_2O$ at 130° give 2:4-dimethylpyrrole-5-carboxyhydrazide, m.p. 182° (decomp.) [corresponding azide, m.p. 122° (decomp.)]. 3-Carbethoxy-2:4-dimethylpyrrole-5-carboxylic acid is transformed by $N_2H_4.H_2O$ at 130° into Et 2:4-dimethylpyrrole-3-carboxylate, m.p. 78°. Et 2:4-dimethylpyrrole-5-acetate and $N_2H_4.H_2O$ at room temp. afford 2:4-dimethylpyrrole-5-acethydrazide, m.p. 157° (decomp.). H. W.

Pyrrylethanones. H. FISCHER and C. BARAT (Annalen, 1934, 512, 217—238; cf. A., 1932, 285).—5-Chloroacetyl-2:4-dimethyl-3-ethylpyrrole (I), m.p. 149° (Cu salt, m.p. 200—202°), is obtained in 75—78% yield by the action of HCl on CH_2Cl-CN and the pyrrole in $CHCl_3-Et_2O$ or in 55—60% yield from $CH_2Cl-COCl$ on the Mg pyrrol bromide. Cl in (I) is very firmly retained, but treatment with $NaOEt$ at 100°, boiling NH_2Ph , or $NHMe_2-MeOH$ at 80° leads respectively to 5-ethoxy-, m.p. 87°, 5-anilino-, m.p. 185°, and 5-dimethylamino- (hydrochloride, m.p. 200°), *-acetyl-2:4-dimethyl-3-ethylpyrrole*. A hydroxylic structure is suggested for (I), since with $NH_2OH.HCl$ and $N_2H_4.H_2O$, respectively, it gives 5-*ω*-hydroxylamino-, m.p. 142°, and 5-*ω*-hydrazino-, m.p. 153°, *-acetyl-2:4-dimethyl-3-ethylpyrrole*. The following compounds are analogously obtained: *Me* 5-chloroacetyl-2:4-dimethylpyrrole-3-propionate, m.p. 118° (Cu salt, m.p. 188°; corresponding *NHPh* derivative, m.p. 170°); 5-chloroacetyl-2-methyl-4-ethylpyrrole, m.p. 122°

(Cu salt, m.p. 220°); 5-chloroacetyl-4-methyl-2-ethylpyrrole, m.p. 109°; 5-chloroacetyl-2:4-diethylpyrrole, m.p. 118°; 5-chloroacetyl-2:3:4-trimethylpyrrole, m.p. 165°; 5-chloroacetyl-2:4-dimethylpyrrole, m.p. 138° (corresponding $NH.NH_2$ compound, m.p. 150°); 5-chloroacetyl-4-methyl-2:3-diethylpyrrole, m.p. 112°; 5-chloroacetyl-2:4-dimethyl-3-propylpyrrole, m.p. 133° (corresponding $OH.NH$ -derivative, m.p. 145°); Et 5-chloroacetyl-2:4-dimethylpyrrole-3-carboxylate, m.p. 192°; Et 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate, m.p. 162°; 2-chloroacetyl-3-methylpyrrole-4-propionic acid, m.p. 182°; Et 5-chloroacetyl-2-methylpyrrole-3-carboxylate, m.p. 220°; Et 3-hydroxy-2-chloroacetyl-5-methylpyrrole-4-carboxylate, m.p. 250° (decomp.); Et 2-hydroxy-3-chloroacetyl-5-methylpyrrole-4-carboxylate, m.p. 208°; 2-chloroacetyl-3-methyl-4-ethylpyrrole, m.p. 118°. 3:3':5:5'-Tetramethyl-4:4'-diethylpyrrylethan-β'-one (III), m.p. 142° (hydrazone; ketazine, m.p. 158°), from chloroacetyl-cryptopyrrole and Mg cryptopyrrol bromide (II) or from $CH_2Cl-COCl$ and (II), does not react with NH_2OH , $NHPh.NH_2$, $NH_2.CO.NH.NH_2$, or $p-NO_2.C_6H_4.NH.NH_2$. It is reduced by Al in $KOH-EtOH-H_2O$ to 3:3':5:5'-tetramethyl-4:4'-diethylpyrrylethan-β'-ol, m.p. 110°. 3:3':5:5'-Trimethyl-5:4-diethylpyrrylethan-β'-one (IV) has m.p. 157°. Cryptopyrrole and $[C.CO_2Me]_2$ in C_6H_6 afford *Me*₂ di-α-di-3:5-methyl-4-ethylpyrrylsuccinate, m.p. 188°, hydrolysed by $KOH-MeOH$ to 3:3':5:5'-tetramethyl-4:4'-diethylpyrrylethane, m.p. 140°. In boiling alkaline solution in presence of air or under the influence of H_2O_2 (III) passes into a compound $C_{36}H_{54}O_2N_4$, m.p. 230°, reduced by Zn and alkali to a substance, $C_{36}H_{52}ON_4$, m.p. 184°, probably a furan derivative. (IV) is similarly dehydrogenated to a compound, $C_{34}H_{46}O_2N_4$, m.p. 215°. (II) and $CH_2Ph-COCl$ or cryptopyrrole and $CH_2Ph-COCl$ in boiling C_6H_5N afford 5- CH_2Ph 2:4-dimethyl-3-ethylpyrryl ketone, m.p. 146° (hydrazone; ketazine, m.p. 155°; oxime, m.p. 120°; Ac_2 , m.p. 160°, and Bz_2 , m.p. 142° derivatives). The following 5- CH_2Ph -pyrryl ketones are obtained similarly: 4-methyl-2-ethyl-, m.p. 120° (non-cryst. hydrazone; ketazine, m.p. 135°; oxime, m.p. 128°); 4-methyl-2:3-diethyl-, m.p. 110° (hydrazone; ketazine, m.p. 145°); 2:4-dimethyl-, m.p. 172° (hydrazone, m.p. 100°; ketazine, m.p. 198°); 2-methyl-4-ethyl-, m.p. 121°; 2:3:4-trimethyl-, m.p. 134°; 2:4-diethyl-, m.p. 100°; 3-carbethoxy-2-methyl-, m.p. 168°; 2:4-dimethyl-3-propyl-, m.p. 130°. 2-methyl-5-phenacylpyrrole-3-carboxylate has m.p. 200°.

H. W.
Preparation of esters of fatty-aromatic acids with amino-alcohols.—See B., 1934, 824.

Dipyridylguanidine and its derivatives. K. S. TOFTSCHIEV (Arch. Pharm., 1934, 272, 775—779).—Dipyridylthiocarbamide (modified prep., 65% yield, the form, m.p. 147°, passes, when kept, into that of m.p. 163°) with NH_3-EtOH , followed by $PbCO_3.Pb(OH)_2$, gives s-dipyridylguanidine, m.p. 144° (70% yield) (hydrochloride, m.p. 197°; picrate, m.p. 225—228°). NH_2Me and NH_2Ph afford similarly s-dipyridyl-methyl- (I), m.p. 72—73° (hydrochloride, m.p. 122°; picrate, m.p. 197—199°), and -phenylguanidine, m.p. 132° (hydrochloride, m.p. 141°; picra

m.p. 218—221°), respectively. (I) is a potent local anæsthetic.

R. S. C.

Nitration of 2-methylindole. F. C. MATHUR and R. ROBINSON (J.C.S., 1934, 1415).—Nitration of dinitro-2-methylindole leads to the 3:?:?(NO_2)₃-compound, m.p. 254—256° (decomp.), oxidised (KMnO_4) to *trinitroindole-2-carboxylic acid*, m.p. 227—229° (*Et* ester, m.p. 198—199°), and condensing with *p*- $\text{NMe}_2\text{C}_6\text{H}_4\text{CHO}$ to *trinitro-2-p-dimethylaminostyrylindole*. One NO_2 is probably in position 4 and the other in 5, 6, or 7.

F. R. S.

Isatogens and indoles. XIV. Reduction of isatogens. P. RUGGLI, O. SCHMID, and A. ZIMMERMANN (Helv. Chim. Acta, 1934, 17, 1328—1334; cf. this vol., 303).—Catalytic hydrogenation (Ni) of 6-nitro-2-phenylisatogen (I) gives 6-amino-2-phenylindoxyl (II), m.p. 230—235° (decomp.) after softening at 225°, and (after treatment of ppt. + catalyst with Ac_2O) 6-acetamido-3-acetyl-2-phenylindoxyl, m.p. 220°. (II) is better obtained by reduction of 6-nitro-2-phenylindoxyl (III). Mild reduction of (I) by $\text{NHPh}\cdot\text{NH}_2$ does not lead to 6-nitro-3-keto-2-phenylindolenine, m.p. 185° [obtained by oxidation of (III) by HNO_2 and reduced by $\text{NHPh}\cdot\text{NH}_2$ to (III)], since the change proceeds to the formation of (III); by suitable interruption, the quinhydrone from (I) and (III) is isolated.

H. W.

Indolenines. VI. Reactions of the compounds of 3:3-dimethylindolenines with acid chlorides. H. LEUCHS and A. SCHLOTZER (Ber., 1934, 67, [B], 1572—1576; cf. A., 1932, 1260).—Further examples of the mobility of halogen in the 2-chloro-1-acylindolines formed by union of indolenines with acyl chlorides are cited. 2-Chloro-1-benzoyl-3:3-dimethylindoline (I) yields the following -1-benzoyl-3:3-dimethylindolines: (with NaOPh in C_6H_6) 2-phenoxy-, m.p. 125—127°; (with NH_2Ph in C_6H_6 at room temp.) 2-anilino-, m.p. 164°; (with $\text{C}_5\text{H}_5\text{N}$ in boiling C_6H_6) 2-pyridinium chloride (hydrate) and the corresponding perchlorate; (in boiling C_6H_6) 2-malonic *Et*₂ ester, m.p. 98—99°; (with AgCN in C_6H_6) 2-nitrile, m.p. 128—129°; (with AlCl_3 and C_6H_6) 2-phenyl-, m.p. 168—169°. (I) and MgPhBr in C_6H_6 give $\text{CPh}_3\cdot\text{OH}$ and 2-phenyl-3:3-dimethylindoline, m.p. 93°. 1-p-Nitrobenzoyl-3:3-dimethyl-2-indolinylpyridinium chloride, m.p. 126—128°, and the corresponding perchlorate are described. 2-Chloro-1-acetyl-3:3-dimethylindolenine and AgOBz in C_6H_6 afford 2-benzoyloxy-1-acetyl-3:3-dimethylindolenine, m.p. 83—85°. (I) and AgNO_2 do not yield the 2- NO_2 -derivative and the nitrite is so readily hydrolysed that only the 2-OH-compound is obtained. 3:3-Dimethylindolenine does not give readily cryst. compounds with $\text{Pr}\cdot\text{COCl}$, $\text{CH}_3\cdot\text{Ph}\cdot\text{COCl}$, or $\text{CHPh}\cdot\text{CH}\cdot\text{COCl}$; the products are heated with 2*N*- NaOH , thereby yielding, respectively, 1-butyryl-, m.p. 82—84°, 1-phenylacetyl-, m.p. 99—102°, and 1-cinnamoyl-, m.p. 124—126°, 2-indolinol.

H. W.

Organic catalysts. X. Carboxylase models. IV. W. LANGENBECK, F. HELLRUNG, and R. JUTTERMANN (Annalen, 1934, 512, 276—286).—1:1'-Anthraquinonylisatin, m.p. 319°, is obtained from 1-anilinoanthraquinone and $(\text{COCl})_2$ in PhNO_2 at 100° and

finally at 150°, and its constitution established by oxidation to anthraquinonylanthranilic acid, m.p. 281°. Its *oxime*, decomp. > 280°, is reduced by SnCl_2 and conc. HCl in AcOH to 3-amino-1:1'-anthraquinonyloxindole (I). 1-Aminoanthracene and $(\text{OH})_2\text{C}(\text{CO}_2\text{Et})_2$ in hot AcOH afford *Et*₂ anthracenedioxindolecarboxylate, hydrolysed to anthracenisatin, the *oxime* of which is reduced to 3-aminoanthracenoxindole (II) hydrochloride. Aminoacenaphthene and $(\text{OH})_2\text{C}(\text{CO}_2\text{Et})_2$ give *Et* acenaphthendioxindolecarboxylate, decomp. about 213°, whence acenaphthenisatin, decomp. > 260°, its *oxime*, decomp. > 235°, and 3-aminoacenaphthenoxindole (III) hydrochloride, decomp. > 260°. 5-Amino- α -naphthol yields successively *Et*₂ 6-hydroxy-1-naphthadioxindolecarboxylate, m.p. 200—201° (decomp.), 6-hydroxy-1-naphthisatin, its *oxime*, and 3-amino-6-hydroxynaphthoxindole (IV) hydrochloride. Similarly obtained are *Et* 7-hydroxy-1-naphthadioxindolecarboxylate, decomp. 220—230°, 7-hydroxy-1-naphthisatin, its *oxime*, and 3-amino-7-hydroxynaphthoxindole (V) hydrochloride (Sn salt, $\text{C}_{24}\text{H}_{22}\text{O}_4\text{N}_4\text{Cl}_6\text{Sn}$): *Et* 8-hydroxy-1-naphthadioxindolecarboxylate, decomp. 220—230°, 8-hydroxy-1-naphthisatin, its *oxime*, and 3-amino-8-hydroxynaphthoxindole (VI); *Et* 5-hydroxy-1-naphthoxindolecarboxylate, decomp. 240°. 2-Amino- α -naphthol hydrochloride and $(\text{OH})_2\text{C}(\text{CO}_2\text{Et})_2$ in AcOH at 70° give a substance (?) $\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}$, m.p. 155°. The carboxylase activity of (I) and (III) is <, and that of (II) approx. equal to, that of the parent compound. (VI) is very feebly active. The activity of (V) is about equal to that of the parent, whereas (IV) is twice as active. Cryst. peptin is only 22 times as active as (IV).

H. W.

Growth and kynurenic acid production on amides of l-tryptophan.—See this vol., 1252.

Synthesis of quinoline and isoquinoline derivatives. Synthesis of derivatives of isocarbo-styryl and carbostyryl. S. J. KANEVSKAJA, M. M. SCHEMJAKIN, and E. M. BANDASS-SCHEMJAKINA (Arch. Pharm., 1934, 272, 770—775).—7:8-Dimethoxy-3-acetylisocoumarin and hot 25% aq. NH_3 give 7:8-dimethoxy-3-acetylisocarbo-styryl, m.p. 212—213° (semicarbazone, decomp. 270—273° after sintering at 240°). Ag nitro-opianate, when heated in vac. in CO_2 , gives 2-nitro-4:5-dimethoxybenzaldehyde, m.p. 130—131° (25% yield), affording with $\text{CH}_2(\text{CO}_2\text{H})_2$ and piperidine a 70% yield of 2-nitro-4:5-dimethoxycinnamic acid, m.p. 281—282° (decomp. from 250°) (*Me* ester, m.p. 174—175°), the *Et* ester of which with $\text{Zn}\cdot\text{HCl}\cdot\text{EtOH}$ gives a 35% yield of 6:7-dimethoxy-3:4-dihydrocarbo-styryl, m.p. 127—128° after sintering at 125°.

R. S. C.

Quinoline derivatives. III. β -2-Amino-4:5-dimethoxybenzoylpropionic acid and its derivatives. M. A. HAQ, J. N. RAY, and M. TUFFAIL-MALKANA (J.C.S., 1934, 1326—1328).— β -2-Amino-4:5-dimethoxybenzoylpropionic acid (I) forms a monohydrate, m.p. 118° (cf. this vol., 83), converted at 110° into the lactam, m.p. 183° (decomp.). 6:7-Dimethoxy-3-acetyl-2-methylquinoline-4-propionic acid forms a piperonylidene derivative, m.p. 240° (decomp.). 3:4-Dimethoxybenzoylbenzoic acid (II) is nitrated to the 2-nitro-4:5-derivative, m.p. 165°, reduced to the lactam (III) of the 2- NH_2 -compound, m.p. 256°.

The monoxime of histazarin Me₂ ether, m.p. 210—212° (decomp.), is converted by the Beckmann transformation into (III). (I) and cyclohexanone yield a substance, m.p. 262°. (II) is reduced (Na—Hg) to 3:4-dimethoxyphenylphthalide, m.p. 144°, nitrated to the 2-nitro-4:5-compound, m.p. 224°. F. R. S.

Anhydronium base formation in the quinoline series. H. LEMPert and R. ROBINSON (J.C.S., 1934, 1419—1422).—CH₂Bz₂, *m*-anisidine (I), and hot AcOH give *Ph* β-methoxyanilinostyryl ketone, m.p. 75—76°, which is converted (HCl) into 7-methoxy-2:4-diphenylquinoline, m.p. 102° (methosulphate, m.p. 230—235°). The anhydronium base (+1.5H₂O), obtained from 7-hydroxy-2:4-diphenylquinoline methosulphate, dissolves in C₆H₆ to a red solution and with MeI gives 7-methoxy-2:4-diphenylquinoline methiodide. This is analogous to the behaviour of 7-hydroxybenzopyrylium salts. (I) is converted by the Skraup reaction into 7-methoxyquinoline, b.p. 145—147°/12 mm. [picrate, m.p. 216°, methiodide, m.p. 204° (decomp.); 7-hydroxyquinoline methiodide, m.p. 245° (decomp.)]. *Me* β-*m*-methoxyanilino-α-propenyl ketone, b.p. 170—178°/10 mm., obtained from (II) and CH₂Ac₂, undergoes ring closure (HCl) to 7-methoxy-2:4-dimethylquinoline, b.p. 180—185°/25 mm. (hydrochloride), the methiodide, m.p. 238° (decomp.), of which is demethylated to 7-hydroxy-2:4-dimethylquinoline methiodide, m.p. 265° (decomp.). Ring closure by POCl₃ gives the 7-derivative and some 5-derivative [5-methoxy-2:4-dimethylquinoline methiodide, m.p. 180° (decomp.)]. 7-Hydroxy- and 7-hydroxy-2:4-dimethylquinoline do not give coloured anhydronium bases, the formation of quinonoid structure being suppressed probably because of the affinity of the N atom for its charge. F. R. S.

Attempts to find new antimalarials. X. 8-Amino-6-γ-aminopropoxyquinoline and some related substances. K. MATEJKA and R. ROBINSON (J.C.S., 1934, 1322—1326).—*p*-γ-Phthalimidopropoxyacetanilide, m.p. 157°, prepared from γ-bromopropylphthalimide (I), *p*-NHAc·C₆H₄·OH, and K₂CO₃, is hydrolysed to *p*-γ-(*o*-carboxybenzamido)propoxyacetanilide, m.p. 177.5°, and is nitrated to the 2-nitro-4-γ-derivative (II), m.p. 162°, hydrolysed (KOH) to 2-nitro-4-γ-aminopropoxyaniline, m.p. 147°, and converted by NaOH into 2-nitro-4-γ-(2-carboxybenzamido)propoxyaniline, m.p. 130.5°. γ-*p*-Nitrophenoxypropylphthalimide, m.p. 183°, is reduced to *p*-γ-phthalimidopropoxyaniline, m.p. 92—94°. (II) and HCl form 2-nitro-4-γ-phthalimidopropoxyaniline, m.p. 172.5°, which by the Skraup reaction gives 8-nitro-6-γ-aminopropoxyquinoline (III), m.p. 108°, the C₆H₄(CO)₂N group being hydrolysed after the closure of the quinoline ring. The non-phthaloylated base or the phthalamic acid does not undergo the reaction. (III) and C₆H₄(CO)₂O give 8-nitro-6-γ-phthalimidopropoxyquinoline, m.p. 209°, reduced to the 8-amino-compound, m.p. 157—158°, which with (I) forms 8-γ-phthalimidopropylamino-6-γ-phthalimidopropoxyquinoline, m.p. 150—152°. This compound with N₂H₄·H₂O followed by HCl leads to 8-γ-aminopropylamino-6-γ-aminopropoxyquinoline trihydrochloride (+3.5H₂O), m.p. 188°. (III) is reduced (SnCl₂) to 8-amino-6-γ-aminopropoxyquinoline, m.p. 106—107° (hydrochloride,

m.p. 211—214°), which is methylated (MeI) and reduced (Fe) to 8-amino-6-γ-dimethylaminopropoxyquinoline methiodide hydrochloride (+0.5H₂O), m.p. 222° (decomp.). F. R. S.

Quinoline derivatives as basic products for preparation of antimalarials. Influence of length of chain in position 8. O. J. MAGIDSON and I. T. STRUKOV (J. Gen. Chem. Russ., 1934, 4, 253—268).—CH₂Cl·CH₂·CO₂Et and NHEt₂ yield NEt₂·CH₂·CH₂·CO₂Et, which with Na in EtOH affords NEt₂·CH₂·CH₂·CH₂·OH (I), also synthesised from CH₂Cl·CH₂·CH₂·OAc and NHEt₂ at room temp. (24 hr.), heating at 100° for 8 hr., and hydrolysing the acetate of (I) so formed. (I) is converted by heating with SOCl₂ in C₆H₆ into diethyl-γ-chloropropylamine hydrochloride, m.p. 62—64°, which when heated for 48 hr. at 100° with 8-amino-6-methoxyquinoline (II) yields 8-γ-diethylaminopropylamino-6-methoxyquinoline (III), b.p. 198—201°/2 mm. (meconate, m.p. 133—134°); the corresponding 6-OEt-compound, b.p. 214—218°/2—3 mm., 238—241°/8—9 mm., yields 6:8-dihydroxyquinoline on hydrolysis with HBr. CHNa(CO₂Et)₂ and NEt₂·[CH₂]₃Cl in EtOH yield Et₂β-diethylaminoethylmalonate, b.p. 136—142°/12 mm., which when heated for 4 hr. at 100° with aq. KOH followed by esterification with EtOH—HCl affords Et γ-diethylaminobutyrate, b.p. 103—105°/17 mm., reduced (Na—EtOH) to 8-diethylamino-*n*-butyl alcohol, b.p. 90—92°/7—9 mm. This is converted by SOCl₂ in C₆H₆ into diethyl-8-chlorobutylamine, which with (II) affords 8-8-diethylaminobutylamino-6-methoxyquinoline (IV), b.p. 200—210°/3 mm. 8-ε-Diethylaminoamylamino-6-methoxyquinoline (V), b.p. 216—221°/2—3 mm. [meconate, m.p. 120—122° (decomp.)], is prepared analogously to (IV), the intermediate products being diethyl-ε-chloroamylamine hydrochloride, m.p. 35—36°, ε-diethylaminoamyl alcohol, b.p. 131—133°/23—24 mm., Et₂ 8-diethylaminovalerate, b.p. 130—131°/25 mm., and Et₂ γ-diethylaminopropylmalonate, b.p. 149—151°/4 mm. 8-γ-Diethylamino-β-hydroxypropylamino-6-ethoxyquinoline (VI), b.p. 240—241 mm., is prepared from 8-amino-6-ethoxyquinoline (VII) and NEt₂·CH₂·CH(OH)·CH₂Cl. 8-γ-Piperidinopropylamino-6-ethoxyquinoline (VIII), b.p. 227—231°/2—3 mm., is obtained from (VII) and α-chloro-γ-piperidinopropane. γ-Piperidinopropylene glycol, b.p. 128—130°/7 mm., m.p. 67—68°, is prepared from piperidine and monochlorohydrin. 8-Ethylamino-6-ethoxyquinoline (IX), b.p. 160—163°/3 mm., m.p. 53 (p-toluenesulphonate, m.p. 68°; hydrochloride, m.p. 200—201°), obtained from (VII) and *p*-C₆H₄Me·SO₃Et at 100—120°, yields with NEt₂·CH₂·CH₂Cl (X) 8-N-β-diethylaminooctyl-N-ethylamino-6-ethoxyquinoline (I), b.p. 192—193°/1 mm. The N-Na salt of (IX) with γ-diethylaminopropylene αβ-oxide yields 8-(N-γ-diethylamino-β-hydroxypropyl)ethylamino-6-ethoxyquinoline (XII), b.p. 207—212°/1 mm. 8-Nitro-6-hydroxyquinoline and (X) yield when reduced with 20% Et (NH₄)₂S 8-amino-6-β-diethylaminoethoxyquinoline [hydrochloride, +2H₂O, m.p. 207—212°; 8-Δ derivative (hydrochloride, m.p. 141°); 8-N ethyl derivative (dihydrochloride, m.p. 182—183°); 8-N-Bz derivative, m.p. 57° (hydrochloride, m.p. 201°); 8-benz-β-diethylaminoamido-derivative (

hydrochloride, m.p. 83°)]. The therapeutic indices (max. tolerated dose/min. lethal dose) are (III) 26.5, (IV) 10.6, (V) 25, (VI) 15, (VIII) 6, (XI) and (XII) 0. R. T.

Carbazole series. Preparation of 1- γ -aminopropylaminocarbazole. M. MOTTIER (Helv. Chim. Acta, 1934, 17, 1130—1135).—1-Aminocarbazole (I) (hydrochloride, m.p. about 308° after blackening at about 250°) and γ -bromopropylphthalimide yield unchanged (I), its hydrobromide, m.p. about 315° after blackening at 295°, and the hydrobromide, m.p. 205—207°, of 1- γ -phthalimidopropylaminocarbazole (II), m.p. 163—164°, or (+H₂O) m.p. 108—125°. (II) is transformed by N₂H₄·H₂O in boiling EtOH and subsequent treatment with HCl into 1- γ -aminopropylaminocarbazole dihydrochloride, m.p. 230.5—231.5° after softening at 191°, whence the base, m.p. 154°. H. W.

Composition and solubility of derivatives of 3:6-diaminoacridine used in therapy. P. GAILLIOT (Bull. Soc. chim., 1934, [v], 1, 796—806).—Commercial 3:6-diaminoacridine methochloride (I) and its hydrochloride (acriflavine) contain much 3:6-diaminoacridine (II) or its hydrochlorides (III) (B, HCl; 4B, 3HCl; B, 2HCl), respectively. (I) is separated from (III) by treatment with Ag₂O and filtration of the pptd. (II). Mixtures of (I) and (II) or their salts have greatly increased solubilities in H₂O, and the solubilities commonly ascribed to (I) and (II) are too high. R. S. C.

Synthesis and action of hydantoins. K. H. SLOTTA, R. BEHNISCH, and G. SZYSZKA (Ber., 1934, 67, [B], 1529—1535).—Berg's method (G.P. 566,094) for the prep. of hydantoins is inapplicable to some acyclic unsaturated keto-compounds (CHMe·CH·CHO; CMe₂·CHAc) and to certain materials containing basic substituents [NMe₂·CH₂Ac; CO(CH₂·NMe₂)₂]. All other carbonyl compounds afford hydantoins in good yield provided that Me or CH₂ is vicinal to CO. The first step in the synthesis is the production of the NH₂-nitrile, this view being supported by the transformation of NH₂·CMe₂·CN into 5:5-dimethylhydantoin (I) under synthetic conditions. Condensation is possible only when the CO₂ can react with primary salt formation; ring closure does not take place with CN·CEt₂·CO·NH₂ or CEt₂(CO·NH₂)₂, whereas NH₂·CMe₂·CO·NH₂ readily affords (I). The following scheme is therefore suggested: R·CO·CH₂R' \longrightarrow R·C(OH)·CHR' \longrightarrow CH₂R'·CR(CN)·NH₂ \longrightarrow CH₂R'·CR(CO·NH₂)·NH₂+CO₂H \longrightarrow

$\begin{matrix} \text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO} \end{matrix} > \text{CR}\cdot\text{CH}_2\text{R}'$. The prep. of the following

hydantoins is described: 5- β -phenylethyl-5-methyl-, m.p. 180°; 5:5-di- β -phenylethyl-, m.p. 171° after softening; 5-phenyl-5-benzyl-, m.p. 210°; 5-benzyl- α -methyl-, m.p. 226°; 5:5-dibenzyl-, m.p. 305° (decomp.); 5-phenyl-5-methyl-, m.p. 197°; 5-3':4':5'-trimethoxyphenyl-, m.p. 310°. CHPh·CHAc is reduced at a Pb or Hg cathode in AcOH-2N-H₂SO₄ to CH₂Ph·CH₂Ac (yield 50%) and diphenyloctadione; in presence of Pb-SiO₂ gel in EtOH the yield of CH₂Ph·CH₂Ac is 80%, rising to 83% when Pd-gelatin in EtOH-H₂O is used. Similarly the yields of CO(CH₂·CH₂Ph)₂ from CO(CH₂·CHPh)₂ are 80% and 79%, respectively, when Pt-SiO₂ gel and Pd-gelatin are employed. H. W.

Syntheses of hydantoins. I. Reactions of α -hydroxy- and α -amino-nitriles. H. T. BUCHERER and W. STEINER. II. Formation of substituted hydantoins from aldehydes and ketones. H. T. BUCHERER and V. A. LIEB (J. pr. Chem., 1934, [ii], 140, 291—316; 141, 5—43).—I. Hydantoins are obtained by the action of technical (NH₄)₂CO₃ on ketocyanohydrins (I) in various media, preferably in H₂O at 30—40°, the yields being excellent. With NH₂·CO₂NH₄ (II), in presence or absence of a suspending medium, the yields are somewhat lower, but normal yields are obtained if the temp. is raised above the dissociation temp. of (II). α -NH₂-nitriles [obtained in 85—90% yield by saturating (I) with NH₃ and subsequent addition of CaCl₂ and Et₂O] similarly afford hydantoins under the influence of (NH₄)₂CO₃, and the probability that they are intermediate products is strengthened by their conversion into hydantoins when their conc. aq. solutions are saturated with CO₂. The mechanism of the change is discussed in detail. The following compounds are described: 5:5-dimethylhydantoin, m.p. 174—175° (Ac derivative, m.p. 123—124°; NO₂-compound, m.p. 140—141°), from OH·CMe₂·CN, hydrolysed by 60% H₂SO₄ at 120—130° to NH₂·CMe₂·CO₂H; OH·CMe₂·CN does not condense with CO(NH₂)₂ or NH₂·CO₂Et; 5-methyl-5-ethylhydantoin, m.p. 145—146°; compound CN·CMe₂·NH·CO·NH·CMe₂·CO·NH₂, m.p. 196—197°, from NH₂·CMe₂·CN (prep. described) and CO₂, and substance, CN·CMeEt·NH·CO·NH·CMeEt·CO·NH₂, m.p. 186—187°, from NH₂·CMeEt·CN and CO₂; ethyl 5-methylhydantoin-5-acetate, m.p. 137°, from CO₂Et·CH₂·CMe(CN)·OH and (NH₄)₂CO₃; (?) ureido-phenylacetamide, m.p. 223°, 5-phenylhydantoin, m.p. 178°, and the substance, (?) CO₂H·CHPh·NH·CO·NH·CHPh·CN, m.p. > 280° (decomp.), from OH·CHPh·CN and (NH₄)₂CO₃; α -imino-dipropionitrile, m.p. 65—67°, and α -ureidopropionamide, m.p. 195—196° (whence 5-methylhydantoin, m.p. 145—146°), from OH·CHMe·CN.

II. Further examination of the prep. of hydantoins from solid (NH₄)₂CO₃ and homogeneous cyanohydrins or from CO₂ and NH₂-nitriles shows 50% EtOH to be the most suitable medium; Et₂O and ligroin can also be used, and change occurs slowly at room temp., but, particularly with ligroin, is apt to be accompanied by pronounced discoloration. Hydantoins are also obtained in good yield directly from ketones, HCN or KCN, and (NH₄)₂CO₃, best in 50% EtOH at 45—60°. The process is particularly applicable to ketones which give unstable cyanohydrins and can be advantageously extended to aldehydes. In place of the ketone or aldehyde, the corresponding H sulphite compound may be employed with advantage and the presence of NaHSO₃ appears to facilitate the production of hydantoins from ketones of which the H sulphite compounds cannot be isolated. N-Methylhydantoins do not appear to result from cyanohydrin, NH₂Me·HCl and Na₂CO₃ or NaOH. Details are recorded of the prep. of the following 5:5-substituted hydantoins: dimethyl-, m.p. 175°, from COMe₂; pentamethylene-, m.p. 215°, from cyclohexanone; methylethyl-, m.p. 146°, from COMeEt; phenylmethyl-, m.p. 197°, from CPhMe; phenylethyl-, m.p.

201—202°, from CPhEt; benzylmethyl-, m.p. 226°, from COMe·CH₂Ph; (?) *dibenzyl*-, m.p. 295°, from CO(CH₂Ph)₂; (?) *dimethyl*di-, m.p. 265—270° (decomp.), from Ac₂; phenyl-, m.p. 178°, from PhCHO or CPh·COMe; *benzyl*-, m.p. 190°, from CH₂Ph·CHO; carbethoxydimethyl-, m.p. 135—137°, from CH₂Ac·CO₂Et. Benzil and CPh·COMe suffer fission between the CO groups, whereas CH₂Ac₂, CHPhBz·OH, and CHPhAc·OH do not give recognisable products. Phenanthraquinone yields a *substance*, m.p. about 305°. Hydrolysis of the hydantoin to the corresponding α-NH₂-acids is effected with 60% H₂SO₄ at 120—130° or, if necessary, 150°. The product is treated with a slight excess of BaCO₃, boiled to remove (NH₄)₂CO₃, filtered, and the filtrate is conc. and, if necessary, treated with EtOH. 1-Benzamidocyclohexane-1-carboxylic acid has m.p. 190°. The synthesis of tyrosine from CH₂Ph·CHO through benzylhydantoin and its *p*-NO₂-, m.p. 240—245° (corresponding *o*-NO₂-derivative, m.p. 213—215°), *p*-NH₂-, and *p*-OH-compounds is described. Attempts to prepare α-amino-β-hydroxy-β-phenylisobutyric acid are recorded. Benzylmethylhydantoin could not be converted satisfactorily into the ω-Br-derivative. If CO₂ is replaced by CS₂ the sense of the reaction appears altered. Thus cyclohexanonecyanohydrin, CS₂, and NH₃ in EtOH-H₂O yield the product (?) (CH₂)₅>C-NH<CS-S>C<(CH₂)₅, m.p. 225°, amongst others. OH·CMe₂·CN, CS₂, and NH₃ in EtOH-H₂O yield the *substance* C₇H₁₄N₂S, m.p. 154—155°, also obtained in addition to a compound, m.p. 297°, when gaseous NH₃ is used; these compounds are also obtained from NH₃·CMe₂·CN and CS₂ in Et₂O.

H. W.

Wada's method for the production of amines from amino-acids. H. T. CLARKE and G. L. FOSTER (Biochem. Z., 1934, 272, 376—379; cf. A., 1933, 616).—Hydantoin is wholly or partly hydrolysed but not decarboxylated when treated by Wada's method, which consequently does not result in the conversion of NH₂-acids into amines. W. McC.

Synthesis of 5-β-hydroxypropylbarbituric acids. J. W. LOUBRIEL (J. Amer. Chem. Soc., 1934, 56, 1968—1969).—*o*-isoPropyl-5-allylbarbituric acid and cold conc. H₂SO₄ give [after hydrolysis (ice)] 5-isopropyl-*o*-β-hydroxypropylbarbituric acid, m.p. 221—222° [O-Bz derivative, m.p. 169—171° (1:3-di-allyl derivative, b.p. 260°/25 mm., prepared by the action of allyl bromide in presence of 10% NaOH and Cu)]. 5-isoButyl-5-β-hydroxypropylbarbituric acid, m.p. 216—217°, is similarly prepared. H. B.

Manufacture of barbituric acid derivatives.—See B., 1934, 941.

Manufacture of *as*-thiocarbamide derivatives.—See B., 1934, 874.

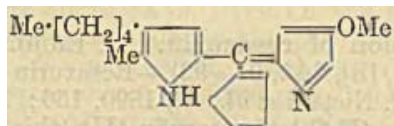
Toad poisons. VII. Constitution of bufotenin and bufotenidine. H. WIELAND, W. KONZ, and H. MITTASCH (Annalen, 1934, 513, 1—25).—Details are given (cf. A., 1931, 1310) for the isolation of bufotenin (I), C₁₂H₁₆ON₂ (cf. *loc. cit.*), m.p. 146—147° [methiodide (II), m.p. 210°; *oxalate*, (−H₂O), m.p. 96·5°; *m*-nitrobenzoyl, m.p. 258° (decomp.), and Ac₂,

m.p. 226° (decomp.), derivatives], and bufotenidine (III), non-cryst. [flavianate, decomp. 195—200°, probably identical with the bufotenin flavianate obtained by Jensen and Chen (A., 1932, 1142) from Ch'an Su; *hydriodide*, m.p. 209°, which is identical with (II); Ac₂ derivative *picrate*, m.p. 173°, and *hydrochloride*, m.p. 230° (decomp.)], from the secretion. (I) contains 2 active H and with MeI and TIOEt in EtOH gives *O*-methylbufotenin *methiodide* (IV), m.p. 183—184° [corresponding *picrate* (V), m.p. 84°, and *flavianate* (VI), decomp. 233°], also obtained from (II) and CH₂N₂. (I) and Et₂O·CH₂N₂ afford (probably) (III). Methylation (Me₂SO₄, *N*-NaOH) of (III) and subsequent treatment with flavianic acid gives (VI), convertible through the acetate into (V). The product from 5-methoxyindole and MgMeI is treated with CH₂Cl·CN and the resulting crude nitrile reduced (Na, EtOH) to β-5-methoxy-3-indolylethylamine, m.p. 121—122° [*picrate*, m.p. 220° (decomp.)], which with MeI and TIOEt in EtOH gives β-5-methoxy-3-indolylethyltrimethylammonium *iodide*, m.p. 182—183° [identical (colour reactions; m.p. of derivatives) with (IV)], and an *iodide*, m.p. 260—270°. (I) is, therefore, 5-hydroxy-3-β-dimethylaminoethylindole, whilst (III) is the corresponding phenol-betaine (cf. *loc. cit.*). β-6-Methoxy-3-indolylethyltrimethylammonium *iodide*, m.p. 182—183° (corresponding *picrate*, m.p. 108—110°), is similarly prepared. Indole-3-aldehyde is methylated (Me₂SO₄, *N*-NaOH) to 1-methylindole-3-aldehyde, m.p. 65° (*phenylhydrazones*, m.p. 170—171°); the *azlactone*, m.p. 178°, from this is reduced (Na-Pb alloy, EtOH) to 1-methyltryptophan, m.p. 289° (decomp.), which does not give the pyrrole reactions. (I), bufothionine (A., 1930, 1466), and the base, C₁₂H₁₄ON₂ (*loc. cit.*) [flavianate, decomp. 260—265°, probably identical with some of the bufotenin flavianates of Jensen and Chen (*loc. cit.*)], are isolated from the skins of *Bufo arenarum*. H. B.

[Aryl]sulphonylation of hexamethylenetetramine. E. HUG (Bull. Soc. chim., 1934, [v], 1, 1004—1006).—Successive additions of PhSO₂Cl (I) and aq. NaOH to conc. aq. (CH₂)₆N₄ (II) at 60° gives 1:3:5-tribenzenesulphonylhexahydro-1:3:5-triazine (III) (trimeric methylenecyclohexanesulphonamide). m.p. 228°; the 1:3:5-tri-*p*-toluenesulphonyl derivative is similarly prepared. (I) and (II) in CHCl₃ afford a 1:1-compound, m.p. 198° (decomp.), which when heated with EtOH or dil. NaOH gives (III). Analogous results are obtained with *n*-C₆H₄Me·SO₂Cl. H. B.

Prodigiosine, the red pigment of *Bacillus prodigiosus*. VI. F. WREDE and A. ROTHHAAS (Z. physiol. Chem., 1934, 226, 95—107; cf. this vol., 330).—Oxidation of the pyrrole (I), C₁₀H₁₇N, with CrO₃ in AcOH yields an oil (a maleimide), which adds on 2H with Pd-C giving *amylsuccinimide* (II), m.p. 87°. Oxidation of (I) with KMnO₄ in COMe₂ affords *n*-hexoic acid (*p*-phenylphenacyl ester, m.p. 69°). (II) was synthesised by the stages: Et₂ *n*-amylmalona b.p. 255—260°, → CO₂Et·CH₂ derivative carboxylic acid → *n*-amylsuccinic acid, m.p. 80°, (II); isoamylsuccinimide, m.p. 89·5°, similarly. (I) was synthesised as follows: Et *n*-amyl ketone (100 *n*-hexoyl chloride and ZnEt₂) → *oximino-ketone*, 1·

130°/10 mm., m.p. 13° (octane- $\beta\gamma$ -dioxime, m.p. 171°), \rightarrow β -amino-octan- γ -one \rightarrow with Et₂ oxalacetate and aq. KOH, pyrrole diester \rightarrow dicarboxylic acid \rightarrow by distillation with soda-lime (I). Hence prodigiosine is:



J. H. B.

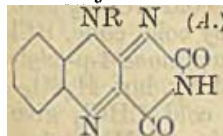
Product of the irradiation of lactoflavin. Lumichrome. P. KARRER, H. SALOMON, K. SCHÖPP, E. SCHLITTLER, and H. FRITZSCHE (Helv. Chim. Acta, 1934, 17, 1010–1013).—Exposure of lactoflavin, preferably in dil. MeOH, to day- or sunlight in presence of air leads to the production of *lumichrome*, decomp. $> 300^\circ$, which does not contain OMe or NMe and is identified as 6:7-dimethylalloxazine. The by-products, sol. in H₂O, give very weak reactions for pentoses.

H. W.

Isolation of the flavin of malt. P. KARRER and K. SCHÖPP (Helv. Chim. Acta, 1934, 17, 1013–1014).—The isolation of malt *flavin*, m.p. 282° (corr.), from green malt is described. In cryst. form and m.p. it does not differ from the flavins of milk, yellow or white of egg, liver, and dandelion.

H. W.

Synthesis of substances analogous to lactoflavin. P. KARRER, H. SALOMON, K. SCHÖPP, and E. SCHLITTLER (Helv. Chim. Acta, 1934, 17, 1165–1169).— $\beta\gamma$ -Dihydroxypropylamine, o -C₆H₄Cl·NO₂, and anhyd. NaOAc at 100–140° yield *o*-nitro- $\beta\gamma$ -dihydroxypropylaniline, m.p. 120°, reduced (PtO₂) to $\beta\gamma$ -dihydroxypropyl-*o*-phenylenediamine, which is transformed by alloxan into 9- $\beta\gamma$ -dihydroxypropylisoalloxazine



(I) [A; R=CH₂·CH(OH)·CH₂·OH], m.p. about 300°, which exhibits intense green fluorescence in H₂O and, particularly, in org. media. When irradiated in dil. MeOH (I) gives exclusively alloxazine (II), whereas in an alkaline medium (II) and 9-methylisoalloxazine are produced. The close similarity of (I) and lactoflavin is evidence of the structure A (R=CH₂·[CH·OH]₃·CH₂·OH] for the latter.

Application of Zeisel's method to lactoflavins results in the formation of small amounts of AgI, which are not produced if sufficient PhOH is present. Possibly an alkyl group is formed by degradation of the side-chain.

H. W.

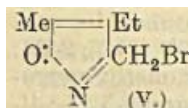
Molecular compounds of pyrroles and pyrrole-dyes. A. TREIBS and P. DIETER (Annalen, 1934, 513, 65–93; cf. A., 1929, 1467).—An investigation of the mol. compounds formed by substituted pyrroles, pyrromethenes, and porphyrins with inorg. salts and acids and various NO₂-compounds. Pyrrole [1:1-compound with C₆H₃(NO₂)₃; 3:1- and 1:1-compounds with H₃Fe(CN)₆] gives an unstable *picrate*, m.p. 69° (decomp.). Monoalkylpyrroles do not form *picrates*. Of the dialkylpyrroles, only the 2:4-derivatives form *picrates*; the 2:3-Me₂ and 3-Me-2-Et derivatives are polymerised to dipyrroles. Most of the tri- and tetraalkylpyrroles give *picrates* (except when large alkyl

groups are present). Compound formation with CaCl₂ occurs only when the pyrrole derivative contains O (not necessarily as CO₂Et); compounds containing Co, Ni, Cr, Mn, Ag, or Zn could not be obtained. The following are described: 1:1-compound, m.p. 111°, of Et 2:4-dimethylpyrrole-3:5-dicarboxylate (*picrate*, m.p. 116°; *perchlorate*, m.p. 123°) and SbCl₃; 1:1-compounds of Et 2:4-dimethylpyrrole-5-carboxylate (*picrate*, m.p. 99°; *perchlorate*) with CaCl₂ and SbCl₃ (m.p. 104°?); 1:1-compounds of Et 2:4-dimethylpyrrole-3-carboxylate (*picrate*, m.p. 81°; *perchlorate*) with CaCl₂ and SbCl₃ (m.p. 97°?); 1:1-compounds of Et 3-acetyl-2:4-dimethylpyrrole-5-carboxylate (*perchlorate*, m.p. 139°) with CaCl₂ and SbCl₃ (m.p. 115°); 1:1-compounds of 3:5-diacetyl-2:4-dimethylpyrrole (unstable *perchlorate*) with CaCl₂ and SbCl₃; 1:1-compounds of 2:4-dimethylpyrrole with SbCl₃ (m.p. 104°), H₃Fe(CN)₆, and H₄Fe(CN)₆; 1:1-compounds of 2:4-dimethyl-3-ethylpyrrole with SbCl₃ (m.p. 118°) and H₄Fe(CN)₆; 1:1-compounds, m.p. 102° and 125–128°, respectively, of SbCl₃ with 5-formyl-2:4-dimethyl-3-ethylpyrrole and 5-carbethoxy-2:4-dimethyl-3-pyrrolpropionic acid; 3:1-compound of 3-methyl-4-ethylpyrrole with H₄Fe(CN)₆; 1:1-compounds of 2:3:4-trimethylpyrrole with H₃Fe(CN)₆ and H₄Fe(CN)₆; 1:1-compound of 2:4-dimethyl-3-pyrrolpropionic acid with H₄Fe(CN)₆; 1:1-compound of cryptopyrrole with H₃Fe(CN)₆. The temp. quoted after the following compounds are those at which decomp. of the *picrate*, *stypnate*, *picrolonate*, and *flavianate*, respectively, occurs: 3:5:3':5'-tetramethylpyrromethene [1:1-compound, decomp. 157° (corr.), with C₆H₂Me(NO₂)₃; *platinichloride*, sinters at 250°, 215°, 200°, 235° (corr.), 273° (corr.); 3:5:3':5'-tetramethyl-4:4'-diethylpyrromethene [1:1-compound with *m*-C₆H₄(NO₂)₂; 1:2-compound, decomp. 150°, with C₆H₂Me(NO₂)₃; 2:3-compound, decomp. 235°, with flavianic acid], 191° (corr.), 203°, 212°, 243°; 4:4'-dicarbethoxy-3:5:3':5'-tetramethylpyrromethene, 208°, 204°, 212°, 240°; 5'-bromo-3:5:4'-trimethyl-4:3'-diethylpyrromethene, 199°, 195°, 193°, 188°; 4:4'-dibromo-3:5:3':5'-tetramethylpyrromethene, 209°, 217°, 221°, 278°; 4:3':5'-tribromo-3:5:4'-trimethylpyrromethene, 167°, 184°, 133° (=dipicrolonate), 240°; 5'-bromo-3:4'-dimethyl-4:3'-diethyl-5-ethoxymethylpyrromethene, 150°, 149°, —, —. *Ætioporphyrin* forms 1:1-compounds with C₆H₃(NO₂)₃ and C₆H₂Me(NO₂)₃, 1:2-compounds with dinitrosalicylic and rufanic (quinizarinsulphonic) acids, a *trisulphate*, a *tri-perchlorate*, a *platinichloride*, C₃₂H₃₈N₄(=B), H₂PtCl₆, and *aurichlorides*, B₂H₂AuCl₄ and B₂H₂AuCl₄; the following *complexes* are also described: 2B₂FeCl₃; 4B₂3FeCl₃·2HCl(?); B₂2SnCl₄; 2B₂5SnCl₄; B₂2HgCl₂; B₂2H₂HgCl₄; B₂4H₃Fe(CN)₆; B₂13H₃Fe(CN)₆. *Mesoporphyrin Me ester*, C₃₀H₄₂O₄N₄(=A), forms 1:1-compounds with C₆H₃(NO₂)₃ and C₆H₂Me(NO₂)₃ and gives the following *complexes*: A₂H₂PtCl₆; 2A₂H₂AuCl₄; 2A₂FeCl₃·2HCl. *Mesoporphyrin (diquinine and diquinidine salts)* and CrO₃ in 20% H₂SO₄ afford the *complex*, C₃₄H₃₈O₄N₄·2CrO₃·3H₂SO₄·6H₂O, which when washed with H₂O gives the unstable *complex*, C₃₄H₃₈O₄N₄·2CrO₃·H₂O. *Hæmatoporphyrin Me₂ ether* forms a *compound*, m.p. 145–150°, with approx. 2 mols. of quinine.

H B

Synthesis of 6-formylpyrroporphyrin and 6-formylphyllporphyrin. H. FISCHER and A. SCHWARZ [and, in part, HIRSCHBECK and K. MÜLLER] (Annalen, 1934, 512, 239—249).—Treatment of the corresponding hæmin ester with a mixture of $\text{CHCl}_3 \cdot \text{OEt}$ and POCl_3 (obtained by the action of PCl_5 on HCO_2Et) and SnCl_4 at room temp. leads to *Me formylpyrroporphyrin ester* (I), $\text{C}_{33}\text{H}_{36}\text{O}_3\text{N}_4$, m.p. 248°, the spectrum of which differs from that of the *b*-porphyrins and the ketoporphyrins of the *a*-series. The *Cu*, m.p. 208°, and *Fe*, $\text{C}_{33}\text{H}_{34}\text{O}_3\text{N}_4\text{FeCl}$, m.p. 265°, salts, the *oxime*, m.p. 260° (*Fe*, m.p. 303°, and *Cu*, m.p. 255°, salts), of (I) are described. (I) and $\text{CH}_2(\text{CO}_2\text{H})_2$ in presence of $\text{C}_5\text{H}_5\text{N}$ —piperidine followed by treatment with HCl and CH_2N_2 give the compound, $\text{C}_{36}\text{H}_{40}\text{O}_4\text{N}_4$, m.p. 261° (*Cu* salt, m.p. 229°). *6-Formylphyllporphyrin Me ester*, m.p. 231°, obtained similarly, gives a *Cu* salt, m.p. 206°, and an *oxime*, m.p. 244°. H. W.

Bile pigments. XIII. Synthesis of hydroxy-hæmopyrrole, of isoneo- and iso-xanthobilirubic acid. Cryptopyrrole ether. H. FISCHER and P. HARTMANN (Z. physiol. Chem., 1934, 226, 116—129; cf. A., 1933, 725).—Oxidation of cryptopyrrole (I) with H_2O_2 (improved prep.) gives hydroxycryptopyrrole (II), the Br-derivative of which combines with 3- β -carbomethoxyethyl-2:4-dimethylpyrrole to form *Me xanthobilirubate*, m.p. 213°. Oxidation of hæmopyrrole with H_2O_2 affords 5-hydroxy-2:4-dimethyl-4-ethylpyrrole (III), m.p. 95°, the Br-derivative (IV) of which combines with *Me* cryptopyrrolecarboxylate to give *Me isoxanthobilirubate*, m.p. 197°. Analogously with *Me opsopyrrolecarboxylate*, (IV) yields *Me isoneoxanthobilirubate*, m.p. 204°. With SO_2Cl_2 , (III) gives the Cl_2 -derivative, m.p. 167°. Bromination of



(II) in MeOH gave a "bromoketocryptopyrrole" (V), m.p. 141° (2 cryst. forms), derived from a "ketocryptopyrrole" (VI), $\text{C}_8\text{H}_{11}\text{ON}$, m.p. 197°, obtained by oxidation of (II) with FeCl_3 in AcOH . A trace of (VI) was obtained by fractional distillation of (II) which had been kept for some time. FeCl_3 oxidation of (II) also gave methylethylmaleimide (VII). Treatment of the BrMg compound of (I) with O_2 gave small yields of (II) and cryptopyrrole ether (VIII), m.p. 222°. Hydrolysis of (VIII) with conc. HCl afforded (VI) and a substance, $\text{C}_8\text{H}_{13}\text{O}_2\text{N}$, m.p. 143°, possibly a hydrate of (VI) or a N-oxide. Oxidation of (VIII) with H_2O_2 gave (VII), under milder conditions dicryptopyrrol peroxide. Oxidation of (VIII) with FeCl_3 in AcOH (cf. A., 1932, 285) gave 5-hydroxy-4:3':5'-trimethyl-3:4'-diethylpyrromethene. Oxidation of 3-acetyl-2:4-dimethylpyrrole with H_2O_2 in $\text{C}_5\text{H}_5\text{N}$ afforded *bis*-(3-acetyl-2:4-dimethylpyrrol 5-peroxide), m.p. 183°. With conc. H_2SO_4 and oleum, coproporphyrin-II *Me* ester (IX) yields coprorhodin-II, converted by CH_2N_2 into the *Me* ester, m.p. 225° (*haemin*). (IX) affords *Ag*, m.p. 274° (decomp.), and *Co* complex salts. J. H. B.

Bacteriochlorophyll.—See this vol., 1265.

Azoformamidoximes. A. QUILICO and R. JUSTONI (Gazzetta, 1934, 64, 577—583; cf. A., 1932, 1146).— α -isoOxazoleazooformamidoxime is reduced by SnCl_2 in HCl to α -isooxazolehydrazoformamidoxime

hydrochloride (I), m.p. 180° (decomp.). Benzeneazooformamidoxime similarly yields phenylhydrazoformamidoxime hydrochloride (II), decomp. 140—150°. NaOH does not liberate the bases from (I) or (II), but yields the original azo-compounds in presence of atm. O_2 . R. K. C.

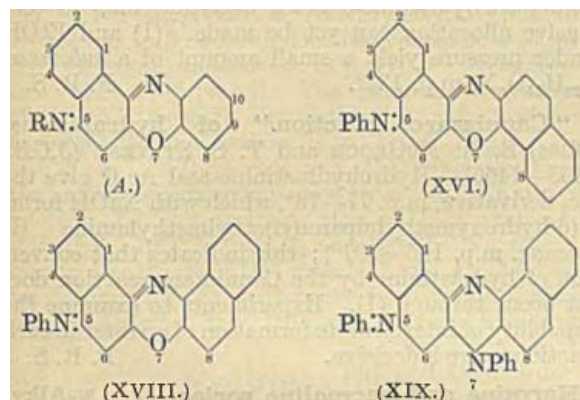
Preparation of resazurin. H. EICHLER (J. pr. Chem., 1934, [ii], 141, 91—92).—Resazurin (I) is best prepared (cf. Nietzki *et al.*, A., 1890, 156; 1892, 163) by oxidation (H_2O_2) of resorufin (II) (this vol., 309) in conc. H_2SO_4 . Dyes are obtained from diazonium salts and (I) and (II) in alkaline solution (aq. NH_3 , NH_4HCO_3 , Na_2CO_3) in presence of $\text{CO}(\text{NH}_2)_2$, $(\text{NH}_4)_2\text{SO}_4$, or NH_4Cl , especially at higher temp. H. B.

Preparation of dibenzoxacarbocyanines.—See B., 1934, 878.

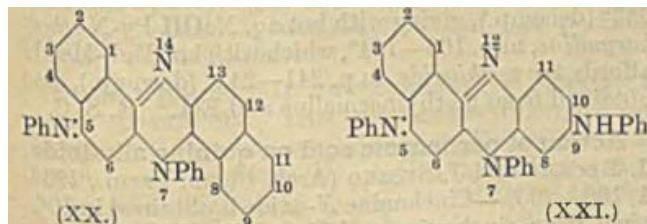
Syntheses of azine dyes. R. LANTZ (Ann. Chim., 1934, [xi], 2, 101—185; cf. this vol., 1011).—1-Anilino- β -naphthol (I) with *o*- $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ (II) and $\text{Cu}(\text{OH})_2$ in air at room temp. gives β -naphthol-1:4-di-(*o*-anisylimine) (III) (*Cu* salt), hydrolysed by cold, conc. HCl to (II) and 2-hydroxy-1:4-naphthaquinone-1-*o*-anisylimine. 1-*p*-Toluidino- β -naphthol (IV), $\text{Cu}(\text{OH})_2$, and NH_2Ph in air give similarly β -naphthol-1:4-di(phenylimine) (V), giving NH_2Ph on hydrolysis. (I), *p*- $\text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{NH}_2$ (VI), and $\text{Cu}(\text{OH})_2$ in air at 50° yield β -naphthol-1:4-di-(*p*-tolylimine) (VII), m.p. about 240° (*Cu* salt), obtained similarly from (IV). (I), $\text{Cu}(\text{OH})_2$, and the appropriate base afford similarly β -naphthol-1:4-di-(*m*-xylilyl-), -(*p*-chlorophenyl-), and -(*o*-tolyl-imine) (*Cu* salts). 1:2-Naphthaquinone-1-phenylimine and (VI) in cold COMe , give NH_2Ph , (I), and (VII), hydrolysed by cold, conc. HCl to (VI) and 2-hydroxy-1:4-naphthaquinone-4-*p*-tolylimine, which is further hydrolysed by hot H_2SO_4 — EtOH to (VI). (V) and (VI) in cold CHCl_3 give β -naphthol-4-phenylimine-1-*p*-tolylimine (VIII), hydrolysed (cold) to (VI) and 2-hydroxy-1:4-naphthaquinone-4-phenylimine (IX), which is further hydrolysed (hot) to NH_2Ph . (VIII) and NH_2Ph in cold CHCl_3 give (V), but (VII) and NH_2Ph afford (VIII). (V) and *p*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NHPH}$ (X) in hot xylene yield β -naphthol-4-phenylimine-1-*p*-phenylaminophenylimine (XI), hydrolysed (cold) to (X) and (IX). (VII) and (IX) react similarly. β -Naphthol-1-imine-4-phenylimine (XII) and (X) in xylene also yield (XI). (I), *o*- or *p*- $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, and $\text{Cu}(\text{OH})_2$ in $\text{C}_5\text{H}_5\text{N}$ in air afford β -naphthol-1-phenylimine-4-*o*- (XIII) or *p*-nitrophenylimine (XIV) (*Cu* salts), respectively. 1-anilino- β -naphthol-4-sulphonate, NH_2Ph , and a little Na_2CO_3 in H_2O in air give (V); (VI), *p*- $\text{C}_6\text{H}_4 \cdot \text{Cl} \cdot \text{NH}_2$, *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, and *p*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ afford similarly (VII) and its *s*-analogues, (VII) being obtained also from Na 1-*p*-toluidino- β -naphthol-4-sulphonate and (VI). The regulated hydrolyses prove the structures of the products. It is proved that replacement of the 1-arylimino-group occurs only after formation of the di-imine. Analogous replacements are discussed.

Passage of air through a solution of (V) or a suspension of its *Cu* salt and a little NH_4Cl in PhNO_2 at 170° gives 5-anilo-as-naphthophenoxazine (XV) ($\text{R} = \text{Ph}$), m.p. 215°, obtained also in better yield from *o*- $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ and (V) in MeOH or $\text{C}_5\text{H}_{11}\text{OH}$, or

the Cu salt in hot PhNO_2 or $\text{C}_5\text{H}_5\text{N}$; it is stable to cold HCl , but with hot 20% HCl gives slowly 5-keto- α -naphthophenoxazine (naphthophenoxazone), m.p. 191° , and is reduced by Zn dust-AcOH-EtOH to a (? *di*)hydro-derivative, m.p. 200° , which is rapidly oxidised by air to (XV). The Cu salt of (XIV) in hot PhNO_2 gives similarly the *p*- NO_2 -derivative of (XV) (*A*; $\text{R}=\text{p-NO}_2\cdot\text{C}_6\text{H}_4$), and (XIII) gives the *o*- NO_2 -compound (not obtained pure). (XI), $\text{NH}_2\text{Ph}\cdot\text{HCl}$, and air give the 9-anilino-derivative of (XV), cryst. (hydrochloride), in 66% yield. 5-Anilino- α -di-as-naphthoxazine (XVI), m.p. 321° (corr.), is



obtained readily from (V) and $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$ in hot xylene, or (V) and 1-bromo- β -naphthylamine (XVII) in hot PhNO_2 , less readily from (XII), $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, ZnCl_2 , and air in PhNO_2 at 140° , or (possibly) (IX) and (XVII) in PhNO_2 . 5-Anilino- α -di-as-naphthoxazine (XVIII), m.p. 254° (corr.), is obtained from (V), $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$, and air in xylene at 100° , (V) and 1-amino- β -naphthol in hot PhNO_2 , 1- α -naphthyl-amino- β -naphthol, NH_2Ph (excess), $\text{Cu}(\text{OH})_2$, and air at room temp., or (XII), $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$, ZnCl_2 , and air in hot PhNO_2 . (I), $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, $\text{Cu}(\text{OH})_2$, and air in cold $\text{C}_5\text{H}_5\text{N}$ give 2-hydroxy-1:4-naphthaquinone-4- β -naphthylimine and the β -naphthylimino-analogue of (XVI). With (I), pure $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$, $\text{Cu}(\text{OH})_2$, and air at 70° condensation and cyclisation give in one operation the α -naphthyl analogue, m.p. 240° (corr.), of (XVIII); impure $\alpha\text{-C}_{10}\text{H}_7\cdot\text{OH}$, containing some β -isomeride, gives also some α -naphthylimino-analogue of (XVI). The Cu salt of (III) with $\text{Cu}(\text{OH})_2$, NH_4Cl , and air in PhNO_2 at 140° probably loses MeOH to give the (impure) *o*-OMe-derivative of (XV) (*A*; $\text{R}=\text{o-OMe}\cdot\text{C}_6\text{H}_4$), m.p. 192° (corr.). (V) and Na 2-amino-phenol-4-sulphonate in $\text{C}_5\text{H}_5\text{N}$ afford the Na 10-sulphonate of (XV). (XII), Na 1-amino- β -naphthol-4-sulphonate, and NaOAc in hot EtOH yield NH_3 and



the Na 9-sulphonate of (XVIII). (V), NaOAc, and 1-amino-4-anilino- β -naphthol [pure or prepared in

solution by reduction (H_2S) of (V)] in hot EtOH give rapidly the 9-anilino-derivative of (XVIII).

(XVIII) and boiling NH_2Ph (6 hr.) afford 5-anilino-7-phenyl- α -di-as-naphthazine (XIX), m.p. 273° (corr.). (XVI) gives more rapidly (2 hr.) 5-anilino-7-phenyl- α -di-as-naphthazine (XX), m.p. 229° , and similar 7-arylnaphthazines are obtained in 50% yield using *o*-anisidine, *o*- and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, *m*- and *p*-xylydine at 190° . The 9-anilino-derivative of (XV) and a trace of 10% Na_2CO_3 in boiling PhNO_2 (22 hr.) afford 9-anilino-5-anilino-7-phenyl- α -naphthophenazine (XXI), m.p. 275° (corr.), also obtained by an exchange of arylimino-groups from the *p*-tolylimino-analogue of (XV) (*A*; $\text{R}=\text{p-C}_6\text{H}_4\text{Me}$), but (XV) itself does not react. The 5-anilino-derivative of (XVII), NH_2Ph , and BzOH in PhNO_2 at 160° give the α -dinaphthazine derivative (XXII), m.p. 338° (corr.) (hydrochloride). R. S. C.

1-[2-Amino-5-[4-methoxybenzthiazole. — See B., 1934, 874.

Chemical examination of the seeds of *Abrus precatorius*, L. III. Constitution of abrine. N. GHATAK (Bull. Acad. Sci. U.P., 1934, 3, 295—299). —Abrine, $\text{C}_{12}\text{H}_{14}\text{O}_2\text{N}_2$ (A., 1933, 104), is monobasic, and gives no FeCl_3 coloration. It contains an alcoholic OH, an NH , and one double linking. There is no amino-acidic group. The following derivatives are described: hydrochloride, m.p. 221.5° (unstable in H_2O), nitrate, m.p. 143° (decomp.), picrate (three cryst. modifications), m.p. 194° (decomp.), Br_2 -, darkens at 220° , m.p. $241\text{—}242^\circ$ (decomp.), NO_2 -, darkens at about 185° , decomp. at about 220° , NO -, m.p. 121° , *Ac*-, m.p. $286\text{—}287^\circ$ (decomp.), and phenylurethane, m.p. 271° . F. S. H. H.

Synthesis of two isomeric *N*-methylconicines. R. LUKES and N. SMETACKOVA (Coll. Czech. Chem. Comm., 1934, 6, 433).—A density calculation in an earlier paper (this vol., 902) is corr.

Physical constants of anabesine.—See this vol., 1165.

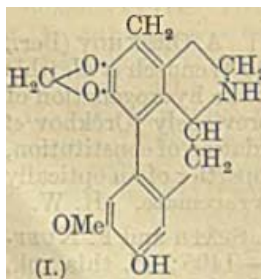
[Constitution of anabesine.] A. OREKHOV (Ber., 1934, 67, [B], 1606).—In reply to Wenusch *et al.* (this vol., 1014) it is pointed out that the hydrogenation of anabesine has been described previously (Orekhov *et al.*, A., 1933, 517). For the elucidation of constitution, it is not valid to compare the properties of an optically active compound with those of a racemate. H. W.

Peganine and vasicine. E. SPATH and F. KUFFNER (Ber., 1934, 67, [B], 1494—1495; cf. this vol., 303, 787).—The identity of Merck's vasicine with peganine (II) is maintained (cf. Narang *et al.*, *ibid.*, 905). Isatoic anhydride, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}\cdot\text{HCl}$, and $\text{H}_2\text{O-NaOMe}$ afford *Me o-aminohippurate*, m.p. $87\text{—}89^\circ$ after softening, transformed by HCO_2H at 100° into the ester, $\text{C}_6\text{H}_4\text{N}(\text{CO}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me})_2$, m.p. $151\text{—}152^\circ$, identical with that obtained by oxidation of (I) with KMnO_4 . H. W.

Synthesis of physostigmine (eserine). X. *dl*-Noresermethole and crystalline *dl*-eserethole.

F. E. KING, M. LIGUORI, and R. ROBINSON (J.C.S., 1934, 1416—1419).— γ -Phthalimido- α -methylbutaldehyde (improved prep.), p -OMe-C₆H₄-NH-NH₂, and HCl give 5-methoxy-3-methyl-3-(β -phthalimidoethyl)-indolenine (*picrate*, m.p. 159—160°), the *methosulphate*, m.p. 170°, of which with N₂H₄·H₂O affords *dl*-noresermethole (*picrate*, m.p. 162—163°, which cannot be successfully methylated, only a minute quantity of *dl*-esermethole *picrate*, m.p. 180—181°, being isolated). *dl*-Eserethole has been obtained crystalline, m.p. 79—80°, but could not be resolved. *dl*-Esermethole methopicate has been obtained in two modifications, hexagonal plates, m.p. 184—186°, and rhomboidal plates, m.p. 192—193°, the latter resembling the derivative from natural eserine. The work of Hoshino and Kobayashi (cf. this vol., 667) is discussed. F. R. S.

Constitution of actinodaphnine. T. P. GHOSE, S. KRISHNA, and E. SCHLITTLER (Helv. Chim. Acta, 1934, 17, 919—930; cf. A., 1933, 168).—Actinodaphnine (I) is C₁₈H₁₇O₄N. It contains :O₂CH₂. NMe is absent, but the presence of NH and phenolic OH, respectively, is established by the prep. of its *phenylthiocarbamide*, m.p. 181°, and methylation by CH₃N₂. *O*-Methylactinodaphnine (II) is converted by MeI and NaOMe in MeOH into the *methiodide*, m.p. 214°, which with NaOH yields the *methine* base (III), C₂₁H₂₃O₄N, m.p. 158—159°, transformed by successive treatment with MeI and Ag₂O into *dimethoxymethylenedioxyvinylphenanthrene* (IV), m.p. 205.5—206°. Oxidation of (IV) yields the corresponding carboxylic acid, decarboxylated by Cu powder in quinoline to *dimethoxymethylenedioxyphenanthrene*, m.p. 204—205°. (II) is oxidised by conc. HNO₃ to mellophanic acid (*Me₂* ester, m.p. 129°). Treatment of (I) with KMnO₄ leads to methylenedioxyhemimellitic acid (*Me₂* ester, m.p. 128—129°), identical with a specimen derived from pukateine. (II) is oxidised by KMnO₄ to *m*-hemipinic acid. Successive treatment of (II) with MeI in COMe₂ and Ac₂O leads to *N*-acetyl-*O*-methylactinodaphnine, m.p. 222—224°, and dicentrene, m.p. 169°. *N*-Methyl-*O*-ethyl- (V), m.p. 198—199°, and *ON*-diethyl-, m.p. 213—214°, -actinodaphnine are described. The Hofmann degradation of (V)



leads through the *methine*, C₂₂H₂₅O₄N, m.p. 142—144°, to the *vinyl* product, C₂₀H₁₈O₄, m.p. 186—187°. Treatment of (V) with H₂SO₄ and phloroglucinol gives the corresponding (OH)₂-compound, decomp. about 160°, the *Me₂* compound of which is subjected to the Hofmann degradation, thus leading to a

H. W.

Stereoisomerides of narcotine and hydrastine. (Miss) M. A. MARSHALL, F. L. PYMAN, and R. ROBINSON (J.C.S., 1934, 1315—1320).—Boiling with KOH-MeOH transforms *l*- α -narcotine into *l*- β -narcotine, m.p. 176°, [α]_D²⁰ -101° in CHCl₃ [*hydrochloride* (+1.5H₂O); *H sulphate*; *picrate*, m.p. 118°; *methiodide*, m.p. 208°; *methotri-iodide*, m.p. 187.3°]. The “phthal-

ide” C atom is probably the one affected. *d*- β -Narcotine is similarly obtained. A mixture of *d*- and *l*- β -narcotine gives β -gnoscopine, which cannot be resolved. Hydrastine with KOH-MeOH affords *l*- α -hydrastine, m.p. 162°, [α]_D²⁰ -163° in CHCl₃ (*hydrochloride*, m.p. about 237°; *picrate*, m.p. 172°; *methiodide*, m.p. 222°). Comparison of the narcotine and hydrastine series suggests that the naturally occurring bases are not stereochemically analogous; natural hydrastine is probably *l*- β -hydrastine (I). Hydrastine-*a* and -*b* have been obtained in small yield from (I) by racemisation processes, but, although the evidence points to hydrastine-*b* being *dl*-hydrastine, no conclusive allocation can yet be made. (I) and EtOH under pressure yield a small amount of a substance, C₂₂H₂₅O₆N, m.p. 134°. F. R. S.

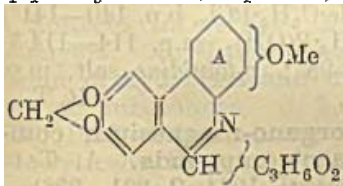
“Cannizzaro reaction” of hydrastinine. (Miss) S. N. MCGEOCH and T. S. STEVENS (J.C.S., 1465—1466).—Hydrohydrastinine and Ac₂O give the *Ac₂* derivative, m.p. 77—78°, which with NaOH forms β -(6-hydroxymethylpiperonyl)ethylmethylamine (I) (*picrate*, m.p. 195—197°); this indicates that conversion of hydrastinine by the Cannizzaro reaction does not occur through (I). Experiments to examine the possibility of intermediate formation of an ester in such reactions were indecisive. F. R. S.

Harmine and harmaline series. I. *N*-Alkyl derivatives of harmine and harmaline. R. KONOVALOVA and A. OREKHOV (Arch. Pharm., 1934, 272, 748—761).—Harmine (I), harmaline (II), and various *N*-alkyl derivatives are ineffective against malaria in birds. The following results confirm the views of Perkin and Robinson (J.C.S., 1919, 115, 943) on the methylation of (I) and the formulæ of (I) and (II). Norharmine (III) and MeI in hot EtOH give a salt, which is stable to NH₃ or cold 10% NaOH, but with hot 10% NaOH gives *N*-methylnorharmine, which with EtI-PhNO₂-PhMe gives the *ethiodide*, m.p. 280—281°, stable to NH₃ and hot 10% NaOH. (III) and EtI in hot PhNO₂-PhMe give the *ethiodide*, m.p. 221—222°, decomposed by hot (not cold) 10% NaOH to *Py-N*-ethylnorharmine, m.p. 183—185°, which affords a stable *methiodide*, m.p. 256°. Benzylidenenorharmine (IV) and MeI in hot EtOH give *Py-N*-methylbenzylidenenorharmine hydriodide, which with cold aq. NH₃ or NaOH gives methylbenzylidenenorharmine, m.p. 192—193°, the *ethiodide*, m.p. 230—231° (prepared in hot PhNO₂-PhMe), of which is stable to hot 10% NaOH or aq. NH₃. (IV) in hot PhNO₂-PhMe affords the hydriodide of the Et derivative, which with hot NaOH-EtOH gives *Py-N*-ethylbenzylidenenorharmine, m.p. 199—200° (*methiodide*, m.p. 250—251°). (II) and EtI in hot EtOH give *Py-N*-ethylharmaline hydriodide, m.p. 232—233° (decomp.), giving with hot aq. NaOH *Py-N*-ethylharmaline, m.p. 163—164°, which with hot MeI-MeOH affords the *methiodide*, m.p. 241—243° (decomp.), also obtained from methylharmaline and EtI. R. S. C.

Action of perbenzoic acid on quinine alkaloids. J. BECKER and J. SUSZKO (Arch. Chem. Farm., 1934, 1, 199—205).—Cinchonine *N*-oxide is obtained in 10% yield from cinchonine and BzO₂H in CHCl₃ at room temp. The -oxide, +2.5H₂O, m.p. 194°, [α]_D²⁰ of cinchonidine (also obtained by the action of H₂O₂;

of quinine, $[\alpha]_D^{20} -26^\circ$, and of quinidine, $[\alpha]_D +100^\circ$, are obtained similarly. R. T.

Tazettine. E. SPÄTH and L. KAHOVEC (Ber., 1934, 67, [B], 1501—1506).—*Tazettine* (I), $C_{18}H_{21}O_5N$, m.p. 210—211° (vac.), $[\alpha]_D^{25} +150.4^\circ$ in $CHCl_3$ (*Ac* derivative, m.p. 125—126.5°), is obtained by extracting the dried corms of *Narcissus Tazetta*, L., with boiling EtOH. It contains 1 OMe. Distillation of (I) with Zn dust yields phenanthridine (prep. from *o*-nitrodiphenyl described), whilst oxidation with $KMnO_4$ (—160) affords 4:5-methylenedioxyphthalic acid (anhydride, m.p. 177—180°; methylimide, m.p. 231°). For comparison, 6:7-methylenedioxyphthalide is oxidised to 3:4-methylenedioxyphthalic acid, m.p. 285° (decomp.) [*anhydride*, m.p. 170.5°; *methylimide*, m.p. 212—213° (vac.)]. The Hofmann degradation of (I) leads through the *methiodide*, m.p. 220° (vac. decomp.), to the *methine base* (II), $C_{18}H_{19}O_4N$, $[\alpha]_D^{25} -40.6^\circ$ in $CHCl_3$ [*picrate*, m.p. 171° (vac. decomp.)], the process being accompanied by loss of OMe and production of a new aromatic ring. (II) is oxidised by $KMnO_4$ (=100) to $H_2C_2O_4$ and $BzOH$. Further successive treatment of (II) with MeI and Ag_2O followed by decomp. of the quaternary base yields 6-phenylpiperonyl alcohol, m.p. 101°, also obtained by converting 6-bromopiperonal by PhI and Cu powder at 210—250° in CO_2 into 6-phenylpiperonal, m.p. 87° [*semicarbazone*, m.p. 298° (decomp.)], which is treated with KOH-MeOH at 100°. (I) is therefore as annexed. Nucleus A contains only one double linking. It may be identical with sekisanine and Kondo's "base VIII."



H. W.

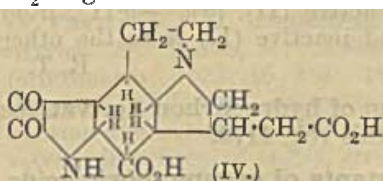
Reduction in morphine series. III. **Dihydro- γ -isomorphine.** L. SMALL and R. E. LUTZ (J. Amer. Chem. Soc., 1934, 56, 1928—1930).—Reduction (H_2 , Pd-BaSO₄, 16% AcOH) of γ -isomorphine (I) gives the diphenolic tetrahydro- γ -isomorphine (II) [*hydrochloride*, m.p. 275—280° (all m.p. are corr.); *hydriodide* (+0.5H₂O), m.p. 280—290°; *perchlorate* (+H₂O), m.p. 215—220°], also prepared by demethylation of tetrahydro- ψ -codeine (A., 1933, 170). (II) is stable only in presence of acids. Reduction (H_2 , PtO₂, AcOH) of the hydrochloride of (I) affords 21% of (II) and 35% of the non-phenolic dihydro- γ -isomorphine (III) (+H₂O), m.p. 128—130° (with loss of H₂O), re-solidifying at 160—170° with m.p. 222—223°, $[\alpha]_D^{25} -35.4^\circ$ in 95% EtOH [*hydrochloride* (+0.5H₂O), m.p. 300—302°; *hydriodide*, m.p. 285—288°; *perchlorate* (+H₂O); *sulphate* (+0.5H₂O), m.p. 131.5—132.5°; *methiodide*, m.p. 255—257°]. (III) is methylated (CH_3N_2) to, and is best prepared by demethylation of, non-phenolic dihydro- ψ -codeine (*loc. cit.*).

γ - ψ -Morphine. L. SMALL and B. F. FARIS (J. Amer. Chem. Soc., 1934, 56, 1930—1934). γ -isomorphine (I) is oxidised [alkaline $K_3Fe(CN)_6$] to the bimol. γ - ψ -morphine (II), $C_{34}H_{36}O_6N_2$, 3H₂O, m.p. (vac.) 282—283°, $[\alpha]_D^{25} +44.8^\circ$ in *N*-HCl [*dihydrochloride* (+2.5H₂O); *dihydrobromide* (+2H₂O); *dihydriodide* (+H₂O); *diperchlorate* (+2H₂O); *sulphate* (+3H₂O); *tartrate* (+7H₂O); *dibenzoate*; *disalicylate*],

methylated (method: Pschorr and Dickhauser, A., 1911, i, 908) to a Me₁ ether [*oxalate* (+5H₂O)]. Methylation (MeI, aq. MeOH-NaOH) of (II) gives the Me₁ ether *methiodide* (+2H₂O), indicating the presence of only 1 phenolic OH in (II). Similar oxidation of the *methiodide* of (I) affords the *methiodide methohydroxide* (+5H₂O) of (II); this with dil. HI gives the *dimethiodide* (+3H₂O), which could not be obtained directly from (II). (II) is acetylated (Ac_2O , C_6H_6) to a *Ac* derivative, m.p. 189—191°, $[\alpha]_D^{25} +57.5^\circ$ in EtOH [*dihydrobromide* (+4H₂O); *dihydriodide* (+3H₂O); *diperchlorate* (+3H₂O)], which readily gives a *dimethiodide* (+6H₂O). Reduction (H_2 , Pd-BaSO₄, AcOH) of the hydrochloride of (II) affords tetrahydro- γ - ψ -morphine (+3H₂O), m.p. (vac.) 254° (decomp.), $[\alpha]_D^{25} +34.3^\circ$ in *N*-HCl [*sulphate* (+2H₂O)], also prepared by oxidation [$K_3Fe(CN)_6$] of dihydro- γ -isomorphine (preceding abstract). Reduction (H_2 , Pd-BaSO₄, dil. AcOH) of (II) gives octahydro- γ - ψ -morphine [*dihydrobromide* (+2H₂O); *diperchlorate* (+2H₂O)], which could not be prepared by oxidation of tetrahydro- γ -isomorphine. Oxidation (as above) of α - and β -isomorphine gives α - (+3H₂O), m.p. (vac.) 276°, $[\alpha]_D^{25} +6.2^\circ$ in *N*-HCl, and β - (+3H₂O), m.p. (vac.) 272°, $[\alpha]_D^{25} -77^\circ$ in *N*-HCl, ψ -morphine, respectively; dihydromorphine affords tetrahydro- ψ -morphine (+2H₂O), m.p. (vac.) 300—302° (decomp.), $[\alpha]_D^{25} -85.9^\circ$ in *N*-HCl [*tartrate* (+5H₂O)]; dihydrodeoxymorphine-D (A., 1933, 1176) yields tetrahydrodideoxy- ψ -morphine (+2H₂O), m.p. (vac.) 318° (decomp.), $[\alpha]_D^{25} -13.4^\circ$ in *N*-HCl; heterocodeine (Mannich, A., 1917, i, 473) furnishes ψ -heterocodeine (the alcoholic Me₂ ether of ψ -morphine) (+2H₂O), m.p. (vac.) 250—252°, $[\alpha]_D^{25} -192^\circ$ in 10% AcOH; a 1:1 mixture of (I) and morphine gives the mixed bimol. compound morphine- γ -isomorphine, m.p. (vac.) 268—269°, the constitution of which is demonstrated by its complete hydrogenation with 3 mols. of H₂.

H. B.

Strychnos alkaloids. LXXXI. Degradation of benzylidenedihydro-brucine and -strychnine to the acid, $C_{16}H_{18}O_6N_2$. H. LEUCHS and H. BEYER. LXXXII. Hydrogenation of diketonucidine methoperchlorate. H. LEUCHS (Ber., 1934, 67, [B], 1577—1582, 1607—1611).—LXXXI. Dihydrobrucine, PhCHO, and NaOEt in boiling EtOH yield benzylidenedihydrobrucine (I), m.p. 243—244° after softening at 240°, $[\alpha]_D^{25} -140.7^\circ$ in $CHCl_3$ [*perchlorate*, m.p. 224—226° (decomp.); *zincchloride*]. Oxidation of (I) with $KMnO_4$ in AcOH-COMe₂ leads to the base (II), $C_{30}H_{32}O_6N_2$, m.p. 246—247° (decomp.) [*sulphate*; *Ac*₁ derivative, m.p. 226—228°], the group $CHPh\cdot C$ becoming $COPh\cdot C\cdot OH$. The analogous substance from benzylidenedihydrostrychnine, m.p. 306° (decomp.) after becoming brown at 280°, is $C_{30}H_{30}O_6N_2$. Oxidation of (I) by $KMnO_4$ in $COMe_2$ -H₂O gives a small amount of (II) and an acid (III), $C_{23}H_{26}O_6N_2$, m.p. 245—246° (decomp.), $[\alpha]_D^{25} +81.9^\circ$ in 0.1*N*-NaOH, which is decomposed by $Ba(OH)_2$ into BaC_2O_4 and a (non-isolated) NH_2 -acid. (III) or the



(IV.)

analogous acid, $C_{15}H_{23}O_5N_2$, from the strychnine series is oxidised by CrO_3 in $3N\cdot H_2SO_4$ to the acid (IV) [*perchlorate* (V), $[\alpha]_D^{25} + 9.0^\circ/d$ in H_2O]. Hydrogenation of (V) (PtO_2) leads to the *perchlorate*, $C_{15}H_{26}O_6N_2\cdot HClO_4$, $[\alpha]_D^{25} - 19.8^\circ/d$ in H_2O . Treatment of (V) with $NH_2\cdot CO\cdot NH\cdot NH_2$ followed by $EtOH\cdot HClO_4$ gives the *semicarbazone* of the *Et ester perchlorate*, $C_{18}H_{25}O_6N_5\cdot HClO_4$, $[\alpha]_D^{25} - 75.6^\circ/d$ in H_2O . With $H_2O_2\cdot Ba(OH)_2$ (IV) yields $BaCO_3$.

LXXXII. 2:3-Diketonicucidine (I) and Me_2SO_4 yield the compound, $C_{17}H_{20}O_3N_2\cdot Me_2SO_4\cdot MeOH$, m.p. $> 300^\circ$, $[\alpha]_D + 117^\circ$ in H_2O (calc. for $MeOH$ -free). The corresponding methoperchlorate, $[\alpha]_D^{25} + 113^\circ$, is hydrogenated (PtO_2) to 2-keto-3-hydroxydihydronucidine methoperchlorate (II), $[\alpha]_D^{25} + 59.2^\circ/d$, and a mixture of isomerides, $C_{18}H_{28}O_3N_2$, m.p. $199\text{--}201^\circ$ after softening at 195° (vac.), $[\alpha]_D^{25} + 63.6^\circ/d$ in abs. $EtOH$ (*perchlorate*, $[\alpha]_D^{25} + 45.4^\circ/d$), and m.p. (indef.) $170\text{--}175^\circ$, $[\alpha]_D^{25} + 36^\circ/d$ in abs. $EtOH$ (*perchlorate*, $[\alpha]_D^{25}$ about $+33^\circ/d$). 2-Keto-3-hydroxydihydronucidine methiodide is described. Oxidation of (II) with CrO_3 in $3\cdot 6N\cdot H_2SO_4$ gives diketodihydronucidine methoperchlorate, $[\alpha]_D^{25} + 138.1^\circ/d$ (*semicarbazone*, $C_{18}H_{25}O_3N_5\cdot MeClO_4$), re-hydrogenated (PtO_2) to (II), and carboxydihydroapocucidine methiodiperchlorate, $C_{16}H_{24}O_3N_2\cdot MeClO_4\cdot HClO_4$, $[\alpha]_D^{25} - 4.7^\circ/d$. Reduction of (I) with $Zn\cdot Hg$ gives 2-keto-3-hydroxynucidine, m.p. $257\text{--}260^\circ$ (vac.) [methiodide (III) and methoperchlorate (IV), $[\alpha]_D^{25} + 44^\circ/d$]. Hydrogenation (PtO_2) of (III) and (IV) gives the quaternary salt of the H_2 -compound and bases sol. in $CHCl_3$. H. W.

Alkaloid from *Mitragyna*, mitrinermine.—See this vol., 1277.

Asymmetric quaternary arsonium compounds, and their attempted resolution into optical antipodes. G. KAMAI (J. Gen. Chem. Russ., 1934, 4, 184—191).—The following substituted *arsines* have been prepared by Wigren's method (A., 1930, 899): $AsMeEtI$ (I), b.p. $62\text{--}63^\circ/12$ mm.; $AsEtPrI$, b.p. $89.5\text{--}90^\circ/11$ mm.; $AsPhEtI$, b.p. $138\text{--}141^\circ/12$ mm.; $AsPhI_2$, b.p. $193\text{--}197^\circ/12$ mm.; $AsPhMeEt$ b.p. $89\text{--}90.5^\circ/12$ mm. (*benziodide*, m.p. 140°); $AsPhEtPr$, b.p. $120^\circ/13$ mm. ($CuBr$ salt, m.p. 134° ; *benzochloride*, m.p. 156°); $As(p\text{-}C_6H_4Me)EtPr$, b.p. $127\text{--}128^\circ/10$ mm. [$CuBr$ salt, m.p. $117\text{--}118^\circ$; *benziodide* (II), m.p. $119\text{--}120^\circ$]; $As(\alpha\text{-}C_{10}H_7)EtPr$, b.p. $181^\circ/10$ mm. (*benziodide*, m.p. 155° ; *phenacyl bromide* compound, m.p. $136\text{--}137^\circ$). (I) and $CH_2I\cdot CH_2\cdot CO_2Et$ in C_6H_6 yield when boiled with Zn the double salt, $AsMeEt\cdot C_2H_4\cdot CO_2Et\cdot ZnI_2$, m.p. 189° , which did not afford *cryst. decomp. products*. (II) and $Ag\ d\text{-}\alpha$ -bromocamphor--sulphonate in aq. $COMe_2$ yield a *cryst. salt*, separated into 3 fractions, respectively of m.p. 137° , $135\text{--}136^\circ$, and $120\text{--}126^\circ$, and $[\alpha]_D^{25} + 49.7^\circ$, $+45.5^\circ$, and $+44.6^\circ$; aq. KI regenerates rapidly racemising optically active (II), $[\alpha]_D^{25} + 9.11^\circ$, from the first fraction, and inactive (II) from the other two. R. T.

Relative strengths of hydrocarbon derivatives of boric acid.—See this vol., 1173.

Dissociation constants of organic boric acids.—See this vol., 1173.

Preparation of mercuric phenyl nitrate. G. H. WOOLLETT and V. A. COULTER (J. Amer. Chem. Soc., 1934, 56, 1922).— $HgPh_2$ in $CHCl_3$ is converted into $HgPhNO_3$, m.p. 188° (decomp.), when shaken with aq. $Hg(NO_3)_2$. The residue after melting decomposes explosively at about 270° . Solubilities in H_2O and $EtOH$ have been determined at 5° and the b.p.

E. S. H.

Antimony and mercury compounds of quinoline and isoquinoline. R. N. SEN and G. K. MUKHERJEE (J. Indian Chem. Soc., 1934, 11, 541—543).—*Na quinolyl-7-stibinate* ($+H_2O$), m.p. $> 300^\circ$, is obtained by treating diazotised 7-aminoquinoline with $SbCl_3$ in HCl , treating the product with $NaOH$, acidifying, and neutralising the ppt. with $NaOH$. *Na quinolyl-3-stibinate* and *Na isoquinolyl-5-stibinate* are similarly obtained. 8-Hydroxy-5-acetoxymercuroquinoline, decomp. $> 280^\circ$, is prepared by addition of $Hg(OAc)_2$ in $AcOH$ to 8-hydroxyquinoline in $NaOH\cdot H_2O$. 5:6-Dibromo-8-hydroxy-7-acetoxymercuro-, decomp. $180\text{--}181^\circ$, and 5-bromo-8-hydroxy-7-acetoxymercuro-, decomp. $231\text{--}232^\circ$, -quinoline are obtained similarly. H. W.

Chloro-*p*-anisylphosphine [*p*-methoxyphosphoryl chloride]. G. KAMAI (J. Gen. Chem. Russ., 1934, 4, 192—193).— $OMe\cdot C_6H_4\cdot PCl_2$, b.p. $140\text{--}141^\circ/11$ mm., yields $OMe\cdot C_6H_4\cdot P(OH)_2$, m.p. $114\text{--}114.5^\circ$ (NH_4Ph salt, m.p. $97\text{--}98^\circ$; *p*-toluidine salt, m.p. $99\text{--}100^\circ$), on hydrolysis. R. T.

Reaction between organo-magnesium compounds and hydroxyazo-compounds. A. TAVRINSCH (Latvian Univ. Raksti, 1934, 2, 321—338).—Quant. yields of the same mol. compounds $MgRX\cdot Az\cdot nEt_2O$ (I) (Az =hydroxyazo-compound) are obtained from Az and either $MgRX$ or $MgR_2 + MgX_2$ in Et_2O . Thus are obtained the compounds of $Ph\cdot N_2\cdot C_6H_4\cdot OH$ with $CH_3Ph\cdot MgCl$, $MgEtBr$ (both $n=2$), $MgPhBr$, $MgMeI$, $MgPhI$; of $Ph\cdot N_2\cdot (C_6H_4\cdot OH)_2$ with $MgPhBr$, $MgEtBr$, and of $Ph\cdot N_2\cdot C_{10}H_6\cdot OH(\alpha)$ with $MgEtBr$ and $MgPhBr$. The compounds $2MgBr_2\cdot 3Ph\cdot N_2\cdot C_6H_4\cdot OH$; $MgBr_2\cdot Ph\cdot N_2\cdot C_6H_4\cdot OH$; $MgI_2\cdot 2Ph\cdot N_2\cdot C_6H_4\cdot OH$; $2MgBr_2\cdot 3Ph\cdot N_2\cdot C_{10}H_6\cdot OH(\alpha)$; $MgPh_2\cdot 2Ph\cdot N_2\cdot C_6H_4\cdot OH$; $MgPh_2\cdot Ph\cdot N_2\cdot C_{10}H_6\cdot OH(\alpha)$, are also prepared and react with MgR_2 and MgX_2 , respectively, to give the compounds of type (I), or with $BeCl_2$ or $ZnCl_2$ to give the compounds $MgPh_2\cdot 2Ph\cdot N_2\cdot C_6H_4\cdot OH\cdot BeCl_2$, and $[MgPh_2\cdot 2Ph\cdot N_2\cdot C_6H_4\cdot OH]_2ZnCl_2$. This stepwise formation confirms the view (Jolibois, A., 1912, i, 753; Schlenk, A., 1931, 718) that a mixture of $MgR_2 + MgX_2$ is equivalent to $MgRX$, the actual constitution of the Grignard reagent being discussed. J. W. B.

Magnesylypyrrole and potassium pyrrole. Behaviour and constitution. B. ODDO (Gazzetta, 1934, 64, 584—594).—A discussion. R. K. C.

Manufacture of triorgano- and organo-metallic compounds.—See B., 1934, 824.

Keratin. D. R. GODDARD and L. MICHAELIS (J. Biol. Chem., 1934, 106, 605—614).—Keratin is sol. in alkaline solutions of Na_2S , KCN , or thioglycolic acid (I) with formation of proteins sol. in acid or alkali, having a definite isoelectric point and digested by trypsin and pepsin, even when the $\cdot SH$ has been

reoxidised to $\cdot S \cdot S \cdot$. The action of (I) is simple reduction of $\cdot S \cdot S \cdot$ to $2 \cdot SH$. Side reactions occur with KCN and Na_2S , causing loss of S. C. G. A.

Crystalline acetyl derivatives of pepsin. R. M. HERRIOTT and J. H. NORTHROP (J. Gen. Physiol., 1934, 18, 35—67).—Cryst. pepsin (I) with CH_3CO in aq. solution at p_H 4.0—5.5 yields three cryst. Ac derivatives, (a) Ac_3 or Ac_4 attached to the NH_2 groups and having the same activity as (I); (b) Ac_{6-11} with 60% of the activity of (I); (c) Ac_{20-30} with 10% of the activity of (I). Hydrolysis of (b) by 2.5*N*-HCl yields (a). Solubilities, NH_2 -N and Ac content, isoelectric point, and sp. activity differ from those of (I), but p_H -activity curves, acid- and alkali-inactivation, and titration curves do not. C. G. A.

Tyrosine-binding power of ovalbumin.—See this vol., 1172.

Sintered glass absorber for determining carbon by wet combustion. P. A. WELLS, O. E. MAY, and C. E. SENSEMAN (Ind. Eng. Chem. [Anal.], 1934, 6, 369—370).—With the apparatus described it is unnecessary to use a large excess of alkali, and washing is simpler than with the glass bead absorber. E. S. H.

Sources of error in organic elementary analysis. X. Importance of exact determination of hydrogen and manipulation of hygroscopic substances. J. LINDNER (Ber., 1934, 67, [B], 1652—1658; cf. A., 1933, 80).—It is shown theoretically that for similar accuracy in ultimate analysis H must be determined to within 0.03% if the permissible error for C is regarded as 0.2%. In micro-analysis, hygroscopic substances can readily absorb very appreciable amounts of H_2O during the customary manipulation. Such substances, after having been brought to a wt.-stable condition, should be weighed in a Pt container and immediately transferred to the combustion tube in which desiccation is effected, the liberated H_2O (I) being absorbed in $CaCl_2$ and the wt. of (I) subtracted from that of the substance. Combustion is carried out immediately desiccation is complete. H. W.

Use of cerium dioxide in the determination of carbon and hydrogen by the Pregl method. G. W. WELLWOOD (Mikrochem., 1934, 15, 237—241).—15—20 mm. of CeO_2 -pumice is inserted following the $PbCrO_4 + CuO$, and Pt gauze is substituted for Ag wire before the PbO_2 . J. S. A.

Direct simultaneous micro-determination of carbon, hydrogen, and oxygen in organic substances. I. Analysis of pure compounds containing carbon, hydrogen, and oxygen, with and without halogens. W. R. KIRNER (Ind. Eng. Chem. [Anal.], 1934, 6, 358—363).—The substance is burnt in O_2 by a modified Pregl micro-method in a closed system, the vol. of O_2 consumed being very accurately measured. The mean error for O in nine compounds (three containing halogen) is 0.4%. Extreme accuracy of C and H determinations and precision in gasometry are essential. Previous methods embody large errors and give approx. accurate results only by cancellation of errors. R. S. C.

ter Meulen method for direct determination of oxygen in organic compounds containing nitrogen. W. W. RUSSELL and N. E. MARKS (Ind. Eng. Chem. [Anal.], 1934, 6, 381—382).—Absorption of the H_2O by NaOH pellets avoids errors due to absorption of NH_3 by $CaCl_2$. R. S. C.

Semimicro-determination of halogens in organic compounds. E. P. CLARK (J. Assoc. Off. Agric. Chem., 1934, 17, 483—487).—Cl and Br are determined by the Carius method, I, except aliphatic, by the Leipert volumetric method, using 26 mg. of material. Aliphatic I is determined by Viebock and Brecher's method (A., 1931, 246). Necessary modifications of apparatus and procedure are described. E. C. S.

Determination of organic halogens. F. E. BEAMISH (Ind. Eng. Chem. [Anal.], 1934, 6, 352—353).—All types of compounds give accurate results by the Na_2O_2 -lactose explosion method. Certain precautions are indicated. R. S. C.

Nickel micro-bomb for micro-determination of organic arsenic. F. E. BEAMISH and H. L. COLLINS (Ind. Eng. Chem. [Anal.], 1934, 6, 379—380).—The substance, containing 1.5—3 mg. of As, is exploded with Na_2O_2 -sugar in a Ni cup and the Na_3AsO_4 formed determined by titration. R. S. C.

Determination of acetyl in organic compounds. M. PHILLIPS (Ind. Eng. Chem. [Anal.], 1934, 6, 321—322).—The substance is distilled with $p\text{-}C_6H_4Me \cdot SO_3H$ in EtOH vapour, and the EtOAc which has distilled is determined. An all-glass apparatus is described. O- and N-Ac can be determined. R. S. C.

Micro-determination of acetyl. A. J. BAILEY and R. J. ROBINSON (Mikrochem., 1934, 15, 233—236).—5—10 mg. of material are refluxed for 12—35 hr. with 5 ml. of 0.04*N*-NaOH, and excess of alkali is titrated back with 0.01*N*-HCl (phenolphthalein). A blank correction for aq. hydrolysis must be applied. J. S. A.

Determination of acetone, butyl and ethyl alcohols in mixtures of the three. C. E. PRELAT (Anal. Asoc. Quím. Argentina, 1934, 22, 67—72).— $COMe_2$ is determined colorimetrically with $o\text{-}NO_2 \cdot C_6H_4 \cdot CHO$ in alkaline solution, and removed afterwards with 2:4- $(NO_2)_2C_6H_3 \cdot NH \cdot NH_2$ if > 10%. Total alcohols are determined by acetylating in C_5H_5N and titrating the excess of AcOH with 0.5*N*-alkali. The alcohols are oxidised with CrO_3 to $PrCO_2H$ and AcOH, and the partition coeff. of the mixed acids between H_2O and Pr^2O is determined, the BuOH and EtOH contents being deduced from a graph. R. N. C.

Application of drop reactions to the identification of organic compounds. IV. Detection of nitroso-compounds. F. FEIGL, V. ANGER, and O. FREHDE. **V. Detection of hydrazine derivatives.** F. FEIGL, V. ANGER, and R. ZAPPERT (Mikrochem., 1934, 15, 181—189, 190—194; cf. this vol., 790).—IV. The Liebermann reaction is applied by melting the substance with a crystal of PhOH, dissolving in a drop of H_2SO_4 (red colour), and making alkaline with 4*N*-NaOH (blue). Alternatively, NO-compounds (I) give with a drop of 1% aq.

$\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$ or $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ (II) intense green to violet colorations (cf. Baudisch, A., 1922, i, 993). NO_2 -compounds may be detected by mixing the EtOH solution with (II) + 1 drop of 4*N*-NaOH or 5% Na_2SO_4 , then reducing electrolytically to (I) between a Ni wire cathode and a Pb wire anode. Hydrazines give deep red or violet colorations with (II).

V. Hydrazine derivatives condense with the yellow dyes produced by coupling $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ with R-acid, crocein acid, Schaffer's acid, or nigrotic acid, to give deep red or violet products. Reaction may be performed on a drop of the AcOH solution in presence of NaOAc. Aromatic and unsaturated aldehydes in presence of 0.5*N*-AcOH + 2% polysulphide-free $(\text{NH}_4)_2\text{S}$ give blue or green colorations with (II).

J. S. A.

Identification of amines as 2:4-dinitrobenzoates. C. A. BUEHLER and J. D. CALFEE (Ind. Eng. Chem. [Anal.], 1934, 6, 351—352).—The prep. of 2:4- $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{CO}_2\text{H}$, m.p. 179°, red or colourless, from 2:4- $\text{C}_6\text{H}_3\text{Me}(\text{NO}_2)_2$ is modified (40% yield). 2:4-Dinitrobenzoates of the following are described (m.p. are corr.): NH_2Ph , m.p. 160.4—162°; *o*-, m.p. 193.2—194.9°, *m*-, m.p. 144.5—146.1°, and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$, m.p. 160.8—162.2°; *m*-4-xylydine, m.p. 175.1—175.5°; *o*-, m.p. 137.9—138.7°, *m*-, m.p. 142.0—142.8°, and *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}_2$, m.p. 164.5—165.1°; *p*- $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}_2$, m.p. 182.6—183.2°; *m*-, m.p. 133.0—133.4°, and *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, m.p. 117.3—118.2°; *p*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, m.p. 204.3—204.5°; *o*-, m.p. 150.5—151.5°, *m*-, m.p. 188.1—189.6°, and *p*- $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 168.3—168.9°; NHPHMe , m.p. 102.6—103.8°; NPhMe_2 , m.p. 102.4—104°; $\text{NHPH}\cdot\text{CH}_2\text{Ph}$, m.p. 121.4—122.2°; NHPHAc , m.p. 87.9—90.9°; NHPH , unstable; *o*-, m.p. 197.5—197.9°, *m*-, m.p. 197.3—197.5°, and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$, m.p. 181.4—182.6° (decomp.); α -, m.p. 199.3—199.7°, and β - $\text{C}_{10}\text{H}_7\cdot\text{NH}_2$, m.p. 181.4—181.8°; benzidine, m.p. 231.8—233° (decomp.); $\text{C}_6\text{H}_5\text{N}$, m.p. 140.9—141.7°; quinoline, m.p. 142.0—142.8°; NH_3 , m.p. 218.5—220.5°; $\text{NH}_2\cdot\text{CH}_2\text{Ph}$, m.p. 199.1—200.1°; NHEt_2 , m.p. 147.5—149.1°; NEt_3 , m.p. 81—82.9°; carbamide, m.p. 129.1—129.9°; NH_2Ac , m.p. 111.1—112.1°; NH_2Bz , m.p. 118.1—119.1°. *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, $\text{NPh}(\text{CH}_2\text{Ph})_2$, and NPh_3 do not form such salts.

R. S. C.

Application of drop reactions to the detection of organic compounds. VI. Detection of aliphatic and aromatic amines with fluorescein chloride. F. FEIGL, V. ANGER, and R. ZAPPERT. VII. Detection of reactive CH_2 and NH_2 groups. F. FEIGL and O. FREHDEN (Mikrochem., 1934, 16, 67—78, 79—86).—VI. On fusion with dichlorofluoran in presence of ZnCl_2 , primary aliphatic amines give rose-coloured compounds with a yellowish-green fluorescence in EtOH and HCl, *sec*-.aliphatic amines a red colour with orange-red fluorescence, and aromatic amines deep reddish-violet colours, but with no fluorescence. Amides and nitriles also give coloured products which show fluorescence, whilst pyrrole derivatives give yellowish-brown products which show blue fluorescence in ultra-violet light. Primary aromatic amines all give characteristic colours with glutacetaldehyde. Owing to the instability of the latter compound, it is better to use 4-pyridylpyridinium di-

chloride, which on addition of NaOH passes into the Na salt of the enolic form of glutacetaldehyde and 4-aminopyridine. Details of the colours and fluorescence effects obtained by these tests with the commoner amines etc. are tabulated.

VII. A little of the sample is treated with 2 drops of Na 1:2-naphthoquinonesulphonate solution (saturated in 50% EtOH) and 2 drops of 0.5*N*-NaOH are added. In presence of active CH_2 or NH_2 groups, a deep coloration is obtained, and on acidifying with AcOH characteristic ppts. This reaction also detects cyclic *tert*. ring bases and oxonium compounds.

J. W. S.

Biochemistry and physiology of cholesterol.

A. Technique of the micro-analysis of cholesterol. I. Reaction kinetics of the Liebermann-Burchardt reaction and a new basis for the correct reading of such reactions in the colorimetry of cholesterol. K. ŠILINK (Mikrochem., 1934, 16, 45—66).—It is concluded that even with the most careful manipulation the intensities of colouring obtained by this method are not identical and the max. are not attained at the same time; the errors are normally 4—8%. Two reactions occur: a colour development, which is accelerated by excess of H_2SO_4 and retarded by traces of H_2O or EtOH, and the colour disappearance which always proceeds normally. Both reactions are accelerated by heating, the former > the latter. A method for calculating the cholesterol content from the intensity-time curve is given.

J. W. S.

Micro-method for determination of free and combined cholesterol. R. SCHOENHEIMER and W. M. SPERRY (J. Biol. Chem., 1934, 106, 745—760).—Cholesterol (I), in a COMe_2 -EtOH extract of 0.2 c.c. of serum or blood, is pptd., either directly or after hydrolysis, as the digitonide (II), isolated by centrifuging, and dissolved in AcOH. The colour produced on addition of Ac_2O and H_2SO_4 is estimated, using 610—620 μ light, for which the weak colour produced by digitonin shows no absorption. In the absence of other sterols the method is comparable in accuracy with the Windaus macro-gravimetric method, and 0.02—0.15 mg. of (I) may be determined. Yoshimatsu's method (Tohoku J. Exp. Med., 1931, 17, 147) involves an error due to the solubility of (II) in 95% EtOH and the Bernoulli colour reaction applied to (II) by Obermer and Milton (A., 1933, 733) gives inconsistent results.

F. S. H. H.

Colorimetric determination of triarylcarybols. S. T. BOWDEN (Analyst, 1934, 59, 618—619; cf. A., 1933, 732).—The material is converted into the chloromethane, which is treated with ZnCl_2 in Et_2O . The highly coloured additive compound is determined colorimetrically.

E. C. S.

Determination of benzene and *m*-dinitrobenzene.—See this vol., 1135, 1252, 1253.

Micro-copper-pyridine reaction for saccharin. II. C. VAN ZIJP (Pharm. Weekblad, 1934, 71, 1146—1151).—Further optical data supporting the contention that the various cryst. forms of the $\text{Cu}\text{-C}_5\text{H}_5$ -saccharin complex are different modifications of the same rhombic crystal (cf. this vol., 1017).

S. C.

[Micro-copper-pyridine reaction for saccharin.] J. J. L. ZWIKKER (Pharm. Weekblad, 1934, 71, 1151—1152).—A reply to the preceding. S. C.

Volumetric determination of inositol.—See this vol., 1246.

Use of iodine-potassium iodide and iodine-sodium iodide in microchemistry. C. VAN ZIJF (Pharm. Weekblad, 1934, 71, 1075—1087).—Characteristic dichroic, microcryst. ppts. are obtained with veronal, dial, propional, rutilal, and luminal with 10% KI-I solution (I), but not with 10% NaI-I solution (II). Trional, tetronal, and sulphonal give similar ppts. with (II) and not with (I), whilst theobromine gives ppts. with (I) and (II), which are not identical in form. CsCl gives a brown ppt. with (I) or (II) and should not be used therefore as a test for caffeine (III), since the latter takes no part in the reaction. RbCl gives no ppt. with (I) or (II) either in presence or absence of (III). The optical and crystallographic properties of the various ppts. are described. S. C.

Photo-electric determination of furfuraldehyde and methyl alcohol. H. MOHLER and H. BENZ (Mitt. Lebensm. Hyg., 1934, 25, 161—165).—Two Se cells connected in opposition are illuminated with the same source after traversing vessels containing H₂O and the reaction mixture (I), respectively, the result being read from the resultant current-furfuraldehyde (II) or MeOH (III) calibration curves; insertion of a filter complementary in colour to that of (I) assists the sensitiveness. Up to 5 mg.-% of (II) in 40 vol.-% EtOH is determined by the NH₂Ph.HCl reaction, and up to 0.6 vol.-% of (III) in 4 vol.-% EtOH by oxidation with H₂SO₄-KMnO₄ and addition of fuchsin-H₂SO₃. J. G.

Micro-determination of hydroxymethylfurfuraldehyde by oxidation with chromic acid; hydroxymethylfurfuraldehyde in sweet wines. T. VON FELLEBERG (Mitt. Lebensm. Hyg., 1934, 25, 249—257).—Fiehe's method (B. 1932, 43, 364) is shortened by washing the phloroglucide (I) with dil. HCl, shaking it with cold K₂Cr₂O₇ and H₂SO₄, and back-titration with Na₂S₂O₃, 0.15 c.c. being added to the amount of 0.1N-K₂Cr₂O₇ (II) consumed to correct for the solubility of (I) in H₂SO₄; each c.c. of (II) = 0.394 mg. of hydroxymethylfurfuraldehyde (III), 3.045 mg. of sucrose, 3.198 mg. of invert sugar, and 1.602 mg. of fructose. Sweet wines to which heated juice has been added contain large quantities of (III),

and since added SO₂ is rapidly fixed by (III) the SO₂ demand and the bound SO₂ are approx. measures, respectively, of the amounts of free and bound (III) present. J. G.

Microchemical identification of caffeine and theobromine. A. KOFER (Mikrochem., 1934, 15, 319—330).—H₂O-free caffeine (I), as sublimate in micro-sublimation, forms rod-like hexagons, m.p. 238°. Hydrated (I), from aq. solution, forms silky monoclinic needles, losing H₂O about 70°. Both forms undergo a characteristic morphological change at 200°, forming a uniform film of polygonal crystals. Theobromine forms highly twinned monoclinic prisms, m.p. 351°. Vals. of n_a etc. are given. J. S. A.

Determination of uric acid.—See this vol., 1278.

Determination of hordenine. Y. RAOUL (Compt. rend., 1934, 199, 425—427).—The method of Stas is modified, the alkaloid being finally purified by sublimation. R. S. C.

Crystal precipitation by salting out. L. ROSENTHALER (Mikrochem., 1934, 16, 37—44).—The character of the ppts. formed when alkaloid salts are salted out by alkali chlorides, sulphates, and nitrates is described. J. W. S.

Polarographic micro-determination of cystine and cysteine in the hydrolysates of proteins. R. BRDIČKA (Mikrochem., 1934, 15, 167—180).—The polarographic determination of cystine in the hydrolysis products of proteins is described, using the method previously described (A., 1933, 964). J. S. A.

Determination of methionine in proteins. H. M. BAERNSTEIN (J. Biol. Chem., 1934, 106, 451—456).—KOAc and Br in glacial AcOH is substituted for AgNO₃-EtOH in the determination of MeI (see A., 1932, 867) resulting from the action of HI on proteins. If the HI contains H₃PO₄, HgCl₂ must be introduced into the absorption train to remove PH₃. HI digests of methionine contain, not free homocysteine, but the thiolactone of homocysteine hydriodide (isolation described). A. E. O.

Determination of the basic amino-acids in small quantities of proteins by the silver precipitation method. R. J. BLOCK (J. Biol. Chem., 1934, 106, 457—462).—The method (cf. A., 1931, 1317) is further modified to permit accurate determinations of the bases in 2—5 g. of protein. Histidine is weighed as the diflavinate, arginine as the flavianate, and lysine as the picrate. A. E. O.

Biochemistry.

Carbon monoxide and respiration. Action on respiration of normal and blocked embryonic cells (*Orthoptera*). J. H. BODINE and E. J. BOELL (J. Cell. Comp. Physiol., 1934, 4, 475—482).—The O₂ consumption of grasshopper embryos in an atm. of varying CO : O₂ ratio is examined. A. G. P.

Determination of small amounts of carbon monoxide in blood. H. BURESCH (Arch. Gewerbe-

path. Gewerbehyg., 1934, 5, 210—228).—Blood is heated with 65% H₃PO₄ at 100—120° in vac. The liberated gas is collected over alkali and CO determined by vol. changes after combustion. A. G. P.

Absorption spectrum of blood after treatment with carbon monoxide and other gases. N. VITA and E. SALMOIRAGHI (Atti Congr. naz. Chim., 1933, 4, 869—871; Chem. Zentr., 1934, i, 1998).—Changes in

spectra due to the action of CO are recorded. Other gases (CO_2 , N_2 , O_2) produce changes which are quite distinct from the above.

A. G. P.

Effect of acidity on the carbon monoxide-combining power of hæmoglobin in the blood of marine fishes. R. W. ROOT and A. A. GREEN (*J. Biol. Chem.*, 1934, **106**, 545—552).—Fish-hæmoglobin (I) can be saturated with CO irrespective of p_{H} , whereas at acid reactions O_2 apparently combines with only a part of (I). In acid solution the dissociation curves at comparable p_{H} val. differ in shape, explained by inactivation of (I) towards O_2 , but not to CO.

C. G. A.

Ultramicro-determination of oxygen content of blood. J. S. DONAL, jun. (*J. Biol. Chem.*, 1934, **106**, 783—797).—The O_2 content of 10 cu. mm. blood samples is determined by introduction of the sample, contained in a capillary, into an evacuated chamber, whence the gases evolved are passed over a hot W filament. The positive ion current produced by the O_2 is amplified and passed through a galvanometer the initial deflexions of which \propto the O_2 content of the samples. Determinations are unaffected by N_2 , CO_2 , and H_2O . The method gives vals. < those obtained by the Van Slyke method (A., 1924, ii, 872).

H. D.

Influence of fatty oils and metal-oil sols on cell respiration. I. W. TRAXI, K. BRAUN, and K. LOCKER (*Biochem. Z.*, 1934, **273**, 109—121).—Respiration of hen's erythrocytes is increased by olive oil (by 30%) and by liver oil (300—400%), but is unaffected by coconut and rape-seed oils and is inhibited by linseed oil. Colloidal metal dissolved in an active oil greatly increases its effect, but is without action with oils which themselves are inactive. The extent of respiratory activation does not run parallel with the I val. of the oil, but is due to the presence of a thermolabile constituent of the oil which does absorb I.

P. W. C.

Glutathione fraction and blood-respiration. Respiration in anoxæmia. H. W. BANSI and M. ROHRICH (*Arch. exp. Path. Pharm.*, 1934, **176**, 609—624).—Under normal respiratory conditions, a fairly const. part ["reversible glutathione" (I), approx. 0.008% of the blood] of the blood-glutathione (II) gives H_2 on reduction of the partial pressure of O_2 to 25—50 mm. Hg. The stable part of (II) is, after hæmolysis, relatively slowly oxidised or decomposed. With circulatory impairment (e.g., anoxæmia), (I) is increased. A small O_2 reserve of the blood produces deoxygenation of oxyhæmoglobin, oxidised (II) being formed in the lungs, and this acts as a H acceptor in the peripheral vessels. The presence of (I) in various diseases and its part in respiration are discussed.

F. O. H.

Coupling of respiration and synthesis of phosphate esters in hæmolysed blood. J. RUNNSTROM and L. MICHAELIS (*Science*, 1934, **80**, 167).

L. S. T.

Action of erythrocytes on optically active mono- and di-phosphoglyceric acids. W. SCHUCHARDT and A. VERCELLONE (*Biochem. Z.*, 1934, **272**, 437—440).—At 6.5—7.5 diphosphoglyceric

acid is not or only very slightly (> 6%) hydrolysed (no AcCO_2H found) by hæmolysed erythrocytes (I) (ox, horse, pig, sheep, rabbit, pigeon, hen), but phosphoglyceric acid is readily attacked (up to 90%), AcCO_2H being produced in the case of pig and pigeon (I).

W. McC.

Rate of escape of hæmoglobin from the hæmolysed red corpuscle. H. FRICKE (*J. Gen. Physiol.*, 1934, **18**, 103—107).—The calc. time required for a decrease of hæmoglobin content to 10% of its original val., assuming complete permeability of the cell, is 0.16 sec. Ponder's experimental val. of 4 sec. corresponds with a permeability (μ_{H}) of 5×10^{-5} cm. per sec.

C. G. A.

Catalytic analogies between peroxidases, blood-pigments, and some salts. A. CASOLARI (*Biochim. Terap. sperim.*, 1933, **20**, 572—576; *Chem. Zentr.*, 1934, i, 1845).— NaCl , LiCl , CaCl_2 , and other salts react with the *o*-toluidine, benzidine, and $p\text{-NH}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ reagents and with tincture of guaiacum. To eliminate the action of these salts in testing for blood (I), the pigments of (I) should first be isolated with NaWO_4 in presence of protein, or with $\text{Al}(\text{OH})_3$. The pigments may also be extracted from the evaporated solution with EtOH or $\text{NH}_3\text{-COMe}$.

H. J. E.

Role of copper in blood formation. J. BENGE (*Z. klin. Med.*, 1933, **126**, 143—151; *Chem. Zentr.*, 1934, i, 1514).—The Cu and Fe contents of the liver, spleen, kidneys, and bone marrow of an anæmic body and of human and animal embryos have been determined. The Cu content is highest in the embryo; it falls in the liver after gastric extirpation.

L. S. T.

Availability of copper in various compounds as a supplement to iron in hæmoglobin formation. M. O. SCHULTZE, C. A. ELVEHJEM, and E. B. HART (*J. Biol. Chem.*, 1934, **106**, 735—744).—Severely anæmic rats show hæmoglobin regeneration when fed with Fe and a Cu supplement in the forms of Cu caseinate, glycine- and alanine-amide biuret, and hæmocyanin from *Limulus polyphemus*. The necessary level of intake is > for CuSO_4 . Hæmatoporphyrin is ineffective under the same conditions, being excreted as such in the fæces.

H. D.

Copper content of blood. S. L. TOMPSETT (*Biochem. J.*, 1934, **28**, 1544—1549).—As determined by the diethylthiocarbamate method (MacFarlane, A., 1932, 1182), normal human blood contains 0.180—0.229 mg. of Cu per 100 ml. approx. equally distributed between plasma and corpuscles. Approx. equal concns. of Cu exist in the bloods of the sheep, pig, ox, horse, and guinea-pig, rabbit's blood giving slightly lower vals. Normal human cerebrospinal fluid contains 0.032—0.067 mg. per 100 ml.

W. O. A.

Creatine and creatinine metabolism.

Creatinine and creatine of blood. M. K. and H. LIEB (*Z. physiol. Chem.*, 1934, **226**, 130—; cf. this vol., 543).—Pincussen's method for creatine (I) and creatinine (II) determination is untrustworthy owing to the decomp. of the $\text{CCl}_3\text{-CO}_2\text{H}$. The "stances determined by the Jaffe reaction behave (I) and (II). There is no reason to doubt the e.

ence of preformed (II) or to regard the (I) found as only a fraction of the true val. Hahn's method (Z. klin. Med., 1933, 125, 458) gives the same vals. as autoclave treatment.

J. H. B.

Natural occurrence of 6-amino-2-hydroxypurine? F. A. SCHÜTZ (Biochem. Z., 1934, 273, 52—55).—6-Amino-2-hydroxypurine could not be detected in pig's blood. This substance is probably not identical with isoguanine.

P. W. C.

Quantitative drop analysis. III. Kjeldahl nitrogen determination and non-protein-nitrogen of blood. P. L. KIRK. **IV. Determination of urea and ammonia.** G. E. GIBBS and P. L. KIRK (Mikrochem., 1934, 16, 13—24, 25—36).—III. A modification of the Kjeldahl method is applicable to the drop-scale with an accuracy of 3%, the amounts of N dealt with being $3.88\text{--}15.52 \times 10^{-6}$ g.

IV. In a micro-method for determination of urea the latter is treated first with urease for 1 hr. and then with K_2CO_3 . The NH_3 produced is either allowed to diffuse into a vessel containing a drop of standard HCl, the experiment being carried out inside a cell with a ground lid, or is distilled in the micro-Kjeldahl apparatus. The determination of NH_3 is similar, but without the urease treatment. The method has been applied to amounts of $1.55\text{--}8.27 \times 10^{-6}$ g. of NH_3 and urea in pure solution, blood, or urine, with an accuracy of 3%.

J. W. S.

Nephelometric determination of protein in serum. A. SCHMITZ (Biochem. Z., 1934, 273, 132—134).—The change of the $(\text{NH}_4)_2\text{SO}_4$ pptn. curve as a result of treatment of plasma or serum for a short time with acid (cf. Fischer, this vol., 795) could not be confirmed.

P. W. C.

Surface tension of horse- and guinea-pig-serum against vaseline and its alteration on heating the serum to the inactivation temperature. F. SEELICH (Biochem. Z., 1934, 273, 135—146).—With normal serum (I), the tension (II) becomes const. after 1.5—3 hr. The velocity of the fall of (II) and the final val. of (II) are dependent on the concn. and previous history of (I). Shortly after establishment of the surface, heat-inactivated (I) causes a quicker fall of (II) than does normal active (I) of the same concn., but the final vals. attained by the (II)-time curves are lower for active than for inactive (I).

P. W. C.

Sheep blood. G. D. SHEARER and J. STEWART (Rep. Cambridge Inst. Animal Path., 1931, 86—120).—Blood-Ca, -P, -Na, -K, and -sugar vals. were followed during pregnancy and after parturition, and on injection of guanidine nitrate, creatinine, K oxalate, Na citrate, NaCl, caseinogen, ovalbumin, *Clostridium chauvei* filtrate, parathyroid extract, anterior pituitary lobe extract, thyroid extract, I, ovarian extract, and placental extract.

CH. ABS.

Determination of the distribution of serum-calcium. S. HERMANN and M. ZENTNER (Arch. exp. Path. Pharm., 1934, 176, 583—590).—Ingestion of Na_2SO_4 or NH_4Cl by rabbits (I) rapidly increases the dissociated Ca and hence decreases the Ca quotient (A., 1932, 81). That the marked variations in the total serum-Ca and body-temp. of (I) are possibly related is

indicated by the constancy of both levels in man. The methods for determining Ca distribution in serum are discussed and that of pptn. by phosphomolybdic acid is upheld.

F. O. H.

Non-diffusible serum-calcium at various calcium, phosphate, and hydrogen-ion concentrations. R. G. SMITH (Biochem. J., 1934, 28, 1615—1623).—When non-diffusible serum-Ca (I) is increased by the addition of Ca to serum, the binding of added Ca by protein and the formation of $\text{Ca}_3(\text{PO}_4)_2$ (II) occur simultaneously. In presence of excess of phosphate the increase of (I) is due to formation of (II). With change of from 8 to 7 there is slight increase of diffusibility of normal serum-Ca; with high Ca concn. this increase is much greater, since the large (II) constituent of (I) breaks down.

C. G. A.

Determination of magnesium in blood-serum. I. J. CUNNINGHAM and S. W. JOSLAND (New Zealand J. Sci. Tech., 1934, 16, 28—29).—The Kramer-Tisdall method yielded unduly low results. Modified procedure is described whereby results obtained agree with those of gravimetric methods.

A. G. P.

Zinc hydroxide powder for preparation of protein-free filtrates of blood. T. V. LETONOFF (J. Biol. Chem., 1934, 106, 693—699; cf. this vol., 793).— $\text{Zn}(\text{OH})_2$ is pptd. from aq. $\text{Zn}(\text{OAc})_2$ by NaOH, the dry powder is added to laked blood, and the pptd. proteins are filtered off after 1 min. The reducing matter of the filtrate is < those from the Somogyi (A., 1930, 801) (I) and Folin-Wu (A., 1919, ii, 308) (II) pptns., but is entirely fermentable. The presence of Zn did not affect the Folin-Wu determination of sugar (A., 1920, ii, 337). Determinations of urea, creatine, and creatinine gave results similar to those obtained by (I) and (II). Total N is < that in (II) filtrates, but > that in (I) filtrates.

H. D.

Constancy of the cholesterol level in rat's blood. R. KOOY and W. ROSENTHAL (Acta Brevia Neerl. Physiol., 1933, 3, 135—138; Chem. Zentr., 1934, i, 1209—1210).—Adrenalectomised rats show a normal blood-cholesterol (I) level. Feeding for a short time with cholesterol did not increase (I). The (I) was normal in rats with beri-beri.

H. J. E.

Cholesterol content of human plasma. IV. Non-sterol unsaponifiable matter of human plasma. V. Nature of the sterols in blood-plasma. J. A. GARDNER and H. GAINSBOROUGH (Biochem. J., 1934, 28, 1631—1634, 1635—1639; cf. A., 1928, 1045).—IV. The non-sterol unsaponifiable matter obtained in the analysis of blood-plasma is an artefact produced by impurities in the reagents and grease in the apparatus used.

V. Schonheimer's finding of β -cholestanol in gallstone cholesterol (A., 1930, 1616) is confirmed, although his analytical method is criticised. Cholesterol dibromide is unstable in EtOH solution, yielding cholesterol on long keeping even at room temp. and more rapidly on boiling.

H. N. R.

Vagus and regulation of the blood-sugar. E. GEIGER, I. BINDER, and A. RUSZTEK (Arch. exp. Path. Pharm., 1934, 176, 355—366).—Section of the neck vagi or subsequent faradic stimulation of the

peripheral end of either nerve produces a diminution of the fasting blood-sugar in dogs (but not rabbits). The sugar-tolerance is increased with left, but decreased with right, vagotomy; with rabbits the final result is a decrease with either vagus, a transient increase following section of the right vagus. The influence of the vagi in controlling the blood-sugar is discussed.

F. O. H.

Central blood-sugar regulation. V. Effect of insulin on pyramidone hyperglycæmia. VI. Effect of chloral hydrate on blood-sugar. VII. Influence of various pharmaceuticals on alimentary hyperglycæmia. F. HOGLER and F. ZELL (*Z. ges. exp. Med.*, 1933, **86**, 158—172, 173—184, 185—120; *Chem. Zentr.*, 1934, i, 1067).—V. Pyramidone hyperglycæmia (I) is insensitive to insulin (II). Pyramidone hypothermia is still more resistant to (II). This resistance is overcome by ergotamine blockade and is reduced by veronal.

VI. Chloral hydrate in moderate doses has no influence on the blood-sugar or (I), and does not hinder hypoglycæmic convulsions after small doses of (II). It hinders Mg hyperglycæmia.

VII. Ergotamine, atropine, veronal, luminal, chloral hydrate, Ca, parathormone, and pyramidone produced no effect, but certain of their combinations influenced the occurrence of alimentary glycæmia. H. J. E.

Central blood-sugar regulation. VIII. Influence of various drugs on alimentary hyperglycæmia after administration of galactose. IX. Behaviour of blood-sugar during fasting after elimination of different brain sections. X. Influence of eliminating various sections of the central nervous system on nutritional hyperglycæmia after administration of specific sugars. XI. Influence of removal of different parts of the central nervous system on pyramidone- and magnesium-hyperglycæmia. XII. Blood pressure and sugar metabolism. F. HOGLER and F. ZELL (*Z. ges. exp. Med.*, 1933, **92**, 181—192, 193—210, 211—221, 222—233, 234—240; *Chem. Zentr.*, 1934, i, 1832—1833).—VIII. Administration of galactose (I) produces varied effects even in the same animal. Ergotamine (II), atropine, veronal (III), luminal, and chloral hydrate (IV) have no definite effect on (I) hyperglycæmia (V). Simultaneous treatment with (II) and (III) prevents (V). Simultaneous administration of (II) and (IV) restricts (V) more strongly than glucose hyperglycæmia. Administration of (I) 30 min. after injection of insulin causes a rapid increase in blood-sugar. A. G. P.

Cuprocollargol, electrocollargol, and blood-glycolysis. B. ZEMPLEN (*Z. ges. exp. Med.*, 1933, **88**, 92—95; *Chem. Zentr.*, 1933, ii, 3715).—Cuprocollargol hinders and electrocollargol accelerates blood-coagulation. In each case coagulation and glycolysis (I) run parallel, the colloidal metal solutions exerting their primary effect on (I). H. J. E.

Fibrinogen formation and blood-coagulation. T. WEDEKIND (*Klin. Woch.*, 1933, **12**, 103—105; *Chem. Zentr.*, 1933, ii, 3715).—Fibrinogen (I) can be formed in the blood. Addition of certain colloidal substances (e.g., Congo-red) to blood increases the

amount of (I). These substances can therefore accelerate blood-coagulation. H. J. E.

Alleged new formation of fibrinogen by Congo-red. B. BELONOSCHKIN and E. WOHLISCH (*Klin. Woch.*, 1933, **12**, 1371—1372; *Chem. Zentr.*, 1934, i, 1515).—Results obtained with citrate-plasma of swine, cattle, and horses showed, contrary to the data of Wedekind (see above), no increase in fibrinogen resulting from the addition of Congo-red. L. S. T.

Glutathione, heavy metals, and blood-clotting. J. KÜHNAU and V. MORGENSTERN (*Z. physiol. Chem.*, 1934, **227**, 145—168; cf. this vol., 1123).—Glutathione (I) acts through the agency of heavy metals, probably as metal complex, on thrombin. The amounts of Cu and Fe present in plasma probably suffice. The inhibition of clotting by reduced (I) at acid reaction represents a Cu anticatalysis, the clotting activation in alkaline medium a Fe catalysis. Thrombin is evidently a proteolytic enzyme related to cathepsin. J. H. B.

Synthesis of immunising antigens by coupling chemically definite haptens to non-antigenic protein derivatives. R. DOERR and P. GIRARD (*Z. Immunität.*, 1933, **81**, 132—136; *Chem. Zentr.*, 1934, i, 1516).—The antigen (I) formed by coupling ovalbumin racemised with *N*-NaOH with diazotised atoxyl has been used for the immunisation of rabbits, but no pptd. antibodies were obtained. (I) reacted, however, with an antiserum prepared from the product obtained by coupling native ovalbumin and diazotised atoxyl. L. S. T.

Immunisation with adsorbed haptens, especially cerebral haptens, without species-non-specific protein. F. PLAUT and H. RUDY (*Z. Immunität.*, 1933, **81**, 87—100; *Chem. Zentr.*, 1934, i, 1515—1516).—Immunisation of rabbits with the adsorbate on kaolin or, preferably, on β -Al(OH)₃ of EtOH cerebral extract of cattle, in certain cases but not invariably, gives rise to the antibody of the cerebral hapten, which can be obtained by adsorption on sol. starch, but not on C. Antisera against adsorbed cholesterol or the adsorbate of spirochætes of syphilis could not be obtained. L. S. T.

Adsorption experiments with alcoholic extracts of organs. T. FISCHER (*Z. Immunität.*, 1933, **79**, 39—52; *Chem. Zentr.*, 1933, ii, 3868).—Kaolin (I), Al(OH)₃, BaSO₄, and Ca₃(PO₄)₂ adsorbed the reactive material from cholesterolised extract of ox heart and EtOH horse-kidney extract, without removing the constituent reacting with lipid anti-sera. BaSO₄ and Ca₃(PO₄)₂ were specially active. The heterogeneous antigen was adsorbed by (I) if sufficient of (I) was used. Adsorption occurs most readily from aq. extract, the adsorbate being removed by EtOH.

Chemical nature of the blood group characteristic. E. JORPES and G. NORLIN (*Z. Immunität.*, 1933, **81**, 152—162; *Chem. Zentr.*, 1934, i, 1832).—One sp. blood-group agglutinin in urine is conc. by pptn with tannin. Evidence of the protein-like character of the receptor is advanced. The constituent of a receptor which inhibits hæmolysis in sheep's blood occurs in the polysaccharide fraction. A. "

Respiratory substance in irradiated protein. P. WELS and R. HESSE (Naturwiss., 1934, 22, 648).—A solution of egg-white irradiated in N_2 with ultra-violet light contains a substance which is readily oxidised and again reduced. Such a solution treated with a stream of O_2 (preferably in presence of traces of $CuSO_4$) loses the power of reducing methylene-blue, but regains it after treatment for several hr. with washed frog muscle or dried muscle powder. The muscle apparently reduces the oxidised active substance. The muscle prep. itself reduces methylene-blue only slowly, but the addition of the oxidised active substance markedly accelerates reduction. Non-irradiated solutions are inactive. W. O. K.

Oxidation-reduction potential. III. The potential and the Becquerel effect in photochemical processes. Irradiation of extracts of visual purple. L. PINCUSSEN, T. SUZUKI, and E. O. SEITZ (Biochem. Z., 1934, 272, 357—363; cf. A., 1932, 880).—The Becquerel effect (I) is reversible and hence can be distinguished from the oxidation-reduction effect (II) which is not. The solvents used for extracting the visual purple (III) (Na cholate or saponin solutions) exhibit (I), but not (II), which is shown by oxidisable material such as dihydroxyphenylalanine and (III). W. McC.

Reducing substances and thiol compounds in the optic lens. H. VON EULER (Svensk Kem. Tidskr., 1934, 46, 201—203).—The average content of glutathione in the normal human lens is approx. 75% of that indicated by the total reducing power (I) (i.e., 0.02—0.04%); approx. 0.01% of ascorbic acid (II) is present. With cataract (12 cases), the vals. of both (I) and (II) are considerably reduced, (II) being entirely absent in 7 cases. In the lens of fish (*Gadus*, *Labrus*, and *Gadiculus*), the indophenol reagent gives vals. of 0.008—0.053%; biological tests indicate that this is due partly to (II). F. O. H.

Determination of enzymes and carbohydrate investigation in the aqueous humour. I. J. BOCK and H. POPPER (Z. ges. exp. Med., 1933, 90, 319—330; Chem. Zentr., 1933, ii, 3706).—The normal aq. humour (I) contains diastase (II). After puncture of (I), the val. of (II) rises rapidly after 4 hr.

H. J. E.

Dielectric constant of muscle. B. N. TARUSOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 353—356).—The val. for the fresh sartorius muscle of the frog was 84, increasing in 15—25 hr. to 86, with a simultaneous rise in the intracellular conductivity (I) and the (I) measured at low frequencies. In 25—40 hr. the dielectric val. falls to 78, but (I) remains const.

H. J. E.

Ammonia-forming substances in the breast-muscle of the pigeon and the fowl. H. DOTZENRODT (Z. physiol. Chem., 1934, 226, 58—72).—The various NH_3 fractions found in the breast-muscle (I) of the pigeon (II) are similar to those in the fowl (III). The free NH_3 val. is much > in frog and rabbit muscle. The PO_4''' fractions differ in that the (III)-(I) contains more insol. residual H_3PO_4 , i.e., phosphatide- H_3PO_4 than (II)-(I). Free adenylic acid (IV) is not present. (IV) determined by the enzymic

method is > that calc. from the $H_4P_2O_7$ vals. PO_4''' is present in about double the amount calc. from the NH_3 determination, which may indicate that (I) contains adenosinediphosphoric acid. J. H. B.

Acetylcholine in fresh spleen and blood. K. GOLLWITZER-MEIER and E. KRÜGER (Arch. exp. Path. Pharm., 1934, 176, 642—646).—Fresh pulped ox- or horse-spleen contains detectable amounts of biologically active acetylcholine (I) which are increased by repeated freezing and thawing or, to a greater extent, by extraction. The spleen (pulp and extract) and blood of cats and dogs are free from (I). Detection of (I) in human blood is vitiated by the high content of K. F. O. H.

Flavins and their distribution in animal tissue. A. CHARIT and N. CHAUSTOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 386—390).—Finely divided tissue well washed with H_2O is extracted for 36—48 hr. with 10 parts of MeOH at 28—36°. The extract is diluted with 3 vols. of H_2O , and an equal vol. of $CHCl_3$ is added to the clear centrifugate. The yellow solution of the flavin in dil. MeOH is determined colorimetrically, using K_2CrO_4 as standard. For rabbit's tissue, the following vals. ($\times 10^{-6}$ g. per g. of tissue) were obtained: kidneys 13.05; liver 6.45; heart 5.53; lungs 8.9; brain 2.7; muscle nil. W. O. K.

Phosphatides. IX. Fatty acids of the phosphatides and of the liquid triglycerides of ox heart-muscle. E. KLENK and F. DITT (Z. physiol. Chem., 1934, 226, 213—220; cf. this vol., 97).—The fatty acids of the phosphatides contain 14 and 21%, respectively, of solid C_{16} and C_{18} acids; liquid acids, C_{18} 45%, C_{20} 14%, C_{22} 1%, the unsaturation increasing with mol. wt. (3.5—6.5 H). The liquid triglycerides contain: solid fatty acids, C_{16} 22%, C_{18} 20%; liquid C_{16} 12%, C_{18} 45%, only traces of higher acids being present. J. H. B.

Fatty substances of shell-fish. III. Fatty substance of oyster and four other shell-fish. M. TSUJIMOTO and H. KOYANAGI (J. Soc. Chem. Ind. Japan, 1934, 37, 436—439B; cf. this vol., 676).—1.5—4% of fatty matter was extracted by EtOH and Et_2O from the "mukimi" (i.e., bared shell-fish) of "kaki" (oyster, *Ostrea gigas*, Thunberg), "ōnogai" (*Mya arenaria*, Linn.), "ezohibari" (*Volsella modiolus*, Linn.), "akanishi" (*Rapana thomasi*, Crosse), and "ushinotsume" (*Cellana nigrolineata*, Reeve). After saponification, the separated fatty acids had I vals.: 180.4 from the $COMe_2$ -insol. oil and 197.4 from the $COMe_2$ -sol. oil (I) (about 67% of total oil) of oyster, and 161.5, 178.4, 157.0, 156.3, respectively, for the acids from the total oil in the other cases. (I) had acid val. 5.2, sap. val. 159.0, I. val. 188.1, unsaponifiable matter 17.98%. The fatty acids of (I) had I. val. 199.1, Et_2O -insol. bromides 64.2%. In each case, the unsaponifiable matter contained *conchasterol*, m.p. 133.5—134.5°, from "hamaguri" (*Meretrix*) oil, 136.5—137.5°, from oyster oil (*Ac* derivative, m.p. 144.5—145.5°), which gives a characteristic red coloration with Ac_2O and H_2SO_4 , previously observed in the case of the sterols from other shell-fish, calamary and "tarabagani" (*Paralithoides*) oils, but absent in the case of fish or whale body- and liver-oils.

The systematic names of "asari" and "karasugai" given in Part I (*loc. cit.*) are revised and given as *Paphia* (*Ruditapes*?) *philippinarum*, Adams and Reeve, and *Cristaria plicata patiosa*, Clessin, respectively.

E. L.

C₂₂-acids of sardine oil. K. KINO (J. Soc. Chem. Ind. Japan, 1934, 37, 442—444B).—C₂₂H₄₄O₂, C₂₂H₄₂O₂ [solid cetoleic and a liquid (isomeric?) acid], C₂₂H₄₀O₂, C₂₂H₃₈O₂, C₂₂H₃₆O₂, and C₂₂H₃₄O₂ have been identified.

E. L.

Ovary oil of fresh mullet. K. KAFUKU and C. HATA (J. Soc. Chem. Ind. Japan, 1934, 37, 455B; cf. B., 1934, 155).—The yellow oil (14%) extracted by Et₂O from the ovaries of fresh mullet (*Mugil japonicus*, L.) was fluid at 20° and sol. in COMe₂, and had d_{4}^{20} 0.8848, n_D^{20} 1.4696, acid val. 5.83, sap. val. 130.3, I val. 119.7, SCN val. 82.9, unsaponifiable matter 45.1% (mainly cetyl alcohol, with 10% of cholesterol and minor amounts of C₁₄H₂₉·OH, C₁₆H₃₁·OH, and C₁₈H₃₅·OH. The fatty acids (d_{4}^{20} 0.8985, n_D^{20} 1.4679, I val. 162.9, SCN val. 95.31, acid val. 194.9) contained palmitic, myristic, zoomaric, and oleic acids and probably highly unsaturated acids such as C₁₈H₂₈O₂, C₂₀H₃₀O₂, and C₂₂H₃₄O₂.

E. L.

Pigmented marine-animal oils. I. Pigments from the angler fish (*Lophius piscatorius*), the prawn (*Nephrops norvegicus*), and the whale. G. N. BURKHARDT, I. M. HELLBRON, H. JACKSON, E. G. PARRY, and J. A. LOVERN (Biochem. J., 1934, 28, 1698—1701).—The red oils from the angler fish (I), the prawn, and the whale yield a violet-black solid, almost certainly astacene. In the oil from (I) a yellow pigment, showing the absorption max. characteristic of taraxanthin, is also present.

C. G. A.

(A) Volumetric determination of inositol.
(B) Determination of inositol in animal tissues. L. YOUNG (Biochem. J., 1934, 28, 1428—1434, 1435—1443).—(A) By a modification of the Fleury and Marque method (A., 1929, 1266) depending on the reduction of KHgI₃ by polyhydric alcohols, inositol (I) (1—5 mg.) may be accurately determined. If glucose is also present it is first removed by fermentation with yeast.

(B) Brain or heart muscle is extracted with 70% COMe₂. The aq. extract after removal of COMe₂ and Et₂O extraction is treated with the acid HgSO₄—BaCO₃ reagent of West and Peterson (A., 1933, 179) to remove N compounds. The filtrate is treated with Ba(OH)₂ and EtOH, which under suitable conditions ppt. the (I). The ppt. is decomposed with H₂SO₄, filtered, conc., and (I) pptd. together with inorg. compounds by COMe₂ and Et₂O. The pptd. (I) is determined as in (A).

W. O. K.

"Bound" water of biological colloids. D. M. GREENBERG and W. E. COHN (J. Gen. Physiol., 1934, 18, 93—96).—The objection by Bull (A., 1933, 1218) to the determination of bound H₂O by ultrafiltration because of an assumed adsorption of the reference substance is shown to be invalid for glucose, which is not adsorbed by caseinogen or gelatin.

C. G. A.

Analysis of separated liver tissues in the characterisation of its electrostructure. R. KELLER and G. KLEPETAR (Biochem. Z., 1934, 273, 180—

185).—Liver connective tissue contains excess of Na, Cl, and Ca, whilst parenchymatous tissue contains excess of glycogen, K, Mg, and P. The results agree with the requirements of the electrostructure of this organ.

P. W. C.

Chloride content of new-born rats. K. A. WINTER (Biochem. Z., 1934, 272, 384—386).—The very high Cl content of unborn and new-born rats decreases greatly during the first month of life, although the abs. amount of Cl increases threefold. Simultaneously the H₂O content decreases, the extent of decrease being different in different organs.

W. McC.

Metallic content of tissues from goat fetuses and kids. H. RAMAGE (Biochem. J., 1934, 28, 1500—1502).—The metal content of the various organs of goat fetuses of different ages was determined by spectro-analysis. The results were variable, but the contents of Fe, Ca, and Cu in the liver appear to be correlated.

W. O. K.

Enzymes of brain. S. EDLBACHER, E. GOLDSCHMIDT, and V. SCHLAPPI (Z. physiol. Chem., 1934, 227, 118—123).—Nucleic acid (I), Mg hoxosediphosphate (II), and Na glycerophosphate (III) are readily hydrolysed by liver and kidney of the guinea-pig, rat, and rabbit; brain hydrolyses (I) and (II) only slightly, (III) not at all. The fission in all cases is greatly influenced by p_H . Brain shows a weak catheptic and no tryptic action.

J. H. B.

Marchi's staining method. II. Fixation. R. L. SWANK and H. A. DAVENPORT (Stain Tech., 1934, 9, 129—135).—The spinal cords of cats and rabbits were fixed with acid, neutral, and alkaline solutions; staining was limited to a chromate- or a chlorate-osmic solution. The presence of acid in the fixative resulted in the staining of normal myelin sheaths. The staining reactions of the granular deposits which occur in most Marchi preps. are very similar to those of degenerating myelin. The granules are partly suppressed by adding KClO₃ to the CH₂O fixative.

H. W. D.

Embedding [of histological material] with low-viscosity cellulose nitrate. H. A. DAVENPORT and R. L. SWANK (Stain Tech., 1934, 9, 137—139).—Low-viscosity cellulose nitrate and celloidin are compared.

H. W. D.

Toad poisons.—See this vol., 1232.

Hydrogen-ion concentration of the vaginal fluid during the menstrual cycle of the macaque. M. Y. CHEN MAI and H. B. VAN DYKE (Chinese J. Physiol., 1934, 8, 203—208).—In the healthy macaque the p_H of the vaginal fluid varies from 4.20 to 8.60 during the cycle.

H. G. R.

Influence of impaired liver function on the histamine-gastric juice reaction. I. In dogs. II. In rats. M. MUTO (Arch. exp. Path. Pharm., 1934, 176, 431—445, 446—455).—I. CHCl₃ narcosis diminishes the secretion of acid (I) but not that of pepsin (II) in the gastric juice (III) produced by histamine in dogs; the vol. of (III) is unchanged. Liver damage by ligation of the hepatic artery ishes total and free (I), Cl' content, and vol. of (III), the (II) level remaining const.; the max. disturbance

occurs within 14 days. Biliary fistulæ and ligation of the bile duct cause similar changes. With gastric fistulæ and diuresis, (I), (II), and vol. and [Cl'] of (III) decrease. The response appears to depend on the presence of an unknown substance of hepatic origin.

II. The changes in histamine-produced (III) in rats due to CHCl_3 - or P-poisoning are > those due to Et_2O , avertin, or atophan, i.e., substances which are less injurious to the liver than CHCl_3 or P. In all cases, free and total (I) and [Cl'] are decreased. Administration of glucose inhibits the effects due to avertin, but not to P. The results are correlated with the preceding data.

F. O. H.

Lipins of milk. I. Fatty acids of the lecithin-cephalin fraction. F. E. KURTZ, G. S. JAMIESON, and G. E. HOLM (J. Biol. Chem., 1934, 106, 717—724).—The lecithin (I)-cephalin (II) fraction of sweet cream buttermilk powder was obtained by extraction with EtOH -petroleum (3:1) and addition to COMe_2 . After emulsification in H_2O and trituration with hot COMe_2 the phospholipins were kept in Et_2O at 0° , when a mixture of sphingomyelin and galactolipins separated. The nitrogenous impurities were removed from the Et_2O -sol. fraction with EtOH and H_2O . The purified material contained 44% of (II) and 56% of (I). The composition of the total fatty acids on hydrolysis was: 5.2% myristic, 16.1% stearic, 1.8% arachidic, 70.6% oleic, and 6.3% of (?) $\text{C}_{22}\text{H}_{36}\text{O}_2$.

H. D.

Influence of different levels of fat intake on milk secretion. L. A. MAYNARD, C. M. MCKAY, H. H. WILLIAMS, and L. L. MADSEN (Cornell Univ. Agric. Exp. Sta. Bull., 1934, No. 593, 14 pp.; cf. A., 1933, 177).—Additions of > 4% of fats to a grain mixture ration did not significantly increase fat or total milk yields.

A. G. P.

Quality of protein in relation to milk production. A. B. FOWLER, S. MORRIS, and N. C. WRIGHT (Scot. J. Agric., 1934, 17, 261—269).—Data recorded show the close relationship between the biological val. of proteins and their lysine contents.

A. G. P.

Br. abortus in the bovine udder and its effect on the chemical composition of the milk. C. P. FITCH and L. M. BISHOP (Cornell Vet., 1934, 24, 25—29).—Cl': lactose, sp. conductivity, and catalase were normal.

CH. ABS.

Irradiated milk: influence of fat content and time of exposure on antirachitic potency. G. C. SUPPLEE, G. E. FLANIGAN, R. C. BENDER, and M. J. DORCAS (J. Dairy Sci., 1934, 17, 483—487).—Low-fat milks attained antirachitic properties more slowly than did high-fat samples. The potency ultimately reached was not \propto the fat content.

A. G. P.

Irradiated milk: reflecting properties and antirachitic activation as affected by the impingement angle of the incident radiation. G. C. SUPPLEE and M. J. DORCAS (J. Dairy Sci., 1934, 17, 607—611).—Milk films exhibit selective reflexion of ultra-violet radiation especially in the range 2550—3300 Å., the effect being most marked with angles of incidence (A) of 30° or less. Relationships are examined between A , the % of reflected radiation, and antirachitic potency attained.

A.

Effect of light on the reducing substance (vitamin-C?) in milk. R. G. BOOTH and S. K. KON (Nature, 1934, 134, 536; cf. A., 1933, 1186).—The ability to reduce the indophenol reagent can be partly restored by treating milk which has been exposed to light with H_2S , which is then removed from the $\text{CCl}_3\cdot\text{CO}_2\text{H}$ filtrate. The longer is the original exposure to light the smaller is the extent to which the reducing power can be restored.

L. S. T.

Effect of variations in protein and salt intake on the nitrogen and chloride content of sweat. D. P. CUTHBERTSON and W. S. W. GUTHRIE (Biochem. J., 1934, 28, 1444—1453).—In resting man the output of N and of Cl' in the sweat is increased with rise in the air temp. (I) when the protein (II) and Cl' content of the diet is const. At const. (I) increase in (II) content of diet results in high excretion of sweat-N, whilst increase in the Cl' intake has no const. effect on sweat-Cl'. In two cases of myxoedema there was a greatly reduced output of both Cl' and N, whilst in two cases of exophthalmic goitre the output of Cl' and N appeared to vary with the severity of the disease as shown by the basal metabolic rate.

W. O. K.

Urobilinogen. R. LEMBERG (Nature, 1934, 134, 422).—Evidence that urobilinogen (I) and mesobilirubinogen (II) are not identical is advanced. Natural urobilin and "urobilin" (III) from (II) show a difference in position of their absorption max. in acid EtOH . With FeCl_3 , (II) and (III) are dehydrogenated to mesobiliverdin and -violins, whereas (I) from normal urine and faeces and from pathological urine is changed only into urobilin. (I) and (II) thus differ in their skeletal system. (I) is not a simple product of reduction of bilirubin by intestinal bacteria, but a product of dismutation or oxidation of bilirubin.

L. S. T.

Biochemical urine analysis. E. FREUND (Wien. klin. Woch., 1933, 46, 1574—1576; Chem. Zentr., 1934, i, 737).—Under normal conditions the urine remains clear after addition of a nucleoprotein extract of an organ. With diseased organs the extract forms a ppt., the amount of which depends on the extent of the disease.

L. S. T.

Method for detection of photodynamic substances in urine. A. PERUTZ and B. LUSTIG (Wien. klin. Woch., 1933, 46, 1579—1580; Chem. Zentr., 1934, i, 737).

L. S. T.

Cole's method for determination of sugar in urine. Determination of galactose. F. KAYSER and N. MASJUS (J. Pharm. Chim., 1934, [viii], 20, 257—263).—The method is satisfactory for glucose and for galactose providing there is < 1% present.

H. G. R.

Rapid determination of urinary sugar. H. HABS (Münch. med. Woch., 1933, 80, 1101—1102; Chem. Zentr., 1933, ii, 3735).—The brown colour produced on boiling with aq. NaOH is matched against standards.

H. J. E.

Changes in the composition of urine due to constriction of the common carotid artery. H. HUNGERLAND (Arch. exp. Path. Pharm., 1934, 176, 306—325).—Bilateral clamping of the common carotid arteries in fasting dogs increases the vol. of the urine,

the difference between the total cation and anion, and the abs. contents of total base, HCO_3' , HPO_4'' , and, more especially, Cl' . $[\text{N}]$ is markedly decreased.

F. O. H.

Acidosis. XXII. Application of the Hender-son-Hasselbalch equation to human urine. **XXIII.** Carbon dioxide tension and acid-base balance of human urine. J. SENDROY, jun., S. SEELIG, and D. D. VAN SLYKE (J. Biol. Chem., 1934, 106, 463—477, 479—500).—XXII. The solubility coeff. of CO_2 in 22 human urines was 0.522 ± 0.08 at 38° , the max. range of variation, chiefly a function of the salt concn. (I), being 0.498—0.536. Hasselbalch's const., pK' , was 6.10 ± 0.07 , the max. range of variation being 5.97—6.21, and was related to (I) by the approx. formula, $pK' = 6.32 - 0.6\sqrt{B}$, where B —normality of total base in the urine. The urea content has practically no effect on pK' .

XXIII. CO_2 tensions (I) in urine (II) can be accurately measured at 38° by equilibrating (II) with 2% of its vol. of air- CO_2 mixture and subsequent micro-analysis of the gas bubble. In both normal and pathological cases the range of (I) was 40—200 mm. (mostly 45—95 mm.); 25% of the vals. were 67 ± 5 mm. (I) > 80 mm. correspond with densities > 1.020, whilst (I) > 120 mm. were frequently found after severe exercise and after taking NaHCO_3 . High (I) were not observed if (II) had been retained in the bladder for > 4 hr. (I) in (II) is probably always > (I) in arterial blood. Gamble's results (A, 1922, i, 494) are in the main confirmed, and all results are compatible with the filtration-reabsorption theory of (II) excretion. A. E. O.

Permeability of the renal tubules of the frog for organic non-electrolytes. F. E. SCHMENGLER and R. HÖBER (Pflüger's Archiv, 1933, 233, 199—221; Chem. Zentr., 1934, i, 1214).—N-free and N-containing org. non-electrolytes (e.g., NH_4Ac , glycerol, or glucose) diffused from the portal vein into the urine, the rate being greater the smaller is the mol. vol. of the substance used. Narcotics did not interfere with this process. The pore permeability is comparable with that of frog's muscle. H. J. E.

Anæmia. Classification and treatment based on volume and hæmoglobin content of the red corpuscles. M. M. WINTROBE (Arch. Int. Med., 1934, 54, 256—280).—Vals. for the no. and vol. of the erythrocytes and for their content and concn. of hæmoglobin in human anæmia indicate four main types of anæmia, viz., macrocytic, normocytic, microcytic (simple and hypochromic). Their response to liver or Fe therapy is discussed. F. O. H.

Ancylostoma anæmia and its treatment by iron. A. G. BIGGAM and P. GHALIOUNGUI (Lancet, 1934, 227, 299—304).—Blood regeneration under different treatment after removal of the cause has been observed in ancylostoma anæmia. The response of red cells and hæmoglobin to reduced Fe, and FeCl_2 , together with the effect of addition of liver, yeast, marmite, Cu, and Mn, is described. The hæmoglobin in the average normal Egyptian adult is approx. 80%. L. S. T.

(A) **Metallic glutamates in nutritional anæmia.**
(B) **Glutamic acid in milk anæmia; effect on**

hæmoglobin regeneration in "cystine-deficient" animals. (c) Cobalt glutamate in nutritional anæmia. E. BRAND and C. J. STUCKY (Proc. Soc. Exp. Biol. Med., 1934, 31, 627—630, 689—692, 739—742).—(A) Fe, Cu, Mg, and Mn (as glutamate or inorg. compounds) increased hæmoglobin and restored growth in anæmic rats; glutamic acid (I) was ineffective.

(B) Fe was ineffective unless supplemented by (I).

(c) Co glutamate and $\text{Co}(\text{NO}_3)_2$ produced polycythæmia in young rats when given as supplement to a whole-milk-Fe-Cu diet. CH. ABS.

Response of the normal guinea-pig to the administration of liver extracts. B. M. JACOBSON (Science, 1934, 80, 211—212).—The no. of reticulocytes in the peripheral blood is increased by oral or parenteral administration of a therapeutically active liver extract. The reaction is sensitive. This reticulocyte response is most probably intimately related to the true hæmatopoietic action of liver in pernicious anæmia. L. S. T.

1:2:5:6-Dibenzanthracene as a carcinogenic agent. M. G. SEELIG (Amer J. Cancer, 1934, 20, 827—833).—The compound is less toxic than tar. CH. ABS.

Tissue metabolism. IV. Comparison of muscle and tumour glycolysis. E. BOYLAND and C. A. MAWSON. **V. Lactic dehydrogenases of yeast and heart muscle.** E. BOYLAND and M. E. BOYLAND (Biochem. J., 1934, 28, 1409—1416, 1417—1421).—IV. The glycolysis of tumour tissue is unaffected by the presence or absence of phosphate and is max. at about p_H 8.0. Cell-free extracts of mouse or rat sarcoma capable of producing lactic acid (I) from glucose or AcCO_2H (II) + α -glycerophosphate (III) could not be prepared, but slices of the tumour, treated with COMe_2 , frequently retained about 0.1 of the glycolytic activity of the original tissue, although they were incapable of reproducing the tumour when injected into animals. A method for producing an active glycolysing extract from rat muscle is described. This extract has max. activity at p_H 7.5 and in presence of $M/30$ phosphate. Tumour slices form some (I) from hexose monophosphate or (II) + (III), but much < do muscle extracts.

V. Solutions of the lactic dehydrogenase of heart muscle (I) and of baker's yeast (II) showed max. activity at p_H 9.3 and 6.4, respectively. The (II) enzyme is independent of co-enzyme (III) and does not attack malate (IV), whilst (I) lactic dehydrogenase requires a (III) and oxidises both lactate and (IV) in alkaline solution, the action being max. with both substrates at the same p_H . W. O. K.

Metabolism of tumours. IV. S. EDLBACHER and F. KOLLER [with M. BECKER] (Z. physiol. Chem., 1934, 227, 99—113; cf. A., 1932, 767).—Fission by arginase (I) and phosphatase (II) is marked in tumour tissue free from necrosis. In the necrotic tissue, (I) and (II) are present probably owing to the degradation of nuclear substance. The conditions for activation of necrosis-(I) differ, however, from those found for (I) of intact tissue. This is probably connected with the small amount of reducing substances such as glutathione and ascorbic acid, which are natura

activators, in necrotic tissue. (I) in tumours must be concerned with change in nuclear substance, since there is no synthesis of urea. J. H. B.

Reducing substances of tissue. S. EDLBACHER and A. JUNG (*Z. physiol. Chem.*, 1934, **227**, 114—117).—The ascorbic acid content (by dichlorophenol-indophenol titration) of intact sarcoma tissue of rats is about 10 times, the I titration val. 4—5 times, that of necrotic tissue. The liver of tumour animals frequently shows vals. < normal. J. H. B.

Influence of various preparations of lactic acid and sugars on the growth of transplanted tumours. II. I. A. PARFENTIEV, V. D. SUNTZEV, and W. K. DEVRIENT (*Amer. J. Cancer*, 1934, **20**, 117—136). CH. ABS.

Fat-soluble oestrogenic substance isolated from spontaneous mammary tumours of mice. P. ZÉPHIROFF and N. DOBROVOLSKAIA-ZAVADSKAIA (*Compt. rend.*, 1934, **199**, 589—591; cf. this vol., 815).—Adenomatous growths in mice yield a fat-sol. substance, stable to acids and alkalis, which produces oestrus, and enlarges the uterus and ovaries of a young rat. Similar extracts from human cancers are inactive. J. L. D.

Thyroxine-inhibiting action of urine in cardiac decompensation. A. HOFMANN and O. LUTEROTTI (*Klin. Woch.*, 1933, **12**, 1941—1942; *Chem. Zentr.*, 1934, i, 1344).—The acceleration of metamorphosis of salamanders living in H_2O , produced by addition of thyroxine to the H_2O , disappears on addition of urine from decompensation subjects. H. J. E.

Binding of potassium in serum in normal and diabetic men. H. WAELSCH and S. KITTEL (*Kolloid-Z.*, 1934, **68**, 342—346).—In the serum of normal men K is mainly bound in a complex and migrates to the anode, but in diabetic subjects a greater proportion is ionised and goes to the cathode. E. S. H.

Effect of intravenous injection of insulin. VI. Hypoglycæmic symptoms in diabetes. K. ROHOLM and T. E. H. THAYSEN (*Acta Med. Scand.*, 1933, **80**, 528; *Chem. Zentr.*, 1934, i, 722).—Insulin produced the same symptoms in both normal and diabetic subjects, the blood-sugar falling to 50—55 mg. per 100 c.c. There was no evidence of hyperadrenalinæmia in diabetics. R. N. C.

Participation of the thyroid gland in increases in metabolism. I. Mechanism of increased metabolism in fever. H. ANTHERS (*Deut. Arch. klin. Med.*, 1933, **176**, 128—137; *Chem. Zentr.*, 1934, i, 720).—Neither in acute fever nor in chronic febrile diseases (tuberculosis) can an increase in the blood-I level be detected. The daily variations in I val. are small and are independent of the fever curve. The increased metabolism in fever must be due to irritation of the central nervous system without participation of the thyroid gland. L. S. T.

Blood-sugar and glycosuria in exophthalmic goitre. W. T. ANDERSEN (*Acta Med. Scand. Suppl.* Vol., 1933, **54**, 9—206; *Chem. Zentr.*, 1934, i, 1066).—In exophthalmic goitre, spontaneous glycosuria was found. The alimentary blood-sugar curve was higher

and more extended than normal. The excretion threshold for sugar was < normal. H. J. E.

Analysis of the di-iodotyrosine- and diet effect in experimental hyperthyrosis. I. ABELIN and A. SCHÖNENBERGER (*Z. ges. exp. Med.*, 1933, **90**, 489—501; *Chem. Zentr.*, 1933, ii, 3713).—Thyroid-free rats rendered thyrotoxic by thyroxine or thyroid powder show after dosage with di-iodotyrosine (I) an increase in wt. and a decreased pulse frequency. The acid-sol. products of hydrolysis of thyroid containing (I) resemble (I) in their action. The liver of the rat is able to absorb vitamin-A in spite of strong hyperthyrosis. H. J. E.

Mechanism of simple hypertension. VII. True and false creatine and creatinine of the blood. Lowering of the blood-creatinine level in simple hypertension. H. BOHN and F. HAHN (*Z. klin. Med.*, 1933, **125**, 458—474; *Chem. Zentr.*, 1933, ii, 3714).—In true hypertension the blood-creatinine (I) is lowered. In uræmia the val. of (I) is high. H. J. E.

Excretion of phenylpyruvic acid in the urine as a metabolic anomaly in conjunction with imbecility. A. FÖLLING (*Z. physiol. Chem.*, 1934, **227**, 169—176).— $CH_2Ph \cdot CO \cdot CO_2H$, although not a normal excretion product, was isolated from the urine of several imbeciles. J. H. B.

Removal of bromine from the blood in cases of mental disorders. J. H. QUASTEL and E. D. YATES (*Biochem. J.*, 1934, **28**, 1530—1535).—In man the rate of removal of Br from the blood (I) after intravenous injection of NaBr and also the rise in (I)-Br following oral administration of NaBr are independent of mental state. The Br removed from (I) is distributed throughout the body-tissues and is only to a small extent excreted in the urine. Br may appear in the gastric juice (II) in concns. > that in (I). During digestion (I)-Br falls and the Br in (II) rises. W. O. K.

Utilisation of galactose in physiological and pathological conditions. V. Significance of galactosæmia and glucosæmia for functional liver diagnosis after oral galactose administration. H. KOSTERLITZ (*Z. ges. exp. Med.*, 1933, **90**, 465—478; *Chem. Zentr.*, 1933, ii, 3876—3877; cf. A., 1933, 971).—After dosage with 40 g. of galactose the concn. in the blood is 20—40 mg. per 100 c.c. In 1.5 hr. it has disappeared from the blood. In icterus simplex the val. can rise to 150 mg. and the effect may last for > 2 hr. H. J. E.

Bilirubin level of the blood-serum in cases of deficient circulation and the effect of mercury diuresis. F. KIRSCH (*Klin. Woch.*, 1933, **12**, 593—596; *Chem. Zentr.*, 1933, ii, 3868).—In cases of congestion of the liver, intravenous salyrgan injection increased the blood-serum-bilirubin (> 1.0 mg. per 100 c.c.). H. J. E.

Anterior pituitary extract and glycogen-storing disease. H. FASOLD (*Z. ges. exp. Med.* 1933, **92**, 63; *Chem. Zentr.*, 1934, i, 1065).—A case of glycogen-storing disease was treated with anterior pituitary extract (I). The excretion of ketones was increased, but there was no rise in the blood-sugar.

Injection of adrenaline (II) had the same effect. (I) increases secretion of (II). H. J. E.

Antimalarial acridine compounds. F. MIETZSCH and H. MAUSS (*Angew. Chem.*, 1934, **47**, 633—636).—The relative efficacy of quinine, plasmoquin, and acridino derivatives (especially atebrin) in the prophylaxis and treatment of various forms of malaria is discussed. F. O. H.

Mechanism of acidosis in experimental uranium nephritis. L. BRULL and C. ROERSCH (*Biochem. J.*, 1934, **28**, 1513—1515).—In dogs poisoned with U nitrate, the excretion of org. and inorg. acids may rise while the acidosis develops. A rise in blood- PO_4''' and $-\text{SO}_4''$ takes place, but the main cause of the acidosis appears to be an increased production of org. acids. W. O. K.

Muscle metabolism in (a) experimental intestinal obstruction, (b) nephrectomised rabbits. W. NONNENBRUCH, Z. STARY, A. BAREUTHER, and H. THELEN (*Arch. exp. Path. Pharm.*, 1934, **176**, 563—572, 573—577).—(a) Following ligation of the ileum in rabbits, the free muscle- PO_4''' increases by 43% within 24 hr., whilst the hexose-mono-(I) and adenylypyro-phosphoric acid (II) decrease by 42 and 59%, respectively. The activity of phosphoric ester synthesis is diminished.

(b) Nephrectomy produces changes in the P distribution and synthesis in muscle similar to those due to intestinal obstruction; the rates of degradation of (I) and (II), however, differ markedly from each other. F. O. H.

Concentration of serum-protein in cedema. H. M. HAND (*Arch. Int. Med.*, 1934, **54**, 215—238).—A low level of serum-protein (I) produces cedema (II) due to the diminution in colloid osmotic pressure (III). Owing to the greater effect of albumin (IV) than globulin on (III), the tendency to (II) follows more closely the level of (IV). An inadequate intake of proteins produces (II), which appears when (I) falls to approx. 5.5% or (IV) to 2.5%. Electrolytes influence the extent and type of (II). F. O. H.

Calcium and phosphorus metabolism in osteomalacia. R. R. HANNON, S. H. LIU, H. I. CHU, S. H. WANG, K. C. CHEN, and S. K. CHOU (*Chinese Med. J.*, 1934, **48**, 623—636).—In osteomalacia with no vitamin-D (I) therapy, the absorption of Ca through the intestinal tract and the urine-Ca are low. Administration of (I) gives increased Ca and P retention, which is sustained for several months after discontinuation of treatment. H. G. R.

Blood-calcium and -potassium in Parkinsonism. C. C. LEE (*Chinese Med. J.*, 1934, **48**, 738—740).—Serum-Ca is low, but -K is normal. H. G. R.

Toxæmias of pregnancy. L. McILROY (*Lancet*, 1934, **227**, 291—296).—A lecture. L. S. T.

Significance of the thyroid gland for the action of vitamin-D and recovery from rickets. A. NITSCHKE (*Klin. Woch.*, 1933, **12**, 1793—1797; *Chem. Zentr.*, 1934, i, 720).—A discussion. L. S. T.

Influence of removal of parathyroid glands on development of rickets in rats. J. H. JONES (J.

Biol. Chem., 1934, **106**, 701—705).—The % of femur ash (I), serum-Ca (II) and -inorg. P (III) were determined on parathyroidectomised rats (IV) put on a high-Ca-low-P rachitogenic (V) and a stock diet on appearance of tetany, and in normal rats on (V). No differences in (I), (II), and (III) were observed between (IV) and normal rats on (V). The (I) and (III) of (IV) on a stock diet were >, and the (II) <, those of (IV) and normal rats on (V). Parathyroidectomy of rachitic rats does not influence the rickets. H. D.

Rickets in chickens; its nature and pathogenesis. J. P. MCGOWAN and A. R. G. EMSLIE (*Biochem. J.*, 1934, **28**, 1503—1512).—Chickens, on a basal diet of yellow maize, dried yeast, dried skim-milk, and NaCl with or without cod-liver oil (I), develop osteoporotic bones. Addition of 1% of CaCO_3 to the diet prevents osteoporosis (II) only when accompanied by (I). The addition of 6% of CaCO_3 causes rickets unless (I) is also administered, when normal bones are formed. The bones of the newly-hatched chick are already osteoporotic, and this fact is the essential cause of the differences observed as compared with mammals. The results are consistent with the view that (II) and rickets are due to deficiency in Ca and P, respectively, and that vitamin-D liberates H_3PO_4 from the phospholipins of the body. W. O. K.

Silicotic lungs. I. Chemical examination. G. GERSTEL (*Arch. Gewerbepath. Gewerbehyg.*, 1934, **5**, 249—264).—Methods for determining SiO_2 , Fe, Al, Ti, and PO_4''' are described. A. G. P.

Possible dietary predisposition to stammering. K. DUNLAP (*Science*, 1934, **80**, 206).—Insufficient meat in the diet of children may be a predisposing factor. L. S. T.

Crystal deposition processes in relation to pathological stone and precipitate formation. A. VON KUTHY (*Kolloid-Z.*, 1934, **68**, 335—341).—The appearance of macro-crystals in supersaturated solutions can be inhibited or strongly retarded by addenda which increase or decrease the solubility, or by high-mol. or surface-active substances. The influence on the velocity of formation of nuclei and the subsequent velocity of growth is distinguished. The observations are discussed in relation to pathological conditions. E. S. H.

Relation between tetany and tetanus. K. LISSAK (*Arch. exp. Path. Pharm.*, 1934, **176**, 425—428).—Tetanus infection (I) in dogs produces a rise in serum-Ca and -inorg. P; during the incubation period no marked change occurs until after the development of paralysis. These symptoms are not influenced by injection of parathyroid hormone. Hence the condition due to (I) is not in any way related to the parathyroid gland. F. O. H.

Metabolic oxidation and radiation. M. COPPSAROW (*Protoplasma*, 1934, **21**, 73—80).—Normal metabolism of organisms is generally accompanied by ultra-violet radiation, which is associated with the activity of respiratory enzymes. A. G. P.

Digestion of plant food and the penetration of enzymes into closed plant cells. W. HEUPKE

(Münch. med. Woch., 1933, 80, 1969—1971; Chem. Zentr., 1934, i, 1211).—It is not necessary for the cell-wall to be broken, as enzymes in the digestive tract can diffuse through the wall and convert the colloidal protein, fat, and carbohydrate in the cell into sol. products capable of diffusing out of the cell.

H. J. E.

Digestion of inulin. W. HEUPKE and K. BLANKENBURG (Deut. Arch. klin. Med., 1933, 176, 182—187; Chem. Zentr., 1934, i, 725—726).—Inulin (I) penetrates the warm intact cell membrane and diffuses through collodion membranes. It is not markedly decomposed in the gastro-intestinal canal. Most of the administered (I) is resorbed in the small intestine, apparently without much change in its mol.

L. S. T.

Intermediate carbohydrate-protein-fat metabolism in relation to the liver function. W. GNEITING (Klin. Woch., 1933, 12, 1807—1810; Chem. Zentr., 1934, i, 726).—The liver was loaded with galactose (I), gelatin, and fat, successively, by the addition of extra quantities of each to the normal diet. In the normal liver the ratio of the amount of the constituent tested in the diet to the amount added was unaltered; in cases of slightly diseased liver the (I) and glycine ratios were less abnormal, whilst in severe cases the (I) ratio showed increased abnormality.

R. N. C.

Carbohydrate metabolism of the liver. II. Sugar output. III. Sugar intake during glucose absorption. C. TSAI and C. L. YI (Chinese J. Physiol., 1934, 8, 245—272, 273—296).—II. The sugar (I) content of the venous blood (II) from the liver (III) of decapitate cats is > that of the arterial and portal (II). Glycogen (IV), accumulated in (III) during the recovery period, is from non-carbohydrate sources and the average (I) formed during the recovery period is 0.27 g. per kg. per hr.

III. During glucose absorption the difference in (I) in the outflowing and inflowing (II) is only 3—5 mg. per 100 c.c.. A reduction in the output of (I) by (III) from 150 to 40 mg. per kg. per hr. was observed. (IV) in (III) increased considerably, but only about 15% of this was due to absorbed (I).

H. G. R.

Carbohydrate metabolism of the goat. Blood-sugar and inorganic phosphate. J. T. CUTLER (J. Biol. Chem., 1934, 106, 653—666).—The resting venous blood-sugar (I) of goats was 24—65 mg. per 100 c.c. (average 46 mg.). The ventricular (I) in each case was 2—4 mg. per 100 c.c. > the venous (I); this discrepancy was not increased by administration of insulin (II). Sugar appeared in the urine of four anaesthetised goats at (I)-levels of 130, 81, 112, and 115 mg., and had disappeared at 80, 67, 89, and 87 mg. per 100 c.c., respectively. Adrenaline (III) and intravenous injection of glucose cause increased (I) and depression of the serum-inorg. P (IV), as in the dog. A min. of 4 units of (II) per kg. of body-wt. is required to produce shock in goats; this shock occurs only after the (I) has been at 10—20 mg. per 100 c.c. for 5—8 hr. The (IV) is reduced by (III).

H. D.

Galactogen. Annual cycle in galactogen and glycogen contents of vineyard snails. F. MAY

(Z. Biol., 1934, 95, 401—430).—Galactogen (I) occurs only in the salivary gland (II) and glycogen (III) in all other organs. The proportions of (I) and (III) in the various organs after the winter period are directly related to nutrient conditions prior to hibernation. The increase in (I) during spring coincides with a decline in (III). The latter is again accumulated after (I) has reached max. val. A considerable amount of (I) is transferred from (II) to the eggs, and much of the reserve (III) is transformed into (I). A general enrichment in (I) and (III) follows egg laying. During hibernation (I) remains practically const. and (III) acts as a maintenance reserve.

A. G. P.

Fate of citric acid in the rabbit. H. LANGECKER (Biochem. Z., 1934, 273, 43—51).—Citric acid (I) is not destroyed to any significant extent in the rabbit's gastro-intestinal canal by bacterial action. Of the organs, particularly the liver, then the kidney, and to a small extent muscle are able to degrade (I), the reaction being enzymic, having a temp. optimum of 38°, occurring rapidly in presence and absence of PhMe, and being inhibited by HCN. Aq. extracts of liver and blood cannot attack (I). A method for determination of acetonedicarboxylic acid (II) in urine, milk, and organs is given. It was not possible to detect (II) as an intermediate product of the degradation of (I) by liver, and liver pulp is unable to accelerate the degradation of (II) in aq. solution. After administration of (II) to rabbits, considerable amounts appear in the urine. (II) could not, however, be detected in normal urine or milk.

P. W. C.

Relation of egg-yolk pigmentation to pimento feeds. W. L. BROWN (Georgia Agric. Exp. Sta. Bull., 1934, No. 183, 8 pp.).—A method is described for determining capsanthin (I) in yolks. (I) appears in yolks about 48 hr. after feeding, and is distributed throughout the yolk after about the sixth egg laid. The pigment is not affected by cold storage of eggs.

A. G. P.

Lipochrome metabolism of the horse. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1934, 226, 255—257).—About 70—80% of the carotene and 60% of the polyene alcohols in the fodder of horses are recovered in the faeces.

J. H. B.

Role of unsaturated fatty acids in nutrition. J. BECKER (Mezoz. Kutat., 1933, 6, 363—371; Chem. Zentr., 1934, i, 1998).—Administration of small amounts of Et₂O extract of ripe nuts [equiv. to 2—3 mg. of linoleic acid (I) daily] counteracted the decrease in live-wt. of rats receiving a fat-free diet. The vitamin-like action is attributed to (I) or to other unrecognised constituents.

A. G. P.

Vital need of the body for certain unsaturated fatty acids. IV. Reproduction and lactation on fat-free diets. V. Reproduction and lactation on diets containing saturated fatty acids as their sole source of energy. VI. Male sterility on fat-free diets. H. M. EVANS, S. LEPKOVSKY, and E. A. MURPHY (J. Biol. Chem., 1934, 106, 431—440, 441—444, 445—450).—IV. Addition of a mixture of linoleic (80%) and oleic acids (I), but not of carotene or of increased amounts of vitamin-A, -D, and -E, to

a fat-free diet (II) effected a marked improvement in reproductive abnormalities in rats. Lactation was possible on (II) together with (I) and increased amounts of all the known vitamins, but normal wt. at weaning was obtained only when 25% of lard or butter-fat was included in the diet.

V. Gestation is unsuccessful on diets with hydrogenated coconut oil as the source of energy, when the essential unsaturated fatty acids [(I), vitamin-F] are absent. Lactation is not normal even when all the known supplements are increased.

VI. Curative feeding of vitamin-A or of essential unsaturated fatty acids, after proved sterility supervening from deficiency in the particular vitamin, results in structural and functional restoration of fertility in male rats. Restoration is much more difficult after sterility due to vitamin-E deficiency.

A. E. O.

Absorption of milk precursors by the mammary gland. VI. Relation of phosphorus to the fat metabolism of lactation. J. H. BLACKWOOD (Biochem. J., 1934, 28, 1346—1354).—Jugular blood contains more lipin-P and less inorg. P than mammary blood, and these facts are independent of lactation. It cannot be concluded that phosphatide acts as fat-precursor during lactation. Inorg. blood-P (I) is significantly decreased during passage through the active mammary gland, and it appears that the P of milk is derived from (I). Lactation requires a high proportion of cholesterol and phospholipins in blood and plasma, the amounts falling until the non-lactating period is reached. I. A. P.

Nitrogen catabolism in invertebrates. I. The snail (*Helix pomatia*). E. BALDWIN and J. NEEDHAM (Biochem. J., 1934, 28, 1372—1392).—The hepatopancreas (I) of the snail contains arginase and xanthine-oxidase but no urease (II), but (II) was extracted in small quantities from the nephridia. Only 2.5% of the urica (III) excreted can be accounted for by the (III) present in the normal diet. Administration of arginine (V) increases the (III) excretion, but no definite evidence could be obtained that other NH_2 -acids (IV) acted as (III) precursors, although injection of (IV) tended to increase (III) excretion, especially if carbohydrate were administered simultaneously; this may, however, be explained as the result of diuresis. (V) is thus the most probable source of (III). Sections of (I) *in vitro* in presence of NH_3 synthesise uric acid.

W. O. K.

Tryptophan metabolism. VII. Growth and kynurenic acid production on amides of *l*-tryptophan. L. C. BAUGUEN and C. P. BERG (J. Biol. Chem., 1934, 106, 615—623).—*Tryptophan-amide*, m.p. 167—170°, $[\alpha]_D^{20}$ — 7.9°, *ethylamide*, m.p. 67—69°, $[\alpha]_D^{20}$ — 14.4°, *diethylamide*, m.p. 183—185°, $[\alpha]_D^{20}$ — 24.7°, *anilide*, m.p. 83—85°, $[\alpha]_D^{20}$ — 9.5°, and *N-ethylanilide*, m.p. 97—99°, $[\alpha]_D^{20}$ — 4.2° (all rotations in EtOH), prepared by treating tryptophyl chloride hydrochloride with the appropriate amine, undergo cleavage *in vivo*, supporting growth when fed to rats as a supplement to a tryptophan-deficient diet and being converted into kynurenic acid in the rabbit.

C. G. A.

Indole cycle in the organism. J. GARCIA-BLANCO and O. VIDAL (Anal. Fis. Quím., 1934, 32, 627—636).—Indican (I) excretion in a case of chronic indicanuria (II) was diminished considerably during digestion, and was not increased by ingestion of tryptophan (III). Rabbits excreted (I) in steadily increasing quantities in starvation, excretion disappearing on feeding; (III) caused slight increase. Indole (IV) injected in large quantities could be detected in the blood stream for 1—2 hr.; indoxyl (V) in small quantities was also present for 4—6 hr. after injection of (IV). Injection or feeding of (IV) produced intense (II). When injected in large quantities (IV) could be detected in the urine and bile. (V) injected as such was eliminated in a shorter period than when it originated from (IV). R. N. C.

Excretion of glyoxaline derivatives in mammalian urine. R. KAPPELLER-ADLER and H. KOHUT (Biochem. Z., 1934, 272, 341—347; cf. A., 1933, 1094).—*l*-Histidine (I) is completely degraded in the organism of pregnant and non-pregnant guinea-pigs (II), but in (II) poisoned with P the power to degrade is eventually lost and unchanged (I), in amounts increasing with the dose of P, appears in the urine.

W. McC.

Proteolysis in regenerating tissues. II. Activity of tissue proteases in different parts of the regenerated tissue. N. V. BROMLEY and V. N. ORECHOVITSCH (Biochem. Z., 1934, 272, 324—331).—The intensity of digestion in different zones of regenerated (I) and of stationary (II) tissue of tadpole tails by the glycerol extracts of the tails is the same. Cathepsin is, however, either present in greater amount or is more active in the adjacent tissues than in the rudimentary tissues of regeneration. The intensity of digestion of (II) of the axolotl by extracts of either the rudimentary or surrounding tissue is somewhat > that of the (II). With the axolotl the amount of desmocathepsin in (I) is > in (II), but of lyocathepsin is about the same.

P. W. C.

Photo-electric determination of p_{H} changes in muscle during contraction. R. MARGARIA and A. VON MURALT (Naturwiss., 1934, 22, 634).—Muscle fibres of the living frog may be stained with bromocresol-purple and bromophenol-blue. By the correct choice of the partial pressure of CO_2 , the indicator may be maintained at the p_{H} of its colour change. When the muscle contracts, the colour of the indicator changes towards the alkaline side. A photo-electric method for determining the p_{H} change is described.

A. J.

Water exchanges of living cells. II. Non-solvent volume determinations from swelling and analytical data. J. L. LEITCH (J. Cell. Comp. Physiol., 1934, 4, 457—473).—A correlation between high permeability to H_2O and high protein: fat ratio is indicated in sea-urchin eggs.

A. G. P.

Changes in carbon dioxide capacity and ionic changes during the development of trout eggs. L. IRVING and J. F. MANERY (J. Cell. Comp. Physiol., 1934, 4, 483—503).—With the development of the eggs there is associated an increase in the content of and capacity for CO_2 , an increased $[\text{HCO}_3^-]$, a decrease

in $[Cl^-]$, and probably an increase in other weak anions (possibly $PO_4^{'''}$ and protein). A. G. P.

Storage of halogens in hens' eggs and animal tissues. III. Fluorine. B. PURJESZ, L. BERKESSY, K. GONCZI, and M. KOVACS-OSKOLAS (Arch. exp. Path. Pharm., 1934, 176, 578—582; cf. this vol., 217).—Parenteral injection of NaF into hens results in storage of F in the eggs and liver and a transient appearance of F in the blood; traces occur in the brain shortly after injection. F is not found in normal human blood. Feeding of F-containing eggs to persons with thyroid diseases results in a fall of temp., pulse-rate, and basal metabolism and an increase in body-wt. F. O. H.

Effect of supplementary feeding with small amounts of iodine on the yield and hatchability of hens' eggs. A. ZAITSCHEK (Bied. Zentr. [Tierernähr.], 1934, B, 6, 102—111).—Addition of 0.114% of I (as KI) to the ration increased the yield and improved the hatchability of eggs without affecting the live-wt. of the hens. A. G. P.

Relation between function and iodine content of the thyroid gland. G. MANSFELD, L. SCHEFFER, and F. VON TYUKODY (Arch. exp. Path. Pharm., 1934, 176, 344—354).—The two lobes of dog's thyroid gland have the same I content (I) (averaging 0.141 and 0.151% of the dry wt., respectively). Extirpation of one lobe produces after 1—2 months an increase of > 100% in (I) of the other lobe; a similar effect occurs when the compensatory hyperplasia (II) is increased by administration of KI. Ingestion of 0.02—100 mg. of KI has no effect on (I). Diminution of (II) by thyroxine ingestion only slightly increases (I). An increase in (I) does not occur during starvation with or without administration of KI, but occurs when the activity of the thyroid gland is increased by thyrotropic hormone. F. O. H.

Cause of the rise in oxygen consumption of frog muscles in excess of potassium. A. H. HEGNAUER, W. O. FENN, and D. M. COBB (J. Cell. Comp. Physiol., 1934, 4, 505—526).—Muscle contraction occurs with 0.035—0.045% of K in Ringer's solution and is accompanied by an increased O_2 consumption and breakdown of phosphocreatine (I). Lactic acid (II) formation begins with 0.06% of K. Breakdown of (I) increases with rising $[K^+]$ up to 0.06%, but at higher concns. resynthesis is accelerated. O_2 consumption is controlled by (I) in presence of 0.04—0.06% K, and probably by (II) at higher $[K^+]$. A. G. P.

Distribution and mode of combination of muscle-calcium. E. WEISE (Arch. exp. Path. Pharm., 1934, 176, 367—377).—The total Ca content of rat's muscle (I) is 0.004—0.0073%. Ultra-filterable Ca is present in fatigued but not in resting (I). The uptake of Ca by minced (I) suspended in Ca-containing solutions depends mainly on a loose adsorption and, to a much smaller extent, on combination with proteins; the normal (I)-Ca probably occurs in the latter form. Neither the Ca level nor the adsorption of Ca by (I) is affected *in vitro* by adrenaline [injection of which into rats does not influence the (I)-Ca], caffeine, guanidine, or K^+ .

Parathyroids and the distribution of magnesium in rats. P. MOLINARI-TOSATTI and M. COPPO (Arch. exp. Path. Pharm., 1934, 176, 625—634).—The Mg content of the bones increases after thyroparathyroidectomy (I) or administration of parathyroid hormone (II); with (II) the brain-Mg also increases, whilst with (I) the muscle-Mg diminishes. Other slight or transient changes occur in the Mg levels of the lungs, liver, skin, spleen, kidney, and heart.

F. O. H.

Magnesium deficiency in animals. V. Changes in mineral metabolism of animals following magnesium deprivation. H. D. KRUSE, M. M. SCHMIDT, and E. V. MCCOLLUM. VI. Chemical changes in the bone, with associated blood changes resulting from magnesium deprivation. E. R. ORENT, H. D. KRUSE, and E. V. MCCOLLUM (J. Biol. Chem., 1934, 106, 553—572, 573—593).—V. During the first six weeks of Mg deficiency the Ca excretion is lowered, particularly in the faeces, but then progressively increases probably due to the nutritive failure (I) which occurs at the same time. The Mg excretion remains const. and low throughout. A progressive increase of N excretion is also probably due to (I). The absence of alkalosis is held to confirm the view that a distinct Mg tetany exists.

VI. Rats on a very low Mg diet have heavier bones (II) which contain a greater % of Ca than do those of normal animals (III). The accelerated growth of (II) occurs during the first 5 days and then becomes parallel with that of (III). The (II) accumulated Mg slowly but steadily over the whole period. Immediately prior to induced convulsions the Mg level of (II) falls and that of the blood rises. C. G. A.

Connexion between biological processes and weather. O. RIESSER and G. KUNZE (Naturwiss., 1934, 22, 653—656).—The effect of weather conditions (e.g., height of the barometer) on the P_2O_5 content of dog's muscle was investigated. A. J. M.

Metabolic changes produced by irradiation. XIII. Effect of irradiation with monochromatic light on blood-sugar and -lactic acid in rabbits. L. PINGUSSEN (Biochem. Z., 1934, 272, 354—356; cf. A., 1933, 1200).—The irradiation produces characteristic changes in the amounts of blood-sugar (I) and -lactic acid (II) and in the ratio (I) : (II) which increase or decrease according to the kind of light used (ultra-violet, blue, green, yellow, red, infrared). The changes are related to the extent to which the light is absorbed by skin and blood. W. McC.

Excretion of rectally absorbed essential oils. H. PAFFRATH and O. BENECKE (Arch. exp. Path. Pharm., 1934, 176, 558—562).—Thyme, cypress, and eucalyptus oils are rapidly absorbed from suppositories (cacao-butter). Only traces of oil are subsequently found in the urine, the greater part occurring in the expired air. F. O. H.

Toxicological determination of benzene. II. Determination in blood. M. PERONNET (J. Pharm. Chim., 1934, [viii], 20, 195—206).—The C_6H_6 is removed by a current of air and converted into $m-C_6H_4(NO_2)_2$, which is determined by the method previously described (cf. this vol., 1135). E. H. S.

Toxicological determination of benzene. III. Determination in various organs. M. PERONNET (J. Pharm. Chim., 1934, [viii], 20, 244—248; cf. preceding abstract).—The colour reaction between fructose and $m\text{-C}_6\text{H}_4(\text{NO}_2)_2$ is utilised, the error being 5% with 1 mg. of C_6H_6 in 150 g. of the organ.

H. G. R.

Absorption and excretion of certain resorcinols and cresols in dogs and man. B. H. ROBBINS (J. Pharm. Exp. Ther., 1934, 52, 54—60).—A colorimetric method for the determination of phenolic compounds (I) in the urine and faeces is described. Dibromobenzoquinonechloroimide (A., 1927, 688) is a satisfactory reagent for most (I) (except *p*-substituted), giving a blue colour in dilutions as high as 1:100,000. Hexylresorcinol, when given in 1-g. doses to man, is excreted in the urine (18%) and faeces (64%). With dogs, 6-hoxyl-*m*-cresol, given orally, is excreted in small amounts in urine and faeces; 6-decyl-*m*-cresol is not excreted in the urine; whilst thymol is excreted only in the urine (23—34%).

A. E. O.

Relative toxicity of chlorine derivatives of the aliphatic series. G. S. BARSOUM and K. SAAD (Quart. J. Pharm., 1934, 7, 205—214).—The toxicity of Cl-substituted derivatives of CH_4 , C_2H_6 , and C_2H_4 determined by administration orally and intravenously to dogs, subcutaneously to rabbits (I), and by application to isolated hearts from toads and (I) increases with the no. of Cl atoms up to CHCl_3 , $[\text{CHCl}_2]_2$, and $[\text{CCl}_2]_2$ in the three series, respectively. All the compounds are cardiac depressants. A. L.

Relation between the oxygen uptake of La Bourboule mineral waters (Choussy spring) and glycaemia of rabbits. R. CLOGNE and A. DRILHON (Bull. Acad. med., 1933, 110, ([3] 97), 85—88; Chem. Zentr., 1933, ii, 3868).—The decrease in glycaemia on injection of the fresh mineral H_2O (I) is attributed to O_2 dissolved in (I).

H. J. E.

Action of curative waters and salt solutions on exudate formation. Antipyretic action of Karlsbad mineral water. E. STRANSKY (Arch. exp. Path. Pharm., 1934, 176, 504—509).—The pleural exudate induced by aq. CuSO_4 (a criterion of pyretic action) in rabbits (I) is diminished by continuous drinking of Karlsbad H_2O (II). No significant change occurs in body-wt., serum-solids, sedimentation velocity of erythrocytes, or in protein and Ca levels of the exudate. The pyretic response of (I) has a seasonal variation which is not affected by (II). Ingestion of aq. SO_4^{--} -Tyrode preps. but not of aq. Na_2SO_4 , NaCl, etc. has an inhibitory action which, in (II), is mainly due to SO_4^{--} . F. O. H.

Action of curative waters on the composition of the blood. II. Serum-cations, -chloride, and -phosphate. III. Serum-colloids. E. STRANSKY (Arch. exp. Path. Pharm., 1934, 176, 510—522, 523—530; cf. A., 1933, 1199).—II. Rabbits on a hay+oats diet and drinking Karlsbad H_2O (I) experience a gain in body-wt. and dry wt. of the serum when compared with controls on H_2O . Similar effects occur with aq. SO_4^{--} and $\text{NaHCO}_3\text{-NaCl}$, respectively. (I) increases the blood-Ca and, less regularly, - K^+ and $-\text{PO}_4^{---}$; - Na^+ and $-\text{Cl}^-$ are un-

changed, whilst $-\text{Mg}^{++}$ diminishes. Equimol. aq. SO_4^{--} merely increases Ca, whilst aq. $\text{NaCl}+\text{NaHCO}_3$ is without action. (I) probably acts on the serum-Ca by complex formation.

III. The binding power or transport function of serum as indicated by trypan-blue or naphthol-yellow-S is increased by (I), whilst the sedimentation velocity of the erythrocytes tends to decrease. The total protein and albumin/globulin levels fluctuate considerably.

F. O. H.

Reversible coagulation in living tissue. XII. W. D. BANCROFT and J. E. RUTZLER, jun. (Proc. Nat. Acad. Sci., 1934, 20, 501—509).—The antagonism between NaCNS and Na amytal has been confirmed and the varying results of other workers are explained.

H. G. R.

Narcotics and brain oxidations. Reversibility of narcotic action *in vitro*. J. H. QUASTEL and A. H. M. WHEATLEY (Biochem. J., 1934, 28, 1521—1529).—The rate of uptake of O_2 by brain slices is reduced in presence of chlorotone, luminal, and hyoscine, but a steady low rate is established so that progressive poisoning does not take place. When the slices are washed in a PO_4^{---} -glucose-NaCl medium so as to remove the narcotic, recovery of cell oxidation takes place between 70 and 100%. Reversibility of action is also observed with mescaline and $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}_2$, but not with indole, which also inhibits cell oxidation.

W. O. K.

Acryl-amides and ureides as hypnotics. W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1934, 23, 788—793).—The following amides are prepared: furylacrylyl-, α -ethyl- β -propylacrylyl-, m.p. 66—67°, α -methyl-, m.p. 125.5—126° (lit. 128°), α -ethyl-, m.p. 135—137° (lit. 128°), α -isopropyl-, forms, m.p. 127—129° and 111—111.5°, α -amyl-, forms, m.p. 124—124.5° and 117°, *p*-methoxy- α -ethyl-, m.p. 170—170.5°, *o*-chloro- α -ethyl-, m.p. 93—94°, and β -methylcinnam-, and α -ethylcinnam-N-ethylamide, m.p. 99.5—100°. The following ureides are prepared: furyl-, m.p. 204—206°, and *n*-propyl-acrylic, m.p. 181—183°, sorbic, m.p. 226—228°, α -methyl-, m.p. 160—162°, α -ethyl-, m.p. 189—190.5°, α -propyl-, m.p. 184—186.5°, α -isopropyl-, m.p. 190—191°, and α -amylcinnamic, m.p. 158—159°. The min. hypnotic doses (usually very large) and (sometimes) min. lethal doses of these substances are recorded. Both series have low resorbability and the ureides undergo rapid intestinal hydrolysis. The furylacrylyl compounds are toxic and non-hypnotic.

R. S. C.

Barbiturates. IV. Effect of barbiturates in experimental nephrosis. W. S. MURPHY and T. KOPPANYI. V. Action of barbiturates in *Sauropsida*. T. KOPPANYI, W. S. MURPHY, and P. L. GRAY. VI. Elimination of ethylisocamylbarbituric acid ("amytal") and ethyl-*n*-butylbarbituric acid ("neonal"). T. KOPPANYI and S. KROP. VII. Experimental analysis of barbital action. T. KOPPANYI and J. M. DILLE (J. Pharm. Exp. Ther., 1934, 52, 70—77, 78—86, 87—90, 91—100).—IV. Nephrotic animals failed to recover from the anaesthesia following administration of barbital (I), but not of other barbiturates which, unlike (I), are not largely eliminated by the kidneys.

V. Unlike mammals, fowls and turtles excrete (I) slowly, the concn. of (I) in the urine being low; they retain (I) in the blood and organs. Other barbituric acid derivatives are more rapidly disposed of in fowls than in mammals.

VI. The fact that about 8% of the administered dose of neonal (II) and amytal (III) is excreted in the urine may be utilised in the diagnosis of poisoning by (II) and (III). Phenylbutyl- and isobutylallyl-barbituric acid are eliminated in the urine only in negligible amounts.

VII. Rabbits receiving daily doses of (I), although showing a lag in excretion, acquire the ability to oxidise (I), since there is no cumulative effect. In cats and dogs, the profound depression after max. excretion of (I) is due to retention of (I) by the brain cells.

A. E. O.

Depressor substances in extracts of the intestinal mucosa. Purification of entero-gastrone. R. K. S. LIM, S. M. LING, and A. C. LIU (Chinese J. Physiol., 1934, 8, 219—236).—The yield of the gastric inhibitory agent has been doubled by extracting mucosa containing 3% of picric acid with EtOH-HCl. The depressor substance (I) which is probably 5—10% histamine, together with the Euler-Gaddum and Felix-Lange substance, is also increased. Removal of (I) is described. H. G. R.

Comparative effects of the intravenous administration to man of acetylcholine and acetyl- β -methylcholine. S. WEISS and L. B. ELLIS (J. Pharm. Exp. Ther., 1934, 52, 113—120).—The general and cardiovascular responses in normal human subjects to the continuous intravenous infusion of acetylcholine (I) and acetyl- β -methylcholine (II) are similar, the velocity of the blood flow remaining essentially unchanged, and no evidence of cumulative action being observed. (II) is about 200 times as potent as (I).

A. E. O.

Physiological properties of certain N-methylated β -phenylethylamines. A. M. HJORT (J. Pharm. Exp. Ther., 1934, 52, 101—112).—The introduction of OMe or O_2CH_2 enhances the toxicity and diminishes the pressor effects of $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NHMe}$ (I). Introduction of phenolic OH into (I) usually decreases the toxicity, the 3-OH- and 3:4-(OH) $_2$ -derivatives being the least toxic and most effective pressor agents of their respective groups, whilst the most toxic derivatives are those substituted in the 2 or 2:5 positions. Isolated smooth muscle is stimulated by all the OAlk- and OH-derivatives of (I) tested. The only purely neurotropic pressor agents are the 3- and 4-OH- and 2:5-(OMe) $_2$ -derivatives (II) [but not the 2:5-(OH) $_2$ -derivative on account of its instability]. Introduction of two OH *o*- to each other does not always result in sympathicotonic activity (III) nor is the pyrocatechol group essential for (III), since (II) possesses (III).

A. E. O.

Sulphæmoglobinæmia. J. C. HEALY (J. Lab. Clin. Med., 1933, 18, 348—353).—Use of NH_4AcPh or acetophenetidide and exposure to NH_2Ph are etiological factors. In presence of NH_2Ph derivatives sulphæmoglobin (I) is formed by interaction of hæmoglobin with H_2S ; if H_2S is not present in the blood, methæmoglobin (II) is formed. The O_2 -

carrying capacity of the blood in sulphæmoglobinæmia is normal or increased. Inhalation of O_2 and CO_2 and ingestion of NH_4Cl cause disappearance of (I). Differentiation of (I) and (II) in presence of one another is described.

CH. ABS.

Influence of drugs on the cerebral control of antibody-formation. E. KRAMER (Arch. exp. Path. Pharm., 1934, 176, 401—407).—The formation of antibody in rabbits is significantly affected by injection of pyrimidone but not by that of nicotine, adrenaline, pilocarpine, an ergot prep., or cocaine.

F. O. H.

Placental permeability to toxic and medicinal substances. III. Caffeine. R. FABRE and M. T. REGNIER (J. Pharm. Chim., 1934, [viii], 20, 193—195).—The distribution of caffeine in the organs of the rabbit and dog after subcutaneous injection was examined. Considerable amounts were found in the placenta.

E. H. S.

Pharmacological action of some members of the tropane group. II. G. S. R. RAO (Quart. J. Pharm., 1934, 7, 227—236).—1-Methyltropine (I) and 1-methyltropacocaine (II) have min. lethal doses for mice by intraperitoneal injection of 0.47 and 1.10 g. per kg., respectively. Their effect on the nervous system is similar to that of tropacocaine (III). (II) has a local anæsthetic action lasting twice as long as that of (III). Both (I) and (II) depress respiration in rabbits and cats, weaken the contraction of isolated intestine, and stimulate the rabbit's, but relax the cat's, uterus.

A. L.

Destruction of cocaine and atropine in the animal body. H. A. OELKERS and W. RAETZ (Klin. Woch., 1933, 12, 1985—1986; Chem. Zentr., 1934, i, 2002).—The rate of decomp. of cocaine and atropine in mice corresponds with the rates of hydrolysis in borate buffer solutions of p_H 7.4—7.5 at 38°. There is no evidence of the existence of sp. enzymes.

A. G. P.

Ergoclavine, a new ergot principle. H. KREITMAIR (Arch. exp. Path. Pharm., 1934, 176, 171—180).—No quant. or qual. distinction exists between the pharmacological properties of ergotoxin, ergotamine, and ergoclavine (this vol., 669).

F. O. H.

Comparative pharmacology of lobeline alkaloids. V. V. SAKUSSOV (Arch. exp. Path. Pharm., 1934, 176, 468—477).—Norlobeline, lobelan, lobelamine, and lobelanidine resemble, but are inferior to, lobeline in their action on the respiratory centre of the cat. Large doses of each alkaloid have a depressor action.

F. O. H.

Physiology and pharmacology of sleep. II. Influence of autonomic poisons. H. DOST (Arch. exp. Path. Pharm., 1934, 176, 478—485).—*apo*-Morphine and, to a smaller extent, picrotoxin induce sleep in canaries. Tetrahydro- β -naphthylamine does not produce the motor and mental stimulation as with other animals, but gives a typical "sleep-curve." Intramuscular injection of ergotamine or eserine induces sleep, as do large doses (0.5—2.0 mg.) of ephedrine or atropine, small doses (0.01—0.5 mg.) of which merely stimulate. The soporific action of insulin is probably of peripheral origin.

F. O. H.

Saliva tests. I. Morphine. J. C. MUNCH (J. Amer. Pharm. Assoc., 1934, **23**, 766—774).—Morphine (I) in the saliva of horses can be detected by the mouse-tail reaction 15—30 min. after administration. 0.0125 mg. of (I) can thus be determined within 5%.

R. S. C.

Evaluation of substances paralysing the stomach and intestines. E. HESSE and G. ZIMMERMANN (Klin. Woch., 1933, **12**, 1986—1988; Chem. Zentr., 1934, i, 2012).—Action of atropine sulphate, syntropine, papaverine hydrochloride, isoquinoline derivatives, and methyloctenylamine in mice is parallel to that in man. Relative activities of the substances are in the order named.

A. G. P.

Diuresis. V. Pituitary and mid-brain in the regulation of water-threshold. S. G. WEINBERG and H. MARX (Arch. exp. Path. Pharm., 1934, **176**, 291—305).—Injection of stimulants (e.g., yohimbine) into the lateral cerebral ventricles of dogs produces no spontaneous or increased diuresis; that of hypo- or hyper-tonic aq. NaCl has a marked antidiuretic action (I), the urinary N and NaCl increasing. With posterior pituitary preps., intraventricular and intravenous administration produce similar effects, which are characterised by high urinary N and NaCl, respectively; the former route gives results which are completely inhibited by "phanodorm" narcosis. The sensitivity of dogs to (I) is considerably increased by continued dosage.

F. O. H.

Assay of *Strophanthus* preparations by the cat method. A. D. MACDONALD (Quart. J. Pharm., 1934, **7**, 182—191).—In the assay of *Strophanthus* by the cat method the toxicity vals. vary less when chloralose or dial is substituted for the Et₂O anaesthetic, and the use of spinal cats further improves the accuracy of determination. The interval between the prep. of the cat and the infusion should be about 4 hr.

A. L.

Biological evaluation of differently prepared infusions of *Digitalis* leaves. A. SARMO (Pharmacia, 1933, **13**, 175—183; Chem. Zentr., 1934, i, 1838).—Various methods of filtration etc. of extracts had no appreciable influence on the resulting concn. (frog injection). Vals. were approx. 59% of those of abs. EtOH extracts.

A. G. P.

Action of *Digitalis* glucosides on pigeons suffering from beri-beri. J. MEHES (Arch. exp. Path. Pharm., 1934, **176**, 141—159).—The response of pigeons to the emetic action of digitoxin, digitalin, tinctures of *Digitalis*, and strophanthin (I) is markedly decreased with the incidence of beri-beri; excepting with (I), where an increase occurs, the toxic action in the heart is also diminished. The abnormality, which is not influenced by starvation and is rapidly corr. by a vitamin-B-rich diet, is probably due to an impaired reflex sensitivity.

F. O. H.

Accumulation of *Digitalis* glucosides. H. WEESE and J. DIECKHOFF (Arch. exp. Path. Pharm., 1934, **176**, 274—282).—Administration of therapeutic doses of digitoxin (I) to cats increases for a period of up to 3 days the work-performance (II), the resistance to fatigue, and the survival period of the heart. With excessive doses, (II) decreases, degeneration of the cardiac muscle producing a diminution in conduction.

The cumulative action of (I) is due to a storage in the heart (which occurs in cats but not dogs or rabbits) and a subsequent delayed poisoning.

F. O. H.

Pharmacological and toxic action of digoxin. A. C. WHITE (J. Pharm. Exp. Ther., 1934, **52**, 1—22).—Digoxin (I) possesses the general characteristics of the *Digitalis* group of cardiac glucosides, its toxicity being about $\frac{1}{3}$ that of ouabain (II). In the guinea-pig, about 3 times as much (I) is required to cause 50% mortality when given orally as when given intramuscularly. (I), (II), and digitoxin all produce cumulative effects.

A. E. O.

Significance of phosphatide-lipo-proteins from the pharmaceutical-chemical and toxicological viewpoint. J. ORIENT (Curierul farmac., 1933, **3**, No. 6, 9—12; Chem. Zentr., 1933, ii, 3877).—CHCl₃, salvarsan, and CH₂O are held in relatively large amounts and PhOH, caffeine, HCN, and adrenaline in smaller amounts by the phosphatide proteins.

H. J. E.

Pectin the principal active agent in apple diet. G. MALYOTH (Klin. Woch., 1934, **13**, 51—54; Chem. Zentr., 1934, i, 1833).—The action of pectin is associated with its physico-chemical properties.

Significance of glutathione and other substances containing -SH and -S-S- groups. H. SCHREIBER (Med. Welt, 1933, **7**, 813—814; Chem. Zentr., 1934, i, 1886).—The importance of glutathione in indirect detoxication in the organism results from its action as catalyst in oxidation-reduction processes and as activator of the protein metabolism of the cell.

A. G. P.

Action of cystine on the toxicity of antimony. L. LAUNOY (Compt. rend., 1934, **199**, 646—648). Toxicity data for cystine (I), Sb thiomalate (II), and mixtures of (I) and (II) with respect to mice are given. 1 mg. of (I) counteracts the effect of 0.1 mg. of (II).

R. S.

Toxicity of naturally-occurring arsenic in foods. E. J. COULSON, R. E. REMINGTON, and K. M. LYNCH (Science, 1934, **80**, 230—231).—Experiments with rats fed on diets containing different amounts of As derived from shrimps and from added As₂O₃ show that there is a difference in the metabolism of the As occurring in shrimp compared with the inorg. As. Only a small % of the former is absorbed and stored in the animal body when such foods are eaten.

L. S. T.

Analysis in arsine poisoning. R. THAUER (Arch. exp. Path. Pharm., 1934, **176**, 531—549).—Following inhalation of AsH₃ by rabbits, dogs, and cats, As occurs in the non-haemolysed blood corpuscles but not in the plasma. Methaemoglobin formation is detectable. The As content of the organs is relatively low, the highest occurring in the spleen (from blood degradation), liver, and kidney. Rapid excretion of As occurs, mainly in the urine. Various species of animals show differences in susceptibility to As₂S₃ poisoning.

O.

Toxicity of cadmium to chewing. J. M. GINSBERG (Science, 1934, **80**, 269).—Cd s are toxic to the tent caterpillar, silk-moth caterp

and confused flour beetle. CdO and $\text{Cd}(\text{OH})_2$ compare well with Pb arsenate. L. S. T.

Lead content of blood in experimental lead poisoning with especial regard to age. M. KASAHARA and K. ARIMICHI (*Z. ges. exp. Med.*, 1934, 92, 629—630; *Chem. Zentr.*, 1934, i, 1520).—After injection of equal amounts of $\text{Pb}(\text{OAc})_2$ per kg. body-wt., the Pb content of blood is less in adult than in young rabbits. L. S. T.

Lead poisoning in children. T. S. RODGERS, J. R. S. PECK, and M. H. JUPE (*Lancet*, 1934, 227, 129—133).—The action of Pb and its effects on the human body are described. L. S. T.

Mercury content of human blood and excreta. A. STOCK and F. CUCUEL (*Angew. Chem.*, 1934, 47, 641—647).—The faeces (I) and urine (II) of men free from contact with Hg [e.g., amalgam dental stoppings (III)] contained $0.25\text{--}3.3 \times 10^{-6}$ and $0.5\text{--}1.0 \times 10^{-7}\%$, respectively. These vals. were increased (approx. $\times 10$) in men with (III) and, to a greater extent, in glass workers etc. The blood- Hg (normally up to $7 \times 10^{-7}\%$) followed a parallel course. Ingested HgCl_2 (0.2 mg.) was excreted over a period of 8 days, approx. 0.1 mg. occurring in both (I) and (II), the distribution of Hg in (I) being more regular than that in (II). F. O. H.

Toxicity of anions (oxalate) and cations (barium) and their detoxication. I, II. S. HERMANN [with M. ZENTNER and T. BUTSCHOWITZ] (*Arch. exp. Path. Pharm.*, 1934, 176, 591—598, 599—608).—I. The variations in the toxicity of $\text{Na}_2\text{C}_2\text{O}_4$ to rabbits (I) is due to differences (both individual and seasonal) in the blood- Ca . The toxic action of $\text{Na}_2\text{C}_2\text{O}_4$ on the heart is readily inhibited by Ca in frogs, but not in (I). The extent and nature of $\text{H}_2\text{C}_2\text{O}_4$ detoxication in (I) and the antagonism to $\text{H}_2\text{C}_2\text{O}_4$ of BaCl_2 , *Digitalis* and *Strophanthus* preps., and cholesterol contra-indicate a simple $\text{Ca}\text{--}\text{H}_2\text{C}_2\text{O}_4$ antagonism.

II. The BaCl_2 -poisoned frog's heart recovers on treatment with Na_2SO_4 , but not with CaSO_4 or Na_2HPO_4 . Orally and, to a much smaller extent, parenterally administered Na_2SO_4 detoxicate subcutaneously injected BaCl_2 in (I). That ingested CaCl_2 detoxifies BaCl_2 indicates that the efficacy of Na_2SO_4 etc. is due to their action on the blood- Ca ; the synergism of BaCl_2 poisoning in (I) by NaHCO_3 is similarly explained. F. O. H.

Detection of hydrocyanic acid in cadavers in cases of poisoning. O. SCHMIDT (*Deut. Z. ges. gerichtl. Med.*, 1933, 21, 334—336; *Chem. Zentr.*, 1933, ii, 3735).—The red colour produced by KCNS with Fe^{III} salts is used. H. J. E.

Hofmeister series in smooth muscle. E. GELLHORN and L. F. MOLDAVSKY (*Protoplasma*, 1934, 21, 270—278).—The ability of Na salts to restore automaticity to smooth muscle is in accordance with the position of the anions in the Hofmeister series, the effects being observed at const. p_{H} . A. G. P.

Physical chemistry of resorption. P. J. JURISIC (*Protoplasma*, 1934, 21, 500—510).—The osmotic polarity shown by frog skin is examined. A. G. P.

Irreciprocal permeability [of frog skin]. P. J. JURISIC (*Protoplasma*, 1934, 21, 511—521).—Surviving frog skin loses its irreciprocal permeability (I) to acid dyes at low hydrostatic pressures, and all diffusible dyes, irrespective of their chemical nature, pass more readily from the internal to the external side than in the reverse direction. The property of (I) is lost at death. A. G. P.

Oxygen-carrying enzymes in respiring cells. O. WARBURG (*Chem. Weekblad*, 1934, 31, 538—543).—A lecture. S. C.

Effect of high-frequency sound waves on oxidase activity. R. J. CHRISTENSEN and R. SAMISCH (*Plant Physiol.*, 1934, 9, 385—386).—Exposure of fruit extracts to high-frequency sound radiation (450,000 cycles) caused marked reduction in oxidase activity, which decreased logarithmically with time of exposure. A. G. P.

Components of the dehydrase system. I. Dehydrogenation of alcohol and Robison-ester. H. VON EULER and E. ADLER (*Z. physiol. Chem.*, 1934, 226, 195—212).—A colourless dehydrase, the flavin enzyme (I), and cozymase (II) all participate in the dehydrogenation of EtOH by yeast extract. In the yeast-enzyme system which dehydrogenates Robison-ester, (I) and (II) are also active. J. H. B.

Specificity of fumarase and enzymic equilibrium. K. P. JACOBSON and A. DA CRUZ (Ber., 1934, 67, [B], 1481—1485).—The results of Ionescu *et al.* (this vol., 927) are directed against von Euler's method of calculating the data of Bourquelot (*J. Pharm. Chim.*, 1914, [vii], 10, 361), but do not refute von Euler's hypothesis of enzymic equilibria, which is supported by observations of the rate of change of fumaric (I) and *l*-malic (II) acid in presence of fumarase (III). The affinity of (III) for (I) appears twice as great as for (II). H. W.

Reversible dehydrogenase systems. II. Reversibility of xanthine-oxidase systems. D. E. GREEN (*Biochem. J.*, 1934, 28, 1550—1560).—The reversibility of the xanthine-oxidase (I) system involving the reactions hypoxanthine (II)—xanthine (III), (III)—uric acid (IV), and (II)—(IV) has been demonstrated colorimetrically and potentiometrically. The theory of two-step oxidation involving two eqivs. at each step is given. The system (II)—(IV) in presence of (I) behaves in accordance with the results predicted by this theory. The prediction of the anaerobic formation of (IV) and (II) from (III) and the partial formation of (III) from (II) and (IV) in presence of (I) has been confirmed. E_0' of (II)—(III) is -0.371 volt at p_{H} 7.0 and for (III)—(IV) is -0.361 volt. W. O. K.

Nature of the action of tyrosinase. C. E. M. PUGH (*Biochem. J.*, 1934, 28, 1693—1697).—The enhanced reduction of methylene-blue by pyrocatechol or *p*-cresol + glycine in presence of tyrosinase (McCance, A., 1926, 203) has been confirmed, but its interpretation as due to activation of H in the substrate is still uncertain. C. G. A.

Activity- p_{H} curve of alanine-deaminase. N. NEUENSCHWANDER-LEMMER and F. VON LEOVEY

(Biochem. Z., 1934, 272, 380—383).—The deaminase of rat kidney readily deaminates *D*-alanine ($\log K = -1.65$) and *DL*-alanine ($\log K = -1.80$), but affects *L*-alanine scarcely or not at all. W. McC.

Carboxylase models. IV.—See this vol., 1229.

Amylases in resting and germinating seeds. IV. Wheat. T. STENSTAM, C. O. BJÖRLING, and E. ÖHLSSON (Z. physiol. Chem., 1934, 226, 265—271; cf. A., 1933, 1343).—The p_H optimum for the saccharogen- (I) and dextrinogen-amylase (II) of wheat is 4 and 5.5, respectively. The activity of (II) in ungerminated wheat is much > in other cereals. The amylases of wheat correspond completely with those of other cereals. The total effect of (I) and (II) when present together is roughly the sum of their separate effects. J. H. B.

Inactivation of amylase by adsorption on protein precipitates. A. OPARIN, S. MANSKAJA, and I. GLASUNOV (Biochem. Z., 1934, 272, 317—323; cf. A., 1933, 1202).—The activity of amylase (I) solutions is reduced by addition of pptd. protein [ovalbumin pptd. by tannin (II)]. Peptone and ovalbumin prevent the inactivation and regenerate the activity if suppressed because they dissolve (I). The degree of inactivation \propto the ratio of dissolved to pptd. protein. If the pptn. takes place at a low temp. the adsorbed (I) remains inactive on drying. The effect of (II) is reduced by boiling prior to the pptn. Nucleic acid acts like (II), but activity is restored and (I) removed from the adsorbent at $p_H \approx 4.1$. W. McC.

Action of papain on the amylase of grain. T. CHRZASZCZ and J. JANICKI (Biochem. Z., 1934, 272, 402—411; cf. A., 1933, 1343).—The activity of the amylase (I) of barley, rye, and wheat, and to a smaller extent that of (I) of oats, buckwheat, and maize, is increased by active papain (II) and, less extensively, by heat-inactivated (II), the saccharifying effect being most powerfully influenced. The starch-liquefying power is less affected and the dextrin-forming power least of all. (II) reduces the activity of (I) of millet because sisto-substances are produced. Active (II) contains no kinase; it acts by producing more (I) or liberating (I) which is bound to protein, physico-chemical factors being also involved. W. McC.

Hydrolysis of starch by enzymes in the malt of cholam (*Sorghum vulgare*). C. N. ACHARYA (Indian J. Agric. Sci., 1934, 4, 476—536).—Active maltase (I) occurs in both malted (II) and unmalted cholam (III) in concns. > those in barley. (I) in (II) is slightly sol. and that in (III) insol. in H_2O . The optimum reaction and temp. of (I) in cholam are p_H 4.2 and 48°, respectively, hence resembling (I) of maize and barley. $PhMe$, $CHCl_3$, CH_2O , asparagine, and emulsin have no action on (I), whilst glycine, pepsin, and diastase accelerate, and alcohols (excepting mannitol) and aspartic acid retard, hydrolysis by (I). Destruction of (I) by heat was investigated. A study of the liquefying (IV) and saccharifying properties (V) of the diastases from cholam and barley malts indicates differences in temp. and p_H optima, heat-resistance, etc. Both produce glucose on heating to 60° and then reacting with starch (cf. A., 1923, i, 1162). Each diastase contains α -[having mainly (IV) but also

some (V) and hydrolysing amylopectins to erythro- and achroo-dextrins and maltose] and β -amylase (hydrolysing amyloses to maltose and dextrins), which can be separated by heating at 62—63° or keeping at 0° at p_H 3.2, respectively. Differences in the two diastases are due to different contents of α - and β -amylase. F. O. H.

Occurrence of maltase and invertase in *Schizosaccharomyces octosporus*. Separation of the enzymes. E. HOFMANN (Biochem. Z., 1934, 272, 417—425; cf. Weidenhagen, A., 1931, 1331).—The fungus (I) contains maltase (II) and invertase (III). Solutions from fresh (I) contain (II), but not (III), which remains in the insol. residue. Solutions from dried autolysed (I) hydrolyse first maltose and then sucrose. The optimum p_H for (II) is 4.7, that for (III) 5.6. The results are not in accord with Weidenhagen's theory. W. McC.

Influence of native proteins on activity of yeast invertase. J. M. NELSON and E. L. SAUL (J. Amer. Chem. Soc., 1934, 56, 1994—1998).—Hydrolysis of sucrose by purified invertase (I) is accelerated by undenatured ovalbumin, edestin (II), pepsin, globin, and ox-serum (III) at $p_H < 4.5$; the denatured proteins, gelatin, gum arabic, glycylglycine, and tryptophan have no influence at p_H 3. Several crude solutions of (I) are unaffected by (II) and (III). H. B.

Specific elution of enzymes. E. G. KRITSCHEVSKAJA (Biochem. Z., 1934, 272, 348—353).—The flowers and leaves of *Convallaria majalis* contain invertase (I), maltase (II), lactase (III), and β -glucosidase (IV), which are adsorbed by $Al(OH)_3$, $Fe(OH)_3$, and $UO_2(OAc)_2$, the adsorbed material remaining active. Elution with NaH_2PO_4 , Na_2HPO_4 , dil. aq. NH_3 , and aq. Na_2CO_3 does not effect separation of the enzymes, but (I), (II), and (IV) are removed by elution with their respective substrates (V), the actions being sp. (I) and (II) adsorbed on charcoal (VI) retain their activity, but cannot be removed by elution with (V). (III) and (IV) on (VI) are inactive. W. McC.

Emulsins of plants. E. HOFMANN (Biochem. Z., 1934, 272, 426—429; cf. this vol., 328).—The seeds of the cherry contain much β -glucosidase (I) and little β -galactosidase (II), those of the mandarin orange much (II) and little (I), and those of the soya bean (II) but not (I). W. McC.

Emulsin. XIV. Enzymic fission of amino-glucosides. B. HELFERICH, A. ILOFF, and H. STREECK. XV. Fission of cresolglucosides and homogeneity of glucosidases of different origin. B. HELFERICH and H. SCHEIBER (Z. physiol. Chem., 1934, 226, 258—264, 272—280; cf. this vol., 59).—With Na and $PhOH$. acetobromoglucosamine hydrochloride affords phenol- β -*D*-glucosaminide 3 : 4 : 6-triacetate (I) [hydrochloride, decomp. 210—240, $[\alpha]_D^{20}$ — 19.2° in $MeOH$; acetate (II)]. With Ac_2O in C_6H_5N , (II) gives phenol- β -*D*-glucosaminide tetraacetate (III). Hydrolysis of (I) with *N*- $NaOH$ yields phenol- β -*D*-glucosaminide (IV), m.p. 167.5—170, $[\alpha]_D^{20}$ — 86° in H_2O . With liquid NH_3 , phenol- β -*D*-glucoside-6-bromohydrin affords phenol-6-amino- β -*D*-glucoside (V), m.p. 176—178°, $[\alpha]_D^{20}$ — 66.2° in H_2O (hydrochloride). With Ac_2O in C_5H_5N , (V) gives 6-amino-

phenol-β-d-glucoside tetra-acetate, m.p. 129—130°, $[\alpha]_D^{25}$ -28.1° in C_6H_6 , -18.3° in $CHCl_3$, which on hydrolysis gives *6-acetamidophenol-β-d-glucoside* (VI), m.p. 228—236°, $[\alpha]_D^{25}$ -73.3° in H_2O . (IV) is resistant to emulsin, but both (V) and (VI) are hydrolysed, (V) much more slowly than (VI). Thus NH_2 has an inhibitory, and $NHAc$ a favourable, effect which is in the 6- < in the 2-position.

XV. The following derivatives of *o*- and *p*-cresol-hexosides were prepared by hydrolysis of the Ac_4 derivatives: *o*-, m.p. 163—164.5°, $[\alpha]_D^{25}$ -68.7° in H_2O , and *p*-cresol-β-d-glucoside, m.p. 170—179.5°, $[\alpha]_D^{25}$ -67.7° in H_2O ; *o*-, m.p. 193—195.5°, $[\alpha]_D^{25}$ -43.5° in H_2O , and *p*-cresol-β-d-galactoside, m.p. 158—161°, $[\alpha]_D^{25}$ -42.1° in H_2O . 2:6-Xylenol-β-d-glucoside tetra-acetate, m.p. 140—142°, $[\alpha]_D^{25}$ -11.18° in $CHCl_3$ (from *m*-3-xylenol and glucose β-penta-acetate), gave 2:6-xylenol-β-d-glucoside (I), m.p. 209—211°, $[\alpha]_D^{25}$ -15.4° in H_2O . The *o*-cresol derivatives were very readily hydrolysed by sweet almond emulsin (II), whilst the *p*-derivatives and (I) were comparable with $PhOH$ compounds. Thus one *o*-Me group is responsible for quick fission. The rates of fission by acids are not in agreement with the enzymic fission. The enhanced velocity of hydrolysis of the *o*-cresol derivatives is not shown with lucerne emulsins (III). The optimum pH for (II) is 5 and for (III) 4. All m.p. are corr. throughout.

J. H. B.

Enzymic hydrolysis of cellobionic acid. C. ANTONIANI (Biochem. Z., 1934, 273, 219—222).—Tables show the considerable degree of hydrolysis of cellobionic acid (Ba salt) with emulsin and with takadiastase.

P. W. C.

Enzymic hydrolysis of cellobiosecarboxylic acid. C. CATTANEO (Biochem. Z., 1934, 272, 430—433).—The acid (Ba salt, $[\alpha]_D^{25} + 3.87^\circ$) is not hydrolysed by takadiastase or *Saccharomyces fragilis*, but is (to the extent of 5—6%) by emulsin and malt extract (70—90%).

W. McC.

Effect of carotene on glycolysis in muscle. C. FRISCH and R. WILLHEIM (Biochem. Z., 1934, 272, 332—336; cf. A., 1932, 1278).—Glycolysis in muscle extracts, freed from co-enzyme by dialysis and reactivated with muscle, liver, or yeast extract, is increased by addition of carotene, which also counteracts the inhibitory effect of added quinone.

W. McC.

Effect of carotene on glycolysis in tumours. C. FRISCH and R. WILLHEIM (Biochem. Z., 1934, 272, 337—340).—Although glycolysis (I) in systems inactivated by dialysis and reactivated by muscle or yeast extracts (II) is increased by addition of carotene, a decrease occurs if extract of tumour (III) or a mixture of it with (II) replaces (II). (III) lacks some inhibitory oxidising factor present in (II) and contains some factor which inhibits (I).

W. McC.

Lysocithin-forming pancreatic lecithase. S. BELFANTI and C. ARNAUDI (Arch. ital. Biol., 1933, 88, 157—165; Chem. Zentr., 1933, ii, 3706).—Active substance is pptd. from the aq. extract of horse pancreas with $EtOH$. The decomp. of lecithin from various sources has been examined. The optimum temp. was 37°, the optimum pH being 6.8—7.0. The enzyme was destroyed at 58—60°.

H. J. E.

Tyndallometric method for measurement of lipase action. E. HERZFELD (Mikrochem., 1934, 15, 227—232).—The lipase prep. is progressively diluted with 1% aq. $NaHCO_3$, and added to an emulsion of tributyrin (I) stabilised by gum arabic. The solution halving the Tyndall effect of (I) in 1 hr. at room temp. contains approx. 0.0002 mg. of lipase.

J. S. A.

Depression of serum-lipase by thyroxine and its prevention. I. J. BAUER and M. H. HOFFMAN.

II. **Stoppage of the reticulo-endothelial system.** G. DELL'ACQUA and W. STRAUSS (Klin. Woch., 1933, 12, 1933—1934, 1935; Chem. Zentr., 1934, i, 1344).—I. Subcutaneous injection of thyroxine (I) in rabbits causes a fall in the serum-lipase. Previous treatment with lipin extract from serum or olive oil (less effective) prevents this action of (I).

II. When the reticulo-endothelial system is blocked with trypan-blue, injection of (I) in rabbits again causes a fall in the serum-lipase.

H. J. E.

Lipolysis as a source of mitogenetic radiation.

A. D. BRAUN (Nature, 1934, 134, 536).—Spectrum analysis of the splitting of monobutyrin by pancreatic lipase gives a spectrum which has no components coincident with the known spectra of fermentation. Tributyrin, triolein, and castor oil emit secondary radiation when irradiated by the monobutyrin system.

L. S. T.

Mitogenetic radiation of the urea-urease system. E. G. PROKOFIEVA (Nature, 1934, 134, 574).—The spectrum of the mitogenetic radiation produced in this system is recorded. All substrates, including urea, subject to enzymic disintegration can emit secondary radiation when irradiated by mitogenetic rays.

L. S. T.

Manometric micro-determination of arginase.

Enzymic study of blood-arginase in rats. L. WEIL and M. A. RUSSELL (J. Biol. Chem., 1934, 106, 505—513).—Urea (I) formed from arginine by the action of arginase is decomposed by urease and the resulting CO_2 measured in the Warburg apparatus. A unit for blood-arginase (II) is defined. Mature male rats tend to possess a higher (II) content than young or castrated male rats, or female rats. No parallelism was found between (II) and blood-(I) content.

A. E. O.

Effect of ascorbic acid on arginase action.

S. EDLBACHER and F. LEUTHARDT (Klin. Woch., 1933, 12, 1843; Chem. Zentr., 1934, i, 725).—Ascorbic acid (I) alone does not activate arginase, but in presence of Cu its action is increased up to 30—50%. Under anaerobic conditions the increase is much less. The action of (I) is due possibly to its O_2 -combining power. In neutral solution the Cu-(I) mixture has a strong inhibiting effect on urease.

L. S. T.

Zymogens of pepsin and rennin. I. S. KLEINER and H. TAUBER (J. Biol. Chem., 1934, 106, 501—504; cf. A., 1932, 881; 1933, 1203).—Contrary to the results of Ege and Lundsteen (this vol., 450), pro-rennin (I) solutions can be freed from preformed rennet activity, either by keeping the carefully neutralised extract under $PhMe$ at 37° for 3—4 days, or by adjusting to pH 9.2, heating at 24° for 40 min.,

and finally neutralising to p_H 7. (I) becomes completely active at p_H 3.6, propepsin (pepsinogen) at p_H 1.6, but partial activation of either may occur in more acid solutions. A. E. O.

Proteolytic enzyme content of latex from fig and related trees. B. H. ROBBINS and P. D. LAMSON (J. Biol. Chem., 1934, 106, 725—728; cf. A., 1930, 1066).—None of the saps of 17 species of the family *Moraceae* from Cuba possessed proteolytic activity (I). Saps from S. American species of the same family possessed high (I). H. D.

Artificial substrates for proteases: protein structure. K. SHIBATA (Acta Phytochim., 1934, 8, 173—178).—Synthetic glycyldiaminopropionic anhydride, $\text{NH} \langle \text{CHR} \cdot \text{CO} \rangle \text{NH}$ ($\text{R} = \text{H}$; $\text{R}' = \text{CH}_2 \cdot \text{NH}_2$) and diaminopropionic anhydride ($\text{R} = \text{R}' = \text{CH}_2 \cdot \text{NH}_2$) are hydrolysed by pepsin (optimum p_H approx. 2.3), and glycyglutamic anhydride ($\text{R} = \text{H}$; $\text{R}' = \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$) and asparagine anhydride ($\text{R} = \text{R}' = \text{CH}_2 \cdot \text{CO}_2\text{H}$) are hydrolysed by trypsin (increasing from p_H 6.0 to $> p_H$ 8.0), cathepsin, and papain. J. W. B.

Digestibility of proteins *in vitro*. VI. **Partial cleavage products from peptic digests of caseinogen.** D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1934, 106, 707—716; cf. A., 1933, 1081).—Caseinogen (I) in 0.1N-HCl was incubated with pepsin at 38° for 1 hr. and then heated to 80°. The flocculent suspension was centrifuged off and washed with H_2O , EtOH, and Et₂O (fraction A). The supernatant fluid was adjusted to p_H 6 and the ppt. centrifuged off (fraction B). The centrifugate was conc. (fraction C). The distribution of N in the hydrolysates of the fractions was determined. Fractions A and B contained no cystine, whilst C contained almost all that in the original (I). 87% of the original P was in A and B. The lysine in A, B, and C was 8.02, 10.68, and 4.52, the tryptophan 0.46, 1.17, and 3.03%, respectively. H. D.

Enzymic histochemistry. IX. **Distribution of pepsin in the mucous membrane of the pig's stomach.** H. HOLTER and K. LINDERSTRØM-LANG. X. **Distribution of acid.** XI. **Distribution of peptidase in the mucous membrane of the pig's stomach and duodenum.** K. LINDERSTRØM-LANG and H. HOLTER. XII. **Distribution of esterase.** D. GLICK. XIII. **Enzyme distribution in the pig's stomach as a function of its histological structure.** K. LINDERSTRØM-LANG, H. HOLTER, and A. S. OHLSEN (Z. physiol. Chem., 1934, 226, 149—172, 173—176, 177—185, 186—191; 227, 1—50; cf. this vol., 561).—IX. The depth distribution of pepsin in the mucous membrane of fundus (I), pylorus (II), and cardia (III) from the inner surface to the muscularis mucosae (IV) was examined. Typical profiles are given. The max. activity is shown at a depth of 2.5 mm., but there is usually a secondary max. at 0.5 mm. (I), (II), and (III) show decreasing activity in that order. Glycerol (V) extraction is not equally effective at all depths of (I). At 1.4 mm. no pepsin is extracted, at 1.8 mm. 100%, and at 2.6 mm. 85% approx. Extraction with

(V)-edestin is complete. Only 20—30% is extracted by (V) from (II) over the total depth; with (V)-edestin the extraction is again complete.

X. Acid was found only in the (I) region, and only at a depth of 1—1.5 mm. from the surface. In some cases it was entirely absent.

XI. The peptidase activity is small at the surface and rises steadily towards the (IV), then falls sharply. The duodenum shows a curve with two max. The (I) region is relatively least active.

XII. The esterase activity is of the same order in all regions examined; there is no typical localisation in different layers. Both epithelium and (IV) show considerable activity.

XIII. A count of the chief types of cells at different depths in the mucous membrane was compared with the enzymic activity in order to assign to the particular types of cell definite enzymic (or acid-producing) properties. The enzyme content per cell was calc. Acid is produced only in (I) by the parietal cells, pepsin chiefly in (I) by the central cells, peptidase in (III), (I), and (II) by the central cells and in the duodenum (VI) by the cylindrical and Brunner cells, esterase in (I), (II), (III), and (VI) chiefly by epithelial cells and interstitial tissue.

Autocatalytic activation of trypsinogen in the presence of concentrated ammonium or magnesium sulphate. M. KUNITZ and J. H. NORTHROP (Science, 1934, 80, 190).—A protein fraction (I) which has a slight activity can be obtained from the mother-liquor from the chymotrypsinogen crystallisation (cf. this vol., 219). (I) becomes very active (approx. 80% of cryst. trypsin) when kept as a suspension (II) in half-saturated $(\text{NH}_4)_2\text{SO}_4$ or MgSO_4 at approx. p_H 7.0 and 30°. Activation is autocatalytic except for a prolonged lag. It occurs rapidly in a fresh suspension inoculated with previously activated (II). L. S. T.

Differentiation of trypsins by the anaphylactic test. C. TEN BROECK (J. Biol. Chem., 1934, 106, 729—733).—Trypsin from swine and cattle, chymotrypsin (I), and chymotrypsinogen (II) act as antigens to guinea-pigs, and may be differentiated by the anaphylactic test in these animals. Precipitins are not easily formed when (I) and (II) are injected into rabbits. H. D.

Activation of cathepsin by hydrogen cyanide and glutathione. T. MAYR and G. BORGER (Biochem. Z., 1934, 273, 56—59).—Curves show the activation of cathepsin hydrolysis of gelatin, serum-albumin, edestin, and peptone by KCN and glutathione individually and when added together. W. C.

Transformation of phosphoglyceric acid by the enzymes of germinated peas and beans. NEUBERG and M. KOBEL (Biochem. Z., 1934, 2, 457—458).—Pulped germinated peas and bean convert the acid, at p_H 6.95, into AcCO_2H . W. McC.

Degradation of *l*-phosphoglyceric acid by fresh bottom yeast. W. SCHUCHARDT and A. CELLONE (Biochem. Z., 1934, 272, 434; cf. A., 1933,

982).—The yeast converts *l*-phosphoglyceric acid into AcCO_2H . W. McC.

Fermentation of diphosphoglyceric acid by yeast. W. SCHUCHARDT and A. VERCELLONE (Biochem. Z., 1934, 272, 435–436; cf. this vol., 927).—The conversion of the acid into AcCO_2H (yield 55% of theoretical) by yeast maceration juice proceeds at p_{H} 5 (acetate buffer). At p_{H} 5.5 in the absence of buffer further degradation occurs, CO_2 (61%), MeCHO (17%), acetoin (16%), and EtOH being produced. W. McC.

Enzymic conversion of phosphoglyceric acid into pyruvic and phosphoric acids. K. LOHMANN and O. MEYERHOF (Biochem. Z., 1934, 273, 60–72).—Enzymic conversion of phosphoglyceric acid (I) into AcCO_2H and H_3PO_4 occurs only in presence of adenylyl pyrophosphate and a Mg salt acting as co-enzyme (II). In the absence of (II), H_3PO_4 is not separated, but a compound is formed which gives a cryst. Ag–Ba salt and is phosphopyruvic acid (III). (III) is hydrolysed on heating for a short time at 100° with *N*-HCl, with alkaline I shows an absorption of 6I and gives CHI_3 and H_3PO_4 , and in muscle extract containing (II) gives AcCO_2H and H_3PO_4 . (I) and (III) exist in enzymic equilibrium, 71% of (I) being present at 20° and the amount of (III) increasing with rising temp. Compared with the dephosphorylation reaction, the equilibrium reaction is more sensitive to F' , less to oxalate, and equally sensitive to citrate. P. W. C.

Enzymic equilibrium reaction between hexose-diphosphoric acid and dihydroxyacetonephosphoric acid. II. Negative heat of enzymic hydrolysis. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1934, 273, 73–79).—Enzymic conversion of hexose diphosphate (I) into dihydroxyacetone phosphate (this vol., 1034) is associated with a heat of reaction of -6000 g.-cal. per mol. of (I) and the synthesis with the same positive heat. P. W. C.

Proportions in the phosphorylation of maltose by fresh bottom yeast, dried yeast, and maceration extract. T. BABA (Biochem. Z., 1934, 273, 207–218).—Curves show the proportion of hexose mono- (I) and di-phosphates to CO_2 formed in the fermentation of maltose by bottom yeast (II), dried yeast (III), and maceration extract (IV). The product after 2 hr. fermentation with (IV) was almost pure (I), and after 7 hr. with (III) or 11 hr. with (II) almost the same mixture of (I) and trehalose mono-phosphates. P. W. C.

Cell-free fermentation. O. MEYERHOF (Biochem. Z., 1934, 273, 80–102).—The kinetics of the fermentation with maceration juice of glucose (I), hexose diphosphate (II), and glycogen (III) in presence and absence of F' , AsO_4''' , and MeCHO are investigated. In the first 1–2 min. of fermentation of (I), formation of hexose monophosphate (IV) precedes that of (II), the ratio of (IV) : (II) being then slowly displaced in favour of (II). In the early phase more H_3PO_4 is esterified than corresponds with the CO_2 eliminated, but the difference is rapidly equalised. In presence of MeCHO the esterification starts with max. velocity, whereas the fermentation increases

during the first 1–2 min. AsO_4''' increases the normal slow and const. fermentation velocity of (II) by 30–50 times, and elimination of PO_4''' is similarly increased. In presence of F' and MeCHO , both (I) + trace of (II) and also (II) + AsO_4''' are oxidised to phosphoglyceric acid, the reaction in both cases beginning at max. velocity. In the fermentation of (II) in presence of AsO_4''' , the max. velocity in presence of MeCHO \propto the concn. of (II), but in its absence is not. During the fermentation of (III) in presence of NaF , (II) accumulates, whilst (III) is oxidised on adding MeCHO to phosphoglyceric acid with greatly increased velocity. P. W. C.

Respiration and fermentation. H. HAEHN (Woch. Brau., 1934, 51, 313–316).—The relation between respiration and fermentation and the reactions of the cell constituents participating in the two processes are discussed. F. O. H.

Growth of yeast in synthetic media and the factors produced by yeast which limit this growth. V. HARTELIUS (Compt. rend. Trav. Lab. Carlsberg, 1934, 20, No. 7, 44 pp.).—In a medium containing 10% of glucose (I) growth (II) occurs exponentially for 12 hr. and then the rate begins to fall due to the accumulation of EtOH and acid. (II) ceases when all the (I) has been used. Fermentation (III) of (I) takes place linearly throughout. If (I) is continually added and the EtOH kept below 4% (II) continues until p_{H} 2.15 is reached. Addition of fresh yeast will lower the p_{H} to 1.8. If the p_{H} is maintained at 3–4 (II) ceases when 8.5% EtOH is formed and (III) at 12.6% EtOH . In N-deficient media the N content (IV) of the yeast falls to 2.5% when (II) ceases. With excess of N (IV) rises to 10% in 12 hr., then falls to a const. val. of 6%. The lower the p_{H} the higher does (IV) become. $[\text{EtOH}]$ has no effect on (IV). C. G. A.

Effect of deuterium on the growth of yeast. O. W. RICHARDS (J. Bact., 1934, 28, 289–294).—In media containing small proportions (1 in 2000) of “heavy” H_2O (I), yeast produced increased yields of dry matter in which the ash and total N contents were < and the glycogen content > when grown in distilled H_2O (II). Cultures in (I) appeared to age more rapidly than those in (II). A. G. P.

First stages of sugar assimilation. Yeast cells. E. WERTHEIMER (Protoplasma, 1934, 21, 522–560).—The first stage of sugar (I) assimilation by yeast consists of a surface adsorption followed by a sp. form of combination in which (I) functions as H-donor. (I) does not penetrate the cell membrane, but easily permeable reaction products are formed at the surface. The mechanism of these changes is examined. A. G. P.

Effect of organic substances on alcoholic fermentation. IV. Irradiated and non-irradiated cholesterol, lecithin, and lysolecithin. E. MAMELI and A. MOSSINI (Giorn. Chim. Ind. Appl., 1934, 16, 377–381; cf. A., 1933, 751).—The increase in the power of accelerating fermentation conferred on cholesterol (I) by ultra-violet rays is not due solely to the presence of an olefinic linking, with or without an alcoholic OH, or to impurities removable

from (I) by washing with or crystallisation from EtOH, or by successive bromination and debromination. Both lecithin (II) and lysolecithin (III), which occur as impurities in (I), accelerate fermentation, the effect being increased more by exposure to ultra-violet light than in the case of (I). The influence of commercial (I), whether irradiated or not, is raised by either (II) or (III). Irradiation of mixtures of (I) with (II) or (III) enhances the effect. The lowered action of (I) caused by bromination and debromination is restored by addition of (II). T. H. P.

Irradiation of *Saccharomyces* with monochromatic ultra-violet light. I. Morphological and respiratory changes. R. H. OSTER (J. Gen. Physiol., 1934, 18, 71—88).—No stimulation was detected. Inhibition of normal-sized colony formation occurs at low energy level; only a few budded cells are produced, but giant cells form which may be associated with division of the nuclear body. At higher incident energy levels the rate of O_2 consumption is lowered and finally growth and reproduction cease. The shape of the curves relating effect to energy are similar for various λ , but different energy is required to produce the same effect at each λ . C. G. A.

Effects of agents on the reduction of indicators and of cytochrome by yeast cells. L. V. BECK and J. P. ROBIN (J. Cell. Comp. Physiol., 1934, 4, 527—544).—The action of HCN, H_2S , Et urethane, and $Na_4P_2O_7$ on the aerobic reduction intensity in yeast cells is examined by the use of a no. of indicators. The rate of cytochrome reduction is decreased by presence of AsO_3''' . A. G. P.

Effect of 2:4-dinitrophenol on the oxygen consumption of yeast. J. FIELD, 2nd, A. W. MARTIN and S. M. FIELD (J. Cell. Comp. Physiol., 1934, 4, 405—420).—The respiratory rate of *Sac. cerevisiae* is increased by small and decreased by larger amounts of 2:4-dinitrophenol. The free undissociated substance is the active biological agent. The inhibition is reversible. A. G. P.

Synthesis of amino-acids by yeasts. II. Isolation of alanine. C. FROMAGEOT and P. DESNUELLE (Biochem. Z., 1934, 273, 24—30).—Alanine synthesised during alcoholic fermentation (A., 1933, 1204) arises from the reduction of a $AcCO_2H-NH_3$ mixture and not from the yeast cells. P. W. C.

Superficial electric moments of particles in a liquid medium.—See this vol., 1068.

Relation between inorganic salt concentration, hydrogen-ion concentration, and physiological processes in *Amoeba proteus*. III. Interaction between salts (antagonism) in relation to hydrogen-ion and salt concentration. R. F. PITTS and S. O. MAST (J. Cell. Comp. Physiol., 1934, 4, 435—455).—Antagonism between Ca and Na or K in respect of rates of locomotion and gel/sol ratio varies considerably with p_H . There is no antagonism between Na and K or between Mg and K or Na. The effects of base ratios in mixed salt solutions are examined in relation to p_H ranges. A. G. P.

Effect of certain chemicals on the division of cytoplasm in *Amoeba proteus*, with particular reference to salt antagonism and the interaction of salts and organic acids. H. W. CHALKLEY and G. E. DANIEL (Protoplasma, 1934, 21, 258—269).—Lactic acid (I) and $AcCO_2H$ (II) in small concns. prevent the completion of cytoplasmic division. This effect is modified or counteracted by addition to the medium of $CaCl_2$ in the case of (I) and of $CaCl_2$ or $NaCl$ in the case of (II). The action of Ca towards (I) is antagonised by Na or K. In respect of (II) the effects of Ca and Na are additive. The mechanism of this phenomenon is examined. A. G. P.

Temperature characteristics for metabolism of *Chlorella*. I. Rate of oxygen utilisation of *C. pyrenoidosa* with added glucose. W. J. CROZIER, P. S. TANG, and C. S. FRENCH (J. Gen. Physiol., 1934, 18, 113—124).—The temp. characteristic, μ , in Knop solution containing 1% of glucose (I) between 1° and 27° is $19,000 \pm 1000$ g.-cal. with indication of a crit. temp. at 20° with shift to a lower μ above it. It is concluded that the normal respiration [without added (I)] does not appear in the determination of μ . C. G. A.

a. Composition of moulds. b. Physiology of nitrate assimilation. I. Influence of source of nitrogen on the gaseous exchange of moulds. S. YAMAGATA (Acta Phytochim., 1934, 8, 107—116, 117—155).—a. The C, H, N, and ash % of *Aspergillus oryzae*, *A. niger*, and *A. melleus* grown at p_H 5.6 at 30—31° on different sources of C (I) (glucose, mannitol, EtOH, and glycerol in 0.5M, saccharic acid and sucrose in 0.25M solution) and N (II) (NH_4Cl , KNO_3 , KNO_2 , and NH_4NO_3) have been determined. The composition depends slightly on the mould (grown from spores or mycelium), but in general the C and H content of the moulds is but slightly altered, but the N content (III) is greatly influenced, by variations in (I) or (II). When the concn. of (I) is small in comparison with that of (II) (e.g., EtOH) (III) is proportionately large. Contrary to Terroine *et al.* (A., 1929, i, 1220) for all (I), (III) is considerably reduced when KNO_3 replaces an NH_4 salt. The ash content varies considerably.

b. Using Tamiya's technique (A., 1932, 1167) determinations of the gaseous exchange and of growth of *A. oryzae* on various (I) and (II) have been made. For all types of (I) the R.Q. for cultures when (II) is KNO_3 is $>$ that when (II) is NH_4^+ . The R.Q. for NO_2^- is intermediate. On the basis of the above analyses the at. composition of the mould is deduced, and it is thus found that, in contrast to Tamiya's val. 0.875 (*loc. cit.*), the combustion quotient of the mould varies between 0.91 and 0.95 according to the nature of (I) and (II). A general formula is deduced whereby the CO_2 evolution and O_2 absorption corresponding with the formation of 1 g. of mould can be calc.; the R.Q. vals. so calc. for an NH_4^+ substrate agree, in all cases, with experimental vals. It is therefore concluded that the R.Q. theory of Tamiya is essentially correct. In agreement with Warburg *et al.* (A., 1921, i, 82) it is found that, with a NO_3^- substrate, the excess of CO_2 from the NO_3^- reduction is liberated, and a means of determining this excess

of CO_2 in the growing cell is derived. The resultant calc. vals. of R.Q. for a NO_3^- substrate also agree with experiment. The energy set free by the combined oxidation-reduction processes in NO_3^- reduction is probably lost as heat, so that on such substrates the growing cell must perform additional work in order to reduce NO_3^- . J. W. B.

Biochemical origin of citric and oxalic acids.
II. Mycelium as seat of acid production. V. S. BUTKEVITSCH, E. V. MENZSCHINSKAJA, and E. I. TROFIMOVA. **III. Role of the mycelium in oxalic acid production.** V. S. BUTKEVITSCH (Biochem. Z., 1934, 272, 364—370, 371—375; cf. this vol., 1139).—II. In proportion to their content of reducing substances (originally present or added) moulds (I) growing on aq. NaOAc produce citric acid, which consequently is derived not from the NaOAc , but from (I). $\text{H}_2\text{C}_2\text{O}_4$ is also produced partly from (I), partly from the sugar of the nutrient medium, and partly from the NaOAc ; it is also produced when Na_2SO_4 replaces NaOAc .

III (cf. Chrzaszcz *et al.*, A., 1933, 982; Bernhauer *et al.*, *ibid.*, 1082). The $\text{H}_2\text{C}_2\text{O}_4$ produced by moulds is derived from the mycelium and accumulates because fixed by bases. The process involves the conversion of 1 mol. of sugar into 3 mols. of $\text{H}_2\text{C}_2\text{O}_4$ and if HCO_2H is produced it is not a precursor of $\text{H}_2\text{C}_2\text{O}_4$. Similarly in the production of succinic and citric acid from sugar AcOH is not necessarily an intermediate.

W. McC.

Production of citric acid by *Aspergillus niger*.
I. In unchanged solutions. **II. In changed solutions.** E. I. SOTNIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 273—278, 279—283).—I. The dry wt. of mycelia grown in media the N of which is present as $\text{Mg}(\text{NO}_3)_2$ (I) varies directly, and the citric acid (II) production and sugar consumption hyperbolically, with the concn. of (I); whether N is present as NO_3^- or as NH_4^+ appears to be immaterial, but Mg^{++} acts specifically only in presence of NO_3^- .

II. The mould (III) is cultivated in 1:3 barley wort- H_2O , containing NH_4NO_3 0.37, ZnSO_4 0.005, and FeCl_3 0.002%, sterilised at 110° , and filtered from the pptd. protein, which inhibits growth. (III) is added to 20% aq. sucrose containing 0.3—0.4% of (I), when (II) is obtained in 60% yield, as compared with 12—43% when Mg^{++} is replaced by other cations. The sp. action of Mg^{++} is observed only with active strains of (III). R. T.

Mould metabolism. O. E. MAY and H. T. HERRICK (J. Bact., 1934, 28, 145—151).—Current views of the mechanism of acid production by moulds are discussed. A. G. P.

Hydrolysis of glucosides and disaccharides by mould enzymes. E. HOFMANN (Biochem. Z., 1934, 273, 198—206).—A table shows the varying degree of hydrolysis of salicin and β -phenylglucoside by EtOH - Et_2O preps. of the mycelium of *A. niger* and *A. oryzae* after growth on various media. The action of β -galactosidase and lactase from *A. oryzae* is inhibited by galactose (I), but not by glucose (II) or glucosureide (III), whereas the β -glucosidase is inhibited by (II), but not by (I) and (III). *A. niger* grown on an inorg. salt solution containing raffinose did, but meli-

biose (IV) did not, effect hydrolysis of the carbohydrate, whereas grown on Raulin's medium (IV) was also attacked but to a smaller extent. P. W. C.

Influence of salts on invertase formation in *Aspergillus niger*. G. ROSSI and G. SCANDELLARI (Atti. Congr. naz. Chim., 1933, 4, 795—799; Chem. Zentr., 1934, i, 1988).—Dry matter yields (I) of *A. niger* were increased by small additions to media of ZnSO_4 or FeSO_4 . Larger amounts decreased (I). Invertase activity (II) showed similar changes with increasing $[\text{ZnSO}_4]$, but the optimum concn. was not the same as for (I). FeSO_4 reduced (II) at all concns. MgSO_4 lowered (I) without affecting (II). A. G. P.

Formation of urea from peptone by various moulds. T. CHRZASZCZ and M. ZAKOMORNY (Biochem. Z., 1934, 273, 31—42).—Tables summarise the formation of urea (I) after 5, 15, 20, and 25 days from 2% peptone with and without glucose by 16 species of *Penicillium*, *Aspergillus*, etc. The amounts of (I) formed vary enormously with the different organisms, increasing with enfeeblement and age of the culture, the formation being completely inhibited by 0.1% glucose with some organisms, with other organisms still proceeding in presence of 1% glucose, but being completely inhibited always with 10% glucose and by smaller amounts of EtOH and AcOH . The production of citric acid and $\text{H}_2\text{C}_2\text{O}_4$ on the other hand increases with increasing sugar concn. P. W. C.

Production of triose during degradation of hexose by microbes and higher plants. C. NEUBERG and M. KOBEL (Biochem. Z., 1934, 272, 445—456).—*B. delbrücki*, *B. coli*, *A. niger*, *A. fumigatus*, and germinated peas and beans produce bound (possibly phosphorylated) triose from K hexosediphosphate. W. McC.

Biochemistry of micro-organisms. XL. Crystalline pigments of species in the *Aspergillus glaucus* series. B. S. GOULD and H. RAISTRICK (Biochem. J., 1934, 28, 1640—1656; cf. this vol., 927).—Three new pigments have been isolated from 25 species of *A. glaucus*: *flavoglaucin* (I), $\text{C}_{19}\text{H}_{28}\text{O}_3$, lemon-yellow needles, m.p. 105° , contains no OMe ; *auroglaucin* (II), $\text{C}_{19}\text{H}_{22}\text{O}_3$, golden-orange needles, m.p. 152° , contains no OMe ; *rubroglaucin* (III), $\text{C}_{16}\text{H}_{12}\text{O}_5$, ruby-red rods, m.p. 172 — 173° . Colour reactions for these products are described. They appear to be series sp., not being found in 19 other species of *Aspergillus*. The *A. glaucus* series is divided into 3 groups: group I (13 species) produces (I) and (II) only; group II (2 species) produces (I), (II), and an unidentified red pigment; group III (10 species) produces (I) and a red pigment [(III) in 4 cases]. H. N. R.

Alleged stimulation of moulds by paraffin in heavy water. T. C. BARNES (Nature, 1934, 134, 573—574).—A reply to criticism (this vol., 1035).

L. S. T.

Bacteria decomposing alginic acid. S. A. WAKSMAN, C. L. CAREY, and M. C. ALLEN (J. Bact., 1934, 28, 213—220).—Decomp. of alginic acid in sea- H_2O is mainly effected by bacteria, species of which are described. A. G. P.

Action of gases under pressure on the growth of micro-organisms. I. Action of oxygen under pressure at various temperatures. A. C. THAYSEN (Biochem. J., 1934, 28, 1330—1335).—O₂ at 10 atm. (I) retarded the growth of *B. mesentericus* (II), *Bact. coli commune*, *Streptococcus lactis acidii*, and *Staphylococcus pyogenes aureus*. At temp. well below the optimum (N) for growth at atm. pressure an increase in the original no. of cells may take place in presence of (I), but there is a marked decrease at the normal N. Raising the temp. a few degrees above N destroys all vegetative cells in > 5 hr., but spores of (II) are not killed. I. A. P.

Respiration physiology of bacteria. I. Effect of hydrocyanic acid and of carbon monoxide on the oxygen respiration of various bacteria. S. YAMAGUTCHI (Acta Phytochim., 1934, 8, 157—172).—The effect of KCN (0.0004M and 0.001M) and of CO (95% CO+5% O₂ compared with 95% N₂+5% O₂ as a standard) on the O₂ consumption (Q_o=c.c. O₂ absorbed per mg. of dried bacteria per hr.) of various bacteria has been determined on a phosphate-glucose substrate at p_H 7.3. With group I [*Micrococcus ochreus* (I), *M. citreus*, and *Sarcina lutea*] both CO and KCN cause an increase in Q_o [59% and 31%, respectively, for (I)]: in group II (*M. agilis*, *S. aurantiaca*, *S. sp.*, *B. pyocyaneus*, *B. fluorescens liquefaciens*, and *B. fluorescens albus*) Q_o is reduced to 25—50% by 0.0004M-KCN, but is unaffected by CO. In group III (*B. coli communis*, *communior*, and *anaerogenes*, *B. sphingidis*, *B. mycoides*, *B. proteus vulgaris*, *Azotobacter chroococcum*, and *B. tumefaciens*) both CO and KCN cause a considerable decrease in Q_o, which is unaffected by light, whereas in group IV (*Staph. aureus*, *citreus*, and *albus* II, *B. mirabilis*, *B. xylinum*, *B. subtilis*, and *B. mesentericus vulgatus*) a similar decrease occurs, but that produced by CO is partly nullified by illumination. The respiratory mechanism is discussed and it is concluded that cytochrome-a forms a CO-complex readily destroyed by light, cytochrome-b forms a light-stable complex with both HCN and CO, and cytochrome-c combines with HCN but not with CO. J. W. B.

Respiration and fermentation of pathogenic bacteria. III. Cytochrome and the oxygen-transporting enzyme; inhibition of the respiration of pathogenic bacteria by CO and HCN. A. FUJITA and T. KODAMA (Biochem. Z., 1934, 273, 186—197).—Facultative anaerobic bacteria (I) which grow readily in blood-containing media and all obligate anaerobes possess no cytochrome (II), their O₂ respiration (III) being scarcely at all inhibited by CO or HCN and probably not being catalysed by Warburg's Fe-containing enzyme (IV). Spectroscopic examination suggests that Warburg's yellow (IV) is present. Some (especially intestinal) (I) show considerable inhibition of (III) by CO and HCN, the CO effect being abolished by light, (III) being catalysed by Fe containing (IV). Pigment-containing (I), e.g., *B. diphtheriae*, *pyocyaneus*, *prodigiosus*, show small inhibitions of (III), the CO effect being again abolished by light. With *B. proteus vulgaris*, inhibition of (III) by CO and HCN occurs, but the CO effect is not abolished by light. Usually, but not

invariably, Gram-negative (I) have a (III) catalysed by Fe. A scheme for dividing (I) into six (II)-types is given. P. W. C.

Pyocyanine and bacterial respiration. O. EHRLSMANN (Z. Hyg., 1934, 116, 209—224).—Increased respiration of bacteria brought about by pyocyanine (I) is small and is not greatly affected by HCN, CO, Na₂AsO₃, or NaF. The disinfectant action of (I) is also small and varies considerably with the species. In respiratory studies with COMe₂ bacteria, lactates (II) served almost exclusively as the oxidisable substance. In presence of (I) and (II) HCN and CO partly inhibit respiration, but urethane has little effect. A. G. P.

Chemistry and physiology of bacterial growth. J. HIRSCH (Z. Hyg., 1934, 116, 182—205).—The P content of cultures of the diphtheria bacillus rose and fell with the cycle of reproductive intensity, but that of N varied irregularly throughout. A. G. P.

Differential *B. coli* detection by means of the neutral-red reaction in relation to the redox potential. O. ACKLIN and R. VUILLEMIN (Mitt. Lebensm. Hyg., 1934, 25, 138—161).—Culture experiments with coli, coliform, typhoid, and paratyphoid-A and -B in ordinary nutrient agar, glucose nutrient agar (I), and in (I) buffered at p_H 5.8 and 7.8, using 1.5% neutral-red as a redox indicator (E₀ -0.320 at p_H 7.0; -0.205 at p_H 5.0), indicate that differentiation is obtained only if the conditions of redox and p_H val. are satisfied. J. G.

Production of lactic acid only by fermentation with *B. coli*. C. CATTANEO and C. NEUBERG (Biochem. Z., 1934, 272, 441—444).—L-Lactic acid, in almost 100% yield, is obtained, instead of the usual mixture, when large amounts of dried (fresh gives poorer yield) *B. coli* act on Na hexosediphosphate in presence of glutathione. W. McC.

Dehydrogenases of *Bacterium coli*. II. Rate of reduction of methylene-blue. III. Co-enzyme of glucose-dehydrogenase. J. YUDKIN (Biochem. J., 1934, 28, 1454—1462, 1463—1473).—II. The rates of reduction of methylene-blue (I) by formic (II), succinic (III), and glucose dehydrogenase (IV) of washed suspensions of *B. coli* have been determined with various concns. of (I) and various dilutions of bacterial suspensions. The reduction of a further quantity of (I), added during the course of the reaction, is abnormally rapid with (II) and (IV), but retarded with (III). The addition of leuco-methylene-blue does not influence the reduction times of (II), (III), or (IV).

III. Boiled suspensions of *B. coli* (I) contain a co-enzyme (II), relatively stable to heat and alkali, which accelerates the reduction of methylene-blue by glucose (III) in presence of (I) suspensions. (I) is probably identical with the cozymase (IV) of yeast and with (II) of the (III) dehydrogenase (V) of liver, as these three are mutually interchangeable, with (II) of Warburg, which activates (I)-(V), not activated by (I) suspensions, probably consists of the same (II) together with other factors. Adenylic acid, in relatively large quantities, exerts a weak activating action on (V) of (I). (II) of (I) is . . .

contained in *B. lactis aerogenes* (VI), *B. dispar* (VII), and *B. alkaligenes*. (VI) and (VII) require a (II) for the dehydrogenation of (III) replaceable by (IV). The same (II) is involved in the oxidation of (III) by O_2 and the production of H_2 from (III) by the enzyme (III)-hydrogenlyase.

W. O. K.

Biology of lactic bacteria. BAUMGARTEL (Milch. Zentr., 1934, 63, 243—246).—A summary.

L. D. G.

Metabolism of some nitrogen-fixing *Clostridia*. W. H. WILLIS (Iowa Agric. Exp. Sta. Res. Bull., 1934, No. 173, 255—284).—N-fixing anaerobes occurred in considerable nos. in acid soils, and varying applications of CaO had little influence on nos. or on the amount of N fixed. In solution cultures with an atm. of N_2 *C. pasteurianum* and *C. butyricum* (I) fixed only small amounts of N. The initial p_H of the media over the range 5.0—9.5 did not appreciably affect the N fixed, but in all cases the final p_H approached 5.0 after 3 weeks. In mixed cultures of soil anaerobes, $CaCO_3$ and $CaCl_2$ increased fixation, the former being rather more effective. In $CaCl_2$ media relatively larger amounts of NH_3 , NH_2-N , and acids were produced. In pure cultures of (I) $CaCO_3$ stimulated the utilisation of glucose and permitted the production of NO_2' and NO_3' . The latter effect was not apparent in $CaCl_2$ media. Fixed N in media also accelerated assimilation of glucose, but fixation of free N_2 ceased. Production of CO_2 was approx. the same from N-free media and from those containing $NaNO_3$, but was high in presence of peptone and very small in $CaCl_2$ media.

A. G. P.

Intermediate product of [bacterial] nitrogen assimilation. G. ENDRES (Naturwiss., 1934, 22, 662).—Evidence is produced that NH_2OH is an intermediate product of *Azotobacter* grown on a lactate medium.

L. D. G.

Microbial activities in soil. I. Nitrogen fixation by *Azotobacter* and activity of various groups of microbes in Palouse silt loam. S. C. VANDECAVEYE and B. R. VILLANUEVA (Soil Sci., 1934, 38, 191—205).—Fixation was favourably influenced by the presence of much org. matter in soil. The activity of the organisms (based on CO_2 production) was independent of total and $NO_3'-N$ contents of the soil, the C:N ratio of the org. matter, or the activity of cellulose-decomposing bacteria. The development of the groups of bacteria examined was not appreciably affected by p_H changes in the range 5.5—8.1. The activity of fungi was high at p_H 5.5 and much depressed at p_H 8.1.

A. G. P.

Anaerobic condition of soils in porous porcelain containers. C. B. CLEVENGER and L. G. WILLIS (Science, 1934, 80, 212).— O_2 does not dissolve and diffuse through the moisture in the walls of porous porcelain containers rapidly enough to supply the micro-organisms within.

L. S. T.

Blue stain for micro-organisms in humus and in soil. L. G. ROMELL (Stain Tech., 1934, 9, 141—145).—4% aq. PhOH containing 0.05% of fast-acid-blue R is recommended.

H. W. D.

Rhizobium. II. Effect of nitrogen source on oxygen consumption by *R. meliloti*, *R. trifolii*,

and *R. phaseoli*. R. H. WALKER, D. A. ANDERSON, and P. E. BROWN (Soil Sci., 1934, 38, 207—217).—*R. trifolii* and *R. phaseoli* react similarly to *R. leguminosarum* (this vol., 811), whereas *R. meliloti* is differently affected by NH_4Cl , $NaNO_3$, urea, and alanine.

A. G. P.

Growth and metabolism of mixed cultures of ammonia-producing micro-organisms. J. E. GREAVES, J. D. GREAVES, and I. HICKMAN (J. Bact., 1934, 28, 159—167).—Ammonification in a no. of soils is examined mathematically. Organisms producing NH_3 in peptone media occur in greater proportions in alkaline than in non-alkaline soils.

A. G. P.

Prodigiosine, the red pigment of *Bacillus prodigiosus*.—See this vol., 1232.

Physiology of pigments of purple bacteria.

II. Bacteriochlorophyll. E. SCHNEIDER (Z. physiol. Chem., 1934, 226, 221—254).—*Bacteriochlorophyll* (I), the pigment of photosynthesising purple bacteria, is closely related to chlorophyll (II) and exists in two modifications, *a* and *b*, *b* predominating. (I), $C_{55}H_{72}O_6N_4Mg \cdot H_2O$ (with 1 OMe), sinters at 94° , yields a series of derivatives by methods similar to those employed in the case of (II): *bacteriopheophytin* (Cu compound), in which introduction of Mg (Grignard) gives a product resembling (I); *bacteriopheophorbide*, separated into *a* and *b*, $C_{35}H_{38}O_6N_4 \cdot 0.5H_2O$, m.p. approx. 220° (decomp.) (*Me* derivative, m.p. 226° ; *oxime*; *Bz* derivative); *bacteriorhodin*; *bacterioporphyrins* (prepared with $Fe-HCO_2H$), HCl no. 6, $C_{33}H_{33}O_6N_4$, HCl no. 12, $C_{34}H_{34}O_6N_4$; *bacteriopheophorbide* 7, $C_{34}H_{34}O_6N_4$, decomp. $< 275^\circ$ (*Me* ester, m.p. 256° and 12, $C_{33}H_{33}O_6N_4$, m.p. 290° (corr.; decomp.) [*Me* ester, m.p. 255° (decomp.); *oxime*]; oxidised bacterioporphyrin [with $Fe-HCO_2H$ from oxidised (I)]; and, from alkaline degradation at high temp., phyllo- and pyrrho-porphyrin. There are marked differences between the (I)-*b* and (II)-*b* derivatives. (I) can be reversibly oxidised and the spectrum is then of the type of (II). The spectrum of (I) is of the second order, probably owing to the presence of a double linking lacking in (II).

J. H. B.

Action of formaldehyde on diphtheria toxin.

II. Immunising property of anatoxins. S. SCHMIDT (Z. Immunität, 1933, 78, 323—339; Chem. Zentr., 1934, i, 1509).—A comparison of the immunising properties of various anatoxins of different combining powers as determined by flocculation reactions (I). In general (I) agree with the immunisation results, but definitive distinctions between the individual antigen vals. of the anatoxins are not clear. Prolonged action of small concns. of CH_2O considerably reduces the immunising effect (II), and well-immunising anatoxins are obtained by the short action of moderate amounts of CH_2O . Addition of adsorbents, e.g., $Al(OH)_3$ increases (II). The immunising val. of an anatoxin depends on its content of flocculating (antitoxin-neutralising) substances.

L. S. T.

Lysis of pneumococci by sodium deoxycholate: effect of varying concentrations of sodium chloride. A. B. ANDERSON and P. D. HART

(Lancet, 1934, 227, 359—360).—NaCl increases the susceptibility of washed pneumococci to lysis by Na deoxycholate. L. S. T.

Comparison of lead, bismuth, and iron as detectors of hydrogen sulphide produced by bacteria. C. E. ZOBELL and C. B. FELTHAM (J. Bact., 1934, 28, 169—176).—The difference in [Pb] in media necessary to detect H_2S and that inhibiting bacterial growth is small in many cases. The ratio of corresponding concns. for Fe averages 1:40 and that for Bi 1:5. Use of $Fe NH_4$ citrate as a detector is suggested, although, where applicable, filter-paper strips soaked in $Pb(OAc)_2$ used externally to the medium are preferable. A. G. P.

Antagonistic action of chemotherapeutic agents. A. HASSKÓ (Z. ges. exp. Med., 1933, 89, 252—259; Chem. Zentr., 1934, i, 1074—1075).—Treatment of trypanosome-infected mice with various $CHPh_3$ dyes (fuchsin, parafuchsin, brilliant-green, and Me- or Et-violet) decreased the subsequent ability of the parasites to take up trypanflavin (I) [(I) was determined colorimetrically after extraction from the blood]. Na thioglycollate did not inhibit the absorption of (I) by trypanosomes. H. J. E.

Nature of the bactericidal and hæmolytic constituents of *B. pyocyaneus* lipins. H. O. HETTCHE (Klin. Woch., 1933, 12, 1804—1805; Chem. Zentr., 1934, i, 716).—50% EtOH extracts from the lipin of *B. pyocyaneus* an acid, mol. wt. 370, which acts hæmolytically and has a bactericidal action on staphylococci. Hydrolysis of the neutral fat with KOH yields palmitic acid and a liquid acid of mol. wt. 340 and I val. 77. The antibacterial action of the acid is directed only against Gram-positive organisms. L. S. T.

Bacterial supersensitivity and enhanced resistance to antiseptics. A. HEGEDUS (Magyar Orvosi Arch., 1933, 34, 467—477; Chem. Zentr., 1934, i, 1992—1993).—A strain of the Flexner bacillus exhibited abnormally high sensitiveness to dyes (I), but not towards $PhOH$, CH_2O , $HgCl_2$, etc. When grown in media containing (I) the organisms developed an increased resistance to (I), but not towards other types of antiseptics. A. G. P.

Titration of dyes for bacteriostatic action. M. V. REED and E. F. GENUNG (Stain Tech., 1934, 9, 117—128).—The bacteriostatic effect (I) of some $CHPh_3$ dyes was tested on *Staphylococcus aureus* and on *B. communior*. (I) is influenced by $[H^+]$, the constituents of the medium, and the amount of inoculum. The therapeutic val. of a dye cannot be assessed by tests *in vitro*. H. W. D.

Immunology and chemistry. A. G. VAN VEEN (Chem. Weekblad, 1934, 31, 567—575).—A lecture. S. C.

Bacillus radiclecola and its bacteriophage in the growth of lucerne. A. DEMOLON and A. DUNEZ (Compt. rend. Acad. Agric. France, 1934, 20, 659—662).—Lucerne-sick soils contain a bacteriophage effecting the lysis of *B. radiclecola* (cf. this vol., 114). A. G. P.

Isolation of the infective principle of virus diseases. W. J. ROBBINS (Science, 1934, 80, 275—

276).—The no. of infective particles is calc. on certain assumptions. L. S. T.

Inactivating effect of ultra-violet light on the virus of rabies. G. SANKARAN and W. A. BEER (Current Sci., 1934, 3, 69—70).—Light from a quartz-Hg vapour lamp inactivates, with or without addition of methylene-blue, a 0.5% centrifuged emulsion of rabies-infected rabbit's brain in 60 sec. Shorter exposures only attenuate the virus. L. S. T.

Biological effect of thymus extract (Hanson). L. G. ROWNTREE, J. H. CLARK, and A. M. HANSON (Science, 1934, 80, 274—275).—Administration of thymus extract to parents accelerates growth and development in young rats, and precocity results. Accruing acceleration in growth and development is also produced in succeeding generations born to thymus-treated parents. L. S. T.

Action of thyroxine on milk and milk-fat production of cows. W. R. GRAHAM, jun. (Biochem. J., 1934, 28, 1368—1371).—Thyroxine administered to lactating cows increased the production of milk-fat and, less regularly, the total milk yield. Dinitrophenol and prolactin occasionally gave similar effects, but these were of doubtful significance. W. O. K.

Detoxication of thyroid hormone. III. E. HESSE, I. CARPUS, and L. ZEPPEMEISEL (Arch. exp. Path. Pharm., 1934, 176, 283—290; cf. A., 1933, 539, 1337).—Thyroxine (I) is detoxified (as evidenced by characteristic morphological changes in the fat depôts, heart, and liver) in the dog by Pr, Cu, and mineral- H_2O containing Fe, Cu, and Ni, whilst Rb, Be, Ba, Hg, Y, La, Ti, Zr, Ce, Nd, Th, Pb, V, Sb, Cr, and U salts are inactive. Pr salts markedly inhibit the diminution in liver-glycogen due to (I) in rats. F. O. H.

Mechanisms in the development of an active resistance to the effects of substances stimulating the thyroid gland in the guinea-pig. L. LOEB (Science, 1934, 80, 252—253).—A discussion. L. S. T.

Action of antithyroid substances on the gaseous metabolism of the rat. Z. DIRNER (Arch. exp. Path. Pharm., 1934, 176, 190—198).—The increase in basal metabolism due to thyroxine is not significantly inhibited in rats by the simultaneous administration of pancreas preps., bone-marrow, Cu acetate, di-iodotyrosine, or antithyroid preps. from blood (cf. A., 1932, 781, 970). F. O.

Effects of moderate doses of viosterol and parathyroid extract on rats. A. F. MORGAN, L. KIMMEL, R. THOMAS, and Z. SAMISCH (J. Biol. Chem., 1934, 106, 531—544).—Viosterol (I) and parathyroid extract (II) have similar and additive effects, increasing the serum-Ca and -P, the ash, Ca, and P kidneys (III), and causing decalcification of bones (I) of rats fed on a normal diet, but the calcification of (III) is more marked in (II)-treated animals and calcification of (IV) more advanced in (I)-treated animals. C.

Parathyrotropic action of anterior extracts. I and II. K. J. ANSELMINO, F. HO MANN and L. HEROLD. Action of anterior pit

ary extracts on the blood-calcium level. H. HOFFMANN and K. J. ANSELMINO (Klin. Woch., 1933, 12, 1944; 1934, 13, 45—47, 44—45; Chem. Zentr., 1934, i, 1343).—I. In rats injected with anterior pituitary extract (I), the parathyroids increased to double or triple their size. Oxyphilic cells and intracellular lipids disappeared, and blood-Ca increased. The active substance in the extract stimulates the parathyroid. The parathyrotropic substance is thermolabile and not ultra-filterable.

II. Histological changes in the parathyroid after injection of pituitary extracts are described.

III. (I) causes a rise in blood-Ca due to its action on the parathyroid. When this organ is removed, no change in blood-Ca occurs. H. J. E.

Anterior pituitary hormone. K. EHREHARDT and H. RUHL (Arch. Gynakol., 1933, 154, 293—308; Chem. Zentr., 1934, i, 1342).—The effect of blood transfusion from a pregnant subject on the hormone reactions of the blood, sweat, and urine of man and of animals has been investigated. H. J. E.

Effect of secretions on gas metabolism. XII. **Effect of hormones of anterior lobe of the pituitary on oxygen consumption.** F. PETER (Biochem. Z., 1934, 272, 387—401; cf. von Ludany and Lengyel, this vol., 565).—Two factors which affect the metabolism are present: the thyrotropic, which increases it, and another (I), which decreases it. (I) acts directly and not through the gonads, although it is associated with the gonadotropic effect. W. McC.

Prolonged gas exchange investigations of the effect of different anterior pituitary preparations on metabolism. M. FEULING (Deut. Arch. klin. Med., 1933, 176, 90—99; Chem. Zentr., 1934, i, 719).—Anteron, prolan, and prehormone showed no metabolic action on man. Preloban depresses, and thyrotropic hormone (I) increases, metabolism. The increase in exchange resulting from 8-day administration of (I) is not enhanced by further additions and exchange quickly falls to normal when addition of (I) ceases. L. S. T.

Effect of anterior pituitary extract on the serum-calcium of cats. H. A. SHAPIRO (Quart. J. Pharm., 1934, 7, 223—226).—Serum-Ca which for the normal domestic cat is 8.2—11.4 mg. per 100 ml. (under paraldehyde anaesthesia) increased 40% in 5 hr. after injection of 2—3 c.c. of "antuitrin." A. L.

Influence of posterior pituitary hormones on urea clearance. T. BJERING (Arch. exp. Path. Pharm., 1934, 176, 255—261).—Injection of a posterior pituitary prep. (I) produced a fall in creatinine filtration [urine vol. \times concn. index (II)] and in the Van Slyke "urea clearance" of normal and, to a smaller extent, nephritic men. Thus (I) lowers the filtration of urea and increases the re-absorption in the tubules, the latter being independent of the (II) o. creatinine.

Content of pressor and oxytocic substances in the posterior pituitary gland. (a) Normal and thirsting animals. A. SIMON and Z. KARDOS. (b) Man. A. SIMON and F. NAGY (Arch. exp. Path. Pharm., 1934, 176, 238—242, 243—247).—(a) With rabbits (I) and guinea-pigs (II), but not cats, depriva-

tion of H₂O markedly diminishes the levels of pressor (III) and oxytocic principles (IV) in the posterior pituitary gland. With (I), hunger has no influence on the two vals. The blood pressure of (II) narcotised with "dial" is sensitive to very small amounts of (III).

(b) The greatest relative and abs. contents of (III) or (IV) in man occur in childhood and middle age, respectively. The levels diminish with old age. A max. content of approx. 30 units is attained with both (III) and (IV), the contents of which in the same gland are generally parallel, but occasionally differ considerably. F. O. H.

Behaviour of melanophore hormone in human blood during the phases of gestation. A. JÖRES and O. HELBRON (Arch. Gynakol., 1933, 154, 243—250; Chem. Zentr., 1934, i, 1341).—During pregnancy the amount of melanophore hormone in the blood undergoes no change. H. J. E.

Adrenal cortical hormone. I. **Methods of preparation.** J. J. PFIFFNER, H. M. VARS, and A. R. TAYLOR. II. **Yield from glands of various species.** H. M. VARS, A. R. TAYLOR, and J. J. PFIFFNER. III. **Distribution studies.** J. J. PFIFFNER and H. M. VARS (J. Biol. Chem., 1934, 106, 625—638, 639—644, 645—651).—I. The max. yield of cortical hormone (I) obtained from ox adrenal gland is about 2500 dog units per kg. and represents 75% efficiency of recovery. All of (I) can be extracted with neutral EtOH or COMe₂. Methods of separating the two hormones of the gland and the nature of the impurities present are discussed.

II. Extracts prepared by the above method and assayed on adrenalectomised dogs yield the following no. of dog units per kg. of gland: man < 165, horse 1500, ox 2500, sheep 3500, pig 3500, dog 2500, shark < 500.

III. Adrenal cortical hormone (I) may be purified by selective distribution between a neutral, acid, or slightly alkaline aq. phase and an immiscible solvent phase. Amorphous products free from adrenaline and containing 200 dog units of (I) per mg. are obtained. C. G. A.

Crystalline insulin. D. A. SCOTT (Biochem. 1934, 28, 1592—1602; cf. A., 1933, 321).—Insulin (I) crystals, prepared by the C₆H₅N-brucine or the saponin method, contain Zn. Addition of Zn, Cd, Ni, or Co facilitates crystallisation. (I) with an ash content of 0.04% (electrodialysis) will not crystallise without addition of traces of one of the above metals. C. G. A.

Limits of resistance of the pigeon to insulin. D. GIGANTE (Atti R. Accad. Lincei, 1934, [vi], 19, 892—896).—Under normal conditions the resistance of the pigeon to insulin is > that of any other birds examined, but doses of 500 units per kg., administered either at once or in portions, cause convulsions and death. T. H. P.

Effect of insulin on the processes of the normal human stomach. K. P. BECKER and E. GEIS (Deut. Arch. klin. Med., 1933, 176, 154—161; Chem. Zentr., 1934, i, 721—722).—The processes of the stomach are excited to different extents by insulin. The HCl and Cl⁻ contents of the gastric juice (I) are

much raised. The increased secretion of (I) through insulin is dependent on the period of hypoglycaemia (II). The excitation of the HCl and Cl' secretion and the mobility persists after the cessation of (II). Total Cl secretion is influenced inasmuch as the HCl fraction rises as the Cl' fraction falls. R. N. C.

Effect of insulin on the production of sugar in the surviving frog liver. B. VON ISSEKUTZ and J. SZENDE (Biochem. Z., 1934, 272, 412—416).—The production of sugar in the surviving frog liver is restricted by administration to the living frog [perfusion causes no restriction (I)] of cryst. or crude insulin. At room temp. 15 hr., and at 30—33° 4 hr., elapse before (I) becomes pronounced.

W. McC.

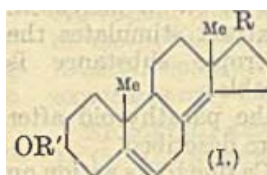
Action of insulin in a severe disturbance of the lipin metabolism. D. MATROSSOWITSCH (Klin. Woch., 1934, 13, 143—145; Chem. Zentr., 1934, i, 1344).—In hypercholesterolaemia, insulin lowers the blood-cholesterol (I), the blood-sugar (II) being raised. This indicates a change of (I) into (II). H. J. E.

Insulin-sugar treatment in experimental pituitary hyperthyrosis. A. LOESER (Klin. Woch., 1934, 13, 83—85; Chem. Zentr., 1934, i, 1344).—In a guinea-pig, the liver of which was rendered glycogen-free by repeated injection of thyrotropic substance, injection of fructose (I) and insulin together [but not of (I) alone] rapidly restored the glycogen supply in the liver. H. J. E.

Crystalline progestin. W. M. ALLEN and O. WINTERSTEINER (Science, 1934, 80, 190—191).—The product obtained by Allen's method (A., 1933, 194) contains (i) a physiologically inactive *hydroxyketone*, $C_{21}H_{34}O_2$, m.p. 190°, (ii) a compound, $C_{21}H_{30}O_2$, m.p. 128°, *progestin* (I), which possesses the characteristic physiological properties of the hormone (progestational proliferation), (iii) a compound, m.p. 120—121°, probably isomorphous with (I), and (iv) a physiologically inert compound, m.p. 70—74°. L. S. T.

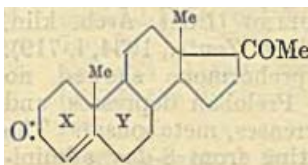
Hormone of corpus luteum. A. BUTENANDT, U. WESTPHAL, and W. HOHLWEG (Z. physiol. Chem., 1934, 227, 84—98).—The hormone is determined by means of its action on the mucous membrane of the uterus of the immature rabbit in which proliferation has been induced by pretreatment with oestrin. Purified corpus luteum extract affords a crude semicarbazone (I), decomp. 260° (yield about 20%), containing all the biologically active material. Hydrolysis of (I) with dil. H_2SO_4 gives an oil which is fractionated at 120°/0.001 mm. into a cryst. sublimate (II) and a residue. When crystallised from aq. EtOH, (II) yields active fractions (III), m.p. 145—155° (70%), and (IV), m.p. 75—85° (30%). With Ac_2O , (III) affords an *acetate*, m.p. 144.5°, of a *keto-alcohol* (V), $C_{21}H_{34}O_2$, m.p. 194° (*oxime*, m.p. 227°). Oxidation of (V) with CrO_3 in Ac_2O gives a *diketone*, m.p. 200.5° [*dioxime*, m.p. 260° (decomp.)]. (V) is inactive. (IV) by crystallisation from EtOH and COMe₂ and fractional sublimation yields the active hormone as a *diketone*, $C_{21}H_{30}O_2$ (or $C_{20}H_{28}O_2$), m.p. 128.5° (*dioxime*, m.p. 243°), and another active cryst. substance, m.p. 120°. J. H. B.

Degradation of stigmasterol to substances with corpus luteum activity; constitution of the corpus luteum hormone. A. BUTENANDT, U. WESTPHAL, and H. COBLER (Ber., 1934, 67, [B], 1611—1616).—Stigmasterol is converted into Me 3-hydroxybismorcholenate (Fernholz, A., 1933, 1290),



which is transformed by MgPhBr in Et₂O and subsequent acetylation into the substance (I) (R=CMe:CPh₂, R'=Ac), m.p. 216—217°. Successive treatments of (I) with Br in CHCl₃, O₃, and Zn dust—AcOH lead to the *OH-ketone acetate* (I; R=Ac; R'=Ac), m.p. 146—147° [semicarbazone, m.p. 240—245° (decomp.)], hydrolysed by 5N-H₂SO₄ to the *OH-ketone* (II) (R=Ac; R'=H), m.p. 190°. Gentle oxidation of (II) with CrO₃ yields a mixture of substances which, unlike (II), have physiological action only slightly inferior to that of the natural hormone (III). The close relationship of (III) to the sterols and pregnandiol is thus established as well as the necessity of the diketonic and unsaturated character for the development of physiological activity. H. W.

Preparation of homogeneous hormones from the corpus luteum. II. K. H. SLOTTA, H. RUSCHIG, and E. FELS (Ber., 1934, 67, [B], 1624—1626; cf. this vol., 931).—Luteosterone D (I) has m.p. 120—121°. It is isomeric with luteosterone C (II), into which it is converted when heated at 120° and seeded. (I) and (II) are diketones, yield a dioxime, and absorb 3H₂ used in saturating the double linking ($\alpha\beta$ to CO) and converting 2 CO into 2 CH·OH. The annexed constitution is assigned, the difference between (I) and (II) lying in the position of rings X and Y (*D cis*, and *C trans*). The physiological action of (I), (II), and (I)+(II) is described. Reply is made to Butenandt *et al.* (this vol., 1039). H. W.



Influence of the corpus luteum on the glycogen content of the liver. E. ENGELHART and O. RIML (Klin. Woch., 1934, 13, 101; Chem. Zentr., 1934, i, 1341—1342).—In the livers of pregnant rabbits, the ovaries of which contained numerous corpora lutea (I), 3—4 times the normal amount of glycogen (II) was found. The livers of guinea-pigs injected with (I) extract were richer in (II) than controls.

H. J. E.

Sexual hormones. I, II.—See this vol., 1221.

Extraction of the male sex hormone from urine. Y. WANG and H. WU (Chinese J. Physiol., 1934, 8, 209—218).—Acidified male urine is treated with Ca(OH)₂ and filtered, excess of Ca(OH)₂ being removed with Na₂CO₃. This overcomes emulsification and pptn. of uric acid in the subsequent C₆H₆ extraction. H. G. R.

Tissue respiration of the seminal vesicle and male sex hormone. W. FLEISCHMANN and KANN (Naturwiss., 1934, 22, 527).—Respiration of mouse seminal vesicles in a Warburg apparatus was

accelerated by an aq. extract of testis, but not by thyroid extract. R. K. C.

Crystalline α -folliculin from stallion's urine. V. DEULOFEU and J. FERRARI (Z. physiol. Chem., 1934, 226, 192—194; cf. this vol., 815).—The identity of the cryst. oestrogenic substance from stallion's urine with α -folliculin is established. J. H. B.

Fate of folliculin in the living body. B. ZONDEK (Lancet, 1934, 227, 356).—After oral or subcutaneous administration of folliculin (I) only small quantities are excreted in human or animal urine in an active state. (I) is not stored in the body, but is inactivated, probably in the liver by means of enzymes. (I) is also inactivated by plants, but not by yeast. L. S. T.

Application of the Kober test to the determination of oestrone and oestriol in human pregnancy urine. S. L. COHEN and G. F. MARRIAN (Biochem. J., 1934, 28, 1603—1614).—A detailed procedure is given for the separation and determination of oestrone and oestriol by a modification of Kober's colour reaction. C. G. A.

Conditions of hypertrophy of seminal vesicles in rats. II. Effect of derivatives of oestrone (menformone). K. DAVID, J. FREUD, and S. E. DE JONGH (Biochem. J., 1934, 28, 1360—1367).—The actions of oestrone, oestradiol and derivatives and related substances on the various sex organs in rats are described. In general, the myotropic and oestrogenic effects run parallel, but some compounds show enhanced myotropic effects. W. O. K.

Effect of oestrone on normal and castrated male rats. V. KORENCHESKY and M. DENNISON (Biochem. J., 1934, 28, 1474—1485).—In normal rats, daily subcutaneous injection of oestrone (60—180 I.U.) decreased the appetite and gain in body-wt., depressed development of the sexual organs, and produced hypertrophy of the adrenals and pituitary. Castrated animals, similarly treated, showed marked stimulation of the seminal vesicles and pituitary, some enlargement of the prostate and, in smaller degree, of the penis and preputial gland. W. O. K.

Effect on male rats of simultaneous administration of male and female sexual hormones and the relation to the assay of the hormones. V. KORENCHESKY and M. DENNISON (Biochem. J., 1934, 28, 1486—1499).—The comb-growth activity of male sex hormone may be measured by its effect on the wt. of the prostate gland in castrated rats, whilst the whole male sex-hormone activity is measured by the effect on the wt. of prostate+seminal vesicles. The presence of oestrin in the prep. is indicated by a marked increase of the seminal vesicles without a corresponding increase in the prostate. New definitions of the rat unit are proposed. W. O. K.

Normal and experimental development of the mammary gland. I. Male and female domestic cat. C. W. TURNER and W. R. DE MOSS
II. Male and female dog. C. W. TURNER and E. T. GOMEZ (Missouri Agric. Exp. Sta. Res. Bull., 1934, No. 207, 35 pp.).—Appropriately timed administration of corporin, theelin, and galactin to the male cat was followed by development of the lobule-

alveolar system and the secretion of milk. Male and female animals responded equally to the oestrogenic hormone. A. G. P.

Chemistry of fertilisation. E. FREUND (Wien. klin. Woch., 1933, 46, 1578—1579; Chem. Zentr., 1934, i, 723).—Clear extracts of the testicle (I) and corpus luteum (II), when mixed and kept for 1—2 hr., developed a copious ppt. which did not appear on mixing either (I) or (II) with kidney or liver extract, or these two with one another. A marked difference exists in the Ca : P ratios of the genital organs, viz., in the testicle, 1 : 4, in spermatozoa, 1 : 1, in the ovary, 1 : 9, and in the corpus luteum, 1 : 12.

R. N. C.
Adsorption of vitamin-A concentrates. D. C. CASTLE, A. E. GILLAM, I. M. HEILBRON, and H. W. THOMPSON (Biochem. J., 1934, 28, 1702—1711).—Five fractions are obtained by chromatographic analysis on $Al(OH)_3$ or $Ca(OH)_2$: (a) strongly adsorbed, violet or violet-blue colour with $SbCl_3$, probably consisting of oxidation products; (b) the main fraction, with an absorption band at 328 m μ corresponding with Karrer's β -vitamin-A, and regarded as the best vitamin-A prep.; (c) strongly coloured red material showing the band at 328 m μ and an inflexion near 430 m μ , blue with $SbCl_3$ but with an extra band between 640 and 660 m μ ; (d) Karrer's α -vitamin-A, small in amount, violet with $SbCl_3$, and closely resembling (a); (e) a yellow substance characterised by three distinct absorption bands at 348, 369, and 389 m μ , giving a blue colour with $SbCl_3$ showing absorption max. at 624 and 579 m μ . C. G. A.

Ultra-violet absorption and Lovibond value of oils and fats containing vitamin-A. B. JOSEPHY (Acta Neerl. Physiol., 1933, 3, 133—135; Chem. Zentr., 1934, i, 1212).—Concordant vals. are obtained from the ultra-violet absorption at 3280 Å. and the Lovibond vals., if the unsaponifiable residue (I) is examined. The cholesterol in (I) must be removed before measuring the absorption, as it causes high vals. H. J. E.

Influence of vitamin-A on serum-cholesterol. H. J. JUSATZ (Klin. Woch., 1934, 13, 95—97; Chem. Zentr., 1934, i, 1346).—Rabbits fed on a vitamin-A-free diet, and given large doses of "Vogan," showed an increase in the serum-cholesterol. The neutral fat level in the serum was also raised. H. J. E.

Fish-liver oils rich in vitamin-A. J. A. LOVERN (Nature, 1934, 134, 422).—Sturgeon-liver oils are comparable with halibut-liver oil. Tunny-liver oil is also rich in vitamin-A, the blue vals. varying from 1927 to 2724. The livers contained 20—25% of oil.

L. S. T.
Vitamin-A and -D contents of oil from the testes of a sturgeon. H. D. BRANION (Sci. Agric., 1934, 14, 614—615).—Neither vitamin was detected. A. G. P.

Fat-soluble vitamin content of liver oil of turbot. H. D. BRANION (Sci. Agric., 1934, 15, 1—11).—The oil has higher proportions of vitamin-A and -D than are shown by medicinal cod-liver oil. Determinations of inorg. blood-P alone are of little val. in assaying -D. A. G. P.

Fish oils as a source of vitamin-D for growing chicks. J. S. CARVER, A. BRUNSTAD, J. L. ST. JOHN, F. W. FRAISER, and W. ATHOW (Washington Agric. Exp. Sta. Tech. Bull., 1933, No. 284, 31 pp.).—The ash of tibiae in chicken cannot be used as an index of calcification. Histological examination is also necessary. 0.5% of sardine oil in the ration prevented rickets if appropriate amounts of Ca and P were supplied. A. G. P.

Origin of vitamin-D in cod-liver oil: vitamin-D content of zooplankton. A. M. COPPING (Biochem. J., 1934, 28, 1516—1520).—Dried copepods contain vitamin-D as demonstrated by prophylactic experiments on rats. They probably constitute an important source of the vitamin-D present in cod liver oil. W. O. K.

Antirachitic factor in Kabuli Chhola oil. N. C. NAG and H. N. BANERJEE (Current Sci., 1934, 3, 68).—The factor is present. L. S. T.

Vitamin-D in the blood and milk of cows fed with irradiated yeast. R. F. LIGHT, L. T. WILSON, and C. N. FREY (J. Nutrition, 1934, 8, 105—111).—Vitamin-D (I) in irradiated yeast is almost completely absorbed. (I) disappears rapidly from the bloodstream and the concn. of (I) in the plasma controls its concn. in the milk. A. G. P.

Do *Symphytum offic.*, L., leaves contain vitamins? Z. MARKUZE (Arch. Chem. Farm., 1934, 1, 205—212).—Vitamin-A, -B₁, -B₂, -C, and -D are absent. Feeding the leaves does not affect the fertility of female rats, or the development of the young. R. T.

Chemical constitution of vitamin-B₁ as deduced from ultra-violet absorption spectra. F. F. HEYROTH and J. R. LOOFBOUROW (Nature, 1934, 134, 461).—In vitamin-B₁ concentrates there is marked correlation between absorption at or near 2600 Å. and biological activity. Absorption curves resemble those of cytosine and have max. at 2650 and 2350 Å. The active material may be built around a pyrimidine of the cytosine type. L. S. T.

Irradiation of yeast oryzanin. F. F. HEYROTH and J. R. LOOFBOUROW (J. Amer. Chem. Soc., 1934, 56, 2010—2011).—Irradiation of oryzanin with light from a Victor quartz lamp destroys the anti-neuritic activity; the absorption curve [which resembles that of cytosine (this vol., 1112)] is rapidly destroyed. Ultra-violet radiation from which most of the radiations of < 2960 Å. have been filtered has little or no effect on the activity or absorption. H. B.

Relation of the vitamin-B complex (particularly vitamin-B₁) to carbohydrate persistence. E. ABDERHALDEN and E. WERTHEIMER (Pflüger's Archiv, 1933, 233, 395—415; Chem. Zentr., 1934, i, 724).—Pigeons on a diet deficient in vitamin-B₁ (I) showed high liver-glycogen (II) when in a convulsive state; administration of (I) resulted in a fall of liver-(II). With a carbohydrate-free diet (caseinogen and fatty acids) (II) still showed high vals. in both liver and heart-muscle. Pigeons fed only with fatty acids developed no convulsions (III), and liver-(II) remained low. Increasing the proportion of fat in

the diet at the expense of the carbohydrate retarded the onset of (III); increasing the carbohydrate at the expense of the fat hastened it. In all cases where no symptoms of (I) deficiency showed the liver-(II) was < 0.35%. A diet of fat alone reduced the susceptibility to (III), apparently by restricting carbohydrate synthesis in the organism. Oryzanin [(I) concentrate] caused rapid fall of liver-(II) in (III). R. N. C.

Proteins and vitamin-B. II. Course of complete avitaminosis-B in pigeons in relation to the digestibility and nature of the proteins in their food. R. LECOQ (Bull. Sci. pharmacol., 1934, 40, 527—531; Chem. Zentr., 1934, i, 724).—Pigeons in avitaminosis-B consume their proteins to replace vitamin-B. R. N. C.

Lactic acid oxidation in the brain of hens in avitaminosis-B. P. E. GALVAO and C. H. FLORENCE (Pflüger's Archiv, 1934, 233, 714—721; Chem. Zentr., 1934, i, 1213).—Oxidation of lactic acid by hen's brain in avitaminosis-B is lower than for normal or fasting animals. The ability to oxidise succinic acid is unchanged. H. J. E.

Distribution of bound and free flavin in plants. H. VON EULER, E. ADLER, and A. SCHLÖTZER (Z. physiol. Chem., 1934, 226, 87—94).—The flavin content of various edible plants is > 1 mg. per kg. of fresh wt. The vals. found agree well with the vitamin-B₂ activity. 75—90% of the flavin in fresh spinach is in non-dialysable form. J. H. B.

Large-scale preparation of ascorbic acid from Hungarian pepper (*Capsicum annuum*). I. BANGA and A. SZENT-GYÖRGYI (Biochem. J., 1934, 28, 1625—1628; cf. A., 1929, 98).—The expressed juice is treated with Pb(OAc)₂, the ppt. decomposed with dil. HCl, and the filtrate rapidly evaporated in vac. Extraction of the residue with COMe₂ and evaporation yields a product containing about 25% of ascorbic acid (I). This is purified by a repetition of the above, by conversion into the Na salt and regeneration, or (best) by further extraction with COMe₂. On treatment with BuOH the syrupy products crystallise. The product, on recrystallisation from MeOH-dioxan, yields pure (I). H. N. R.

Vitamin-C content of human tissues. M. YAVORSKY, P. ALMADEN, and C. G. KING (J. Biol. Chem., 1934, 106, 525—529).—The order of concn. of vitamin-C in human tissues is adrenal (I), brain, pancreas, liver, spleen, kidney, lung, heart (II), and muscle, the average vals. ranging from 0.55 mg. per g. in (I) to 0.04 mg. per g. in (II), although great individual variation occurs. The average for each tissue below the age of 10 years was > for above. Approx. 20% of cases showed evidence of latent scurvy. C. G. . .

Vitamin-C in aqueous humour; its place in the physiology and pathology of metabolism. H. K. MÜLLER, W. BUSCHKE, GUREWITSCH, and F. BRÜHL (Klin. Woch., 1934, 20—21; Chem. Zentr., 1934, i, 2000).—The aqueous humour (I) in cattle and dogs contains 0.02% ascorbic acid (II), which originates from the

bolism of the lens. Administration of $C_{10}H_8$ causes loss of (II) from (I). A. G. P.

Vitamin-C in invertebrates. M. VAN EEKELEN (Acta Néerl. Physiol., 1933, 3, 119—120; Chem. Zentr., 1934, i, 1214).—Results of titrations with 2:6-dichlorophenol-indophenol are recorded.

H. J. E.

Urinary excretion of ascorbic and dehydro-ascorbic acids in man. S. W. JOHNSON and S. S. ZILVA (Biochem. J., 1934, 28, 1393—1408).—The indophenol-reducing power of human urine (I) approx. measures the ascorbic acid (II) content as assayed biologically. The (II) content of normal (I) is variable, depending in part on the diet and on the amount of (II) already stored in the body. After large doses of (II) the fraction excreted is smaller than after smaller doses. Even with large doses no dehydroascorbic acid (III) is found in (I). When the subject is saturated or approaching saturation the rate of urinary excretion after ingestion of (II) rapidly rises to a max. at 4 hr. and then gradually returns to its initial rate in about 24 hr. Excretion of (II) at night is < during the day and is not affected by diuresis. (III) administered by the mouth raises the (II) content of (I).

W. O. K.

Human daily requirements of dietary ascorbic acid. G. GOTHELIN (Nature, 1934, 134, 569—570).—The min. daily dose of cryst. ascorbic acid which insures to the guinea-pig protection against pre-scorbutic alterations in the molar teeth is 1.33 mg. The calc. min. daily dose required by adults weighing 60 kg. for protection against detectable pre-scorbutic alterations is 19—27 mg.

L. S. T.

Tolerance of ascorbic acid in infancy. E. KRAMÁR (Deut. med. Woch., 1933, 59, 1428—1429; Chem. Zentr., 1934, i, 1347).—Doses of ascorbic acid of 15—50 mg. could be administered without any ill-effects.

H. J. E.

Pharmacology of ascorbic acid. H. KREITMAIR (Arch. exp. Path. Pharm., 1934, 176, 326—339).—Ascorbic acid is not toxic to rats and rabbits and has a negligible action on respiration, activity of heart, smooth muscle, etc., but it stimulates blood-regeneration in sponin-anæmia in cats. It synergises the action of adrenaline, choline, thyroxine, and the anti-anæmia factor of liver, but has no influence on that of insulin, di-iodotyrosine, and the female sex hormones.

F. O. H.

Ascorbic acid and toxic infections. E. HARDE (Compt. rend., 1934, 199, 618—620).—The adrenal cortex of guinea-pigs (I) killed by injection of a lethal dose (d) of diphtheria toxin shows a diminished vitamin-C (II) content similar to that observed in scorbutic animals. Mice, which synthesise (II), are resistant to 10d, (II) still being found in the cortex, but after death by oral infection with *B. typhi murium* [which probably prevents the synthesis of (II), and to which they are very susceptible], (II) could not be detected. The resistance of (I) is increased up to 1—2d by (II) injected or given orally. Thus (II) has a protective action against infections which cause lesions of the adrenal cortex and of the gastrointestinal tract.

J. ,

Chemical determination of vitamin-C. Z. KOŁODZIEJSKA (Arch. Chem. Farm., 1934, 1, 244—252).—Minor modifications of Tillmans' method are suggested. Lemon, but not orange, juice may be used for standardising 2:6-dichlorophenol-indophenol. The results obtained by titration are in close agreement with those given by biological assay. R. T.

Determination of ascorbic acid. E. MARTINI and A. BONSIGNORE (Biochem. Z., 1934, 273, 170—177).—Under the action of light, ascorbic acid (I) donates 2H to methylene-blue (II). (I) is extracted from tissue with 8% $CCl_3 \cdot CO_2H$ and the determinations in terms of decoloration of (II) are carried out in citrate- $NaHCO_3$ buffer, $Na_2S_2O_3$ being also added to prevent reoxidation of the leuco-base. Glutathione and cysteine do not interfere with the determination. Determinations in animal tissues and plant juices are recorded.

P. W. C.

Deficiency disease in chicks resembling scurvy. H. DAM and F. SCHONHEYDER (Biochem. J., 1934, 28, 1355—1359).—Chicks reared on a diet containing vitamin-A-free caseinogen, marmite, sol. starch, and salts with cod-liver oil concentrates develop a disease characterised by hæmorrhages, damage to the mucous membrane of the gizzard, anæmia, and defective growth. Subcutaneous administration of ascorbic acid is without effect, but replacement of the starch by cereals (I) brings about a cure. The disease is ascribed to the lack of a factor occurring in (I).

W. O. K.

Chlorophyll unit in photosynthesis. W. ARNOLD and H. I. KOHN (J. Gen. Physiol., 1934, 18, 109—112).—In six species of plants the min. no. of chlorophyll (I) mols. present for each mol. of CO_2 reduced is 2000—3000, suggesting the existence of a (I) unit.

C. G. A.

Influence of ultra-violet rays on green and colourless strains of *Euglena gracilis*. O. JIROVEC (Protoplasma, 1934, 21, 577—587).—Chlorophyll has a protective action against ultra-violet rays.

A. G. P.

Phæophytin formation in leaf-organs after the action of heat and cold. M. ROSEN (Kl. Mitt. Ver. Wasser-, Boden-, Lufthyg., 1933, 9, 194—206; Chem. Zentr., 1934, i, 1337—1338).—In Rosaceæ phæophytin formation occurs readily due to the effect of heat or cold. In Cruciferae leaves this is seldom the case.

H. J. E.

Apparatus for the measurement of respiratory rate [of plants]. R. H. LANDON and W. G. BRIERLEY (Science, 1934, 80, 75).

L. S. T.

Plant respiration. III. Relationship between respiration in air and in nitrogen of certain fat-storing seeds during germination. W. LEACH and K. W. DENT (Proc. Roy. Soc., 1934, B, 116, 150—169).—Seedlings of *Helianthus*, *Cucurbita*, and *Ricinus* on transference from air to N_2 showed a rapid fall, followed by a slower fall, in rate of CO_2 output. On return to aerobic conditions the respiration rate rose rapidly to normal; the R.Q. first fell to a low figure and then rose to normal.

L. D. G.

Relation between root respiration and absorption. L. HENDERSON (Plant Physiol., 1934, 9, 283—

300).—Rates of CO_2 evolution and of O_2 absorption are correlated with the intake of H_2O by roots.

A. G. P.

Retention of carbon dioxide in the intercellular atmosphere of pears and apples. F. GERHARDT and B. D. EZELL (Science, 1934, 80, 253—254).—After treatment with 35% CO_2 for 24 hr. at 18° , the intercellular $[\text{CO}_2]$ in Bosc pears and Jonathan apples is approx. 80 and 50%, respectively. After removal from the gas 70% of the accumulated CO_2 is lost in 8 hr., and in 14 hr. a normal val. is reached.

L. S. T.

Carbon dioxide content of the gas from pea pods. Z. I. KERTESZ (Plant Physiol., 1934, 9, 339—350).—The higher CO_2 content of air from growing pea pods during darkness is attributable to the altered proportions of respiration and photosynthesis. The $[\text{CO}_2]$ remains const. throughout the day. The freezing of picked pods increased the CO_2 content, which again increased on subsequent storage at 25° . When pods were sealed with paraffin wax and stored at room temp. CO_2 increased very rapidly.

A. G. P.

Production of alcohol and acetaldehyde by tomatoes. F. G. GUSTAFSON (Plant Physiol., 1934, 9, 359—367).—The presence of EtOH and MeCHO is established in tomatoes under all conditions. The proportion of EtOH , but not of MeCHO , increases with time in anaerobiosis. Other compounds associated with anaerobic respiration were formed only in minute amounts.

A. G. P.

Effects of humidity on metabolism in tomato and apple. G. T. NIGHTINGALE and J. W. MITCHELL (Plant Physiol., 1934, 9, 217—236).—Tomato plants grown with complete nutrients in an atm. of 35% R.H. contained less chlorophyll and more carbohydrate (I) than those grown at 95% R.H. Low humidity caused the formation of much insol. protein-N in the plants, and high humidity gave rise to much H_2O -sol. N. Growth of apple trees at 40% R.H. is associated with accumulation of (I) and the condensation of simpler forms of org. N to form complex protein.

A. G. P.

Influence of thyroxine on the growth of plants. E. E. DAVIS (Plant Physiol., 1934, 9, 377—384).—Injection of thyroid material into bulbs accelerated the flowering period and increased the no. of flowering heads. Roots of plants grown in media containing thyroxine were stunted.

A. G. P.

Micro-organisms and plant growth. H. NICOL (Nature, 1934, 134, 218; cf. this vol., 934).

L. S. T.

Micro-organisms and plant growth. W. B. MERCER (Nature, 1934, 134, 218; cf. preceding abstract).—For many years yeast has been recognised as a fertiliser on the Keuper Marls around Burton-on-Trent. It has been commonly used as a dressing on grassland, giving an effect resembling that of nitrogenous manure.

L. S. T.

Relation of hydrogen ions to the growth rate of the *Avena* coleoptile. J. BONNER (Protoplasma, 1934, 21, 406—423).—The action of acid solutions in increasing the plasticity of cell walls is confirmed in *Avena* coleoptiles. The increased growth rates in

acid buffer solutions are inhibited by concns. of HCN comparable with those which inhibit the action of "growth substance" (I). The acidity of cells is not increased by (I). The presence of (I) in plants is established even after the removal of hormone-producing tips. The acceleration of growth in acid buffers is due to the conversion of (I), already in the plant from an inactive salt into an active non-dissociated form.

A. G. P.

Growth substance and plant growth. S. L. MALOWAN (Protoplasma, 1934, 21, 306—322).—A review.

A. G. P.

Growth hormone of plants. VI. Distribution of the growth substance in plant tissues. K. V. THIMANN (J. Gen. Physiol., 1934, 18, 23—34).—Extraction by acid CHCl_3 can be used for determination of the growth hormone (I). The concn. decreases steadily from the tip to the base in both *Avena* coleoptiles (II) and roots (III). The amount of (I) diffusing out of (III) into glucose-agar is never > the amount obtainable by extraction, indicating that production does not occur in (III) as it does in (II). (I) is inactivated by the oxidising enzymes of plant tissues.

C. G. A.

Root-forming substance. F. LAIBACH, A. MÜLLER, and W. SCHAFER (Naturwiss., 1934, 22, 588—589).—Constituents of the aq. extract of pollen and of the Et_2O extract of human urine stimulate the formation of roots on cut stems of a no. of plants.

A. G. P.

Transverse and longitudinal transport of growth-promoting substance in plant organs. K. KOCH (Planta, 1934, 22, 190—220).—Effects of removal and of darkening *Avena* coleoptiles on geotropic response with and without the presence of auxin are examined. The anionic character of the growth substance is demonstrated.

A. G. P.

Growth-promoting substance in roots poisoned with erythrosin. P. BOYSEN-JENSEN (Planta, 1934, 22, 404—410).—Treatment of seed with erythrosin tends to inhibit the formation and activity of growth-promoting substance.

A. G. P.

Inhibition of the development of lateral buds by growth hormone. F. SKOOG and K. V. THIMANN (Proc. Nat. Acad. Sci., 1934, 20, 480—485).—An impure prep. of growth hormone from *Rhizopus*, auxin B, and heteroauxin inhibit the growth of lateral buds of decapitated *Pisum* (to an equal extent in equiv. concns.), but do not cause an increase in stem length or thickness. The plants are not injured and later develop normally. Auxin A, inactivated by age, is without effect.

R. S. C.

Sensitivity of the plagiogeotropism of lateral roots. H. VON WITSCH (Jahrb. Wiss. Bot., 1934, 79, 790—812).—Traces of salts of Cu (such as may occur in distilled H_2O in contact with metallic Cu), Pb, Ag, Fe, Cd, Co, and Hg cause abnormal deflexion of lateral roots of plants grown in H_2O cultures. Ca or K salts reduce the toxic action of Cu on plants without affecting its geotropic action.

A. G. P.

Catalase, redoxase, and development factors of barley mutants. H. VON EULER, H. HELLSTROM, D. BURSTROM, and H. LARSSON (Svensk Kem.

Tidskr., 1934, 46, 66—70; cf. A., 1932, 550; this vol., 696).—The root extracts of chlorophyll-normal and chlorophyll-defective varieties of barley do not differ greatly in catalase activity (which is small), O_2 absorption, or in the presence of factor-B (which is fairly abundant). Small additions of yeast extract accelerate growth more than does urine with higher auxin content, even if it also contains folliculin (I). (I) is not detected in pea pods by ultra-violet spectroscopic investigation. Inter-relationships of the various growth factors are briefly discussed. J. W. B.

Metabolism of etiolated seedlings as affected by ammonium nutrition. L. BURKHART (Plant Physiol., 1934, 9, 351—358).—Rates of absorption and utilisation of NH_4^+ by *Cucurbita pepo*, *Phaseolus vulgaris*, *Lupinus albus*, and *L. luteus* grown in darkness with complete nutrients were dependent on the type and amount of non-N reserves (I) in the plants, and differed with variety and stage of growth. Feeding with NH_4^+ disturbed the utilisation of reserve protein and (I) and in some cases restricted protein regeneration. Little evidence was obtained to indicate that amides serve as efficient detoxicants of NH_4^+ . Injury by NH_4^+ is associated with low concns. of reducing sugars in the plants and is largely controlled by the nature of the (I) in the seed. A. G. P.

Relation of nitrate-nitrogen to carbohydrate and nitrogen content of onions. A. L. WILSON (Cornell Univ. Agric. Exp. Sta. Mem., 1934, No. 156, 30 pp.).—N-deficient onions have subnormal proportions of sol. and insol. N in all parts of the plant and a higher sugar (I) : N ratio. Supplies of soil N > that for normal growth depress the yield of bulbs without affecting that of tops. Manuring with N does not cause appreciable variations in the (I) content of the plant, but high NO_3^- dosage tends to decrease the rate of accumulation and max. storage of (I) in bulbs. The nature of the stored (I) differs with variety. Prior to bulbing (I) accumulates in all parts of the plant and subsequently is translocated into the bulb. Sol. N remains const. in leaves and neck, but increases steadily in the bulb with advancing growth. Insol. N is substantially const. in bulbs but decreases in neck and leaves. A. G. P.

Effect of variations in nutrient media on the nitrogen, phosphorus, and potassium contents of plants, with special reference to tomato. R. P. BARTHOLOMEW, V. M. WATTS, and G. JANSSEN (Arkansas Agric. Exp. Sta. Bull., 1933, No. 288, 42 pp.).—Nutrient media of very different composition may produce the same dry matter yield in tomatoes. The actual intake of N, P, and K by plants is partly controlled by the concn. of these elements in the nutrient. Deficiency of K may increase the absorption of N and P, and deficiency of P may increase intake of N by stems. Generous supplies of N tend to increase the P uptake of leaves; high K supplies increase the P of stems. Absorption of Mg and Ca is not directly influenced by that of N, P, and K, but is probably influenced by physiological reactions caused by these nutrients. Antagonism between nutrient elements may develop in the metabolic centres of plants as well as at the surface of the absorbing membrane. A. G. P.

Effect of type of endosperm on carbohydrate distribution in the mature maize plant. W. B. KEMP and P. R. HENSON (J. Amer. Soc. Agron., 1934, 26, 519—524).—Plants producing no grain accumulate more carbohydrates (I) in stems and leaves than do grain-bearing plants. Withdrawal of (I) from leaves to grain is greater for dent than for sugar grain.

A. G. P.

Significance of potassium in the production of living plant tissue. J. STOKLASA (Ernähr. Pflanze, 1934, 30, 299—307).—The germination and growth of a no. of crop plants were increased by exposure to radiation from K compounds. A. G. P.

Influence of the time of harvesting on the composition and feeding of hay. I. POIJÄRVI (Nord. Jordbr., 1933—1934, May, 520—524).—With increasing age of the grass the protein content and frequently the ash content decrease while the fibre content increases. The earlier the stage of growth, the higher is the digestibility. NUTR. ABS. (m)

Seasonal changes in the chemical composition of pasture grasses. H. B. STENT (Dept. Agric. N. Rhodesia, Ann. Bull., 1933, 14—23).—Monthly cutting of natural veld grass gives material of a higher protein and P_2O_5 content and lower fibre content. Results are given for the seasonal variation in composition of this grass and *Digitaria setivalva*, *Chloris gayana*, *Urochloa pullulans*, and *Brachiaria dictyoneum*. NUTR. ABS. (m)

Distribution of proteolytic activity in stems of normal plants and grafts. K. SILBERSCHMIDT (Planta, 1934, 22, 313—367).—In tobacco and *Datura* plants max. proteolytic activity (I) of the expressed juice of stems occurs in the lower apical section. The (I) of young flowering plants is > that in corresponding sections of fruiting plants. In heteroplastic (II) and homoplastic (III) grafts, sap from the zone of union has a similar (I) to that of adjacent zones, but that from the upper section of *Datura* stocks has a higher (I) with (II) than in (III) grafts. A. G. P.

Photosynthesis and free nitrogen assimilation by leguminous plants. E. B. FRED and P. W. WILSON (Proc. Nat. Acad. Sci., 1934, 20, 403—409).—N fixation by clover plants increases with a rise in the CO_2 content of the atm. (0.03—0.1%). Excessive carbohydrate (I) formation in the early stages of growth may lead to delayed N fixation. A positive correlation exists between increasing (I) content and the no. of root nodules occurring in inoculated plants. P. G. M.

Fixation of nitrogen by germinating seeds of leguminous plants. F. S. ORCUTT, A. M. SHANNON, and P. W. WILSON (J. Bact., 1934, 27, 55—56).—No evidence was obtained of N fixation by germinating peas in the absence of bacteria (cf. Vita, A., 1933, 103). A. G. P.

Colour and growth in the ocean. Theory of complementary colour adaptation in northern marine algæ. C. MONTFORT (Jahrb. wiss. Bot., 1934, 79, 493—592).—The interdependence of pigmentation, light colour, and assimilation in green, brown, and red algæ is examined in relation to the natural distribution of the species. A. G. P.

Specific alkalinity and distribution of algae in sea-shore pools. R. LAMI (Compt. rend., 1934, 199, 615—617).—With adequate illumination the p_H finally attained by the H_2O in the neighbourhood of various algae *in vitro* (I) and *in situ* (II) is a sp. const. of the alga, although (I) is slightly $>$ (II), but with insufficient light it is dependent on the intensity of the latter and is not characteristic of the species. The implications on the distribution of algae are briefly discussed. J. W. B.

Light energy balance of submerged water plants, especially marine algae. A. SEYBOLD (Jahrb. wiss. Bot., 1934, 79, 593—654).—The influence of intensity and quality of light on the C assimilation of coloured marine algae is examined. A. G. P.

Carbohydrate, nitrogen, and base element relationships of peas grown in water culture under various light exposures. O. E. STREET (Plant Physiol., 1934, 9, 301—322).—High wet and dry wts. of plants are associated with nutrients rich in $Ca(NO_3)_2$, high sugar contents with much Mg, and high polysaccharide contents with much K. The org. N in the plants was not consistently affected by the composition of the nutrient. Shorter exposure of plants to light tended to produce greater proportions of crude ash, higher K, and lower Ca and Mg contents. High-Mg media produced relatively small, and high-Mg and -Ca media large, proportions of ash in plants. A. G. P.

Effect of failure of pollination on composition of maize plants. A. M. BRUNSON and W. L. LATSHAW (J. Agric. Res., 1934, 49, 45—53).—Prevention of pollination results in abnormally high accumulation of protein (I) and N-free extract in other organs, and a reduction in the % of crude fibre (II), especially in cobs and stems. Greatest changes in composition occur in the cobs, in which poorly filled ears have high proportions of fat, ash, and (I). The effects of these changes on the val. of maize silage and fodder are examined. A. G. P.

Influence of electricity on the ash content and organic composition of plants. J. O. MUSSO (Z. Pflanz. Düng., 1934, A, 35, 31—37).—The intake of mineral matter by plants is influenced by the potential gradient between the soil and the atm. In soil of positive potential (I) plants accumulate more ash constituents than when grown in soil of negative potential. In (I) plants produce more protein per unit of dry matter. A. G. P.

Effect of rubidium sulphate and palladium chloride on the growth of plants. W. E. BRECHLEY (Ann. Appl. Biol., 1934, 21, 398—417).—Over a considerable range of concn. Rb_2SO_4 had no effect on the germination or growth of a no. of crops in H_2O cultures. Root injury was caused by $PdCl_2$ to extents which varied with the concn. applied and with the species of plant treated. A. G. P.

Absorption of calcium from nutrient solutions in presence or absence of boron. K. WARINGTON (Ann. Bot., 1934, 48, 743—776).—The presence of B in nutrient solutions (I) increased the amount of Ca absorbed by *Vicia faba*, and also the period during which the weekly intake of Ca was increasing.

Renewal of the (I) at 7—14-day intervals raised the Ca intake from B-free solutions, but depressed that from (I) containing B. From a series of corresponding solutions the Ca absorption \propto the amount supplied, although in presence of B the level of intake was raised. The N and K contents of plants were related to the total dry matter production but not to the amount of Ca supplied. The N/Ca and K/Ca ratios of plants grown in complete (I) declined with age, the rate of decline being increased by B.

A. G. P.
Calcium, phosphorus, and nitrogen content of grasses and legumes and the relation of these elements in the plant. H. A. DANIEL (J. Amer. Soc. Agron., 1934, 26, 496—503).—Analytical data for numerous species are recorded and inter-relationships are examined. A. G. P.

Composition of salts on leaves of some desert plants. R. E. CHAPMAN (Ann. Bot., 1934, 48, 777—780).—The salt accumulations consisted largely of Ca^{++} , Na^+ , Cl^- , and SO_4^{--} with relatively small amounts of K^+ , Mg^{++} , Fe, N, and P. No carbohydrates were present. A. G. P.

Fruit of two Greek species of citrus containing sulphate. A. TEGOPOULOS (Z. Pflanz. Düng., 1934, A, 35, 77—78).—Practically all the SO_4^{--} in both species was sol. in H_2O . Only traces of Mg and very little Ca appeared in H_2O extracts. The distribution of SO_4^{--} in various parts of the fruit is examined. A. G. P.

Iodine content of potatoes. J. F. MCCLENDON, E. BARRETT, and T. CANNIFF (Biochem. J., 1934, 28, 1209—1211).—I is determined by ashing, extraction with CCl_4 , and comparison with a standard in a micro-colorimeter. The content is $85—226 \times 10^{-8}$ g. per kg. dry wt. C. G. A.

Distribution of molybdenum in biological material. I. Spectrographic study of the occurrence of molybdenum in plants grown in the Province of Quebec. A. DINGWALL, R. R. MCKIBBIN, and H. T. BEANS (Canad. J. Res., 1934, 11, 32—39).—Mo was detected spectroscopically in the ash of a large no. of plants grown on a Mo-free soil in Jacques Cartier county. In other districts Mo could not be detected. H. N. R.

Hydrocyanic acid, the toxic entity of *Molinia caerulea*, Moench. A. JHILLER and R. ZITTI (Compt. rend., 1934, 199, 617—618).—The toxic character of the inflorescence (before and during flowering) of *M. caerulea* is due to the presence of a HCN-generating complex, the decomp. of which is accelerated by emulsin; it is absent from the fruit and all other parts of the plant. J. W. B.

Dry matter content of annual lespedezas, lucerne, and soya beans. R. E. STITT (J. Amer. Soc. Agron., 1934, 26, 533—535).—Analyses of plants at varying stages of growth are recorded. A. G. P.

Phytochemical investigation of living *cyamus muticus*, L. T. POTJEWIJD (Pharm. Weekblad, 1934, 71, 1009—1016).—In Egyptian henbane, *H. muticus*, L., cultivated in Holland, tropine identified in the leaves of the youngest plants, but in more mature specimens. Tetramethyldiam

butane was present in the first stages of growth only in parts above ground, in half-grown plants chiefly in the corolla. There is no suggestion that this base is an intermediate in the synthesis of more complex alkaloids. Atropine was occasionally identified and is probably a degradation product in moribund leaves. Hyoscyamine occurred in all parts of the plant at all stages of growth, the amount increasing to a max. at the flowering stage. The total alkaloid content, 0.0177%, is < that in plants cultivated in Egypt. S. C.

Chemical composition of New Mexico Pinto and Bayo beans. M. L. GREENWOOD (New Mexico Agric. Exp. Sta. Bull., 1933, No. 213, 11 pp.).—Analytical data are recorded. A. G. P.

Leaves of *Pentstemon cobaea*, Nutt. L. E. HARRIS and R. A. CONNER (J. Amer. Pharm. Assoc., 1934, 23, 796—798).—These leaves, after extraction with ligroin, yield to EtOH crystals, m.p. 163°. The amounts of extract obtained by various solvents are given (max. 38%, by hot H₂O). R. S. C.

Phytochemistry of the root-bark of *Phyllanthus engleri*, Pax. M. G. BREYER-BRANDWIJK (Quart. J. Pharm., 1934, 7, 167—178).—The root-bark of *P. engleri* extracted with light petroleum and Et₂O, respectively, gave two different resins, a third being present in the EtOH extract of the residue. Extraction of the bark with COMe₂ yielded a toxic glucoside, and in addition the bark contained rubber and starch, but no protein. A. L.

[Composition of] dandelions. E. BENNETT (Science, 1934, 80, 142).—The dandelion has a high protein (15.76%) and a low fibre (9.79%) content and contains much Ca, Mg, and P. L. S. T.

Absorption spectra of some carotenoid pigments at liquid-air temperatures and application to the carotenoid pigments of cow-pea leaves (*Vigna sinensis*). G. E. HILBERT and E. F. JANSEN (J. Biol. Chem., 1934, 106, 97—105).—Absorption spectra of α - and β -carotenes, carrot "carotene," "leaf xanthophyll," and lycopene studied at liquid air temp. show more bands in the ultra-violet and a considerable sharpening of the bands. In mixtures of α - and β -carotenes, absorption max. are shifted towards shorter λ with increasing concn. of α -carotene. Xanthophyll is present as an ester in cow-pea leaves in negligible amount and the major proportion of the carotene is the β -form. H. G. R.

Pigment of the India red pummelo (*Citrus grandis*, Osbeck). M. B. MATLACK (J. Washington Acad. Sci., 1934, 24, 385—386).—The crystals of pigment isolated from the pulp and locular membranes have been identified spectroscopically as lycopene (cf. A., 1928, 765). W. O. K.

Microchemical properties of hydroxyflavone compounds and the possibility of distinguishing them from tannins. A. GUILLIERMOND and R. GAUTHERET (Compt. rend. Soc. Biol., 1933, 112, 537—540; Chem. Zentr., 1933, ii, 3891—3892).—Microchemical tests are given for the detection of the hydroxyflavone (I) occurring in white and yellow tulip flowers and, in smaller concns., in many other cells, and for the detection of tannin (II). In *Chrys-*

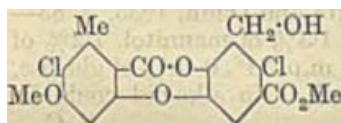
anthemum frutescens two types of cell are found, the vacuoles of one containing a mixture of (I) and (II), and those of the other only (II). H. J. E.

Tannin content of Labiatae. H. VOLLMER (Arch. exp. Path. Pharm., 1934, 176, 207—216).—Of 40 species examined, 3 had > 15%, 11 had 10—15%, 22 had 5—10%, and 4 had < 5% of tannin in the dried material. The relation between % tannin and the astringent action in mice of aq. extracts of peppermint and ground-ivy was investigated. F. O. H.

Tannin content of indigenous Tubuliflorae. H. VOLLMER (Arch. exp. Path. Pharm., 1934, 176, 550—557).—The tannin contents of roots and leaves of Boraginaceae, Solanaceae, and Convolvulaceae used as herbs were determined and correlated with the costive action of their extracts on mice. F. O. H.

Reactions of lichen-thallus. Y. ASAHINA (Acta Phytochim., 1934, 8, 47—64).—The colour reactions of a large no. of lichen acids and their derivatives of the depsidone group with KOH (photomicrographs of cryst. forms given) and with NH₂Ph, benzidine, and *p*-C₆H₄(NH₂)₂ (reactions with -CHO) are tabulated and discussed in detail. J. W. B.

Lichen substances containing chlorine. T. J.



NOLAN, J. KEANE, and J. HARDIMAN (Chem. and Ind., 1934, 762).—A neutral, chlorinated depside, m.p. 215°, for

which the annexed formula is suggested, has been isolated from a lichen from the Irish coast. S. C.

Structure of the cell-wall of wood fibres. G. J. RITTER (Paper Ind., 1934, June, 178—183).—The major portion of the lignin is located in the middle lamella, the remainder in the cell-wall. Cellulose and hemicellulose form the major part of the cell-wall, which is composed of several thin layers arranged as concentric sleeves which can be loosened chemically and separated mechanically by slipping them off endwise. The layers can be split up into fibrils by both chemical and mechanical means, and these may be further subdivided into fusiform bodies, which are themselves composed of smaller spherical units. A cementing material of hemicellulosic nature is believed to exist between the layers and fibrils of the cell-wall of delignified fibres. When this is removed by suitable solvents, the layers and fibrils can be separated mechanically. H. A. H.

Structure of the starch granule. M. SAMEC (Z. ges. Getreide-Mühlenw., 1934, 111; Woch. Brau., 1934, 51, 270—271).—The manner in which the subsidiary constituents of starch (P₂O₅, SiO₂, proteins, fatty acids) are arranged in the granule is discussed. T. H. P.

Rye gum. T. VON FELLEBERG (Mitt. Lebensm. Hyg., 1934, 25, 257—260).—The product isolated by the method of Tillmans, Holl, and Jariwala (B., 1929, 70) gives all the reactions of pure pentosan. J. G.

Ethyl alcohol and acetaldehyde in certain kinds of cacti. F. G. GUSTAFSON (Biochem. Z., 1934, 272, 172—179).—Small amounts of MeCHO (0.45—6.3 mg. per kg.) and EtOH (2.2—46 mg. per kg.)

are present in the fresh plants under normal aerobic conditions. After exclusion of air, formation of MeCHO is only slight and attains a max. after 24 hr., whilst EtOH accumulates and may be regarded as an end-product of anaerobic respiration. P. W. C.

Origin, composition, and structure of cellulose in the living plant. W. SEIFRIZ (Protoplasma, 1934, 21, 129—159).—A review. A. G. P.

Carbohydrates in the bulbs of *Narcissus tazetta*. IV. Y. KIHARA (J. Agric. Chem. Soc. Japan, 1934, 10, 318—319).—When hydrolysed by *Eulota* extract the reducing power (I) of the glucomannan increased; takadiastase did not increase (I). CH. ABS.

Biochemistry of *Salix repens*. L. M. WATTIEZ (Bull. Acad. roy. Méd. Belg., 1932, [v], 12, 433—446; Chem. Zentr., 1933, ii, 3710).—"Salireposide" is the benzoate of a *heteroside*, m.p. 172—173°, mol. wt. about 300. Acid hydrolysis yields β -glucose (59.71%) and a black insol. substance with reducing properties (39.77%). Enzymic hydrolysis yields β -glucose and a keto-phenolic substance, $C_7H_7O_3$. H. J. E.

Chemical examination of the leaves of *Nyctanthes arbor-tristis*. Linn. J. B. LAL and S. DUTT (Bull. Acad. Sci. Agra and Oudh, 1933, 3, 83—86).—The leaves afforded 1.3% of mannitol, 1.2% of a resin, 1% of a *glucoside*, m.p. 71°, 0.48% of glucose, and a trace of essential oil. No alkaloid could be detected. S. C.

Non-basic constituents of the leaves and roots of *Adlumia fungosa*. Greene. L. MARION (Canad. J. Res., 1934, 10, 759—764).—The H_2O -insol. constituents of this plant comprise an *alcohol* (?), $C_{28}H_{56}O_2$, m.p. 82—83°, b.p. 255—256°/1.5 mm., oxidised by CrO_3 to an *acid*, m.p. 59°; a sterol (*adlumiasterol*), $C_{39}H_{68}O_2$, m.p. 151—152° (*monoacetate*, m.p. 136—137°); a red *pigment*, m.p. 286°; a phenolic substance, $C_8H_{16}O$, m.p. 115°; fumaric acid; 3:4-methylenedioxypthalide, probably derived from adlumine; and a *phytosterolin*, $C_{33}H_{56}O$, m.p. 295° (*tetrabenzoate*, m.p. 184—185°; *tetraacetate*, m.p. 157°), which, on hydrolysis, gives a sterol, m.p. 135—136°, possibly identical with that obtained from the seeds of *Asclepias syriaca*. H. N. R.

Digitonin and phytosterol from the seed of *Digitalis purpurea*. O. GISVOLD (J. Amer. Pharm. Assoc., 1934, 23, 664—666).—The seeds yielded 1.16% of digitonin, part directly by EtOH extraction and part as an insol. sterol digitonide. C. G. A.

Occurrence of sterol glucosides in soya-bean oil. E. JANTZEN and W. GORDEN (Biochem. Z., 1934, 272, 167—171).—Sitosterol occurs in the oil both free and esterified, but also as sitosteryl- β -glucoside. In the phosphatide fraction of the oil, the amount of sterol as glucoside is > the sum of free and esterified sterol, whereas in the oil itself the reverse is true. The glucoside is absent from olive oil. P. W. C.

Occurrence of a phytosterol in African oil palm (*Elaeis guineensis*). K. S. MARKLEY and M. B. MATLACK (Science, 1934, 80, 206).—Crystals, m.p. approx. 136.5°, giving a positive Liebermann-Bur-

chard reaction have been obtained from the EtOH mother-liquor remaining after the separation of most of the carotene from the unsaponifiable fraction of palm oil. The palm-oil phytosterol probably consists chiefly of sitosterol. L. S. T.

Calosterol, a sterol present in the juice of *Calotropis gigantea*. K. P. BASU and M. C. NATH (Biochem. J., 1934, 28, 1561—1564).—From the milky juice of the tubers *calosterol*, $C_{28}H_{44}O$, m.p. 202—203°, +100.6° in $CHCl_3$ (*hydrate* $C_{28}H_{44}O \cdot H_2O$; *benzoate*, m.p. 239—240°, $[\alpha]_{D}^{25} + 121.6^\circ$; *acetate*, m.p. 211—212°, $[\alpha]_{D}^{25} + 105^\circ$ in $CHCl_3$), has been isolated. The uptake of Br indicates the presence of 3 double linkings, whilst by catalytic reduction 2 H, were absorbed. W. O. K.

Crystalline substance from the ethereal oils of Manila elemi resin. M. MLADENOVIC (Monatsh., 1934, 64, 177—182).—From the phellandrene (I) fraction, b.p. 170—180°, of the steam-distilled essential oils of elemi resin is obtained a *substance*, $C_{10}H_{18}O$, (II), m.p. 168°, $[\alpha]_D^{25} + 10.39^\circ$ in EtOH, which, contrary to Clover (A., 1907, i, 542), is not obtained by atm. oxidation of (I), since repetition of the distillation on the mother-liquor gives no more cryst. material. Reduction of (II) with H_2 -Pd-C in EtOH (H_2 absorption equiv. to 2 double linkings) affords an oil from which separates a cryst. *substance*, $C_{10}H_{20}O$, m.p. 65°, closely resembling (? identical with) menthol. J. W. B.

Presence of a substance of oleaginous appearance in the epidermal cells of the leaves of *Haworthia cymbiformis*. N. SOSTER (Atti R. Accad. Lincei, 1934, [vi], 19, 735—740).—This substance (cf. Guillermond, Compt. rend. Soc. Biol., 109, 1182) contains a phenolic derivative and possibly flavone compounds. T. H. P.

Two species of the genus *Ledum*. R. A. CAIRN and E. V. LYNN (J. Amer. Pharm. Assoc., 1934, 23, 666—672).—Neither *L. grænländicum* (I) nor *L. columbianum* (II) contains alkaloids or is toxic to rats or rabbits. The leaves of (I) yield 0.15% of an oil containing 20% of *l*-borneol (III), 15% each of phellandrene, *l*- α -caryophyllene (IV), and ledum camphor (V), and small quantities of phenols (VI), AcOH (VII), and azulene (VIII). The flowers gave 0.058% of an oil with different consts. The leaves of (II) gave 0.35—0.56% of an oil containing 3% of *l*- α -pinene, 17% of (III), 15% each of (V) and a terpene (probably *l*- β -pinene), 10% each of *d*- α -phellandrene, (IV), and *columbenol* (IX), $C_{15}H_{22}O$, m.p. 55.7°, b.p. 277° (some decomp.), $[\alpha]_D^{25} + 5.2^\circ$ in EtOH, probably alcohol, and small quantities of (VI), (VII), and (VIII). The flowers gave 0.59% of an oil having different consts., containing 10% of (IX). C. G. A.

Higher hydrocarbons in tobacco smoke. A. WENUSCH (Biochem. Z., 1934, 273, 178—179).—A hydrocarbon, m.p. 70—72°, containing 84.9% C is isolated from cigar and cigarette smoke. P. W. C.

Kaoliang oil. T. INABA and K. KITAGAWA (J. Soc. Chem. Ind. Japan, 1934, 37, 434b).—The Et_2O -extracted oils from the germ (I) and the bran (II) *Andropogon sorghum*, Brot, had respectively: n_D^{20} 1.4604, 1.4570; acid val. 6.68, 96.47; sap. val. 180.9, 185.8; I val. 115.4, 110.8; Ac val. 15.9, 18.8; Helmer

val. 94.45%, 90.01%; Reichert-Meissl val. 0.53, 0.73; Polenske val. 0.39, 0.46%; unsaponifiable matter 2.82%, 8.04%. The fatty acids from (I) contained 10.3% of solid acids (mainly palmitic, with traces of arachidic acid), 42.9% of oleic acid, and 46.8% of α - and β -linoleic acids (by thiocyanometric analysis). The acids of (II) consisted of 7.7% of solid acids, with 43.1% of oleic and 49.2% of linoleic acid.

E. L.

Oil from *Pentaclethra macrophylla*, Benth. P. DENIS (Matières grasses, 1933, 25, 9987—9988, 10015—10017; Chem. Zentr., 1934, i, 1902).—Analytical data for the oil are given. The fatty acids include a C_{24} acid, m.p. 79.7°, stearic, oleic, linoleic, and a OH-acid.

A. G. P.

Organ-protein of plants. A. KIESEL, A. BELOZERSKY, P. AGATOV, N. BYSCHICH, and M. PAVLOVA (Z. physiol. Chem., 1934, 226, 73—86).—The types of N-linking and constituent NH_2 -acids of the leaf- and root-proteins of potato, sugar-beet, and red beet (leaf only), and of the leaf- and seed-proteins of *Citrullus edulis* and *C. colocynthis* were compared.

J. H. B.

Exudation of glutamine from perennial ryegrass. A. W. GREENHILL and A. C. CHIBNALL (Biochem. J., 1934, 28, 1422—1427).—The exudation observed on the leaves of the grass treated with $(NH_4)_2SO_4$ consists essentially of glutamine.

W. O. K.

Cystine, tryptophan, and tyrosine contents of the soya bean. F. A. CSONKA and D. B. JONES (J. Agric. Res., 1934, 49, 279—282).—Varietal differences in the proportions of these NH_2 -acids are recorded.

A. G. P.

Alkaloid from *Mitragyna*, mitrinermine. RAYMOND-HAMET and L. MILLAT (Compt. rend., 1934, 199, 587—589).—The bark contains mitrinermine, $C_{22}H_{28}O_4N_2$, m.p. 202—216°, which contains two $\cdot OMe$, and occurs only in *M. inermis*.

J. L. D.

Rôle of the steric factor in the biogenesis of alkaloids. J. SUSZKO (Arch. Chem. Farm., 1934, 1, 212—228).—The optical activity of naturally occurring alkaloids does not support the hypothesis of their origin from NH_2 -acids.

R. T.

Determination of minute amounts of chlorophyll. P. A. HICKS and T. E. PANISSET (New Phytol., 1934, 33, 199—210).—A colorimetric method to deal with MeOH extracts from 5—20 mg. of fresh plant material is described. Relationships between respiration rates and chlorophyll contents of *Lemna* fronds are examined.

A. G. P.

Determination of phytin-phosphorus. R. S. HARRIS and L. M. MOSHER (Ind. Eng. Chem. [Anal.], 1934, 6, 320—321).—The HCl extract of the plant is treated with NH_4CNS and then with a slight excess of standard $FeCl_3$, kept 10—20 min., filtered (double hardened paper), and matched colorimetrically against aq. $FeCl_3$ added to HCl- NH_4CNS solution. Results are reproducible within $\pm 0.05\%$.

R. S. C.

Combustion method for the determination of iodine in plant material. J. S. McHARGUE, D. W. YOUNG, and R. K. CALFEE (Ind. Eng. Chem. [Anal.], 1934, 6, 318—319).—The plant material with CaO

and CuO is burnt in a closed system in a slow stream of air, the issuing gases being washed with aq. KOH. A hot aq. extract of the residue, combined with the KOH, is evaporated, just redissolved in H_2O , and extracted thrice with EtOH. The EtOH is evaporated, the residue dissolved in H_2O , acidified (H_2SO_4), reduced (SO_2), and treated with $NaNO_2$ and CS_2 . The I in the CS_2 is determined colorimetrically. Results are recorded for various materials.

R. S. C.

Effect of hydrogen sulphide on *Elodea canadensis*. H. ZINKERNAGEL (Kl. Mitt. Ver. Wasser-, Boden-, Lufthyg., 1933, 9, 188—193; Chem. Zentr., 1934, i, 1508).— H_2S at dilutions of 1:1250 to 1:19,600 produces fading in the leaves owing to the conversion of chlorophyll into phaeophytin (I). Sunlight changes the fading into bleaching owing to the disappearance of (I).

L. S. T.

Influence of radium on plants. A. LEPAPE and R. TRANNOY (Ann. agron., 1934, 4, 319—354).—An amplified account of earlier work (this vol., 1049). Ra withdrawn from soil by plants occurred mainly in leaves and stems.

A. G. P.

Toxic action. VII. Toxicity of aliphatic esters towards potato tuber. K. W. DENT. VIII. Toxicity of normal aliphatic alcohols towards various plant tissues. F. M. CARTER (Protoplasma, 1934, 21, 62—72, 615—629).—VII. Toxicity (I) of esters, as measured by Stiles' method (A., 1932, 206), increased with mol. wt. whether of the acidic or alkyl group. Pr^oOAc was more toxic than Pr^iOAc . Isomeric esters composed of different alkyl and acid groups possess different (I), the highest acid radical being usually associated with greatest (I).

VIII. Toxicities of EtOH, PrOH, and BuOH increased in the order named. (I) is paralleled by surface activity. Among alcohols relative (I) is probably const. for all tissues.

A. G. P.

Carbon dioxide formation by clean and scabby potatoes. B. F. LUTMAN (J. Agric. Res., 1934, 48, 1135—1144).—Scabbed potatoes respired more rapidly than healthy ones during the first month of storage. The rates were subsequently equalised until, when sprouting began, healthy samples became the more active. Respiration rates obtained by passing CO_2 -free air through jars containing tubers were uniformly > those obtained by sampling air in the jars.

A. G. P.

Nutritional requirements of the root-rot fungus, *Phymatotrichum omnivorum*. W. N. EZEKIEL, J. J. TAUBENHAUS, and J. F. FUDGE (Plant Physiol., 1934, 9, 187—216).—Essential nutrients for the fungus include PO_4''' , K, Mg, and probably SO_4'' . Traces of Ca, Fe, and Cl occurring as impurities in the media suffice for normal requirements. Peptone, urea, NH_2 -acids, NH_4' , and NO_3' served as sources of N. C requirements were met by pentose and hexose monosaccharides, disaccharides, starch, and, to a smaller extent, by mannitol. In glucose media growth and acid formation continued until the sugar concn. fell to < 1%. The reaction of the media subsequently changed rapidly towards alkalinity. Growth reached max. in slightly alkaline media and was inhibited at pH 3.0. No evidence of accumul-

ations of staling products was obtained. Addition of carrot juice markedly increased growth, but cod-liver oil and rice bran extract had little effect. A. G. P.

Application of the Altmann freezing-drying technique to plant cytology. T. H. GOODSPEED and F. M. UBER (Proc. Nat. Acad. Sci., 1934, 20, 495—501).—The technique gives precise and uniform fixation of plant tissues. H. G. R.

Is it possible to detect manganese histochemically? V. BUREAU (Arch. Biol., 1934, 45, 391—396).—The method based on the pptn. of MnNH_4PO_4 in plant tissues by use of $\text{NaNH}_4\text{HPO}_4$ in the presence of NH_3 is not of general application. In some cases the reagent does not penetrate plant cells. A. G. P.

Amines in cytological fixing fluids. C. ZIRKLE (Protoplasma, 1934, 20, 473—482).—Amines (notably diisoamylamine and $\text{C}_5\text{H}_5\text{N}$) fix mitochondria in the presence of chromic acid at p_{H} 5.0. The effects of using other amines in conjunction with Cu dichromate and of variations of p_{H} on the fixation of (I) and chromatin are examined. A. G. P.

Standardisation of biological stains. V. A. R. PETERSON, H. J. CONN, and C. G. MELIN (Stain Tech., 1934, 9, 147—155).—Methods are described for qual. and quant. analysis and biological tests of the following dyes: pyronin-G and -B, neutral-red, safranine, nigrosin H_2O -sol, brilliant-cresyl-blue, cresyl-violet, Nile-blue A, thionine, methylene-blue, methylene-azure, azure C, toluidine-blue O, indigotin, and carmine. H. W. D.

Histochemical detection of fats. I. R. WASICKY and E. AMARANT (Sci. Pharm., 1934, 5, 1—4; Chem. Zentr., 1934, i, 2012—2013).—Fats are decomposed by pancreatic lipase at 37° . Saturated fatty acids crystallise in needles and unsaturated acids remain in drop form. Further differentiation of acids is made by customary reactions. A. G. P.

Determination of bromine in blood. F. HARTNER (Mikrochem., 1934, 15, 195—206).—10 c.c. of blood are heated with HNO_3 in presence of 3—4 c.c. of 10% AgNO_3 , oxidation being completed by addition of KMnO_4 . MnO_2 is removed by $\text{H}_2\text{C}_2\text{O}_4$, and the $\text{AgCl} + \text{AgBr}$ collected on a glass filter and washed free from org. matter with COMe_2 . The ppt. is reduced by Zn in presence of H_2O , dissolution of Cl' and Br' being completed by treatment with 0.005N- Na_2S . The solution, containing Br', is acidified with H_2SO_4 and H_3PO_4 , 2 c.c. of 0.5% MnSO_4 are added, and S'' is oxidised by KMnO_4 . Br' is then determined as in A., 1933, 477. J. S. A.

Determination of total lipin in plant and animal tissues. J. S. CHEN (Chinese J. Physiol., 1934, 8, 195—202).—The material is first extracted with Et_2O - EtOH (1 : 3) and the extract re-extracted with light petroleum. The unextracted residue is mainly phospholipin. H. G. R.

Modification of the Folin method for determining uric acid. E. HERZFELD (Mikrochem., 1934, 15, 305—312; cf. A., 1930, 630).—Loss of uric acid (I) during deproteinisation (II) may be avoided

by effecting (II) with excess of the uric acid reagent (III). (I) forms sol. complex compounds with excess of (III), which may be extracted quantitatively by washing. 2 c.c. of body-fluid are treated with 10 c.c. of (III), and the protein is filtered off and washed. (I) in the filtrate may then be determined both titrimetrically with 0.01N- KMnO_4 and colorimetrically. Urine and other $\text{PO}_4^{''}$ -containing fluids should first be treated with Folin's $\text{UO}_2(\text{OAc})_2$ reagent. J. S. A.

Detection of volatile amines in biological materials. A. WACEK and H. LOFFLER (Monatsh., 1934, 64, 161—166).— NH_3 in biological fluids (0.01—0.03 c.c.) is retained on addition of an excess of HgO , followed by aq. NaCl and Na_2CO_3 , whilst NMe_3 is liberated and detected by 2 : 4- $\text{C}_{10}\text{H}_5(\text{NO}_2)_2\cdot\text{OH}$ (I). After such removal of NMe_3 other volatile toxic amines (NHMe_2 , $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, etc.) are liberated by increasing the alkalinity (2.5% NaOH), the characteristic cryst. compounds with (I) (vinylamine, m.p. 132° ; propenylamine, m.p. 120° , and diallylamine, m.p. 116°) being described. Normal urine contains NHMe_2 and a little NMe_3 , the latter being greatly increased in patients suffering from severe burns. NMe_3 is present in pus. $\text{NH}(\text{CH}_2\cdot\text{CH}:\text{CH}_2)_2$ injected into the bloodstream of a rabbit is detected in blood samples up to the time of the animal's death. J. W. B.

Determination of magnesium [in biological material] using 8-hydroxyquinoline. M. JAVILLIER and J. LAVOLLAY (Ann. Falsif., 1934, 27, 326—333).—Ca is pptd. as oxalate from a solution of the ash at p_{H} 5, and removed by centrifuging. Mg is then pptd. at about p_{H} 8.4 with 8-hydroxyquinoline (I), traces of co-pptd. metals being removed by washing with ammoniacal 96% EtOH . Mg is determined bromometrically. If the $\text{PO}_4^{''}$ is > 15 times the amount of Mg, Mg must be added to bring the total Mg within this ratio. Relatively large amounts of Fe and Al are removed by treatment at p_{H} 5 with (I), after pptn., but before removal of the CaC_2O_4 . E. B. H.

Clinical determination of calcium. R. GILLE (Compt. rend. Soc. Biol., 1934, 110, 490—492; Chem. Zentr., 1934, i, 2011).—Serum is decomposed with HNO_3 - HClO_4 . Ca is pptd. as CaC_2O_4 , dissolved in HNO_3 , and heated with HCl . Alkali soap solution is added and the opalescence is compared with that given by standard solutions. A. G. P.

Thiolacetic acid as a reagent for determination of inorganic iron content of biological materials. S. L. TOMPSETT (Biochem. J., 1934, 28, 1536—1543). The $\text{CCl}_3\cdot\text{CO}_2\text{H}$ filtrate from the yolk of hen's egg or from serum contains no Fe, whilst that from whole blood contains small quantities. The total inorg. Fe may be determined by adding thiolacetic acid to the fluid before pptn. of the proteins with $\text{CCl}_3\cdot\text{CO}_2\text{H}$. The colour developed in the filtrate after addition of NH_3 is compared with a standard. The whole of the Fe in the hen's egg (about 1 mg.) is inorg. Human serum contains 0.2 mg. and whole blood about 1 mg. of inorg. Fe per 100 ml. Normal human urine contains < 0.01 mg. per litre, but in cases of nephritis > 2 mg. per litre may be found. W. O. K.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1934.

General, Physical, and Inorganic Chemistry.

Photographic intensity measurements of lines of the Paschen series of hydrogen in the infra-red solar spectrum. A. H. ROSENTHAL (*Nature*, 1934, 134, 533—534). L. S. T.

General expression for the intensity of hydrogen lines. L. McLEAN (*Phil. Mag.*, 1934, [vii], 18, 845—874).—Mathematical. A formula has been obtained for the total intensity of H lines in the general case of the transition $n \rightarrow n'$. M. S. B.

Resonance bands of the HD molecule in the region 1650—1000 Å. K. MIE (*Z. Physik*, 1934, 91, 475—492).—Analysis of rotation lines and bands in this region gives results in agreement with H₂ analysis; the zero point energy is 5.359 kg.-cal. A. B. D. C.

Dispersion of helium in the ground level according to wave mechanics. H. KORWIEN (*Z. Physik*, 1934, 91, 1—36).—Theoretical. A. B. D. C.

Interference measurements in the spectra of noble gases. W. F. MEGGERS and C. J. HUMPHREYS (*J. Res. Nat. Bur. Stand.*, 1934, 13, 293—309).—The wave-lengths of lines in the first spectra of He, Ne, Ar, Kr, and Xe have been measured between 3948 and 10,830 Å. E. S. H.

C state of Li₂. W. H. FURRY (*Physical Rev.*, 1933, [ii], 43, 361—362; cf. A., 1933, 1095). L. S. T.

New band system in nitrogen. J. KAPLAN (*Nature*, 1934, 134, 538; cf. this vol., 823).—Of new N bands, 2536, 2635, and 2740 Å. increase in intensity as pressure is reduced, and are (0,1), (0,2), and (0,3) bands of a new system. L. S. T.

Situation of the $A(^3\Sigma)$ level in the nitrogen molecule. L. VEGARD (*Nature*, 1934, 134, 697; cf. this vol., 1051). L. S. T.

Effect of inert gases on the afterglow spectrum of nitrogen. J. OKUBO and H. HAMADA (*Sci. Rep. Tôhoku*, 1934, 23, 281—288).—The intensity max. of the bands in the afterglow spectrum with $v'=-11$ and -6 are displaced towards longer wave-lengths with increasing partial pressure of inert gas at const. N₂ pressure, the effect being He>Ne>Ar. For the first positive bands of N₂ excited by a very weak current, the max. at $v'=-11$ is displaced towards longer wave-lengths, but not that at $v'=-6$, in presence of He or Ne. J. W. S.

Light excitation in neon by lithium ions. A. J. DEMPSTER and R. E. HOLZER (*Physical Rev.*, 1933, [ii], 43, 365—366).—Light excitation of Ne by Li⁺ has been observed at 160 volts, approx. 150 volts < the

ionisation potential observed by Beeck and Mouzon (A., 1932, 105). L. S. T.

Nuclear magnetic moments from the polarisation of resonance radiation. I. Sodium, $3^2S_{1/2}-3^2P_{3/2,1/2}$. L. LARRICK. II. Sodium, $3^2S_{1/2}-3^2P_{3/2,1/2}$. A. ELLETT and N. P. HEYDENBURG (*Physical Rev.*, 1934, [ii], 46, 581—583, 583—589).—I. An increase of 16.5—50% for 0—300 gauss range of field strength in the polarisation of Na D line resonance radiation, due to the Paschen-Back effect of the hyperfine structure, is observed, and is calc. and plotted on the assumption of a nuclear moment of 3/2.

II. Detailed calculations on the change in polarisation, due to the Paschen-Back effect of the hyperfine multiplet, of Na resonance radiation excited by unpolarised light are given. Measurements as a function of intensity of applied field were made. The hyperfine structure separation const. for $4^2P_{3/2}$ is $(1.87 \pm 0.05) \times 10^{-4}$ cm.⁻¹ N. M. B.

Spin interaction with exchange for alkali atoms. E. DAVID (*Z. Physik*, 1934, 91, 289—317).—Inverted alkali doublets cannot be explained without spin interchange. A. B. D. C.

Isotope effect in the band spectrum of sodium hydride. E. OLSSON (*Nature*, 1934, 134, 697—698). L. S. T.

Absorption spectra of mixed vapours of sodium and potassium with mercury, cadmium, and zinc. E. MATUYAMA (*Sci. Rep. Tôhoku*, 1934, 23, 334—342).—The absorption spectra of mixtures of vapours of Hg, Cd, or Zn with Na or K show two types of band, one having intensity fluctuations and appearing in very narrow regions with K alloys, the other, with discrete heads, appearing with Na alloys. It is considered that the two types of bands occur for both series of mixtures, but that they are masked by the Na₂ and K₂ band systems. J. W. S.

Hyperfine structure in the Al III line, 5722.6 Å. R. C. WILLIAMS and G. B. SABINE (*Physical Rev.*, 1933, [ii], 43, 362).—No hyperfine structure has been detected with certainty. L. S. T.

Nuclear mechanical moment of cobalt. K. R. MORE (*Physical Rev.*, 1934, [ii], 46, 470—473).—Components and interval ratios in the hyperfine structure of the lines $\lambda\lambda$ 4191, 4234, 6082, 6231, 6450, and 6592 of the arc spectrum give a val. of $I=7/2$. The estimated nuclear magnetic moment is of the order 2—3 small magnetons. N. M. B.

Selenium arc spectrum Se I. K. W. MEISSNER, O. BARTELT, and L. ECKSTEIN (Z. Physik, 1934, 91, 427—443). A. B. D. C.

Selenium arc spectrum Se II. O. BARTELT (Z. Physik, 1934, 91, 444—470). A. B. D. C.

Magnetic extinction of the fluorescence of diatomic selenium molecules. J. GENARD (Compt. rend., 1934, 199, 784).—The fluorescence of Se_2 excited by the Hg lines $\lambda\lambda$ 4047, 4359 Å. is decreased 40—50% by a field of 43,000 gauss, different terms of the same series being differently affected. H. J. E.

Absorption spectra due to excitation of inner electrons. VII. The rubidium spectrum between 900 and 600 Å. due to excitation of the $(4p)^6$ shell (Rb I). H. BEUTLER (Z. Physik, 1934, 91, 131—142). A. B. D. C.

Band spectra of rubidium in absorption and in emission. E. MATUYAMA (Sci. Rep. Tôhoku, 1934, 23, 308—321).—The spectrum due to Rb_2 mols. includes bands at 4300, 4800, 6800, and 8600 Å. of discrete vibrational structure, diffuse bands due to polarisation mols. and appearing only in emission, and a continuous spectrum at 6000 Å. The vibration quantum of the ground state is 58 cm^{-1} . J. W. S.

Multiplets in the Ag III spectrum. B. V. R. RAO (Proc. Indian Acad. Sci., 1934, 1, 28—33).—From the Moseley diagram for the terms of the isoelectronic sequence Rh I, Pd II, and Ag III, the terms $4d^3F5s^4F'$ and 2F , and $4d^3F^o p^4F'$ and $^2F'$ of Ag III are identified. The approx. ionisation potential is 29.25 volts.

N. M. B.

Band fluorescence of cadmium vapour. J. ŚWIETOSŁAWSKA (Z. Physik, 1934, 91, 354—360).—The long-wave limit and first fluctuation max. of these bands vary with the exciting wave-length.

A. B. D. C.

Wave-length shifts of the spectral lines of antimony due to change of pressure. T. YUASA (Sci. Rep. Tokyo Bunrika Daigaku, 1934, 2, 57—72).—Comparison of the emission spectra of Sb at pressures of a few cm. Hg and atm. pressure indicates that the higher are the principal and inner quantum nos. defining the spectral terms the greater is the wave-length change due to pressure and the greater the change in mode of appearance.

J. W. S.

Continuous emission spectra of iodine. K. ASAGOE and Y. INUZUKA (Sci. Rep. Tokyo Bunrika Daigaku, 1934, 2, 73—87).—Data are given for the intensity max. of the bands excited in a Geissler tube containing I vapour, over the range 2560—4735 Å. The effects of intensity of excitation and of pressure are discussed.

J. W. S.

Intensity distribution of hyperfine structure components of the caesium line at 4555 Å. and the nuclear moment of the caesium atom. H. BARTH (Z. Physik, 1934, 91, 272—283).—This moment is $5/2$.

A. B. D. C.

Absorption band spectra of caesium. E. MATUYAMA (Sci. Rep. Tohoku, 1934, 23, 322—333).—Bands at 7200, 7600, 8200, and 8700 Å. have been observed near the resonance lines in the spectrum of Cs vapour. The bands at 7200 and 7600 Å., together

with the previously known band at 6300 Å., have been analysed. The vibration quantum for the normal state of the Cs_2 mol. is 40 cm^{-1} . Relationships are developed between the vibration quanta of diat. mols. and the at. wts. of the constituent atoms. J. W. S.

Fifty-three electron spectra of caesium and barium: Cs III and Ba IV. (Miss) M. A. FITZGERALD and R. A. SAWYER (Physical Rev., 1934, [ii], 46, 576—580).—The separations of the lowest levels $5s^25p^2\ ^2P$ have been predicted and observed. The separations found were 13,870 and 17,830 cm^{-1} in the case of Cs III and Ba IV, respectively. New terms and classifications are tabulated.

N. M. B.

Nuclear magnetic moment of lanthanum. O. E. ANDERSON (Physical Rev., 1934, [ii], 46, 473—476; cf. this vol., 824).—From an investigation of the hyperfine structure of 25 lines, in order to determine the overall widths of each member of the $5d^26s^4F$ levels, a nuclear g -factor of 0.719 and a magnetic moment of 2.5 small magnetons are calc. The interaction energy between the d as well as the s electrons and the nucleus must be considered in accounting for the observed intervals.

N. M. B.

Nuclear moment of terbium. H. SCHULER and H. GOLLNOW (Naturwiss., 1934, 22, 730).—Investigation of the hyperfine structure of the Tb spectrum in the range 6500—4000 Å. shows that no line is split into > four components. The nuclear moment is $3/2$.

A. J. M.

Nuclear moment of lutecium. H. SCHULER and T. SCHMIDT (Naturwiss., 1934, 22, 714).—Hyperfine structure of the Lu spectrum gives $5/2$ for the nuclear moment.

A. J. M.

Rare gas-mercury vapour lamps. W. GERLACH and K. SIEBERTZ (Z. Physik, 1934, 91, 37—42).—Hg discharge tubes with Ne transform suddenly from Hg to Ne discharge near 12° , and with A near 0° .

A. B. D. C.

Concentration of excited atoms in the mercury discharge at high pressures. V. FABRIKANT and V. PULVER (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 435—442).—Concn. of Hg atoms in the 2^3P_0 , 2^3P_1 , and 2^3P_2 states and its dependence on conditions have been determined from absorption measurements.

H. J. E.

Hyperfine structure of some Hg II lines. B. VENKATESACHAR and L. SIBATYA (Proc. Indian Acad. Sci., 1934, 1, 8—13).—Data for the $\lambda\lambda$ 3983.96, 2847.67, and 2262.33 ultra-violet spark lines are tabulated and discussed.

N. M. B.

Spectrum of trebly-ionised mercury. T. S. SUBBARAYA (Proc. Indian Acad. Sci., 1934, 1, 39—43).—From the fundamental multiplets and term vals. a classification of about 200 lines of Hg^{IV} is tabulated.

N. M. B.

Effect of temperature and pressure on the mercury afterglow. D. W. CARPENTER and W. M. NIELSEN (Physical Rev., 1934, [ii], 46, 607—612).—Measurements were made of the rate of escape of resonance radiation from a length of Hg vapour 4 cm. thick, for the pressure range 0.133—0.720 mm. Hg and temp. range 390 — 585° abs. Results are discussed in relation with the predictions of Kenty's

theory of radiation diffusion (cf. *ibid.*, 1932, [ii], 42, 823). N. M. B.

Dark interval in mercury fluorescence. (LORD) RAYLEIGH (Proc. Roy. Soc., 1934, A, 146, 272—280).—Using direct photography through suitable filters, the various features of the Hg fluorescence spectrum have been separated. The phenomenon of the dark interval occurs only in the visual Hg fluorescence, which has continuous spectrum, photographic max. 4850 Å., and visual max. in the green. The appearance of the dark interval is dependent on the source of excitation. L. L. B.

Space-charge distribution in the mercury arc. J. PAWLIKOWSKI (Acta phys. polon., 1933, 2, 59—66; Chem. Zentr., 1934, i, 2097). H. J. E.

Continuous transition from the glow to the arc discharge in mercury vapour at higher pressures. E. MATULA (Acta phys. polon., 1932, 1, 433—446; Chem. Zentr., 1934, i, 2097). H. J. E.

Absorption series of the thallium arc spectrum (Tl I) and their perturbation terms $6s(6p)^{2/4}P_{1,2}$. H. BEUTLER and W. DEMETER (Z. Physik, 1934, 91, 143—150). A. B. D. C.

Absorption spectra due to excitation of inner electrons. VIII. Thallium spectrum between 2500 and 1400 Å. due to excitation of the $(6s)^2$ shell (Tl I^b). IX. Thallium spectrum between 900 and 600 Å. due to excitation of the $(5d)^{10}$ shell (Tl I^c). Comparison of terms of the Tl I^c spectrum with ultra-soft X-rays. H. BEUTLER and W. DEMETER (Z. Physik, 1934, 91, 202—217, 218—229). A. B. D. C.

Specific isotope effect in the hyperfine spectrum of the lead atom. (MISS) B. H. DICKINSON (Physical Rev., 1934, [ii], 46, 598—604).—Mathematical. The method of Hughes (cf. A., 1930, 1328) is used to calculate the sp. isotope separation of Pb²⁰⁶ and Pb²⁰⁸ levels. N. M. B.

Production of spectrally pure carbon electrodes.—See this vol., 1194.

Investigations of gas discharges with an electrolyte as cathode. W. BRAUNBEK (Z. Physik, 1934, 91, 184—201).—Glow discharges obtained with H₂SO₄, KOH, and NaOH as electrodes show that metals are not necessary for production of free electrons. A. B. D. C.

Production of light from discharges in gases. S. DUSHMAN (Gen. Elec. Rev., 1934, 37, 260—268).—A review. Data on luminous efficiencies, ionisation, and resonance potentials are tabulated.

CH. ABS. (e)

Nuclear magnetic moments and their origin. A. LANDE (Physical Rev., 1934, [ii], 46, 477—480).—The origin of the nuclear moments is, in most cases, one proton or one neutron only. Analysis of hyperfine structure gives magnetic moments: proton ~ 2.0 magnetons, neutron ~ -0.6 magneton. N. M. B.

Spectral multiplets belonging to configurations of the type d^4ms and d^4msns . R. A. MERILL (Physical Rev., 1934, [ii], 46, 487—501; cf. this vol., 576).—Mathematical. N. M. B.

Calculation of optical terms and in particular of ionisation potentials of bivalent metals by means of the statistical potential of Fermi. U. FANO (Atti R. Accad. Lincei, 1934, [vi], 20, 35—39).—Theoretical. O. J. W.

Limitation of the potential theory of the broadening of spectral lines. H. KUHN and F. LONDON (Phil. Mag., 1934, [vii], 18, 983—987).—The spectral intensity of an atom, moving in a perturbing field, agrees with the "occurrence distribution" for infinitely slow motion only, of the atom. The amount of deviation in other cases, and its dependence on the velocity, are discussed. M. S. B.

Pressure shift and broadening of spectral lines. H. KUHN (Phil. Mag., 1934, [vii], 18, 987—1003).—Inter-at. forces may be studied by determining the effect of pressure on spectral lines. Small vals. of $\Delta\nu$ are due to the simultaneous presence of many neighbouring atoms and the shift of the max. $\propto d^2$. Larger vals. of $\Delta\nu$ are due to the influence of single atoms only. M. S. B.

Corona discharge in various gases. H. F. BOULIND (Phil. Mag., 1934, [vii], 18, 909—921).—The discharge between concentric cylinders through O₂, H₂, CO₂, and air has been studied for different vals. of p . The mobilities of the ions have been calc. for all the gases except CO₂ in which the discharge is disruptive. M. S. B.

Electron energies in the negative glow. K. G. EMELEUS and D. KENNEDY (Phil. Mag., 1934, [vii], 18, 874—878).—A recalculation of the fraction (about 1/6) of the energy of the cathode dark space which becomes available as the energy of fast electrons entering the negative glow, has been made from Linder's data (A., 1931, 1210). M. S. B.

Scattering of light by liquid surfaces. S. JAGENNATHAN (Proc. Indian Acad. Sci., 1934, 1, 115—119).—The Mandelstamm-Gans theory of light scattering is criticised. A Hg surface can be cleansed for light-scattering experiments by scraping with a clean steel edge. Such a surface shows a polarisation of light scattered nearly parallel to the Hg surface with the electric vector normal to the surface. J. W. S.

Production of X-rays by swiftly-moving mercury ions. W. M. COATES (Physical Rev., 1934, [ii], 46, 542—548).—Using an improved tube (cf. this vol., 1283) the production of soft X-rays (4—9 Å.) by Hg ions of energies up to 2.38×10^6 e.v. was investigated. By absorption measurements in Al and in air the wave-length of the radiation was determined for Al, S, Br, Mo, Ag, Sn, and Pb targets. No radiation was detected from Li, Be, C, O₂, Na, Ni, or Cu. The X-ray intensity increased rapidly with the energy of the ions above crit. min. energies of 700 kv. for Br, Mo, and Al, and 400 kv. for Pb and Ag. Ag gave one X-ray quantum per 1 in 2000 Hg ions. A theory of excitation of X-rays by positive ions is proposed. N. M. B.

Natural width of X-ray lines. L. PINCHERLE (Atti R. Accad. Lincei, 1934, [vi], 20, 29—35).—The natural widths of X-ray lines are calc. on the basis

of quantum mechanics and compared with recent experimental data. O. J. W.

Absorption coefficients for X-rays. H. LAY (Z. Physik, 1934, 91, 551—555).—Absorption coeffs. of various elements are given for wave-lengths between 0.5 and 5.3 Å. A. B. D. C.

K satellites of potassium and calcium. H. TAZAKI (J. Sci. Hiroshima Univ., 1934, A, 4, 185—190; cf. this vol., 3).—Using K and KCl as emitting substances $K\alpha_5$ and $K\alpha_6$, and from Ca and CaO $K\alpha_5$, were observed and measured; respective wave-lengths are 3688.2, 3683.6, and 3310.3 X. From KCl $K\alpha_5$ was not found. N. M. B.

Two-crystal study of the structure and width of K X-ray absorption limits. W. H. ZINN (Physical Rev., 1934, [ii], 46, 659—664; cf. Barnes, A., 1933, 993).—Structure on the short wave-length side of the main absorption limit or in the limit itself was found in the case of Se, SeO_2 , Na_2SeO_4 , Rb, RbCl, Zr, ZrO_2 , $\text{Zr}(\text{SO}_4)_2$, Mo, Mo_2O_3 , and MoO_3 . Intensity and location are discussed with reference to Kronig's theory of sec. structure. Widths of absorption limits were approx. const. for elements of at. no. < 32, and, above this, increase as (at. no.)⁴. N. M. B.

Anomaly in the niobium K absorption limit. C. J. BURBANK (Physical Rev., 1933, [ii], 43, 83).

L. S. T.

Fluorescence efficiency in the L region. H. LAY (Z. Physik, 1934, 91, 533—550).—L fluorescence is determined for elements from at. no. 40 to 92, and K fluorescence from 8 to 54. A. B. D. C.

Structure and width of the L_{III} absorption limits of tantalum, tungsten, and gold. H. SEMAT (Physical Rev., 1934, [ii], 46, 688—691).—Using the free metals and Ta_2O_5 , K_2TaF_7 , H_2WO_4 , Au_2O_3 , and $\text{KAu}(\text{CN})_2$, data and curves are given. The widths, in volts, increase with at. no.

N. M. B.

Intensities of satellites of $L\beta_2$. (Miss) A. W. PEARSALL (Physical Rev., 1934, [ii], 46, 694—697).—The integrated intensity, investigated in the at. no. range 40—53, is about 4% of that of $L\beta_2$ for Nb (41), rises to a max. of 52% for Ag (47), and falls rapidly to < 1% for Te (52), disagreeing with Druyvesteyn's theory. N. M. B.

Continuous and discontinuous Compton spectrum of hydrogen. F. SCHNAIDT (Ann. Physik, 1934, [v], 21, 89—112).—Theoretical. The intensities of the continuous and discontinuous Compton spectra of H are calc. using the proper function for H.

A. J. M.

Structure of the Compton modified band. G. E. M. JAUNCEY (Physical Rev., 1934, [ii], 46, 667—668).—The intensity distribution in the Compton band gives directly the component velocity distribution function of the electrons producing the band.

N. M. B.

Effect of electron binding on the magnitude of the Compton shift. P. A. ROSS and P. KIRKPATRICK (Physical Rev., 1934, [ii], 46, 668—673).—Measurements of Compton shift for 90° scattering of the wave-lengths 0.435, 0.496, and 0.631 Å. by C and Be are < h/mc , the val. required by the Compton

formula, the max. discrepancy being 2.4%, observed for λ 0.631 scattered from C, but agree with a proposed formula (cf. *ibid.*, 45, 223) and with the results of Bloch (cf. following abstract). N. M. B.

Compton line. F. BLOCH (Physical Rev., 1934, [ii], 46, 674—687).—Mathematical. From Wentzel's theory, formulæ for the intensity distribution in the Compton line are developed. The interaction of the electrons with the at. nucleus gives a broadening of the line and a shift of the position of max. intensity from Compton's val. N. M. B.

Sparking potentials at low pressures. A. J. DEMPSTER (Physical Rev., 1934, [ii], 46, 728—730).—The no. of electrons set free by the impact of a positive ion on a Ni cathode, calc. from data for the efficiency of ionisation by electrons of various velocities and sparking potentials in air, increases with the velocity of the ion from approx. 4 at 3000 volts to 85 at 30,000 volts, results much > those given by direct observations. An explanation is proposed. N. M. B.

Quartz lamp as pre-ioniser. R. HELLMANN (Z. Physik, 1934, 91, 569—572).—Oscillographic measurements show that light emission from a quartz lamp varies, and care should be taken in using it to illuminate metals to obtain const. photo-emission for ionisation measurements. A. B. D. C.

Coefficient of electron ionisation for nitrogen at low pressures. R. HELLMANN (Z. Physik, 1934, 91, 556—568).—Townsend's coeff. is determined for pressures from 1.6 to 15 mm. A. B. D. C.

Emission of electrons under the influence of chemical action. IV. Reactions of liquid NaK_2 with gaseous SOCl_2 , S_2Cl_2 , SO_2Cl_2 , HgCl_2 , S_2Cl_4 , and with mixtures of gases, and a new method of determining the contact potential difference. A. K. DENISOFF and O. W. RICHARDSON (Proc. Roy. Soc., 1934, A, 146, 524—564; cf. this vol., 937).—The electron emission from NaK_2 when acted on by SOCl_2 , S_2Cl_2 , SO_2Cl_2 , HgCl_2 , and $(\text{SCl})_2$ at very low pressures has been studied, and experiments with the mixtures $\text{COCl}_2 + \text{COS}$, $\text{COCl}_2 + \text{S}_2\text{Cl}_2$, and $\text{SOCl}_2 + \text{S}_2\text{Cl}_2$ are described. It is proved that the electron currents originating from chemical action possess the additive property and exhibit saturation with true zero applied p.d. A new method is described for determining the contact p.d. between the alloy drop and the surrounding Pt electrode in presence of different gases. A general method of analysis of electronic spectra is given, based on the comparative study of different electronic spectra and on some considerations of the kinetics and the electronic yield of the chemical reactions. The electronic spectra, having been thus analysed, are then applied to test the fundamental relation between the dissociation energy, involved in a certain reaction, and the max. energy of the emitted electrons of the group originating from the reaction with the corresponding mechanism. L. L. B.

Small-angle inelastic scattering of electrons in helium, hydrogen, and mercury. S. N. VAN VOORHIS (Physical Rev., 1934, [ii], 46, 480—483).—Measurements for the initial energies range 100—300 volts and 0—15° scattering angles show that scatter-

ing per unit solid angle reaches a max. at a fairly small angle and decreases to a lower val. at zero angle. The position of the max. is a function of energy, and not of momentum as predicted by Born's theory.

N. M. B.

Determination of the variation of the mass of electrons in rapid cathode rays. H. STARKE and M. NACKEN (*Ann. Physik*, 1934, [v], 21, 67—88).—The results obtained for the variation of the mass of the electron with its velocity by Abraham's and Lorentz's theory are compared.

A. J. M.

[So-called] electric moment of the electron. G. RACAH (*Atti R. Accad. Lincei*, 1934, [vi], 20, 39—40).—Theoretical.

O. J. W.

Activation of nitrogen by electron impacts. J. OKUBO and H. HAMADA (*Sci. Rep. Tôhoku*, 1934, 23, 289—295).—The production of active N, as indicated by a sensitive thermopile, increases suddenly when the accelerating potential of the electrons reaches 16 volts, the first ionisation potential of N. Above this potential the production of active N increases continuously with the accelerating potential. At pressures of 0.1—10 mm. the primary production of N_2^+ is essential to the formation of active N, and the probability of its formation by single collisions with high-speed electrons is very small.

J. W. S.

Approximate phases in electron scattering. F. L. ARNOT and G. O. BAINES (*Proc. Roy. Soc.*, 1934, A, 146, 651—662).—A no. of phases for Kr have been calc. by Jeffreys' and Born's methods, and these are compared with the exact phases determined by Holtsmark. For the special case of the zero-order phase Jeffreys' expression for a repulsive is $>$ for an attractive field by the term $1/4\pi$, but the error decreases as the order of the phase increases. The cause of the error is discussed. A theoretical scattering curve for 121-volt electrons in Kr has been calc., and is in good agreement with Arnot's experimental curve.

L. L. B.

Scattering of electrons in bromine vapour. F. L. ARNOT and J. C. McLAUCHLAN (*Proc. Roy. Soc.*, 1934, A, 146, 662—672).—Theoretical angular distribution curves for elastically scattered electrons of energies from 15 to 339 volts are given for Br. Satisfactory agreement is obtained with the experimental curves (this vol., 577). An approx. Hartree at. field for Br is given.

L. L. B.

Production of heavy high-speed ions without the use of high voltages. D. H. SLOAN and W. M. COATES (*Physical Rev.*, 1934, [ii], 46, 539—542).—A tube previously described (cf. A., 1932, 106) is improved to withstand application of 79,000 volts, by decreased heating of electrodes due to lowering their resistance and capacity, and yields Hg ions with energies of 2,850,000 e.v., and beam intensity of the order 10^{-8} amp.

N. M. B.

Ionisation of gases by atom beams. A. ROS-TAGNI (*Nature*, 1934, 134, 626).—Vals. for the effective cross-sections of ionisation of A and He by their own atoms with an energy varying between 50 and 700 e.v. are recorded graphically. The vals. for He are approx. 0.1 those of the corresponding vals. for A.

L. S. T.

Production of pairs by collisions of heavy particles. W. HEITLER and L. NORDHEIM (*J. Phys. Radium*, 1934, [vii], 5, 449—454).—Mathematical.

N. M. B.

Temperature variation of the total current-carrying elements of air. II. A. BECKER and I. SCHAPER (*Z. Physik*, 1934, 91, 422—426; cf. A., 1933, 4).—Potentials up to 6000 volts indicate decrease of the influence of recombination with rise of temp.

A. B. D. C.

Constitution of metallic sodium. II. E. WIGNER and F. SEITZ (*Physical Rev.*, 1934, [ii], 46, 509—524; cf. A., 1933, 660).—Mathematical. Correlations between electrons with parallel spin are investigated, and the Fermi zero-point energy is calc. Results show that the electrons behave as if they were entirely free; binding energy is 9 kg.-cal. and lattice const. 4.86 Å., against observed vals. of 26.9 kg.-cal. and 4.23 Å., respectively. Investigation of correlations between electrons with anti-parallel spins leads to binding energy of 23.2 kg.-cal. and lattice const. 4.75 Å. The cause of the discrepancies is discussed.

N. M. B.

Measurement of nuclear spin by the method of molecular beams. Nuclear spin of sodium. I. I. RABI and V. W. COHEN (*Physical Rev.*, 1934, [ii], 46, 707—712).—Using a focussed velocity spectrum method, sensitive to very low intensities and slow at. and mol. beams, the angular momentum of the nucleus is measured directly by its effect on the space quantisation of the angular momentum of the extra-nuclear configuration in a magnetic field. The spin of the Na nucleus is $3/2$.

N. M. B.

Nuclear spin of caesium. V. W. COHEN (*Physical Rev.*, 1934, [ii], 46, 713—717).—The spin of the Cs atom was measured by its effect on the Stern-Gerlach pattern of the neutral Cs atom. The val. obtained was $7/2$, and from the known magnetic field the hyperfine structure separation for the normal state is 0.295 ± 0.01 cm. $^{-1}$

N. M. B.

Comparison of some physical and chemical at. wts. G. P. BAXTER (*J. Chem. Educ.*, 1934, 11, 441—444).—A discussion.

CH. ABS. (e)

Periodic classification of the elements. M. LEMARCHANDS and M. JACOB (*Bull. Soc. chim.*, 1934, [v], 1, 1070—1075).—Considering the total chemical energy of an element to be made up of energy of oxidation (or reduction) and "metallic (or non-metallic) energy," it is pointed out that the assignment to the elements of appropriate vals. for these two quantities throws some light on their chemical properties, notably with C.

F. L. U.

Investigation of isotopes of oxygen and hydrogen by the mass-spectrograph. H. MUCKENTHALER (*Physikal. Z.*, 1934, 35, 851—857).—The ratio $O^{18} : O^{16}$ in ordinary O_2 is about 1 : 1000. H^1 diffuses more rapidly than H^2 through heated Pd.

A. J. M.

Systematics of isotopes. J. MATTAUCH (*Z. Physik*, 1934, 91, 361—371).—The selection rule that there are no isobars to isotopes of odd elements and no isobars of odd mass no. gives a scheme of isotopes in agreement with those so far found.

A. B. D. C.

Segregation of polonium in bismuth crystals. A. B. FOCKE (Physical Rev., 1934, [ii], 46, 623—628).—Geiger counter measurements of no.-distance relations for α -particles emitted normally through cleavage surfaces were made in order to determine the distribution of Po present as an impurity in single Bi crystals. The Po is segregated into small regions having nearly regular spacings, which are unaffected by speed of growth of the Bi crystal and by subsequent heat treatment. The addition of Te suppresses certain layers.

N. M. B.

Energy of a β -ray of radium-B. F. A. SCOTT (Physical Rev., 1934, [ii], 46, 633—640).—The measured energy of the most intense line of the β -ray spectrum of Ra-B obtained by magnetic focussing was $(2.6145 \pm 0.0001) \times 10^5$ e.v., taking e/m as 1.760×10^7 . The val. of $H\rho$ for this line was 1931.8 gauss cm.

N. M. B.

Technique of the counter-controlled cloud chamber. P. M. S. BLACKETT (Proc. Roy. Soc., 1934, A, 146, 281—299; cf. A., 1933, 441).—The breadths of the tracks formed when Geiger counters are used to actuate a cloud chamber can be calc. by taking into account the diffusion of the ions, during the time τ , from the moment of their formation to that of drop formation. The breadth of the track varies as $\tau^{1/2}$.

L. L. B.

Neutrons from aluminium and beryllium. R. JAEKEL (Z. Physik, 1934, 91, 493—510).—Energy distributions are given for neutrons excited by Rn, Ra-A, and Ra-C' α -rays.

A. B. D. C.

Induced radioactivity. F. H. NEWMAN and H. J. WALKER (Nature, 1934, 134, 537).—A further discussion of the authors' hypothesis (this vol., 939, 1054).

L. S. T.

Disintegration of boron by swiftly-moving protons. M. G. WHITE and E. O. LAWRENCE (Physical Rev., 1933, [ii], 43, 304—305).—The yield of α -particles from B for voltages $> 5 \times 10^5$ is practically the same as that from Li (A., 1933, 205, 1225). The results indicate that for Li and B the effective collision cross-section for disintegration does not increase perceptibly with the speed of the proton above 4 or 5×10^5 volts.

L. S. T.

Fermi effect in aluminium. II. I. KURTSCHATOV, L. MISOVSKI, B. KURTSCHATOV, G. SCHTSCHEPKIN, and A. VIBE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 422—424; cf. this vol., 1152).—The product with a half-period of 12—13 hr., formed on bombarding Al with neutrons, was separated from Al and Mg and shown to be Ra-Na (I) (pptn. with added NaCl with K pyroantimonate). The process is $\text{Al}^{27} + n = \text{Ra-Na}^{24} + \text{He}^4$. The disintegration mechanism of (I) is discussed.

H. J. E.

Active phosphorus and its β -ray energy spectrum. J. AMBROSEN (Z. Physik, 1934, 91, 43—48).—S bombarded with neutrons gives active P, which was separated from S; the β -ray spectrum was then investigated.

A. B. D. C.

Energy spectrum of positrons from radio-phosphorus $^{30}_{15}\text{P}$ (activated aluminium). Y. NISHINA, R. SAGANE, M. TAKEUCHI, and R. TOMITA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934,

25, 1—7).—The energy spectrum of positrons from radio-P from activated Al was investigated by the measurement of 1484 Wilson tracks in a uniform magnetic field, and extended up to about 4×10^6 e.v. Indications of > 1 intensity max., changing in position with time after activation, were obtained.

N. M. B.

Artificial disintegration by radium-C' α -particles. Aluminium and magnesium. W. E. DUNCANSON and H. MILLER (Proc. Roy. Soc., 1934, A, 146, 396—419).—An electrical counting method for counting α -particles and protons in the presence of strong β - and γ -radiations is described. Experiments in which Al is bombarded by the α -particles from Ra-C' indicate the presence of 3 excited α -particle levels in the resulting nucleus, and 2 resonance levels in the potential barrier at energies $>$ those found by Chadwick and Constable (A., 1932, 318). Similar experiments on Mg indicate 2 excited α -particle levels in the resulting nucleus, and 2 resonance levels in the potential barrier above an energy of 5.25×10^6 e.v.

L. L. B.

Artificial radioactivity produced by neutron bombardment. E. FERMI, E. AMALDI, O. D'AGOSTINO, F. RASSETTI, and E. SEGRÈ (Proc. Roy. Soc., 1934, A, 146, 483—500).—Out of about 60 elements investigated, > 40 could be activated by neutron bombardment. No special difference was noted between light and heavy elements. The cross-sections for neutron impact for the elements which can be most intensely activated are of the order of the geometrical cross-section of the nucleus. Thus a high % of the neutrons which hit the nucleus produce an active atom. The active product is sometimes an isotope of the original atom (at. no. Z); in other cases its at. no. is lower by one or two units. Light and heavy elements appear to differ in this respect: for light elements the at. no. of the active product is usually $< Z$, whilst for heavy, non-spontaneously radioactive elements the active product is an isotope of the bombarded element. The emitted electrons always have a negative charge.

L. L. B.

Theory of artificial disintegration. K. C. KAR (Current Sci., 1934, 3, 106—107; cf. this vol., 127, 580).

L. S. T.

Nuclear structure and excited radioactivity. G. GUEBEN (Nature, 1934, 134, 626).—Theoretical.

L. S. T.

Gamow's theory of radioactivity. H. SAINI (Arch. Sci. phys. nat., 1934, [v], 16, 80—101).—A crit. survey of the scope and deficiencies of Gamow's theory.

N. M. B.

Mass of the neutron and the constitution of atomic nuclei. A. VON GROSSE (Physical Rev., 1933, [ii], 43, 143).—The assumption that the masses of all neutrons are not identical would remove the difficulty of accounting for the difference in energy emission by the same substance during a β -disintegration.

L. S. T.

Constitution of nuclei. II. K. GUGGENHEIMER (J. Phys. Radium, 1934, [vii], 5, 475—485; cf. this vol., 939).—Relations between the abundance of different atoms and the affinity of the nuclei for

neutrons, protons, and α -particles, the transformation of neutrons into protons, and the various types of binding in the nucleus are discussed. N. M. B.

Annihilation of electrons and positrons. Y. NISHINA, S. TOMONAGA, and H. TAMAKI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 7—12).—Mathematical. A relativistic calculation is made of the cross-section for the annihilation by recombination of an incident positron and a K , L , II , III , electron belonging to a bare at. nucleus. N. M. B.

How far do cosmic rays travel? F. ZWICKY (Physical Rev., 1933, [ii], 43, 147—148).—An examination of the two hypotheses of the origin of cosmic rays. L. S. T.

Counter-tube determinations with ultra-ray corpuscles. H. MAASS (Physikal. Z., 1934, 35, 858—861).—Two counter tubes were used with the method of double coincidence, the effect of absorbers placed alternately between and above the two tubes being determined. For thicknesses of Fe > 8 cm. above the tube, an increase in secondary radiation was noted, which was probably due to the existence of an ultra- γ -radiation as a component of the ultra-radiation. A. J. M.

Analysis of cosmic radiation at high altitudes. P. AUGER and L. LEPRINCE-RINGUET (Compt. rend., 1934, 199, 785—787).—High altitude measurements indicate two groups of cosmic rays differing in penetrating power. H. J. E.

Very high altitude survey of the effect of latitude on cosmic-ray intensities, and an attempt at a general interpretation of cosmic-ray phenomena. I. S. BOWEN, R. A. MILLIKAN, and H. V. NEHER (Physical Rev., 1934, [ii], 46, 641—652).—Detailed results and conclusions are described in relation to contemporary theory. Energies of cosmic-ray components indicate exclusively an origin in matter-annihilation. N. M. B.

Theory of the origin of the cosmic rays. L. G. H. HUXLEY (Phil. Mag., 1934, [vii], 18, 971—983).—A simple mathematical treatment is given. The equations obtained are in agreement with the properties of the cosmic radiation on the assumption that the potential of the earth lies between 6×10^{10} and 10^{11} volts, probably about 7×10^{10} volts, and that the corpuscles all carry charges of similar sign opposite to that of the charge on the earth. Possible agencies by which the earth's charge may be maintained are considered. M. S. B.

Coincidence test of the corpuscular hypothesis of cosmic rays. D. S. HSIUNG (Physical Rev., 1934, [ii], 46, 653—658).—Double and triple coincidences obtained with three Geiger-Müller counters arranged vertically and certain interpositions of Pb absorbers are due to penetrating ionising particles, and not to secondary particles produced by photons which traverse the Pb. N. M. B.

Distribution of photo-electrons of the M shell of hydrogen-like atoms. J. KREISLER (Acta phys. polon., 1933, 2, 7—22; Chem. Zentr., 1934, i, 2397).—Theoretical. H. J. E.

Atomic nuclei and the periodic system. L. MEITNER (Naturwiss., 1934, 22, 733—739).—A lecture.

Investigations on free alkali metals (1930—1933). H. ALTERTHUM and R. ROMPE (Physikal. Z., 1934, 35, 814—836).—A review.

De Broglie theory of photons. J. L. DESTOUCHES (Compt. rend., 1934, 199, 779—781).—Theoretical. H. J. E.

Molecular screening constants. P. DAS (Indian J. Physics, 1934, 9, 35—43).—Using the Hylleraas method the heats of dissociation of LiH, BeH, and Li₂, and the term vals. of H₂, are calc. N. M. B.

Determination of e/m and mass of individual charged particles in colloids. K. KRISHNAMURTI (Current Sci., 1934, 3, 107).—The motion of single colloid particles in a cataphoretic cell under a given p.d. has been observed in the field of the ultramicroscope and the val. of e/m calc. L. S. T.

Interpretation of e^2/mc^2 and h/mc . B. PODOLSKY (Physical Rev., 1934, [ii], 46, 734—738).—Equations are re-written on the assumption that m and e need not enter into the electrodynamics and quantum mechanics of electrons, positrons, and photons. Results are discussed. N. M. B.

Method of determining atom form factors. B. VON S. NAGY (Z. Physik, 1934, 91, 105—110).—Theoretical. A. B. D. C.

Approximate wave functions and atomic field for mercury. D. R. HARTREE (Physical Rev., 1934, [ii], 46, 738—743).—Tables of preliminary results are given. N. M. B.

Averages over portions of configuration space. G. HELLER and L. MOTZ (Physical Rev., 1934, [ii], 46, 502—505).—Mathematical. N. M. B.

Perturbation calculation in many-electron [valency] problem. G. GELMAN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 442—446).—Theoretical. H. J. E.

Approximation treatment for many-electron systems. C. MÖLLER and M. S. PLESSET (Physical Rev., 1934, [ii], 46, 618—622).—Mathematical. A perturbation theory method is developed. N. M. B.

Problems involving permutation degeneracy. R. SERBER (J. Chem. Physics, 1934, 2, 697—710; cf. this vol., 580).—Mathematical. F. L. U.

Application of the Dirac vector model to the d^1 configuration. M. OSTROFSKY (Physical Rev., 1934, [ii], 46, 604—607).—Mathematical. N. M. B.

Nuclear energy levels and the model of a potential hole. H. MARGENAU (Physical Rev., 1934, [ii], 46, 613—615).—Mathematical. N. M. B.

Vacuum in Dirac's theory of the positive electron. R. PEIERLS (Proc. Roy. Soc., 1934, A, 146, 420—441).—Mathematical. The problem of the charge and current induced in the vac. by an electromagnetic field has been studied from the viewpoint of Dirac's theory (where the positive electron is a "hole" in an infinite distribution of electrons in states of negative energy). Essential modifications seem to be

needed in the fundamental concepts underlying the theory. L. L. B.

Uncertainty of the electromagnetic field of a particle. G. LEMAITRE (Physical Rev., 1933, [ii], 43, 148).—From Heisenberg's uncertainty principle it is concluded that for instantaneous determinations the field of an electron, proton, or at. nucleus is practically undetermined. Bohr's view, that the field of the nucleus determines the orbit of the electron and that the radiation of a moving electron can be neglected, is supported. L. S. T.

Electron counter and demonstration of Gurtwisch radiation.—See this vol., 1194.

Interpretation of line spectra in crystals. F. H. SPEDDING (Physical Rev., 1933, [ii], 43, 143—144).—The theories of Deutschbein (A., 1932, 983) and Tomaschek (A., 1933, 5) are discussed in relation to the absorption spectra of solids. L. S. T.

Emission spectra of the vapours of the sodium and potassium halides. H. HAMADA (Sci. Rep. Tôhoku, 1934, 23, 296—307).—The emission spectra of NaCl, NaBr, and NaI show a continuous region with max. intensity near the Na D line, this continuum being widest for NaCl and narrowest for NaI. This spectrum differs from that of Na vapour in being emitted by quantised mols., held loosely together by polarisation forces, whereas the Na spectrum is emitted by quasi-mols. Similar results are obtained with K halides. J. W. S.

Band spectrum of manganese oxide. A. K. S. GUPTA (Z. Physik, 1934, 91, 471—474).—The energy of dissociation of the lower state is given as 4.4 volts. A. B. D. C.

Test for free radicals of short life. O. OLDENBERG (J. Chem. Physics, 1934, 2, 713—714).—Using a C arc in dry N₂ as source of radiations and high resolving power, the absorption spectrum of H₂O vapour has been photographed after the cessation of an electric discharge through it. Bands due to OH have been observed, their persistence being > 1/8 sec. It is not yet known whether the observed decay relates to the average life of OH radicals or to that of combining O and H atoms. F. L. U.

Sensitisation of the photochemical effect in crystals of the alkali halides. A. D. VON LUPKE (Ann. Physik, 1934, 21, [v], 1—14).—The prep. of crystals of KCl showing ultra-violet bands is described. Light absorption in these bands changes the ultra-violet centres into colour centres. The addition of foreign substances (K₂O, KOH, K₂CO₃, KNO₃) causes some photochemical sensitisation. A. J. M.

Ultra-violet bands of beryllium chloride. W. R. FREDRICKSON and M. E. HOGAN, jun. (Physical Rev., 1934, [ii], 46, 454—458).—A band system in the range 3468—3700 Å., using a Be arc in Cl₂, was photographed. Four heads are found for each band; the system is due to a ²Π—²Σ transition, and only partial rotational analysis was possible. The isotope effect for Cl₂ was observed in -1 and +1 sequences and the ²R₂₁ head of the (0,0) band. From the heats of dissociation electronic extinction appears to be due to the ¹D → ¹P transition in the Be atom. N. M. B.

Spectrophotometric investigation of aqueous cobalt chloride solutions. G. SPACU and J. G. MURGULESCU (Z. physikal. Chem., 1934, 170, 62—70).—The relation of the absorption coeff. of unit thickness of 0.25—1.0M-CoCl₂ solutions containing KCl for 546 mμ to the Co and Cl concns. may be accounted for by assuming that the reactions [Co,6H₂O]⁺⁺+Cl⁻=D₁ and [Co,6H₂O]⁺⁺+2Cl⁻=D₂ occur, where the products D₁ and D₂ have different absorption coeffs. R. C.

Spectrophotometric investigation of aqueous cupric chloride solutions. G. SPACU and J. G. MURGULESCU (Z. physikal. Chem., 1934, 170, 71—80).—The absorption coeffs. of 0.25—1.5M aq. CuCl₂ solutions in which the total [Cl⁻] is varied up to 4N by addition of KCl have been determined at 436, 650, and 680 mμ to find the causes of the deviations from Beer's law. In the red the deviations are ascribed to [Cu,4H₂O]⁺⁺+Cl⁻⇌X, where X may be either [Cu,3H₂O,Cl]⁺ or CuCl⁺. In the blue CuCl₄²⁻ is responsible. R. C.

Spectra of indium halides. M. WEHRLI and E. MIESCHER (Helv. phys. Acta, 1933, 6, 457—458; Chem. Zentr., 1934, i, 2252).—InCl, InBr, and InI each show 3-band systems, two of which overlap. H. J. E.

Spectra of gallium halides. E. MIESCHER and M. WEHRLI (Helv. phys. Acta, 1933, 6, 458—459; Chem. Zentr., 1934, i, 2252—2253).—The band systems of GaCl, GaBr, and GaI resemble those of the In salts, but are displaced to shorter wave-length. The isotope effect for Ga⁶⁹ and Ga⁷¹ was observed. H. J. E.

Diffuse band systems in the absorption spectrum of thallos chloride vapour. H. NEUTMIN (Phys. Z. Sovietunion, 1934, 5, 580—585).—13 diffuse bands were observed on the long-wave side of the continuum at 2513 Å.; 4 bands occur on the long-wave side of the continuum at 3113 Å. The dissociation energy of TlCl into Tl and Cl is 109 kg.-cal. TlCl has 2 unstable upper electronic states. CH. ABS. (e)

Ultra-violet absorption by potassium nitrate, nitrites, and carbon disulphide at low temperatures. G. RODLOFF (Z. Physik, 1934, 91, 511—532).—Absorption spectra of KNO₃, KNO₂, NaNO₂, and CS₂ have been determined to -250° in the region 4400—2400 Å. Near -180° the KNO₂ and CS₂ continuous bands show structure at 600 cm.⁻¹ intervals, and at -250° these show further structure; NaNO₂ shows this second structure at -180°. A. B. D. C.

Optical absorption spectrum of three isomerides of potassium pentachlororuthenite. S. AOYAMA and T. FUKUROI (Sci. Rep. Tôhoku, 1934, 23, 420—425; cf. this vol., 1295).—Curves are given for the absorption spectra between 3400 and 4400 Å. of HCl solutions of K₂RuCl₆ and samples of K₂RuCl₅ and K₂Ru(H₂O)Cl₅ prepared in different ways. The existence of three isomerides of K₂RuCl₅ is confirmed, and geometrical models are suggested. J. W. S.

Absorption spectra of the rare earths. W. PRANDTL and K. SCHEINER (Z. anorg. Chem., 1934, 220, 107—112).—Absorption spectra of solutions of the rare earths have been determined between 7000

and 2200 Å. at 5 different concns. The relation between the variations in absorption spectra and at. structure is discussed. M. S. B.

Action of penetrating radium radiation on dissolved substances. G. GUÉBEN (Arch. Phys. biol., 1933, 10, 292—303; Chem. Zentr., 1934, i, 2555).—The ultra-violet absorption spectra of aq. KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, KI , CaI_2 , NaOEt , and cinnamic or malonic acid were changed by exposure to rays from radioactive material. Aq. AgNO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, and fumaric or maleic acid were unchanged. H. J. E.

Rotational and vibrational structure of the fourth positive bands of carbon monoxide. D. N. READ (Physical Rev., 1934, [ii], 46, 571—575).—The rotational structure of 12 of the fourth positive bands of CO has been measured and analysed. Rotational consts. of the normal state are: $B_0 = 1.9170$, $\alpha = 0.01738 \text{ cm}^{-1}$, against $B_0 = 1.84$ by infra-red band measurements. Data for 64 band heads below 2270 Å. are tabulated. N. M. B.

Energy of the C-OH linking and molecular structure in alcohols. Y. HUKUMOTO (Nature, 1934, 134, 538).—Investigation of a continuous absorption spectrum in the ultra-violet which corresponds with the immediate dissociation of a mol. into its constituents shows that for the normal aliphatic alcohols the energy of the C-OH linking increases as the series is ascended. L. S. T.

Chemical reactivity and light absorption. III. N. R. DHAR and P. K. KAR (J. Indian Chem. Soc., 1934, 11, 629—634; cf. this vol., 975).—Absorption of light of longer λ by reacting systems involving I than by the reactants, and increased total absorption, are observed in the ultra-violet and visible, but not the infra-red regions. The relative magnitudes of the absorption changes in the several mixtures are in the same order as the respective heats of reaction. J. G. A. G.

Absorption of light in organic compounds. N. Q. CHAKO (J. Chem. Physics, 1934, 2, 644—653).—An attempt is made to correlate the width and strength of absorption bands with chemical constitution and the nature of the solvent. Examination of data relating to a large no. of substances reveals the present inadequacy of a theoretical basis for such a correlation. F. L. U.

Absorption spectrum of acetylene in the region 2350—2050 Å. A. JONESCO (Compt. rend., 1934, 199, 710—713).—Approx. 80 bands of C_2H_2 have been examined with a precision $3\text{--}5 \text{ cm}^{-1}$ 10—12 of these are represented by $\nu = \nu_0 + 1034.6V - V^2$ ($\nu_0 = 43,277$, 42,639, and 42,062 cm^{-1}), $V = 0, 1, 2, 3, 4, 5$; another frequency interval often appearing is approx. 2700 cm^{-1} . The frequency 1034.6 cm^{-1} is identified with the vibration ν_1' of the final state of the mol. R. S. B.

Ultra-violet absorption of some aromatic hydrocarbons. AUBERT and T. GHEORGHIU (Ann. Office nat. Comb. liq., 1933, 8, 451—478; Chem. Zentr., 1934, i, 510).—In the region 2200—2800 Å. selective absorption was observed for C_6H_6 , PhMe, PhEt, PhPr, and PhBu. Continuous absorption was

observed for $\text{C}_6\text{H}_4\text{Et}_2$, amylbenzene, mesitylene, ψ -cumene, and $\text{C}_6\text{H}_3\text{Et}_3$. H. J. E.

Ultra-violet absorption of some aromatic hydrocarbons. II. Mono-*n*-alkylbenzenes. M. PESTEMER and O. GUBITZ (Monatsh., 1934, 64, 426—438).—The extinction-wave no. curves for the series of compounds from PhMe to $n\text{-C}_6\text{H}_{13}\text{Ph}$ have been determined in C_6H_{14} and MeOH and the results compared. The effect of alkyl substitution and of the change from a non-polar to a polar solvent is discussed. M. S. B.

Ultra-violet absorption by aromatic aldehydes and ketones. (MME.) RAMART-LUCAS and J. SÉGAL (Bull. Soc. chim., 1934, [v], 1, 1049—1054).—Absorption between λ 2200 and 3750 Å. has been measured in EtOH and C_6H_{14} solutions of PhCHO, $\text{C}_6\text{H}_4\text{Me}\cdot\text{CHO}$, $p\text{-C}_6\text{H}_4\text{Pr}^s\cdot\text{CHO}$, $o\text{-C}_6\text{H}_4(\text{OH})\cdot\text{CHO}$, $p\text{-C}_6\text{H}_4(\text{OMe})\cdot\text{CHO}$, $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COMe}$, and $p\text{-C}_6\text{H}_4(\text{OMe})\cdot\text{COMe}$, and in EtOH solutions of semi-carbazones of the aldehydes. F. L. U.

Absorption spectra of the nitroanilines and of the corresponding nitroacetanilides. (MLE.) G. GLORZ (Bull. Soc. chim., 1934, [v], 1, 1148—1152).—The absorption of the *o*-, *m*-, and *p*-compounds between λ 2200 and 6000 Å. has been measured, and differences are noted and discussed. F. L. U.

Ultra-violet absorption spectra of derivatives of uracil. J. E. AUSTIN (J. Amer. Chem. Soc., 1934, 56, 2141—2144; cf. A., 1932, 320).—Ultra-violet absorption spectra curves of EtOH solutions of uracil (I), 1- and 3-methyl-, 1:3-dimethyl-, 1:3-diethyl-, 1-methyl-3-ethyl-, 3-benzyl-1- and -5-methyl-, 1-benzyl-3-methyl-, and 5:6-dihydro-uracil, 2-keto-4-methoxy- and -4-ethoxy-1-methyl- and 2-keto-4-methoxy-1-tetra-acetylglucosido-1:2-dihydropyrimidine, and 2:4-dimethoxy- and 2:4-diethoxy-pyrimidine are given. The 1:4-, 1:3-, and 2:4-derivatives show an absorption max. at 36,400, 37,800, and 38,800 cm^{-1} , respectively, irrespective of the nature of the substituents. The results indicate that (I) (and, by analogy, hydantoin) is predominantly the 2-hydroxy-4-keto-derivative. H. B.

Fluorescence spectrum of ethylamine vapour. A. V. BANOV and N. A. PRILESHAIEVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 497—499).—Five fluorescence bands between 2700 and 3500 Å. excited by $\lambda\lambda$ 2300—2800 Å. were observed, the frequency difference between the band max. corresponding with the 1450 cm^{-1} Raman frequency of NH_2Et . H. J. E.

Photochemical studies. XVIII. Fluorescence of acetone vapour. C. F. FISK and W. A. NOYES, jun. (J. Chem. Physics, 1934, 2, 654—658; cf. this vol., 852).—The intensity of the fluorescence radiation of COMe_2 vapour free from O_2 has been studied as a function of the incident intensity and of the pressure. The results are discussed with reference to the mechanism of photochemical decomp. F. L. U.

Displacement of absorption spectra of azo-compounds. M. HORIO and S. YAMASHITA (J. Soc. Chem. Ind. Japan, 1934, 37, 491—497b).—The absorption spectrum of azobenzene (non-polar) is nearly the same as vapour, as liquid, or as solute in polar or non-polar liquids. For the polar substances

hydroxy-, amino-, and trihydroxy-azobenzene the spectra in the liquid state or dissolved in polar solvents differ from those of the solid or of solutions in non-polar solvents. A. G.

Relation between absorption spectra and constitution of dyes. VI.—See this vol., 1344.

Spectra and latent energy of flame gases. W. T. DAVID (Nature, 1934, 134, 663).—Mainly a discussion. In CO-air combustion the latent energy in const.-pressure combustion is $>$ in closed-vessel explosions. It appears that the greater is the latent energy in the CO flame gases the greater is the relative intensity of the ultra-violet radiation. L. S. T.

Halogen molecules and their spectra. J-J-like coupling. Molecular ionisation potentials. R. S. MULLIKEN (Physical Rev., 1934, [ii], 46, 549—571).—Relations and rules, with comparisons with observed vals., for mol. and at. ionisation potentials are discussed. Electron configurations of N_2 , CO, X_2 , HX (X=halogen), and O_2 are examined. New low-energy states of X_2 and XY are predicted, and observed absorption spectra of XY and X_2 mols. are interpreted, with suggestions for interpreting observed fluorescence and emission spectra. Indications of J-J-like coupling from the vac. ultra-violet (λ 1600—1950) bands of XY are examined. N. M. B.

Photographic method for the study of mechanical models of vibrating molecules. D. H. ANDREWS and J. W. MURRAY (J. Chem. Physics, 1934, 2, 634—636).—The method and some of its applications are described. F. L. U.

Nature of the red shift in the infra-red emission bands in flame spectra. V. N. KONDRATEV (J. Exp. Theor. Phys., Russia, 1933, 3, 265—272).—The shift is explained by means of the superposition of single bands, which correspond with the oscillation quanta emitted by the mols. when strongly oscillating as a result of the reaction taking place. The magnitude of the shift is related to the energy of oscillation; hence analysis of infra-red flame spectra can be used to determine the chemical processes proceeding in the burning zone. CH. ABS.

Structure of the ozone molecule and its infra-red bands. G. HETTNER, R. POHLMAN, and H. J. SCHUMACHER (Z. Physik, 1934, 91, 372—385).—The spectrum was investigated to 27μ . The 7.6μ band is ascribed to N_2O_5 , and a new intense band is given at 14.1μ . The mol. is an isosceles triangle of vertical angle 19.5° . A. B. D. C.

Infra-red spectrum and the molecular structure of ozone and sulphur dioxide. R. M. BADGER and L. G. BONNER (Physical Rev., 1933, [ii], 43, 305—306).—Disagreement with the views of Gerhard (A., 1933, 208) on the structure of O_3 and with those of Bailey and co-workers (A., 1931, 144) on SO_2 is expressed. L. S. T.

Infra-red absorption spectrum of silane. W. B. STEWARD and H. H. NIELSEN (J. Chem. Physics, 1934, 2, 712).—Positions and intensities of 4 bands are given. The spectrum appears to be similar to that of CH_4 . F. L. U.

Near infra-red absorption of solutions of hydroxides and hydrolysing salts. W. GORDY (J. Chem. Physics, 1934, 2, 621—623; cf. this vol., 1154).—Observations were made on aq. solutions of KOH, NaOH, LiOH, NaOAc, Na_2CO_3 , $ZnCl_2$, and $ZnBr_2$ in the region 0.60—2.80 μ . Bands at 2.60 and 1.81 μ are characteristic of the hydroxide mol., and that at 2.30 μ of OH'. The remaining bands are accounted for as harmonics of 2.30, 3.65, and 5.20 μ . F. L. U.

Near infra-red absorption spectrum of monodeutero-acetylene. A. MCKELLAR and C. A. BRADLEY, jun. (Physical Rev., 1934, [ii], 46, 664—666).—Using absorbing columns up to 20 ft. in length at atm. pressure, the spectrum, photographed for the range 6000—10,500 \AA ., showed a band with origin at 10,302 \AA ., attributed to $C_2H^1H^2$. The calc. interat. distances are $C-C=(1.247\pm0.008)\times10^{-8}$, $C-H^1=C-H^2=(0.940\pm0.036)\times10^{-8}$ cm. N. M. B.

Rotation-vibration spectrum of acetylene (C_2H_2). G. HERZBERG and J. W. T. SPINKS (Z. Physik, 1934, 91, 386—399).—A C_2H_2 band at 1.174 μ and two weak bands at 1.016 and 1.037 μ have been photographed and the lines measured; this gives variation of inter-nuclear separation with rotation, and also a new allocation of band frequencies. A. B. D. C.

Infra-red and Raman spectra of methyl compounds. A. ADEL and E. F. BARKER (J. Chem. Physics, 1934, 2, 627—629).—The appearance of an intense extra band in the infra-red and Raman spectra of the Me halides is explained by resonance interaction between the ν_1 and $2\nu_4$ levels. Comparison of a no. of Me compounds indicates that the phenomenon is characteristic of the Me group. F. L. U.

Influence of temperature on the absorption of organic liquids in the region of the near infra-red. B. BLOCH and J. ERRERA (Compt. rend., 1934, 199, 713—715).—Absorption bands in the region 1.5 μ due to C-H, C-O, C-Cl, and N-H in org. compounds are not influenced by temp. With alcohols the band due to O-H at 1.6 μ decreases in intensity as temp. rises, and a band at 1.4 μ appears at approx. 20° , and becomes well marked at approx. 90° . MeOH, EtOH, BuⁿOH, $C_5H_{11}OH$, and $C_6H_{15}OH$ have been examined. $OH\cdot CH_2\cdot CH_2Cl$ (I) behaves like an alcohol, which disagrees with the quantum resonance supposed by Zahn to exist between (I) and $^-\cdot O\cdot CH_2\cdot CH_2Cl^+$. The C-H band of (I) at 1.74 μ is not influenced by temp. R. S. B.

Infra-red spectra of the chlorine derivatives of ethylene. T. Y. WU (Physical Rev., 1934, [ii], 46, 465—469).—Data for regions of absorption and band envelopes are given for the infra-red absorption spectra of $CH_2\cdot CHCl$, *cis*- and *trans*- $C_2H_2Cl_2$, C_2HCl_3 , and C_2Cl_4 in the region 2—25 μ . Analysis and the Raman spectra are considered. N. M. B.

Vibrational spectrum of water vapour. L. G. BONNER (Physical Rev., 1934, [ii], 46, 458—464).—Mathematical. From a treatment of the non-linear triat. XY_2 type mol. the vibrational energy expression is obtained. Application of the results to the H_2O mol. gives the primary binding consts. and vibration frequencies for infinitesimal amplitudes. A prediction

of the infra-red vibrations spectrum of the symmetrically substituted H_2O mol. is given. N. M. B.

Electric moments and infra-red spectra. A correction. R. S. MULLIKEN (J. Chem. Physics, 1934, 2, 712—713; cf. this vol., 942). F. L. U.

Infra-red absorption of cellulose esters. Cellulose acetate. O. B. ORLOV and D. A. FEDOROV (J. Tech. Phys., Russia, 1933, 3, 1124—1131).—By addition of plasticisers, cellulose acetate films equiv. in absorptive properties to glass can be obtained.

CH. ABS.

Plotnikov effect or longitudinal light scattering in liquids. R. S. KRISHNAN (Proc. Indian Acad. Sci., 1934, 1, 44—47).—The effect (halo produced around a pencil of transmitted light) was more conspicuous in liquids not free from dust than in pure liquids, and disappeared completely when the AcOH , EtOH , MeOH , H_2O , petrol- Et_2O , $[\text{CH}_2\cdot\text{OH}]_2$, and castor oil had been purified by repeated distillation in vac., indicating that the effect is not a mol. phenomenon, but is due to the presence of dust. N. M. B.

Normal frequencies of vibration of symmetrical pyramidal molecules AB_3 with application to the Raman spectra of trihalides. J. B. HOWARD and E. B. WILSON, jun. (J. Chem. Physics, 1934, 2, 630—634).—Theoretical. Interat. distances are calc. for trihalides of P, As, Sb, and Bi.

F. L. U.

Raman spectrum of sulphur in the solid and liquid states. C. S. VENKATESWARAN (Proc. Indian Acad. Sci., 1934, 1, 120—121).—No difference could be detected between the structure or positions of the Raman lines for the liquid state and the rhombic form of S. Hence the liquid state seems to differ from the solution state, for which small shifts in the frequencies have been recorded.

J. W. S.

Intensity of Raman effect in water. A. CARRELLI and F. CENNAMO (Nuovo Cim., 1933, [ii], 10, 329—332; Chem. Zentr., 1934, i, 2095).—In the band groups of H_2O excited by λ 3665, 4047 Å., three max. occur at 3230, 3450, and 3560 cm^{-1} .

H. J. E.

Raman spectra and molecular constants of phosphorus trifluoride and phosphine. D. M. YOST and T. F. ANDERSON (J. Chem. Physics, 1934, 2, 624—627).—Raman lines for liquid PF_3 were found at 890, 531, 840, and 486 cm^{-1} , and for liquid PH_3 at 2306, 979, and 1115 cm^{-1} . A regular pyramidal structure is indicated for PF_3 . Entropies are calc.

F. L. U.

Raman spectra of sulphuric acid solutions. R. M. BELL and M. A. JEPPESEN (J. Chem. Physics, 1934, 2, 711—712).—The Raman spectrum of aq. H_2SO_4 at different concns. shows a gradual shift of frequency with concn. among two groups, rather than a shift among three different frequencies as reported by Woodward and Horner (this vol., 473). F. L. U.

Raman spectrum of nitrosylsulphuric acid. W. R. ANGUS and A. H. LECKIE (Nature, 1934, 134, 572).—The Raman spectrum of a solution of this acid in H_2SO_4 shows in addition to displacements due to H_2SO_4 a line corresponding with a displacement of 2340 cm^{-1} together with a no. of faint lines.

L. S. T.

Raman and ultra-violet absorption spectra of metal carbonyls and alkyls. A. B. F. DUNCAN and J. W. MURRAY (J. Chem. Physics, 1934, 2, 636—643; cf. this vol., 10).—Raman lines, and the limits of absorption at -78° and room temp., are given for $\text{Ni}(\text{CO})_4$, PbMe_4 , and PbEt_4 . The results are discussed. The calc. symmetry no. for $\text{Ni}(\text{CO})_4$ is 6·3, indicating a plane square rather than a tetrahedral configuration.

F. L. U.

Multiplicity of some Raman frequencies of the nitrate group in nitrates with more than one valency. Z. OLLANO and G. FRONGIA (Nuovo Cim., 1933, [ii], 10, 306—315; Chem. Zentr., 1934, i, 1451—1452).—The frequencies, 1440, 1030, 980, and 720 cm^{-1} , are simple for aq. solutions of Na, K, NH_4 , and Hg^+ nitrates; in those of Mg, Mn, Ba, and Al, Ce^{+++} , La, and Bi, 1440 cm^{-1} is broad and complex, probably double, and 720 cm^{-1} is double with an interval of 30—40 cm^{-1} between the components. The doublet structure of this frequency, which corresponds with vibrations perpendicular to the symmetry axis of the NO_3 pyramid, is attributed to the presence of $[\text{M}(\text{NO}_3)]^+$ or $[\text{M}(\text{NO}_3)_2]^+$ and $[\text{M}(\text{NO}_3)_2]^{++}$ ions in conc. solutions in spectroscopically detectable amounts.

L. S. T.

Raman spectrum of deuteriobenzene. J. W. MURRAY, C. F. SQUIRE, and D. H. ANDREWS (J. Chem. Physics, 1934, 2, 714—715).—The Raman spectrum of C_6H_5 obtained by polymerisation of C_2H_2 shows a line at 943 cm^{-1} . This agrees with the frequency (945 cm^{-1}) calc. from the shift of the 992 line of C_6H_6 due to substituting six H^2 atoms for the H^1 atoms.

F. L. U.

Influence of high temperature on the Raman bands of benzene. S. C. SIRKAR (Current Sci., 1934, 3, 113—114).—The changes which many of the lines in the Raman spectrum of C_6H_6 undergo between 35° and 160° are described and discussed. L. S. T.

Raman effect of furan and three derivatives. L. MEDARD (Bull. Soc. chim., 1934, 1, [v], 934—942; cf. this vol., 830).—The characteristic olefinic C:C frequency, 1600 cm^{-1} approx., is absent from the Raman spectrum of furan (I), doubtful in the case of furfuraldehyde (II), but present in those of 2-methylfuran and furfuryl alcohol. The frequencies characteristic of the (I) ring are 610, 745, 880, 1150, 1390, 1500, 3126, and 3160, and are not found in tetrahydromethylfuran. (I) has no frequencies at 919—930, 1220—1237, and 1458—1476, possibly owing to its symmetry or the absence of side-chain-nuclear vibrations. The frequencies of the C:O in (II) are modified.

J. G. A. G.

Application of the Raman effect to organic chemistry. III. Tetramethylethylene. IV. Configuration of anethole, isosafrole, and isoeugenol. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 25, 31—35, 36—45).—III. The following frequencies, in cm^{-1} , have been found in the Raman spectrum of $\text{CMe}_2\text{:CMe}_2$ at 18° : 1665, due to tetra-substituted C:C, 1378 (corresponding with 1342 for C_2H_4), 1447, due to substituted CH_2 ; 2997, 2903, 2853, 1017, 954, and 894, all analogous to frequencies appearing in Raman spectra of saturated and unsaturated hydrocarbons. It is inferred that

substitution of the H atoms of C_2H_4 by Me increases the strength of the double linking.

IV. The Raman spectra of anethole (I), isosafrole (II), and isoeugenol (III) have been determined at approx. 20° . The C:C frequencies, in cm^{-1} , are 1644 (I), 1641 (II), and 1646 (III). The influence of the OMe has been studied with *p*-methoxystyrene, for which the C:C frequency is 1620, as against 1636 for styrene. From this effect, and from the influence of OMe on the CO frequency of PhCHO, it is inferred that the C:C frequencies of (I), (II), and (III) correspond not with the frequency 1645 of *cis*-CHPh:CHMe, but with the frequency 1663 of *trans*-CHPh:CHMe. It is supposed that (I), (II), and (III) exist in the *trans*-form. Other frequencies observed are: 3046 (I), 3056 (II), and 3060 (III), due to aromatic CH; 2991, 2904, 2820 (I), 2995, 2902, 2855 (II), and 2990, 2916, 2850 (III), due to aliphatic CH; 1492, 1432 (I), 1483, 1434 (II), and 1452, 1430 (III), due to CH_2 .

R. S. B.

Raman effect. Raman spectrum of organic substances. XXIII (Poly-substituted benzenes. IV). XXIV. (Benzoyl, phenylacetyl, and cinnamoyl compounds.) K. W. F. KOHLRAUSCH and A. PONGRATZ (Monatsh., 1934, 64, 361—373, 374—384).—XXIII. Data have been obtained for a no. of compounds $C_6H_5Me_2X$ ($X=Cl, Br, I, \text{ or } CN$). The results are discussed.

XXIV. The frequency ω of the CO has been determined for a no. of derivatives $CH_2Ph\cdot COX, BzX$, and $CHPh:CH\cdot COX$. In the Cl-derivative a duplication of the CO ω takes place, but not in the only Br-derivative, BzBr, examined. Association of the CO group with the C:C linking increases intensity, but lowers ω .

M. S. B.

Line emission and absorption of chromium phosphors. III. Behaviour at low temperatures and in a magnetic field. O. DEUTSCHBEIN (Ann. Physik, 1934, [v], 20, 828—842; cf. A., 1932, 1076).—Between 78° and 14° abs. there is no marked change in the sharpness and position of the lines emitted by Cr phosphors. The intensity ratio of some of the lines, however, varies considerably between these temp. The variation of the intensity with temp. makes possible an arrangement of the terms, and the term scheme of the Al_2O_3 -Cr phosphor has been accurately derived. The principal lines (I) and some of the secondary lines (II) are split in a magnetic field, (I) into more components than (II). (I) are more strongly degenerate than (II).

A. J. M.

Natural fading in single crystals of phosphorescent zinc compounds. V. V. ANTONOV-ROMANOVSKI (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 432—435).—The dependence of the decay of phosphorescence on the crystal size (approx. size 10 — $100\ \mu$), temp., and intensity of the exciting light has been measured. The decay was slower in small than in large crystals.

H. J. E.

Radiation damping and the polarisation of fluorescence radiation. G. BREIT and I. S. LOWEN (Physical Rev., 1934, [ii], 46, 590—597).—Mathematical. The case in which the distance between two or more energy levels is comparable with their natural

breadth is considered in a systematic treatment of emission, absorption and fluorescence, and the calculation of the polarisation of fluorescence radiation. Results are given for the polarisation of H_α excited by absorption of the second line of the Lyman series.

N. M. B.

Behaviour of calcite in ultra-violet light. A. KOHLER and H. LEITMEIER (Zentr. Min., A, 1933, 401—411; Chem. Zentr., 1934, i, 2103—2104).—Observations on the luminescence phenomena are recorded for 300 specimens.

H. J. E.

Phosphorescence of glass solarised by soft X-rays. H. KERSTEN and C. H. DWIGHT (J. Opt. Soc. Amer., 1934, 24, 285—286; cf. this vol., 40).—The variation of the intensity of the phosphorescence with time of excitation, and the rate of its decay have been investigated by measurement of blackening produced on a photographic film.

J. W. S.

Ionisation potentials of formaldehyde and halogen derivatives of methane. T. N. JEWITT (Physical Rev., 1934, [ii], 46, 616—617).—Vals. measured by a mol.-ray method for $CH_2O, MeCl, MeBr$, and MeI were 11.3, 10.7, 10.0, and 9.1 volts, respectively.

N. M. B.

Electrolytic valve action in molten salts. H. GRUNERT (Z. Physik, 1934, 91, 49—69).—Valve action has been investigated for Ta and Al electrodes in molten $NaNO_3, KNO_3$, their eutectic mixture, and $K_2Cr_2O_7$.

A. B. D. C.

Emission of electrons from cold metal surfaces. C. C. CHAMBERS (J. Franklin Inst., 1934, 218, 463—484).—By repeating Del Rosario's work it is found that the cold electron current did not commence until voltages much $>$ those found by others because of extremely good vac. conditions and freedom from impurities. The formula of Fowler and Nordheim is applicable in the measurable regions in form directly, and in magnitude only if irregularities in the surface are such as to raise the field at the surface to a sufficiently high val.

W. R. A.

Surface photo-electric effect in metals. I. K. MITCHELL (Proc. Roy. Soc., 1934, A, 146, 442—464).—Theoretical. The theories of the surface photo-electric effect in metals proposed by Wentzel and Fröhlich are shown to be incorrect. The photo-electric emission due to a single surface is calc. by two methods which lead to the same result. The theoretical spectral distribution curves for K are compared with experiment.

L. L. B.

Effect of out-gassing potassium on the selective photo-electric effect. F. KLAUER (Ann. Physik, 1934, [v], 20, 909—918).—The K was submitted to seven-fold distillation in vac. The sensitivity is very small for freshly prepared layers, but increases on keeping, gas probably being taken up from the walls. The introduction of a very small pressure of intensively dried H_2 has no effect on the sensitivity. The selective photo-effect with the alkali metals is to be ascribed to the fact that the ordinary metals always contain H_2 .

A. J. M.

Semi-conductors. G. DECHÊNE (Ann. Physique, 1934, [xi], 2, 241—345).—The discontinuities of potential at the junction of a semi-conductor

(HgO , PbCl_2 , ZnO , Na_2CO_3), and a metallic electrode when a current passes, are attributed to the formation of a space charge in the thin layer of semiconductor; this hypothesis allows an explanation of the influence of temp., illumination, pressure, and modifications with time. From the capacity of the contact the order of magnitude of the layer in which the potential variation takes place is deduced as 10^{-2} or 10^{-3} cm. Evidence is given that the complex ionising electromagnetic radiation emitted above a crit. potential, when the electrode is in grid form, originates in the adjacent air, and not in the semiconductor. The intensity of the radiation varies with time, with the resistivity of the substance, and with the voltage at the grid. N. M. B.

Effects produced on illuminating cuprous oxide in a magnetic field. I. K. KIKOIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 418—421).—When a plate of Cu_2O with its surface parallel to the magnetic field is illuminated perpendicularly, an e.m.f. of the order of 20 volts is set up in the plate in a direction perpendicular to that of illumination and to the field. Measurements under varied conditions are recorded. H. J. E.

Voltaic and thermal potential of cuprous oxide. G. MONCH (Z. Physik, 1934, 91, 124—130).—These are independent, the voltaic being a surface and the thermal a vol. effect. A. B. D. C.

Crystal photo-effect. G. MONCH and R. STUHLER (Z. Physik, 1934, 91, 253—263; cf. A., 1933, 1230). A. B. D. C.

Crystal photo-effect. G. MONCH (Z. Physik, 1934, 91, 264—271).—Theoretical. Classical and quantum-mechanical theories are discussed; Frenkel's theory (A., 1933, 1103) agrees best with absence of photo-effect in synthetic Cu_2O crystals. A. B. D. C.

Behaviour of the normal cathode fall at the m.p. of the metal. A. WEHNELT and H. KURZKE (Ann. Physik, 1934, [v], 20, 919—920).—Sn, Pb, and Hg in A were used. Sn and Pb show a sudden increase in the cathode fall at the m.p. For Hg there is a decrease. A. J. M.

High-voltage polarisation in crystals of salt-petre. H. M. BRYEVICH and B. M. HOCHBERG (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 545—554).—The temp. dependence of the vol. charge from 30° to 74° and the effect of added AgNO_3 on the vals. have been measured. CH. ABS. (e)

Electronic and lattice conduction of heat in metals. E. GRUNEISEN and H. REDDEMANN (Ann. Physik, 1934, [v], 20, 843—877).—The thermal conductivity of Ag, Cu, Pd, and the alloys Au-Ag, Au-Cu, Cu-Pd, and Au-Pd was determined at -183° , -195° , and -255° . The rule of the linear isotherm, and Norbury's relationship, hold only up to a certain degree of lattice distortion, above which the heat-resistance increases more slowly than is indicated by the rule. The addition to another metal of metals which cause the same change of resistance does not alter the heat-resistance by the same amount. The results may be explained by assuming that the conductivity is made up of two parts, one being the electronic, the other the

lattice, conduction, the latter being not so greatly affected by deformation of the lattice as the former.

A. J. M.

Electrical conductivity of amber at different pressures. F. SEIDL (Z. Physik, 1934, 91, 318—322).—This conductivity was determined at atm., low and high vac. pressures. A. B. D. C.

Conductivity of compressed mercuric sulphate. W. SCISZOWSKI (Acta phys. polon., 1932, 1, 457—463; Chem. Zentr., 1934, i, 515).—When HgSO_4 is pressed between a Zn and a Pt electrode a current passes more feebly in the direction $\text{Zn} \rightarrow \text{HgSO}_4$ than in the reverse direction. A resistant layer forms near the Zn-HgSO_4 interface. H. J. E.

Electrical conductivity of semi-conductors. A. N. ARSENEVA and B. V. KURCHATOV (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 149—152).—The electrical conductivity of pure MoO_3 is $6.1 \times 10^{13} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temp.; vals. increase rapidly with increase in concn. of Mo_2O_5 . Farkas' theory is preferred to that of Wilson and Bronstein. CH. ABS.

Elucidation of the form of zwitter ions by dielectric measurements. W. KUHN and H. MARTIN (Ber., 1934, 67, [B], 1526—1529).—Approx. calculation of the dipole moment of hexaglycylglycine leads to 3.4×10^{-18} , which is too small to permit the conception that the mol. is rod-like (cf. Wyman *et al.*, A., 1933, 459). Reasons are advanced in favour of the view that measurements of the dielectric const. do not afford evidence in favour of a stiff, stretched form of the mols. of NH_2 -acids. H. W.

Ionic polarisation in solid bodies. I. V. KURCHATOV (J. Exp. Theor. Phys., U.S.S.R., 1933, 3, 133—135).—Vals. of γ in Errera's formula and in $\gamma = \{[(\epsilon - 1)/(\epsilon + 2)] - [(\eta_0^2 - 1)/(\eta^2 + 2)]\} / [(\epsilon - 1)/(\epsilon + 2)]$, in which ϵ is the dielectric const. for a frequency $\eta_0 = 10^6$ hertz, are tabulated for LiF, NaF, KF, RbF, MgF_2 , CaF_2 , SrF_2 , BaF_2 , LiCl, NaCl, KCl, RbCl, LiBr, NaBr, KBr, RbBr, LiI, NaI, KI, and RbI. The former vals. are the less trustworthy. CH. ABS.

Variation of the dielectric constant of Rochelle salt crystals with frequency and applied field strength. A. ZELENY and J. VALASEK (Physical Rev., 1934, [ii], 46, 450—453).—Measurements perpendicular to the a axis at 0° over the frequency range $30\text{--}30 \times 10^6$ cycles per sec. show uniform decline from 62,000 at 30 cycles to 220 at 10^7 cycles and an abrupt fall to negative vals. (inductive reactance) at 14×10^6 cycles, independently of the size and mounting of the crystal. N. M. B.

Polarity of chemical compounds. VII. K. HIGASHI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1167—1175).—Theoretical. Muller's rule for the influence of solvent on observed dipole moment (μ) disagrees with experiment with EtOH , Bu^OH , $\text{C}_5\text{H}_{11}\text{OH}$, $\text{C}_{16}\text{H}_{33}\text{OH}$, $\alpha\text{-C}_{10}\text{H}_7\text{OH}$, and NH_2Ph in polar and non-polar solvents. The influence of the solvent is correlated with the shape of the solute mol., and ϵ for the solvent. μ observed for mols. with small or negative Kerr consts. (K) should increase with increasing ϵ , but should decrease with increasing ϵ for mols. with large positive K . This explains the anomalies to Müller's rule. R. S. B.

Dielectric properties of acetylenic compounds.
IV. Arylhalogenoacetylenes. Positive iodine.
 C. J. WILSON and H. H. WENZKE (J. Amer. Chem. Soc., 1934, **56**, 2025—2027; cf. this vol., 717).—The dipole moments of several arylhalogenoacetylenes (I) have been determined. The C to I moment has the + end towards the I atom; the C to Br moment and the C to Cl moment in (I) are < the corresponding moments in substituted C_6H_6 . The Br and Cl are less negative than in derivatives of paraffins, ethylenes, or benzenes.

E. S. H.

Effect of the solvent in dipole moment measurements: moment of ethylene bromide.
 M. A. G. RAU and B. N. NARAYANASWAMY (Proc. Indian Acad. Sci., 1934, **1**, 14—27).—Data for the polarisations of $C_2H_4Br_2$ in C_6H_6 , PhMe, CCl_4 , and cyclohexane at infinite dilution and over the temp. range 10—40° are tabulated. The calc. moments vary widely with the solvent, and increase by about 0.08—10⁻¹⁸ e.s.u. over the temp. range. Potential energies between the rotating parts of the mol. are calc.

N. M. B.

Index of refraction of water and its thermal history. V. K. LA MER and M. L. MILLER (Physical Rev., 1933, [ii], **43**, 207—208).—No difference in the val. of n for H_2O dependent on thermal treatment has been detected.

L. S. T.

Refractivity of cellulose and its derivatives.
I. Influence of non-cellulosic impurities on refractivity of cellulose fibres. II. Influence of oxidation and hydrolysis on [refractivity of] cellulose fibres. K. KANAMARU (Helv. Chim. Acta, 1934, **17**, 1047—1066, 1066—1072).—I. Measurements of n_D , both parallel to (n_\parallel) and perpendicular to (n_\perp) the fibre axis have been made with ramie, hemp, jute, Manila hemp, straw, and bamboo fibres, at each stage of a process of purification consisting of extraction by EtOH, Et_2O , H_2O , and 1% NaOH, and of chlorination. Vals. of n_\parallel increase, and of n_\perp decrease, with purification, the latter converging to 1.524 at 21° for all varieties, whereas the former varies with the material. Purified hemp cellulose has $n_\parallel - n_\perp$ 0.071. Measurement of the double refraction can be used as a criterion of purity for a given variety of cellulose fibre.

II. Oxy- and hydro-cellulose behave similarly to the above, in that with progressive degradation first n_\parallel , and later n_\perp , increases. Only the former reaches the val. characteristic of the cellulose micelle. This indicates that n_\parallel may depend on the configuration of the main chain, n_\perp being influenced by chemical changes in the side-chains.

F. L. U.

Refractive dispersion of organic compounds.
V. Oxygenated derivatives of cyclohexane. Inadequacy of the Ketteler-Helmholtz equation. C. B. ALLSOPP. **VI. Refractivities of the oxygen, carbonyl, and carboxyl radicals. Origin of optical rotatory power and of the anomalous rotatory dispersion of aldehydes and ketones.** T. M. LOWRY and C. B. ALLSOPP (Proc. Roy. Soc., 1934, **A**, 146, 300—312, 313—326).—V. The refractive indices of $C_6H_{11}OH$ at 25° and of cyclohexanone and $C_6H_{11}CO_2Et$ at 20° have been determined for 6708—2366 Å. It is found that, although the rotatory

dispersion of optically active ketones is largely dominated by the ketonic absorption band, the contribution of this band to the refractive dispersion is extremely small. At wave-lengths covered by, or near to, the absorption bands, the Ketteler-Helmholtz equation is inadequate.

VI. Using the above data, vals. are deduced for the refractivities of the $\cdot O$, $\cdot C=O$, and $\cdot CO\cdot O$ radicals over the range 6708—2400 Å. $\cdot C=O$ exhibits an anomalous dispersion in the region covered by the absorption band with max. 2880 Å. $\cdot O$ also shows a slight anomaly, in a region of complete transparency. The refractivity of $\cdot CO\cdot O$ is of a normal type. The rotatory dispersion of *sec.*-BuOH can be accounted for by means of the term $\frac{R_A R_B R_C R_D}{R_A + R_B + R_C + R_D}$ where R_A, R_B, R_C, R_D are the refractivities of the four radicals. The experimental vals. for the primary alcohols and for the *sec.* alcohols with branched chains are beyond the range of the formula, even when multiplied by Boys' factor $(\mu^2 + 2)(\mu^2 + 5)$. The origin of the anomalous rotatory dispersion of aldehydes and ketones is discussed.

L. L. B.

Molecular refraction of crystallised organic compounds and its applicability to questions of constitution. A. NEUHAUS (Ber., 1934, **67**, [B], 1627—1636).—From consideration of the different forms of the α -follicular hormone (I) it is shown that the refraction increments (Eisenlohr, von Auwers, *et al.*) for C, H, O, and the double linking deduced from org. liquids are valid in high degree for the cryst. condition. The empirical and constitutional formulæ of the (I) have thus been confirmed. Consideration of available data shows that the relationships and possibilities developed above are generally applicable to cryst. org. compounds containing C, H, and O or C, H, O, and N. Several homogeneous hydrocarbons present exceptions, obviously of an ordered type. The constitution of the hormones of the corpus luteum is discussed.

H. W.

Remarkable properties of a doubly-refracting liquid. G. VAN IJERSON (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 367—376).—Bands are observed when Cd phosphoglycerate (I) in presence of NaOAc in a capillary is viewed between crossed nicols. Other examples of double refraction with this gelatinous liquid, especially after mechanical agitation, have been studied. It is inferred that fibrils of (I) align themselves in the direction of flow of the liquid.

Surface of double refraction and fringes with certain crystalline plates. C. GAUDEFRY (Compt. rend., 1934, **199**, 731—734).—Theoretical. The author's equation of double refraction is discussed. When the angle between the two optic axes of a crystal is 90° or nearly so, and a crystal plate cut parallel to these axes is placed perpendicular to the incident convergent beam, the whole field is uniformly lit. With parallel rays the retardation of the plate is const., whatever the inclination to the incident beam. Diaspore obeys these conditions. R. S. B.

Stereochemical structure. VII. Rotatory powers and racemisations of the optically active benzoins. R. ROGER and A. MCGREGOR (J.C.S., 1934, 1545—1550; cf. this vol., 476).—Rotatory

powers of the optically active benzoin in (a) COMe_2 , EtOH , CHCl_3 , CS_2 , CCl_4 , dioxan, and (b) NH_2Ph , $\text{C}_5\text{H}_5\text{N}$, piperidine, NHEt_2 , NEt_3 , are given. The vals. in (a) satisfy the Rupe and Lowry-Dickson criteria. *D*-Benzoin is levorotatory between λ 6563 and 4358 in group (a) solvents and in NH_2Ph and $\text{C}_5\text{H}_5\text{N}$, but dextrorotatory in the others. The rotatory powers are not directly \propto to the dipole moment of the solvent. Vals. in CHCl_3 and dioxan decreased with rise of temp. It is suggested that the optically active benzoin contains a centre of fixed asymmetry (the mandelyl complex) and a centre of induced asymmetry (the PhCO group) the relative contributions of which to the optical rotation may be altered by the solvent. The influence of the material of the containing vessel, various solvents, and catalysts on the rate of racemisation has been studied.

R. S.

Rotatory dispersion curves. II. Configuratively related substituted fatty acids. P. A. LEVENE and A. ROTHEN (J. Chem. Physics, 1934, 2, 681—688; cf. this vol., 12).—Rotatory dispersion curves of acids of the types $\text{SH}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ and $\text{SO}_3\text{H}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ and of their Na salts have been measured in the visible and ultra-violet regions. The results agree with the rule previously reported, that in members of homologous series the total rotation of consecutive members may differ in sign, but the signs of the partial rotations remain const.

F. L. U.

Extent of the validity of the "rule of shift." P. A. LEVENE, A. ROTHEN, and G. M. MEYER (Science, 1934, 80, 101—102).—Max. mol. rotations of correlated *p*-nitrophenyl esters of α -substituted AcOH and EtCO_2H in the homogeneous state and in C_7H_{16} are recorded. The need for the exercise of caution in using the "rule of shift," which postulates that in configuratively related substances an identical substitution brings about a shift of rotation in the same direction, to correlate the configurations of substances the two-component partial rotations of which are of opposite sign is pointed out.

L. S. T.

Effect of concentration, temperature, and wave-length of light on the Verdet constant of cerous chloride solutions. F. G. SLACK, R. L. REEVES, and J. A. PEOPLES, jun. (Physical Rev., 1934, [ii], 46, 724—727).—Data are tabulated for a concn. range up to almost saturated solution, for the temp. range 10—45°, and for wave-lengths 5893, 5461, and 4481 Å. Curves for the Verdet const. as a function of temp. and concn. are given. N. M. B.

Kerr effect in solutions. V. A. JOFFE (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 491—496).—Vals. are recorded for PhNO_2 (up to 30%) in paraffin oil, C_6H_6 , CCl_4 , and C_7H_{16} . The mol. const. for PhNO_2 remains const. in each solvent up to a crit. concn., and then decreases, owing to association.

H. J. E.

Dispersion of the electro-optical Kerr effect in carbon dioxide. G. G. QUARLES (Physical Rev., 1934, [ii], 46, 692—694).—Data for the range 4000—7500 Å. are given. The abs. val. of the Kerr const. *B* for CO_2 is $(0.249 \pm 0.003) \times 10^{-10}$ at 17.5°, 5890 Å., and 1 atm. pressure.

N. M. B.

Magnetic circular dichroism of solutions of cuprammonium hydroxide and the corresponding salts (nitrate and sulphate). R. CORDONNIER (Compt. rend., 1934, 199, 667—668; cf. A., 1933, 765).—Data are tabulated. The effects \propto mol. concns.

H. J. E.

Dependence of polarisation on the strength of the electric field for seignetto-electrics outside the region of spontaneous orientation. I. V. KURCHATOV (J. Exp. Theor. Phys., U.S.S.R., 1933, 3, 181—188).

CH. ABS.

Physico-chemical test for mitogenetic (Gurwitsch) rays. M. HEINEMANN (Nature, 1934, 134, 701).—The coagulation of unstable inorg. sols, e.g., Au sol, is used to detect these rays.

L. S. T.

Structure hypotheses for the heteropoly-compounds. A. ROSENHEIM [with E. BRAUER and (FRL.) E. MATERNE] (Z. anorg. Chem., 1934, 220, 73—95).—Recent work on poly- and heteropoly-anions indicates that there is no reason to discard the views on the structure of these anions based on Werner's coordination theory.

M. S. B.

Stereochemistry of the free triarylmethyl radical. Total asymmetric synthesis. G. KARAGUNIS and G. DRIKOS (Z. physikal. Chem., 1934, B, 26, 428—438).—A more detailed account of an investigation, the principal results of which have been recorded (A., 1933, 1041).

R. C.

Significance of chemical linking energies. C. T. ZAHN (J. Chem. Physics, 1934, 2, 671—680).—A general theoretical discussion in which energies associated with linking interaction are taken into account.

F. L. U.

Multiple linkings in organic substances. V. S. GUTRIIA (J. Gen. Chem. Russ., 1934, 4, 408—419).—Theoretical.

R. T.

Merkel diagram for secondary valency compounds and its technical application. H. BRAUER (Z. ges. Kalte Ind., 1933, 40, 167—170; Chem. Zentr., 1934, i, 2326).—The relation between the heat content and concn. of the more volatile component is represented graphically. The method is illustrated for $\text{CaCl}_2 \cdot n\text{NH}_3$ ($n=1, 2, 4$, or 8) at 0.5—16 atm. Technical applications are discussed.

H. J. E.

Vibrations of tetrahedral pentatomic molecules. III. Comparison with experimental data. IV. Isotopic shifts. (Miss) J. E. ROSENTHAL (Physical Rev., 1934, [ii], 46, 730—733; cf. A., 1934, 719).—III. From data for 9 mols. of the type XY_4 the vibrations may be explained on the basis of valency forces only in the case of CH_4 ; for the others an additional repulsive force must be postulated.

IV. Certain relations between the frequencies of the isotopic mols. are independent of the vals. of the force consts.

N. M. B.

Diamagnetism of organic liquid mixtures at different temperatures. S. R. RAO and P. S. VARADACHARI (Proc. Indian Acad. Sci., 1934, 1, 77—97).—The vals. of χ for C_6H_6 , CHCl_3 , and PhNO_2 - COMe_2 mixtures at 15—50°, as measured by the Quinke method with intense magnetic fields, obey the additivity law. χ for the pure liquids shows no

variation between 15° and 50°. It is concluded that association produces no change in the sp. susceptibility of org. liquids, and that the additive law holds unless chemical combination occurs. J. W. S.

Paramagnetic saturation in a single crystal. W. J. DE HAAS, J. VAN DEN HANDEL, and C. J. GORTER (Physical Rev., 1933, [ii], 43, 81).—The magnetisation of a mono-axial single crystal of Dy Et sulphate has been determined as a function of temp. and field strength in the directions of the optical axis and a secondary axis perpendicular to it. L. S. T.

Dependence of the magnetic susceptibility of water and potassium iodide solutions on temperature. G. TAMMANN (Z. Physik, 1934, 91, 410—412).—Cabrera and Fahlenbrach's results (cf. this vol., 841) are explained by variation of the mol. aggregation of H₂O with temp. A. B. D. C.

Magnetochemical investigations. X. Manganous chalcogenides. H. HARALDSEN and W. KLEMM. **XI. Magnetic behaviour of some rhenium compounds.** W. SCHUTH and W. KLEMM (Z. anorg. Chem., 1934, 220, 183—192, 193—198).—X. Magnetic susceptibilities of MnO, MnS, MnSe, and MnTe have been determined between 90° and 728° abs. and the effective magneton nos., μ_{eff} , calc. increases with rise of temp. and approaches the val. for aq. Mn^{II} salts or for salt hydrates. The vals. for the different compounds vary in the order MnSe > MnS > MnO > MnTe, which is unexpected, since the metallic character increases in order of increasing mol. wt. from MnO to MnTe. It is suggested that the behaviour is due, not to the interaction of cation and anion only, but also to the influence of the cations on one another.

XI. Compounds of Re^{VII} have a very slight paramagnetism varying with temp. The metallic character of the compounds ReO₃, ReO₂, and ReS₂ practically suppresses the ionic paramagnetism, whilst in the trihalides the absence of paramagnetism is probably due to the formation of larger mols. At higher temp.

for ReOCl₄, ReCl₅, and the complex halogen compounds of Re^{IV} approximates to the val. to be expected if the magnetism is due to electronic spin only. At room temp. and at low temp., however, the magnetism is < this val. M. S. B.

Magneto-chemical characteristics of the oxides of nickel. S. S. BHATNAGAR and G. S. BAL (J. Indian Chem. Soc., 1934, 11, 603—616).—Pure NiO is green; black samples owe their colour, in part, to adsorbed O. Magnetic susceptibility determinations at 25—366° show that the high vals. recorded in the lit. are due to traces of Ni formed by reduction during the prep. of the NiO. The val. of χ for NiO is 9.56×10^{-6} . The existence of other Ni oxides was not confirmed. J. G. A. G.

Classical model of ferromagnetism and its additional quantising at low temperatures. G. HELLER and H. A. KRAMERS (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 378—385).—Theoretical. Quantising the classical model leads to the theory of Bloch and Moller. R. S. B.

Discussion on energy distribution in molecules in relation to chemical reactions. (Proc. Roy. Soc., 1934, A, 146, 239—271).—C. N. HINSHEL-

WOOD. Attention was directed to the independent modes of activation of the mols. taking part in a reaction. Sp. linkings in a compound undergoing decomp. may be activated to a high vibrational level. Experiments support the hypothesis that mols. with activation energy differently located may behave as virtually independent entities kinetically; in a mol. like CH₂O the chance that the activation energy is communicated to the mol. so as to cause rapid decomp. is relatively > in a substituted mol. such as EtCHO. Bimol. reactions in solution where the observed rate is nearly equal to the rate of encounter of the appropriate activated mols., and reactions of the same order where the reaction velocity is many powers of ten < the activation rate, were discussed.

J. E. LENNARD-JONES discussed the problem with reference to the electronic structure of mols. and electronic orbitals.

M. W. TRAVERS criticised previous results obtained by Hinshelwood and Hutchinson on the pyrolysis of MeCHO (A., 1926, 804). Investigation by a different experimental method leads to other conclusions.

M. POLANYI discussed the accumulation of energy in a mol. and its transfer into elongation of a certain linking.

C. ZENER dealt with the factors which may greatly reduce the probability that a mol. should dissociate following collision with a second mol., if the combined energies of the two mols. are sufficient for this dissociation.

E. J. BOWEN directed attention to the difficulty of satisfactory chemical analysis in the experimental investigation of this subject.

R. G. W. NORRISH emphasised the importance of investigating every possible photochemical and spectroscopic aspect of this problem: the absorption spectrum, fluorescence, products of decomp., and the quantum yield at different wave-lengths. The photochemical decomp. of certain aldehydes and ketones was discussed.

H. W. THOMPSON spoke on the correlation of certain spectroscopic results with the corresponding photochemical data. The conditions for the occurrence of a dissociation process were discussed. The absorption spectra of several metal-alkyl compounds and compounds containing the chromophoric group SO₂ were considered.

C. J. M. FLETCHER described the experimental results supporting the hypothesis of the association of the energy of activation with different parts of the mol., for the different activated states which exist for the aldehydes.

E. K. RIDEAL directed attention to the connexion between the no. of squared terms (S) involved in a reaction and E , the energy of activation, and showed how these magnitudes could be correlated with constitutional factors. The effect of increasing chain length in a series of compounds containing a const. end-reacting group on the relation between E and S was described.

A. R. UBBELOHDE discussed the physical tests used to check the chemical equations. L. L. B.

Molecular rotation in ice at 10° abs. Free energy of formation and entropy of water. W. F.

GIAUQUE and M. F. ASHLEY (Physical Rev., 1933, [ii], 43, 81—82).—Preliminary vals. calc. are $H_2 + 0.5O_2 = H_2O(g)$, $\Delta F_{298.1} = 54,670$ g.-cal. per mol.; $H_2 + 0.5O_2 = H_2O(l)$, $\Delta F_{298.1} = 56,720$; $H_2O(g)$, $S_{298.1} 45.17$ (abs. 47.92) g.-cal. per degree per mol.; and $H_2O(l)$ $S_{298.1} 16.9$. A comparison of vals. indicates a lack of equilibrium between *o*- and *p*- H_2O in ice, and rotation of *o*- H_2O in ice. L. S. T.

Budde effect in halogens. T. S. NARAYANA (Indian J. Physics, 1934, 9, 91—109).—The effect was absent in pure super-dried Cl_2 ; it was observed in moist Cl_2 and Br, but decreased with drying; it was absent in Cl_2 and Br above 500 and 550 $m\mu$, respectively. The effect was shown by dry Cl_2 when heat losses from the walls of the Pyrex bulb were arrested, and by dry air-halogen mixtures. The effect \propto pressure and the square root of light intensity. Theories are reviewed and a mechanism is proposed. N. M. B.

Effect of temperature on the rotational heat of methane. R. RENNER (Physikal. Z., 1934, 35, 811—814).—Theoretical. A. J. M.

Intramolecular forces in octahedral models, particularly sulphur hexafluoride, on the basis of normal frequencies. A. EUCKEN and F. SAUTER (Z. physikal. Chem., 1934, B, 26, 463—472).—Theoretical. From the observed normal frequencies of SF_6 (this vol., 1055) and a calculation of the normal frequencies of an octahedral model, an attempt has been made to determine the nature of the intramol. forces in SF_6 . As a first approximation, the intramol. force system may be regarded as a combination of a Coulomb central force system with an angular force system. In so far as the intramol. forces can be regarded at all as central forces, they behave in respect of sign and magnitude like Coulomb forces effective between the centres of the atoms, considered fully ionised. R. C.

Rotational wave equation of tetramethylmethane for zero potential and a generalisation. L. J. B. LA COSTE (Physical Rev., 1934, [ii], 46, 718—724).—Mathematical. The exact solution is similar to that for the rigid spherical top. N. M. B.

Determination of parachor in solution. I. S. K. RAY (J. Indian Chem. Soc., 1934, 11, 671—679).—The surface tension and d of solvent and solution have been determined in the systems $C_{10}H_8$ - C_6H_6 , $-CCl_4$, $-CHCl_3$, α - $C_{10}H_7$ -OH- C_5H_5N , $-EtOAc$, coumarin- C_6H_6 , $-CHCl_3$, $-C_5H_5N$, 8-hydroxyquinoline- C_6H_6 , $-CCl_4$, xanthone- $CHCl_3$, $-C_5H_5N$, phenanthrene- C_6H_6 , $-CCl_4$, $-COMe_2$, anthracene- $PhNO_2$, dithiolthiadiazole- $EtOH$, and the parachors of the solutes have been calc. on the assumption that they obey the straight-line mixture law. E. S. H.

Parachor of benzyl alkyl ethers. T. C. HUANG and K. P. SUNG (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 303—306).—The parachors of benzyl Me, Et, Pr^a , Pr^i , Bu^a , Bu^i , and isoamyl ethers have been determined and appear to be normal. H. N. R.

Molecular organic compounds. V. Parachors of the phenol-amines in solution. C. A. BUEHLER and E. H. SPREEN (J. Amer. Chem. Soc., 1934, 56, 2061—2062; cf. A., 1932, 841).—The

parachors of the 1:1-compounds (f.p. quoted after base) of $PhOH$ with NH_2Ph , 30.4° (corr.), *o*- $C_6H_4Me \cdot NH_2$, 34.7° (corr.), *m*- $C_6H_4Me \cdot NH_2$, $-3.5 \pm 0.5^\circ$, and *p*- $C_6H_4Me \cdot NH_2$, 28.8° (corr.), determined (method: Hammick and Andrew, A., 1929, 638) in solutions of either component, are const. for a given temp., but increase with rise in temp. (cf. *loc. cit.*). Mol. wt. determinations (in $PhOH$) indicate that the compounds are generally undissociated. H. B.

Theory of liquids. II. T. S. WHEELER (Proc. Indian Acad. Sci., 1934, 1, 105—114; cf. this vol., 1159).—Formulae are deduced relating the attractive force coeff. to the parachor and giving the force between mols. at the distance of closest approach. Expressions for surface tension and internal latent heat of vaporisation are developed to include attractive and repulsive forces, and the force consts. calc., from the equations of state of certain gases by the Lennard-Jones method applied to these formulae. J. W. S.

Variation of refractive index for X-rays with angle of incidence. F. JENTZSCH (Z. Physik, 1934, 91, 151—166; cf. this vol., 125).—Data are given for glass. A. B. D. C.

Effect of pressure on the intensity of X-rays scattered from nitrogen at small angles. G. G. HARVEY (Physical Rev., 1934, [ii], 46, 441—445).—Scattering curves at 60, 80, and 100 atm. resemble those for a solid or liquid, and this is due to the closeness of the scattering centres. At small angles the scattering from a "permanent" gas diminishes owing to intermol. interference. N. M. B.

Absorption spectrum of X-rays. S. AOYAMA and T. FUKUROI (Sci. Rep. Tōhoku, 1934, 23, 405—418).—No difference could be detected in the X-ray absorption spectra of α - K_2RuCl_5 and α - $K_2RuCl_5 \cdot H_2O$, but marked difference was observed between β - K_2RuCl_5 and β - $K_2Ru(H_2O)Cl_5$. This is attributed to the co-ordination of the H_2O to the Ru in the β -salt, but not in the α -salt. Differences can be observed between the Debye-Scherrer photographs of the α - and β -salts, but not between those of the β - and γ -salts. The latter also give the same absorption spectra. J. W. S.

Crystallite orientation in a polycrystalline metal during plastic flow. R. E. GIBBS and N. RAMLAL (Phil. Mag., 1934, [vii], 18, 949—956).—X-Ray measurements on Cd wire show that, when a polycryst. metal flows, the β -flow, which gradually diminishes with time, is connected with a rotation of the axes of the crystallite, thus confirming the conclusions of Andrade *et al.* (A., 1933, 14). M. S. B.

Complete X-ray diagram of fibre structures. K. HUTINO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1187—1197).—Intensity distributions are treated theoretically for various planes of the Debye-Scherrer sphere. R. S. B.

Obtaining monocrystals with a given axial orientation. P. A. POLIBIN and A. I. FREUMAN (J. Exp. Theor. Phys., U.S.S.R., 1933, 3, 162—164).—Bridgman's method was applied to Zn, Cd, and Sn. CH. ABS.

Suggested form of crystallographic presentation. M. A. PEACOCK (Amer. J. Sci., 1934, [v],

28, 241—254).—The two-circle presentation is combined with an improved conventional presentation.

C. W. G.

Change in the properties of (I) deformed polycrystalline crystals, (II) monocrystals, when subjected to a period of rest. M. O. KORNFEELD (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 563—566, 567—570).—I. Rest does not restore completely the properties of deformed polycryst. Al. Laue photographs show overlapping of the grain boundaries (I). During rest changes occur at (I).

II. Data are recorded for the relative limits of fluidity before and after rest for deformed mono- and poly-crystals.

CH. ABS. (e)

Complexity of the solid state. A. SMITS and N. F. MOERMAN (Nature, 1934, 134, 698—699).—Irradiation by X-rays accelerates the establishment of the inner equilibrium in SO_3 . The v.p.-time of irradiation curve increases linearly to a const. val. at 76.0 mm. after 598 min. at 24.8°. The thermal reaction taking place is different from the reaction produced by X-rays, which is of zero order. X-Rays appear to split up polymerised mols. in the solid phase.

L. S. T.

Distortion of the crystal lattice of α -brass. W. A. WOOD (Nature, 1934, 134, 572).—X-Ray spectra of cold-rolled α -brass show that deformation of the alloy is accompanied by changes in the average size and shape of the unit cell, and in the latent energy of the crystal lattice.

L. S. T.

Absorption of X-rays and chemical linkings. A. SOLTAN (Acta phys. polon., 1932, 1, 317—326; Chem. Zentr., 1934, i, 1609).—Absorption measurements on H_2O and gaseous or liquid O_2 showed no deviation from the additive law attributable to an effect of chemical linking.

H. J. E.

Inertness and chemical activity of the rare gases. IV. Differences in the properties of the platinum-helium compound and pure platinum: action of aqua regia on both substances. V. X-Ray spectrogram of the cathodic deposit of the platinum-helium compound with excess of platinum. H. DAMIANOVICH (An. Inst. Invest. cient. tech., 1931, 2, 15—23, 24—32; Chem. Zentr., 1934, i, 2543—2544).—IV. The solubility of the Pt-He compound in dil. aqua regia increases with the He content. With 20 c.c. of He per g. of Pt the material is 74% sol. The insol. residue is different from the He-containing material. A definite compound is probably formed.

V. X-Ray photographs for the Pt-He compound show a ring characteristic of amorphous material. It disappears after heating. Colloidal PtS_2 or Bi_2S_3 give a similar ring.

H. J. E.

Crystal structure of Tl_2Sb_2 . F. R. MORRIS and A. WESTGREN (Svensk Kem. Tidskr., 1934, 46, 153—156).—A slight distortion of the previously proposed structure leads to a much better agreement with the intensities of the powder photograms. Each Sb atom is surrounded by four Tl atoms distant 3.10 Å., one distant 3.38 Å., and four distant 3.48 Å. R. P. B.

Crystal structure of copper sulphate pentahydrate. C. A. BEEVERS and H. LIPSON (Proc. Roy. Soc., 1934, A, 146, 570—582).— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has

a 6.12, b 10.7, c 5.97 Å., 2 mols. per unit cell. The Cu atoms lie on the special positions (000) and ($\frac{1}{2}$ $\frac{1}{2}$ 0), and the S on the general position (0.01, 0.29, 0.64). Four of the H_2O mols. are arranged in squares around the Cu atoms, and the 2 O make approx. octahedra with these. The fifth O is not co-ordinated, but is in contact with 2 O atoms and 2 H_2O mols. All the H_2O mols. show 2 O linkings each, in agreement with the theory proposed by Bernal and Fowler (A., 1933, 1106). The cryst. structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ explains the existence of the three successive stages of dehydration.

L. L. B.

Filiform sulphur and its structure. K. H. MEYER and Y. Go (Helv. Chim. Acta, 1934, 17, 1081—1093).—If a thread of plastic S is repeatedly stretched to 12—15 times its initial length it becomes microcryst. and no longer contracts. The resulting filiform S is found by X-ray analysis to have an elementary cell with a 26.4 \pm 0.1, b 9.26 \pm 0.05, c 12.32 \pm 0.05 Å., β 79° 15', space-group C_{2h}^{21} , containing 112 atoms. Filiform S retains its structure up to 50°, above which it becomes non-cryst. and contracts to 1/10 of its initial length. Both X-rays and light convert it rapidly into rhombic S. The analogy between the physical properties of S and rubber is noted.

F. L. U.

X-Ray study of a long X-cut quartz crystal vibrating under the transverse piezoelectric effect. M. Y. COLBY and S. HARRIS (Physical Rev., 1934, [ii], 46, 445—450; cf. A., 1933, 557).—Analysis of Mo $K\alpha$ reflexion for the crystal non-oscillating, oscillating at its fundamental frequency under the transverse piezoelectric effect, and oscillating at its second harmonic frequency shows that there is no elastic deformation of the spacing of the (110) planes $> 1.45 \times 10^{-5}$ per unit dimension, and that any increase in intensity of reflected X-rays produced by piezoelectric oscillations of the crystal is due to a reduction of secondary extinction.

N. M. B.

Crystal structure of thallium cyanide. M. STRADA (Atti R. Accad. Lincei, 1934, [vi], 19, 809—811).— TlCN is body-centred cubic. If the CN group is considered as a single entity the unit cell contains 1 mol. with a 3.82 Å., but if the C and N are assumed to occupy distinct positions in the lattice the unit cell then contains 8 mols. with a 7.64 Å. The CN' ion has an apparent radius 1.81 Å.

O. J. W.

Structure of heteropoly-acids. R. SIGNER and H. GROSS (Helv. Chim. Acta, 1934, 17, 1076—1080).—12-Silico-, 12-boro-, and meta-tungstic acids are shown by powder diagrams to have the same structure as 12-phosphotungstic acid (this vol., 479). Both the pentahydrates and higher hydrates were examined. The chemical properties are shown to be simply related to the structure in each case.

F. L. U.

Crystal structure of some phosphates and arsenates of tervalent metals. I. Phosphate and arsenate of aluminium. M. STRADA. II. Arsenate and phosphate of yttrium. M. STRADA and G. SCHWENDIMANN (Gazzetta, 1934, 64, 653—662, 662—674).—I. AlPO_4 and AlAsO_4 have a tetragonal structure of the SiO_2 type, space-group S_6 , with a 4.85 \pm 0.005, 4.90 \pm 0.005, c 6.60, 6.64 Å., c/a 1.362,

1.355, respectively, and 2 mols. per unit cell. The P and As atoms have an S_4 , and the O atoms a C_4 , symmetry. The calc. radius of the As^{5+} ion is 0.518 Å.; the distances Al-O, P-O, and As-O are 1.91, 1.80, and 1.878 Å., respectively.

II. *Anhyd. YAsO₄* was prepared by heating to 500° the dihydrate obtained by pptg. a solution of the nitrate with Na_2HAsO_4 . It belongs to the tetragonal system, space-group D_{2h}^{19} , 4 mols. per unit cell, a 6.890, c 6.269 Å., d_{calc} 5.053, d_{obs} 4.561. YPO_4 has the same structure as xenotime, with a 6.862, c 6.174 Å., d_{calc} 4.174, d_{obs} 3.785. The following ionic radii have been calc.: Y 1.027, O 1.216, As^{5+} 0.521, P^{5+} 0.422, AsO_4 1.738, PO_4 1.638 Å. O. J. W.

X-Ray analysis of the structure of dibenzyl. J. DHAR (Indian J. Physics, 1934, 9, 1—20; cf. this vol., 948).—The C_6 rings have a plane hexagonal structure, and lie in parallel planes separated by about 0.23 Å. Full data and discussions are given.

N. M. B.

X-Ray analysis of the crystal structure of dibenzyl. I. Experimental and structure by trial. J. M. ROBERTSON (Proc. Roy. Soc., 1934, A, 146, 473—482).— $[CH_2Ph]_2$ has a 12.77, b 6.12, c 7.70 Å., β 116°; space-group C_{2h}^2 ($P 2_1/a$), 2 mols. per unit cell, each possessing a centre of symmetry. Quant. intensity measurements have been made of the reflexions from about 100 crystal faces. The mol. extends in 3 dimensions, instead of being planar as in the aromatic compounds previously examined. The planes of the C_6 rings, although parallel, are at right angles to the plane containing the zig-zag of the connecting CH_2 groups. L. L. B.

Shape of the dibenzyl molecule. J. M. ROBERTSON (Nature, 1934, 134, 381).—A double Fourier analysis confirms previous views (see above) as opposed to those of Dhar (this vol., 948). L. S. T.

Determination of the atomic positions in *p*-dinitrobenzene by the Fourier analysis method. K. BANERJEE (Phil. Mag., 1934, [vii], 18, 1004—1008).—X-Ray measurements have been made on crystals of p - $C_6H_4(NO_2)_2$. Structure factors for the different planes have been calc. on certain assumptions and compared with the observed structure factors. A rough agreement has been observed. The planes of the NO_2 groups are inclined to the plane of the C_6 ring. M. S. B.

X-Ray studies on choleic acids. Y. Go and O. KRATKY (Z. physikal. Chem., 1934, B, 26, 439—452).—Of a no. of compounds of deoxycholic acid (I) with fatty acids, almost all give the same X-ray diagram, indicating the presence of the same basic lattice, composed of (I) mols., in each. Apparently the fatty acid mols. are arranged one behind another, forming canals extending through the basic lattice. Choleic acids containing EtOH of crystallisation have also been obtained. R. C.

X-Ray crystallographic measurements on derivatives of cardiac aglucones.—See this vol. 1354.

X-Ray diagram of ring-thread structure and orientation of micelles in films. I. SAKURADA and K. HUTING (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 193—210). A. J. M.

Cybotactic condition in the region of the critical point. I. Ethyl ether. R. D. SPANGLER. II. *iso*Pentane. C. A. BENZ and G. W. STEWART (Physical Rev., 1934, [ii], 46, 698—703, 703—706).—I. X-Ray diffraction-ionisation curves are given for 37 combinations of vals. of pressure, temp., and sp. vol. in the neighbourhood of the crit. point. Results, interpreted on the cybotactic theory, show that groups are very sensitive to changes in sp. vol., but show less dependence on temp. and pressure; that groups disappear at approx. the same sp. vol. at various temp. and pressures; that groups may appear in the gaseous state, and that beyond a certain sp. vol. no groups appear and the curves are of the gas type.

II. Curves for *isopentane*, obtained similarly to the above, show that the sp. vol. is unique in determining the extent of cybotactic groups; the sp. vol. at which these groups disappear is 90% > the crit. vol.; above the crit. pressure the formation of groups increases with decrease in sp. vol.; the internal description of liquefaction above the crit. pressure, passing from gas to liquid, is the same for Et_2O and *isopentane*.

N. M. B.

Explosive antimony. I. Microscopy of polished surfaces. C. C. COFFIN and S. JOHNSTON (Proc. Roy. Soc., 1934, A, 146, 564—570).—Details are given of the microscopical examination of polished surfaces of explosive Sb, before and after explosion.

L. L. B.

Molecular structure as determined by a new electron diffraction method. I. Experimental. II. Halogen-carbon linking distance in some simple benzene derivatives. H. DE LASZLO (Proc. Roy. Soc., 1934, A, 146, 672—689, 690—700).—I. An apparatus is described for obtaining photographic records of the scattering of fast electron beams by the vapour of any substance which will vaporise in a vac. up to 1000° without decomp. It is possible to record many more interference max. than were previously observed; these new high-order max. are particularly sensitive to changes in chemical structure, hence making possible more accurate determinations of inter-at. distances and mol. spatial configurations.

II. The electron diffractions of C_6Cl_6 , C_6Br_6 , s - $C_6H_3Br_3$, s - $C_6H_3I_3$, p - $C_6H_4Br_2$, and p - $C_6H_4I_2$ have been measured. The results agree with the theoretical scattering curves based on a model of C_6H_6 as a regular flat hexagonal ring with C-C distance 1.41 Å. The halogen-C distances are C-Cl 1.69±0.01, C-Br 1.88±0.01, C-I 2.05±0.01 Å. These distances are independent of the no. of similar atoms substituted at the same time in the C_6H_6 ring, and all the atoms lie in the plane of the ring. The C-halogen distances are about 0.06 Å. < those generally accepted for aliphatic compounds. L. L. B.

Structure of carbon. Investigation by electron diffraction. F. TRENDLENBURG [with E. FRANZ and O. WIELAND] (Z. tech. Physik, 1933, 14, 489—495; Helv. phys. Acta, 1933, 6, 477—478; Chem. Zentr., 1934, i, 2249).—Specimens of graphite (I) and soot gave results characteristic of the (I) lattice. Intensity variations with crystal size were studied. H. J. E.

Electron diffraction investigations of the aluminium silicates and other substances of the layer lattice type. F. TRENDLENBURG and O. WIELAND (Wiss. Veröff. Siemens-Konz., 1934, **13**, No. 3, 31—41).—A comparison of X-ray and electron diffraction photographs of kaolin, pholerite, pyrophyllite, agalmatolite, talc, $\text{Mg}(\text{OH})_2$, and PbI_2 shows, as with graphite, a difference in the intensities in the lines corresponding with the same indices in the photographs taken with the two types of rays. This intensity variation depends on the condition of the surface. Surfaces which are parallel to the cleavage planes are smooth towards electrons, and intense, sharp interferences are not found. Crystals which show good cleavage (e.g., calcite), and those which have no decided cleavage (e.g., quartz), show little or no difference in the intensities of the electron and X-ray interference. A. J. M.

New method of investigating the diffraction of slow electrons by crystals. W. EHRENBURG (Phil. Mag., 1934, [viii], **18**, 878—901).—A rapid visual method, requiring the use of a fluorescent screen, for determining the scattering of slow electrons by a crystal, is described. The results obtained with a Cu crystal are compared with those obtained by Farnsworth (A., 1933, 761). M. S. B.

New method for determining electron diffraction patterns produced by thin films. W. COCHRANE (Phil. Mag., 1934, [vii], **18**, 956—970).—Instead of using the photographic method, small parts of the diffracted electron beam were allowed to pass successively into a Faraday cylinder and were measured with an electrometer. Films of celluloid, Au, Al, and Ag were used and the experimental vals. for the intensities of the diffracted rays were found to agree with those given by Born's theory. Methods for the prep. of the very thin films used are described. M. S. B.

Drift of magnetic permeability at low inductions after demagnetisation. R. L. SANFORD (J. Res. Nat. Bur. Stand., 1934, **13**, 371—376).—To obtain consistent results a period of 18—24 hr. should elapse after demagnetisation before the test is made. E. S. H.

Magnetisation of the permanent oxide magnet at high temperatures. Y. KATO, T. TAKEI, N. KAWAI, and H. AIKAWA (J. Chem. Soc. Japan, 1934, **55**, 584—589).— $\text{CoO-Fe}_2\text{O}_3$ and the solid solution of $\text{CoO-Fe}_2\text{O}_3$ and Fe_3O_4 are more strongly magnetised at 300° than at room temp. CH. ABS. (c)

Structural demagnetising field of ferromagnetics. T. KAHAN (J. Phys. Radium, 1934, [vii], **5**, 463—470).—A new method for investigating the structural demagnetising factor is described. Applied to the thermal variation of the factor for specimens of Ni and Co marked decrease in the factor with rise of temp. is found, thereby confirming the existence of the factor, since the geometrical demagnetisation factor is independent of temp. N. M. B.

Magnetic Hall effect in crystalline media. M. KOHLER (Ann. Physik, 1934, [v], **20**, 878—890).—Theoretical. The compatibility of the dependence of the magnetic Hall effect on the crystallographic

orientation of the crystal used with the symmetry of the crystal is examined. A. J. M.

Magnetic resistance changes in crystalline media. M. KOHLER (Ann. Physik, 1934, [v], **20**, 890—908).—Theoretical. Assuming that the resistance change (I) \propto the square of the field strength, the dependence of (I) on the crystallographic orientation of the current and the magnetic field is investigated. A. J. M.

Magneto-caloric effect and other magnetic phenomena in iron. H. H. POTTER (Proc. Roy. Soc., 1934, **A**, **146**, 362—387).—The magneto-caloric effect and other magnetic phenomena in Fe have been studied in the region of the Curie point. The results demand that the intramol. field factor N is independent of σ , but shows a rapid increase with increasing T near the Curie temp. The Weiss magneton nos. of Ni and Fe in the paramagnetic state are discussed. L. L. B.

Large Barkhausen discontinuities and their propagation in Ni-Fe alloys. II. R. E. REINHART (Physical Rev., 1934, [ii], **46**, 483—486; cf. this vol., 588).—Relationships between longitudinal field, intensity of magnetisation, and velocity of propagation were investigated. The behaviour of propagation phenomena for pure Ni is the reverse of that for 10% Ni-Fe alloy, the difference being related probably to differences in magnetostrictive properties. N. M. B.

Anomalous case of magnetic viscosity. A. V. MITKEVITSCH (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 426—431).—Data are recorded. The relation between magnetic viscosity and lag due to eddy currents is discussed. H. J. E.

Electric strength of rock-salt exposed to X-rays. A. VOROBEV (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 424—425).—Resistance to sparking through the crystal was lowered 30—40% during exposure to X-rays, indicating that electrons are important in the sparking mechanism. H. J. E.

Optical constants of polished and sputtered molybdenum surfaces. R. D. SUMMERS (J. Opt. Soc. Amer., 1934, **24**, 261—263).—The refractive index, index of absorption, and reflectivity of opaque films of Mo, sputtered in air and in H_2 , as measured by Drude's method at λ 5780, 5460, and 4360 Å., vary with the conditions of sputtering and are \ll for the metal in mass. The optical consts. for massive Mo polished under kerosene are the same as for the metal polished in air. The low vals. for sputtered films are attributed to lattice distension by occluded gas. J. W. S.

Optical constants of thin metal films in the long-wave infra-red. W. WOLTERSDORFF (Z. Physik, 1934, **91**, 230—252).—Reflexion and transmission curves are given for Al, Ag, Sb, and Bi between 21 and 91 μ . A. B. D. C.

Effect of temperature on the reflectivity of copper, silver, and gold. Y. FUJIOKA and T. WADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **25**, 9—19).—The reflectivities (r) of Cu, Ag, and Au have been measured for λ 2500—6500 Å. at

—180°, 0°, and 100°. r for Ag agrees with the val. calc. from dispersion theory. R. S. B.

Total radiation of iron in the region of temper colours. R. HASE (Arch. Eisenhüttenw., 1934—1935, 8, 93—96).—The emissivity (E) of clean Fe remains const. below 300° in spite of the formation of a dark-coloured film on the surface, and then increases rapidly with increasing oxidation to a const. max. at 450° and higher, E being then 80—90% of black-body radiation. Above 1400° the oxide film goes into solid solution in the Fe, and E then falls, since the surface becomes clean again. The oxide film in the region of temper colours has an effect on E when it exceeds 0.5 μ in thickness. A. R. P.

Oscillation energy of particles in a crystal lattice. S. FRANCHETTI (R. Ist. lombardo Sci. Lett. Rend., 1933, [ii], 66, 731—742; Chem. Zentr., 1934, i, 2249).—Theoretical. H. J. E.

Metallic binding. H. BOMKE (Z. Physik, 1934, 91, 400—409).—Binding forces between metal atoms, liquid or solid, are electrostatic; a positive ionic lattice with distributed electron cloud gives a min. potential for the crystal, and gives the heat of sublimation in terms of the lattice energy. On this scheme, metals fall into two groups. A. B. D. C.

Plasticity and mosaic structure of cast and recrystallised metals. U. DEHLINGER and F. GISEN (Physikal. Z., 1934, 35, 862—864).—The mosaic structure of Al is often as stable in the pure metal as in the impure. Recryst. Al shows stronger mosaic structure than the cast metal. The results of this and previous work (this vol., 16) are summarised. A. J. M.

Elastic constants of single crystals of iron. R. KIMURA and K. OHNO (Sci. Rep. Tōhoku, 1934, 23, 359—364).—The results are not in agreement with Cauchy's relation. The compressibility calc. is in fairly good agreement with Bridgman's experimental val. J. W. S.

Photo-electric determination of the elastic limit of rock-salt crystals. M. N. PODASCHYEVSKI (Z. Physik, 1934, 91, 97—104).—Sensitivity of the primary internal photo-electric current of X-irradiated NaCl to plastic deformation is used to determine the elastic limit. A. B. D. C.

Effect of salt on the hardness of rock-salt crystals. V. D. KUZNETZOV and A. A. BOROBEOVA (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 555—562).—Hardness determinations are recorded for NaCl, dry, and after wetting with saturated aq. NaCl (I) or (I) + AcOH. H₂O alters the hardness of tempered, but not of untempered, crystals. CH. ABS. (e)

Torsional modulus of nickel at high temperatures with simultaneous magnetisation. II. W. MOBIUS (Physikal. Z., 1934, 35, 806—811; cf. A., 1932, 683).—At field strengths about 20—30 gauss there are min. in the isotherms of the torsional modulus, for all temp. almost up to the Curie point. Probably the orientation of elementary circuits caused by the field is partly destroyed by the torsion of the wire; vibrational energy being used up in this way, the modulus thus becomes smaller. A. J. M.

Allotropy of liquid benzene. H. W. DEINUM (Rec. trav. chim., 1934, 53, 1061—1063).—The conclusions of Menzies and Lacoss (A., 1932, 452) are criticised. A formula for the v.p. of C₆H₆ between 0° and 100° is given. F. L. U.

Little-known properties of metals. E. RAUB (Mitt. Forsch. Probieramts. Edelmetall. Schwäb-Gmund, 1933, 7, 51—64; Chem. Zentr., 1934, i, 1601—1602).—I. The toxic and bactericidal action of metals is discussed. The amounts of metals which go into solution during use of eating utensils are too small to produce hygienic disturbances; they exert a favourable effect by killing bacteria. No bacterial cultures could be developed in the remnants of food from a Ag cover.

II. [With H. NANN.] The cause of metallic odour has been sought in the different phases of production. Ag alloys with additions of Se and Te are odourless. Treatments with electrolytic baths, with purifying, burnishing, and cleansing media produced a slight odour. S compounds [*e.g.*, allyl sulphide, mustard oil (I), onion, leek, and mustard juices] produce the characteristic "Ag odour." The action of these substances, with phenylallylthiocarbamide instead of (I), on Cu, Ni, Zn, Al, Fe, alpukka, brass, Cr, Au, Pd, and Pt is quite different; the odour produced varies in strength and in nature. After Ag, alpukka, brass, and Cu react the strongest. Direct Cr-plated brass smells strongly, but Ni- and Cr-plated brass remain odourless. Treatment with dil. HCl, or nascent H, or heating to 300° removes the odour. L. S. T.

Pressure coefficients of acoustic velocity for organic liquids. J. C. SWANSON (J. Chem. Physics, 1934, 2, 689—693).—Acoustic velocities have been determined at 22.7—25.5° and at pressures up to 300 kg. per sq. cm. for EtBr, CCl₄, CHCl₃, Et₂O, C₅H₁₂, CS₂, C₆H₆, PhMe, and NH₂Ph. F. L. U.

Interpretation of the anomalous sound absorption in air and oxygen in terms of molecular collisions. H. O. KNESER (J. Acoustical Soc. Amer., 1933, 5, 122—126).—Knudsen's results (*ibid.*, 112) are discussed. CH. ABS.

Electric resistance of magnesium and its alloys. K. TAKAHASHI and W. EDA (Kinz. no Kenk., 1933, 10, 127—136).—8% Al added to Mg increases the resistivity (I) from 4 to 14 ohm⁻⁶ per c.c. Addition of Cu increases (I) only slightly; the order is Al, Sn, Zn, Ag, Cd, Ni, Cu. CH. ABS.

Superconductivity and Fermi-Dirac statistics. J. A. KOK (Nature, 1934, 134, 532—533).—Theoretical. L. S. T.

Superconductivity of alloys and its magnetic destruction. W. J. DE HAAS and J. VOOGD (Comm. Kamerlingh Onnes Lab. Leiden, Suppl. 73, 1—21; Chem. Zentr., 1934, i, 668).—The properties of the crystal lattice are of paramount importance for superconductivity (I). In general, alloys with a lattice of superconducting components show only a relatively small displacement of the transition point (II), whilst in those which possess a lattice other than that of superconducting components (II) is markedly displaced. The superconducting compound Au₂Bi has a lattice different from those of its non-superconducting

components. The magnetic field necessary for destroying (I) increases with a fall in temp. more markedly in alloys than in the pure components. L. S. T.

Determination of the magnitude of motion of conductivity electrons. E. PATAI (Physikal. Z., 1934, 35, 837).—Apparatus for this determination makes use of the superconductivity of Pb, and its disappearance at a definite temp. A. J. M.

Effect of temperature on electrical resistance. W. J. DE HAAS and J. VOOGD (Comm. Kamerlingh Onnes Lab. Leiden, Suppl. 73, 22—34; Chem. Zentr., 1934, i, 668).—A summary of measurements of the electrical resistance of pure metals at low temp. Vals. of R/R_0 at 4·5—1·13° abs. are given for many metals. L. S. T.

Resistance of liquid metals. N. F. MOTT (Proc. Roy. Soc., 1934, A, 146, 465—472).—The fact that the electrical resistance of most normal metals in the liquid state just above the m.p. is about twice that of the solid metal just below the m.p., whilst with certain abnormal metals, such as Bi, Ga, and Sb, the conductivity increases on melting, is discussed from the point of view of the wave-mechanical theory of electronic conduction. The change of resistance on melting can be accounted for by the change in at. frequency, for normal metals. The behaviour of abnormal metals is explicable qualitatively. L. L. B.

(A) **Theory of heat conduction by liquids.** (B) **Conductivity number of chemically related substances in the liquid state.** A. KARDOS (Forsch. Ingenieurwes., A, 1934, 5, 14—24; Z. tech. Physik, 1934, 15, 79—80; Chem. Zentr., 1934, i, 2099—2100).—A. A method of calculating the thermal conductivity of liquids is developed.

B. The above theoretical vals. are compared with observed vals. for series of related liquids.

H. J. E.

Heat-capacity curves of the simpler gases. VI. H. L. JOHNSTON and E. A. LONG (J. Chem. Physics, 1934, 2, 710).—A correction (cf. this vol., 951). F. L. U.

Specific heat of liquids at the b.p. N. A. DE KOLOSOWSKI (J. Gen. Chem. Russ., 1934, 4, 269—272).—Sp. heat at the b.p., T , is given by $MC = kT^3$, where M is the mol. wt. of a member of a homologous series, for which k is a characteristic const. R. T.

Specific heats of silver and zinc at liquid helium temperatures. W. H. KEESOM and J. A. KOK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 377—378).—The influence of surface on the sp. heat of a Zn block with increased ratio surface/vol. is insufficient to explain the rapid fall in $\theta = 7.745TC^{-\frac{1}{2}}$ (C = at. heat) below the crit. temp. of He. The sp. heat of Ag cooled without admission of He is identical with the val. determined in presence of He. The fall in θ is not due to adsorbed He, and is attributed to the heat capacity of free electrons. For Ag, agreement with Sommerfeld's formula for the heat capacity of free electrons is obtained, but with Zn no definite conclusion results. R. S. B.

Thermodynamic functions of nitrous oxide and carbon dioxide. L. S. KASSEL (J. Amer. Chem. Soc., 1934, 56, 1838—1842).—The free energy, heat

content, and sp. heat of N_2O have been calc. up to 1500° abs. and of CO_2 up to 1000° abs., from spectroscopic data. Equilibrium consts. of the water-gas and producer-gas reactions and the thermal decomp. of CO_2 have been calc. for a wide range of temp. E. S. H.

Latent heat of vaporisation [of ethyl alcohol]. S. OOURI, S. ANJO, and Y. KUYABARA (Bull. Waseda Appl. Chem. Soc., 1934, 22, 1—4).—The val. for EtOH at the b.p. is 207·74 g.-cal. CH. ABS.

General rule for the determination of b.p. at different pressures. Y. H. LI (J. Chinese Chem. Soc., 1934, 2, 108—116).—From Trouton's rule and the Clausius-Clapeyron equation an expression is derived which permits the b.p. of a liquid to be calc. at any required pressure, if its b.p. at another pressure and the b.p. of another liquid at the two different pressures are known. The expression is more trustworthy than Trouton's rule because the ratio of the Trouton consts. of the two liquids remains const. throughout the whole range of pressures, whereas the individual vals. may vary separately. J. W. S.

B.p. of divinyl ether. W. A. LOTT and W. G. CHRISTIANSEN (Pub. Chem. Pharm. Res. Labs. E.R. Squibb and Sons, 1934, 12 pp.).—Discrepancies in recorded vals. are discussed. The b.p. is $28.3 \pm 0.2^\circ$. A distillation apparatus is described. CH. ABS. (e)

B.-p. correction. C. S. HOYT (J. Chem. Education, 1934, 11, 405).—For all normal liquids the correction of the b.p. for each mm. deviation of the barometer from 760 mm. equals the abs. b.p. divided by 8000 (or another const. in the case of certain groups of related mols. and polar liquids). CH. ABS. (e)

Entropy of polyatomic molecules. J. O. HALLFORD (J. Chem. Physics, 1934, 2, 694—696).—The calc. entropies of 7 org. compounds having 4—7 rotational degrees of freedom agree well with experimental vals. F. L. U.

Temperature variation of the second virial coefficient of helium. N. G. WHITELAW (Physica, 1934, 1, 749—751).—Vals. calc. from the Joule-Thomson effect (cf. A., 1933, 218) are compared with direct determinations. H. J. E.

Properties of real gases according to the thermodynamic equation of state. I. Dependence of the Joule-Thomson effect of helium on pressure and temperature. V. JACYNIA (Z. Physik, 1934, 91, 349—352).—The Joule-Thomson effect for He is tabulated between -150° and 500° and from 0 to 100 kg. per sq. cm. A. B. D. C.

Limits of validity of the theorem for preliminary choice of arbitrary functions in the thermodynamic equation of state. V. JACYNIA (Z. Physik, 1934, 91, 353; cf. this vol., 1070). A. B. D. C.

Phenomenon of fusion in relation to a new equation of state and the lattice structure of solids. II. S. FRANCHETTI (Atti R. Accad. Lincei, 1934, [vi], 19, 800—803; cf. this vol., 1062).—Theoretical. O. J. W.

n-Paraffin hydrocarbons of high mol. wt. L. IVANOVSKY (Petroleum, 1934, 30, No. 42, 1—3).—From vals. reported in the lit. for the physical properties of *n*-paraffins of high mol. wt. (particularly C_{20} to

C₄₀), an attempt has been made to correlate the latter (as represented by the no. of C atoms in the mol.) with d_4^{25} , n_D^{25} , m.p., and mol. vol. In the last case only is the relation linear; curves for d and n against no. of C atoms are coincident. C. C.

Rhenium fluorides. A correction. O. RUFF and W. KWASNIK (Z. anorg. Chem., 1934, 220, 96; cf. this vol., 1083).—A corr. val. for the v.p. of ReF₅ is: $\log p = -1507.9/T - 7.5818$. Hence the heat of vaporisation is 6893 g.-cal., Trouton's const. 21.5, and crit. temp. 208.8° approx. B.p. by extrapolation is 47.6° and v.p. at m.p. 261.4 mm. M. S. B.

Vapour pressure of metals with high b.p. E. BAUR and R. BRUNNER (Helv. Chim. Acta, 1934, 17, 958—969).—V.p. of Zn, Mg, Pb, Ag, Mn, Al, Cu, Si, Sn, Cr, Au, and Be have been measured. Their logs. in every case $\propto 1/T$. The b.p. at 760 mm. are calc. The results agree generally with those of other workers. The b.p. of Al is, however, 2270°, not 1800° as reported by Greenwood (A., 1909, ii, 720). F. L. U.

Viscosity law. K. H. MEYER and H. MARK (Z. Elektrochem., 1934, 40, 728; cf. this vol., 952).—Polemical. E. S. H.

Mechanism of viscosity of liquids. A. D. GOLDHAMMER (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 484—490).—Theoretical. H. J. E.

Gold-manganese phase diagram. H. BUMM and U. DEHLINGER (Metallwirt., 1933, 13, 23—25; Chem. Zentr., 1934, i, 2238).—X-Ray observations show a small two-phase region between the cubic face-centred mixed crystals and tetragonal γ -Mn. A new body-centred tetragonal phase (50 at.-% Mn; a 3.28. c 3.14 Å.) has been detected below 700°. H. J. E.

Crystal structure of thallium-bismuth solutions. A. ÖLANDER (Z. Krist., 1934, 89, 89—92).—The powder photographic method has been used and the hexagonal phase (34—46 at.-% Tl) has received special attention. B. W. R.

Modification of aluminium-silicon alloys. J. A. KLAJATSCHKO (Kolloid-Z., 1934, 69, 215—218).—A discussion, directing attention to the possible stabilising influence on the disperse system of small amounts of a third constituent. E. S. H.

Equilibria in alloyed bronzes. III. Copper-rich copper-manganese-tin alloys. J. VERO (Mitt. berg-hütt. Abt. kgl. Hochschule Berg-Forstw., 1933, 5, 128—155; Chem. Zentr., 1934, i, 1703; cf. Veszelka, A., 1933, 1111).—Mn (up to 4%) produces a lowering of the crystallisation and transition temp. of binary Sn bronzes. With > 4% Mn a new Mn-rich phase (X) is formed by separation from the γ mixed crystals. The phase relations for Cu-rich alloys with 0—15% Mn are discussed. H. J. E.

Magnetic study of mixed crystals of the system sulphur-selenium. S. S. BHATNAGAR and P. L. KAPUR (J. Indian Chem. Soc., 1934, 11, 701—705).—The magnetic susceptibility of solid solutions containing \pm 10% Se in S has been determined. The composition curve does not follow the mixture rule. E. S. H.

“Meta-alite,” a metastable form of alite. S. SOLACOLU (Zement, 1934, 23, 587—591).—Chemical, microscopical, and X-ray analysis of the product of the reaction $3\text{CaO} \cdot \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2 + \text{CaO}$ at 1900° shows the existence of a metastable solid solution of CaO and $2\text{CaO} \cdot \text{SiO}_2$. T. W. P.

Refractivity and density of binary and ternary mixtures of water, acetaldehyde, and paraldehyde, and their analytical application. M. STRADA and A. MACRI (Giorn. Chim. Ind. Appl., 1934, 16, 335—341).—Vals. of d and n for the ternary and three binary systems are recorded. The ternary diagram (which contains a large heterogeneous area) may be employed for the rapid and accurate analysis of mixtures by physical measurements. H. F. G.

Anomalies in the molecular polarisation of acetone and dichloroethane. M. KUBO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1221—1233).—The mol. polarisations of COMe_2 and $\text{C}_2\text{H}_4\text{Cl}_2$ have been measured in mixtures of CCl_4 and C_6H_6 , and are abnormally large. The results seem to show that COMe_2 combines with 2CCl_4 , and that $\text{C}_2\text{H}_4\text{Cl}_2$ combines with C_6H_6 to give a complex $\text{C}_2\text{H}_4\text{Cl}_2 \cdot \text{C}_6\text{H}_6$ which is much more polar than free $\text{C}_2\text{H}_4\text{Cl}_2$. R. S. B.

Binary mixtures. II. Diminution of viscosity by tetrahydronaphthalene. L. PIATTI (Angew. Chem., 1934, 47, 732—733).—Addition of 30 vol.-% of tetrahydronaphthalene reduces the curvature of the viscosity-temp. graph of partly resinsified cresol. H. W.

Constitution of solutions of aldehydes in alcohols. Phenylacetaldehyde in benzyl alcohol. A. MÜLLER (Helv. Chim. Acta, 1934, 17, 1231—1239).—Measurements have been made of the thermal change on mixing $\text{CH}_2\text{Ph} \cdot \text{CHO}$ with $\text{CH}_2\text{Ph} \cdot \text{OH}$, and of the viscosity and capillary spreading of the mixtures. The results, in conjunction with existing data on the refractive index, support the view that a semi-acetal $\text{CH}_2\text{Ph} \cdot \text{CH}(\text{OH}) \cdot \text{O} \cdot \text{CH}_2\text{Ph}$ is formed in equilibrium with unchanged aldehyde, probably in the enolic form. The reaction is probably general. F. L. U.

Equilibria in liquid mixtures and solutions. B.p. and composition of the vapours of (A) aqueous ethylene glycol and ethylene oxide; (B) the system ethyl alcohol-ether. V. A. KIREEV (J. Appl. Chem. Russ., 1934, 7, 489—494, 495—496).—A. [With A. A. POPOV.]—B.p. data are given for the systems $[\text{CH}_2\text{OH}]_2 \cdot \text{H}_2\text{O}$ and $(\text{CH}_2)_2\text{O} \cdot \text{H}_2\text{O}$, and the composition of the vapour phases is determined at the b.p.

B. [With E. M. CHATSCHADUROVA.]—B.p. and composition of the vapour phase are determined for $\text{EtOH} \cdot \text{Et}_2\text{O}$. R. T.

Theory of concentrated solutions. XI. Thermodynamic properties of concentrated solutions of organic nitrogen compounds of the aliphatic series. N. I. JOUKOVSKY (Bull. Soc. chim. Belg., 1934, 43, 397—446).—The v.-p. curves and mol. heats of fusion of MeCN and CS_2 , the mol. heats of fusion of EtCN , Pr^iCN , and Bu^iCN , and the v.-p. curves of NEt_3 , MeNO_2 , $\text{CH}_2\text{CH} \cdot \text{CH}_2 \cdot \text{NCS}$, Et_2O , and MeOH have been determined. F.-p. data are

given for the following binary mixtures: MeCN-EtCN, -PrⁿCN, and -BuⁿCN; EtCN-PrⁿCN and -BuⁿCN; PrⁿCN-BuⁿCN (ideal solutions); C₆H₆-MeCN and -EtCN (non-ideal), -PrⁿCN, -BuⁿCN (ideal), -MeNO₂ (non-ideal), -CH₂:CH-CH₂:NCS, and -NEt₃ (ideal); PhNO₂-MeCN and -MeNO₂ (approaching ideality), -CH₂:CH-CH₂:NCS (almost ideal), and -NEt₃ (abnormal); HCO₂H-MeCN (ideal), -MeNO₂ (non-ideal), -CH₂:CH-CH₂:NCS [crit. solution temp. (*T*) 39.8°], -NEt₃ (compound formation); HCO₂NH₂-Et₂O (*T* > 195°), -MeOH (almost ideal), -CS₂ (*T* > 120°), -HCO₂H (equimol. compound), -PhNO₂ (*T* 108.2°), -C₆H₆ (*T* > 150°); CS₂-NEt₃ (ideal solution). Miscibility data for CS₂-MeCN, CS₂-MeNO₂, HCO₂H-CH₂:CH-CH₂:NCS, PhNO₂-HCO₂NH₂, and HCO₂H-NEt₃ are recorded. Compositions of vapour and liquid phases are given for Et₂O with MeCN, MeNO₂, CH₂:CH-CH₂:NCS, NEt₃ (almost ideal); CS₂ with MeCN, MeNO₂, CH₂:CH-CH₂:NCS, NEt₃ (ideal); MeOH with MeCN (azeotrope at 30% MeCN and 30°), MeNO₂ (azeotrope at 10% CH₃NO₂ and 30°), CH₂:CH-CH₂:NCS (almost ideal) and vals. of *n* for Et₂O-MeCN (which shows a max.), MeOH-MeCN, and MeOH-MeNO₂. Activity coeffs. have been calc. for all the mixtures studied, and the results are discussed in relation to the dielectric const. of the components and to previous work R. S.

Critical opalescence of binary mixtures. A. ROUSSET (Compt. rend., 1934, **199**, 716-718).—The apparent absorption coeffs. of the following mixtures have been measured within approx. 0.2° of the crit. temp.: H₂O-PrⁿCO₂H (I), NH₂Ph-cyclohexane (II), H₂O-NEt₃ (III), C₆H₁₄-PhNO₂ (IV). The absorption, and hence the intensity of diffusion of light, $\propto \lambda^{-n}$, where *n*=4 for (III) and (IV) up to the crit. temp. (*T*_c); for (I) and (II) *n*=4 when *T*-*T*_c 0-15°, but decreases when *T*-*T*_c approaches 0. Diffusion intensities have been measured in two opposite directions equally inclined to the incident beam for (I)-(IV), and for CS₂-MeOH (V), NH₂Ph-turpentine (VI). (III), (IV), and (V) show complete symmetry, but in the case of (I), (II), and (VI) forward is > backward diffusion, and this dissymmetry increases as *T*-*T*_c decreases. Ornstein and Zernicke's theory does not hold for (I)-(VI), but results with (III), (IV), and (V) agree with Rocard's theory. R. S. B.

Striæ in chemical processes. VI. **Striæ formed by mixing liquids of the same refractive index.** E. SCHALLY and F. NAGL (Monatsh., 1934, **64**, 385-398).—If one solution is allowed to flow into another stationary solution of the same high *n* val., striæ may be observed by the striæ microscope. If there is a reversal in the alternation of light and dark shades due to the striæ, when the stationary and flowing solutions are interchanged, they are called *D*-striæ. Pairs consisting of aq. inorg. salts or of aq. salt+aq. sugar, CO(NH₂)₂, or CS(NH₂)₂ solutions have been examined for varying differences of *n*. There are essential changes in the *D*-striæ when the two solutions no longer have equal *n*. A third internal shadow is obtained if the more rapidly diffusing substance flows into the more strongly refracting. Observations have also been made with org. solutes in CCl₄, using monochromatic light to obviate colour

disturbances. Between isomeric solutes in solutions of equal *n* there are no *D*-striæ, or feeble ones only. For homologues the shadows vary in accordance with the increasing mol. wt. *D*-striæ are always to be expected where the two solutes have different rates of diffusion. M. S. B.

Equilibria in tetrahalide systems. P. A. POND and E. B. CRONE (J. Amer. Chem. Soc., 1934, **56**, 2028-2031).—The solubility-temp. curves have been determined for TiBr₄ and GeCl₄, respectively, in liquid SO₂. PbCl₄ does not form such a partly miscible system. There is no evidence of compound formation. E. S. H.

Mutual solubility and surface tension. V. V. SEMENTSCHENKO and E. A. DAVIDOVSKAJA (J. Gen. Chem. Russ., 1934, **4**, 632-646).—The rule that substances which lower (raise) the tension at liquid-liquid interfaces increase (reduce) the mutual solubility of the liquids is verified for the systems MeOH-C₆H₁₄ and nicotine-H₂O in presence of alkali chlorides and aliphatic acids. R. T.

Solubility of hydrogen in water under pressure and at high temperatures. V. IPATIEV, jun., and V. P. TEODOROVITSCH (J. Gen. Chem. Russ., 1934, **4**, 395-399).—Deviations from Henry's law are observed above 200° at 100 atm. R. T.

Solubility of calcium carbonate. J. PIA (Int. Rev. ges. Hydrobiol. Hydrog., 1933, **29**, 84).—Lit. data have been recalcd. and the results tabulated. CH. ABS.

Solubility of ammonium chromate in water. J. I. GERASIMOV (J. Gen. Chem. Russ., 1934, **4**, 721-722).—Solubility data are given for the range 0-75°. R. T.

Solubility of stereoisomerides of cystine.—See this vol., 1381.

Polytherm of CoCl₂-H₂O. H. BENRATH (Z. anorg. Chem., 1934, **220**, 142-144).—The solubility curve of CoCl₂ in H₂O indicates the existence of the hydrate CoCl₂·4H₂O at 46-48° approx. It forms hard, bluish-red, monoclinic crystals which, unlike CoCl₂·6H₂O, show no pleochroism. M. S. B.

Permeability of palladium to hydrogen. III. **Fractionation of electrolytic hydrogen.** IV. V. LOMBARD and C. EICHNER (Bull. Soc. chim., 1934, **1**, [v], 945-954, 954-967; cf. this vol., 250, 497).—III. Full details are given of results already published (*ibid.*, 977).

IV. Progressive changes in the permeability of Pd to H₂ have been investigated. Traces of O₂ increase the rate of diffusion, *D*, of H₂. *D* of H₂ from admixture with N₂ through Pd into a vac. is given by *D*=*K*P_{N₂}^{1/2}, and the *D* of H₂ into N₂ increases with rate of flow of N₂. J. G. A. G.

(A) **Passage of active hydrogen through a mercury column.** C. RECZYŃSKI and B. SKOROBHATYJ. (B) **Sorption of gas in the mercury arc at high vapour pressure.** B. SKOROBHATYJ (Acta phys. polon., 1932, **1**, 413-418, 419-426; Chem. Zentr., 1934, i, 498).—A. When a Hg arc has been maintained in H₂ for a short time, H₂ diffuses from the apparatus through a Hg column 1 m. long

(after the arc is extinguished). The process probably occurs at the Hg-glass interface.

B. Sorption of N_2 in a Hg arc, attributed to Hg nitride formation, has been studied. H_2 is taken up more rapidly than N_2 . H. J. E.

Diffusion of vapours through gas films. T. K. SHERWOOD and E. R. GILLILAND (Ind. Eng. Chem., 1934, 26, 1093—1096).—The gas film coeff. \propto (diffusivity \times total pressure)^{0.56}, to (Reynold's no.)^{0.83}, and to the mol. wt. of the diffusing vapour, and inversely \propto the mean pressure of the non-diffusing gas. Hence the performance of a packed tower for any sol. vapour can be calc. from its known performance with another vapour. Equations are given connecting the absorption coeff. with the height of packing equiv. to a theoretical plate, but this method of calculation is not recommended. A. G.

Diffusion in liquids. VI. Micro-diffusion apparatus for coloured and colourless liquids. R. FURTH and R. ZUBER. **VII. Zuber's micro-diffusion method applied to diffusion measurements at very low concentrations.** K. SITTE (Z. Physik, 1934, 91, 609—616, 617—621).

A. B. D. C.

Distribution of H_2O and H_2O in various systems. H. ERLÉNMEYER and H. GARTNER (Helv. Chim. Acta, 1934, 17, 970—973).—When anhyd. Na_2SO_4 is mixed with H_2O containing H_2O and allowed to crystallise at 0° the resulting crystals contain the same proportion of H_2O as does the solution. Et_2O , shaken in bulk with H_2O , effects no change, but when droplets of Et_2O are caused to rise through H_2O there is a small increase of $[H_2O]$ in the Et_2O phase, indicating adsorption of H_2O at the interface. Rapid and complete exchange occurs between the H atoms of H_2O and H_2O_2 , whilst none is detectable between those of H_2O and KH_2PO_3 . F. L. U.

Hydration of salts with heavy water; constitution of salt hydrates. J. N. E. DAY, E. D. HUGHES, C. K. INGOLD, and C. L. WILSON (J.C.S., 1934, 1593—1599).—Using heavy H_2O with a known H^2 content corresponding with an excess d over that of normal H_2O of about 2000/10⁶ the following salt hydrates were formed from the anhyd. salt: $SrCl_2 \cdot 6H_2O$; $CuSO_4 \cdot 5H_2O$; $Li_2SO_4 \cdot H_2O$; $Na_2CO_3 \cdot 10H_2O$; $K_2C_2O_4 \cdot H_2O$. Measurements were made of the d of the H_2O recovered from the cryst. hydrate and from the solution. The results for the five salts, which illustrate the cation, anion, and carbonyl types of hydration, show that the differences of selectivity for light and heavy H_2O in the formation of cryst. hydrates are negligibly small, if real. This result is to be expected on the physical theory of hydration (Fajans, Born, Magnus, Garrick), but not on the structural theory (Werner, Sidgwick). It would seem, therefore, that any structure involved in the linking of hydrate H_2O can at best have but a loose and evanescent character. O. J. W.

Adsorption of oxygen and hydrogen on bright platinum. H. REISCHAUER (Z. physikal. Chem., 1934, B, 26, 399—412).—H is not appreciably adsorbed at 20—700° at pressures below 5×10^{-2} mm. O is not adsorbed below about 120°, but at higher

temp. there are two kinds of activated adsorption, with differing heats of activation and different temp. ranges. The total amount adsorbed in the two ways together is 5 O_2 mols. for each atom of the Pt surface, but the partition of the surface between the two kinds of adsorption depends on the previous treatment of the Pt. The rate of adsorption is effectively independent of the pressure, which may be explained by supposing that adsorption proper occurs on only a limited no. of the surface atoms, from which the O diffuses over the surface. In the adsorption with the smaller heat of activation, the O_2 adsorbed first is taken up more rapidly than that adsorbed later and reacts particularly readily with H. Heating in knallgas increases the no. of active Pt atoms. The true surface of the Pt foil used was apparently about 2.5 times as great as the apparent surface. R. C.

Adsorption of vapours of mutually soluble liquids. V. KIREJEV and N. D. SOLUGUB (Kolloid-Z., 1934, 69, 222—225).—The adsorption of mixed vapours of $EtOH$ and Et_2O in air by active C and SiO_2 gel at partial pressures of the vapours 2—30 mm. has been studied in respect of amount and composition. The composition of the adsorbed mixture is influenced by a selective adsorption factor, which is greatest at small concns. of vapour. Temp. has little influence when the amount of vapour mixture is const., but the degree of saturation is important in determining the amount of mixture adsorbed.

E. S. H.

Adsorption of salol and aspirin from alcoholic solutions by active carbon. M. PÉRONNET and P. CRÉTE (J. Pharm. Chim., 1934, [viii], 20, 359—367).—Salol (I) and aspirin are rapidly adsorbed from $EtOH$ solutions by active C and in neither case is hydrolysis evident. (I) is the more readily adsorbed and Freundlich's law is followed. S. C.

Adsorption. Silica gel and its applications. A. TRAVERS (Bull. Soc. Ind. Mulhouse, 1934, 100, 485—522).—A lecture. E. S. H.

Desorption of ether from active-charcoal powder by water vapour in relative motion. E. BOYE (Kolloid-Z., 1934, 69, 218—222; cf. this vol., 1066).— Et_2O is desorbed from highly-active C by superheated H_2O vapour more slowly than from less active C. The amount of desorbed Et_2O corresponding with a given amount of H_2O vapour varies inversely as the activity of the C; the relations between this quantity, max. adsorption, and surface are worked out. The technical significance of the results is discussed. E. S. H.

Theory of ionic adsorption. H. MÜLLER (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 34—38).—Data for $NaCl$, $CaCl_2$, and Na_2SO_4 with glass, graphite, and collodion have been studied mathematically.

CH. ABS.

Theory of a unimolecular adsorption layer. N. FOKS (J. Phys. Chem. U.S.S.R., 1933, 4, 562—566).—An adsorption isotherm equation is developed statistically. CH. ABS. (e)

Solvation of molecules and the equation of state of an adsorbed layer. S. E. BRESLER, B. A. TALMUD, D. L. TALMUD, and Y. B. KHARITON (J.

Phys. Chem. U.S.S.R., 1934, 5, 107—115).—The effect of cations and anions on the dehydration (I) of insol. layers of cetyl alcohol and oleic acid adsorbed on aq. electrolytes and glucose is in the order of the lyotropic series. (I) is related to the electrostatic effects of polar groups in the adsorbed layer. CH. ABS. (e)

Two-dimensional equation of state and structure of surface layers. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1934, 9, 363—393).—Mathematical.

E. S. H.

Relation between surface tension of solutions and solubility of physiologically important fatty acids. F. ERODI (Biochem. Z., 1934, 273, 273—278).—The influence of p_H on the solubility and on the surface tension of solutions of stearic, oleic, linoleic, linolenic, and arachidic acids has been examined. The micelles formed by the unsaturated acids are smaller, and these are consequently more easily resorbed in the animal system.

W. McC.

Interference colours of thin films of oxides, sulphides, or iodides on metals. U. R. EVANS (Kolloid-Z., 1934, 69, 129—137).—Published work is reviewed in the light of optical theory. E. S. H.

Friction and adhesion. IV. Theory of adhesion of small particles. B. DERJAGUIN (Kolloid-Z., 1934, 69, 155—164; cf. this vol., 1169).—A mathematical treatment for deformable and non-deformable particles.

E. S. H.

Influence of time of contact between mineral and air bubbles on flotation. I. SVEN-NILSSON (Kolloid-Z., 1934, 69, 230—231).—A certain induction time is necessary to enable an air bubble to adhere to a mineral surface. The time may be < 0.1 sec. or > 1 day, depending on the size of the bubble, treatment of surface, and presence of other reagents.

E. S. H.

Effect of salts on the electric charge of surfaces in liquids. H. A. ABRAMSON and H. MULLER (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 29—33).—For graphite, glass, quartz, cellulose, collodion, and paraffin oil with ions which do not produce reversal of sign of charge, concn.: p.d. is complex, but concn.: surface d of electric charge gives a simple curve resembling the adsorption curve. CH. ABS.

Surface phenomena at the boundary between solid and solution. Change in the heat of wetting in surface-active materials by the introduction of an electrolyte. V. LJIN, V. V. SEMENTSCHENKO, and V. I. IVANOV (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 571—578).—The heat of wetting (H) of C with aq. NaCl and Pr^sOH and with an EtOH solution of *sec.*-BuOH has been measured. The electrolyte increases H .

CH. ABS. (e)

Theory of the diffuse double layer. H. MULLER (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 1—8).—A discussion.

CH. ABS.

Surface conductance. K. S. COLE (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 23—28).—A mathematical discussion of Smoluchowski's diffuse layer and ionic concept of surface conductance.

CH. ABS.

Theory of electrophoretic migration. H. MULLER (Cold Spring Harbor Sympos. Quant. Biol.,

1933, 1, 9—13).—The validity of Smoluchowski's formula is discussed.

CH. ABS.

Streaming potential measurements. D. R. BRIGGS (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 14—22).—A formula has been developed. The variation in streaming potential (I) of ovalbumin has been measured; the (I) equation is invalid for very low pore diam. and for low hydrostatic potentials.

CH. ABS.

Electro-osmosis. IV. S. IMAI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1198—1220).—The electrokinetic potential (ζ) of electrolytes has been measured using a diaphragm of sintered powdered SiO_2 . For acid solutions, $\zeta = \zeta_0 e^{-\beta c} - (\zeta_0 - \zeta_\infty) e^{-\gamma c}$, where ζ_0 is the val. obtained by extrapolating the $\log \zeta - c$ curve to $c = 0$, ζ_∞ is the val. of ζ for conductivity H_2O , and β and γ are consts. For alkaline solutions, $\zeta = \zeta_0' + k \log c - \alpha e^{\delta \log c}$, where α , k , and δ are consts., and for salt solutions, $\zeta = \zeta_0' + k \log 1/c + \alpha e^{-\delta \log 1/c}$.

R. S. B.

Liesegang stratification developed in the diatomaceous gyttia from Lake Haruna, and problems related to it. K. SUGAWARA (Bull. Chem. Soc. Japan, 1934, 9, 402—409).—A periodic structure is shown by the $\text{Fe}(\text{OH})_3$ formed by diffusion of atm. O_2 through the lake deposits, which were stored in glass tubes. The deposits contained about 63% SiO_2 , and Fe^{II} salts in the capillary-bound H_2O .

E. S. H.

Physico-chemical properties of solutions in condensed gases. V. Determination of the mol. wt. of substances dissolved in liquid ammonia at room temperature. A. I. SCHATENSTEIN and A. M. MONOSZON (J. Phys. Chem. U.S.S.R., 1933, 4, 691—695).—Vals. for $\text{CO}(\text{NH}_2)_2$ (I), *d*-glucose (II), quinhydrone (III), NH_4Cl , and NH_4NO_3 are recorded. The degree of association of (I) is independent of temp. NH_4Cl is strongly associated, (II) unassociated, and (III) dissociates into benzoquinone and quinol.

CH. ABS. (e)

Properties of electrolytic solutions. XIII. F.p. of solutions in benzene. F. M. BATSON and C. A. KRAUS (J. Amer. Chem. Soc., 1934, 56, 2017—2020; cf. this vol., 486).—The f.p. const. of C_6H_6 is 5.075° . The f.p. of solutions of *tri*soamylammonium picrate, AgClO_4 , and *tetra*soamylammonium picrate and thiocyanate in C_6H_6 have been determined. At very low concns. the f.p. curves approach those based on the formula wt. of the electrolyte. At higher concns. the deviations increase, especially for electrolytes having electrically symmetrical ions.

E. S. H.

Compressibility of aqueous solutions. II. W. G. THOMAS and E. P. PERMAN (Proc. Roy. Soc., 1934, A, 146, 640—650).—The compressibility coeffs. of aq. solutions of KCl, KBr, KI, CaBr_2 , SrBr_2 , BaBr_2 , AcOH , and CH_2O have been measured at 30° at pressures up to 100 atm., using an improved form of Perman and Urry's method (A., 1930, 154). Results (obtained by W. D. URRY) are also given for solutions of glucose, sucrose, and raffinose.

L. L. B.

Dilatometric study of complex formation in solutions of chlorides. A. V. TITOV (J. Gen. Chem.

Russ., 1934, 4, 567—576).—The complex salts Na_2ZnCl_4 , NaCoCl_3 , NaHgCl_3 , and Na_2CdCl_4 are indicated by max. increase in vol. on mixing solutions of the constituent salts; solutions of the individual salts exhibit a decrease in vol. on dilution. Complex formation does not take place appreciably in the systems MgCl_2 - NaCl , CaCl_2 - NaCl , CaCl_2 - NH_4Cl , and NH_4Cl - NaCl . R. T.

Constitution of iodic acid and its salts. I. M. R. NAYAR and T. R. GAIBOLA. II. [Raman spectra.] M. R. NAYAR and P. SHARMA (Z. anorg. Chem. 1934, 220, 163—168, 169—171).—I. F.-p. determinations in aq. solution indicate that HIO_3 is polymerised in conc. solutions. In dil. solutions the mols. are simple. KIO_3 does not polymerise. Electrical conductivity measurements do not support the view that HIO_3 is dibasic.

II. Raman spectral data support the above conclusions. M. S. B.

Anionic weight of some sulpho-salts in aqueous solution. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1934, 220, 172—176).—From measurements of the dialysis coeff. in aq. solution the following anionic formulæ have been deduced: $[\text{As}(\text{H}_2\text{O})_2\text{S}_4]'''$, $[\text{Sb}(\text{H}_2\text{O})_2\text{S}_4]'''$, $[\text{Sn}(\text{H}_2\text{O})_2\text{S}_4]'''$, $[\text{Mo}(\text{H}_2\text{O})_2\text{S}_4]'''$, $[\text{GeS}_3]'$, $[\text{V}(\text{HS})_2\text{SO}]'$, $[\text{W}(\text{WS}_3)_3\text{S}_3]'$, $[\text{As}(\text{AsS}_3)_3\text{S}_3]'''$. M. S. B.

Anionic weights of complex cyanides in aqueous solution. H. BRINTZINGER and H. OSSWALD (Z. anorg. Chem., 1934, 220, 177—179).—The formulæ of complex cyanides of Fe, Co, Ni, Cu, Ag, Zn, Cd, and W have been determined by measurements of the dialysis coeffs. The ferro- and cobalto-cyanide ions are abnormally large and the following alternative formulæ are suggested: $[\text{Fe}(\text{or Co})(\text{CN})_6]_6'''$ or $[\text{Fe}(\text{or Co})(\text{CN})_6(\text{H}_2\text{O})_{12}]'''$. M. S. B.

Mobility of small selenium spheres in air at high speeds. A. S. BERKOWITSCH (Helv. phys. Acta, 1934, 7, 170—202; Chem. Zentr., 1934, i, 3171).—The velocity \propto applied force. The particles also obey the Millikan law of fall. H. J. E.

Sedimentation equilibrium in colloidal suspensions. S. LEVINE (Proc. Roy. Soc., 1934, A, 146, 597—623).—An expression is derived for the distribution in the sedimentation equilibrium. Departure from Perrin's law is indicated, varying, according to the charges on the particles and the concn. of the electrolyte, from $n=1.6 \times 10^{13}$ to $n=4.0 \times 10^{14}$, with corresponding limiting concns. lying between $n=2.1 \times 10^{14}$ and $n=5.5 \times 10^{15}$. L. L. B.

Dispersion analysis of fine suspensions. N. N. ZAPRUDSKI (Tzvet. Met., 1933, No. 5, 15—23).—A review and discussion. Electrical methods give promising results. CH. ABS.

Physico-chemical state of silicate dusts in salt solutions. I. Stability of dust suspensions. II. Solubility of silicate dusts. E. A. NAUMAN (Arch. Sci. biol. U.S.S.R., 1933, 33, 533—550, 551—557).—I. The influence of electrolytes on the stability of suspensions of porcelain dust is examined.

II. Solubility data are recorded. CH. ABS. (p)

Electrophoresis of cholesterol suspensions. L. S. MOYER (Biochem. Z., 1934, 273, 122—131).—

Cholesterol (I) sols possess very different electrokinetic properties according to their method of prep. Suspensions of powdered (I) crystals gave the best results, and curves showing the electrophoretic velocity at varying p_H are given. Addition of glucose does not alter the electrophoretic behaviour. P. W. C.

Preparation of colloidal solutions through the silent electric discharge. II. S. MIYAMOTO (Kolloid-Z., 1934, 69, 179—181; cf. this vol., 841).—Sols of As, Sb, and Hg_2Cl_2 in H_2O , EtOH , $\text{Bu}^\text{t}\text{OH}$, and amyl alcohol can be prepared by the method previously described. E. S. H.

Preparation of hydrosols of sparingly-soluble metal salts by electrolysis. N. PESKOV and B. SAPROMETOV (Kolloid-Z., 1934, 69, 181—185).—When a very dil. salt solution is electrolysed under certain conditions, an insol. compound of the salt anion and the cathode metal is dispersed. When the medium is a gelatin gel periodic pptn. structures are formed. E. S. H.

Formation of emulsions in definable fields of flow. G. I. TAYLOR (Proc. Roy. Soc., 1934, A, 146, 501—523).—Experiments have been made on the deformation and bursting under controlled conditions of a drop of one liquid suspended in another. Measurements of the interfacial tension of the liquids, their viscosities, and the rate of deformation of the outer fluid are described. An expression is found for small distortions from the spherical form which occur at slow speeds. L. L. B.

Relation between particle size of highly-polymerised substances and viscosity of their solutions. R. OBOGI and E. BRODA (Kolloid-Z., 1934, 69, 172—178).—The results of measurements of the viscosity and osmotic pressure, at 25° and 40°, of fractionated, homogenised solutions of cellulose acetate show that up to a particle wt. about 60,000 the variation of viscosity with mol. wt. is in fair agreement with Staudinger's relation. Experimental difficulties prevent the confirmation of the rule at higher mol. wt. E. S. H.

Colloid chemistry of metal soaps. I. Dipole moment. W. OSTWALD and R. RIEDEL (Kolloid-Z., 1934, 69, 185—199).—The dielectric polarisation, n , and d of solutions of Al, Mg, and Cd soaps in C_6H_6 and the solubilities of the soaps have been measured. $n \propto$ concn. and decreases with increasing no. of C atoms. The dielectric mol. polarisation and dipole moment increase with the no. of C atoms, the increase being linear except for myristate and laurate. E. S. H.

Anomalous osmotic pressures of colloid solutions at equilibrium. D. R. BRIGGS (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 152—165).—Anomalous osmotic pressures of aq. gum arabic against NaCl at varying pressure, p_H , and concn. of EtOH , Na^+ , and Cl^- are found. The sign of the charge carried by the colloid appears to be the determining factor. CH. ABS.

Colloidal nature and related properties of clays. W. W. MEYER (J. Res. Nat. Bur. Stand., 1934, 13, 245—258).—Weathering tends to produce a compound of isoelectric p_H equal to the p_H of the

weathering solution, and therefore to reduce the content of fine particles; the sp. surface thus varies inversely with the p_H of the weathering solution and with the degree of weathering. A low $\text{SiO}_2:\text{M}_2\text{O}_3$ ratio causes a min. ion concn. at the surface of the particles, and therefore also influences the particle size and activity, since the colloidal properties of a clay are due to the ionic atm. surrounding the particles. Coagulation and deflocculation are discussed in terms of the difference of ionic charge between the particles and their atms.; in coagulated clay the imbibed H_2O film is thin and mol. attraction occurs, whereas in the deflocculated condition the film is sufficiently thick to prevent such attraction. This view is in accord with the relative ease of deflocculation of different clays, and the differences in behaviour of deflocculating agents. The plasticity, shrinkage on drying, and transverse strength when dry of ceramic clays are discussed. H. F. G.

Stability of colloids and the theory of rapid coagulation. H. MÜLLER (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 60—64).—A discussion. Smoluchowski's theory is supported.

CH. ABS.

Bound water in hydrophilic colloid systems. A. V. DUMANSKI, A. G. KULMAN, and O. N. GOLOSOVA (J. Appl. Chem. Russ., 1934, 7, 585—591).—The capacity for binding H_2O increases in the series potato < soft wheat < hard wheat < maize < rye < soya meal. The colloids of flour, dough, and bread are highly hydrated; their affinity for H_2O varies during the process of baking, and falls rapidly in bread with time after baking. R. T.

"Bound" water of biological colloids.—See this vol., 1246.

Lyophilic colloids. IV. "Disintegration-sheath" theory and stability of hydrophilic colloids. S. M. LIEPATOV (Kolloid-Z., 1934, 69, 199—202; cf. A., 1934, 1069).—The adsorption of the easily-sol. fraction of the colloid at the surface of the micelle brings about an orientation of lyophilic groups, which strengthens the binding between the solvent and the micelle surface. The sheath thus formed weakens the attraction field between the mols. The theory is applied to the mechanism of gelation.

E. S. H.

Effect of movement on the electrical conductivity of hydrosols. W. S. URBANSKI (Acta phys. polon., 1933, 2, 181—192; Chem. Zentr., 1934, i, 835).—The electrical resistance of a V_2O_5 hydrosol increases when it flows past an electrode. A limiting val. is reached. The effect decreases on dilution. A well-dialysed Fe_2O_3 sol behaves similarly.

H. J. E.

Influence of light on hydrophobic sols in relation to their natural stability. W. HELLER (Compt. rend., 1934, 199, 723—724).—The velocity of growth of particles (v), at 20° , of dialysed $\text{Fe}(\text{OH})_3$ sol, which was kept in the dark for approx. 200 days, has been studied by means of magnetic double refraction. v decreases with time in the dark, but increases if the sol is then exposed to diffused daylight, especially for the sols dialysed for the longest time (least stable). The mechanism is discussed. R. S. B.

Changes in charge, conductivity, stability, and composition of colloidal arsenious oxide on exposure to light. C. B. JOSHI, P. M. BARVE, and B. N. DESAI (Current Sci., 1934, 3, 105).—The charge on the colloidal particles decreases and the conductivity increases with an increase in the period of exposure to electric light. The amount of free H_3AsO_3 increases, whilst the total S decreases. The flocculation vals. with KCl at first increase and then decrease; those with MgCl_2 decrease continuously. On exposure to light the As_2S_3 hydrolyses to H_3AsO_3 and H_2S which is photochemically oxidised to SO_2 . L. S. T.

Interpretation of dielectric constant anomalies in emulsions. A. PIEKARA (Acta phys. polon., 1933, 2, 225—228; Chem. Zentr., 1934, i, 1628; cf. Urban'ski, this vol., 1171).—Polemical. H. J. E.

Application of quantitative filtration analysis to the study of the transformation of aluminium hydroxide suspension into the jelly state. V. A. POKROVSKI (Kolloid-Z., 1934, 69, 202—205).—By Ostwald's method (A., 1925, ii, 198) the ripening of gel-like suspensions of $\text{Al}(\text{OH})_3$ and the effect of temp. thereon can be studied. E. S. H.

Colloidal behaviour of sericin. V. H. KANEKO (Bull. Chem. Soc. Japan, 1934, 9, 409—421; cf. this vol., 1069).—The rate of gelatinisation of sericin depends on p_H and is greatest at the isoelectric point (p_H 4.5). Syneresis occurs over the region p_H 3.5—4.8. The variation of setting point with concn. has been determined. When the sol is frozen, sericin is pptd. in the form of fibres, which are incompletely sol. on thawing. Sericin gel has been used as a medium for the prep. of periodic pptn. structures of several substances, and the rate of diffusion of inorg. salts and org. dyes in the gel has been determined. E. S. H.

Nephelometric investigation of protein solutions. E. M. MYSTKOWSKI (Biochem. Z., 1934, 273, 161—169).—The passage from the sol to the gel condition does not run parallel with changes of Tyndall effect, considerable increase in turbidity occurring without conversion into gel. Tables and curves summarise the effect of NaCl , CaCl_2 , Na_2SO_4 , MgCl_2 , and MgSO_4 at varying p_H on the degree of turbidity. P. W. C.

Theory of dominating forms. I. Chemical equilibria as electrostatic phenomena. II. Theory of hydrides. J. V. CHODAKOV (J. Gen. Chem. Russ., 1934, 4, 328—358, 359—371).—Theoretical. R. T.

Third law of thermodynamics. W. H. RODEBUSH (J. Chem. Physics, 1934, 2, 668—670).—Theoretical. F. L. U.

Thermodynamics of hydrocarbon reactions. A. V. FROST (Khim. Tverd. Topl., 1933, 4, 171—185).—Equilibrium consts. for the following reactions have been calc. from experimental data: $\text{C}_6\text{H}_6 + 3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12}$; $\text{PhMe} + 3\text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{11}\text{Me}$; $2\text{C}_6\text{H}_6 \rightleftharpoons \text{Ph}_2 + \text{H}_2$; C (graphite) + $2\text{H}_2 \rightleftharpoons \text{CH}_4$; C (amorphous) + $2\text{H}_2 \rightleftharpoons \text{CH}_4$; 2C (graphite) + $2\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_4$; $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$; 2C (graphite) + $3\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$.

CH. ABS. (e)

Equilibria in a chemical system. Hydrogen sulphide-propylene-isopropyl mercaptan-*n*-propyl mercaptan. F. T. BARR and D. B. KEYES (Ind. Eng. Chem., 1934, 26, 1111—1114).—The standard free energy changes for the reaction $\text{H}_2\text{S} + \text{C}_3\text{H}_8 = \text{PrSH}$ are $-14,600 + 28.80T$ (Pr^β) and $-14,600 + 30.00T$ (Pr^α). Dynamic measurements have been made with NiS on kieselguhr as catalyst. The total mercaptan formation decreases with rising temp., but at 250—300° the equilibrium ratio of the two is nearly const. at 65 Pr^β to 35 Pr^α . A. G.

Bivalent dissociating systems. M. GEX (Arch. Phys. biol. Chim.-Phys. Corps organ., 1933, 10, 257—291; Chem. Zentr., 1934, i, 827).—Mathematical.

L. S. T.

Factors determining electrolytic dissociation and energy of dissociation of salt molecules. W. J. C. ORR and J. A. V. BUTLER (Phil. Mag., 1934, [vii], 18, 778—792).—Theoretical. A method of calculating energies of dissociation of salt mols. in the vapour state is given. Experimental vals. for the alkali metal halides are generally in agreement with those calc. The origin of the difference in electrolytic behaviour between these and salts of metals of the transitional series is to be sought in the homopolar nature of the latter. F. L. U.

Thermodynamic dissociation constant of benzoic acid at 25°, from conductivity measurements. G. H. JEFFERY and A. I. VOGEL (Phil. Mag., 1934, [vii], 18, 901—909).—Conductivity data have been obtained for BzOH and NaOBz . A method of applying the solvent correction is given. The thermodynamic dissociation const. is 6.373×10^{-5} .

M. S. B.

Ionisation constant of *n*-butyric acid from 0° to 60°. H. S. HARNED and R. O. SUTHERLAND (J. Amer. Chem. Soc., 1934, 56, 2039—2041).—Determinations have been made at 5° intervals by measuring the e.m.f. of the cells $\text{H}_2 | \text{HX}(m_1), \text{NaX}(m_2), \text{NaCl}(m_3) | \text{AgCl} | \text{Ag}$. The max. val. is 1.575×10^{-5} at 8°. The heat of ionisation has been calc. E. S. H.

Classical dissociation constant of bromophenol-blue in aqueous salt solutions. M. KILPATRICK (J. Amer. Chem. Soc., 1934, 56, 2048—2050).—Data have been obtained for the yellow-purple colour change in solutions of different salts up to 3*M*. The application of various equations is discussed.

E. S. H.

Ionisation of calcium, magnesium, and strontium citrates. A. B. HASTINGS, F. C. McLEAN, L. EICHELBERGER, J. L. HALL, and E. DA COSTA (J. Biol. Chem., 1934, 107, 351—370).—Determination of Ca^{++} by the frog's heart method (cf. this vol., 1422) and by equilibration experiments with CaCO_3 as the solid phase indicate that the dissociation of Ca citrate (I) takes place in two stages, viz., $\text{Ca}_3\text{Cit}_2 \rightleftharpoons \text{Ca}^{++} + 2\text{CaCit}^-$ (complete dissociation); and $\text{CaCit}^- \rightleftharpoons \text{Ca}^{++} + \text{Cit}^{---}$ (partial dissociation). In logarithmic form, $p\text{Ca}^{++} + p\text{Cit}^{---} - p\text{CaCit}^- = pK_{\text{CaCit}^-} = 3.22 \pm 0.025$ at 22° and $p_{\text{H}} 7.4$. Mg and Sr citrates behave similarly, the corresponding vals. for pK_{MgCit^-} and pK_{SrCit^-} being 3.22 and 2.70 ± 0.06 , respectively. A structure is suggested for the Ca salt. A. E. O.

Complexes formed by mercuric chloride and alkali metal chlorides in aqueous solution. C. TOURNEUX (Bull. Soc. chim., 1934, [v], 1, 1043—1049).—Equilibrium consts. for the reactions $\text{KCl} + 2\text{HgCl}_2 \rightleftharpoons \text{KHg}_2\text{Cl}_5$ and $2\text{KCl} + \text{HgCl}_2 \rightleftharpoons \text{K}_2\text{HgCl}_4$ are calc. for temp. between 0° and 100°. The variations of K with temp. are in accordance with van 't Hoff's law. F. L. U.

Solutions containing zwitterions: erratum. J. G. KIRKWOOD (J. Chem. Physics, 1934, 2, 713; cf. this vol., 962). F. L. U.

Activity in mixtures of strong electrolytes. I. L. BRULL (Gazzetta, 1934, 64, 607—614).—The activity coeffs. of ZnCl_2 in aq. solutions of alkali chlorides have been determined from e.m.f. measurements of the cell $\text{Hg}, \text{Zn} | \text{ZnCl}_2 + \text{MCl} | \text{Hg}_2\text{Cl}_2 | \text{Hg}$, where $\text{M} = \text{Li}, \text{Na}, \text{or K}$. The results are compared with the vals. calc. by the theory of Bonino (this vol., 254). O. J. W.

Apparent and true activity coefficients in solutions of electrolytes. L. BRULL (Gazzetta, 1934, 64, 615—623).—The true activity coeffs. for dil. solutions of CdCl_2 are calc. assuming the existence of CdCl^+ ions. O. J. W.

Principles involved in the phase rule. F. J. TROMP (J. Chem. Met. Soc. S. Africa, 1934, 35, 34—40).—In place of the usual equation $F = C + 2 - P$ it is proposed to substitute $F = V - E$, in which V , the no. of intensive properties, is defined as 2 + the total no. of mol. fractions of every constituent of every phase in which it occurs. E is the total no. of independent equations relating to the constituents, including mol. fraction, arbitrary, and free energy equations. Examples are given. F. L. U.

System PbO-SiO_2 . R. F. GELLER, A. S. CREAMER, and E. N. BUNTING (J. Res. Nat. Bur. Stand., 1934, 13, 237—244).—Three compounds exist, viz., $4\text{PbO}, \text{SiO}_2$ (m.p., incongruent, $725 \pm 1^\circ$), which occurs in three forms, transitions occurring at $720 \pm 2^\circ$, and at $120 - 155^\circ$; $2\text{PbO}, \text{SiO}_2$ (m.p., congruent, $743 \pm 3^\circ$); and PbO, SiO_2 (m.p., congruent, $764 \pm 3^\circ$). Eutectics occur at $714 \pm 3^\circ$ and 25 mol.-% SiO_2 ; $716 \pm 3^\circ$ and 40.5 mol.-% SiO_2 ; and $732 \pm 3^\circ$ and 61 mol.-% SiO_2 . H. F. G.

System silica-alumina. II. Reactivity of kaolinite and a new group of silicates. O. REBUFFAT (Giorn. Chim. Ind. Appl., 1934, 16, 433—435).—The eutectic point of the system tridymite (I)-hydrated kaolinite (II), $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$, is at 1620° with 10% Al_2O_3 . As suspected from the m.-p. diagrams, (I) reacts with (II) slowly at 600—700°, forming the compound $\text{Al}_2\text{O}_3, 3\text{SiO}_2$. Similarly, (II) reacts at 1000° with β -stannic acid, forming the compound $\text{Al}_2\text{O}_3, 2\text{SiO}_2, \text{SnO}_2$, and with TiO_2 , forming a compound which is probably analogous. D. R. D.

Equilibria in the system $\text{KBr-KBrO}_3\text{-H}_2\text{O}$. J. I. GERASIMOV (J. Gen. Chem. Russ., 1934, 4, 723—727).—Equilibrium data at 0—80° are given.

R. T.

Equilibrium diagrams of salts for salt baths. IV. Barium chloride-calcium chloride-sodium chloride system. T. SATO and T. AMANO (Kinzoku no Kenkyu, 1934, 11, 305—316).—The eutectoid

points in the systems $\text{BaCl}_2\text{--CaCl}_2$, $\text{BaCl}_2\text{--NaCl}$, and $\text{CaCl}_2\text{--NaCl}$ correspond with 617° (CaCl_2 54 mol.-%), 656° (BaCl_2 40 mol.-%), and 501° (NaCl 54 mol.-%), respectively. The system $\text{CaCl}_2\text{--NaCl}$ affords no indication of the compound $4\text{NaCl}\cdot\text{CaCl}_2$. The eutectoid in the ternary system corresponds with 453° (BaCl_2 16, CaCl_2 47, NaCl 37 mol.-%).

CH. ABS. (e)

Polytherms of the ternary system $\text{MnCl}_2\text{--}(\text{LiCl})_2\text{--H}_2\text{O}$. H. BENRATH (Z. anorg. Chem., 1934, 220, 145—153; cf. A., 1932, 697).—The following ternary compounds are formed: $\text{MnCl}_2\cdot 4\text{LiCl}\cdot 10\text{H}_2\text{O}$, stable from $<0^\circ$ to approx. 28° ; $\text{MnCl}_2\cdot 2\text{LiCl}\cdot 2\text{H}_2\text{O}$, above 53° ; $\text{MnCl}_2\cdot 2\text{LiCl}\cdot 2\text{H}_2\text{O}$, above 73° ; $\text{MnCl}_2\cdot \text{LiCl}\cdot 5\text{H}_2\text{O}$, at $<0^\circ$ to 26° ; $\text{MnCl}_2\cdot 2\text{LiCl}\cdot 4\text{H}_2\text{O}$, at $23\text{--}76^\circ$ approx. In addition, the following occur as stable solid phases in the system at $0\text{--}100^\circ$: $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$, $\text{MnCl}_2\cdot 2\text{H}_2\text{O}$, $\text{LiCl}\cdot 2\text{H}_2\text{O}$, $\text{LiCl}\cdot \text{H}_2\text{O}$, and LiCl .

M. S. B.

Double decomposition in the absence of a solvent. XXV. Irreversible mutual system $\text{TlCl} + \text{KI} \rightarrow \text{TlI} + \text{KCl}$. E. M. TSCHERNOMORDIK (J. Gen. Chem. Russ., 1934, 4, 456—465).—The phase diagrams indicate limited solid solution formation, and absence of compound formation.

R. T.

Equilibrium of sulphides of metals with hydrogen chloride. I. System zinc sulphide-hydrogen chloride. II. System manganese sulphide-hydrogen chloride. E. V. BRITZKE, A. F. KAPUSTINSKI, and B. K. VESELOVSKI (J. Phys. Chem. U.S.S.R., 1934, 5, 77—84, 103—106).—I. Vals. of $\log K_p$ determined by a static method are 1.14 and 1.67 at 565° and 635° abs., respectively.

II. The dissociation pressure of MnS derived from the MnS--HCl reaction at $680\text{--}1000^\circ$ and from the MnS--H_2 reaction at 1373° abs. give the heat of formation of MnS as 44,900 g.-cal.

CH. ABS. (e)

Heat of formation of iron carbide, Fe_3C . G. NAESER (Mitt. Kaiser-Willh.-Inst. Eisenforsch., 1934, 16, 1—7; Chem. Zentr., 1934, i, 3181—3182).—The val. varies from +8 to -3.9 kg.-cal. per mol. according to the state of the C.

H. J. E.

(A) **Affinity of metals for sulphur.** E. V. BRITZKE and A. F. KAPUSTINSKI. (B) **Heat of formation of disulphides and trisulphides of arsenic.** (C) **Heat of formation of double compounds of pentoxide and trioxide of arsenic, and the heat of formation of arsenic sulphate.** E. V. BRITZKE, A. F. KAPUSTINSKI, and L. G. CHENTZOVA (J. Phys. Chem. U.S.S.R., 1934, 5, 85—90, 91—96, 97—102).—A. With increase in the radii of the metal ions the electrolytic dissociation consts. of the sulphides decrease, whilst the thermal dissociation consts. increase.

B. The heats of formation (I) of solid As_2S_2 and As_2S_3 from solid As and rhombic S are calc. as 28.9 and 34.7 kg.-cal.

C. The val. of (I) for $\text{As}_2\text{O}_3\cdot\text{SO}_3$ from solid As_2O_3 and gaseous SO_3 , and of solid $\text{As}_2\text{O}_3\cdot\text{As}_2\text{O}_5$ from solid As_2O_3 and solid As_2O_5 are 23.03 and -24.5 kg.-cal., respectively. The heats of dissolution of As_2O_3 and As_2O_5 in 0.83N-NaOH are 9.61 and 63.23 kg.-cal., respectively.

CH. ABS. (e)

Affinity. LXI. Construction and use of a high-temperature calorimeter with closed reaction space. W. BILTZ, G. ROHLFFS, and H. U. VON VOGEL (Z. anorg. Chem., 1934, 220, 113—141).—A calorimeter for the determination of heats of dissolution in a sealed glass bomb is described. By measuring the heats of dissolution of Zn and ZnO , and also of CaO and CaCO_3 , in aq. HCl at 90° , the heats of formation of ZnO from Zn and of CaCO_3 from CaO, respectively, have been calc. and found to be in good agreement with other determinations. The calorimeter has been employed in the determination of the heats of formation (kg.-cal. per g.-mol.) of the following compounds: AuSn 8.2; AuSn_2 5.5; AuSb_2 approx. 3.4; Au_3Zn 24; AuZn 11; AuZn_2 22; CuO 36.4; Cu_2O 39.4. The val. of the heat of dissociation of 4CuO into $2\text{Cu}_2\text{O}$ and O_2 , calc. from the heats of formation of the oxides, is 66.8 kg.-cal. at 20° .

M. S. B.

Heats of combustion and formation of the normal aliphatic alcohols in the gaseous and liquid states, and the energies of their atomic linkings. F. D. ROSSINI (J. Res. Nat. Bur. Stand., 1934, 13, 189—202).—Existing data are reviewed and correlated with the author's val. (157.0 kg.-cal.) for the increase of the heat of combustion caused by the addition of the CH_2 group, and "best" vals. for the heats of evaporation, combustion, and formation are selected. The energy of dissociation, at 0° abs., of $\text{C}_n\text{H}_{2n+1}\cdot\text{OH}$ into its constituent atoms $\propto n$, when n is >6 ; the deviations, which correspond with lower stability, for $n < 6$, are attributed, as in the case of the paraffin hydrocarbons, to the presence of different types of C-C, C-H, and C-O linkings.

H. F. G.

Electrolytic transport of water in normal lanthanum chloride solutions. J. BABOROVSKÝ and O. VIKTORIN (Chem. Listy, 1934, 28, 257—258).—Higher vals. are found at 3.12 than at p_H 1.92.

R. T.

Conductance of solutions of electrolytes. T. SHEDLOVSKY, A. S. BROWN, and D. A. MACINNES (Trans. Electrochem. Soc., 1934, 66, 237—250).—The equiv. conductance of KCl and NaCl solutions at 25° has been redetermined up to 0.12 and 0.22M, respectively, and the results are shown to be accurately represented by Shedlovsky's modified Debye-Hückel-Onsager equation (A., 1932, 699). The application of the theory to the dissociated part of weak and intermediate electrolytes is discussed and illustrated by new data for $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ at 25° , the thermodynamic dissociation const. of which is found to be $1.39(5) \times 10^{-3}$.

H. J. T. E.

Ionic radius in aqueous solutions of electrolytes. L. BRULL (Gazzetta, 1934, 64, 624—634).—The ionic radii obtained from mobility data are compared with the parameter a in the theory of Bonino (this vol., 254). This quantity is identified with the diameter of the hydrated ion. The following hydration vals. are derived: Li^+ 7.5, Na^+ 3.0, K^+ 1.0, Ca^{++} 8.0, Sr^{++} 4.5, Ba^{++} 3.5, Zn^{++} 8.0.

O. J. W.

Estimation of limiting equivalent conductivity from the streaming currents. K. GOSTKOWSKI (Acta phys. polon., 1933, 2, 215—218; Chem. Zentr., 1934, i, 827).—Electrokinetic potential V and Λ_∞ are

connected by the equation $\Lambda_{\infty}/\Lambda'_{\infty} = KV/V'$. Λ_{∞} for HCl calc. from known data for KCl and HCl is 444, and by comparison with $\text{Pb}(\text{NO}_3)_2$ instead of KCl, 446; using Λ_{∞} for NaOH (204.5) it is 409. This val. for NaOH is too small, and when the new val. of 222 is used Λ_{∞} for HCl is 444. L. S. T.

Behaviour of aqueous solutions in a high-frequency electric field. P. V. ZMAKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 450—453).—Observations have been made on the effect of high-frequency discharges in aq. $\text{CH}_2\text{Cl}-\text{CH}_2\text{OH}$, NaOAc, NaI, $\text{Al}_2(\text{SO}_4)_3$, and other solutions contained in a glass tube with a H_2O -vapour cloud (I) over the solution. The discharge is accompanied by chemical change (e.g., aq. NaI forms I). The solution must first be warmed to 70—90° to produce (I). H. J. E.

Salt error of the quinhydrone electrode and the activity coefficient of the hydrogen ion in concentrated neutral salt solutions. A. URMANCZY (Magyar chem. Fol., 1933, 39, 124—137; Chem. Zentr., 1934, i, 3322).—Data are recorded for aq. KCl, NaCl, BaCl_2 , CaCl_2 , MgCl_2 , KNO_3 , NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, K_2SO_4 , Na_2SO_4 , and MgSO_4 at 25°. At salt concn. $> N$ the salt error (I) \propto the equiv. salt concn. For NO_3' and Cl' , (I) is negative. For SO_4'' it is positive. The activity coeff. of H' in 0.01N-HCl containing neutral salts is calc. Its logarithm \propto the salt concn. H. J. E.

Effect of certain substances used in photography on the potential of the silver bromide electrode. V. A. VEIDENBACH (J. Appl. Chem. Russ., 1934, 7, 339—342).—The potential E at a AgBr electrode in the cell $\text{Ag}|\text{AgBr}-x\text{KBr}|\text{saturated } \text{NH}_4\text{NO}_3|\text{saturated KCl}-\text{HgCl}_2|\text{Hg}$ is unaffected by gelatin, Na_2SO_3 , and Na_2SO_4 ; these substances can hence influence only the developer, its oxidation-reduction potential, or the process of formation of the image. KBr lowers E , and thus retards development. R. T.

Physico-chemical properties of solutions in condensed gases. VI. Electrode potentials in liquid ammonia. V. A. PLESKOV and A. M. MONOSZON (J. Phys. Chem. U.S.S.R., 1933, 4, 696—702).—Referred to $\text{Pb}|0.1N-\text{Pb}(\text{NO}_3)_2=0$ at -50° , the observed electrode potentials, ϵ , are Zn -0.848 ; Cd -0.510 ; H₂ -0.331 ; Cu 0.103 ; Ag 0.472 , and Hg 0.414 . Activity coeffs. in 0.1N solution, based on $\epsilon=0$ for Pb and also on $\epsilon=0$ for Pb in aq. solution, are recorded. CH. ABS. (e)

Phenomena at the contacts between electrodes and electrolytes. I. So-called electrode-electrolyte resistance to the passage [of a current]. E. DENINA (Gazzetta, 1934, 64, 527—563).—A crit. summary of the various methods used for the measurement of the so-called "transfer resistance" at an electrode-electrolyte interface during the passage of an electric current. Experimental data and the theories of the nature of this resistance are discussed. O. J. W.

A. Influence of electrolytes on the electrification of water forced through a capillary tube. T. MALARSKI and K. GOSTKOWSKI. **B. Relation between electrokinetic potential and equivalent**

conductivity. K. GOSTKOWSKI (Acta phys. polon., 1932, 1, 465—482, 483—486; Chem. Zentr., 1934, i, 520).—A. The effect of 1-, 2-, 3-, and 4-valent cations and anions on the potential has been measured.

B. The electrification of electrolyte solutions on passing through a capillary [measured by the potential (V) of a Pt plate in the issuing liquid] is related to the equiv. conductivity (λ_{∞}) by $\lambda'_{\infty}/\lambda''_{\infty} = K(V''/V')$, where $K-1$ approx. H. J. E.

Diffusion in liquids. VIII. Theory of the "boundary layer" of dilute electrolyte solutions. IX. Diffusion of dilute electrolytes into one another. X. Potential difference between dilute electrolytes in contact. K. SITTÉ (Z. Physik, 1934, 91, 622—641, 642—650, 651—659).—VIII. The theories of Planck and Henderson are discussed, and formulae representing first approximations are obtained.

IX. Experiment shows no essential difference between diffusion of electrolytes into one another and their separate diffusion into H_2O ; the formation of a "boundary layer" as postulated by Planck could not be observed. Both colourless and coloured electrolytes were used.

X. Chang's observed time variation of potential difference (cf. A., 1933, 468) can be explained by ordinary diffusion processes. A. B. D. C.

Electric boundary layer disturbance. IV. Effect of an alternating electric field on the permeability potential of a membrane. M. SHIKATA and K. KITAO (Bull. Agric. Chem. Soc. Japan, 1934, 10, 90—91).—The p.d. between the sides of a collodion membrane (I) separating KCl solutions of different concn. almost disappears when (I) is placed for 10—30 sec. in a 220-volt a.c. field of 60 cycles. In 5—10 min. it returns to the normal val. CH. ABS. (e)

Electrolytic metal potentials in pure buffer solutions. S. BODFORSS (Kungl. Fysiogr. Sällskapet I Lund Forhandl., 1933, 3, 33 pp.; Chem. Zentr., 1934, i, 829).—The slip potentials (I) of different metals have been measured in various salt and buffer solutions (e.g., phosphate, tartrate, acetate, sulphate) in an atm. of H_2 . Renewal of the metal surface by rotation causes the potential to become negative with increasing velocity of rotation, and this potential tends towards a limiting val. (II). (II) for Sn, Bi, Cd, and Pb is reached at 600—1000 r.p.m. With Cu, Ag, W, and Ni, (II) is reached at such a high rotation (> 2000 r.p.m.) that (I) is quickly destroyed. For most metals (II) is a linear function of p_{H} and is independent of the nature of the anion concerned. It is improbable that the metals function in the sense of a Pt- H_2 electrode. The stationary potentials can generally be satisfactorily determined. They are more noble than (I) and are dependent on p_{H} and the anions present. L. S. T.

Acidity of substituted phenols and thiophenols. G. SCHWARZENBACH and H. EGLI (Helv. Chim. Acta, 1934, 17, 1176—1182).—Normal acidity potentials (A., 1930, 1526) of PhOH and PhSH with Cl, Br, I, Me, OH, and OMe as substituents have been determined at 20° in 48.95 and 95 vol.-% EtOH.

F. L. U.

Influence of a substituent on the acidity of an organic acid. I. G. SCHWARZENBACH and H. EGLI (Helv. Chim. Acta, 1934, 17, 1183—1196).—The question of the extent to which the influence of a substituent on acidity is purely electrostatic is discussed. From the results recorded (preceding abstract) it appears that the acidity of thiophenols with *m*-substituents is 200 mv., and with *p*-substituents 205 mv., > that of the corresponding phenols. The relation of acidity to the composition of the solvent depends on the nature and position of the substituent. These facts are best interpreted by assuming that the influence of a substituent is partly electrostatic, but that another effect is superimposed whereby the electronic structure of the atom carrying the acid H is modified, thus altering the energy of expulsion of a proton. F. L. U.

Reduction potential of organic compounds. J. HIRADE (J. Biochem. Japan, 1934, 20, 161—191).—The reduction potential (I) of various org. compounds in 0.05*M* aq. solution at p_H 7—12 at 38° has been determined colorimetrically and electrometrically with plain (II) and platinised Pt electrodes (III). (I) attains an equilibrium or "limit" val. (IV) only after a long time, and the use of a "quasi-equilibrium" point (V) is advocated; (V) is generally attained more rapidly with (III) than with (II). Conc'n. of the substance has little effect on the time necessary for attainment of (IV). The vals. of (V) are significantly influenced by and, unlike those of (IV), are dependent on the nature of the electrode. F. O. H.

Reversible oxidation-reduction potentials in dye systems. B. COHEN (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 195—204).—Chemical const's. of a series of indophenols, aminoindophenols, indamines, thiazines, oxazines, indigotin-sulphonates, safranines, neutral-red, rosindulines, and rosindones are presented. CH. ABS.

Reversible two-step oxidation. L. MICHAELIS (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 224—229).—Electrometric titration curves are given for pyocyanine and a series of "viologens." CH. ABS.

Effect of animal charcoal on oxidation-reduction processes. F. JOHNE and H. WEDEN (Biochem. Z., 1934, 273, 147—153).—Animal C at neutral and faintly acid p_H in presence of O_2 oxidises $K_4Fe(CN)_6$ almost completely to $K_3Fe(CN)_6$, but in strongly alkaline (0.2*N*-NaOH) solution the reverse reaction occurs quantitatively, whilst at between these limits equilibrium mixtures of the two compounds are formed. The potentials of the various mixtures at alkaline, neutral, and faintly acid p_H agree accurately with those of the O_2 electrode at the same p_H . In more strongly acid solution, however, partial reduction occurs. P. W. C.

Titration curves of some phosphoric esters containing three carbon atoms and of inosinepyrophosphoric acid. M. KIESSLING (Biochem. Z., 1934, 273, 103—108).— p_K vals. for α - and β -glycerophosphoric, phospho- and diphospho-glyceric, dihydroxyacetone-, pyruvic acid-, synthetic glycer-aldehyde-, and hexosediphosphoric, and phosphoric

acid are recorded. The 3-carbon phosphoric esters are always stronger acids than H_3PO_4 in the first stage, and frequently but not always in the second stage of dissociation. Titration curves for Lohmann's inosinepyrophosphoric acid (I) and adenylypyrophosphoric acids before and after hydrolysis and the analogy between free adenylic and inosinic acids provide fresh evidence for the existence of (I). P. W. C.

Liquid potential and the activity coefficients of the ions. Z. SZABÓ (Magyar chem. Fol., 1933, 39, 145—153; Chem. Zentr., 1934, i, 3036).—A graphical method for calculating the potential at the liquid boundary from the mean activity coeff. of the electrolyte is described. H. J. E.

Cell using the oxidation energy of alcohol. V. KARPEN (Compt. rend., 1934, 199, 708—710).—In the cell graphite|33% aq. HNO_3 |NaOH+MeOH (50 g. NaOH+50 c.c. MeOH)|platinised Pt with a porous diaphragm separating the two solutions, the anode polarises owing to oxidation, but recovers on breaking circuit for a few min., after which the e.m.f. is 1.83 volt. The reaction at the cathode is $2HNO_3 + 8H = 5H_2O + N_2O$, and at the anode $MeOH + 2O + NaOH = HCO_2Na + 2H_2O$. The e.m.f. is close to the val. calc. from the energy changes. Analogous results are obtained when MeOH is replaced by other reducing agents. R. S. B.

Electrochemistry of gallium. H. C. FOGG (Trans. Electrochem. Soc., 1934, 66, 221—229).—The amphoteric character of Ga is compared with that of Al, and observations on the electrodeposition of the metal and its electrode potential are reviewed. H. J. T. E.

Anodic behaviour of thallium in the hydrogen halide acids. O. PIP (Z. Physik, 1934, 94, 329—335).—Electrolytic valve action is shown by Cl' and Br'. A. B. D. C.

"Dead space" correction in gas reaction rate measurements. A. O. ALLEN (J. Amer. Chem. Soc., 1934, 56, 2053—2054).—A formula is derived for the effect on the measured pressure of the "dead space," or part of the reaction system external to the controlled-temp. bath. E. S. H.

Cause of changes in rate of some gas reactions. M. W. TRAVERS, R. V. SEDDON, and P. F. GAY (Nature, 1934, 134, 662).—A discussion. L. S. T.

Emission wave theory of periodic reactions. III. F. M. SCHEMJAKIN (J. Gen. Chem. Russ., 1934, 4, 444—451).—A mathematical derivation of the formula $\lambda v = \text{const.}$ (this vol., 363) is given. R. T.

"After-burning" in gas explosions. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1934, 2, 659—664; cf. A., 1933, 368).—Conclusions reached by other workers (A., 1927, 317; 1933, 30; this vol., 368) are criticised, and experiments are recorded which show that with properly designed explosion vessels the ratio max. pressure: initial pressure in H_2 - O_2 mixtures is independent of the radius of the vessel. "After-burning" is fictitious and cannot invalidate the determination of heat capacities of gases by the explosion method. F. L. U.

Effect of unequal temperature distribution on the maximum pressure developed in explosions

in a closed vessel. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1934, 2, 665—668; cf. preceding abstract).—A method of calculating the difference in max. pressure due to the existence of a temp. gradient is given. For O_3 explosions the difference amounts to < 0.2—0.5%, and for $H_2 + O_2 +$ inert gas to 0.2—0.8%. F. L. U.

Activation energies of reactions involving oxygen. I. Reaction $O + H_2 = H_2O$. R. S. BEAR and H. EYRING (J. Amer. Chem. Soc., 1934, 56, 2020—2025).—Theoretical. The activation energies of excited and normal O atoms with H_2 mols. are deduced. E. S. H.

Non-explosive thermal decomposition of azoimide. R. MEYER and H. J. SCHUMACHER (Z. physikal. Chem., 1934, 170, 33—40).—The decomp. at 306—330° under 30—200 mm. in quartz or hard glass vessels is largely heterogeneous and follows the unimol. law. Traces of impurities have a powerful catalytic action, and easily cause explosion. At least 94% of the product of reaction consists of NH_3 and N_2 ; only 6% of the HN_3 decomposes into N_2 and H_2 . The primary (wall) reaction is possibly $HN_3 = NH + N_2$ (exothermic). After preservation of HN_3 in glass at room temp. for some months it undergoes thermal decomp. more slowly, but has a greater tendency to explode. R. C.

Kinetics of the oxidation of gaseous hydrocarbons. II. Oxidation of ethane. E. W. R. STEADIE and A. C. FLEWES (Proc. Roy. Soc., 1934, A, 146, 583—597).—In the oxidation of C_2H_6 and its mixtures with MeCHO and C_2H_4 there is a long period of inhibition, which decreases as the total pressure is raised. Heating to a high temp. or long pumping intensifies the inhibition period, whilst packing diminishes it. Aldehydes, H_2 , and the products of the reaction reduce or eliminate it; N_2 increases it. Chains started by C_2H_4 can be continued by C_2H_6 . Analysis shows that H_2 and C_2H_4 are present at the end of the inhibitory period and throughout the reaction. It is concluded that the inhibition period is a surface effect leading to the formation of C_2H_4 , and that the primary process in the oxidation of C_2H_6 is dehydrogenation, followed by a chain oxidation of the C_2H_4 thus produced. Further cracking of the paraffin occurs during the oxidation of the olefine. L. L. B.

Mechanism of thermal decomposition of hydrocarbons. Kinetics of decomposition of ethane and propane. A. I. DINTZES and A. V. FROST (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 510—515).—The decomp. of C_2H_6 (at 678°/1.7—22.3 mm.) and of C_3H_8 (at 616—666°/1.05—78 mm.) in a quartz bulb does not follow a unimol. law. A chain mechanism for the hydrocarbon cracking reaction is suggested. H. J. E.

Kinetics and mechanism of decomposition of hydrocarbons. II. Thermal decomposition of octane and of β -dimethylhexane under atmospheric pressure. A. I. DINTZES and A. V. FROST (J. Gen. Chem. Russ., 1934, 4, 610—615).—80—90% of *n*-octane (I) decomp. at 500—570° is accounted for by the reactions $CH_4 + C_7H_{14} \leftarrow (I) \rightarrow C_2H_6 + C_6H_{12}$, proceeding with equal velocity; variations

in temp. influence only the velocity of these reactions, according to the equation $\log \frac{14.70 - 14,100/T + 0.09}{0.09}$. Of the olefines formed, 60—70% undergo intensive decomp. to yield a mixture of H_2 , CH_4 , C_2H_6 , C_3H_8 , C_3H_6 , and C_4H_8 . Under analogous conditions, 75—85% of decomposed β -dimethylhexane (II) yields CH_4 and C_7H_{14} , 40% of which is further decomposed as in the case of (I). Cu does not catalyse the decomp. of (II). R. T.

Thermal reaction between chlorine and gaseous formaldehyde. I. R. SPENCE and W. WILD (J.C.S., 1934, 1588—1593; cf. A., 1933, 1036).—Explosions, accompanied by the emission of light, terminated the slow reaction at 150°, and also occurred in vessels activated by a long series of slow reactions. In the explosion, any excess of CH_2O is decomposed ($CH_2O = CO + H_2$), whilst during the slow reaction, CH_2O is polymerised in addition to the main reaction, $CH_2O + Cl_2 = CO + 2HCl$. The reaction velocity is greatly affected by the state of the surface, and the process is probably of the homogeneous chain type. J. G. A. G.

Induced decomposition of acetaldehyde. A. O. ALLEN and D. V. SICKMAN (J. Amer. Chem. Soc., 1934, 56, 2031—2034).—The decomp. of MeCHO is induced by the decomp. of azomethane (I) occurring when their mixture is heated at about 300°. A kinetic examination of the reaction suggests that the Me radicals from the (I) start a chain-type decomp. of MeCHO. E. S. H.

Thermal decomposition of formaldehyde. C. J. M. FLETCHER (Proc. Roy. Soc., 1934, A, 146, 357—362).—The thermal decomp., $CH_2O \rightarrow CO + H_2$, is a homogeneous bimol. reaction over the pressure range 30—400 mm. Simultaneous condensation reactions occur. The energy of activation over a temp. range 510—607° is 44,500 g.-cal. The rate of reaction is approx. equal to the rate of formation of activated mols., according to the usual expression $Z \times e^{-E/RT}$. L. L. B.

Modes of activation of aldehyde molecules in decomposition reactions. C. N. HINSHELWOOD, C. J. M. FLETCHER, F. H. VERHOEK, and C. A. WINKLER (Proc. Roy. Soc., 1934, A, 146, 327—333).—The curves representing the variation with pressure of the time of half-decomp. of MeCHO and of N_2O show that the reactions are kinetically composite. This can be explained on the assumption of a no. of different modes of activation of the mols., which are characterised by a study of the behaviour of CH_2O , MeCHO, EtCHO, and $CCl_3 \cdot CHO$. L. L. B.

Thermal decomposition of propaldehyde. C. A. WINKLER, C. J. M. FLETCHER, and C. N. HINSHELWOOD (Proc. Roy. Soc., 1934, A, 146, 345—356).—The thermal decomp. of EtCHO has been reinvestigated over the pressure range 400—0.5 mm. The reaction is kinetically complex and is interpreted as the resultant of several homogeneous quasi-unimol. reactions. The chemical nature of the reaction products varies a little with the pressure. The influence of H_2 on the reaction has been studied. The energy of activation shows a well-defined variation with pressure. L. L. B.

Thermal decompositions of aldehydes. W. A. BONE (Chem. and Ind., 1934, 53, 813—814).—Polemical. In explaining the thermal decomp. of MeCHO (cf. preceding abstracts) the authors have overlooked the possibility that at the temp. employed MeCHO may be in equilibrium with $(\text{CH}_2)_2\text{O}$ and $\text{CH}_3\cdot\text{CH}\cdot\text{OH}$. H. A. P.

Thermal decomposition of acetaldehyde. M. W. TRAVERS (Nature, 1934, 134, 569).—The view that the thermal decomp. of MeCHO is a homogeneous reaction unaffected by the character of the containing vessel (see above) is further criticised.

L. S. T.

Homogeneous unimolecular decomposition of seous methyl nitrite. E. W. R. STEACIE and T. SHAW (Proc. Roy. Soc., 1934, A, 146, 388—395).—The thermal decomp. of gaseous $\text{MeO}\cdot\text{NO}$ ($\rightarrow \text{NO} + 0.5\text{CH}_2\text{O} + 0.5\text{MeOH}$) is a homogeneous first-order reaction, and proceeds at a measurable rate between 190° and 240°. The rate of reaction is given by $K = 1.84 \times 10^{13} e^{-36400/RT}$ sec.⁻¹ L. L. B.

Influence of fluid velocity on heterogeneous reactions. III. Extension of the fundamental equation and some of its applications. S. UCHIDA (J. Soc. Chem. Ind. Japan, 1934, 37, 456—457B).—Mathematical analogies with heat transfer processes are developed (cf. A., 1933, 911; this vol., 36). A. J. H.

Keten. II. Rate of polymerisation.—See this vol., 1336.

Velocity of decomposition of nitric esters at relatively low temperatures. M. LAMBREY (Compt. rend., 1934, 199, 725—726).—Guncotton (I), containing (a) 13.34% N, stabilised by boiling with H_2O , and (b) 13.80% N, stabilised by Muraour's method, when heated at 30° gives off NO with decreasing velocity, the total evolution being 0.5 mg. per kg. of (I). On raising the temp. a further quantity is evolved. It is inferred that an impurity is present. After evacuating (I) at 50° decomp. is uniform when residual impurity has been removed, and is such that 0.001 of (I) decomposes in 1100 years at 43°; the rate is 0.1 of this at 36.5°. Method (a) also favours removal of impurity. Similar results have been obtained with pentaerythrityl tetranitrate, and with (I) + glyceryl trinitrate. R. S. B.

Chemical kinetics of ion reactions. V. Neutral salt action in concentrated salt solutions. A. VON KISS (Magyar chem. Fol., 1933, 39, 162—168; Chem. Zentr., 1934, i, 3435).—In six ion reactions of zero order (e.g., for $\text{CH}_2\text{Br}\cdot\text{CO}_2' + \text{S}_2\text{O}_3'' = \text{S}_2\text{O}_3\cdot\text{CH}_2\cdot\text{CO}_2'' + \text{Br}'$) the log. of the velocity coeff. \propto the concn. of the added salt (for certain salts and concn. ranges). H. J. E.

Determination of velocity of hydrolysis of acid anhydrides by the aniline-water method. II. S. E. VLES (Rec. trav. chim., 1934, 53, 961—966; cf. A., 1933, 1250).—Velocities of hydrolysis of AcCl , BzCl , COCl_2 , ClCO_2Me , and ClCO_2Et have been compared. F. L. U.

Factors affecting -onium salt formation. W. C. DAVIES and W. P. G. LEWIS (J.C.S., 1934, 1599—1604).—The rates of addition (I) at 35° of alkyl

halides, RX , to substituted dimethyl- (II) and diethyl-anilines (III), phenyldiethylphosphines, and AsPhEt_2 have been determined in COMe_2 , aq. COMe_2 , and aq. EtOH , and the following products are described: *p*-chlorophenyltrimethylammonium iodide, m.p. 200—202° (decomp.), phenyltriethylphosphonium bromide, m.p. 187—188°, and *p*-phenoxyphenyltriethylphosphonium iodide, m.p. 181—182°. The (I) of $\text{RBr} < \text{RI}$, and $\text{MeX} > \text{EtX} > \text{Bu}^n\text{X}$. The reactivity of the PhEt_2 bases is phosphine > arsine > amine, parallel with the order of dipole moments, and that of (II) is > (III) owing to steric factors. Substituents in the Ph group of (II) afford the following order of reactivity: $\text{OEt} > \text{OMe} > p\text{-Me} > \text{H} > p\text{-Cl} > p\text{-Br} > p\text{-I} > m\text{-NO}_2 > p\text{-NO}_2$. The reaction involves (a) anionisation of the halogen in RX and (b) the co-ordination of the base, by its lone electron pair, to the $\cdot\text{CH}_2$ in RX . Step (b) determines the velocity, which is accelerated by electron-releasing groups (e.g., *p*-Me) and retarded by electron-attracting substituents (e.g., *p*- NO_2) in the bases. J. G. A. G.

Beckmann change. II. Kinetics of the spontaneous rearrangement and solvent effects. A. W. CHAPMAN (J.C.S., 1934, 1550—1555; cf. A., 1933, 952).—The velocity of the Beckmann rearrangement of benzophenoneoxime picryl ether (I) has been determined at 70—100° in polar and non-polar solvents. Consistent with the view that the transformation involves the development of electric charges at the ends of the linkings concerned in the migration of the picryloxy- and hydrocarbon groups, the velocity is markedly increased by substances containing polar groups, including (I) and its change product. The catalytic activities of compounds with one principal dipole are in the same order as the dipole moments, and non-polar compounds with equal and opposite dipoles in each mol. are catalysts when the dipoles are sufficiently separated. In CCl_4 at infinite dilution, mols. of (I) can be activated only by collision with solvent mols., and the activation energy, E , is 30,250 g.-cal., but when activation occurs by collisions between solute mols., E falls to approx. 23,000.

J. G. A. G.

Hydration of unsaturated compounds. III. Rate of hydration of trimethylethylene in aqueous solutions of acids. H. J. LUCAS and Y. P. LIU (J. Amer. Chem. Soc., 1934, 56, 2138—2140; cf. this vol., 369).—The rate of hydration of $\text{CHMe}\cdot\text{CMe}_2$ (I) (to $\text{CMe}_2\text{Et}\cdot\text{OH}$) by dil. HNO_3 (II) at 25° and 35° and const. ionic strength is unimol. with respect to both [(I)] and [(II)]. The ratio k_{35}/k_{25} is 2.83 [for two concns. of (II)]; the heat of activation is 18.92 kg.-cal. For a fixed concn. of (II), the rate is increased by addition of KNO_3 . (I) is hydrated at a much slower rate than isobutene (*loc. cit.*). The rate of hydration of (I) by the following acids (concn. approx. 0.1M) at 25° decreases in the order quoted: $\text{H}_2\text{S}_2\text{O}_8$, H_2SO_4 , HCl , HClO_4 , HBr , (II), *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{H}$, picric acid, $\text{H}_2\text{C}_2\text{O}_4$, AcOH . H. B.

Mutarotation of arabinose. C. N. RIBER and N. A. SORENSEN (Kong. Norske Vidensk. Selsk. Skr., 1933, No. 7, 1—49; Chem. Zentr., 1934, i, 2737—2738).—Pure arabinose, m.p. 160°, has $[\alpha]_D^{20} + 105.46^\circ$ in H_2O . The concn. and n of an aq. solution can be

calc. from the d by Berner's equations, and from them the mol. solution vol. (I) and refraction (II). The vol. change on dissolution is calc. by following the process of evaporation dilatometrically. Mutarotation of arabinose takes place according to the equation $[\alpha]^{20}_D = +105.46^\circ + 76.49 \times 10^{-0.029t} + 9.55 \times 10^{-0.108t}$, and therefore is not a unimol. reaction. The calc. initial $[\alpha]$ ($+191.5^\circ$) agrees better than the hitherto accepted val. ($+174^\circ$) with that derived from the Hudson rule ($+203^\circ$). In differences of mol. $[\alpha]$, (I), and (II) between glucosides and sugar, β -arabinose resembles α -D-galactose. The name "anomerism" is proposed for such cases. From a comparison with the corresponding α -galactose derivative the vals. $[\alpha]^{20}_D + 84^\circ$, (I) 92.24 ml., and (II) 30.9 are calc. for non-cryst. β -arabinose. Saturation experiments at 0° show that for the modifications present besides α -arabinose, $[\alpha] = +46^\circ$ approx., so that a third form must exist. This third form contains no CHO group, since the Schiff and Angeli reactions are negative, and the CHO absorption band is absent from the spectrum.

R. N. C.

Kinetics of the bromination of nitroethane in hydrogen halides. R. JUNELL (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 27, 6 pp.).—The two phases of the bromination of EtNO_2 in $N\text{-HBr}$ at $69.85 \pm 0.05^\circ$ to $\text{C}_2\text{H}_4\text{Br}\cdot\text{NO}_2$ and $\text{C}_2\text{H}_3\text{Br}_2\cdot\text{NO}_2$ have unimol. velocity coeffs. ($\times 10^{-4}$) of 2.5 and 27.7 and in $N\text{-HCl}$ of 2.8 and 32.0, respectively. The vals. are independent of $[\text{Br}]$ (cf. A., 1929, 516).

F. O. H.

Kinetics of the bromination of α -carboxydiethyl- and methyl- α -carboxyethyl-sulphone in aqueous solutions. L. RAMBERG and A. MELLANDER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 31, 6 pp.).—With initial concns. of $> 0.1M$ per litre of the reactants, the unimol. velocity coeffs. at 35° in $N\text{-HBr}$ are dependent on $[\text{sulphone}]$, but independent of $[\text{Br}]$, and have vals. ($\times 10^{-3}$) of 0.379 and 0.68—0.69 for the Me and Et compounds, respectively. With lower concns. the reaction deviates from a unimol. one. The racemisation coeff. of l - and bromination coeff. of $dl\text{-CHMe}(\text{SO}_2\text{Et})\cdot\text{CO}_2\text{H}$ at 25.15° and under identical conditions of concn. etc. have vals. ($\times 10^{-3}$) of 0.273 and 0.249, respectively.

F. O. H.

Velocity of bromination of bromosulphoacetic and α -sulphopropionic acids in hydrobromic acid. L. RAMBERG and E. SAMÉN (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 35, 6 pp.).—The unimol. velocity coeff. (I) ($\times 10^{-5}$) for the bromination of $\text{SO}_3\text{H}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$ (II) is $72.4\text{--}72.5$ (in $N\text{-HBr}$ at 60°), whilst those for $\text{SO}_3\text{H}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ (III) are $1.04\text{--}1.22$ (in $N\text{-HBr}$ at 60°), 0.79 (in $0.5N\text{-HBr}$ at 60°), and 8.7 (in $N\text{-HBr}$ at 80°). As with α -carboxyalkylethylsulphones (cf. preceding abstract), the reaction with (II) is unimol. with excess of Br; with equivs. of the reactants, the reaction becomes "sesquimol." as it approaches completion. With (III) such deviations are slight. Other variations of (I) with temp. are discussed. $\text{CH}_2(\text{SO}_3\text{H})_2$ is extremely slowly brominated at 60° (cf. A., 1929, 909).

F. O. H.

Kinetics of the bromination of aliphatic $\alpha\alpha$ -disulphones in aqueous solution. L. RAMBERG and E. SAMÉN (Arkiv Kemi, Min., Geol., 1934, 11, B,

No. 40, 6 pp.).—The bromination of $\text{CHMe}(\text{SO}_2\text{Me})_2$ (I) or $\text{CHMe}(\text{SO}_2\text{Et})_2$ (II) in $0.5N$ - or $N\text{-HBr}$ is a bimol. reaction even with large excess of Br. (I) has velocity coeffs. ($\times 10^{-3}$) of $4.67\text{--}4.84$ (at 80° in $N\text{-HBr}$) and (II) of $1.91\text{--}1.92$ (at 60° in $N\text{-HBr}$), $5.31\text{--}5.69$ (at 60° in $0.5N\text{-HBr}$), and $7.40\text{--}7.42$ (at 80° in $N\text{-HBr}$). Br does not react with MeSO_2Et (III) at 80° . Aq. (I) and (II), but not (III), develop absorption bands in the ultra-violet region on treatment with alkali.

F. O. H.

Velocity of bromination and racemisation of α -phenylsulphinopropionic acid. L. RAMBERG and I. HEDLUND (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 41, 4 pp.).—The velocity coeff. of racemisation of $d\text{-CHMe}(\text{SO}_2\text{Ph})\cdot\text{CO}_2\text{H}$ at 25.11° in $N\text{-HBr}$ is 34.8×10^{-5} , whilst that of bromination under parallel conditions is $52.3\text{--}53.9 \times 10^{-5}$ at 30° and 31.8×10^{-5} at 25° (equiv. to 32.2×10^{-5} at 25.11°). The data are compared with those for $\text{CHMe}(\text{SO}_2\text{Et})\cdot\text{CO}_2\text{H}$ (cf. preceding abstract).

F. O. H.

Kinetics of salt formation of nitroethane. R. JUNELL (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 34, 5 pp.).—The reaction $\text{EtNO}_2 + \text{NaOH} \rightarrow \text{CHMe}\cdot\text{NO}_2\text{Na}$ was followed by Br titrations. It is bimol. ($k=36$ at 0.05°), and is slightly retarded by NaCl or by replacing NaOH by $\text{Ba}(\text{OH})_2$.

A. G.

Rearrangement of nitroethane in acid solution. R. JUNELL (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 30, 6 pp.).—Acethydroxamic acid (I) is determined in the presence of EtNO_2 and AcOH by oxidation with KBrO_3 and HCl and determination of excess of oxidising agent. The formation of (I) from EtNO_2 in $N\text{-HCl}$ is a unimol. reaction, and the coeff. (0.25×10^{-3} at 69.85°) is nearly the same as that (0.28×10^{-3}) of the bromination of EtNO_2 . Probably in both cases the slow stage is the formation of $aci\text{-EtNO}_2$, which then yields rapidly either (I) or $\text{C}_2\text{H}_4\text{Br}\cdot\text{NO}_2$.

A. G.

Velocity of decomposition of diazo-compounds in water. XV. E. YAMAMOTO, R. GOSHIMA, and J. HASHIMA (J. Soc. Chem. Ind. Japan, 1934, 37, 512—515B).—Decomp. velocity coeffs. for temp. of $0\text{--}60^\circ$ are recorded for the diazo-compounds from β -naphthylamine-5:7- and -6:8-disulphonic acids and 8-amino- α -naphthol-3:6-disulphonic acid.

A. G.

Kinetics of alkaline hydrolysis of betaine-amides.—See this vol., 1340.

Influence of the gaseous medium on the luminosity accompanying detonation of explosives. A. MICHEL-LEVY and H. MURAOUR (Chim. et Ind., 1934, 32, 783—786).—From detonation experiments with (a) crystals of PbN_6 placed at intervals in the form of an isosceles triangle and detonated at the apex, and (b) a mixture of $\text{C}(\text{NO}_2)_4$ and PhMe placed in a circular groove in a brass plate, it is concluded that the luminous effects (I) accompanying detonation are due to the shock wave propagated in the surrounding medium (II). (I) vary with the nature of (II), luminosity decreasing in the order $\text{A}, \text{N}_2, \text{CO}_2, \text{C}_4\text{H}_{10}$, i.e., as the sp. heat increases. Results are recorded photographically.

C. C.

Kinetics of benzylation of cellulose. A. L. BERNOULLI, M. SCHENK, and F. ROHNER (Helv. Chim. Acta, 1934, 17, 897—918).—Benzylation of natural cellulose (I) by Bz_2O is very slow and incomplete except after pretreatment of (I) with NaOH , or in presence of a mixture (II) of $\text{C}_5\text{H}_5\text{N}$ and CH_2PhCl (2:1) which disperses it. In measuring the velocity of the reaction at 94° BzCl diluted with $\text{C}_5\text{H}_5\text{N}$ and a hydrocarbon was used for (I), viscose, and mercerised cotton, and Bz_2O for viscose dispersed in (II). The reaction in every case is topochemical and heterogeneous. In dispersed cellulose the solution units are not single mols., but crystallites.

F. L. U.

Kinetics of evaporation of mercury in the presence of thin layers of capillary-active substances. S. L. PUPKO and M. A. PROSKURNIN (J. Phys. Chem. U.S.S.R., 1933, 4, 523—528).—Using an ionisation manometer, the speed of evaporation (I) of Hg was found to decrease rapidly under a unimol. layer of oleic acid, or with a triolein layer $<$ unimol. If the Hg is covered with a film of oleic acid (4 mols.) (I) increases gradually, probably because of evaporation of the film itself.

CH. ABS. (e)

Oxidation reactions initiated by hydrogen atoms. K. H. GEIB and P. HARTECK (Z. physikal. Chem., 1934, 170, 1—19).—In $\text{H}_2\text{--O}_2$ mixtures at -190° to 100° H atoms cause formation of amounts of H_2O which are of the same order at all the temp. Below -80° H_2O_2 is also formed. H atoms bring about formation of CO_2 from CO and O_2 and oxidation of CH_4 and other hydrocarbons, although under the experimental conditions they react with neither CO nor CH_4 . The exact mechanism is undecided; a considerable no. of reactions are apparently involved, their relative importance varying with temp. and concn. The energies of activation of $\text{H} + \text{O}_2 \rightarrow \text{H}_2 + \text{O}_2$ and $\text{H} + \text{O}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{OH}$ are too small to be measured. H atoms may form HO_2 with O_2 , a reaction which renders impossible long reaction chains, since the further reaction of HO_2 involves a finite heat of activation. Attempts to detect the presence of OH radicals in the reaction mixtures by means of their optical absorption failed.

R. C.

Behaviour of carbon suboxide, and the reaction $\text{C}_3\text{O}_2 \rightleftharpoons \text{CO}_2 + \text{C}_2$ in the homogeneous gas phase. A. KLEMENC, R. WECHSBERG, and G. WAGNER (Z. physikal. Chem., 1934, 170, 97—111; cf. this vol., 969).—The polymerisation of C_3O_2 is an irreversible reaction catalysed by the walls of the vessel, and apart from a period of induction follows the unimol. law. When C_3O_2 is heated at 200° or above, CO_2 and CO are formed both from the gas and from the solid polymerisation product. The rate of formation of CO_2 in the former reaction is reduced by addition of CO_2 , which, however, does not alter the rate of formation of CO . These observations are explained if the decomp. of C_3O_2 occurs by way of $\text{C}_3\text{O}_2 \rightleftharpoons \text{CO}_2 + \text{C}_2$, the equilibrium const. of which is calc. from the observed reaction velocity at 200° to be $\sim 10^{-7}$. The C_2 formed polymerises to graphite, preventing the establishment of a permanent equilibrium. The presence of C_2 in the decomp. system at 200° is proved by the appearance in the

absorption spectrum of the head of the Swan band, 4737 \AA . Addition of O_2 to the reacting system increases the formation of CO_2 and CO .

R. C.

Oxidation of carbon monoxide catalysed by nitrogen dioxide. R. H. CRIST and O. C. ROEHLING (Science, 1934, 80, 338).—The rates of reaction at 500° have been investigated. The effect of NO_2 increases to a max. The catalysed reaction is sensitive to small amounts of H_2 or H_2O vapour, the rate increasing with an increase in concn. The appearance in the system of at. H chains, which increase the total rate of oxidation, is probable.

L. S. T.

Kinetics of the decomposition of chloral and its catalysis by iodine. F. H. VERHOEK and C. N. HINSHELWOOD (Proc. Roy. Soc., 1934, A, 146, 334—344).—The thermal decomp. of CCl_3CHO is predominantly homogeneous, and the principal primary change is $\text{CCl}_3\text{CHO} \rightarrow \text{CHCl}_3 + \text{CO}$. Subsequent decomp. and condensation reactions also occur. The relation between reaction rate and initial pressure corresponds with that characteristic of a quasi-unimol. reaction. The rate is $>$ that of MeCHO or EtCHO , but the energy of activation is 49,000 g.-cal., as great as for MeCHO . The reaction is accelerated by I , the catalytic reaction being of the first order with respect to the CCl_3CHO , and its rate increases in $<$ direct proportion to $[\text{I}]$. The catalysis is relatively less effective than with MeCHO .

L. L. B.

Hydrolysis of phenylalanine. E. BAUR and H. SCHINDLER (Biochem. Z., 1934, 273, 381—388; cf. A., 1933, 940).—Aq. extracts (I) (containing Ca^{++} , Mg^{++} , Fe^{+++} , NH_4^+ , Cl^- , SO_4^{--} , PO_4^{--} , but no org. matter) of animal C accelerate the hydrolytic deamination of phenylalanine and shift the position of the "unilateral" equilibrium, (I) acting like an enzyme which combines with or is adsorbed on the reaction product $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{OH}$. The other product is NH_4HCO_3 .

W. McC.

Glutathione as an inductor in the oxidation of lucose. C. C. PALIT and N. R. DHAR (J. Indian chem. Soc., 1934, 11, 661—669).—Glucose is oxidised by air at room temp. in presence of glutathione, especially when phosphates are added. Addition of $\text{Ce}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, or $\text{Cu}(\text{OH})_2$ increases the rate of oxidation. The induced reaction is further accelerated by light and by photosensitisers.

E. S. H.

Addition of gaseous hydrogen chloride and hydrogen bromide to propene under the influence of catalysts. Equilibrium α -bromopropene β -bromopropene. L. G. BROUWER and J. P. WIBAUT (Rec. trav. chim., 1934, 53, 1001—1010).—At room temp. HCl combines with CH_2CHMe slowly in presence of SiO_2 gel, more quickly if the latter is impregnated with a suitable metal chloride such as BiCl_3 . The product is mainly Pr^aCl (I) with no Pr^cCl (II). The reaction with HBr occurs smoothly in presence of purified SiO_2 gel at room temp., giving (I) as the main product, with 1—2% of (II). Neither reaction is affected by the presence of O_2 . The "peroxide effect" observed with HBr does not occur with HCl . At 250° and 275° the equilibrium proportions of (I) and (II) are about 2:1. The rate of transformation is very slow.

F. L. U.

Catalysts for elimination of carbon monoxide from nitrogen-hydrogen mixtures.—See B., 1934, 959.

Hydrogenation of sulphur-containing compounds. I. Mechanism of decomposition of thiophen in presence of sulphides of metals and hydrogen. II. Decomposition of various sulphur-containing compounds in presence of MoS_2 and hydrogen. B. L. MOLDAVSKI and Z. I. KUMARI (J. Gen. Chem. Russ., 1934, 4, 298—306, 307—309).—I. The catalytic action of sulphides on hydrogenation of thiophen to tetrahydrothiophen, BuSH , and C_4H_{10} and H_2S at $210\text{--}270^\circ/30$ atm. diminishes in the order $\text{MoS}_2 > \text{CoS} > \text{NiS} = \text{MnS} > \text{CdS}$. CuS is a negative catalyst at $> 250^\circ$, and a positive one at $< 250^\circ$.

II. The velocity of elimination of S from R_2S heated at $230^\circ/30$ atm. H_2 diminishes in the order $\text{R} = \text{CH}_2\text{Ph} > \text{CH}_2\text{CH} > \text{Et} > \text{Pr} > \text{iso-C}_5\text{H}_{11}$, and from RSH in the order $\text{R} = \text{Ph} > \text{Et} > \text{iso-C}_5\text{H}_{11}$.

R. T.

Mechanism of heterogeneous catalysis. E. AUDIBERT (Ann. Mines, 1933, [13], 4, 138—162; Chem. Zentr., 1934, i, 815).—Taylor's theory of active centres is criticised. The anomalies in the strength of the adsorption fields are assumed to depend on the local irregularities of crystal structure of the adsorbing atom. Promoters are substances which can form mixed crystals with the catalyst.

L. S. T.

Activity and structure of copper-zinc catalysts for the decomposition of methyl alcohol. N. N. ZOLOTOV and M. I. SCHAPIRO (J. Gen. Chem. Russ., 1934, 4, 679—682).— ZnO-CuO catalyst used for the decomp. of MeOH undergoes reduction at $< 220^\circ$, the CuO being reduced completely, and the ZnO partly. In consequence, α -brass is formed, the Zn content of which increases with duration of contact.

R. T.

Influence of certain physical and chemical factors on the activity of charcoal. V. Effect of treating charcoal with aqueous nitrates and oxidising salts on its adsorptive and catalytic activity. E. V. ALEXEEVSKI and A. P. MUSAKIN (J. Gen. Chem. Russ., 1934, 4, 669—678).—Highly active C is obtained by soaking ordinary wood C in aq. nitrates, ZnCl_2 , or KMnO_4 , and then washing with aq. HNO_3 . The adsorptive capacity (I) falls in the series $\text{KMnO}_4 > \text{ZnCl}_2 > \text{AgNO}_3 > \text{Schweitzer's reagent} > \text{Cu(NO}_3)_2 > \text{Al(NO}_3)_3 > \text{Fe(NO}_3)_3 > \text{Pb(NO}_3)_2 > \text{NH}_4\text{VO}_3 > \text{KNO}_3 > \text{KClO}_3 > \text{untreated C}$. The catalytic activity of the C in the reaction of decomp. of H_2O_2 varies inversely with the (I).

R. T.

Rapid catalytic preparation of sodamide in liquid ammonia.—See this vol., 1330.

Catalytic oxidation of trioses and related compounds.—See this vol., 1335.

Chlorination of naphthalene with chlorine.—See this vol., 1342.

Synthesis of acetone in presence of catalysts.—See this vol., 1336.

Heavy hydrogen. III. Electrolytic separation of the hydrogen isotopes. A. FARKAS and L. FARKAS. IV. Hydrogenation and exchange reaction of ethylene with heavy hydrogen. A.

FARKAS, L. FARKAS, and E. K. RIDEAL (Proc. Roy. Soc., 1934, A, 146, 623—629, 630—639).—III. In the electrolysis of a mixture of light and heavy H_2O a preferential liberation of H_1^2 takes place. The gas evolved may reach equilibrium with the H_2O , corresponding with the reaction $\text{H}_2\text{O} + \text{H}_1^2\text{H}^2 \rightleftharpoons \text{H}_1^2\text{H}_2\text{O} + \text{H}_2$, the equilibrium const. being about 3.8 at room temp.

IV. Two reactions are involved in the interaction of C_2H_4 with H_1^2 and H_2^2 at a catalytically active Ni surface; an exchange reaction $\text{C}_2\text{H}_4 + \text{H}_1^2\text{H}^2 \rightleftharpoons \text{C}_2\text{H}_3\text{H}^2 + \text{H}_1^2$, and the usual reaction $\text{C}_2\text{H}_4 + \text{H}_1^2\text{H}^2 \rightleftharpoons \text{C}_2\text{H}_5\text{H}^2$. The steric factors and the temp. coeffs. of these reactions are dissimilar.

L. L. B.

Electrolysis of salt solutions by means of electrodes immersed in distilled water. P. JOLIBOIS (Compt. rend., 1934, 199, 706—708).—Salt solution at the bottom of two beakers is covered with distilled H_2O without mixing—the two salt layers are joined by an inverted U. On electrolysis at 300 volts of Cu, Ni, Ag, Zn, Mg, U, and Th salt solutions with Pt electrodes in the distilled H_2O , colloidal hydrated oxide (I) of the metal is produced at the surface of separation salt solution- H_2O in the cathodic vessel. (I) then migrates to the cathode, and is deposited as such, or may be retained by a filter. Pb hydrated oxide passes through the latter, and gives some Pb on the Pt. With metals forming sol. oxides the anodic and cathodic H_2O contain after electrolysis acid and base, respectively. The basic and acidic portions of a salt may thus be separated without the formation of metal.

R. S. B.

Electrodeposition of chromium from aqueous chromic acid solutions containing hydrofluoric acid.—See B., 1934, 1015.

Europium, a rare member of the rare-earth group. B. S. HOPKINS (Trans. Electrochem. Soc., 1934, 66, 167—174).—The separation of Eu from Sm and Gd, and the properties of the metal and its compounds, are reviewed.

H. J. T. E.

Production of metals of the cerium group. F. TROMBE (Trans. Electrochem. Soc., 1934, 66, 231—235).—Recent work by the author and others on the electrolytic extraction of pure La and Nd from their fused chlorides and of pure Ce from a bath containing fused CeCl_3 , KCl , and CaF_2 is reviewed, and some properties of these metals are summarised.

H. J. T. E.

Formation of oxides of nitrogen in a high-current electric discharge. N. G. ZALOGIN and G. M. EGOROVA (J. Phys. Chem. U.S.S.R., 1934, 5, 20—31).—A max. yield of N oxides was obtained with 87—90% O_2 (6 mg. HNO_3 per litre of gas passed). Change of discharge strength at const. frequency changes the abs. yield, but not the mixture giving the max. yield. The yield increases with $[\text{O}_3]$ in the discharge, but the products are the same as those in absence of O_3 .

CH. ABS. (e)

Photolysis of water and the action of light on electrodes. R. AUDUBERT (J. Phys. Radium, 1934, [vii], 5, 486—496).—In order to investigate the action of light on electrodes, photo-potentials were measured using electrodes of Cu_2O , CuO , CuI , Ag_2S , and Hg_2I_2 .

in various org. solutions rendered conducting by the addition of NaI or KI. Data on the influence of electrode surface layers, activity of the metallic ions, $[H^+]$, and light intensity are tabulated. Theories of the mechanism are discussed. N. M. B.

Case of photochemical retardation of reaction. M. TRAUTZ and H. E. HAAS (Z. wiss. Phot., 1934, **33**, 129—144; cf. this vol., 1079).—The early experiments of Chastaing (Ann. Chim. Phys., 1877, **11**, 145), and of Thomas on the photochemical oxidation of $FeSO_4$, Na_2SO_3 , Cu_2Cl_2 , $MeCHO$, alkaline pyrogallol, and $PhCHO$, by light of different colours, have been repeated, using similar apparatus and procedure. The results are detailed. Some of the work of Trautz has also been tested. The case of $PhCHO$ has been established; blue light accelerates, and infra-red light retards, the oxidation. Some positive and some negative results were obtained with Na_2S solutions. Other cases showed no retardations. J. L.

Formation of carbonyl chloride from chloroform and oxygen sensitised by irradiated chlorine. H. J. SCHUMACHER and K. WOLFF (Z. physikal. Chem., 1934, **B**, **26**, 453—462).—The formation of CCl_4 from $CHCl_3$ and Cl_2 in light (this vol., 740) is suppressed in presence of O_2 and the above reaction occurs. The velocity is given by $d[COCl_2]/dt = kI_{abs}[CHCl_3]$, the temp. coeff. is 1.23 ± 0.05 , and the quantum yield at 65° and a $CHCl_3$ pressure of ~ 100 mm. is $260 \pm 15\%$. R. C.

Dependence of the gradation of photographic layers on the wave-length of light. F. BURKI and W. BRUCKNER (Helv. Chim. Acta, 1934, **17**, 1239—1262; cf. B., 1930, 486).—The blackening of five varieties of plates and cut films by light of λ 400—700 m μ has been measured. If the gradation G is plotted against time of exposure (t) and intensity (I), the I curves are steeper than the t curves, the Schwarzschild coeff. p being consequently > 1 . With emulsions of average sensitivity the difference between G vals. on the t and I scales is smaller for extreme than for intermediate wave-lengths. With the most sensitive panchromatic emulsions the differences between G_t and G_I are marked, but less variable, p being 0.66—0.86 compared with 0.51—0.97 for ordinary emulsions. With the most sensitive emulsions the limiting val. of G is attained much earlier with long than with short wave-length. In most cases the p - λ curve is a fairly exact mirror-image of the sensitivity curve. F. L. U.

Nature of colour-sensitising. Y. I. BOKINIK (Kino-Photo Ind., 1933, **3**, 84—89).—The mechanism of the energy transfer from the adsorbed dye to the $AgBr$ is discussed. CH. ABS. (e)

Photo-decomposition of formic acid vapour. E. GORIN and H. S. TAYLOR (J. Amer. Chem. Soc., 1934, **56**, 2042—2047).—The products of decomp. of single HCO_2H mols. (I) are (a) $CO + H_2O$, (b) $CO_2 + H_2$; the ratio is displaced in the direction of (b) by increase of light frequency or rise of temp. Double HCO_2H mols. (II) give (b) exclusively in the region 1900—2540 Å. Decomp. of the two mol. species is independent; the quantum yield is 1, independently of temp. and pressure over considerable ranges. The

ultra-violet absorption spectrum of (II) is continuous, whilst that of (I) is banded. E. S. H.

Photolysis of amides and amines in sunlight. G. G. RAO and K. M. PANDALAI (J. Indian Chem. Soc., 1934, **11**, 623—627).—The hydrolysis of aliphatic and aromatic amides is photo-sensitised by TiO_2 . The NH_3 formed is oxidised to NO_2' in the presence of $CaCO_3$. Aliphatic amines are more easily oxidised photosensitively with ZnO to NO_2' than are aromatic amino-derivatives. J. G. A. G.

Photolysis of amino-acids in sunlight. G. G. RAO and N. R. DHAR (J. Indian Chem. Soc., 1934, **11**, 617—622).—The rate of formation of NH_3 in the oxidation, photo-sensitised with TiO_2 , ZnO , and Al_2O_3 , of glycine and alanine is $>$ of aspartic and glutamic acids. It is inferred that the reaction proceeds $R \cdot CH \cdot NH_2 \cdot CO_2H + (O) \longrightarrow RCHO + NH_3 + CO_2$. o - $NH_2 \cdot C_6H_4 \cdot CO_2H$ probably first forms NH_2Ph and CO_2 , but hippuric acid does not react. The significance of these results in soil chemistry is considered. J. G. A. G.

Mutual influences of dyes and of fatty acids in photo-reactions. M. HORIO and S. MONDEN (J. Soc. Chem. Ind. Japan, 1934, **37**, 488—490B).—The photochemical formation of peroxide from linoleic acid is accelerated by the fluorescent dyes eosin (I) and erythrosin, but not by the non-fluorescent dye Victoria-blue (II), and the bleaching of (I) and (II) is accelerated by linoleic acid. Replacement of air by O_2 hinders the bleaching. A. G.

Photo-reactions of liquid and dissolved ketones. I. [Acetone and benzophenone.] E. J. BOWEN and E. L. A. E. DE LA PRAUDIERE. II. [Diacetyl.] E. J. BOWEN and A. T. HORTON (J.C.S., 1934, 1503—1504, 1505—1506).—The m.p. of $COPhMe$ and $COPh_2$ (I) were not changed by exposing the molten substances to the full light of the Hg arc, but (I) afforded benzpinacol in C_6H_6 and hexane (quantum efficiency, γ , 0.04), but not in CCl_4 . The rate of reaction of pure $COMe_2$ (γ 0.05) was in hexane or with added $MeOH$; diacetone alcohol was probably formed. Unlike the photo-reactions of the vapours, gases were not evolved either from these liquids or from liquid $MeCHO$. The results are consistent with the ketone having a primary non-reactive excited level, capable of deactivation on collision, which can pass into a second reactive level (which does not dissociate instantly) after approx. 10^{-12} sec.

II. Gas was not evolved from solutions of $[CHO]_2$ and Ac_2 irradiated with 4360—3660 Å. In hexane and Et_2O , Ac_2 polymerises and γ (0.9—0.1) decreases as the concn. is increased. The results are interpreted by the above hypothesis of two excited levels. J. G. A. G.

Heterogeneous and topochemical reactions. H. W. KOHLSCHUTTER (Angew. Chem., 1934, **47**, 753—756).—A lecture.

Separation of hydrogen isotopes by fractional desorption. H. S. TAYLOR, A. J. GOULD, and W. BLEAKNEY (Physical Rev., 1933, [ii], **43**, 496—497).—Desorption of electrolytic H_2 from adsorbent C at liquid air temp. gave a 3- to 5-fold enrichment of H^1H^2 over that initially present in the H_2 . L. S. T.

Effect of fractional crystallisation on the isotopic composition of water. E. S. GILFILLAN, jun. (J. Amer. Chem. Soc., 1934, 56, 2201).—Evidence is adduced to show that one crystallisation should change the d of ordinary H_2O by 0.22 ± 0.01 p.p.m.

E. S. H.

Preparation of water of minimum conductivity. K. GOSTKOVSKI (Z. physikal. Chem., 1934, 170, 149—152).—Triply distilled H_2O is cooled so that about half freezes, and the ice is then separated, melted, and distilled in vac. in an apparatus lined with paraffin wax. H_2O of conductivity almost as low as that of Kohlrausch and Heydweiller is obtained.

R. C.

Preparation of protium oxide and determination of the proportion of deuterium in the hydrogen of normal water. E. H. INGOLD, C. K. INGOLD, H. WHITAKER, and R. WHYTLOW-GRAY (Nature, 1934, 134, 661).—The d of purified H_2O practically free from H^2 has been compared by a float method with that of purified ordinary H_2O . The d of the nearly pure "light H_2O " ("protium oxide") is $<$ that of purified London and Leeds tap- H_2O by 12 p.p.m. at 20° . The d of these two tap-waters is identical and is taken as standard. The calc. mol. proportion of H_2O in the standard is approx. 1 in 9000, a proportion $<$ is usually assumed. The calc. at. wt. of H^1 is 1.00789 on the scale $O^{16}=16$ and corr. to the chemical scale by Mecke and Childs' factor this becomes 1.00767, or by Babcock and Naudé's factor, 1.00777.

L. S. T.

Reaction between sodium nitritopentacyanide and alkali sulphides. IV. G. SCAGLIARINI and F. MONFORTE (Atti R. Accad. Lincei, 1934, [vi], 20, 41—43; cf. A., 1931, 1013).—The coloured reaction product of $Na_2[Fe^{III}(CN)_5NO]$ with Na_2S is due to the formation by hydrolysis of $Na_4[Fe^{II}(CN)_5NO_2]$, which then reacts with the Na_2S to give $Na_4[Fe(CN)_5NOS]$.

O. J. W.

Copper carbonates. A. S. COCOSINSCHI (Bull. Soc. chim., 1934, [v], 1, 1065—1067; cf. A., 1930, 307).—Reply to a criticism by Poulenc-Ferrand (A., 1932, 1098).

F. L. U.

Copper carbonates. (MME.) POULENC-FERRAND (Bull. Soc. chim., 1934, [v], 1, 1067—1069).—A rejoinder to Cocosinschi (preceding abstract).

F. L. U.

Principles of the genetic development of material. VIII. V. KOHLSCHUTTER. **Chemical reactions in crystals.** III. Thermal decomposition of cupric formate. M. CHRISTEN [with (FRL.) L. JACUBOVICZ] (Helv. Chim. Acta, 1934, 17, 1094—1119; cf. A., 1933, 38).—The decomp. of different forms of $(HCO_2)_2Cu$ at 200° was studied by chemical analysis and microscopically in order to determine the influence of cryst. form on the course of the change. The compounds examined were $(HCO_2)_2Cu$ anhyd., and with 2 and $4H_2O$, $(HCO_2)_2Cu \cdot 2(HCO_2)_2Ba$ anhyd., and with $4H_2O$, and $(HCO_2)_2Cu \cdot 3Cu(OH)_2$. In no case did the reaction conform to either of the usual equations. The main gaseous product was CO_2 , with H_2 , CO , and CH_4 in proportions which varied with the nature of the solid. The residue was Cu in every case. No simple relation

between cryst. structure and the solid reaction was observed.

F. L. U.

Amphoteric behaviour of metal hydroxides. VII. Halogen hydroxo- and pyrocatechol hydroxo-salts of bivalent heavy metals. R. SCHOLDER (Z. anorg. Chem., 1934, 220, 209—218).—The following compounds have been prepared:

$Na_5[CuX(OH)_6(H_2O)_6] \cdot 6H_2O$ (X is Cl , Br , or I); $Na_3[ZnI(OH)_4(H_2O)_4] \cdot 8H_2O$; $Na_3[SnI(OH)_4(H_2O)_4]$; $Ba_{1.5}[Sn_2(OH)_6I(H_2O)]$ (the corresponding Sr compound loses 1 mol. H_2O when dried over H_2SO_4); $Na_2[Pb(C_6H_5O_2)(OH)_2] \cdot 4H_2O$; $Na_3[Zn(C_6H_5O_2)_2(OH)] \cdot 9H_2O$. $Ni(OH)_2$ dissolves in conc. $NaOH$ in presence of at least 0.5 mol. of pyrocatechol to 1 Ni to form a complex pyrocatechol-hydroxo-anion.

M. S. B.

Complex salts of 2 : 2'-dipyridyl with bivalent copper. F. M. JAEGER and J. A. VAN DIJK (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 395—400).—Aq. Cu malonate with 1, 2, and 3 equivs. of alcoholic dipyridyl (dipy) yields after heating, in each case, dark blue crystals of $[Cu, dipy, C_3H_2O_4, (H_2O)_2]$, sol. in $EtOH$, gives off H_2O at 95° , gradually changes in contact with aq. solution into $[Cu, dipy, (H_2O)_2] \cdot C_3H_2O_4$. Aq. $CuSO_4$ yields with 1 and 2 equivs. of cold alcoholic dipy pale blue crystals of $[Cu, dipy, SO_4] \cdot 2H_2O$, sparingly sol., gives off H_2O at 100° ; with 3 equivs., dark blue crystals of $[Cu, dipy_3]SO_4 \cdot 7H_2O$. Cold aq. $CuCl_2$ yields with 1 equiv. of alcoholic dipy green crystals of $[Cu, dipy, Cl_2]$, sparingly sol.; with 2 equivs. blue crystals of $[Cu, dipy_2, (H_2O)_2]Cl_2 \cdot 4H_2O$ or $[Cu, dipy_2]Cl_2 \cdot 6H_2O$, decomp. at 100° to give the mono-dipy salt; with 3 equivs., violet crystals of $[Cu, dipy_3]Cl_2 \cdot 7H_2O$. Crystal data are recorded in most cases.

R. S. B.

Energy of formation of magnesium oxide and its reduction by carbon. W. D. TREADWELL and J. HARTNAGEL (Helv. Chim. Acta, 1934, 17, 1372—1384).—The free energy of formation of MgO and of its reduction by C are calc. Experiments in which an equimol. mixture of MgO and C were heated by an arc in an atm. of A showed that reduction occurred readily, but about 75% of the Mg formed was re-oxidised by the CO in spite of rapid cooling.

F. L. U.

Preparation of phosphorescent substances.

VI. Zinc sulphide. N. F. SHIROV (J. Appl. Chem. Russ., 1934, 7, 343—358).—Of 61 mixtures examined, the most intense phosphorescence was given by the product of heating a mixture of Zn 2, S 1, H_3BO_3 0.3, and $ZnSiO_3$ 0.8 g. In general, the effect of adding ZnO , ZnF_2 , $ZnSiO_3$, $ZnHBO_3$, $ZnHPO_4$, $ZnHAsO_4$, $ZnMoO_4$, $ZnWO_4$, $ZnSe$, or $ZnTe$, or the corresponding Cd salts, is to increase the wave-length of the phosphorescence. The above method is not suitable for factory practice, owing to the violence of the reaction; activation of ZnS by ignition is recommended.

R. T.

Conditions of formation and certain properties of zinc nitride. V. A. SUCHONSKI and K. M. GORBUNOVA (J. Gen. Chem. Russ., 1934, 4, 587—593).—The products of condensation of Zn vapour in N_2 , or of passing NH_3 through molten Zn at 600° , contain

only traces of Zn_3N_2 , 5–40% yields of which are obtained from Zn dust and NH_3 at 550° . The heat of formation of Zn_3N_2 is 24,060 g.-cal.+28%. The dissociation const. of Zn_3N_2 has been calc. from Nernst's equation for the range $37\text{--}537^\circ$. R. T.

Sputtering applied to purification of mercury by electric arc still. R. K. COWSIK (Indian J. Physics, 1934, 9, 21–33).—An arc still fails to eliminate traces of Ag, Cu, and Sn, which are removed from Hg by a gas-heated still. These metals show marked sputtering in a discharge tube, and investigations with these metals and one such as Mg, which shows negligible sputtering, indicate that the impurity in the distillate from an arc must be due to sputtering at the cathode. Detailed purification of Hg and an automatic apparatus for circulating a fine spray of Hg through HgNO_3 solution are described.

N. M. B.

Action of mercuric oxide on cadmium chloride and of cadmium oxide on mercuric chloride. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 1099–1101).—The reaction is represented by $\text{CdCl}_2 + \text{HgO} + \text{H}_2\text{O} \rightleftharpoons \text{HgCl}_2 + \text{Cd(OH)}_2$. With excess of CdCl_2 , $\text{CdCl}_2 \cdot \text{Cd(OH)}_2 \cdot 6\text{H}_2\text{O}$ is formed. F. L. U.

Action of mercuric oxide on chlorides of silver, thallium, and lead. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 1085–1087).— HgO does not react in presence of H_2O with AgCl or TlCl . With PbCl_2 the reaction $\text{PbCl}_2 + \text{HgO} + \text{H}_2\text{O} = \text{Pb(OH)}_2 + \text{HgCl}_2$ occurs, $\text{PbCl}_2 \cdot 2\text{PbO}$ being formed as an intermediate product. F. L. U.

Action of mercuric oxide on cobalt chloride. E. MONTIGNIE (Bull. Soc. chim., 1934, [v], 1, 943–944).—The reaction $\text{HgO} + \text{CoCl}_2 \rightleftharpoons \text{HgCl}_2 + \text{Co(OH)}_2$ is reversible. With small quantities of HgO , $\text{CoCl}_2 \cdot 3\text{CoO} \cdot 3\text{H}_2\text{O}$ is formed, whilst with large quantities HgCl_2 separates. J. G. A. G.

Mercuric oxycyanide. F. C. J. BIRD (Quart. J. Pharm., 1934, 7, 581–583).— $\text{HgO} \cdot \text{Hg(CN)}_2$ is apparently decomposed in cold H_2O , since an insol. residue is obtained, but it is sol. in hot H_2O and remains in solution on cooling to 15.5° . Below 15.5° crystals separate. C. G. A.

Composition and stability of Donovan's solution. C. MORTON and F. R. C. BATESON (Quart. J. Pharm., 1934, 7, 447–452).—Cryoscopic, conductometric, and potentiometric measurements show that the addition of HgI_2 to aq. solutions of AsI_5 gives rise to the complex electrolyte $\text{HgI}_2 \cdot 2\text{HI}$ together with one containing more HI. C. G. A.

Reduction of aluminium oxide by carbon in the arc. W. D. TREADWELL and J. HARTNAGEL (Helv. Chim. Acta, 1934, 17, 1384–1389).—Experiments similar to those with MgO (this vol., 1317) were made with mixtures of Al_2O_3 and C. The sublimate contained Al and Al_4C_3 in approx. equal proportions. Use of a high vac. did not appreciably increase the yield of Al. F. L. U.

Reactions of aqueous solutions of aluminium and chromium salts when rendered basic and on gelatin and hide substance. A. KUNTZEL (Collegium, 1934, 518–533).—On addition of NaOH , a

cryst. ppt., which disappears after some time, is obtained from aq. $\text{Al(NO}_3)_3$, but a definite pptn. point is given by $\text{Cr(NO}_3)_3$. Al salts exert a strong buffering effect on NaOH whilst Cr salts exert much less. When rendered basic, Cr salts form monohydroxo-salts, and the conductivity titration curve shows a point of inflexion corresponding with this. Al salts do not form such basic salts, and their conductivity titration curve shows no inflexion. The hydrolysis of Cr salts finishes with the formation of basic salts and their condensation products. Al carbonato-complexes are very unstable, in contradistinction to those of Cr. The m.p. of gelatin can be raised to 100° by treatment with aq. Cr salts, but not with aq. Al salts. The so-called alum tannage is essentially a pickling effect. Technical alum leather is a combination tannage. Al salts combine with the surface only of the hide fibres and fibrils, whilst Cr salts, owing to their property of forming complexes, unite the principal valency chains in the collagen mols. D. W.

Systematic degradation of ultramarine-blue. K. LESCHIEWSKI and H. MÖLLER (Ber., 1934, 67, [B], 1684–1690).—Finely-divided ultramarine-blue (I) is boiled with successive quantities of $\text{NH}_2\text{Ph} \cdot \text{HCl}$ in H_2O containing an excess of NH_2Ph . The alkali (II) and S components of (I) are thereby independently degraded, nearly all the (II) and only about 0.25 of the S being removed. The final product (III) is grey and does not exhibit cryst. structure. It has distinctly acidic properties and becomes yellow when boiled with aq. NH_3 . (III) absorbs alkali from molten NaNO_3 , becoming green and bluish-green when washed and heated at 700° . Loss of (II) proceeds similarly to a washing-out process, and for this reason the blue colour of (I) disappears continuously without sharply-defined break. S and the SiO_2 skeleton appear closely allied. Disappearance of the lattice coincides with disappearance of the blue colour, which can persist or be developed only when S and (II) are present in a cryst. arrangement the structure of which is governed by the ultramarine lattice.

[With E. PODSCHUS.] Treatment of (I) with successive portions of boiling 5N- NaOH causes most removal of S in the initial stage, the filtrate from which is yellow and contains S'' and S_n'' . The filtrates from the succeeding stages are colourless and contain mainly SO_3'' , finally only in traces. Otherwise only loss of SiO_2 takes place, so that the ratio $\text{SiO}_2 : \text{Al}_2\text{O}_3$ is reduced from 1.2 to 1.0. The action of conc. NaOH on (I) therefore leads to a colourless compound, $\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{30}\text{S}$. Maintenance of the blue colour depends essentially on the existence of the ultramarine lattice. Both are completely stable in boiling 2.5N- NaOH , whereas in 5N- NaOH the colour is slowly discharged in consequence of a transformation of the lattice, but not of a decomp. H. W.

Measurements on bi- and quadri-valent compounds of the rare earths. V. Cerium tetrafluoride. W. KLEMM and P. HENKEL (Z. anorg. Chem., 1934, 220, 180–182).— CeF_4 is obtained as a white powder by the action of F₂ on CeCl_4 without the application of external heat, or of F₂ on Ce_2S_3 or Ce_2S_4 . It is not very sol. in H_2O , is stable at 400°

in a vac. and in H_2 at 200° , but is reduced at 300° to CeF_3 . It is practically non-magnetic. d varies considerably (3.1–4.7) according to the method of prep. Pr and Nd form the trifluorides only.

M. S. B.

Crystallisation of carbon under high pressures. J. BASSET (J. Phys. Radium, 1934, [vii], 5, 471–474).—Attempts have been made to crystallise C as diamond over wide ranges of pressure, temp., and time by the liberation of C by the reduction of metallic oxides in presence of C leading to the decomp. of carbide during cooling, by the decomp. of carbonates, org. and inorg. solid and liquid C compounds, metallic carbides, and gaseous compounds. In all cases there was no definite evidence of the formation of any modification other than graphite. N. M. B.

Oxidation of silicon at low temperatures. A. SANFOURCHE (Compt. rend., 1934, 199, 726–729).—Finely-divided Si readily oxidises at room temp. Samples of fused Si (I) and Si extracted from Si–Ag (II) and Si–Al (III) alloys were decomposed by heating in Cl_2 free from O_2 . The $SiCl_4$ formed was collected in H_2O and determined; the residue from the Si was SiO_2 . Fe formed $FeCl_3$ which condensed on the tube. (I), (II), and (III) contained, respectively, 0.46, 3.01, and 8.60% of SiO_2 [HNO_3 was used in preparing (III)]. This accounts for the supposed partial solubility of Si in HF.

R. S. B.

Volatile transport of silica. (FRL.) R. D. TERZAGLI (Amer. J. Sci., 1934, [v], 28, 391; cf. A., 1926, 36; 1929, 38, 1251).

C. W. G.

Modifications of lead oxide. K. SCHERINGA (Pharm. Weekblad, 1934, 71, 1197–1198).—Some samples of yellow PbO (I) turn red on keeping in subdued light due to the formation of Pb_3O_4 (II). The yellow form of (I) is obtained pure by crystallisation from hot 30% NaOH solution, in which the red form (III) is insol. (III) is obtained by boiling the pharmaceutical product with 50% NaOH. (III) reacts with acid benzidine solution alone; (II) reacts in presence of H_2O_2 and (I) fails to react. S. C.

[Constitution of azoimide and the azides.] A. HANTZSCH (Ber., 1934, 67, [B], 1674–1675; cf. A., 1933, 1129).—Polemical against Franklin (this vol., 477).

H. W.

Amphoteric oxide hydrates, solutions of their hydrolysing salts, and their high-molecular compounds. XXVI. Polyvanadates crystallising from aqueous solutions of potassium vanadate of different $[H^+]$. K. F. JAHR and G. JANDER (Z. anorg. Chem., 1934, 220, 201–208).—From feebly acid K vanadate solutions, the salts $K_3H_4V_5O_{16}$.aq. and $K_2H_5V_5O_{16}$.aq. crystallise. In strongly acid solutions, which contain excess of V, the compound $2K_2O.6V_2O_5$ forms crystals similar in form and colour to the other two salts, and there are grounds for supposing that it, also, is a salt of pentavanadic acid. The formation of this anhyd. salt from an aq. solution appears to indicate that H_2O is not necessarily essential for the formation of isopolyacids.

M. S. B.

Isolation of 0.1 gram of the oxide of element 91 (protoactinium). A. V. GROSSE and M. S. AGRUSS

(J. Amer. Chem. Soc., 1934, 56, 2200).—The working-up of Ra residues is described.

E. S. H.

Metallic element 91. A. V. GROSSE (J. Amer. Chem. Soc., 1934, 56, 2200–2201).—Pa has been prepared by two methods from Pa_2O_5 (cf. preceding abstract). The metal does not oxidise in the air.

E. S. H.

Chromic anhydride. G. A. KIRKHOF, O. I. KORZINA, and K. Y. ASTROVA (Khim. Farm. Prom., 1934, 1, 38–40).—Technical $Na_2Cr_2O_7$ (1 mol. in 440 c.c.) is aged for 2 days at -5° with 1 mol. of H_2SO_4 , Na_2SO_4 is sucked off, and the filtrate treated with H_2SO_4 . Cr_2O_3 is centrifuged off. Alternatively $CaCrO_4$ is pptd. from a neutral solution by $CaCl_2$, converted into $CaCrO_4.0.5H_2O$ by boiling, washed, and decomposed by H_2SO_4 . $CaSO_4$ is separated and the filtrate treated with H_2SO_4 as above.

CH. ABS. (c)

Sodium paratungstate. R. H. VALLANCE and E. G. K. PRITCHETT (J.C.S., 1934, 1586–1588).—Electrometric and refractivity experiments establish that the cryst. products of the titration of hot aq. Na_2WO_4 with HCO_2H and 1 : 1 aq. HCl are identical. The product, $Na_{10}(W_{12}O_{41}).28H_2O$ (I), does not contain acidic or nuclear H. The max. increase in the rotatory power of tartaric acid does not coincide with the addition of a simple mol. proportion of (I), and micelle formation probably accompanies chemical combination between the reactants. J. G. A. G.

Preparation of fluorine. A. TIAN (Bull. Soc. chim., 1934, [v], 1, 1010–1014).—Earlier methods (A., 1926, 139; 1931, 1248; B., 1927, 297) are reviewed and modified. F_2 is determined by reaction with dry KI.

J. G. A. G.

Damp mixtures of chlorates and sulphur and other reactions of damp chlorates. J. AMIEL (Compt. rend., 1934, 199, 787–789).—A reply to Taradoire (this vol., 1186).

H. J. E.

Direct oxidation of iodine and iodides at high pressures. J. BASSET and M. DODE (Compt. rend., 1934, 199, 668–670).—On heating I in O_2 or O_2+N_2 at 250 – 400° for 1–4 hr. at pressures of $O_2 > 2000$ kg. per sq. cm., 0.2–2% of I_2O_5 is formed. Under similar conditions KI forms KIO_3 , a 90% yield of almost colourless KIO_3 being formed in 5–6 hr. at 410° .

H. J. E.

IF_5 , IOF_3 , and the possibility of the production of lower iodine fluorides. O. RUFF and A. BRAIDA (Z. anorg. Chem., 1934, 220, 43–48).— IF_5 has d^{20}_{40} 3.75 approx., d^{193}_{40} 4.07; m.p. 9.6° ; b.p. $98 \pm 1.5^\circ$. If p is the v.p., $\log p = 11.764 - 3035/T$ and $8.3 - 2205/T$ for solid and liquid IF_5 , respectively. IOF_3 has been obtained as fine white crystals by the action of IF_5 on I_2 and F_2 containing O_2 , at the temp. of liquid air. It is decomposed at 400° and by numerous reagents. It behaves differently from the previously known $IOF_3.5H_2O$. No proof of the existence of lower fluorides has been obtained.

M. S. B.

Structure of oxides of manganese, and the rational analysis of manganese ores. A. M. ZANKO and V. F. STEFANOVITSCH (J. Gen. Chem. Russ., 1934, 4, 404–407).—Potentiometric data indicate that Mn_3O_4 reacts in hot $2N-H_2SO_4$ as

follows: $\text{Mn}_2\text{O}_3 + 4\text{H}_2\text{SO}_4 \longrightarrow \text{MnSO}_4 + \text{Mn}_2(\text{SO}_4)_3$ (I) $+ 4\text{H}_2\text{O}$; (I) $+ 3\text{H}_2\text{O} \longrightarrow \text{MnSO}_4 + \text{H}_2\text{MnO}_3 + 2\text{H}_2\text{SO}_4$. Potentiometric titration of Mn^{III} in Mn ores is recommended. R. T.

Chemistry and electrochemistry of rhenium. IV. Action of reducing agents on sulphuric acid solutions of potassium perrhenate. H. HOLEMANN (Z. anorg. Chem., 1934, 220, 33—42).— KReO_4 can be titrated potentiometrically in H_2SO_4 solution to Re^{VI} , Re^{V} , or Re^{IV} , depending on the reducing agent employed. The acid concn. must always be higher than for reduction in HCl solution. FeSO_4 , SnSO_4 , and $\text{Ti}_2(\text{SO}_4)_3$ reduce to the Re^{V} stage, and the course of the titration can be followed by the colour changes only, and not by any sudden change of potential. CrSO_4 reduces Re^{VII} to Re^{IV} , but the intermediate Re^{VI} and Re^{V} stages can be recognised in conc. acid solution only. CrSO_4 is, on the whole, less suitable for potentiometric reduction than CrCl_2 . The valency stages and the related colour changes can also be observed in the reverse direction by oxidation with KMnO_4 . M. S. B.

Quinquevalent rhenium. W. F. JAKÓB and B. JEZOWSKA (Z. anorg. Chem., 1934, 220, 16—30).—The production of Re^{V} as the first stage in the reduction of Re^{VII} by 2 equivs. of HI (cf. A., 1933, 1254) is confirmed. The next stage is the reduction by a third equiv. of HI to Re^{IV} , which may also be obtained by the decomp. of Re^{V} compounds as follows: $3\text{Re}^{\text{V}} \rightarrow 2\text{Re}^{\text{IV}} + \text{Re}^{\text{VII}}$. The equilibrium moves to the left in strongly acid solution at room temp. The valency of Re in its compounds can be determined by both iodometric and oxidation methods. By the action of conc. HCl and KI on HReO_4 , K_2ReOCl_5 is obtained as yellowish-green crystals stable in dry air. The morphological characteristics of the crystals are given. In HCl solution the colour changes from yellow to bluish-green as the concn. of acid diminishes. Conc. H_2SO_4 gives a reddish-brown solution. A strongly acid solution is stable in air, but gives HReO_4 with oxidising agents. Acid solutions, on dilution, ppt. a black hydroxide $\text{ReO}_2 \cdot x\text{H}_2\text{O}$, and with H_2S a black sulphide. The compound previously described as $\text{K}_2[\text{Re}(\text{OH})_2\text{Cl}_5]$ (*loc. cit.*), is probably $\text{K}_2\text{ReOCl}_5 \cdot \text{H}_2\text{O}$. $(\text{NH}_4)_2\text{ReOCl}_5$ has also been obtained as greenish-yellow crystals isomorphous with the K salt. The relation between the salts X_2ReOCl_5 and the ReCl_5 prepared by Geilmann *et al.* (A., 1933, 1259) is indicated. M. S. B.

Preparation of perrhenic acid. J. T. DOBBINS and J. K. COLEHOUR (J. Amer. Chem. Soc., 1934, 56, 2054).— HReO_4 is prepared by oxidation of ReO_2 with H_2O_2 . E. S. H.

Preparation of a stable form of ferrous chloride. F. E. CARTER (Quart. J. Pharm., 1934, 7, 389—391).—Solutions of FeCl_2 can be stabilised against oxidation by addition of 1% (wt./vol.) of citric acid. C. G. A.

Ferromagnetic variety of iron sesquioxide. H. FORESTIER and G. GUIOT-GUILLAIN (Compt. rend., 1934, 199, 720—723).—A new ferromagnetic variety of Fe_2O_3 has been prepared by decomp. of $\text{Fe}_2\text{O}_3 \cdot 4\text{BeO}$ (I). The ppt. obtained by adding aq. $\text{Fe}(\text{NO}_3)_3$ +

aq. $\text{Be}(\text{NO}_3)_2$ to aq. NH_3 is dried and becomes magnetic when heated at 720° for 6 min., with a Curie point at 220° , but long heating above 700° destroys the magnetism. There is a second Curie point at 675° , when stable Fe_2O_3 is formed. X-Ray analysis suggests that the magnetic material consists of BeO, and rhombohedral Fe_2O_3 corresponding with slightly deformed oligist (II). (II) can be isolated by dissolving the BeO in dil. HCl, and has the same magnetic properties as decomposed (I). R. S. B.

Behaviour of ferrous salt solutions on oxidation with bromine. RODT and CHARISIUS (Mitt. Materialprüf., 1934, 271).—When aq. FeBr_3 is boiled Br is slowly evolved, and if the solution is evaporated to dryness the residue consists almost entirely of FeBr_2 and not of Fe_3Br_8 as stated in the lit. These facts should be borne in mind in the iodometric determination of Fe^{III} after oxidation of Fe^{II} with Br.

A. R. P.
Separation of metallic sulphates by selective dissociation. L. WÖHLER and K. FLICK (Ber., 1934, 67, [B], 1679—1683).—The total tensions of NiSO_4 and CoSO_4 have been measured by the air-buffer method; the production of basic sulphates is not observed. The following quant. separations of metallic sulphate have been effected by selective dissociation of sulphate mixtures in a current of SO_3 at temp. $> 800^\circ$ and in SO_2 - O_2 mixtures at higher temp.: Co and Ni; Fe and Zn; Fe and Ti; Fe and Al; Fe and Mn; Zn and Mn; Cr^{III} and Al; Cr^{III} and Fe^{III} . Al, Fe, and Ti are quantitatively isolated from bauxite and total Ti from the red residue of the Bayer process for the prep. of Al_2O_3 . H. W.

Complex periodides. II. G. SPACU and P. SPACU (Bul. Soc. Științe Cluj, 1934, 7, 367—373; Chem. Zentr., 1934, ii, 582; cf. this vol., 41).—The following compounds have been prepared:
 $[\text{Co en}_2(\text{NO}_2)_2]\text{I}_3$, $[\text{Co en}_2(\text{NO}_2)_2]\text{I}_2$,
 $[\text{Co en}_2(\text{CNS})_2]\text{I}_2$, $[\text{Co en}_2(\text{CNS})_2]\text{I}_3$,
 $[\text{Co en}_2(\text{Cl})_2]\text{I}_2$, $[\text{Co en}_2\text{I}_2]\text{I}_2$,
 $\{\text{Co}[\text{Co}(\text{OH})_2\text{en}_2]\text{I}_6$, I_3 , and $[\text{Cr en}_3]\text{I}_3 \cdot 2\text{I}_2$.
H. J. E.

Substituted cyanocobaltates. Diaquotetra-cyanocobaltic acid. Cobaltic cyanide. P. R. RAY and T. GUPTACHAUDHURI (Z. anorg. Chem., 1934, 220, 154—162).—By oxidation of 2SO_3 in $\text{Na}_5[(\text{SO}_3)_2\text{Co}(\text{CN})_4]$ (A., 1933, 476) and subsequent removal and replacement by $2\text{H}_2\text{O}$, the salt $\text{Na}[(\text{H}_2\text{O})_2\text{Co}(\text{CN})_4]\text{H}_2\text{O}$ is obtained. The Ag, K ($0.75\text{H}_2\text{O}$), NH_4 , Li ($3.5\text{H}_2\text{O}$), Ba ($3.5\text{H}_2\text{O}$), Sr ($1.5\text{H}_2\text{O}$), and Ca ($3.5\text{H}_2\text{O}$) salts have been obtained and also the compound $(\text{PbO}_2) \cdot \text{Pb}[(\text{H}_2\text{O})_2\text{Co}(\text{CN})_4]_2$ and the free acid. The acid and its salts cannot be cryst. from solution, but on evaporation they give a red glass suggesting the probability of polymerisation. This view is supported by electrical conductivity data, which indicate a basicity of approx. 3, and by determinations of d which show that the mol. vol. of the anion is small. By heating $\text{H}[(\text{H}_2\text{O})_2\text{Co}(\text{CN})_4]$, deep blue $\text{Co}(\text{CN})_3$ is formed. It is insol. in H_2O , but is gradually transformed into red $\text{Co}(\text{CN})_3 \cdot 2\text{H}_2\text{O}$. The transition temp. to anhyd. $\text{Co}(\text{CN})_3$ is 118° . The magnetic susceptibility of the hydrate, 14.61, is only slightly $>$ that of the anhyd. salt, 13.58. M. S. B.

Complex cobaltioxalates. G. SPACU, J. G. MURGULESCU, and M. VANCEA (Z. anorg. Chem., 1934, 220, 1—15).—Measurements of the electrical conductivity and extinction coeff. of solutions of Durrant's salt show its constitution to be

$[(C_2O_4)_2Co(OH)(OH_2)]K_2$ (I). The action of acids results in the following decomp.: $(I) + HCl = [(C_2O_4)Co(OH_2)_2]K$ (II) + KCl and $2(II) = 2CoC_2O_4 + K_2C_2O_4 + 2CO_2 + 4H_2O$. The decomp. of (II) is shown by the spectro-photometric method to be unimol. The results have been confirmed by a comparison of the absorption spectra of chromioxalates and cobaltioxalates. No salts of the ion $[(C_2O_4)_2Co(OH_2)]'$ could be pptd. M. S. B.

Stability of $[Co(NH_3)_6](NO_3)_3$ in water containing H_2O . H. ERLÉNMEYER and H. GARTNER (Helv. Chim. Acta, 1934, 17, 1008—1010; cf. preceding abstract).—Dissolution of $[Co(NH_3)_6](NO_3)_3$ in H_2O containing H_2O , followed by recovery of the H_2O , shows that complete exchange occurs between the H of the H_2O and of the NH_3 . Similar exchangeability of H atoms in the NH_3 of the solid crystals could not be detected. F. L. U.

Isolation of precipitates in quantitative analysis by centrifuging. A. I. AMANTOV (J. Appl. Chem. Russ., 1934, 7, 630—631).—Centrifuging is in many cases preferable to filtration. R. T.

Rational concentration of solutions for titration. S. K. TSCHIRKOV (J. Appl. Chem. Russ., 1934, 7, 646—655).—The optimum concn. of standard solutions is, for acids, $N = (K[HR] - [R']\sqrt{k_w})Va/[R']$, and for alkalis, $N = ([R'] - K[HR]\sqrt{k_w})Va/[K[HR]]$, where K is the dissociation const. of the indicator HR , k_w that of H_2O , V is the final vol. of the solution, and a the no. of drops delivered per ml. of standard solution. R. T.

Magneto-optic method of chemical analysis. F. G. ŠLACK (J. Franklin Inst., 1934, 218, 445—462).—Work on time lags in the Faraday effect and the magneto-optic method of chemical analysis is reviewed. Min. were observed, but no positive conclusions could be reached. Observed phenomena are described as a type of N -ray phenomena and are subject to the same physiological and psychological effects. W. R. A.

Comparison of the colorimetric, electrometric, and catalytic methods for determining hydrogen-ion concentration. M. KILPATRICK, E. F. CHASE, and L. C. RIESCH (J. Amer. Chem. Soc., 1934, 56, 2051—2053).—Tests on $AcOH$ - $NaOAc$ solutions by the three methods give concordant results. The classical dissociation const. of $AcOH$ increases slightly between 25° and 35° . E. S. H.

Determination of acidity in non-aqueous solutions. O. TOMIČEK and J. FELDMANN (Coll. Czech. Chem. Comm., 1934, 6, 408—421).—Acid-alkali titrations in simple alcohols, C_6H_6 , $COMe_2$, and similar org. solvents and their mixtures have been studied by the indicator and potentiometric methods. Besides the H_2 and quinhydrone electrodes the Sb and Te electrodes are suitable. The Te electrode is serviceable in non-aq. solutions over the range p_H 5.3—11.5. E. S. H.

Photometric micro-analysis of water. XII. Iron.—See B., 1934, 1038.

Micro-titration of bromides and iodides in presence of chlorides. I. BELLUCCI (Gazzetta, 1934, 64, 688—695).—The aq. solution of the three halides is acidified slightly with H_2SO_4 and a few cg. of $NaNO_2$ are added. The liberated I is separated by means of CCl_4 and titrated with $0.002N$ - $Na_2S_2O_3$. The aq. layer is made slightly alkaline with $NaOH$, evaporated to dryness on the H_2O -bath, and the bromide dissolved out with $COMe_2$ and titrated by Volhard's method using $0.01N$ - $AgNO_3$. O. J. W.

Microchemical detection of elementary sulphur. A. SCHONBERG (Nature, 1934, 134, 628).—A well-ground mixture of the specimen and $CH_2Ph \cdot N \cdot C(C_6H_4 \cdot OMe \cdot p)_2$ (from $CH_2Ph \cdot NH_2$ and dianisyl ketone chloride, or from the ketone and $CH_2Ph \cdot N_3$) is heated in a m.-p. tube to 210° for 5 min. and then extracted with C_6H_6 . If the unknown contains elementary S (< 0.04 mg.) the extract is coloured blue owing to the formation of pp' -dianisyl thioketone (I). When a crystal of $HgCl_2$ is added, the blue colour decreases in intensity within a few hr., and its surface is coloured an intense red owing to the formation of an additive compound of (I) and $HgCl_2$. L. S. T.

Detection of sulphurous acid and its salts and of tin. H. FREYTAG (Ber., 1934, 67, [B], 1477—1480).—The green photo-product of 2-benzylpyridine (A., 1933, 1256) becomes red in presence of traces of SO_2 . The moist reagent paper is adapted for the detection of S in org. compounds and natural sulphides which are burnt in air, and for the detection of sulphites from which SO_2 is best liberated by acids and detected in the gas phase. Sn^{II} as $SnCl_2$ in HCl causes similar change from green to red. H. W.

Colour reaction for sulphites. Z. RUDNITSKI (J. Appl. Chem. Russ., 1934, 7, 402—405; cf. A., 1933, 687).—The reaction serves for the detection of $< 5 \times 10^{-5}$ g. of SO_3'' in 100 ml. of solution. Heavy metals and CN' , but not other ions, interfere. R. T.

Determination of substances in low concentration. V. Sulphates, sulphites, and sulphides. M. V. ALEXEEVA (J. Appl. Chem. Russ., 1934, 7, 616—622).—Köszegi's method (A., 1929, 782) serves for determination of 0.01—0.1 mg. of SO_4'' . 0.002—0.01 mg. of H_2S in 10 ml. of solution can be determined by Mecklenburg and Rosenkranzer's method (A., 1914, ii, 380). Gurevitch's method (A., 1930, 879) for the simultaneous determination of S'' and SO_3'' gives good results when the SO_4'' produced is determined nephelometrically. R. T.

Determination of sulphate in water-soluble sulphates. L. SUMEGI (Magyar chem. Fol., 1933, 39, 180; Chem. Zentr., 1934, i, 3088).—Excess of aq. $BaCl_2$ of known concn. is added. Excess of $BaCl_2$ is pptd. as $BaCO_3$ with $(NH_4)_2CO_3$, the ppt. being added to a known vol. of N - HCl and the excess of HCl determined with N - $NaOH$. H. J. E.

Potentiometric determination of selenocyanate in the presence of iodide. G. SPACU and P. SPACU (Z. anal. Chem., 1934, 98, 179—183).—The titration

is made in a neutral solution containing MgSO_4 using 0.1N- AgNO_3 and a Ag wire indicator electrode. Mechanical agitation is necessary to overcome adsorption of iodide by the AgI ppt. The potential of pptn. of AgI is -0.16 volt and that of AgCNSe $+0.06$ volt against the N- Hg_2Cl_2 electrode.

A. R. P.

Gravimetric determination of tellurium as dioxide by means of pyridine. A. JILEK and J. KOTA (Coll. Czech. Chem. Comm., 1934, 6, 398—407).— TeCl_4 is dissolved in HCl containing NH_4Cl , the solution is almost neutralised with aq. NH_3 , Me-orange is added, and $\text{C}_5\text{H}_5\text{N}$ run in dropwise until the colour change is complete. The cryst. ppt. of TeO_2 is collected in a Gooch crucible, dried rapidly at 120° , and weighed.

E. S. H.

Determination of nitrate-nitrogen by the Devarda process.—See this vol., 1422.

Colour reactions of solutions of some organic substances in concentrated sulphuric acid with nitrates and other oxidising agents. M. EITEL (Z. anal. Chem., 1934, 98, 227—234).— H_2SO_4 solutions of phenols and quinones not substituted in the nucleus give colour reactions with NO_3^- (I), to a smaller extent with other oxidising agents, but not with NO_2^- . *p*-Benzoquinone (about 0.01% solution) gives a reddish-brown colour; the blackish-green (0.02%) solution of phenanthraquinone shows a reddish colour with traces of (I) in solid substances. Diphenylglycine [colourless 0.1% H_2SO_4 solution (II)] gives a sensitive green coloration with aq. solutions of (I). 10 mg. of (I) per litre of solution may be detected by adding 1 c.c. to 5 c.c. of H_2SO_4 + 10 drops of (II). Benzidine similarly detects 0.1 mg. of (I) per litre, and 2:7-diaminofluorene (III) 0.001 mg. per litre. NO_3^- and $\text{K}_2\text{S}_2\text{O}_8$ give reddish-yellow colorations with (III).

J. S. A.

Detection of nitrates and iron in water.—See B., 1934, 990.

Determination of cyanide-nitrogen by the Kjeldahl method. A. TETTAMANZI (Atti R. Accad. Sci. Torino (Cl. Sci. fisich.), 1932—1933, 68, 153—160; Chem. Zentr., 1934, i, 2166).—N in both simple and complex cyanides may be determined by the Kjeldahl method. NaCN and KCN must be examined as solids. HCN is evolved from their solutions. $\text{K}_2\text{Pt}(\text{CN})_4$ is exceptional. After long heating with conc. H_2SO_4 , $\text{Pt}(\text{CN})_2$ is pptd. on dilution.

H. J. E.

Colorimetric micro-determination of arsenic.—See this vol., 1422.

Determination of arsenic in sulphur.—See B., 1934, 960.

Determination of arsenic, antimony, tin, and bismuth in lead glances and similar minerals. H. BILTZ and K. HOEHNE (Z. anal. Chem., 1934, 99, 1—12).—The application of the procedure of A., 1930, 1144 to the determination of As, Sb, and Sn in various Pb glances is described. For the determination of Bi, the mineral is dissolved in HCl and evaporated with HNO_3 . The solution is neutralised with Na_2CO_3 and just re-acidified (Me-orange). Bi is then pptd. by a suspension of HgO , redissolved in HNO_3 , and

evaporated down with H_2SO_4 . Any PbSO_4 is removed and Bi in the solution determined colorimetrically.

J. S. A.

Chemical and microscopical determination of arsenic, antimony, tin, and bismuth in the chief Silesian lead sulphides. K. HOEHNE (Chem. Erde, 1934, 9, 219—268).—The results of microscopical examination and chemical analysis of 111 different specimens of mineral PbS , 14 samples of ZnS , and other minerals are described. Methods of determining As, Sb, Sn, and Bi, present as impurities, are recommended from among those published; the accuracy attainable is As 0.01, Sb 0.03, Sn 0.005, Bi 0.002—0.005%. The geological significance of these impurities is discussed.

E. S. H.

Complex mercury-arsenic compounds and their identification. H. KUHL and B. CZYŻEWSKY (Pharm. Zentr., 1934, 75, 660—666).—Satisfactory As mirrors are unobtainable in the Marsh test when Hg is present. This is due to the formation of a stable, black amalgam. Microscopic evidence is given of the formation of Hg-As double salts. Hg As sulphate when heated gives Hg_3AsO_4 and a sublimate consisting of characteristic octahedral crystals of $\text{As}_2(\text{SO}_4)_3$ surrounded by haloes of yellow HgO .

S. C.

Colorimetric determination of silica in boiler water.—See B., 1934, 991.

Use of boron trioxide in determination of minerals. H. VERSLUYS (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 407—408).—A review and extension of the use of B_2O_3 as a flux for examining minerals by bead tests.

R. S. B.

Volumetric determination of potassium with methylene-blue following its precipitation as potassium picrate. A. BOLLIGER (J. Biol. Chem., 1934, 107, 229—234).—K is pptd. as picrate by an EtOH solution of Ca picrate and the ppt. titrated with a standard methylene-blue solution (this vol., 47, 1017). The method is applicable to solutions containing twice as much Na as K (0.04—10 mg. K).

C. G. A.

Standard carbonate-free sodium hydroxide solutions. W. W. KAY and H. L. SHEEHAN (Biochem. J., 1934, 28, 1795—1797).— CO_2 -free NaOH is prepared by pptn. of Na_2SO_4 with $\text{Ba}(\text{OH})_2$.

H. G. R.

Standardisation of sodium thiosulphate solution by means of $\text{Cu}(\text{NH}_4)_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. A. V. FILOSOFOV (J. Appl. Chem. Russ., 1934, 7, 628—629).—Aq. $\text{Na}_2\text{S}_2\text{O}_3$ is conveniently standardised by means of $\text{Cu}(\text{NH}_4)_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$.

R. T.

Optimum conditions of precipitation of sodium silicofluoride. V. J. ANOSOV and S. K. TSCHIRKOV (J. Appl. Chem. Russ., 1934, 7, 503—508).— Na_2SiF_6 is obtained in 90% yield by adding a 50% excess of 20% aq. NaCl to 5—6% aq. H_2SiF_6 , pptn. being complete after 5 min.

R. T.

Determination of calcium and magnesium. A. M. VASILIEV and R. G. HENDEL (Zavod. Lab., 1933, No. 5, 12—14).—Ca is pptd. as CaC_2O_4 , and, without filtering, Mg as MgNH_4PO_4 ; the washed ppt. is dissolved in H_2SO_4 , the phosphate titrated

with NaOH (Me-orange), and the $\text{H}_2\text{C}_2\text{O}_4$ with KMnO_4 .
CII. Abs.

Volumetric determination of cadmium. G. SPACU and M. KURAŠ (Z. anal. Chem., 1934, 99, 26—28).—To the Cd^{++} solution is added excess of 0.1N- NH_4CNS and $\text{C}_5\text{H}_5\text{N}$, pptg. $\text{Cd}(\text{CNS})_2 \cdot 2\text{C}_5\text{H}_5\text{N}$. The liquid is filtered, $\text{C}_5\text{H}_5\text{N}$ neutralised with HNO_3 (using α -dinitrosophenol), and the excess of CNS^- titrated back with AgNO_3 using diphenylcarbazone as indicator.
J. S. A.

Volumetric determination of lead. I. TANA-NAEV (Z. anal. Chem., 1934, 99, 18—22).—Pb is pptd. as PbFCl from neutral (Me-orange) solution by addition of $\text{NaF} + \text{NaCl}$, each 0.2N. Excess of Cl^- or F^- is titrated back with AgNO_3 or AlCl_3 , respectively. Cu or Zn does not interfere.
J. S. A.

Potentiometric titration of thallic salts by sodium thiosulphate. F. ČUŤA (Coll. Czech. Chem. Comm., 1934, 6, 383—397).— Ti^{+++} is reduced by $\text{S}_2\text{O}_3^{--}$ at 90° in presence of HgI_2 as catalyst according to the equation $4\text{Ti}^{+++} + \text{S}_2\text{O}_3^{--} + 5\text{H}_2\text{O} = 4\text{Ti}^+ + 2\text{SO}_4^{--} + 10\text{H}^+$. The reaction can be used for determining Ti^{+++} by electrometric titration with $\text{Na}_2\text{S}_2\text{O}_3$, using a Pt electrode. The mean error is about $\pm 0.66\%$. The titration can be carried out in presence of Br , Cl_2 , Cl^- , Br^- , Hg^{++} , Cd^{++} , SO_4^{--} , PO_4^{--} , and ClO_4^- , but Cu^{++} , Fe^{+++} , and As^v interfere.
E. S. H.

Application of electrolytic reduction methods in analytical chemistry. III. Direct determination of copper and iron by electrolytic precipitation and reduction. G. GALFAJAN (Z. anal. Chem., 1934, 99, 32—34; cf. A., 1933, 138).—Cu may be deposited and Fe^{+++} simultaneously reduced in 10—20% H_2SO_4 solution, using a Pt cathode.
J. S. A.

Quantitative precipitation of copper with gallotannic acid. M. B. DARBINIAN and A. G. KANKANIAN (Z. anal. Chem., 1934, 99, 29—32).—Gallotannic acid ppts. Cu quantitatively in presence of NH_4OAc , but not in ammoniacal solution. Cu^{++} is thereby reduced to Cu^+ .
J. S. A.

Coloured precipitate for colorimetric determinations. V. CUVÉLIER (Z. anal. Chem., 1934, 99, 15—18).—Co-pptn. of Cu or Co with Zn as $\text{ZnHg}(\text{CNS})_4$ gives mixed crystal ppts. of colour \propto the Cu (Co) content. Incomplete pptn. with insufficient $(\text{NH}_4)_2\text{Hg}(\text{CNS})_4$ leads to increased sensitivity by concentrating the Cu in the ppt. relative to the Zn. The sensitivity for Cu is $>$ in colorimetry with aq. NH_3 .
J. S. A.

Spectrographic detection and determination of minute quantities of impurities in copper.—See B., 1934, 965.

Determination of copper in red lead.—See B., 1934, 971.

Electrolytic determination of copper in aluminium alloys.—See B., 1934, 1015.

Alkalimetric determination of mercury as amido-compounds. S. ŠKRAMOVSKÝ and R. UZEL (Časopis. czechoslov. Lék., 1934, 14, 33—45).—The amido-compound (I) is pptd. from HgCl_2 solution by treatment with NH_3 in the presence of alkali chloride and hydroxide. After brief heating excess of

NH_3 is neutralised (cold) with HCl . Addition of $\text{S}_2\text{O}_3^{--}$ or I^- produces the complex $\text{Hg}(\text{S}_2\text{O}_3)_2^{--}$ or HgI_4^{--} with the liberation of $2(\text{OH}^-)$ for each Hg^{++} present. The liquid is then titrated with HCl or H_2SO_4 (Me-red). In the analysis of HgCl_2 tablets eosin must be destroyed by KClO_3 or alternatively bromocresol-green or Congo-red may be used as indicator. Any Hg or Hg_2Cl_2 present in the sample is converted into HgCl_2 by HCl-HNO_3 prior to pptn. of (I).
A. G. P.

Detection of mercury in presence of all the cations. M. SCHTSCHIGOL (Khim. Farm. Prom., 1934, No. 1, 44—45).—The sample is treated with excess of 10% KI and 30% NaOH , heated, and filtered. The filtrate containing K_2HgI_4 is treated with 1 c.c. of glycerol and 2—3 c.c. of aq. NaOH , and boiled for several min. Darkening of the solution or a black ppt. indicates Hg .
CH. Abs. (e)

Pyroelectric concentration for the spectral determination of Y, La, and other rare earths in lead minerals. S. PIÑA DE RUBIES and J. DOETSCH (Z. anorg. Chem., 1934, 220, 199—200).—About 1 g. of the mineral is volatilised in the arc and two or three spectrum photographs are taken during the process. The rare earths begin to emit when a considerable portion of the mineral has been volatilised and they have become more conc. Y, La, Yb, Gd, and Er only have, so far, been definitely shown to be present by this method.
M. S. B.

Determination of aluminium in aluminium and its alloys.—See B., 1934, 890.

Detection of small quantities of indium, gallium, and thallium. E. PIETSCH and W. ROMAN (Z. anorg. Chem., 1934, 220, 219—224).—A pptn. method for the detection of In, Ga, or Tl by the use of quinizarin in presence of aq. NH_3 and NH_4Cl is described. It is very much less sensitive for Tl than for In or Ga. The last two elements can also be detected by this method in presence of comparatively large quantities of Al and Zn, if NH_4Et in place of NH_4Cl is added to the Al, and $\text{C}_5\text{H}_5\text{N}$ together with the NH_4Cl to the Zn.
M. S. B.

Potentiometric determination of iron in ores.—See B., 1934, 1013.

Drop reaction for cobalt. L. M. KUHLEBERG (J. Appl. Chem. Russ., 1934, 7, 406—408).—1 ml. of solution is made acid with HCl , Al is added, and the solution is filtered after 2.5 min. The filtrate is boiled for 2 min. with 2—3 drops of HNO_3 , made neutral with aq. NH_3 , and acid with AcOH , and 0.1 ml. of reagent (I) [saturated aq. $(\text{NH}_4)_2\text{Hg}(\text{CNS})_4$] is added. $\text{Fe}(\text{CNS})_3$, if present, is decolorised with saturated aq. NaF , and 0.5 g. of ZnSO_4 and 1 ml. of (I) are added, when a blue ppt. indicates $< 2.5 \times 10^{-10}$ g. of Co.
R. T.

Volumetric determination of cobalt. G. SPACU and M. KURAŠ (Bul. Soc. Științe Cluj, 1934, 7, 377—383; Chem. Zentr., 1934, i, 2797).—Co is pptd. with 0.1N- NH_4CNS and $\text{C}_5\text{H}_5\text{N}$ as the complex $[\text{Co}(\text{C}_5\text{H}_5\text{N})_4(\text{CNS})_2]$, and excess of NH_4CNS determined with 0.1N- AgNO_3 , using $\text{HNO}_3 + \text{aq. Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ as indicator. The method is applicable

in presence of all elements not pptd. under these conditions. H. J. E.

1-Nitro- β -naphthol as precipitant for cobalt and palladium. C. MAYR (Z. anal. Chem., 1934, 98, 402—408).—Co⁺⁺ is oxidised to Co⁺⁺⁺ by adding 30% H₂O₂ to the slightly acid solution. Co(OH)₃ is pptd. by NaOH and redissolved in AcOH. Excess of 1-nitro- β -naphthol (I), as 1% solution in 50% aq. AcOH, then ppts. Co(C₁₀H₆·O·NO₂)₃ of stoichiometric composition (cf. A., 1933, 1025); this is dried at 130°. Using AcOH concns. < 25—35%, Co may be quantitatively separated from Ni, Zn, Cr, and Al. Small amounts of Fe may first be pptd. with cupferron; larger amounts (e.g., in analysis of Co steels) should first be quantitatively removed by pptn. with ZnO (cf. A., 1914, ii, 494). With Pd in > 5% AcOH solution, (I) ppts. Pd(C₁₀H₆·O·NO₂)₂, dried at 130—140°.

J. S. A.

Determination of chromium in steels containing vanadium and molybdenum.—See B., 1934, 1014.

Spectral analysis by sensitive lines within the range of the glass spectrograph: measurements in the spark spectrum of a high-% molybdenum-iron alloy. W. KRAEMER (Z. anal. Chem., 1934, 98, 240—245).—Results are given for an 80:18% Mo-Fe alloy (see A., 1933, 1110).

J. S. A.

Colorimetric determination of bismuth. Y. YAMAMOTO (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1265—1266).—To the Bi solution 1 g. of Na K tartrate and 5—10 c.c. of 1% aq. gum arabic are added, and then sufficient aq. NH₃ to make the solution alkaline ($p_H > 8$). A few drops of 10% aq. Na₂S are added, and the solution is diluted to 100 c.c. The reddish-brown colloidal Bi₂S₃ produced is matched against a standard. 1.5 mg. per litre can be determined with an error > 2%. The Bi₂S₃ sol can be boiled without coagulation, and its colour intensity does not vary on keeping over-night.

R. S. B.

Colour reaction of bismuth. J. V. DUBSKÝ and A. OKAČ (Chem. Obzor, 1934, 9, 3—4; Chem. Zentr., 1934, i, 3498).—Dimercaptodiazole (0.7 g. C₆H₄N₂S₂ in 35 c.c. 0.1N-KOH) gives with a Bi salt in dil. HCl a red ppt. (limiting concn. 1:28,000, 0.0012 mg. Bi).

H. J. E.

"VIKP" thermoelectric relay. S. A. PAVLOV and N. K. BARAMBOIM (J. Appl. Chem. Russ., 1934, 7, 437—438).—A simple and inexpensive electric thermo-regulator is described.

R. T.

High-frequency calorimeter for investigating the dielectric loss of liquids. L. PUNGS and H. RIECHE (Z. tech. Physik, 1933, 14, 483; Chem. Zentr., 1934, i, 1676).

L. S. T.

Thermal leakage rates of Dewar bottles. W. P. WHITE (Rev. Sci. Instr., 1934, 5, 379).—The heat flow depends on how the throat of the bottle is filled.

C. W. G.

Attainment of temperatures below 1° abs. by demagnetisation of Gd₂(SO₄)₃·8H₂O. W. F. GIAUQUE and D. F. MACDOUGALL (Physical Rev., 1933, [ii], 43, 768).—Temp. of 0.53°, 0.34°, and 0.25° abs. have been reached.

L. S. T.

Chemical intensification of X-ray spectrograms. E. WAINER (Physical Rev., 1933, [ii], 43, 303).—The use of U baths improves the contrast and detail of X-ray spectrograms used for qual. chemical analysis.

L. S. T.

Application of the photo-cell in spectrography. W. KROLL (Metall u. Erz, 1934, 31, 105—107; Chem. Zentr., 1934, i, 3496).—A crit. discussion.

H. J. E.

Spark apparatus for spectral analysis. O. FEUSSNER (Zeiss Nachr., 1933, 4, 6—13; Chem. Zentr., 1934, i, 576).—For reproducibility in quant. spectrum analysis the discharge should be extinguished after a min. no. of high-frequency oscillations. A suitable apparatus is described.

H. J. E.

Direct-reading, two-crystal X-ray spectrometer. F. K. RICHTMYER and S. W. BARNES (Rev. Sci. Instr., 1934, 5, 351—355).—Wave-lengths are read directly to 10⁻⁵ Å.

C. W. G.

Portable vacuum spectrograph. T. H. OSGOOD (Rev. Sci. Instr., 1934, [ii], 5, 368—369).—The camera and X-ray tube may be detached from the pumping system for removal to a dark-room.

C. W. G.

Grating microspectrograph and its application to microchemistry. E. E. JELLEY (Phot. J., 1934, 74, 514—521).—A description of the instrument and its use in determining the optic axial angles of biaxial crystals is given. A new technique of micro-identification of org. substances depends on the production of characteristic birefringence spectrograms of wedge-shaped crystals obtained by fusion of the unknown, and of known substances having approx. the same m.p. Illustrations are given for PhSO₃·NHPh, NHAcPh, antipyrine, *m*-nitroaniline, *p*- and 2:4-di-nitrophenol.

N. M. B.

Application of Henner cylinders to Hahn and Klockmann's colorimetric procedure. N. P. KOMAR (J. Appl. Chem. Russ., 1934, 7, 420—423).—A colorimeter serving for determinations by Hahn and Klockmann's method (A., 1931, 54) is described.

R. T.

Foundations and applications of absolute colorimetry. XI. Highly stable grey solution. A. THIEL (Chem. Fabr., 1934, 7, 383—384; cf. this vol., 912).—Extinction measurements show the solution to be practically ideal as a light-weakening medium.

E. S. H.

Physical methods in the chemical laboratory. XXII. Light absorption and chemical composition. A. SMAKULA (Angew. Chem., 1934, 47, 657—665).—The val. of absorption spectra in determining, e.g., the no. and positions of ethylenic linkings is described and discussed, many typical curves being reproduced. The relation between absorption bands and mol. refraction and m.p. is discussed.

H. F. G.

Derivation of photometric standards for tungsten filament lamps. H. T. WENSEL, W. F. ROESER, L. E. BARBROW, and F. R. CALDWELL (J. Res. Nat. Bur. Stand., 1934, 13, 161—168).—The C-filament standard lamps are compared with a black body immersed in Pt at the m.p., and the gas-filled W-filament lamps with a black body in Ir at the m.p. The relative brightnesses of the black bodies is calc.

from the observed brightnesses at one wave-length. Test lamp results agreed to within 1% with those made with vac. W standards. H. F. G.

Application of photo-cells as actinometers. H. LUX (Fotograf. Ind., 1934, 32, 168—172; Chem. Zentr., 1934, i, 2948).—Since the spectral sensitivity of photo-cells (I) varies with wave-length and the sensitivity max. of plates varies, the uncontrolled use of (I) in actinometry leads to errors unless corrections are applied. H. J. E.

Use of the prism for the determination of the principal indices of refraction in crystals. II. A. CAVINATO (Atti R. Accad. Lincei, 1934, [vi], 19, 812—816; cf. this vol., 984).—A further discussion of the previous theoretical paper. O. J. W.

Identification of crystalline substances by means of the petrographic microscope. T. N. McVAY (Bull. Amer. Ceram. Soc., 1934, 13, 255—260).—A scheme of examination is outlined and the technique of thin-section and immersed grain petrography described with special reference to determination of *n*. Canada balsam is being replaced by "Kollolith," which is particularly suitable for mounting friable materials. "Arochlor 4465 and 5460" are media having a high *n* (1.65). An extensive bibliography is given. J. A. S.

Densitometry and photographic printing. Illumination of the negative and its effect on density. C. TUTTLE (J. Opt. Soc. Amer., 1934, 24, 272—278).—Practical optical systems which yield density vals. intermediate between the specular (projection) and diffuse (contact) vals. are discussed. J. W. S.

Dose measurement of super-hard X-rays. R. JAEGER (Physikal. Z., 1934, 35, 841—844).—A comparison of various chambers is made. A. J. M.

Method of measuring electrolytic conductivities without metallic electrodes. E. DENINA and F. S. DE PAOLINI (Gazzetta, 1934, 64, 675—687).—The method (a) previously described (A., 1933, 1265) has been improved, and abs. conductivities can be measured with a high degree of accuracy. O. J. W.

Laboratory arrangement for electrolytic fractionation of hydrogen isotopes. II. H. ERLIENMEYER and H. GARTNER (Helv. Chim. Acta, 1934, 17, 1226—1231; cf. this vol., 262).—Details of procedure are described. F. L. U.

Apparatus for electrodialysis. P. D. WATSON and P. N. PETER (Rev. Sci. Instr., 1934, [ii], 5, 362—365).—The dialysis chamber consists of permanent diaphragms of alundum or porcelain. The p_H of the solution therein is regulated by a siphon device. C. W. G.

High-pressure Wilson expansion chamber. L. M. MOTT-SMITH (Rev. Sci. Instr., 1934, [ii], 5, 346—350).—Spectroscopic photographs at pressures up to 20 atm. show tracks not markedly different from those obtained at 1 atm. C. W. G.

Meaning and calibration of the p_H scale. D. A. MACINNES (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 190—194).—The p_H of solutions is related to the potentials of galvanic cells containing

the solution, but cannot be interpreted as a measure of $[H^+]$. H^+ activity cannot be defined thermodynamically. CH. ABS.

Absolute measurement of coefficients of magnetisation and magnetic susceptibilities of liquids. G. DUPOUY and C. HAENNY (Compt. rend., 1934, 199, 781—783).—A narrow quartz bar (I) 18 cm. long is suspended in the liquid (II) (20 c.c.) between the poles of a magnet, the susceptibility of (II) being deduced from the apparent susceptibility of (I), as measured by the Gouy method. The method is adaptable for liquefied gases or gases, and the temp. may be varied. H. J. E.

Microburette for the determination of quantities of the order of 0.2×10^{-6} g. W. DUSING [with H. FURST] (Chem. Fabr., 1934, 7, 313—317).—The burette consists of a capillary tube, inclined at about 30° to the horizontal, in which operates a steel plunger moved by a micrometer screw at the lower end. A drop of Hg separates the steel from the reagent. The upper end of the tube is bent down at 90° . The total vol. contained may be 50—100 cu. mm., and readings may be taken to within 0.005 cu. mm. Typical titrations and results are described. $2-4 \times 10^{-6}$ g. of H_2SO_4 or HCl may be determined with an error generally $< 1\%$, and similar results are obtained for $H_2C_2O_4$ -KMnO₄, I-Na₂S₂O₃, and BaCl₂-K₂CrO₄ titrations. H. F. G.

Apparatus for constant delivery of equal weights of two or more liquids. R. H. LAMBERT (Science, 1934, 80, 361—362). L. S. T.

Simple immersion filter for the volumetric determination of precipitates, especially in Bertrand's sugar determination. J. BLOM (Z. anal. Chem., 1934, 98, 178).—The filter consists of a thick-walled glass tube expanded into a small funnel (I) at the lower end. (I) is fitted with a Pt gauze cone which is filled with asbestos for use, suction being applied at the upper end of the tube. Asbestos and ppt. are stirred up with the solution for the titration. A. R. P.

Gas stopcocks lubricated with metaphosphoric acid. A. PINKUS (Bull. Soc. chim. Belg., 1934, 43, 462—466).—The portion lubricated with HPO₃ is separated by a groove in the plug from the upper end, which is lubricated with an org. grease. Such stopcocks can be used for long periods without renewing the HPO₃. R. S.

Hot-wire indicator vacuum gauge. H. MURMANN (Z. tech. Physik, 1933, 14, 538—540; Chem. Zentr., 1934, i, 896).—A vac. gauge in which the temp. of a wire carrying a const. current (45 m.-amp.) is used to indicate pressure is described. L. S. T.

Check valve for vacuum pumps. G. NARASIMHAMURTHY (J. Indian Chem. Soc., 1934, 11, 659—660). A device for overcoming back suction is described. E. S. H.

Automatic recording micro-osmometer for colloidal osmotic pressures. F. URBAN (Rev. Sci. Instr., 1934, [ii], 5, 375—377).—The vol. of solution required is small, the Cellophane membrane is rigidly supported, no gaskets or washers are used, and the

osmotic pressure is continuously and automatically balanced. C. W. G.

Purification of inert gas by mischmetal. C. C. VAN VOORHIS, A. G. SHENSTONE, and E. W. PIKE (Rev. Sci. Instr., 1934, [ii], 5, 367—368).—Mischmetal heated as cathode in a d.c. discharge is effective in cleaning Ne. C. W. G.

Quantitative addition tube. J. GREENSPAN (J. Amer. Chem. Soc., 1934, 56, 2053—2054).—A device to assist adding a weighed amount of solid through a narrow opening. E. S. H.

Automatic gas-holder using concentrated sulphuric acid. A. PINKUS (Bull. Soc. chim. Belg., 1934, 43, 467—470; cf. this vol., 750).—An all-glass apparatus is described for the storage and supply at const. pressure of Cl_2 etc. Movement of the aspiratory liquid is controlled by glass valves. R. S.

Determination of dielectric constant of conducting liquids. A. N. TSCHILAEV (J. Gen. Chem. Russ., 1934, 4, 273—289).—A resonance method for determining the dielectric const., D , of conducting and non-conducting liquids and solids is described; the mean error is $\pm 0.5\%$. The D of dil. aq. NaCl , KCl , and CuSO_4 rises continuously with increasing concn. R. T.

Extraction apparatus for solids and liquids. E. L. MAYS and F. L. WARREN (J.C.S., 1934, 1652).—The boiling solvent (I) and the material (II) to be extracted are in separate flasks, and interposed between the reflux condenser and (II) is a device for returning the extract to (I) when the vol. with (II) reaches a predetermined level. J. G. A. G.

Laboratory apparatus. B. KISCH (Biochem. Z., 1934, 273, 349).—(a) To the neck of a reagent bottle (I) (for solids) with ground hollow stopper (II) a side tube (with or without stopcock) is sealed and a hole is bored at the appropriate level in the wall of (II). (I) may be evacuated and used for storing hygroscopic or oxidisable substances. (b) Observation of the evolution of minute amounts of gas in eudiometers is facilitated by introducing an additional wide-bored stopcock into the lower part of the measuring tube. W. McC.

Stirring apparatus for flasks. BERG (Chem.-Ztg., 1934, 58, 842).—A vertical screw rests in a guide lying on the neck of the flask and carries at the lower end two hinged vanes. When inserting these lie longitudinally, but rapid rotation of the screw causes them to take up a lateral position, and the whole works up and down the flask by manual operation. C. I.

Electromagnetic torsion viscosimeter. G. BERRAZ (An. Inst. Invest. cient. tecn., 1931, 2, 79—84; Chem. Zentr., 1934, i, 2455).—A closed glass tube loaded with Hg is caused to rotate in the liquid. The viscosity of the liquid is deduced from the current required in an electromagnetic control system to restore equilibrium. H. J. E.

Determination of density and viscosity of gases with the Schilling-Bunsen apparatus. W. SCHILLER (Forsch. Ingenieurwes. Ausg. A., 1933, 4, 225—229; Chem. Zentr., 1934, i, 2455).—Results with this method (flow through a nozzle) depend on both the d and viscosity of the gas. Experiments with air and H_2 are described. H. J. E.

Constant-rate dropping device for liquids. H. F. PIERCE (Science, 1934, 80, 339). L. S. T.

Apparatus for determining specific gravity of solutions. J. CIOCHINA (Z. anal. Chem., 1934, 98, 416—417).—The heights of balanced columns of liquid are compared. J. S. A.

Automatic device for maintaining constant pressure. C. CHANDRASEKHARIAH (Current Sci., 1934, 3, 112—113).—An automatic, electrically-controlled arrangement for maintaining pressure to within ± 0.5 cm. Hg is described. L. S. T.

Technique of ultrafiltration. J. J. QUIGLEY (Amer. J. Hyg., 1934, 20, 218—224).—An ultra-filter for large quantities, and the prep. of cellulose nitrate-impregnated alundum thimbles are described. CH. ABS. (e)

Drop weight as a function of the drop velocity and diameter of the drop surface. A. ADLER (Physikal. Z., 1934, 35, 864—867).—The drop velocities for best results in the drop wt. method of determining surface tension are given for H_2O , C_6H_6 , MeOH , and Et_2O . A. J. M.

Evaporation technique for aluminium. J. STRONG (Physical Rev., 1933, [ii], 43, 498).—The technique of the evaporation of Al from a W helix is described. Al mirrors thus made are superior to those of Ag. Reflectivity for ultra-violet light is greater, the mirrors do not tarnish, and they are inert to corrosive agents. They can be washed with soap and H_2O without damage or scratching. L. S. T.

Aluminium-magnesium mirrors. H. W. EDWARDS (Physical Rev., 1933, [ii], 43, 205).—Metals evaporated in a vac. and deposited on glass show high reflexion in the visible spectrum. Al-Mg mirrors reflect 94%. L. S. T.

Geochemistry.

Atmospheric ozone investigations conducted at Scoresby Sound during the polar year. A. DAUVILLIER (J. Phys. Radium, 1934, [vii], 5, 455—462).—Chemical, spectrographic, and photo-electric measurements of the daily atm. $[\text{O}_3]$ were obtained and plotted for a year. A large increase after night-fall, reaching a max. of 57 mg. per 100 cu. m. of air,

and returning to normal val. after sunrise, was observed. Theories of formation and variation with time and locality are reviewed. Results can be interpreted only on the auroral theory. N. M. B.

Origin of helium in beryllium minerals. O. HAHN (Naturwiss., 1934, 22, 744).—He could be

formed by the effect of γ -rays on Be, which emits a neutron, becoming Be^8 , which then breaks down to 2He^4 .

A. J. M.

Examination of the gases of boric acid soffioni, with special reference to their content of helium and other noble gases. U. SBORCI (Mem. R. Accad. Italia, 1934, 5, 667—713).—The following data are given for various Tuscan soffioni: wt. of vapour expelled per hr., ratio of gas to condensable vapour, temp., yields of NH_3 and H_3BO_3 , and composition and radioactivity of the gas. In most cases the gas contains about 0.002% He and 0.001% A by vol. and has in some cases a radioactivity of the order of 10^{-5} millicurie per litre.

D. R. D.

Mineral waters of the upper Adige and the Trentino. Chemical and physico-chemical investigations. I. M. BETTI and G. B. BONINO (Mem. R. Accad. Italia, 1933, 5, 1—56).—Physical properties, physico-chemical consts., and chemical analyses are recorded.

D. R. D.

Changes in the composition of natural waters. A. MASSINK and L. G. M. B. BECKING (Rec. trav. chim., 1934, 53, 1047—1060).—The composition of a natural H_2O may be conveniently represented on triangular diagrams, each relating to three selected components (e.g., Na, Ca, Mg). Lines on such diagrams can indicate any continuous change in composition with geographical position or with time. Examples of the application of the method are given. The freshening of the Zuiderzee is discussed. In certain special cases the composition may be determined graphically on the basis of a single measurement of electrical conductivity.

F. L. U.

Mineral waters of Venice. Ferruginous water of Romano d'Ezzelino. G. BRAGAGNOLO (Annali Chim. Appl., 1934, 24, 483—486).—Composition and physico-chemical consts. are given.

T. H. P.

Mud and salt water of eight mud lakes. P. KASCHINSKI, E. GUBAREVA, N. VESSELOVSKI, and K. LASAREV (Hydrochem. Mater., 1931, 7, 3—123; Chem. Zentr., 1934, i, 524—525).—Analytical data are recorded. The absorption of H_2O by the mud and the adsorption of methylene-blue by the washed mud were studied.

H. J. E.

Condition of silicic acid in mineral waters. L. FRESSENIUS (Arch. Med. Hydrology, 1932, 10, 81—82).—Rather < 1% of the SiO_2 content of waters is mol. dispersed chiefly as dissolved disilicic acid. The latter is more active therapeutically than is colloidal SiO_2 .

CH. ABS. (p)

Physico-chemical variables in a Minnesota lake. H. J. OOSTING (Ecolog. Monogr., 1933, 3, 493—533).—Data for Ham Lake (N. of Minneapolis) are recorded.

CH. ABS.

Proportion of heavy water in the water of crystallisation of minerals. E. H. RIESENFELD and H. E. RIESENFELD (Ber., 1934, 67, [B], 1659—1660).—Examination of the H_2O of crystallisation (I) from gypsum and polyhalite shows that no such enrichment in H_2O has occurred as to enable (I) to be used technically for further enrichment. The pycnometer is insufficiently sensitive to establish a

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difference in the ratio $\text{H}_2^{18}\text{O} : \text{H}_2^{16}\text{O}$ in (I) and ordinary H_2O .

H. W.

Occurrence of heavy water from the geochemical viewpoint. V. VERNADSKY (Compt. rend., 1934, 199, 694—696).—It is suggested that the following should be examined for their content of H_2^{18}O : the remains of Quaternary glaciers, isolated salt lakes, salt hydrates formed by the evaporation of ancient lakes, volcanic vapours, chlorites, and micas. The concn. of H_2^{18}O by gravitation is discussed.

R. S. B.

Agency of algæ in the deposition of travertine and silica from thermal waters. E. T. ALLEN (Amer. J. Sci., 1934, [v], 28, 373—389).—Geologically the influence of algæ is unimportant, and inorg. causes involving loss of CO_2 account satisfactorily for the deposits.

C. W. G.

Relation between colour and composition of autunite from Lurisia. L. FRANCESCONI and R. BRUNA (Gazzetta, 1934, 64, 650—652).—The range of colour of various samples of autunite from sulphur-yellow to yellowish-green runs parallel to the increasing arsenate content of the sample.

O. J. W.

Pleochroism of minerals in the ultra-violet. N. MELANCHOLIN (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 505—506).—Results of the examination of a series of minerals are recorded.

H. J. E.

Interglacial kieselguhr from Ober-Ohe and its chemical and geological relation to recent saproliths. W. BENADE and R. POTONIE (Mitt. Lab. preuss. geol. Landesanst., 1933, 59—71; Chem. Zentr., 1934, i, 2914).—The dry material contains 20—30% of org. matter. The material sol. in org. liquids and the non-hydrolysable material are > in recent saproliths.

H. J. E.

Specific gravity of lapis lazuli. B. W. ANDERSON and C. J. PAYNE (Nature, 1934, 134, 627).—Of 500 specimens 95% had d 2.75—2.90, the extreme limits being 2.45 and 2.94, in contrast with the generally-accepted vals. between 2.38 and 2.45.

L. S. T.

Nickel-bearing goslarite, epsomite, and melanterite from County Durham. J. A. SMYTHE (The Vasculum, 1933, 19, 12—17; Mineralog. Abs., 5, 283).—The sol. salts from a barite-witherite vein are homogeneous isomorphous mixtures with up to 12.79% $(\text{Fe}, \text{Mn})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ in the goslarite and epsomite, and 11—55% $(\text{Mg}, \text{Zn}, \text{Ni})\text{SO}_4 \cdot 7\text{H}_2\text{O}$ in melanterite.

CH. ABS. (e)

Effect of heating on physical and chemical properties of fused basic rocks. K. KANI (J. Japan. Assoc. Min. Pet., 1931, 5, 124—130, 166—176).—Several rocks were fused at 1350° and held at 1050°, the thermal expansion, heat loss and absorption, and changes in microscopic properties and in the solubility in HCl being recorded.

CH. ABS. (e)

Corundum in the region of Sludyanski (Ural) phlogopite deposits. A. SULOEV and A. PONO-MOREV (Min. Suir., 1934, 9, No. 3, 31—33).

CH. ABS.

Weathering of silicate minerals. O. TAMM (Arkiv Kemi, Min., Geol., 1934, 11, A, No. 14, 27 pp.).—By rotation in H_2O or C_6H_6 hard minerals are reduced

to particles of dimensions $< 1 \mu$: K feldspar particles obtained by grinding in C_6H_6 absorb 5–6% H_2O not lost at 105° , have a considerable buffer action at p_H 6–10, and are considerably decomposed by H_2O with dissolution of K silicate. When ground in H_2O the particles reversibly exchange K^+ for H^+ at p_H 6–10. In this and other respects they behave like muscovite particles ground in C_6H_6 , and it is probable that the feldspar lattice is converted by H_2O into the muscovite lattice. Particles of desmin, a typical zeolite, react reversibly with H_2O at p_H 6–9. Wollastonite particles buffer strongly at p_H 8 owing to their considerable solubility (0.245 g. per litre). A. G.

Crystal morphology of vesuvianite. G. KALB (Z. Krist., 1934, 89, 18–23).—External morphology only. B. W. R.

Lilac ortho-pyroxenes from Koratagere, Mysore State. B. R. RAO and M. B. R. RAO (Current Sci., 1934, 3, 114–115).—A few of the outcrops of the cordierite-hypersthene rocks near Bidaloti show a violet or lilac orthopyroxene which has the usual characteristics of hypersthene (I). It is closely associated with the normal pink to green pleochroic (I), cordierite (II), and biotite (III), and is probably a derived species from the reconstruction of the altered products of (II) and (III). L. S. T.

Petrology of the alkaline stock at Pleasant Mountain, Maine. W. F. JENKS (Amer. J. Sci., 1934, [v], 28, 321–340).—Chemical and Rosiwal analyses are given. C. W. G.

Occurrence of pyrites deposits at Lam in the Bavarian forest. F. HEGEMANN and A. MAUCHER (Chem. Erde, 1934, 9, 173–199).—The nature of the deposits is described and their mode of origin discussed. E. S. H.

Biological origin of deposits of iron and sulphur. G. BARGAGLI-PETRUCCI (C.R. Intern. Geol. Congr., 1930, 2, 309–314).—Bacteria of the type of *Bacillus ferrigenus* deposit Fe and S from bog- H_2O , producing ore deposits. CH. ABS. (e)

Separation in the system Cu-Fe-S and its significance as a "geological thermometer." H. BORCHERT (Chem. Erde, 1934, 9, 145–172).—A study of Cu pyrites, cubanite, and other minerals belonging to the system Cu-Fe-S has been made, particularly with regard to the temp. of separation of the various phases and the behaviour on oxidation. The geological bearing of the results is discussed. E. S. H.

"Terra Roxa" in Sao Paulo, Brazil. F. W. FREISE (Econ. Geol., 1934, 29, 280–293).—The rock disintegration is discussed. CH. ABS. (e)

Radioactive phlogopite from the Kira-Kira region in Eastern Transbaikalia. J. SHAFRANOVSKI (Trans. Geol. Prosp. Serv. U.S.S.R., 1931, 50, 765–769).—Analytical data are recorded. The radioactivity is due to the presence of a small quantity of zircon. CH. ABS. (e)

Calcite marble. G. W. BAIN (Econ. Geol., 1934, 29, 121–139).—In the Vermont marble deposits, the development of cryst. marbles was due to thermal metamorphism of bituminous limestone by hot solu-

tions flowing along bedding planes, the flow channels being marked by bands of chlorite, actinolite, and mica. CH. ABS. (e)

Iron ores of Minas Del Rif, Spanish Morocco. A. HEIM (Econ. Geol., 1934, 29, 294–300).—The ore at Uixan is a massive, bluish hæmatite (Fe 60–64, SiO_2 6, S 1–3%). That at Setolazar is of sedimentary origin with magmatic intrusions of hæmatite and magnetite. CH. ABS. (e)

Ore base of Pribalkhashstroy (Russian Mid-Asia). M. P. RUSAKOV (Tsvet. Met., 1933, No. 2–3, 27–40).—Porphyritic Cu ores discovered near Lake Balkhash, Kasakstan, are described. CH. ABS.

Paragenesis of the oxidised ores of copper. G. M. SCHWARTZ (Econ. Geol., 1934, 29, 55–75).—The paragenesis is discussed. Two oxidation sequences are observed: (1) sulphides are oxidised to cuprite, then to black oxide, which is hydrated and carbonated to malachite (I); (2) sulphides are replaced directly by (I). CH. ABS. (e)

Rich ores of Goldfield, Nevada. C. F. TOLMAN and J. W. AMBROSE (Econ. Geol., 1934, 29, 255–279).—The development of the ores is traced. The approx. formula of goldfieldite is $Cu_6Sb_2(S,Te)_9$. CH. ABS. (e)

Weathering of feldspars in relation to soil formation. P. ZEMYATCHENSKI (Trans. Dokuchaev Inst. Soil Sci., 1933, 8, No. 1, 1–42).—Atm. action on feldspars in N.W. U.S.S.R. and the Murman coast produces a material resembling muscovite in optical properties, but much higher in H_2O . CH. ABS. (e)

Feldspars of the Chibina massif. B. KUPLETSKI (Mem. Soc. Russe Min., 1931, [ii], 60, 51–64).—The feldspars contain BaO. Anorthoclase from the Kukiswumtschor Mts. contains 2.44% of Fe orthoclase. CH. ABS. (e)

Grunerite from Mt. Humbolt, Michigan. N. SUNDIUS (Geol. Foren. Stockholm, 1934, 56, 98–100; Chem. Zentr., 1934, i, 2730).—The % composition was SiO_2 50.08, TiO_2 0.01, Al_2O_3 0.25, Fe_2O_3 0.58, FeO 38.55, MnO 1.58, MgO 6.24, CaO 0.45, Na_2O and K_2O trace, H_2O 2.05%. H. J. E.

Specific gravity of Japanese acid clay. K. YAMAMOTO and H. ISHIKAWA (Mem. Fac. Sci. Eng. Waseda Univ., 1934, 11, 11).—Japanese acid clay has d 2.4–2.5, after treatment with alkaline solutions 2.5–2.6, and with acid solutions 2.2–2.4. The d after heating depends on the temp., and is max. (2.5–2.6) after heating at 200–400°. A. G.

Lignites of the Moscow Basin. R. A. WAEHNER (Brennstoff-Chem., 1934, 15, 365–368).—These lignites appear to have originated in the remains of plants allied to the conifers and belonging to a more recent geologic age than the bituminous coal flora. The lignites contain no cellulose, 5–6% of humic acids, and 1.3–2.5% of bitumen. The fossil lignin, which constitutes about 90% of the lignites, is a partly esterified hydroxycarboxylic acid similar in constitution to the lignin of present-day plants. The results are discussed briefly in relation to the mechanism of the formation of lignites. A. B. M.

Mineral formations in the Sredni coal seam in the Karaganda coal basin. N. A. VOLKOV, V. I. LUCHITZKI, and S. D. CHETVERIKOV (Min. Suir., 1934, 9, No. 2, 48—50).—The minerals are quartzine, kaolinite, and celestine. CH. ABS.

Evolution of mineral coals. I, II. J. V. LEWIS (Econ. Geol., 1934, 29, 1—38, 157—202).—A discussion. CH. ABS. (e)

Soil profiles and the accompanying forest vegetation in the neighbourhood of Montpellier. E. BLANCK, J. BRAUN-BLANQUET, and W. HEUKESHOVEN (Chem. Erde, 1934, 9, 200—220).—The chemi-

cal and mineralogical nature of the soil is compared with the type of vegetation. E. S. H.

Geography of the podsol stage of soil formation. V. A. KOVDA (Trans. Dokuchaiev Soil Inst., 1934, 10, No. 2, 1—30).—The conception of a unique podsol zone in the cold region must be replaced by a more exact conception of podsolised soils in different thermic zones: subpolar-cold (dwarf podsoles), cool temperate (podsoles of the forest zone), warm temperate (podsolised soils of Precaucasia, "zheltozems") subtropical (podsoles of Abkhazia, Mediterranean, America), and tropical (podsoles of Java, Brazil). A. M.

Organic Chemistry.

Slow oxidation of propane. R. N. PEASE and W. P. MUNRO (J. Amer. Chem. Soc., 1934, 56, 2034—2038).—Org. peroxides, aldehydes (mainly CH_2O), and alcohols (mainly MeOH) are formed as secondary products, but the primary reaction is unknown. When the interior of the reaction bulb is coated with KCl , peroxides are almost completely eliminated, whilst the reaction rate is not materially altered.

E. S. H.

Action of oxides of nitrogen on hydrocarbons. I. Action of nitric oxide on saturated hydrocarbons in presence of catalysts. M. S. PLATONOV and S. P. SCHAIKIND (J. Gen. Chem. Russ., 1934, 4, 434—437).—The products of reaction of NO with $n\text{-C}_5\text{H}_{12}$, $\text{-C}_6\text{H}_{14}$, and $\text{-C}_7\text{H}_{16}$ in presence of $\text{Al}_2\text{O}_3\text{-CeO}_2\text{-ThO}_2\text{-kaolin}$ at $450\text{--}500^\circ$ were NH_3 15—20, NO 30, CO 1—10%, and unsaturated hydrocarbons, CH_4 , and N_2 , and in presence of V_2O_5 at $290\text{--}310^\circ$, or of Pt-black at $250\text{--}300^\circ$ H_2O , CO , N_2 , and unchanged hydrocarbons. Carboxylic acids and nitriles were not detected. R. T.

Thermal decomposition of octane and of β -dimethylhexane.—See this vol., 1311.

Syntheses by means of unsaturated compounds. B. A. KAZANSKI (Uspekhi Khim., 1934, 3, 116—162).—A comprehensive review.

CH. ABS. (e)

Addition of gaseous hydrogen chloride and bromide to propene.—See this vol., 1314.

Rate of hydration of trimethylethylene.—See this vol., 1313.

Conjugated oxidation of unsaturated hydrocarbons and aldehydes. Oxidation of octene with acetaldehyde or benzaldehyde. V. V. FIGULEVSKI (J. Gen. Chem. Russ., 1934, 4, 616—621).—The oxidation of MeCHO (I) and of PhCHO (II) by atm. O_2 is inhibited by octene (III), and diminishes with increasing O_2 concn. The oxidation of (III) is activated by (I) or (II); in particular, AcO_2H (IV) and BzO_2H formed as intermediates convert (III) into octene oxide. The velocity of oxidation of (III) by (IV) is $>$ that of (I) by (IV). R. T.

Decenes produced from methylisopropylcarbinol by sulphuric acid. N. L. DRAKE, G. M. KLINE, and W. G. ROSE (J. Amer. Chem. Soc., 1934,

56, 2076—2079).— $\text{CHMePr}^3\cdot\text{OH}$ and 75% H_2SO_4 at 80° give a mixture (A) of approx. equal amounts of γ - δ -trimethyl- Δ^2 -heptene (I) and γ - δ -tetramethyl- Δ^2 -hexene (II), since ozonolysis of (A) affords MeCHO , δ -dimethylhexan- β -one (III) [from (I)], b.p. $154.4^\circ/768$ mm. [semicarbazone, m.p. 169.5° ; 2:4-dinitrophenylhydrazone, m.p. $146.5\text{--}147^\circ$; oxime (IV), b.p. $101^\circ/13$ mm.], and γ - δ -trimethylpentan- β -one (V) [from (II)], b.p. $147.2^\circ/766$ mm. [semicarbazone, m.p. 148° ; p-nitrophenylhydrazone, m.p. 73° ; 2:4-dinitrophenylhydrazone, m.p. 109.5° ; oxime (VI), b.p. $113^\circ/27$ mm.]. (III) is oxidised (NaOBr) to β - β -dimethylvaleric acid (VII), b.p. $103\text{--}104^\circ/13$ mm., $213^\circ/778$ mm. (amide, m.p. 76.5° ; anilide, m.p. $105.5\text{--}106^\circ$; Me, b.p. $49\text{--}50^\circ/17$ mm., and p-phenylphenacyl, m.p. 74° , esters); (V) similarly gives α - β -trimethylbutyric acid, b.p. $76^\circ/5$ mm., $103\text{--}104^\circ/20$ mm., m.p. 24.5° (amide, m.p. 106° ; anilide, m.p. 104.5° ; Me, b.p. $46^\circ/18$ mm., and p-phenylphenacyl ester, m.p. 68.5°). (IV) and PCl_5 in Et_2O afford the N-Ac derivative, b.p. $125^\circ/13$ mm., of β - β -dimethylbutylamine [N-2:4:6-trinitrophenyl, m.p. $88\text{--}88.5^\circ$, prepared by the action of $s\text{-(NO}_2)_3\text{C}_6\text{H}_2\text{Cl}$ in EtOH , and benzenesulphonyl, m.p. $59\text{--}59.5^\circ$, derivatives]; the amine is also prepared by reduction (Na , EtOH) of $\text{CMe}_2\text{Et}\cdot\text{CN}$. (VI) is similarly rearranged to the N-Ac derivative, b.p. $130\text{--}131^\circ/20$ mm., m.p. $68\text{--}68.5^\circ$, of α - β -trimethylpropylamine (N-2:4:6-trinitrophenyl, m.p. 107° , and benzenesulphonyl, m.p. 96° , derivatives; aurichloride), also prepared by reduction (Na , EtOH) of $\text{CMeBu}^2\cdot\text{N}\cdot\text{OH}$. The above amines are obtained from their Ac derivatives by hydrolysis with aq. H_3PO_4 at $230\text{--}240^\circ$ (sealed tube). γ -Methyl- γ -ethylpentan- β -one (2:4-dinitrophenylhydrazone, m.p. $92\text{--}92.5^\circ$) is prepared (method: Nyberg, A., 1922, i, 802) for comparison with (III). α -Methyl- α -ethylpropionic acid (amide, m.p. 78.5° ; anilide, m.p. 88.5° ; p-phenylphenacyl ester, m.p. 76°) is synthesised (from $\text{CMeEt}_2\cdot\text{MgCl}$ and CO_2) for comparison with (VII). (I) and (II) are also present in the "diamylene" obtained as a by-product during chlorination of mixed pentanes. Whitmore's theory of the polymerisation of olefines by acid catalysts explains the formation of (I) but not of (II). H. B.

Sodium in liquid ammonia as a dehydrohalogenation agent and its use in the synthesis

of acetylenes. T. H. VAUGHN (J. Amer. Chem. Soc., 1934, **56**, 2064—2065).—Na (2 mols.) in liquid NH_3 is added with vigorous stirring to $\text{CHPh}:\text{CHBr}$ in Et_2O —liquid NH_3 , the mixture is then partly evaporated, and treated with H_2O (and a little HCl); $\text{CPh}:\text{CH}$ (I) is thus obtained in 96% yield. $\text{CClPh}:\text{CH}_2$ similarly gives 15% of PhEt ; α -chloro-*p*-methylstyrene affords 63% of *p*-tolylacetylene; β -bromo- Δ^8 -decene yields 56% of Δ^8 -decene; $(\cdot\text{CHBrPh})_2$ furnishes (with 15 mols. of Na) 73% of dibenzyl; $\text{CHBrPh}:\text{CH}_2\text{Br}$ gives (with 3 mols. of Na) 66% of (I). The acetylenes are contaminated with hydrogenation products.

H. B.

Rapid catalytic preparation of sodamide in liquid ammonia and its uses in preparation of acetylenic materials. T. H. VAUGHN, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, **56**, 2120—2122).— NaNH_2 (I) is readily prepared from Na and liquid NH_3 in presence of Na oxides and NH_3 -sol. Fe, Ni, or Co salts. The method adopted is: Na (1 g.) is added to a mixture of liquid NH_3 (500 c.c.) and $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (?) (0.3 g.), air is then bubbled through the solution until the blue colour disappears, and Na (25 g.) is added in small pieces. (I) thus prepared is more sol. and more reactive than commercial NaNH_2 . $\text{Cl}:\text{CBu}$ is converted by (I) in liquid NH_3 into $\text{CH}:\text{CBu}$; $\alpha\beta$ -dibromo- Δ^8 -heptene, b.p. 93—96°/11 mm. [from amylacetylene (II) and Br in CCl_4 at -34°], similarly gives (II); $(\cdot\text{CHBrPh})_2$ affords stilbene; $\text{CHBr}:\text{CHPh}$, $\text{CH}_2:\text{CClPh}$, and $\text{CH}_2\text{Br}:\text{CHBrPh}$ all yield $\text{CH}:\text{CPh}$; β -bromo- Δ^8 -octene furnishes hexylacetylene; *p*- $\text{C}_6\text{H}_4\text{Me}:\text{C}:\text{CH}$; $\alpha\beta$ -dibromodecane affords octylacetylene. α -Ethyl- β -amylacetylene is not rearranged by (I).

H. B.

Preparation of derivatives for identification of alkyl chlorides. H. W. UNDERWOOD, jun., and J. C. GALE (J. Amer. Chem. Soc., 1934, **56**, 2117—2120; cf. Schwartz and Johnson, A., 1931, 597).—The AlkCl (I) (18 studied) is converted into MgAlkCl and thence by ArNCO into $\text{Alk}:\text{CO}:\text{NHAr}$ ($\text{Ar}=\text{Ph}$, *p*- $\text{C}_6\text{H}_4\text{Me}$, and α - C_{10}H_7); the *p*-toluidides are useful for distinguishing between (I) of similar b.p. The following are new: α -methylbutyr-*p*-toluidide, m.p. 92.5—93°, and α -naphthylamide, m.p. 128—129°; α -dimethylpropion-*p*-toluidide, m.p. 119—120°, and α -naphthylamide, m.p. 146—147°; isohexo-*p*-toluidide, m.p. 61.5—62.5°, and α -naphthylamide, m.p. 110—111°; $\alpha\alpha$ -dimethylbutyr-*p*-toluidide, m.p. 83—83.5°, and α -naphthylamide, m.p. 137—138°; α -methylvaler-*p*-toluidide, m.p. 90—91°, and α -naphthylamide, m.p. 102.5—103.5°; α -ethylbutyr-*p*-toluidide, m.p. 107.5—108.5°, and α -naphthylamide, m.p. 117—118°; α -methylhexoanilide, m.p. 91—92°.

H. B.

Kinetics of salt formation and of bromination of nitroethane. Rearrangement of nitroethane.—See this vol., 1313.

Hydrogenation of acetic and trifluoroacetic anhydrides. Trifluoroethyl alcohol. F. SWARTS (Bull. Soc. chim. Belg., 1934, **43**, 471—481).—Mainly a detailed account of work already reported (this vol., 170). The formation of CMeF_3 from $(\text{CF}_3\text{CO})_2\text{O}$ is not due to secondary reduction of $\text{CF}_3\text{CH}_2\text{OH}$ (I), as this is not hydrogenated under the experimental

conditions. (I) with HNO_3 and H_2SO_4 gives $\beta\beta$ -tri-fluoroethyl nitrate, b.p. 66–15°, and with AcCl , the acetate, b.p. 77–8°. $\text{CF}_3\text{CO}:\text{NH}_2$ is slowly hydrogenated (Pt-black- Et_2O) to (I). With H_2 at 21°/30–45 atm. and Pt-black, Ac_2O yields C_2H_6 , EtOAc , and AcOH .

H. N. R.

Non-saponifiable matter of shea-nut fat. I. I. M. HEILBRON, G. L. MOFFET, and F. S. SPRING (J.C.S., 1934, 1583—1585).—Acetylation of the unsaponifiable resin (I), m.p. 65—85°, (5%) obtained (in addition to illipene; Hopkins *et al.*, B., 1932, 30) from shea-nut fat affords β -amyirin acetate, and an acetate, m.p. 141°, $[\alpha]_D^{25} +22.4^\circ$ in CHCl_3 (2 double linkings by BzO_2H), hydrolysed by 3% KOH-EtOH to an alcohol, $\text{C}_{30}(\text{29})\text{H}_{(50)48}\text{O}$, m.p. 109.5°, $[\alpha]_D^{25} -11.9^\circ$ in CHCl_3 (*Bz* derivative, m.p. 130°). From the product of benzooylation of (I) are isolated lupeol and β -amyirin benzoates.

J. W. B.

Action of sodium hypobromite on dimethylpinacols. J. PALMEN (J. pr. Chem., 1934, [ii], **141**, 113—122).—*s*-Dimethylpinacols, $\text{OH}:\text{CMeR}:\text{CMeR}:\text{OH}$, are converted by shaking with an excess of cold alkaline NaOBr into CBr_4 (66—95% of 2 mols.) and RCO_2H [31—90% of 2 mols. (or 1 mol. of dibasic acid)]. Thus, $(\cdot\text{CMe}_2\text{OH})_2$ gives AcOH ; $(\cdot\text{CMeEtOH})_2$ affords EtCO_2H ; $(\cdot\text{CPhMeOH})_2$ yields BzOH ; 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydrophenanthrene furnishes diphenic acid; santene glycol gives *cis*-cyclopentane-1 : 3-dicarboxylic acid; 1 : 2-dihydroxy-1 : 2-dimethylcamphane affords camphoric acid.

H. B.

Condensation of polyhydric alcohols, sugars, and hydroxy-acids with aldehydes under the influence of phosphorus pentoxide. J. W. PETTE (Rec. trav. chim., 1934, **53**, 967—987).—Condensation of polyhydric alcohols with aldehydes in presence of P_2O_5 , HCl , and H_2SO_4 gives (the product being dependent on the conditions): tri-benzylidene-, m.p. 223—224°, $[\alpha]_D^{25} -16.5^\circ$, -(4-methoxy-, m.p. 235°, $[\alpha]_D^{25} -21^\circ$, -(4-methyl-, m.p. 255°, $[\alpha]_D^{25} -6.5^\circ$, -(2-nitro-, m.p. 222°, $[\alpha]_D^{25} -62^\circ$, -(3-nitro-, m.p. 268°, $[\alpha]_D^{25} -36^\circ$, and isomeric forms of -(4-nitro-, m.p. 296°, $[\alpha]_D^{25} -54^\circ$, and m.p. 152°, $[\alpha]_D^{25} -7^\circ$; di-(4-nitro-, m.p. 315—320°, $[\alpha]_D^{25} +106.5^\circ$ in $\text{C}_5\text{H}_5\text{N}$; tri-(2-, m.p. 260°, $[\alpha]_D^{25} +36^\circ$, -(3-, m.p. 212°, $[\alpha]_D^{25} -23^\circ$, and -(4-chloro-, m.p. 187°, $[\alpha]_D^{25} +7^\circ$, and -(4-chloro-3-nitro-benzylidene)-mannitol, m.p. 300—302°; di-benzylidene-, -(4-methoxy-, m.p. 219—220°, -(4-methyl-, m.p. 235°, -(2-, m.p. 241°, -(3-, m.p. 269°, and -(4-nitro-, m.p. 286°, -(2-, m.p. 222°, -(3-, m.p. 193°, and -(4-chloro-, m.p. 235°, and -(4-chloro-3-nitro-benzylidene)-erythritol, m.p. 253°. Condensation of sugars with aldehydes appears to be facilitated by low temp. *d*-Tartaric, citric, and *dl*-mandelic acids condense with aldehydes to give di-(4-methoxy-, m.p. 155°, $[\alpha]_D^{25} +112^\circ$, -(3-, m.p. 165°, $[\alpha]_D^{25} +72^\circ$, and -(4-nitro-, m.p. 163°, $[\alpha]_D^{25} +39^\circ$, -(2-, m.p. 171°, $[\alpha]_D^{25} -34^\circ$, -(3-, m.p. 172°, and -(4-chloro-benzylidene)-*d*-tartaric acid, m.p. 187°, $[\alpha]_D^{25} +95^\circ$; 3-, m.p. 163°, and 4-nitrobenzylidenecitric acid, m.p. 180°; benzylidene-, m.p. 103°, 2-, m.p. 95°, 3-, m.p. 104°, and 4-nitro-, m.p. 106°, and 2-, m.p. 74°, 3-, m.p. 63°, and 4-chloro-benzylidene-mandelic acid, m.p. 77°. All rotations are in CHCl_3 , unless otherwise stated.

F. R. S.

Migration of the phosphoric radical during the hydrolysis of sodium methyl β -glycerophosphate. Transition from β - into α -glycerophosphates. O. BAILLY and J. GAUME (Compt. rend., 1934, **199**, 793—795).—Successive treatment of Na β -glycerophosphate with Me_2SO_4 and CaCl_2 affords *Ca Me β -glycerophosphate*, m.p. 255° (block; decomp.). Hydrolysis of Na Me β -glycerophosphate with NaOH at 100° gives about 33% of Na α -glycerophosphate (corresponding Ba salt also isolated), whilst 66% transition is observed when hydrolysis is effected by acid.

H. W.

Xylosephosphoric acids. II. P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1934, **107**, 75—83; cf. A., 1933, 1141, 1144).—The homogeneity of the isopropylidenexylose 5-benzoate previously used has been confirmed by conversion into isopropylidenexylose 5-benzoate 3-*p*-toluenesulphonate (I) unaccompanied by any by-product. 5-Carbobenzyloxyisopropylidenexylose (II) and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\text{Cl}$ give 5-carobenzyloxyisopropylidenexylose 3-*p*-toluenesulphonate (III), m.p. 128.5—129.5°, $[\alpha]_D^{20} - 25^\circ$ in CHCl_3 , which on hydrogenation (Ni) and benzylation yields (I), identical with that prepared above. Hydrolysis of (III) with $\text{Ba}(\text{OMe})_2$ yields xylose 3-*p*-toluenesulphonate, m.p. 123—124°, $[\alpha]_D^{20} + 40.2^\circ$ in EtOH (rate of glucoside formation similar to 3-methylxylose). (II) on successive phosphorylation, acid hydrolysis, and hydrogenation (Ni) yields a xylosephosphoric acid (Ba salt). The rates of hydrolysis of a no. of xylosephosphoric acids are given, the rate being much higher with a 3-derivative. It is concluded that the migration previously observed (*loc. cit.*) is real, and a mechanism, involving an intermediate *ortho*-bridge, is proposed.

H. N. R.

Mannose monophosphate. III. Phosphomannonic acid and its lactones. V. N. PATWARDHAN (Biochem. J., 1934, **28**, 1854—1862).—Mannose monophosphate (I) oxidised by Br in presence of aq. $\text{Ba}(\text{OH})_2$ yields phosphomannonic acid (II), isolated as the amorphous neutral Ba salt, $(\text{C}_6\text{H}_{10}\text{O}_{10}\text{PBa})_2\text{Ba}$. (II) heated in aq. solution (III) in a sealed tube for 1 hr. yields the γ -lactone, m.p. 125—125.5°, $+54.1^\circ$, but when (III) is evaporated in vac. at room temp. the δ -lactone, m.p. 127.5—128.5°, $[\alpha]_{546}^{20} + 60.6^\circ$, is formed. The rate of dephosphorylation (IV) of (II) in *N*-HCl at 100° falls after 8 hr. and attains a const. val. equal to the rate of (IV) of the lactones under comparable conditions. (I) is undoubtedly mannose 6-phosphate.

A. E. O.

Bromination of aliphatic $\alpha\alpha$ -disulphones.—See this vol., 1313.

Addition of iodine and thiocyanogen to unsaturated compounds. B. P. CALDWELL and F. A. PRONTKOWSKI (J. Amer. Chem. Soc., 1934, **56**, 2086—2089).—The nos. quoted after the following compounds are the I val. (Hanus) and $(\text{SCN})_2$ val. [determined by Kaufmann's method (B., 1926, 447); reaction time ≤ 30 and ≥ 48 hr.], respectively: oleic 91.38, 86.18, erucic 75, 73, ricinoleic 119.87, 87.82, furoic 9.12, 5.2, maleic 0, 0, acrylic 1.77, 0.64, crotonic 7.01, 0.92, and cinnamic acid 26.26, 1.12; Et 0.22, 0.6, phenacyl 0.63, 2.7, and *p*-nitrobenzyl maleate 0, 1; Et 30.31, 0.5, phenacyl 11.82, 1.05, and *p*-nitrobenzyl

cinnamate 8.98, 1.79; citronellol 162.4, 173.8; citronellol acetate 133.3, 114.1. Allyl alcohol gives indefinite vals. The results are discussed in connexion with the effect of negative groups (near to the C:C) retarding addition.

H. B.

Detection and determination of volatile fatty acids. I. *n*-Butyric acid. L. KLINC (Biochem. Z., 1934, **273**, 1—23).— PrCO_2H (I) can be detected by oxidation in H_2SO_4 solution with H_2O_2 using $\text{FeNH}_4(\text{SO}_4)_2$ as catalyst with subsequent pptn. as the insol. $\text{Hg}(\text{CN})_2$ complex. Methods are described for the determination of 5—20 mg. of (I) by macro-iodometric, of 0.5—5 mg. by micro-iodometric, methods and of 0.006—0.06 mg. nephelometrically. A modification of the methods permits determination of (I) in presence also of HCO_2H , AcOH , EtCO_2H , and lactic acid.

P. W. C.

Migration of the double linking of oleic acid on heating in presence or absence of metals. K. H. BAUER and M. KRALLIS (Fettchem. Umschau, 1934, **41**, 194—196; cf. A., 1931, 1034).—Ozonolysis of the "solid" acids (Twitchell separation) from the products showed that Δ^7 -isoleic acid (I) as well as the Δ^6 isomeride (II) was formed when oleic acid was heated with a Ni-kieselguhr catalyst (=2%, or 5%, of Ni) at 200° or 250° for 8 hr. in a Normann beaker. In parallel experiments, but when the Ni was omitted or replaced by a Cu or Cu-Ce catalyst, (II) was formed, but (I) could not be identified. The amount of "solid" acids produced was much greater at the higher temp.; it was not much affected by the presence or absence of Ni, but was notably reduced when the Cu catalysts were used.

E. L.

New eicosenoic acid from pilot-whale oil.—See this vol., 1381.

Gadoleic acid in see-whale and humpback-whale oils.—See this vol., 1381.

Highly unsaturated C_{24} -acid in herring, cod-liver, pilot-whale, and aburazame liver-oils.—See this vol., 1381.

Synthesis of higher aliphatic compounds. IV. Synthesis of *n*-triacontanoic acid from stearic acid. (MRS.) G. M. ROBINSON (J.C.S., 1934, 1543—1545).—Condensation of Et α -bromoundecate with $\text{CHAcNa}\cdot\text{CO}_2\text{Et}$ affords Et α -acetylbrassyate (I), b.p. 202°/0.5 mm., hydrolysed by boiling $\text{AcOH}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ to μ -ketomyristic acid, m.p. 75° (reduced to myristic acid). Condensation of (I) with stearoyl chloride and Na in dry Et_2O , and subsequent hydrolysis with boiling 5% H_2SO_4 , affords μ -keto-*n*-triacontanoic acid, m.p. 104°, reduced (Clemmensen) to *n*-triacontanoic acid (II), the Et ester, m.p. 70.5°, of which is reduced by Na-BuOH at 150° to *n*-triacontan- α -ol (III) (Ac derivative, m.p. 69°; iodide, m.p. 68.5°). (II) and (III) are identical with specimens isolated from lucerne (Chibnall *et al.*, this vol., 391). A similar synthesis using the chloride of (II) affords μ -keto-*n*-dotetracontanoic acid, $\text{Me}[\text{CH}_2]_{28}\cdot\text{CO}[\text{CH}_2]_{11}\cdot\text{CO}_2\text{H}$, m.p. 110°.

J. W. B.

Aldol condensations. II. Synthesis of unsaturated aliphatic α -keto-acids. F. G. FISCHER and O. WIEDEMANN (Annalen, 1934, **513**, 251—259).—

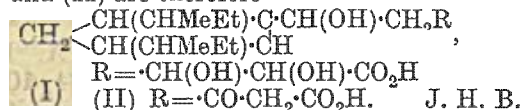
Crotonaldehyde (I), MeCHO, and a little piperidine give (cf. Kuhn and Hoffer, A., 1930, 1406) $\Delta^{\alpha\gamma}$ -hexadienal (II), b.p. 64—65°/11 mm., $\Delta^{\alpha\gamma\epsilon}$ -octatrienal (III), b.p. 62—64°/0.4 mm., m.p. 56°, and $\Delta^{\alpha\gamma\epsilon\eta}$ -decatetraenal, b.p. 110—115°/0.5 mm., m.p. 108—109° [which, like (III), can be kept for several weeks in N₂]. Addition of 40% NaOH (3—4 c.c.) to a shaken emulsion of (I) (0.05 g.-mol.) and a saturated aq. solution of AcCO₂Na (0.05 g.-mol.) at 0° gives (after 15—20 min.) a little of the Na salt (separated) of α -keto- $\Delta^{\beta\delta}$ -hepta-dienoic acid, m.p. 89° (decomp.) [phenylhydrazone, m.p. 147° (decomp.)]; p-nitrophenylhydrazone, m.p. 188° (decomp.)]. (II) similarly affords α -keto- $\Delta^{\beta\gamma\epsilon}$ -nonatrienoic acid, m.p. 116° (decomp.) [semicarbazone, m.p. 185°; oxime, m.p. 167°; phenylhydrazone, m.p. 152—153° (decomp.)]; p-nitrophenylhydrazone, m.p. 185° (decomp.)], whilst (III) gives α -keto- $\Delta^{\beta\gamma\epsilon\eta}$ -undecatetraenoic acid, m.p. 135° (decomp.). These acids are coloured (cf. Kuhn and Hoffer, *loc. cit.*), are decomposed by warm aq. alkali, and undergo ready autoxidation (air) (they can be kept in N₂); they are reduced (catalytically) to the saturated α -CO-acids. H. B.

ψ -Halogens. XXVIII. Reaction of the silver salts of dibasic (polybasic) acids with iodine in presence of cyclohexene. L. BRCKENBACH, J. GOUBEAU, and H. KOLB (Ber., 1934, 67, [B], 1729—1734; cf. this vol., 995).—The action of I on a suspension of Ag₂S in cyclohexene-Et₂O gives a mixture of 55% free S, 2% of cyclohexene-1:2-sulphide, and 10% of di-2-iodocyclohexyl sulphide. Ag₂SO₄ gives a black tar which separates I when distilled and is completely decomposed, probably owing to oxidation by liberated SO₃. Ag₂WO₄ slowly absorbs I. Ag₂CO₃ affords di-2-iodocyclohexyl carbonate, whilst Ag₂C₂O₄ affords di-2-iodocyclohexyl oxalate, m.p. 118—119°, and a substance, (C₆H₄O)_x. Ag₂ succinate gives a little succinic acid and a product which could not be purified, whereas o-C₆H₄(CO₂Ag)₂ affords o-C₆H₄(CO₂H)₂ and di-2-iodocyclohexyl o-phthalate, m.p. 126°. H. W.

Complex cobaltioxalates.—See this vol., 1321.

Plant growth substances. X. Constitution of auxin-*a* and -*b*. F. KOGL and H. ERXLEBEN (Z. physiol. Chem., 1934, 227, 51—73; cf. this vol., 1044).—Oxidation of auxin-*a* (I), its lactone, or auxin-*b* (II) with alkaline KMnO₄ gives a dicarboxylic acid (III), C₁₃H₂₄O₄, m.p. 129°, [α]_D²⁰ -11.9° in 96% EtOH, mol. surface 46—52 Å.² (di-p-phenylphenacyl ester, m.p. 169°). Oxidation of dihydroauxin-*a* with CrO₃ in AcOH affords H₂C₂O₄ and a ketone (an oil), C₁₃H₂₄O, [α]_D²⁰ -9.5° in 96% EtOH (p-nitrophenylhydrazone, m.p. 125.5°). On heating with boiling Ac₂O and distillation in vac., (III) yields the anhydride, m.p. 95.5—96°. With Br and red P, (I) gives the $\alpha\alpha$ -Br₂-acid (IV), C₁₃H₂₂O₄Br₂, m.p. 90°. The Me₂ ester of (IV) (obtained by way of Ag₂ salt and MeI) by Grignard reagent and oxidation of the resulting diglycol with Pb(OAc)₄ affords a 1:3-diketone (an oil), [α]_D²⁰ +9.5° in 96% EtOH, since hydrolysis with aq. KOH gives a C₅-acid (V) and a C₆-ketone (VI). (V) yields a p-phenylphenacyl ester, C₁₉H₂₀O₃, m.p. 71°, [α]_D²⁰ +9.9° in 80% EtOH, which is identical with the corresponding derivative of (+)- α -methyl-n-butyric acid. (VI) gives a 2:4-dinitrophenylhydrazone, m.p. 72°, identical with the derivative from Me sec.-Bu ketone.

Hence (III) is $\alpha\alpha'$ -di-sec.-butylglutaric acid. The "ketone half" although racemic as isolated must possess the same configuration as the "acid half" of the 1:3-diketone. The KMnO₄ oxidation of (II)-acetal lactone yields, in addition to (III), *cis*-glutaconic acid, m.p. 134°. Oxidation of dihydroauxin-*a* with Pb(OAc)₄ gives glyoxylic acid (identified by colour reaction), and an aldehyde, which on oxidation with KMnO₄ gives an acid, C₁₆H₃₀O₃ (p-phenylphenacyl ester, m.p. 120°). This indicates 2 OH groups at α and β . (I) and (II) are therefore



Synthesis of long-chain aliphatic $\omega\omega'$ -dicarboxylic acids. E. SCHWENK and H. PRIEWE (J. Amer. Chem. Soc., 1934, 56, 2101—2102).—*m*-Tolyl adipate, m.p. 85—87° [prepared by slow addition of POCl₃ (1 mol.) to the acid (1 mol.) and *m*-cresol (2 mols.) at about 120°], is rearranged by AlCl₃ at 165° to $\alpha\delta$ -di-(2-hydroxy-4-methylbenzoyl)butane, m.p. 122—123°, reduced (Clemmensen) to $\alpha\zeta$ -di-(2-hydroxy-4-methylphenyl)hexane, m.p. 102—103°. This is reduced (H₂ and Ni in methylcyclohexane at 230° and 100 atm.) to $\alpha\zeta$ -di-(2-hydroxy-4-methylcyclohexyl)hexane, b.p. 205—208°/1.5 mm., which is oxidised (CrO₃, AcOH) to $\alpha\zeta$ -di-(2-keto-4-methylcyclohexyl)hexane, m.p. 60—65°, or $\epsilon\mu$ -diketo- $\beta\delta$ -dimethylhexadecane- $\alpha\pi$ -dicarboxylic acid (I), m.p. 70—71°, according to the conditions used. Clemmensen reduction of (I) gives $\beta\delta$ -dimethylhexadecane- $\alpha\pi$ -dicarboxylic acid, m.p. 64—68°. H. B.

Ketolic condensations of ethyl acetoacetate with formaldehyde. H. GAULT and J. BURKHARD (Compt. rend., 1934, 199, 795—797).—CH₂Ac·CO₂Et is added gradually to 30% CH₂O containing K₂CO₃ at \geq 8°. When the mixture gives no colour with FeCl₃, it is saturated with (NH₄)₂SO₄ and extracted with Et₂O at -10°. The extract is dried successively with anhyd. MgSO₄ and P₂O₅ at -10° to -15° and Et di- $\alpha\alpha$ -hydroxymethylacetoacetate (I) is pptd. by light petroleum. When dry, (I) is stable at room temp., it gives an Ac₂ derivative, b.p. 114°/14 mm., and is transformed by NH₃ into a ketimine, m.p. 185°. Et δ -hydroxy- $\alpha\gamma$ -diacetylbutane- $\alpha\gamma$ -dicarboxylate (II) (viscous acyclic and solid cyclic forms) is obtained from (I) and CH₂Ac·CO₂Et in presence of aq. K₂CO₃ or from CH₂Ac·CO₂Et and CH₂O followed by further addition of CH₂Ac·CO₂Et. Gradual addition of 30% CH₂O to CH₂Ac·CO₂Et in presence of K₂CO₃-H₂O-EtOH at 28—30° gives Et₂ $\alpha\epsilon$ -dihydroxy- $\beta\delta$ -diacetylpentane- $\beta\delta$ -dicarboxylate, m.p. 100°, also obtained from (II) and CH₂O. H. W.

Hydroxytetronic acid. F. MICHEEL and F. JUNG (Ber., 1934, 67, [B], 1660—1664; cf. A., 1933, 1143).—Hydroxytetronic acid (I), m.p. 153° (prep. from Et benzoylglycollate and K described), is transformed by CH₂N₂ into the Me₂ ether, $\begin{array}{c} \text{C} \\ | \\ \text{C} \cdot \text{OMe}' \end{array}$, b.p. 128°/13 mm., which does not react with alkali or I and is converted by the successive action of O₃ in AcOH and MeOH-NH₃ into oxamide and OH·CH₂·CO·NH₂, m.p. 116°. (I) is transformed by NHPH·NH₂ in AcOH into $\alpha\beta$ -diketo- γ -hydroxybutyro-

lactonediphenylhydrazone, labile form, m.p. about 180°, stable variety, m.p. 238°, also obtained from $\alpha\beta$ -diketo- γ -hydroxybutyrolactone (II), prepared by oxidising (I) with $\text{Cu}(\text{OAc})_2$ and removal of Cu by salicylaldehyde or with $p\text{-O}_2\text{C}_6\text{H}_4\text{O}$; it is regarded as

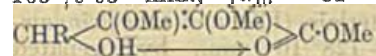
$\text{CH}_2\text{--}\begin{array}{c} \text{CO} \\ \text{C:N-NHPh} \\ \text{C:N-NHPh} \end{array}$ The corresponding *di-p-nitrophenylhydrazone* has m.p. 295°. (II) is unstable, but, immediately after prep., is reduced by H_2S to (I); on keeping or, particularly, on warming in H_2O it loses CO_2 and the residue is converted by $\text{NHPh}\cdot\text{NH}_2$ into $\text{CO}_2\text{H}\cdot\text{CMe:N}\cdot\text{NHPh}$. (II) and 1:3:4- $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2$ give the *quinoxaline* derivative, $\text{C}_{11}\text{H}_8\text{O}_2\text{N}_2$.

H. W.

Preparation of citroanilide. F. DI MENTO (Annali Chim. Appl., 1934, 24, 464—468).—Pebal's method (Annalen, 1852, 82, 87) gives poor yields. By heating citric acid with NH_2Ph , first at 60—70° and later at 120—130°, citroanilide, m.p. 199°, mixed with very little citromonoanilic acid and citrodianilide, m.p. 179°, is obtained.

T. H. P.

Methyl ethers of ascorbic acid. W. N. HAWORTH, E. L. HIRST, and F. SMITH (J.C.S., 1934, 1556—1560).—*l*-Ascorbic acid (I) with $\text{CH}_2\text{N}_2\text{--Et}_2\text{O}$ at -10° gives mainly (90%) its 3- (II), m.p. 121°, $[\alpha]_D^{20} +29^\circ$ in H_2O (absorption band at 245 $\text{m}\mu$; slow reaction with I in acid solution; intense blue with FeCl_3 ; Na salt, $[\alpha]_D +49.3^\circ$ in H_2O), and its (?) 2-*Me* derivative (III), m.p. 162°, $[\alpha]_D^{20} +200^\circ$ in H_2O (band at 280 $\text{m}\mu$; transient colour with FeCl_3 ; Na salt $[\alpha]_D^{20} +223^\circ$ in H_2O). After ozonolysis of (II) the action of NH_3 gives $[\text{CO}\cdot\text{NH}_2]_2$ and *l*-threonamide, m.p. 88—90°, $[\alpha]_D^{20} +58^\circ$ in H_2O . With excess of CH_2N_2 in MeOH at -5° (II) gives the 2:3- Me_2 derivative (IV) (non-reducing, identical with a specimen obtained directly from (I). With $\text{MeI--Ag}_2\text{O}$ (IV) gives 2:3:5:6-tetramethyl-*l*-ascorbic acid (V) (band at 235—240 $\text{m}\mu$), the ozonolysis product of which with MeOH--NH_3 gives only $[\text{CO}\cdot\text{NH}_2]_2$ and 3:4-dimethyl-*l* threonamide and no erythronamide, the presence of which in previous work (A., 1933, 1143) arose from the presence of isomeric forms of (IV). With NaOH or $\text{Ba}(\text{OH})_2$ (IV) and (V) both yield salts of the corresponding open-chain acid, lactonisation to the original compound occurring on acidification. With $\text{Me}_2\text{SO}_4\text{--}40\%\text{ KOH}$ in aq. COMe_2 and subsequent esterification ($\text{Ag}_2\text{O--MeI}$) (IV) affords a *Me* tetramethylketogulonate, b.p. 105°/0.03 mm., $[\alpha]_D^{20} -51^\circ$ in MeOH , probably

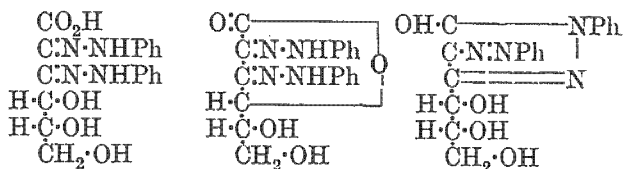


$[\text{R}=\text{OMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})\cdot]$, which resists further methylation and attack by O_3 , oxidation with HNO_3 and subsequent methylation affording $\text{Me}_2\text{C}_2\text{O}_4$ and *Me d*-dimethoxysuccinate. Similar methylation of (V) gives a mixture of the open-chain acid $\text{HO}\cdot\text{CHR}\cdot\text{C(OMe):C(OMe)\cdot CO}_2\text{H}$ and some fully methylated derivative, subsequent treatment with $\text{Ag}_2\text{O--MeI}$ affording, respectively, (V) and $\text{MeO}\cdot\text{CHR}\cdot\text{C(OMe):C(OMe)\cdot CO}_2\text{Me}$. (III) gives no $\text{H}_2\text{C}_2\text{O}_4$ on ozonolysis (? double linking between C_1 and C_2) and with $\text{CH}_2\text{N}_2\text{--Et}_2\text{O}$ affords a *Me* ether, $[\alpha]_D^{20} +107^\circ$ in MeOH (band at 270 $\text{m}\mu$), which isomerises to (IV) when heated. With $\text{MeI--Ag}_2\text{O}$ (III) affords mainly (V). These results establish the superior acid-

ity of the 3-OH in (I), and the presence of labile derivatives indicates that (I) can react in > one structural modification.

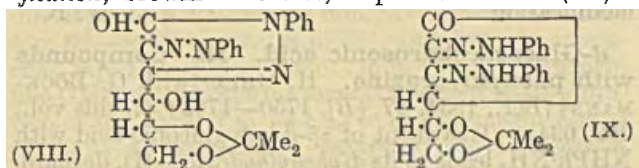
J. W. B.

d-Glucosaccharosonic acid. III Compounds with phenylhydrazine. H. OHLE [with G. BOCKMANN] (Ber., 1934, 67, [B], 1750—1762; cf. this vol., 392, 634).—Treatment of $\alpha\beta$ -diketogluconic acid with $\text{NHPh}\cdot\text{NH}_2$ leads to its *diphenylhydrazone* (I), decomp. 159—160°, $[\alpha]_D^{20} +241^\circ$ to -92° in $\text{C}_6\text{H}_5\text{N}$, $[\alpha]_D^{20} +107.8^\circ$ to $+1192^\circ$ in 0.2*N*- NaOH , the corresponding



lactone (II), m.p. 202—203° (slight decomp.), $[\alpha]_D^{20} -93.5^\circ$ in $\text{C}_6\text{H}_5\text{N}$, and 4-benzeneazo-1-phenyl-3- $\alpha\beta$ -trihydroxypropylpyrazolone (III), m.p. 215—216° (slight decomp.), $[\alpha]_D^{20} -53.1^\circ$ in $\text{C}_6\text{H}_5\text{N}$, $+1305^\circ$ in 0.08*N*- NaOH . In presence of mineral acid (I) and (II) are mainly produced, whereas in presence of AcOH (I) is scarcely formed and (III) appears. Recrystallisation from COMe_2 or EtOAc converts (I) partly into (II); $\text{C}_6\text{H}_5\text{N}$ behaves similarly, whilst dil. NaOH at 20° accelerates the production of (III). In contrast to (I) and (III), (II) is insol. in cold, dil. alkali, whereas boiling alkali transforms it into (III). (III) yields a *Na* salt ($+2\text{H}_2\text{O}$), m.p. 131—132°, $[\alpha]_D^{20} +1054^\circ$, or ($+1\text{H}_2\text{O}$), m.p. 187—191°, $[\alpha]_D^{20} +1125^\circ$. (III) is transformed by Ac_2O in $\text{C}_6\text{H}_5\text{N}$ at 100° into the Ac_3 derivative (IV), m.p. 109—110°, $[\alpha]_D^{20} +37.6^\circ$ in CHCl_3 , $+54.4^\circ$ in $\text{C}_6\text{H}_5\text{N}$, $+74.2^\circ$ in C_6H_6 , whilst the fourth OH is not affected by boiling Ac_2O . (IV) and CH_2N_2 give a non-cryst. *Me* derivative, hydrolysed by *N*- NaOH to 4-benzeneazo-5-methoxy-1-phenyl-3- $\alpha\beta$ -trihydroxypropylpyrazole (V), m.p. 165—166°, $[\alpha]_D^{20} +672^\circ$ in $\text{C}_6\text{H}_5\text{N}$, better obtained from (III) and CH_2N_2 in COMe_2 . Reductive fission of (III) with SnCl_2 and conc. HCl gives NH_2Ph , whereas 4-amino-1-phenyl-3- $\alpha\beta$ -trihydroxypropylpyrazolone could not be isolated as such or as its salts. Oxidation of (V) by KMnO_4 in COMe_2 gives 4-benzeneazo-5-methoxy-1-phenylpyrazole-3-carboxylic acid (VI), m.p. 180—181°, converted by boiling alkali into 4-benzeneazo-1-phenylpyrazolone-3-carboxylic acid (VII). (VII) with a large excess of CH_2N_2 gives *Me* 4-benzeneazo-5-methoxy-1-phenylpyrazole-3-carboxylate, m.p. 133—134°, transformed by partial hydrolysis into (VI). *Me* 4-benzeneazo-1-phenylpyrazolone-3-carboxylate, m.p. 136.5—137.5°, is obtained in poor yield from (VII) and MeOH--HCl . (III), COMe_2 , and conc. H_2SO_4 yield 4-benzeneazo-1-phenyl-3- α -hydroxy- $\beta\gamma$ -isopropylidenedioxypropylpyrazolone (VIII), m.p. 181—182°, $[\alpha]_D^{20} -73.8^\circ$ in $\text{C}_6\text{H}_5\text{N}$ [*Na* salt, slow decomp. $> 200^\circ$ after softening at 170°; *Me* ether, m.p. 137—138°, $[\alpha]_D^{20} +475.6^\circ$ in C_6H_6 (*Me* in pyrazole system); *Ac* derivative, m.p. 152—153°, $[\alpha]_D^{20} -14.22^\circ$ in C_6H_6 , which yields a resinous *Me* derivative]. (VIII) does not react with CPh_3Cl . (III) and CPh_3Cl give an amorphous product converted by $\text{COMe}_2\text{--conc. H}_2\text{SO}_4$ into (VIII). (IV) is transformed by $\text{COMe}_2\text{--H}_2\text{SO}_4$ into the compound (IX), alizarin-red needles, m.p.

224—225°, accompanied by a (?) desmotropic modification, brownish needles, m.p. 223—224°. (IX) is



insol. in dil. alkali, sol. in NaOH-EtOH, and from the solution CO₂ ppts. (VIII).

Ascorbic acid is converted by oxidation with p-O-C₆H₄·O and treatment of the product with NHPH-NH₂ into the lactone of αβ-diketo-*l*-idonic acid di(phenylhydrazine), m.p. 212—214° (decomp.), transformed by alkali into 4-benzeneazo-3-*l*-threo-glyceryl-1-phenylpyrazolone, m.p. 210—211° (decomp.), [α]_D +1155° in 0.2*N*-NaOH, which does not depress the m.p. of (III), but is not identical therewith, since its isopropylidene derivative has m.p. 170—171°, [α]_D²⁵ -31.3° in C₅H₅N.

d-Glucosaccharosonic acid couples with PhN₂Cl, but the product does not yield the substances described above when acted on by NHPH-NH₂. H. W.

Velocity of bromination of bromosulphoacetic and α-sulphopropionic acids.—See this vol., 1313.

Velocity of bromination and racemisation of α-phenylsulphinopropionic acid.—See this vol., 1313.

Kinetics of bromination of α-carboxydiethyl- and methyl-α-carboxyethyl-sulphone.—See this vol., 1313.

Reaction of aldehydes with metals and their catalytic hydrogenation under pressure. J. VON BRAUN and G. MANZ (Ber., 1934, 67, [B], 1696—1712).—Hydrogenation of aldehydes, CH₂R·CHO (I), in presence of Ni in a steel bomb causes partial conversion into the corresponding primary alcohol; the remainder of (I) is in part condensed to the αβ-unsaturated alcohol, in part transformed into CH₂R·CH(OX)·CHR·CHO (X=metal) (II), both of which are hydrogenated to CH₂R·CH₂·CHR·CH₂·OH. A smaller portion of (II) escapes the action of H and passes through CHO·CHR·CH(CH₂R)·O·CH(OX)·CH₂R and R·CH<CH(CH₂R)·O>C(OX)·CH₂R into the glycol ester, CH₂R·CH(OX)·CHR·CH₂·O·CO·CH₂R.

The phenylimido-chloride of fencholic acid, m.p. 165°, is converted by NH₂Ph in Et₂O into the *diphenylamidine*, C₂₂H₂₃N₂, m.p. 236°, which is reduced by Na and EtOH to the *diamine*, C₉H₁₇·CH(NHPH)₂, m.p. 216°, whence fencholaldehyde (I) is obtained by means of HCl and steam. Hydrogenation (Ni in steel autoclave, 200°/50 atm.) of (I) gives exclusively the corresponding primary alcohol, b.p. 104—105°/15 mm. Similarly campholaldehyde affords campholcarbinol, b.p. 100°/18.5 mm., m.p. 60°. *n*-Decaldehyde gives *n*-decyl alcohol, b.p. 118—119°/13 mm., and β-*n*-octyl-*n*-dodecyl alcohol (II), b.p. 230°/17 mm. (II) is transformed by HBr at 120° into the corresponding bromide (III), b.p. 195°/4 mm., converted by the successive action of Mg and acid into β-*n*-octyldodecane, b.p. 200°/14 mm., better obtained by hydrogenation (Pd) of β-*n*-octyl-Δ⁸-dodecene, b.p. 193—195°/12 mm., derived

from (III) by action of KOH-EtOH-H₂O. The residue from distillation of the hydrogenated product affords decoic acid when hydrolysed. Pr^oCHO is hydrogenated at 200° to Bu^oOH and β-ethyl-*n*-hexyl alcohol (IV), b.p. 84—86°/15 mm. (IV) is transformed by conc. HBr at 120° into β-ethyl-*n*-hexyl bromide, b.p. 73—76°/15 mm., which with NMe₃ in C₆H₆ at 100° yields the quaternary bromide, m.p. > 200° after softening, transformed by successive treatment with Ag₂O and distillation with alkali into dimethyl-β-ethyl-*n*-hexylamine, b.p. 177—179° (methiodide, m.p. 215°), and β-ethyl-Δ⁸-hexene (V), b.p. 116—118°. Ozonisation of (V) affords COEtBu^o, b.p. 140—142° (semicarbazone, m.p. 103°). Hydrogenation of Pr^oCHO in an autoclave without catalyst causes separation of Cu (from packing rings), giving unchanged Pr^oCHO, α-ethyl-Δ⁸-pentalen, b.p. 172° (identified by hydrogenation and conversion into α-ethylvaleraldoxime, b.p. 104—106°/10 mm., which is transformed by PCl₅ in Et₂O into α-ethylhexonitrile, b.p. 75°/10 mm., hydrolysed by HCl at 120° to α-ethyl-*n*-hexoic acid, b.p. 122—124°/10 mm.), and monobutyl-β-ethyl-*n*-hexane-αγ-diol (VI), b.p. 148—150°/10 mm., which contains 1 OH (Zerevitinov). (VI) is hydrolysed to Pr^oCO₂H and β-ethylhexane-αγ-diol (VII), b.p. 131—133°/12 mm., converted by 1 Pr^oCOCl into (VI) and by 2 Pr^oCOCl into the dibutyl derivative, b.p. 154—158°/12 mm., also obtained from (VI) and Pr^oCOCl in C₅H₅N. Conc. HCl or HBr at 120° converts (VI) into the unstable αγ-dichloro-, b.p. 50°/0.2 mm., and αγ-dibromo-, b.p. 82°/0.2 mm., -β-ethyl-*n*-hexane, respectively. Oxidation of (VII) with Beckmann's mixture in a current of steam leads to β-hydroxy-α-ethyl-*n*-hexaldehyde, b.p. 100—103°/12 mm. [oxime, b.p. 140—145°/(?)12 mm.], and *n*-heptane-γδ-dione (VIII), b.p. 147—149° (dioxime, m.p. 172°; phenylosazone, m.p. 106°). (VIII) is also obtained by oxidation of (VI), which affords mainly the keto-ester, COPr^o·CHEt·CH₂·O·COPr^o, b.p. 130—134°/12 mm. Treatment of (VI) with PCl₃ in CH₂Cl₂ followed by distillation under diminished pressure and subsequent hydrolysis leads to Pr^oCO₂H and β-ethyl-Δ⁸-hexenyl alcohol (IX), b.p. 68—71°/12 mm. (Ac derivative, b.p. 79—81°/? pressure). (IX) and PBr₃ in C₆H₆Cl₂ give β-ethyl-Δ⁸-hexenyl bromide, b.p. 68—70°/12 mm., which with NMe₃ in C₆H₆ readily yields the quaternary bromide, m.p. about 175°, and is converted by NH₄CNS in EtOH into the thiocarbimide, C₈H₁₅N·C·S, b.p. 105—110°. When heated with PhCHO, Pr^oCHO yields unchanged materials, (IX), and α-ethylcinnamaldehyde, b.p. 126—128°/10 mm., hydrogenated to β-benzyl-*n*-butyl alcohol, b.p. 126—128°/10 mm. Pr^oCHO reacts with finely-divided metals in N₂, evolution of H₂ being most marked with Zn and, particularly, Mg. The amount of glycol ester is invariably small, whereas that of the acetaldehyde derivative diminishes in the sequence Mg, Co, Ni, Fe, Cu, Cr; in absence of metal Pr^oCHO remains unchanged. When heated under pressure at 200°, Pr^oCHO is extensively altered, and the ratio of the products is considerably affected only by the more active metals, which themselves appear to undergo change. (Pr^oCHO)₃ is less readily affected than is Pr^oCHO.

Hydrogenation of heptaldehyde under pressure leads

to heptyl alcohol and β -*n*-amyl-*n*-nonyl alcohol (X), transformed by HBr into β -*n*-amyl-*n*-nonyl bromide, b.p. 154—156°/11 mm., which with NMe_3 in C_6H_6 gives the non-cryst. quaternary bromide (XI) (corresponding *platinichloride*, decomp. 218°). Treatment of (XI) with Ag_2O and fission of the base yields *dimethyl- β -*n*-amyl-*n*-nonylamine*, b.p. 143—145°/11 mm. (non-cryst. *methiodide*, *hydrochloride*, and *picrate*), and β -*n*-amyl- Δ^{α} -*nonene*, b.p. 117—118°/11 mm., ozonised to *n*-amyl *n*-heptyl ketone, b.p. 128—129°/11 mm., m.p. 18.5° (non-cryst. *semicarbazone*). When heated in an autoclave at 200—210° in N_2 heptaldehyde gives α -heptylideneheptaldehyde (XII) [hydrogenated to (X) and oxidised by KMnO_4 (=4 O) to hexoic and heptoic acid], and the *heptoyl* derivative, b.p. 176—178°/0.3 mm., of β -*n*-amyl*nonane- α -diol*, oxidised by Beckmann's mixture to the *diketone*, $\text{C}_6\text{H}_{13}\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_5\text{H}_{11}$, b.p. about 110°/12 mm. The behaviour of heptaldehyde towards metals in glass closely resembles that of $\text{Pr}^{\alpha}\text{CHO}$. The view that (XII) can arise by direct condensation is supported by the isolation of α -*n*-amylcinnamaldehyde, b.p. 155—158°/13 mm., from heptaldehyde and PhCHO .

Pressure hydrogenation of *isovaleraldehyde* (XIII) gives *isoamyl* alcohol (about 60%) and ϵ -*methyl- β -isopropyl-*n*-hexyl alcohol*, b.p. 92—95°/11 mm. ϵ -*Methyl- β -isopropyl-*n*-hexyl bromide*, b.p. 92—95°/11 mm., and NMe_3 give the quaternary bromide, m.p. 152°, whence *dimethyl- ϵ -methyl- β -isopropyl-*n*-hexylamine*, b.p. 196—198° (*methiodide*, m.p. 132°), and ϵ -*methyl- β -isopropyl- Δ^{α} -*n*-hexene*, b.p. 150°, ozonised to *Pr $^{\beta}$ - γ -methylbutyl ketone*, b.p. 58°/10 mm. (*semicarbazone*, m.p. 119°). Decomp. of (XIII) in an autoclave in N_2 at 200° is less extensive than that of $\text{Pr}^{\alpha}\text{CHO}$, giving unchanged material, α -*isovalerylideneisovaleraldehyde*, and the glycol ester (XIV), $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CH}(\text{OH})\cdot\text{CHPr}^{\beta}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Pr}^{\beta}$. Treatment of (XIV) with PCl_5 in CH_2Cl_2 followed by distillation and hydrolysis leads to heptoic acid and ϵ -*methyl- β -isopropyl- Δ^{β} -hexenyl alcohol*, b.p. 80—85°/12 mm. The behaviour of (XIII) towards cold metals is very similar to that of $\text{Pr}^{\alpha}\text{CHO}$. MeCHO becomes blue and green after prolonged contact with Cu and Co, respectively, and yields crotonaldehyde and, possibly, γ -hydroxy-*n*-butyl acetate. H. W.

Preparation of $\alpha\beta$ -unsaturated aldehydes by the chromous chloride method. J. VON BRAUN and W. RUDOLPH (Ber., 1934, 67, [B], 1735—1739; cf. this vol., 393).— $\delta\delta$ -*Dimethyl- $\Delta^{\alpha\gamma\eta}$ -decatrienoic acid* is converted into the corresponding phenylimido-chloride, which is reduced by CrCl_2 in Et_2O ; the product is treated with 10% $\text{H}_2\text{C}_2\text{O}_4$ and steam, thereby giving $\delta\delta$ -*dimethyl- $\Delta^{\alpha\gamma\eta}$ -decatrienal*, b.p. 81—82°/0.15 mm., in nearly 30% yield; the *semicarbazone*, *p*-nitrophenylhydrazone, and NaHSO_3 compound are described. Citronellal and $\text{CH}_2(\text{CO}_2\text{H})_2$ give a mixture of acids, b.p. 178—180°/12 mm., transformed by PCl_5 into the mixed chlorides, b.p. 110—114°/0.4 mm., from which a cryst. *anilide* (I), m.p. 49—51°, is isolated. (I) is transformed into the phenylimido-chloride, converted by CrCl_2 in Et_2O into $\delta\delta$ -*dimethyl- $\Delta^{\alpha\gamma\eta}$ -decadienal*, b.p. 108—110°/12 mm. (*oxime*, b.p. about 140°/12 mm.; *semicarbazone*, m.p. 135° after softening at 120°; non-cryst. *p*-nitrophenyl-

hydrazone). Citral is reduced under pressure (Ni and H_2) to $\gamma\gamma$ -dimethyloctan-1-ol, which is oxidised to inactive dimethyloctanal, condensed with $\text{CH}_2(\text{CO}_2\text{H})_2$ in $\text{C}_5\text{H}_5\text{N}$ at 40—50° to $\delta\delta$ -*dimethyl- Δ^{α} -decanoic acid* (II), b.p. 168—170°/12 mm. (II) is transformed through the *chloride*, b.p. 97°/0.2 mm., *anilide*, b.p. 225°/0.2 mm., m.p. 70°, and phenylimido-chloride into $\delta\delta$ -*dimethyl- Δ^{α} -decanal*, b.p. 122—125°/14 mm. (*semicarbazone*, m.p. 142°). Pentenoanilide yields Δ^{α} -pentenal, b.p. 125—128° (*semicarbazone*, m.p. 180°; *p*-nitrophenylhydrazone, m.p. 123°). H. W.

Production of a mixture of aldehydes and acids containing eight to ten carbon atoms. Factors affecting the yields of aldehydes and acids in the vapour-phase oxidation of a liquid hydrocarbon fraction. C. Q. SHEELY and W. H. KING (Ind. Eng. Chem., 1934, 26, 1150—1153).—Detailed results of the effects of hydrocarbon ratio (I), reaction time (II) (3.5, 5.2, and 10.4 sec.) and temp. (III) (335°, 387°, 444°), and of the v.p. of the HNO_3 catalyst (IV) (0—150 mm.) within the limits given in parentheses, on the yields of C_8 — C_{10} aldehydes (V) and acids (VI) formed by the atm.- HNO_3 vapour oxidation of liquid hydrocarbons (cleaner's naphtha, b.p. approx. 165—216°) in the vapour phase at 645 mm., are tabulated and discussed. Optimum conditions [19.73% yield of (V) and 25.39% yield of (VI), on hydrocarbon burned] are (I) 37.3, (II) 3.5, (III) 444°, and (IV) 67.5 mm. The (V) obtained compared favourably (80% purity by $\text{NH}_2\text{OH}\cdot\text{HCl}$ assay) with the best market samples for perfumery, the estimated cost being only about 10% of the market price. The yield of (VI) is increased by increasing (IV), lowest yields being obtained at 444°. No alcohols are formed unless HNO_3 is absent. J. W. B.

Atmospheric oxidation. III. Catalytic oxidation of trioses and related compounds. H. A. SPOEHR and H. W. MILNER (J. Amer. Chem. Soc., 1934, 56, 2068—2074).—*dl*-Glyceraldehyde (I) is readily oxidised (to CO_2) by air in presence of a mixture of Na ferropyrrophosphate (II) and Na_2HPO_4 at 37.9°. There is no induction period and the largest amount of CO_2 is produced during the first 24 hr. The decrease in the rate of formation of CO_2 is more pronounced with very small concns. of (I), and may be due to condensation or rearrangement of (I). Much more oxidation occurs when (I) is added in, e.g., 5 successive portions at intervals of 3 days, rather than at the beginning. The initial rate of oxidation of (I) is much lower in the absence of Fe. The rate of oxidation of $\text{CO}(\text{CH}_2\cdot\text{OH})_2$ is slightly < that of (I). $\text{CH}_2\text{Ac}\cdot\text{OH}$ (Nef, A., 1905, i, 3) is also oxidised readily; AcCO_2H (III) is also formed. Glycerol also undergoes oxidation to CO_2 , but at a slow initial rate. AcCHO is oxidised more slowly than any of the above compounds, whilst (III) is unaffected (or oxidised exceedingly slowly). Lactic acid and $\text{Pr}^{\beta}\text{OH}$ are oxidised in presence of (II) (not with Na ferripyrophosphate) to (III) and COMe_2 , respectively. Volatile aldehydic products (but no CO_2) are obtained from EtCHO , $\text{Pr}^{\alpha}\text{OH}$, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$, and $(\text{CH}_2)_3(\text{OH})_2$. Experiments with glucose (cf. A., 1924, i, 836; 1926, 385) under sterile conditions and in presence of HgCl_2 or $\text{Hg}(\text{CN})_2$

indicate that micro-organisms are not responsible for the production of CO₂ (cf. Theriault *et al.*, A., 1933, 680).
H. B.

Physical interpretation of the Lapworth-Robinson theory. H. A. C. McKAY (Chem. and Ind., 1934, 870—871).—The Lapworth-Robinson pos-

tulation ($\text{>C}=\text{O}$) of the reactivity of the CO group is more satisfactorily represented by the view that the structures (i) $\text{>C}=\text{O}$ and (ii) $\text{>C}\rightarrow\text{O}$ (coordinate linking) lead, by a linear combination of eigenfunctions ($a\psi_1 + b\psi_2$), to a resonance state. Reaction of the CO involves (ii) rather than (i); the condition for reaction is $b \gg a$, i.e., when the internuclear distance between C and O is large. This is represented by a potential-energy diagram, which gives a probable val. for the energy of activation (I) of CO. Electromeric and inductive effects are ascribed to changes in (I).
H. B.

Constitution and properties of keto-anils. M. MONTAGNE (Compt. rend., 1934, 199, 671—673).—The anils derived from COEtPr (I) and CPhEt react with MgMeI at 80°, but not at room temp. The Grignard derivative of the anil from (I) with Ac₂O yields a mixture of two Ac derivatives, b.p. 178—185°/19 mm., one of which is hydrolysed by cold H₂SO₄ to yield NH₂Ph and COPr·CHMeAc, the other being stable to HCl but hydrolysed by boiling 48% HBr to yield NH₂Ph and (I). Direct acetylation of the anil yields almost exclusively the stable Ac derivative. The anil probably reacts in the imino-form towards MgMeI, and the formation of two Ac compounds by subsequent acetylation is due to partial addition of Ac₂O at the double linking and elimination of MgI·OAc.
A. E. O.

Keten. II. Rate of polymerisation. F. O. RICE and J. GREENBERG (J. Amer. Chem. Soc., 1934, 56, 2132—2134; cf. this vol., 1091).—Keten (I) does not polymerise appreciably in the gaseous phase at room temp. during several hr.; polymerisation occurs (erratically) at one or more points of the vessel. Liquid (I) is stable at -80° provided it is freed (by distillation) from C particles, traces of rubber, or resinous material; polymerisation occurs rapidly at 0° (in sealed tubes). The rate (approx. bimol.) of polymerisation of (I) in different solvents at 0° is determined. Polymerisation is independent of the presence or absence of O₂ (or peroxides) or inhibitors (quinol; anthraquinone). In general, the rate is slower in solvents of low dielectric const. The energy of activation of the polymerisation process in COMe₂ is 11,000 g.-cal. (from measurements at 0° and 20°).
H. B.

Photo-reactions of liquid and dissolved ketones. I. [Acetone and benzophenone].—See this vol., 1316.

Syntheses of ketones and β-diketones with the help of boron trifluoride. H. MEERWEIN and D. VOSSEN (J. pr. Chem., 1934, [ii], 141, 149—166).—Mainly a more detailed account of work previously reviewed (A., 1933, 360). The following appears to be new. C₆H₆ (1 mol.), Ac₂O (2 mols.), and BF₃ at 0° give 13.7% of CPhMe; cyclohexene similarly affords 27% of 1-acetyl-Δ¹-cyclohexene; 1-keto-1:2:3:4-

tetrahydronaphthalene yields 83% of the 2-Ac derivative, b.p. 173—175°/12 mm., m.p. 55—56°; COEt₂ furnishes βδ-diketo-γ-methylhexane and some CH₂Ac₂ (from the Ac₂O); COMe₂ gives CH₂Ac₂; deoxybenzoin does not react with Ac₂O, but is converted into α-benzoyl-αβγ-triphenyl-Δ²-propene. The compound BF₃·Ac₂O, m.p. 194°, of Bowls and Nieuwland (A., 1931, 1404) is actually (CHAc₂·CO)₂O·3BF₃ (cf. *loc. cit.*). (Pr²CO)₂O and BF₃ at 0° similarly give BF₃·2Pr²CO·H, b.p. 68—70°/15 mm., and the compound, (Pr²CO·CMe₂·CO)₂O·3BF₃, m.p. 117—119°, which is decomposed by warm H₂O to CO₂ and COPr². The Cu salts of αα-dipropionylethane and αα-di-n-butylpropene have m.p. 172—174° and 171—172°, respectively. CH₂BzAc and BF₃ give a 1:1-compound (cf. Morgan and Tunstall, A., 1924, i, 1359).
H. B.

Synthesis of acetone from acetylene and steam in presence of catalysts. M. S. PLATONOV, V. A. PLAKIDINA, and K. K. BELTISTOV (J. Gen. Chem. Russ., 1934, 4, 421—433).—The highest yields of COMe₂ from 10:1 H₂O-C₂H₂ using different catalysts are: 2ZnO-V₂O₅-kaolin (I) 50—60, 2ZnO-V₂O₅ 50, 2CdO-V₂O₅ (II) 50, Fe₂O₃ 40, MnO-V₂O₅ 1.3, ZnO-V₂O₅-CaCO₃ 21—25, CdO-CaCO₃ 15, ZnO-Fe₂O₃ 16, Fe₂O₃-V₂O₅-kaolin 12, CeO₂-ThO₂-kaolin 26, ThO₂-Al₂O₃ 13, ZnO-MgO-CaCO₃ 14, ZnO-MgO-V₂O₅-CaCO₃ 12.4% of theory. The optimum temp. using (I) is 425—450°, 470° for (II), and 450° for Fe₂O₃. The yields of MeCHO and AcOH, obtained as by-products, increase as the temp. falls below the optimum. The yield of COMe₂ increases with increasing concn. of H₂O in the vapour phase, but is independent of the velocity of flow up to 12,000 vols. per hr. per vol. of catalyst. (I) undergoes partial inactivation with time, but may be regenerated by passing air at 350—500°. (II) undergoes reduction to metallic Cd, which is volatilised into the receiver; for this reason (II) cannot be reactivated.
R. T.

Iodometric determination of acetone. W. H. HATCHER and J. F. HORWOOD (Canad. J. Res., 1934, 11, 378—381).—The effects of the concn. of COMe₂ (I), NaOH (II), and I, and of the order of addition, in the determination of (I) by Messinger's method show that the two main factors are (a) the enolisation of (I) by (II) which is rapid, and (b) the reaction I₂+OH' → HIO+I'. With the correct order of addition, (I), (II), I, using a min. concn. of (II) 0.03N (better 0.048N) the rapid action (b) concurrently with (a) completes the formation of CHI₃ in approx. 10 min. With addition orders, (I), I, (II), or (II), I, (I), (a) and (b) are in conflict, (b) also removing OH', and the absorption of I is incomplete even after prolonged periods.
J. W. B.

Highly-polymerised compounds. CII. Polymethyl isopropenyl ketones. H. STAUDINGER and B. RITZENTHALER (Ber., 1934, 67, [B], 1773—1783).—Polymerisation of cold COMe·CMe·CH₂ occurs readily at room temp., giving a very viscous, hard eucolloidal material (I) which is sol. and hence consists exclusively of thread mols. Since (I) is reduced by HI and As to a complex hydrocarbon, it must have the structure ·CAcMe·CH₂·[CAcMe·CH₂]_x·CAcMe·CH₂·. Polymerisation of COMe·CMe·CH₂ at 100° leads to

$\beta\zeta$ -dimethyl- Δ^8 -octene- $\gamma\gamma$ -dione, which is not an intermediate in the production of (I). Polymerisation with SnCl_4 affords black, resinous products, whereas Florida earth is inactive. Irradiation of $\text{COMe}\cdot\text{CMe}\cdot\text{CH}_3$ by the Hg-vapour lamp gives a product (II) with mean degree of polymerisation 480 which swells slightly, is much less hard than (I), and is pptd. as a powder by addition of MeOH to its solution in COMe_2 . (I) does not react with $\text{NHPh}\cdot\text{NH}_2$, NH_2Ph , etc. In relatively very viscous solutions (II) obeys the Hagen-Poiseuille law, whilst with (I) the deviations in solutions of low viscosity are so small that they do not affect the calculation of mol. wt. In more viscous solutions the deviations are more marked and of approx. the same magnitude as those observed with polystyrenes of similar degree of polymerisation. Variation of concn. of solutions of (I) or (II) causes variations similar to those produced by the polymeric-analogous polystyrenes. η_{sp}/c of (I) appears independent of temp. The degree of polymerisation of (I) is about 1400. H. W.

Diacetylene. K. F. ARMSTRONG and R. ROBINSON (J.C.S., 1934, 1650).—Oxidation of $(\cdot\text{CH}_2\text{Ac})_2$ (I) with SeO_2 in boiling H_2O affords (15% yield, together with a liquid mixture of isomerides, b.p. $87\text{--}91^\circ/15$ mm.) $\beta\epsilon$ -diketo- Δ^7 -*n*-hexene, m.p. $75.5\text{--}76.5^\circ$ (*bis*-2 : 4-dinitrophenylhydrazones, m.p. $291\text{--}292^\circ$), reduced by H_2 (1 mol.)— Pt-SiO_2 in MeOH or AcOH to (I). J. W. B.

Synthesis and structure of dipropionylacetone and of di-*n*-butyrylacetone. S. S. DESHPANDE, Y. V. DINGANKAR, and D. N. KOPIL (J. Indian. Chem. Soc., 1934, 11, 595—602).—2 : 6-Diethyl-4-pyrone (I) with hot aq. $\text{Ba}(\text{OH})_2$ gives the Ba salt (II) of dipropionylacetone (III), which with dil. HCl affords the ketone as a yellow oil, α -form (IV), m.p. $117^\circ/6$ mm., which changes on keeping into a red β -form (V), reconvertible into (IV) on distillation. Boiling with very dil. MeOH-HCl reconverts (III) into (I). (IV) with $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-NH-NH}_2$ (VI) (1 mol.) in EtOH gives 1-*p*-nitrophenylimino-2 : 6-diethyl-4-pyridone, m.p. 78° (VII) (platinichloride, m.p. 198°), but (V) with (VI) (2 mols.) gives the *p*-nitrophenylhydrazone (VIII), m.p. 164° (platinichloride, m.p. 157°), of (VII). (VIII) cannot be obtained from (VII) and (VI), but on hydrolysis ($\text{AcOH} + \text{HCl}$ gas) it gives (VII). (II) with the hydrochloride of (VI) (2 mols.) in Et_2O , gives at room temp. the $\gamma\epsilon$ -(or $\gamma\gamma$)-di-*p*-nitrophenylhydrazone, m.p. 148° , of (III). Di-*n*-butyrylacetone (IX), b.p. $136^\circ/4$ mm. (one form), from 2 : 6-di-*n*-propyl-4-pyrone (X) readily reverts to (X) on distillation. Pure (IX) (from Cu salt) with (VI) (1 mol.) gives the ζ -*p*-nitrophenylhydrazone (XI), m.p. 71° , which in contact with conc. HCl and PtCl_4 changes to the platinichloride of 2 : 6-di-*n*-propyl-4-pyrone-*p*-nitrophenylhydrazone. Hydrolysis of (XI) gives (IX). With 2 mols. of (VI), (XI) gives 1-*p*-nitrophenylimino-2 : 6-di-*n*-propyl-4-pyridone-*p*-nitrophenylhydrazone, m.p. 140° . The reactions of (III) and (IX) are readily explained on the basis of open-chain formulæ (cf. diacetylacetone, J.C.S., 1921, 119, 1550). Both ketones give violet colorations with FeCl_3 . F. S. H. H.

Diacetylmonoxime. A. K. PLISOV (J. Gen. Chem. Russ., 1934, 4, 290—297).—The yields of Ac_2

obtained when $\text{CAcMe}\cdot\text{NOH}$ (I) is treated with various substances are : NO 85, NO_2 44, N_2O_3 85, HNO_3 60, HgNO_3 87, $\text{Cu}(\text{NO}_3)_2$ 48, and NaNO_3 37% of theory. (I) when heated at $140\text{--}145^\circ$ with CuO or MnO_2 yields chiefly Ac_2 , NH_3 , and N_2 : $3(\text{I}) \longrightarrow \text{NH}_3 + \text{N}_2 + 3\text{Ac}_2$; at higher temp. the reaction $(\text{I}) \longrightarrow \text{AcOH} + \text{MeCN}$ predominates. R. T.

Structure of the nitrogen and oxygen chains of the organic compounds suitable for the formation of complex salts. I. Iron salts of the oximino-ketones. L. CAMBI (R. Ist. lombardo Sci. Lett., Rend., 1933, [ii], 66, 791—798; Chem. Zentr., 1934, i, 1603—1604).—Three series of salts are distinguished : green, basic salts with the ratio oximino-ketone (I) : $\text{Fe} < 2 : 1$; blue, neutral salts, and blue acid salts. Reactions with alkali cyanides and magnetic susceptibility data indicate a linking of Fe^{II} to N. The analogy between the groupings of the glyoximes and (I) is pointed out, both forming similar complex salts with metals. Such relationships also exist between 2 : 2'-dipyridyl and phenanthroline, on the one hand, and pyridine-2- and quinoline-2-carboxylic acids on the other. Where the formation of a six-membered ring is possible, typical red complex salts of Fe^{III} in general appear, and where a stable five-membered ring can be formed, blue or violet complex salts of Fe^{II} are produced. Examples are the Fe^{III} salts of benzoylacetone and the Fe^{II} salts of benzoyl-acetaldehyde and of oxalylacetone. L. S. T.

Immersion filter for Bertrand's sugar determination.—See this vol., 1325.

Forms of arabinose. E. MONTGOMERY and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2074—2076).—Very slow crystallisation (from $\text{C}_5\text{H}_5\text{N}$ at 6° or aq. COMe_2 at room temp.) of arabinose (I) gives the pure β -form (II), $[\alpha]_D$ (in H_2O) $+187.8^\circ$ (1 min.) $\longrightarrow +105.1^\circ$ (const.), whence $[\alpha]_D$ (initial) $+201.5^\circ$. Details are given for the prep. from (I) of the compounds, $\beta\text{-C}_5\text{H}_{10}\text{O}_5\cdot\text{CaCl}_2\cdot\text{H}_2\text{O}$, m.p. 210° (decomp.) (cf. Dale, this vol., 635) [giving $[\alpha]_D$ (initial) $+201.7^\circ$ for (II)], and $\alpha\text{-C}_5\text{H}_{10}\text{O}_5\cdot\text{CaCl}_2\cdot 4\text{H}_2\text{O}$, m.p. 204° (darkens at 185°) (cf. Austin and Walsh, this vol., 635) [giving $[\alpha]_D +89.4^\circ$ in H_2O , for α -*L*-arabinose (III)]. The above vals. for (II) and (III) agree with those calc. ($+200^\circ$ and $+87^\circ$, respectively) from the rotations of α - and β -methylarabinosides by isorotation rules. All $[\alpha]_D$ are determined at $20\pm 0.5^\circ$. H. B.

Preparation of arabinose from gum acacia (gum kordofan). H. C. CARRINGTON, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1934, 1653).—An improved prep. of arabic acid (I) from gum acacia, and its hydrolysis by $0.01N\text{-H}_2\text{SO}_4$ at 95° to *L*-arabinose [18 g. from 100 g. of (I)], are described. J. W. B.

Mutarotation of arabinose.—See this vol., 1312.

Methylation of *l*-rhamnose. J. MINSAA (Kong. Norske Vidensk. Selsk. Forhandl., 1934, 6, 177—179; Chem. Zentr., 1934, i, 2738).— α -Methylrhamnoside (I), m.p. $109\text{--}110^\circ$, $[\alpha]_D^{20} -62.5^\circ$, is prepared by Fischer's method. β -Methylrhamnoside is obtained from the mother-liquor from (I) by distillation in vac. Cryst., anhyd. rhamnose has $[\alpha]_D^{20} +44^\circ$. R. N. C.

Powell and Whittaker's method for the determination of pentosans. T. S. KRISHNAN (J.

Indian Chem. Soc., 1934, 11, 651—657).—In the above method, the determination of furfuraldehyde (I) by Br absorption gives erratic results, but accurate vals. may be obtained, even for very small quantities (for which the phloroglucinol pptn. method fails), if the temp. be maintained at 30°. At lower temp. the absorption of Br is not \propto the amount of (I). F. S. H. H.

Inter-relationships amongst oligosaccharides. E. F. ARMSTRONG and K. F. ARMSTRONG (Chem. and Ind., 1934, 912—913).—The probable modes of synthesis (in nature) of various polysaccharides are discussed. Sucrose [fructofuranose(2)- α -(1)glucose; the nos. indicate the points of attachment of the sugar units] (I) and glucose (II) under the influence of β -glucosidase give gentianose [fructofuranose(2)- α -(1)glucose(6)- β -(1)glucose], hydrolysed by invertase (III) to gentiobiose [glucose(6)- β -(1)glucose] (IV), which occurs only in glycosides. Oxidation of (IV) to the glycuronic acid and subsequent decarboxylation affords primeverose [glucose(6)- β -d-(1)xylose]. Galactose (V) and (I) with α -galactosidase give raffinose [fructofuranose(2)- α -(1)glucose(6)- α -(1)galactose] (VI), hydrolysed by (III) to the unknown (in nature) melibiose [glucose(6)- α -(1)galactose], convertible [as for (IV)] into vicianose [glucose(6)- β -l-(1)arabinose]. (V) and (VI) afford stachyose [fructofuranose(2)- α -(1)glucose(6)- α -(1)galactose(6)- β -(1)galactose], hydrolysed by (III) to manninotriose [glucose(6)- α -(1)galactose(6)- β -(1)galactose]. (I) and (II) with α -glucosidase (maltase) give melezitose [glucose(1)- α -(6)fructofuranose(2)- α -(1)glucose], hydrolysed [dil. acid, not by (III)] to turanose [glucose(1)- α -(6)fructofuranose] (cf. Pacsu, A., 1931, 1149). H. B.

Action of chloroacetic anhydride on sugars, cellulose and its acetates. K. BRASS and E. KURZ (Cellulosechem., 1934, 15, 99—102).—Glucose with $(\text{CH}_2\text{Cl}-\text{CO})_2\text{O}$ (I) and AcOH with or without ZnCl_2 or H_2SO_4 at 65° gives mixtures; a *tetra*(chloroacetate), $+3\text{C}_5\text{H}_5\text{N}$, m.p. 131°, $[\alpha]_D^{25} +44.23^\circ$ in CHCl_3 , and $+4\text{C}_5\text{H}_5\text{N}$, m.p. 116°, $[\alpha]_D^{25} +35.22^\circ$ in CHCl_3 , are isolated in poor yield. Fructose gives similarly a *tri*(chloroacetate), $[\alpha]_D^{25} -10.49^\circ$ in CHCl_3 , and $+2\text{C}_5\text{H}_5\text{N}$, hygroscopic. Cellulose triacetate, (I), and a little H_2SO_4 at 70° give α -glucopyranose 2 : 3 : 4-triacetate 1 : 6-di(chloroacetate). Cellulose under various conditions gives only mixed cellobiose derivatives.

R. S. C.

Molecular combinations of β -methyl-*d*-glucoside, -*d*-xyloside, and -*l*-fucoside with potassium acetate. A. J. WATERS, R. C. HOCKETT, and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2199).—Compounds, $\text{C}_7\text{H}_{14}\text{O}_6\cdot\text{KOAc}$, m.p. 181—182° (corr.), $[\alpha]_D^{20} -22^\circ$ in H_2O , $\text{C}_7\text{H}_{14}\text{O}_5\cdot\text{KOAc}$, m.p. 208—212° (corr.), $[\alpha]_D^{20} +8.9^\circ$ in H_2O , and $\text{C}_6\text{H}_{12}\text{O}_5\cdot\text{KOAc}$, m.p. 171—172° (corr.), $[\alpha]_D^{20} -41.3^\circ$ in H_2O , are obtained by mixing conc. EtOH-solutions of anhyd. KOAc and β -methyl-*d*-glucoside, -*l*-fucoside, and -*d*-xyloside, respectively. The glucoside can be recovered by pptn. of K as K H tartrate (in 50% EtOH); acetylation (Ac_2O) gives the glycoside acetates. Similar compounds could not be prepared from α - and β -methyl-*d*-arabinosides, -*d*-galactosides, and -*d*-lyxosides, and α -methyl-*d*-glucoside, -*d*-xyloside, and -*l*-fucoside.

H. B.

Further method of preparation of sugar derivatives with seven-membered rings (septanoses). F. MICHEEL and W. SPRUCK (Ber., 1934, 67, [B], 1665—1667; cf. A., 1933, 596, 1278).—Galactose Et, mercaptal is converted by CPh_3Cl and $\text{C}_5\text{H}_5\text{N}$ and treatment of the product with Ac_2O into 6-*triphenylmethylgalactosedi Et*, mercaptal 2 : 3 : 4 : 5-*tetra*-acetate (I) (impure), $[\alpha]_D^{20} -10.8^\circ$ in $\text{C}_5\text{H}_5\text{N}$. Addition of HgCl_2 in COMe_2 to (I) and CdCO_3 in $\text{COMe}-\text{H}_2\text{O}$ at 15—20° leads to 6-*triphenylmethylgalactose hydrate* 2 : 3 : 4 : 5-*tetra*-acetate, m.p. 152°, $[\alpha]_D^{20} -47^\circ$ to -15° in $\text{C}_5\text{H}_5\text{N}$, converted by $\text{HCl}-\text{CHCl}_3$ or $\text{HBr}-\text{AcOH}$ into *al*-galactose hydrate 2 : 3 : 4 : 5-*tetra*-acetate, m.p. 140°, whence α - and β -galactoseptanose penta-acetate (*loc. cit.*). H. W.

aldehydo-*d*- β -Galaheptose hexa-acetate. R. M. HANN and C. S. HUDSON (J. Amer. Chem. Soc., 1934, 56, 2080).—*d*- β -Galaheptose, EtSH, and conc. HCl at room temp. give *d*- β -galaheptose Et mercaptal, m.p. 133° (corr.), $[\alpha]_D^{20} +37.8^\circ$ in H_2O , acetylated (Ac_2O , $\text{C}_5\text{H}_5\text{N}$) to the hexa-acetate, m.p. 105° (corr.), $[\alpha]_D^{20} +26.6^\circ$ in CHCl_3 , which is converted by HgCl_2 in aq. $\text{COMe}_2 + \text{CdCO}_3$ into aldehydo-*d*- β -galaheptose hexa-acetate, m.p. 196° (corr.), $[\alpha]_D^{20} +39.9^\circ$ in CHCl_3 .

H. B.

Thio-sugars. A. L. RAYMOND (J. Biol. Chem., 1934, 107, 85—96).—*iso*Propylidenexylose 5-*p*-toluenesulphonate (I) and NaSEt in COMe_2 , yield 5-ethylthiolisopropylidenexylose (II), m.p. 66.5—67.5°, $[\alpha]_D^{22} -57.5^\circ$ in EtOH. Acid hydrolysis of (II) gives 5-ethylthiolxylose, m.p. 81—82°, $[\alpha]_D^{22} -42.2^\circ$ in EtOH. Similarly, with NaSMe (I) yields 5-methylthiolisopropylidenexylose, m.p. 91.5—92°, $[\alpha]_D^{22} -53.9^\circ$ in EtOH, hydrolysed to 5-methylthiolxylose (III), m.p. 74—75°, $[\alpha]_D^{20} -23.0^\circ$. The behaviour of these products on oxidation is discussed, as also the rate of glycoside formation, confirming the structures assigned. Neither (III) nor its osazone, m.p. 162—163°, $[\alpha]_D^{22} -32.8^\circ$ in $\text{C}_5\text{H}_5\text{N}-\text{EtOH}$, is identical with the natural product from yeast (A., 1925, i, 338; 1926, 52), which thus cannot be 5-methylthiol-xylose, -lyxose, -2-ketoxylene, or -2-ketolxylose. *iso*Propylideneglucose 6-*p*-toluenesulphonate and KSMe in dioxan yield 6-methylthiolisopropylideneglucose, b.p. 140—155°/0.1 mm., $[\alpha]_D^{22} -3.5^\circ$ to -7.6° in EtOH. This on hydrolysis yields 6-methylthiolglucose (IV) as a syrup (*p*-bromophenylosazone, m.p. 184—185°, $[\alpha]_D^{20} -48^\circ$ in $\text{C}_5\text{H}_5\text{N}-\text{EtOH}$), the structure of which is confirmed by its similarity to 6-methylglucose in rate of glucoside formation. 2-Bromomethylglucoside and KSMe in COMe_2 give a methylthiolmethylhexoside, m.p. 128.5—129.5°, $[\alpha]_D^{20} -52.6^\circ$ in H_2O ; the hydrolysis product gives no osazone, whence the SMe probably occupies position 2.

H. N. R.

Carbohydrates of grass. Isolation of a polysaccharide of the levan type. S. W. CHALLINOR, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1934, 1560—1564).—From an aq. extract (freed from protein and insol. polysaccharides) of dried rough-stalked meadow grass (*Poa trivialis*) is isolated a H_2O -sol. polysaccharide (I), $[\alpha]_D^{20} -41^\circ$ in H_2O {Ac derivative, softens 110°, m.p. indef., $[\alpha]_D^{20} +23^\circ$ in CHCl_3 ; Me_3 ether (II), $[\alpha]_D^{20} -60^\circ$ in CHCl_3 }, closely resembling levan (III), and giving only fructose (IV)

on hydrolysis; (II) similarly hydrolyses to 1:3:4-trimethylfructose. Examination of the aq.-EtOH extract from which (I) has separated and of its methylation and acetylation products shows the presence of glucose, (IV), a trace of galactose (as mucic acid), and (?) gentiobiose (isolated as heptamethylmethylgentiobioside). (III) contains 10—12 fructofuranose units linked at positions 2 and 6. J. W. B.

Alleged synthesis of starch. M. ROSA and C. H. LIBERALLI (Rev. Soc. Brasil. Quim., 1933, 4, 313—346).—An exhaustive discussion of the reactions involved leads the authors to condemn the theoretical basis of A. Barreto's alleged synthesis of starch [by treating the acetal prepared from CH_2O and EtOH with excess of MgO ; Rev. Chim. Ind. (Rio de Janeiro), 1933, 2, No. 20, 455; 1934, No. 21, 7]. Experimental attempts to repeat the process gave no evidence of the formation of any carbohydrate; the colour reaction with I given by the crude reaction product is not due to starch, but to a hypiodite of Mg (cf. Petraschenj, A., 1927, 847). E. L.

Importance of Knecht's compound for the nitration of cellulose. C. TROCUS (Cellulosechem., 1934, 15, 104—107).—The ratio $1\text{C}_6\text{H}_{10}\text{O}_5 : 1\text{HNO}_3$ for Knecht's compound (I) is confirmed by Schreinemaker's method; the structure $\left[(\text{C}_6\text{H}_8\text{O}_3) \begin{smallmatrix} \text{HO} \\ \text{HO} \end{smallmatrix} \text{H} \cdots \text{OH}_2 \right] \text{NO}_3$, is suggested, by analogy with $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ (II), since (I) exists (proof by X-ray analysis) only in those HNO_3 concns. in which (II) does not occur. (I) may be formed during nitration of cellulose by local alteration in the concn. of the acid and may thus take part in the reaction. R. S. C.

Fractionation of cellulose acetate. W. HERZ (Cellulosechem., 1934, 15, 95—99).—Fractional pptn. of cellulose acetate from COMe_2 by H_2O gives products which, according to osmotic pressure measurements, have mol. wts. 27,000—80,000. is recorded for 3 solvents and gives K_m val. in agreement with Staudinger's results. R. S. C.

Preparation of cellulose stearates by Clark and Malm's procedure. I. SCHETTLE and M. KLIUTSCHKIN (J. Appl. Chem. Russ., 1934, 7, 558—563).—The H_2O content of air-dry cotton-wool does not interfere with esterification according to Clark and Malm's method; the highest degree of esterification (distearate) is obtained by heating a 1:3:6 mol. mixture of cellulose, stearic acid, and $(\text{CH}_2\text{Cl} \cdot \text{CO})_2\text{O}$ at 100° for 60 hr. R. T.

Resolution of co-ordinated inorganic compounds into optical isomerides. II. Resolution of triethylenediaminezinc chloride and sulphate. P. NEOGI and G. K. MUKHERJEE (J. Indian Chem. Soc., 1934, 11, 681—685).—Triethylenediaminezinc chloride (I) (*d*-tartrate + $3\text{H}_2\text{O}$, $[\alpha]_D^{25} + 181^\circ$; *d*-camphorsulphonate + H_2O , $[\alpha]_D^{25} + 18.1^\circ$; *d*-bromocamphorsulphonate + $5\text{H}_2\text{O}$, $[\alpha]_D^{25} + 42^\circ$) is resolved by fractional crystallisation of its *d*-camphornitronate (prep. by interaction with Na *d*-camphornitronate), the *d*-triethylenediaminezinc *d*-camphornitronate + $2\text{H}_2\text{O}$, $[\alpha]_D^{25} + 16^\circ$, which separates first, being converted into the corresponding chloride, $[\alpha]_D^{25} + 94.2^\circ$, and sulphate,

$[\alpha]_D^{25} + 87.7^\circ$, both racemising completely in 2—3 hr. in solution. Crystallisation of the salt formed from the hydroxide of (I) with nitrocamphor affords *l*-triethylenediaminezinc camphornitronate, $[\alpha]_D^{25} - 42.6^\circ$, converted by dil. HCl into a solution of the non-cryst. *l*-chloride. All $[\alpha]_D$ vals. are in H_2O . J. W. B.

Mechanism of oxidation processes. XL. Hydrolytic fission of amino-acids by charcoal. H. WIELAND, I. DRISHAUS, and W. KOSCHARA [with W. KAPITEL] (Annalen, 1934, 513, 203—218; cf. A., 1924, i, 1172).—*dl*-Alanine (I) (2.5% aq. solution) and animal C (II) (as used by Baur, A., 1923, i, 97; 1931, 1366) at 100° in N, give [after 8 hr. (when reaction practically ceases)] about 19% of the CO_2 required by the scheme: $\text{NH}_2 \cdot \text{CHMe} \cdot \text{CO}_2\text{H} - 2\text{H} \rightarrow \text{NH} \cdot \text{CMe} \cdot \text{CO}_2\text{H} \rightarrow \text{CO}_2 + \text{MeCHO} + \text{NH}_3$; the NH_3 and MeCHO are determined also. Contrary to Baur (*loc. cit.*), lactic acid and EtOH are not produced in detectable amounts. The recovered (II) is inactive towards (I), provided the recovery is done in N_2 ; partial reactivation occurs in presence of O_2 . The extent of the above decomp., using (II) previously heated in N_2 at 250 — 300° , is about 3%. The activity of (II) is not completely lost by previous heating in H_2 at 700 — 1000° . $\text{H}_2\text{C}_2\text{O}_4$ is also oxidised by (II) to the extent of 3.3% in 1 hr.; much less oxidation occurs using (II) previously heated in N_2 at 700° . Contrary to Wunderly (A., 1924, ii, 841; 1933, 264), aspartic acid is similarly dehydrogenated: $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} - 2\text{H} + \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + \text{MeCHO} + \text{NH}_3$. H. B.

β -Hydroxyglutamic acid. J. M. GULLAND and C. J. O. R. MORRIS (J.C.S., 1934, 1644—1649).—In the neutralisation (Congo-red) of the 25% H_2SO_4 hydrolysate of caseinogen (I) with $\text{Ba}(\text{OH})_2$ the whole of the β -hydroxyglutamic acid (II) is adsorbed by the pptd. BaSO_4 , from which NH_2 -acids are eluted with 1% HCl at 25° . After treatment (described) to remove glutamic (III), aspartic (IV), mono- NH_2 -carboxylic and basic NH_2 -acids, proline and hydroxyproline, decomp. of the Ag salts of the residue affords a gum which extraction with AcOH at room temp. and then EtOH at 50° separates into an EtOH-insol. powder containing (III), pyrrolidonecarboxylic acid and an impure acid containing S and N, and an EtOH-sol. gum [10% of (II) as $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{R}) \cdot \text{CH} \cdot \text{R}$ (V) ($\text{R} = \text{N} \cdot \text{NHC}_6\text{H}_4 \cdot \text{NO}_2 \cdot p$) by oxidation with chloramine-*T* (VI), which is regarded as the only trustworthy test for the presence of (II)], hydrolysis of which with 2*N*-HCl [17% of (II) due to its formation from hydroxypyrrolidinecarboxylic acid] and removal of (III), (IV), and *l*-leucine gives a product from which (II) is separated by H_3PO_4 - P_2O_5 at 0° , the Ba salt so obtained decomp. on crystallisation to give cryst. (II) + H_2O , similar in properties to Dakin's specimen (A., 1919, i, 150). Determination of (II) is best effected by electrodialysis (improved technique described) of the product obtained by elution of the BaSO_4 ppt. with 90% AcOH, the anode liquor being freed from methionine by $\text{Bu}^\alpha\text{OH}$, and oxidised with (VI), to determine (II) as (V). This method indicates 0.33% of (II) in (I). J. W. B.

Oxidation of cystine with permonosulphuric acid. G. TOENNIES (J. Amer. Chem. Soc., 1934,

56, 2198).—Oxidation of cystine with 1 and 2 mols. of H_2SO_5 (Gleu, A., 1931, 326) appears to give the mono- and di-sulphoxide, respectively; with 10.7 mol. equivs., 5 O (theoretical amount for oxidation to cysteic acid) are absorbed. The product from cystine perchlorate (in MeCN) and 1 mol. equiv. of H_2SO_5 (in 75% MeOH) probably undergoes dismutation when neutralised ($\text{C}_5\text{H}_5\text{N}$). H. B.

Separation of isomeric forms of inactive cystine. H. S. LORING and V. DU VIGNEAUD (Proc. Soc. Exp. Biol. Med., 29, 41—42; Chem. Zentr., 1934, i, 2270).—The product of racemisation of L-cystine with conc. acid yields two isomeric forms on fractionation of the hydrochlorides. A. G. P.

Nitration of chitin. P. SCHORIGIN and E. HAIT (Ber., 1934, 67, [B], 1712—1714).— H_2SO_4 – HNO_3 is unsuitable for the nitration of chitin (I) owing to its hydrolysing action. Better results are obtained by dissolution in HNO_3 (d 1.5) and treatment of the product, whereby 1.5 OH groups are esterified with formation of chitin nitrate (II), inflames at 165°. Treatment of (II) with HCO_2H gives sol. and insol. portions which do not differ considerably in chemical constitution. H. W.

Amido- and imido-chlorides of non-aromatic acids. IX. J. VON BRAUN and W. RUDOLPH (Ber., 1934, 67, [B], 1762—1770; cf. this vol., 393).—In accordance with the electronic theory, the stability of the imido-chlorides, $\text{X}\cdot\text{CHY}\cdot\text{CCl}_2\cdot\text{N}\cdot\text{R}$, increases when R is changed from Et to POCl_2 or SO_2Ph ; CO_2Et appears to offer insufficient protection to prevent migration of H, whilst polymerisation occurs when $\text{R}=\text{CN}$. Instability towards heat increases in the sequence CCl_3 , CHCl_2 , CH_2Cl , Me. The action of PCl_5 on amides proceeds in accordance with the scheme: $\text{X}\cdot\text{CO}\cdot\text{NH}_2 + \text{PCl}_5 \longrightarrow \text{X}\cdot\text{CCl}(\text{NH}_2)\cdot\text{OPCl}_2 \longrightarrow \text{X}\cdot\text{C} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{PCl}_3 \longrightarrow \text{X}\cdot\text{CCl}\cdot\text{N}\cdot\text{POCl}_2$. POCl_3 is

not an intermediate, since $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2$ and POCl_3 immediately yield $\text{CCl}_3\cdot\text{CN}$, and $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2$ and PCl_5 afford $\text{CCl}_3\cdot\text{CCl}\cdot\text{N}\cdot\text{POCl}_2$ in 100% yield. All acid amides are readily converted into nitriles when warmed with POCl_3 , and for this purpose 1/2 to 1/3 mol. of POCl_3 suffices. Hence for this conversion 1/4 mol. of PCl_5 is adequate, but the advantage of POCl_3 rests in its liquid form and easier manipulation and on its smaller liability to attack the OH and CO groups. PSCl_3 and amides also yield nitriles, but reaction is more complex than with POCl_3 . With thioamides and POCl_3 the nitriles contain S.

$\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ and PCl_5 at 100° give unchanged material, PCl_3 , POCl_3 , and the *imido-chloride*, $\text{CHCl}_2\cdot\text{CCl}\cdot\text{N}\cdot\text{CO}_2\text{Et}$, b.p. 115—118°/11 mm., transformed by cold H_2O into *dichloroacetylurethane*, m.p. 98°, and by NH_2Ph in Et_2O into the *amidine*, $\text{CHCl}_2\cdot\text{C}(\text{NHPh})\cdot\text{N}\cdot\text{CO}_2\text{Et}$, m.p. 143°, b.p. 160°/0.5 mm. $\text{CN}\cdot\text{NHAc}$ and PCl_5 yields mainly $\text{CN}\cdot\text{N}\cdot\text{CClMe}$, which could not be obtained pure. $\text{SO}_2\text{Ph}\cdot\text{NHAc}$ yields the *imido-chloride* $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{CClMe}$, b.p. 130°/0.5 mm., which gradually passes into MeCN and PhSO_2Cl and is transformed by NH_2Ph into the *amidine* $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{CMe}\cdot\text{NHPh}$, m.p. 157°. *Benzenesulphonchloroacetamide*, m.p. 106°, from PhSO_2NH_2

and $\text{CH}_3\text{Cl}\cdot\text{COCl}$ at 140°, yields the *imido-chloride* $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{CCl}\cdot\text{CH}_2\text{Cl}$ (I), b.p. 160—164°/0.5 mm., transformed by NH_2Et in C_6H_6 into the *base* $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{C}(\text{NEt}_2)\cdot\text{CH}_2\cdot\text{NEt}_2$ (*picrate*, m.p. 145°). The slight lability of H in (I) is shown by the prolonged heating at 120° required for the production of the *imido-chloride* $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{CCl}\cdot\text{CHCl}_2$, b.p. 160°/0.5 mm., converted by H_2O into *benzenesulphonchloroacetamide*, m.p. 137°. Action could not be caused to proceed to the compound $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{CCl}\cdot\text{CCl}_3$, b.p. 158°/0.2 mm., m.p. 88°, which is obtained from *benzenesulphontrichloroacetamide*, m.p. 157° (from $\text{PhSO}_2\cdot\text{NH}_2$ and $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2$ and PCl_5 at 100° yield the compound $\text{CCl}_3\cdot\text{CCl}\cdot\text{N}\cdot\text{POCl}_2$, b.p. 140°/11 mm., m.p. 80°, quantitatively. Contrary to Wallach, the substance $\text{CHCl}_2\cdot\text{CCl}\cdot\text{N}\cdot\text{POCl}_2$, b.p. 92—94°/0.3 mm., m.p. 39°, behaves similarly. $\text{CH}_3\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ and PCl_5 yield the compound $\text{CH}_2\text{Cl}\cdot\text{CCl}\cdot\text{N}\cdot\text{POCl}_2$, b.p. 100°/0.2 mm., which when gradually heated decomposes into POCl_3 and (?) $\text{CN}\cdot\text{CH}_2\text{Cl}$ and with NH_2Ph in Et_2O gives the substance $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{PO}(\text{NHPh})_2$, m.p. 156°. $\text{CMeCl}\cdot\text{N}\cdot\text{POCl}_2$ could not be obtained in appreciable amount, passing into POCl_3 and MeCN. The following transformations are effected by POCl_3 : $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2$ to $\text{CCl}_3\cdot\text{CN}$; NH_2Bz to PhCN ; *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2$ to *o*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CN}$; lauramide to lauritrile, b.p. 140—142°/12; adipamide to adipodinitrile; cyclopentylacetamide, m.p. 215°, to cyclopentylacetoneitrile, m.p. 35°; methylacetoacetamide to methylacetoacetoneitrile, b.p. 68—70°/12 mm.

H. W.
Kinetics of alkaline hydrolysis of betaine-amides. D. B. LUTEN, jun., and T. D. STEWART (J. Amer. Chem. Soc., 1934, 56, 2151—2158; cf. A., 1932, 1211).—Contrary to the previous assumption (*loc. cit.*) $\text{CN}\cdot\text{CR}_2\cdot\text{NR}_3\text{I}$ (I) are hydrolysed rapidly by dil. alkali to $\text{NH}_2\cdot\text{CO}\cdot\text{CR}_2\cdot\text{NR}_3$ (II), which then undergo slow hydrolysis to $\text{CO}_2\cdot\text{CR}_2\cdot\text{NR}_3$. The simpler (II) hydrolyse according to complex laws (involving fractional exponents); the rate of hydrolysis of the more complex, less reactive (II) is approx. unimol. with respect to each reactant. Variations in ionic strength and temp. have little effect. A reaction mechanism is discussed. $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ (III), m.p. 198—199° (lit. 191°), $\text{NH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NEt}_3\text{I}$ (IV), m.p. 154—156° (lit. 150.5—152.5°), and $\text{NH}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{NMe}_3\text{I}$, m.p. 234—236°, are prepared by hydrolysis [dil. $\text{Ba}(\text{OH})_2$; subsequent neutralisation with H_2SO_4] of the appropriate (I); (III) and (IV) are also obtained from $\text{CH}_2\text{I}\cdot\text{CO}\cdot\text{NH}_2$ and NR_3 . H. B.

Condensation of reductone with carbamide. H. VON EULER and C. MARTIUS (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 26, 6 pp.).—Condensation of reductone (I) (A., 1933, 937) (2 and 1 mol.) with $\text{CO}(\text{NH}_2)_2$ (1 mol.) in presence of aq. mineral acids yields *di-* and *mono-(β -dihydroxyallylidene)carbamide*, respectively; the latter, decomp. 180—185°, is stable to cold conc. H_2SO_4 or HCl, hot POCl_3 , and Ac_2O . $\text{NH}_2\cdot\text{CO}\cdot\text{NHPh}$ affords the corresponding *Ph* derivative, whilst (I) or its Na derivative [from (I) and NaOEt] in EtOH yields no isolable products when condensed with guanidine, $\text{CS}(\text{NH}_2)_2$, or ascorbic acid. F. O. H.

Preparation of amino-nitriles. G. A. MENGE (J. Amer. Chem. Soc., 1934, 56, 2197—2198).—OH·CH₂·CN and liquid NH₃ at room temp. (sealed tube) give about 95% of NH₂·CH₂·CN (*platinichloride*). Other NH₂-nitriles can be prepared similarly.

H. B.

Cyanide and ferrocyanide from calcium cyanamide. L. WOHLER, E. KRALL, and O. DORNHÖFER (Angew. Chem., 1934, 47, 733—734).—The technical conversion of CaCN₂ into alkali cyanide can be effected economically only with the finely-divided fresh dry product. Na₂CO₃, not NaCl, must be used with C, which is advantageously replaced by CaC₂ or Al₄C₃. Fusion with K₂CO₃ and Fe filings or, preferably, powdered Fe₂O₃ effects quant. conversion of CaCN₂ into K₄Fe(CN)₆.

H. W.

Molecular compounds of boron trifluoride with water, alcohols, and organic acids. H. MEERWEIN and W. PANNWITZ (J. pr. Chem., 1934, [ii], 141, 123—148).—Largely a more detailed account of work previously reviewed (A., 1933, 360). The following appears to be new. BF₃·2H₂O (I), b.p. 58.5—60°/1.2 mm., is also prepared from B₂O₃ and 40% HF. BF₃·H₂O gives *cineol*, BF₃·H₂O·(C₁₀H₈O)₂, m.p. 71—73° (decomp.), and *dioxan*, BF₃·H₂O·C₄H₈O₂, m.p. 128—130° (decomp.), salts. The following compounds are described: BF₃·2HCO₂H [decomp. rapidly at 75° into (I) and CO], b.p. 43—44°/11 mm.; BF₃·2AcOH, b.p. 53—54°/10 mm.; BF₃·2EtCO₂H, b.p. 60—60.5°/12 mm.; BF₃·2Pr^oCO₂H, b.p. 64°/11 mm.; BF₃·2CHMe·CH·CO₂H, b.p. 81—82° (partial decomp.)/12.5 mm.; BF₃·HCO₂H, m.p. —21° to —20°; BF₃·AcOH, m.p. 23—24°; BF₃·EtCO₂H, m.p. 28—29°; BF₃·Pr^oCO₂H, m.p. 29—30°; BF₃·CHMe·CH·CO₂H, m.p. 35—36°; BF₃·NaOH; BF₃·KOH; BF₃·NaOMe; BF₃·KOME; BF₃·BzOH, m.p. 90—91.5° (decomp.); BF₃·CH₂Ph·CO₂H, m.p. 56—59° (decomp.); BF₃·H₂C₂O₄, m.p. 57—58° (decomp.); BF₃·CO₂H·CH·CH·CO₂H, m.p. 75—82° (from maleic acid); BF₃·CO₂H·CH₂·CH₂·CO₂H, m.p. 82—84° (decomp.). Mol. refractions of several of the compounds are determined.

H. B.

β-Halogenoethylarsines. A. G. SOARE (Bul. Chim. Soc. Romane, 1933, 36, 75—78).—Prolonged agitation of aq. Na₃AsO₃ with CH₂Cl·CH₂·OH at \pm 5° to 10° gives non-cryst. β-hydroxyethylarsenic acid (Ca salt), which passes into non-cryst. β-hydroxyethylarsine oxide (I) when its aq. solution is evaporated in SO₂ at 60°. Treatment of (I) with KBr and cold, conc. H₂SO₄ affords As β-bromoethyl dibromide, b.p. 110°/25 mm., m.p. 36°, which yields C₂H₄ quantitatively with warm aq. NaOH.

H. W.

Determination of thallium in organic compounds. S. S. NAMETKIN and N. MELNIKOV (Z. anal. Chem., 1934, 98, 414—416).—The substance is dissolved in conc. H₂SO₄ at 70—80° and oxidised by addition of KMnO₄. Excess of KMnO₄ is destroyed by H₂C₂O₄ or H₂O₂ and Br-H₂O added. Excess of Br is removed, and Tl determined iodometrically (cf. A., 1928, 725).

J. S. A.

Thermal decomposition of organic compounds from the viewpoint of free radicals. IX. Combination of methyl groups with mercury. F. O.

RICE and B. L. EVERING (J. Amer. Chem. Soc., 1934, 56, 2105—2107).—The HgAlk₂ (I) obtained by combining the fragments formed in the thermal decomp. (method, A., 1932, 1108) of C₃H₈ or C₄H₁₀ with Hg is converted by EtOH-HgBr₂ into HgAlkBr, and thence by I in aq. KI into AlkI. This and EtOH-NMe₃ give NMe₃I, thus showing that (I) is largely HgMe₂. (I) is accompanied by a small amount of an unstable compound, probably (·HgMe)₂. HgMe (Kraus, A., 1913, i, 1314) decomposes when allowed to warm to about room temp.: 2HgMe → Hg + HgMe₂. Et and higher radicals are not formed in the above decomp.

H. B.

Nitration of the monobromotoluenes. M. C. GEERLING and J. P. WIBAUT (Rec. trav. chim., 1934, 53, 1011—1030).—Nitration of *o*-C₆H₄MeBr, containing about 20% of *o*-C₆H₄Br·OH, which ensures mononitration, with HNO₃ at 0° gives (%) 18.2 of 1 : 2 : 3-, 20.15 of 1 : 2 : 4-, 37.3 of 1 : 2 : 5-, and 25.0 of 1 : 2 : 6-NO₂-derivatives (thermal analysis). Similarly, nitration of *m*-C₆H₄MeBr yields (%) 54.45 of 1 : 3 : 6-, 32.55 of 1 : 3 : 4-, and 13.0 of 1 : 3 : 2-NO₂-derivatives. The results agree with calc. vals.

F. R. S.

Aromatic sulphonyl fluorides. III. W. STEIN KOFF and R. HUBNER (J. pr. Chem., 1934, [ii], 141, 193—200; cf. A., 1930, 1566; Covie and Gibson, A., 1934, 287).—PhEt and FSO₃H give *p*-ethylbenzenesulphonyl fluoride, b.p. 124—125°/14 mm., 238—239° (2-NO₂-derivative, b.p. 179°/15 mm.), which with MgMeI (I) and MgPhBr (II) affords *di-p*-ethylbenzenesulphonylmethane (24% yield), m.p. 131°, and *p*-ethyl-diphenyl sulphone (32%), m.p. 91.5—92°, respectively. 1 : 3 : 4-C₆H₃Me₂·SO₂F (III) with (I) and (II) gives *di*-(*m*-4-xylenesulphonyl)methane (39%), m.p. 155.5—156°, and *phenyl m*-4-xylyl sulphone (33%), m.p. 87°, respectively. *m*-Xylene-2 : 4-disulphonyl fluoride and (I) give 2 : 4-dimethanesulphonyl-*m*-xylene (Polak and Schädler, A., 1918, i, 497) and small amounts of two compounds, both C₁₇H₁₈O₆F₂S₄, m.p. 135° and 272°; with (II), 2 : 4-dibenzenesulphonyl-*m*-xylene, m.p. 232—233°, results. The Grignard reagent from (CH₃)₂Cl₂ and (III) afford *ae-di*-(*m*-4-xylenesulphonyl)-pentane (27%), m.p. 98°. *m*-Chloro-, b.p. 90°/22 mm. (NO₂-derivative, m.p. 85°), and *m*-bromo-benzenesulphonyl fluoride, b.p. 122°/23 mm. (NO₂-derivative, m.p. 104°), are prepared (Sandmeyer) from *m*-NH₂-C₆H₄·SO₂F.

H. B.

Volume effects of alkyl groups in aromatic compounds. V. Monosulphonation of *p*-cymene. R. J. W. LE FEVRE (J.C.S., 1934, 1501—1502).—Sulphonation of *p*-cymene with 15% oleum at 0—10° occurs mainly (90%) in the 2-position, *i.e.*, *o* to the Me, small amounts of the 3-sulphonate also being formed. The relative amount of 2-substitution and the total yield of (SO₃H)₁ derivative both decrease with rise in temp. Substitution with ClSO₃H also occurs mainly in the 2-position, since with NH₃ the product affords the 2-sulphonamide. *p*-Cymene-3-sulphonic acid could not be obtained by oxidation of the 3-SH compound.

J. W. B.

Preparation of *m*-fluorobenzotrifluoride. D. AELONY (J. Amer. Chem. Soc., 1934, 56, 2063).—Thermal decomp. (apparatus used described) of *m*-trifluoromethylbenzenediazonium borofluoride [from *m*-

$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CF}_3$ by a modification of Balz and Schiemann's method (A., 1927, 654)] gives *m*-fluorobenzotrifluoride, b.p. 99.5—100.5°/762 mm. CPhF_3 is prepared in 75.5% yield by a modification of Swarts' method (A., 1913, i, 841; 1916, i, 133). H. B.

Synthesis of styrene. J. S. SALKIND, I. P. BERKOVICH, and M. K. AMUSIN (Plast. Massui, 1934, No. 1, 14—20).— PhEt , prepared in 75% yield from C_6H_6 and EtCl , is converted into styrene (75—80% yield) by forming CHClPhMe (I), which is boiled with quinoline. Alternatively (I) is hydrolysed by boiling with 5—10% aq. NaOH , and the $\text{CHPhMe}\cdot\text{OH}$ dehydrated by heating with 3—5% of KHSO_4 .

CH. ABS. (e)

Synthesis of some aromatic and hydroaromatic hydrocarbons. S. LANDA and J. ČECH (Coll. Czech. Chem. Comm., 1934, 6, 423—432).— α -*Diphenyl- Δ^8 -hexadecene* (I), b.p. 274—275°/12 mm., m.p. 21.5—22.5°, from α -diphenylhexadecan- α -ol (modified prep.) and ZnCl_2 at 125°, is hydrogenated (Pt-black) in Et_2O to α -diphenylhexadecane, b.p. 279—281°/15 mm., m.p. 24°, which with H_2 and Ni at 100°/85 atm. affords α -dicyclohexylhexadecane, b.p. 269—271°/15 mm., m.p. 18.5—19.5°. Et palmitate with $\text{CH}_3\text{Ph}\cdot\text{MgCl}$ gives α -phenyl- β -benzylheptadecan- β -ol (II), m.p. 28°, and some (III). Dehydration of (II) by ZnCl_2 affords α -phenyl- β -benzyl- Δ^8 -heptadecene (III), b.p. 290—292°/16 mm., m.p. 58.5°, which is hydrogenated (Pt) to α -phenyl- β -benzylheptadecane (IV), b.p. 294—296°/16 mm., m.p. —34.5° to —35°. (III) or (IV) with H_2 and Ni at 180°/90 atm. gives α -cyclohexyl- β -cyclohexylmethylheptadecane, b.p. 288—290°/17 mm., m.p. —36.5° to —37.5°. The constitutions of (I) and (III) are proved by oxidation with KMnO_4 ; (I) gives COPh_2 and pentadecic acid (V); (III) gives $\text{CO}(\text{CH}_2\text{Ph})_2$ and (V). (I) and (III) are fluorescent. Physical consts. are recorded for the hydrocarbons. F. S. H. H.

Octachloronaphthalene. II. Chlorination of naphthalene with chlorine. Relative activities of various halogen carriers. V. SCHVEMBERGER and V. GORDON (J. Gen. Chem. Russ., 1934, 4, 529—551).— C_{10}Cl_8 can be obtained without the use of catalysts by passing Cl_2 over C_{10}H_8 without heating for 1 hr., gradually raising the temp. from 100° to 170° for the 2nd—7th hr., and gradually to 200° from the 8th to the 36th hr. The reaction time is shortened to 6 hr. by adding 0.3—1% of AlCl_3 , FeCl_3 , AuCl_3 , TiCl_3 , ZrCl_4 , SbCl_3 , BiCl_3 , or TeCl_4 to the C_{10}H_8 . UCl_4 , AgCl , and SbCl_5 are less active than the above, whilst BeCl_2 , SiCl_4 , TiCl_4 , SnCl_2 , PbCl_2 , ThCl_4 , PCl_3 , PCl_5 , AsCl_3 , SeCl_2 , SeCl_4 , CrCl_3 , MnCl_2 , ICl_3 , CoCl_2 , and NiCl_2 are inactive. R. T.

Hydrocarbons of high mol. wt. I. Alkylated aromatic hydrocarbons. II. Aliphatic branched-chain hydrocarbons. M. LERER (Ann. Off. nat. Comb. liq., 1933, 8, 681—733; Chem. Zentr., 1934, i, 1647—1649).—I. The Na additive compound of anthracene reacts readily (best in Et_2O or liquid NH_3) with alkyl halides giving 9:10-dialkyl-9:10-dihydroanthracenes (I) together with small amounts of 9:10-dialkylanthracenes [also from (I) with Pt-black at 280°]; the method may be extended to C_{10}H_8 . The following are described: 9:10-diiso-

amyl-9:10-dihydro-, b.p. 134—138°/high vac.; 9:10-diisoamyl-, m.p. 134°; 9:10-di- β -octyl-9:10-dihydro-, b.p. 180—190°/high vac.; 9:10-di- β -octyl-, m.p. 65°; 9:10-diethyl-9:10-dihydro-; 9:10-diethyl-anthracene, m.p. 145—145.5°; 1:4-diisobutyl-1:2:3:4-tetrahydronaphthalene, b.p. 170—175°/16 mm.; 4:4'-disobutyl-1:1'-dinaphthyl, m.p. 80—81°; 1:4-diisobutyl-naphthalene, b.p. 185°/11 mm.; 9:10-dibenzoyl-, b.p. 195—200°/high vac., and 9-benzoyl-9:10-dihydroanthracene, m.p. 97.5—98.5°. d , n , and η are recorded for the liquid products.

II. β -Octyl alcohol (improved prep.) is converted by NaOH into η -methylpentadecan- α -ol (I), b.p. 158—160°/12 mm., which, on passage over Al_2O_3 -asbestos or Cu at 300°, gives diotene (II), $\text{C}_{16}\text{H}_{32}$, b.p. 142—146°/12 mm., 148°/12 mm. (probably a mixture). A triotene [η -methyl- α -n-hexyl- Δ^8 - or Δ^8 -heptadecene], b.p. 211—214°/13 mm., is similarly prepared from "tricapryl alcohol" (III). (I) with I and red P gives η -iodo- α -methylpentadecane, b.p. 184—188°/12 mm.; this with Na in PhMe affords $\eta\mu$ -dimethyl- α -di-n-hexyloctadecane, b.p. 256°/13 mm. The bromide from (III) and HBr on similar treatment yields η -dimethyl- $\alpha\mu\epsilon$ -tetra-n-hexyldocosane, b.p. 200—205°/0.003 mm. Mg β -octyl bromide and Me palmitate yield a mixture, $\text{C}_{32}\text{H}_{64}$, b.p. 170—175°/0.1 mm. Attempts to determine the constitution of (II) by oxidation with KMnO_4 were fruitless. d , n_D^{20} , and η are recorded for most of the liquid products. H. N. R.

Substitution of chlorine in aromatic compounds by amino-groups. I. Preparation of aniline from chlorobenzene. II. Preparation of *p*-nitroaniline from *p*-chloronitrobenzene using copper catalysts. N. N. VOROSHOV, jun. (J. Gen. Chem. Russ., 1934, 4, 310—323, 324—327).—I [with V. A. KOBELEV; cf. this vol., 1077]. Max. yields (89—90%) of NH_2Ph are obtained from PhCl (1 mol.), NH_3 (5 mols.), and Cu_2O (0.2 mol.) at 200—230°/70 atm.; the by-products are PhOH , 4—5%, and NHPh_2 , 1—2%. The yield of NH_2Ph increases with increasing abs. and relative $[\text{NH}_3]$, of PhOH with increasing $[\text{OH}']$, and of NHPh_2 with increasing $[\text{NH}_4\text{Ph}]$; addition of NH_4Cl retards the reaction. These results point to the mechanism: $\text{PhCl} + \text{Cu}(\text{NH}_3)_2^+ \text{ (I)} \rightarrow \text{PhCl}\cdot\text{Cu}(\text{NH}_3)_2^+ \text{ (II)}$; $\text{(II)} + \text{NH}_3 \rightarrow \text{(I)} + \text{NH}_2\text{Ph} + \text{HCl}$; $\text{(II)} + \text{OH}' \rightarrow \text{(I)} + \text{PhOH} + \text{Cl}'$; $\text{(II)} + \text{NH}_2\text{Ph} \rightarrow \text{(I)} + \text{NHPh}_2 + \text{HCl}$; $\text{(I)} + \text{Cl}' \rightarrow \text{Cu}(\text{NH}_3)_2\text{Cl}$. The reaction velocity \propto concn. of (I). The catalytic activity of Cu^I is $>$ that of Cu^{II} .

II [with M. I. KRILOVA]. *p*- $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ (III) of 94—97% purity is obtained in 90—98% yield by heating *p*- $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ (IV) (1 mol.) with aq. NH_3 (6 mols.) and Cu^{II} [0.1 mol. as CuSO_4 , CuCl_2 , or $\text{Cu}(\text{OH})_2$], for 30 min. at 217—240°/70 atm. In presence of Cu_2O or Cu smaller yields of less pure (III) are obtained. The velocity of reaction \propto concn. of $\text{Cu}(\text{NH}_3)_4^{++}$ and of (IV). R. T.

Preparation of nitrogen-substituted sulphonanilides. G. H. YOUNG (J. Amer. Chem. Soc., 1934, 56, 2167).—*p*-Toluenesulphon-N-n-, m.p. 56°, and -iso-, m.p. 99.5—100°, -propyl-, and -sec-butyl-, m.p. 75.5°, -anilides are prepared from *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NHPh}$, RBr , and KOH . H. B.

Derivatives of 3:5-dinitroaniline. J. J. BLANKSMA and G. VERBERG (Rec. trav. chim., 1934, 53, 988—1000).—4-Bromo-3:5-dinitrobenzoyl chloride, m.p. 90°, with the appropriate reagent affords *Me*, m.p. 125°, and *Et* 4-bromo-3:5-dinitrobenzoate, 4-bromo-3:5-dinitro-, m.p. 188°, and -3:5-dinitro-4-amino-benzamide, and 4-bromo-3:5-dinitrobenzazide, m.p. 116°. The azide with H_2SO_4 yields 4-bromo-3:5-dinitroaniline m.p. 207° (*Ac* derivative, m.p. 263°), with *MeOH* forms 4-bromo-3:5-dinitrophenyl-methylurethane, m.p. 189°, and with *EtOH* gives *Et* 4-bromo-3:5-dinitrophenylcarbamate, m.p. 167°. The chloroazide similarly affords *Me*, m.p. 176°, and *Et* 4-chloro-3:5-dinitrophenylcarbamate, m.p. 153°. 2-Chloro-3:5-dinitrobenzoyl chloride forms *Me* and *Et* esters, 2-chloro-3:5-dinitrobenzamide, 3:5-dinitro-2-aminobenzamide, m.p. 284°, and 2-chloro-3:5-dinitrobenzazide, m.p. 64°. The azide is converted into 2-chloro-3:5-dinitroaniline, m.p. 168° (*Ac* derivative, m.p. 153°), *Me*, m.p. 119°, and *Et* 2-chloro-3:5-dinitrophenylcarbamate, m.p. 98°. 2-Bromo-3:5-dinitrobenzoyl chloride gives *Me*, m.p. 109°, and *Et* 2-bromo-3:5-dinitrobenzoate, m.p. 74°, and 2-bromo-3:5-dinitrobenzamide, m.p. 216°, and -benzazide, decomp. 67°. The azide leads to 2-bromo-3:5-dinitroacetanilide, m.p. 142—143°, solidifying and re-melting at 181°, *Me*, m.p. 123°, and *Et* 2-bromo-3:5-dinitrophenylcarbamate, m.p. 121°, solidifying and remelting at 131°.

Reaction of some of the compounds with NH_2Ph under different conditions results in *Me*, m.p. 188°, and *Et* 3:5-dinitro-4-anilinophenylcarbamate, m.p. 151°, 3:5-dinitro-4-aminoacetanilide, m.p. 234°, 4:6-dinitro-2-anilinodiphenylamine, m.p. 129°, *Me*, m.p. 143°, and *Et* 3:5-dinitro-2-anilinophenylcarbamate, m.p. 102°, and 5:7-dinitro-1-phenyl-2-methylbenzimidazole, m.p. 192°.

F. R. S.

Nitration of 3:5-dinitroaniline derivatives. J. J. BLANKSMA and G. VERBERG (Rec. trav. chim., 1934, 53, 1037—1046).—3:5-Dinitrophenylcarbamide, m.p. 89°, gives with the reagent indicated the following products: H_2O , *s-di*-3:5-dinitrophenylcarbamide, m.p. 306°; *MeOH*, *Me* (I), m.p. 127°, and *EtOH*, *Et* 3:5-dinitrophenylcarbamate (II), m.p. 83°; NH_3 , 3:5-dinitrophenylcarbamide, m.p. 206°; NH_2Me , *N-3*:5-dinitrophenyl-*N'*-methyl-, m.p. 179°, and NH_2Et , -ethylcarbamide (III), m.p. 155°. 3:5-Dinitroaniline with $ClCO_2Me$ gives (I) and with $EtNCO$ yields (III). 3:5-Dinitroacetanilide is not nitrated further by HNO_3 or $HNO_3-H_2SO_4$ at -15° . (III) and HNO_3 yield *N'-nitro-N-3*:5-dinitrophenyl-*N'*-ethylcarbamide, m.p. 98°. (I) is nitrated (HNO_3) to 3:5-dinitrophenylnitromethylurethane, m.p. 125° (which with $MeOH-NH_3$ forms the NH_4 salt of 3:5-dinitrophenylnitroamine, decomp. 190°), and *Me* 2:3:5-trinitrophenylcarbamate (IV), m.p. 143°. Similarly (II) and HNO_3 afford 3:5-dinitrophenylnitrourethane, m.p. 102°, and *Et* 2:3:5-trinitrophenylcarbamate (V), m.p. 118°. (I) is nitrated with $HNO_3-H_2SO_4$ to (IV) and *Me* 3:4:5-trinitrophenylcarbamate, m.p. 169°, whilst (II) similarly gives (V) and a compound, m.p. 144°.

F. R. S.

Preparation of monoguanidines of possible physiological significance. C. E. BRAUN and W. M.

4 S

RANDALL (J. Amer. Chem. Soc., 1934, 56, 2134—2136).—*S*-Methylisothiocarbamide sulphate and the appropriate NH_2R in *EtOH* give γ -phenylpropyl-, m.p. 173—174°, δ -phenylbutyl-, m.p. 175—176°, hexahydrobenzyl-, m.p. 275—276°, decomp. 280—282°, and β -cyclohexylethyl-, m.p. 295—297°, -guanidine sulphate. α -Phenyl- α -benzyl-, m.p. 248—5°, and $\alpha\alpha$ -dibenzyl-, m.p. 191—192°, -guanidine hydrochloride are prepared from $CN\cdot NH_2$ and $CH_2Ph\cdot NHPH_2\cdot HCl$ (in *EtOH*) and $(CH_2Ph)_2NH_2\cdot HCl$ (in amyl alcohol at 140—150°), respectively. $CS(NH\cdot CH_2Ph)_2$, $CH_2Ph\cdot NH_2$ (I), and HgO in *EtOH* give $\alpha\beta\gamma$ -tribenzylguanidine (hydrochloride, m.p. 203—204°; trihydrochloride, m.p. 258—259°), whilst (I) and *S*-methylbenzylisothiocarbamide hydriodide, m.p. 103—104° (from $NH_2\cdot CS\cdot NH\cdot CH_2Ph$ and *EtOH-MeI*) afford $\alpha\gamma$ -dibenzylguanidine [hydrochloride, m.p. 186° (lit. 176°)].

H. B.

Isomerism of the crystalline liquid *p*-phenetoleazoxybenzoic esters. D. VORLANDER and A. FROLICH (Ber., 1934, 67, [B], 1556—1571).—*p*-Azoxyphenetole (I) is monomorphic cryst. liquid, and in this state forms mobile droplets, according to *n*, more closely related to the amorphous melt than to the solid crystals. The monomorphic azoxybenzoic esters (II) give viscous rodlets resembling in many respects the solid crystals. The main cause of the differences in the cryst.-liquid phases, in visible crystal structure, and in Röntgen interferences lies in the differing viscosity of the phases. The *p*-phenetoleazoxybenzoic esters (III) are regarded as "bastards" of (I) and (II), and the properties of each parent are developed separately, and not simultaneously. Two cryst.-liquid phases are formed. Depending sharply on temp., (III) have the cryst.-liquid characteristics of either (I) or (II) with slight mutual restrictions. The following details are cited: *p*-azoxyphenetole, amorphous liquid \rightleftharpoons (168°) cryst. liquid (137°) cryst. solid II \rightarrow cryst. solid I (from light petroleum); *Et p*-azoxybenzoate, amorphous liquid (121°) cryst. liquid (113°) cryst. solid II \leftarrow cryst. solid I (also cryst. liquid \rightarrow cryst. solid I directly); *p*-phenetoleazoxybenzoic acid-a, dark yellow needles, -b, paler yellow leaflets or plates, m.p. 241° (corr.) to turbid cryst. liquid after softening at 238—239° (corr.), partly vaporising when heated further without attaining the amorphous-liquid phase, and their derivatives; *Et* ester-a, amorphous liquid (115°) cryst. liquid (100—102°) cryst. solid; *Et* ester-b, amorphous liquid (112°) cryst. liquid I \rightleftharpoons (82—83°) cryst. liquid II \rightleftharpoons (74—76°) cryst. solid II (also liquid II \rightarrow solid I \rightarrow solid II) (respective NO_2 -derivatives, m.p. 135° and m.p. 124—126°); chloride-a, softens at 144°, transparent amorphous melt, 150—152°; chloride-b, softens at 102—104°, viscous cloudy melt, 122—124°, clear amorphous melt, 128—130°; allyl ester-a, having 3 cryst.-solid and 2 cryst.-liquid forms; allyl ester-b, cryst. solid \rightleftharpoons (70—72°) cryst. liquid II \rightleftharpoons (91°) cryst. liquid I \rightleftharpoons (99°) amorphous liquid; *Me* ester-a, softens at 135°, cloudy, mobile, cryst. liquid at 138°, amorphous liquid at 156°; *Me* ester-b, softens at 111°, cloudy, mobile, cryst. liquid at 114°, amorphous liquid at 148°.

H. W.

Polymethylbenzenes. IX. Addition of ethyl diazoacetate to durene. L. I. SMITH and P. O. TAWNEY. **X. Reaction with aromatic diazonium compounds.** L. I. SMITH and J. H. PADEN (J. Amer. Chem. Soc., 1934, 56, 2167—2169, 2169—2171).—IX. Slow addition of $\text{CHN}_2\cdot\text{CO}_2\text{Et}$ to durene at 140—145° gives a little Et fumarate, (mainly) *Et* β -2:4:5-trimethylphenylpropionate, b.p. 130—136°/4 mm. [free acid (I), m.p. 96—97° (lit. 92°) (amide, m.p. 152—154°)], and tarry material. 2:4:5-Trimethylbenzylidenemalonic acid, m.p. 183—185° (decomp.) [the Et ester, b.p. 182—186°/11 mm., is prepared from 2:4:5- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CHO}\cdot\text{CH}_2(\text{CO}_2\text{Et})_2$, and piperidine], heated at 190—200° gives 2:4:5-trimethylcinnamic acid, m.p. 154—155°, reduced (H_2 , PtO_2 , 95% EtOH) to (I).

X. 2:4:6-Trinitrobenzeneazo-pentamethylbenzene, m.p. 176° (decomp.), and -isodurene, m.p. 164° (decomp.), prepared by slow addition of C_6HMe_5 (II) and isodurene, respectively (in AcOH), to diazotised picramide (III) (in conc. H_2SO_4) [prepared by a slight modification of Blangey's method (A., 1926, 62)] at < 2°, are reduced (SnCl_2 , conc. HCl, AcOH) to amino-pentamethylbenzene (IV) and -isodurene (V), respectively. Durene (VI) and bromodurene do not react with (III). Other diazotised amines could not be coupled with (II), (VI), or *s*- $\text{C}_6\text{H}_4\text{Me}_3$. Diazotised (IV) and (II) in AcOH-conc. H_2SO_4 give a hydrocarbon, $\text{C}_{22}\text{H}_{30}$, m.p. 212—213.5°, which is not decamethyldiphenyl (m.p. 239—241°). (II) does not react with diazotised (V), ψ -cumidine, or mesidine.

H. B.

Colour of thiol and methylthiol azo-dyes of α - and β -naphthol. A. LUSZCZAK and L. GRUN (Monatsh., 1934, 64, 349—360).—The absorption spectra of the following dyes have been determined: 2:4'-nitrobenzeneazo-1-hydroxy-3-thiol-, -3-methylthiol-, -4-thiol-, -4-methylthiol-, -5-thiol-, -5-methylthiol-naphthalene; 1:4'-nitrobenzeneazo-2-hydroxy-6-thiol-, -6-methylthiol-, -7-thiol-, -7-methylthiol-, -8-thiol-, -8-methylthiol-naphthalene. The SH and SMe dyes of the α -series show marked displacement of the absorption bands towards the red and higher extinction in comparison with those of the β -series. The extinction curves of dyes with SH or SMe in the α -position of the C_{10}H_8 nucleus are more complex than those of compounds with similar groups in the β -position, whether OH is α - or β -. The position of OH and SH or SMe exerts a very marked and individual influence on the colour of the dyes. H. W.

Relation between absorption spectra and chemical constitution of dyes. VI. Influence of chromophore position in bisazo-dyes. J. A. FUNKHOUSER and W. R. BRODE (J. Amer. Chem. Soc., 1934, 56, 2172—2173).—The absorption spectra of 4 mono- and 16 bis-azo-dyes in 30% EtOH, conc. HCl, and 3% NaOH are determined as previously described (cf. A., 1928, 1171); the positions of the max. are tabulated. Comparison of *m*- (I) and *p*- (II) $\text{-NAr}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NAr}'$ (Ar and Ar' both contain OH, e.g., $\text{Ar}=\text{p-OH}\cdot\text{C}_6\text{H}_4$; $\text{Ar}'=2\text{-hydroxy-7-sulpho-}\alpha\text{-naphthyl}$) shows that (II) have more intense and better defined absorption bands; introduction of CO_2H into Ar or Ar' produces broader but less intense bands.

The spectra of (I) are similar to the spectra obtained by addition of the bands of $\text{NAr}\cdot\text{NPh}$ and $\text{NPh}\cdot\text{NAr}'$; (II) show a distinct shift in the intensity distribution with intensified bands (hyperchromic effect) at lower frequencies (hypsochromic effect). *p*-Coupling of N:N groups promotes an effect similar to the conjugation of chromophores (III) to form a single (III) in the mol.; *m*-substituted (III) do not influence each other appreciably. Bisazo-dyes have broader and less sharply defined bands than monoazo-dyes of similar structure. H. B.

Absorption spectra of azo-compounds.—See this vol., 1287.

Formation of certain aromatic hydrazines. A. J. BERLIN (J. Gen. Chem. Russ., 1934, 4, 728—732).—When SO_2 is passed through a suspension of NH_2Ph (I) in aq. NaOH and NaNO_2 at 0—5°, the reactions $2(\text{I})+\text{HNO}_2\rightarrow\text{PhN}_2\cdot\text{NHPH}$ (II) $\rightarrow\text{NHPH}\cdot\text{NH}_2$ (III)+(I) take place, whilst when the solution is not cooled (II) decomposes to yield PhOH, N_2 , and (I). With *o*-anisidine in place of (I), 2-hydrazinoanisole-*o*-sulphonic acid, $+0.5\text{H}_2\text{O}$; decomp. 232—235°, is obtained. R. T.

Action of bases on nitrophenylhydrazines: 2:4-dinitrophenylhydrazine. A. K. MACBETH and J. R. PRICE (J.C.S., 1934, 1637—1639).—2:4-(NO_2) $_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ with boiling aq. NH_3 (*d* 0.945) gives 70% of 6-nitro-1-hydroxy-1:2:3-benzotriazole (I), 17% of *m*- $\text{C}_6\text{H}_4(\text{NO}_2)_2$ (II), 5% of an amorphous acid (III), and a trace of *mm'*-dinitroazoxybenzene (IV). With boiling 10% aq. N_2H_4 82.5% of (I), 1% of (II), and 1% of (III), with boiling 10% $\text{N}_2\text{H}_4\cdot\text{EtOH}$ 90% of (I) are formed. With 0.04—0.37*N*-aq. $\text{Ba}(\text{OH})_2$ at 60° traces of NH_3 are formed; the amount of (I) decreases from 70 to 16%, whilst that of (II) and (IV) increases from 10 to 27 and 10.5 to 49%, respectively, with increasing concn. 0.1*N*-NaOH gives the same result as 0.1*N*- $\text{Ba}(\text{OH})_2$. With 0.2—7.5*N*-aq. NaOH at 15±2° the amount of (I) is a min. (8.5%) and those of (II) and (IV) are a max. (33 and 52%, respectively) at about 2.4*N*, whilst the amount of (III) increases with increasing concn. (12% at 7.5*N*). R. S. C.

Influence of *o*-substituents on the reactivity of aromatic compounds. G. LOCK (Oesterr. Chem. Ztg., 1934, 37, 159—161, 167—170).—A crit. summary of lit. data relating to the effect of *o*-substituents on reactions, in which the superposition of steric and chemical (polar) factors, and the variation of the effect in different reactions, are discussed. J. W. B.

Derivatives of 3:5- and 4:6-dibromo-*o*-phenetidine. E. BUREŠ and B. TUSAROVA (Časopis českoslov. Lek., 1934, 14, 1—14; Chem. Zentr., 1934, i, 2581—2582).—3:5-Dibromo-*o*-phenetidine (I), m.p. 57° (hydrochloride, decomp. > 100°; sulphate, unstable; picrate, m.p. 145°; Ac_2 derivative, m.p. 108°; Bz_1 derivative, m.p. 151°; *N*-Et derivative, b.p. 152°), is prepared by treating *o*-phenetidine with Br in AcOH. From the diazotised base are obtained (by heating) 3:5-dibromophenetole, b.p. 268° (4- NO_2 -derivative, m.p. 128°) (with H_2SO_4 and Na_2SO_4) 3:5-dibromo-2-hydroxyphenetole (fuming liquid), and (Sandmeyer) 2-chloro-3:5-dibromophenetole, m.p. 46°; 2:3:5-

tribromophenetole, m.p. 72°, and 3:5-dibromo-2-iodophenetole, m.p. 62°. The Ac derivative, m.p. 79°, of *o*-phenetidine with Br in AcOH gives 4:6-dibromo-2-acetamidophenetole, m.p. 141°, hydrolysed to 4:6-dibromo-*o*-phenetidine (II), m.p. 60° (hydrochloride, decomp. > 150°; Ac₂ derivative, m.p. 151°; Bz₁ derivative, m.p. 159°; N-Me₂ derivative, liquid). From (II) by diazotisation the following are prepared: 4:6-dibromophenetole, m.p. 270—272°; 2-NO₂-derivative, m.p. 46°; 2-OH-derivative, a fuming liquid resembling PhOH; 2-Cl-derivative, slightly fuming crystals, m.p. 61°; 2-Br-derivative, m.p. 73°; 2-I-derivative, m.p. 69°.

R. N. C.

Condensation products from phloroglucinol and aromatic amines. [Diaryldiaminophenols.]—See B., 1934, 954.

Constituents of *Ginkgo biloba*, L., fruit. I—III. S. FURUKAWA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 304—313, 314—319, 320—324).—I. Ginkgol Me ether (I) (cf. A., 1928, 1291) in CHCl₃ at 0° with O₃ during 30 hr. followed by hydrolysis affords *n*-heptonic acid and its aldehyde, H₂C₂O₄, and azelaic acid, which indicates the presence of a pentadecenyl group. Dihydroginkgolic acid with COMe₂-KMnO₄ gives impure palmitic acid (also obtained from dihydroginkgol), which is probably identical with cyclogallipharic acid (cf. A., 1904, i, 587). When heated, ginkgol affords *m*-cresol [oxidised to *m*-OH·C₆H₄·CO₂H, which is also obtained by oxidation of (I)] and a mixture of aliphatic hydrocarbons, which indicates that OH is *m* to the pentadecenyl side-chain (cf. A., 1907, i, 1032).

II. Bilobol (II) (A., 1928, 1291) with MeI in boiling EtOH-NaOEt affords a Me₂ ether, b.p. 250—252°/6 mm., oxidised by O₃ in CHCl₃ at 0° to the same products as (I). Dihydrobilobol with KMnO₄ affords palmitic acid. Dry distillation of (II) affords probably orcinol or β-orcinol.

III. Et *m*-methoxybenzoylacetate (prep. described) with tridecyl iodide in boiling EtOH-NaOEt during 5 hr. affords a product, hydrolysed to *m*-methoxyphenyl tetradecyl ketone, b.p. 250—258°/10 mm., which is reduced (Clemmensen) to *m*-methoxypentadecylbenzene, m.p. 22°, and demethylated to dihydroginkgol.

J. L. D.

Cationoid reactivity of aromatic compounds. II. Action of potassium cyanide on 1-nitroso-β-naphthol and 1-benzeneazo-β-naphthol. W. BRADLEY and R. ROBINSON (J.C.S., 1934, 1484—1489; cf. A., 1932, 622).—Cationoid activity of 1-nitroso-β-naphthol (I) is shown by its reaction with aq. KCN at 80—90° to form 1-amino-2-hydroxy-4-cyanonaphthalene (II). 1-Benzeneazo- (III) and 1-*p*-sulphobenzeneazo-β-naphthol similarly give (II), indicating that these compounds probably have the hydrazone structure. Five other hydroxyazo-compounds react similarly, two only slowly, and four not at all. (II), m.p. 200—201° (decomp.) (hydrochloride, by dry HCl gas in Et₂O), is insol. in HCl and unstable in air or dil. aq. NaOH, reduces Fehling's solution, and cannot be diazotised or smoothly hydrolysed, but its structure is shown by the following reactions. It gives a Ac₂ derivative (IV) (by hot Ac₂O-C₅H₅N), m.p. 163—164°,

by Me₂SO₄-aq. NaOH 1-dimethylamino-2-methoxy-4-cyanonaphthalene, m.p. 93—93.5° (sol. in dil. HCl; hydrolysed by cold, conc. H₂SO₄ or hot 33% NaOH to 4-dimethylamino-3-methoxy-1-naphthoamide, m.p. 183°, further hydrolysed by hot conc. HCl to the acid), and with CrO₃-H₂SO₄ 4-cyano-1:2-naphthoquinone, m.p. 175—176° (decomp. slowly by aq. NaOH). This quinone affords 4-cyano-1:2-benzphenazine, m.p. 247°, hydrolysed by hot 40% NaOH to 1:2-benzphenazine-4-naphthoic acid, m.p. 305°, and is reduced (SO₂ in hot EtOH) to 4-cyano-1:2-dihydroxynaphthalene, m.p. 210—211°, the Me₂ ether, m.p. 109° (obtained by MeI and K₂CO₃ in hot COMe₂; Me₂SO₄-aq. NaOH gives a substance, m.p. > 300°, of which with hot 25% KOH gives 3:4-dimethoxy-1-naphthoic acid, m.p. 161—161.5°. (IV) and hot, dil. KOH yield 1-acetamido-2-hydroxy-4-cyanonaphthalene, m.p. 224° [K and Na salts; oxidised (KMnO₄) to *o*-C₆H₄(CO₂H)₂], the Me ether (V) (by MeI-K₂CO₃-COMe₂), m.p. 275°, of which is also obtained [Sandmeyer; K₂Ni(CN)₄] from 1-acetamido-4-amino-2-methoxynaphthalene (VI), m.p. 196°. 1-Nitro-2-methoxynaphthalene with Zn-EtOH-conc. HCl gives 2-methoxy-α-naphthylamine, m.p. 55° (lit. 54° and 84°), the Ac derivative, m.p. 178—179° (lit. 175°), of which with HNO₃ (*d* 1.42) in AcOH at < 5° gives the 4-NO₂-derivative, m.p. 251°, indifferent to Zn-HCl or Na₂S, but reduced to (VI) by hot aq. Na₂S₂O₄. (VI) in C₆H₆ with aq. CrO₃-H₂SO₄ yields 2-methoxy-1:4-naphthoquinone, m.p. 184—185° (lit. ? 146—147°), also obtained by hydrolysis and subsequent oxidation of (V). A by-product in the formation of (II) from (III) is a substance, probably C₁₇H₁₃O₂N₃, m.p. 235° (decomp.) [Me ether, m.p. 206° (sinters at 196°; decomp. 215°)]. (I) and *p*-C₆H₄Me·SO₂H in EtOH give 1-amino-2-*p*-toluenesulphonyloxy-4-naphthyl-*p*-tolylsulphone, m.p. 151—152°, which by alkaline hydrolysis and subsequent acetylation yields 1-diacetamidido-2-acetoxy-4-naphthyl-*p*-tolylsulphone, m.p. 191—192°.

R. S. C.

Derivatives of hydroxydiphenyls. II. Nitrogen and halogen derivatives of 4-hydroxydiphenyl. J. C. COLBERT, W. MEIGS, and A. H. STUERKE (J. Amer. Chem. Soc., 1934, 56, 2128—2130; cf. this vol., 291).—3-Chloro-4-hydroxydiphenyl (I), b.p. 176.6°/5 mm. (cf. *loc. cit.*) [Me ether, m.p. 93° (all m.p. are corr. unless stated otherwise)], and HNO₃ in AcOH give 3-chloro-5-nitro-4-hydroxydiphenyl, m.p. 89—90° [4'-Br-derivative, m.p. 193—194°; the hydrochloride and Bz₂ derivative of the corresponding NH₂-derivative have m.p. 180° (decomp.) and 181—182°, respectively], the structure of which is established by chlorination in AcOH to 3:4'-dichloro-5-nitro-4-hydroxydiphenyl, m.p. 190—192° (uncorr.) [the hydrochloride and Bz₂ derivative of the corresponding NH₂-compound have m.p. 210° (decomp.) and 217—218°, respectively], which is also prepared from 3-nitro-4-hydroxydiphenyl (II) (benzoate, m.p. 111°) and Cl₂ in AcOH. The structure of (II) is established since acetylation and benzylation of the NH₂-derivative causes rearrangement (A., 1925, i, 808). (I) is also nitrated to 3-chloro-5:4'-dinitro-4-hydroxydiphenyl, sublimes at 200°. 3:5-Dichloro-4-hydroxydiphenyl, b.p. 188.7°/5 mm. (cf. *loc. cit.*) (Me ether, m.p. 54°; 4'-Br-derivative, m.p. 136.5—138°), and HNO₃ in AcOH give the 4'-NO₂-derivative, m.p. 214—215°.

4-Hydroxydiphenyl (2:4-dinitro-, m.p. 115°, and 2:4:6-trinitro-, m.p. 224°, -phenyl ethers) and Cl_2 in AcOH give Cl -, Cl_2 -, or Cl_3 -derivatives according to the time of reaction (cf. *loc. cit.*); more prolonged chlorination affords a mixture containing Cl_5 -, m.p. 115—118° (uncorr.), and Cl_7 -, m.p. 142—145° (uncorr.), -derivatives. H. B.

Polymorphism of aromatic disulphides. I. CHMELNITZKAJA and V. MICHELS (J. Gen. Chem. Russ., 1934, 4, 452—455).—When reduced with N_2H_4 ($p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot$)₂ yields two forms of ($p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot$)₂ (I), m.p. 83° [Ac_2 derivative (II), m.p. 216°], and m.p. 143—144° (Ac_2 derivative, m.p. 181—182°). (II) is converted into Ginsberg's γ -form, m.p. 122°, by exposure to light. A fourth form, m.p. 172°, of (II) is obtained by heating (I) successively with 30% NaHSO_3 and Ac_2O . R. T.

Pyrocatechol complex salts and their constitution. G. SPACU and M. KURAŠ (J. pr. Chem., 1934, [ii], 141, 201—217).—The complexes $[\text{M}^{\text{II}}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2[\text{H}_2(\text{C}_5\text{H}_5\text{N})_2]$, described by Weinland and Sperl (A., 1926, 165), are best formulated as $[(\text{C}_5\text{H}_5\text{N})_2\text{M}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2]$ (A). The Zn salt (I) (A, $\text{M}=\text{Zn}$) is obtained (i) from $o\text{-C}_6\text{H}_4(\text{OH})_2$ (II), ZnCl_2 , and $\text{C}_5\text{H}_5\text{N}$ in H_2O , (ii) as the monohydrate from (II) and aq. $[(\text{C}_5\text{H}_5\text{N})_2\text{Zn}](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$, and (iii) as the dihydrate from (II) and aq. $[(\text{C}_5\text{H}_5\text{N})_2\text{Zn}](\text{OAc})_2$. Dry (I) is converted by dry NH_3 into the complex, $[(\text{NH}_3)_2\text{Zn}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2]$. (II), ZnCl_2 , and $(\text{CH}_2\cdot\text{NH}_2)_2$ in H_2O give the complex $[\text{enZn}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2]$, also obtained from (II) and $(\text{Zn en}_3)\text{Cl}_2\cdot 2\text{H}_2\text{O}$ in aq. NaOAc . The Cd (III) (A, $\text{M}=\text{Cd}$) and Ni (A, $\text{M}=\text{Ni}$) complexes are also prepared. The complex, $[\text{enCd}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2]$, is obtained from $(\text{Cd en}_3)\text{Cl}_2$ and (II). (II) and $\text{Zn}(\text{OAc})_2$ in H_2O give the salt, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{Zn}\cdot\text{OAc}(\text{H}_2\text{O})$ (IV), whilst $\text{Cd}(\text{OAc})_2$ and (II) in EtOH afford the salt, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{Cd}\cdot\text{OAc}$ [converted by aq. $\text{C}_5\text{H}_5\text{N}$ into (III)]. ZnCl_2 (1 mol.), (II) (2 mols.), and an excess of $\text{C}_5\text{H}_5\text{N}$ in hot H_2O give the complex, $\text{C}_6\text{H}_4\begin{matrix} \text{O}\cdot\text{Zn}(\text{C}_5\text{H}_5\text{N})\cdot\text{O} \\ \text{O}\cdot\text{Zn}(\text{C}_5\text{H}_5\text{N})\cdot\text{O} \end{matrix}\text{C}_6\text{H}_4$, colourless [monohydrate, prepared from (IV) and aq. $\text{C}_5\text{H}_5\text{N}$ at 100°]; when the reaction mixture is cooled slowly in the dark, a red complex (V) of the same composition as (I) is obtained. (V) loses 1 mol. of $\text{C}_5\text{H}_5\text{N}$ at 70° and decomposes from 150°. The complex obtained from (II), ZnSO_4 , and $\text{C}_5\text{H}_5\text{N}$ using Weinland and Sperl's method (*loc. cit.*) contains Zn and N in the ratio 1:2.47; the use of more dil. solutions gives a complex of the composition $4[\text{Zn}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2][\text{H}_2(\text{C}_5\text{H}_5\text{N})_2] + \text{C}_6\text{H}_4(\text{OH})_2$. (II), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$, and $\text{C}_5\text{H}_5\text{N}$ in aq. NaOAc afford the complex, $[(\text{C}_5\text{H}_5\text{N})_2\text{Co}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2](\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})$.

H. B.

Halogen hydroxo- and pyrocatechol hydroxo-salts of bivalent heavy metals.—See this vol., 1317.

Homologues of resorcinol. R. ROBINSON and R. C. SHAH (J.C.S., 1934, 1491—1498).—Additional evidence is cited to confirm the nuclear methylation of β -resorcylic acid by MeI - KOH (J.C.S., 1895, 67, 900). Et , glutaconate does not condense with Me ketones. The Na derivative of Et , α -acetoglutarate

and $\text{Pr}\cdot\text{COCl}$ in Et_2O lead to a mixture of γ -aceto- and γ -butyro-butyric (I) acids. Et C -butyrylacetate (modified prep.) is hydrolysed ($\text{NH}_3\text{-Et}_2\text{O}$) to Et butyrylacetate, which with NaOEt and $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ gives Et_2 butyrogutarate, whence only a poor yield of (I) was obtained. Et butyrylacetate is best cyclised by NaOEt in Et_2O , giving 2-ethyl-dihydroresorcinol, m.p. 175—177° (decomp.), which with Br under most conditions gives tars, but affords (excess Br ; cold CHCl_3) a Br_2 -, m.p. 75—77°, and [cold AcOH ; Br (3 mols.); NaOAc (3 mols.)] a Br_3 -derivative, m.p. 92—94° (decomp.). Nuclear alkylation of resacetophenone (II) (improved prep.) is best effected by KOH (4 mols.) and MeI (5 mols.) under stated conditions; the resulting 2-hydroxy-4-methoxy-3-methylacetophenone, m.p. 80—82°, is reduced (Clemmensen) to 6-methoxy-3-ethyl- o -cresol, b.p. 128—131°/15 mm. (p -nitrobenzoyl derivative, m.p. 135—137°), which with hot HBr (d 1.7) gives 2-methyl-4-ethylresorcinol, m.p. 88—90° [Me_2 ether, b.p. 115—118°/15 mm., oxidised (KMnO_4 ; 70—80°) to 2:6-dimethoxy-3-ethylbenzoic acid, m.p. 114—120°, or, finally, to an acid, m.p. 200—205° (decomp.)]. Ethylation of (II) affords in poor yield a mixture of $O\text{-Et}$, and $C\text{-Et-O-Et}$ derivatives. β -Resorcyaldehyde gives a mixture of $O\text{-Et}$ -aldehyde and some 2-hydroxy-4-ethoxy-3-ethylbenzaldehyde, m.p. 58—60°, and β -resorcylic acid gives a similar mixture. Me β -resorcyate (by $\text{MeOH-H}_2\text{SO}_4$, not by HCl), m.p. 118—119°, affords similarly, but smoothly, Me 2-hydroxy-4-ethoxy-3-ethylbenzoate (III), m.p. 52—53°, Me 2-hydroxy-4-ethoxybenzoate, m.p. 77—79°, Me 2:4-diethoxybenzoate (IV), m.p. 51—54°, and a mixture of (III) and (IV), which is best separated by way of the respective acids, (V) and (VI). (V) is hydrolysed and decarboxylated by hot HI (d 1.7) to 2-ethylresorcinol, m.p. 95—97°, which gives (Gattermann) 2:4-dihydroxy-3-ethylbenzaldehyde, $+0.5\text{H}_2\text{O}$, m.p. 115—118° [2:4-dinitrophenylhydrazine, m.p. 295° (decomp.)]; pyrylium salt with 5:6-dimethoxy-1-hydrindone and HCl in AcOH , reduced (Clemmensen) to 4-methoxy-2-ethylresorcinol, m.p. 98—99°. The last-mentioned substance is probably identical with the dihydric phenol obtained from citrinin (A., 1931, 1092), but the latter decomposes when kept (m.p. 65—70° after 2—3 years). 4-Ethylresorcinol gives (Gattermann) 2:4-dihydroxy-5-ethylbenzaldehyde, m.p. 130—131° [2:4-dinitrophenylhydrazine, m.p. 279° (decomp.)], reduced to 6-methyl-4-ethylresorcinol, m.p. 60—63°, b.p. 150—155°/20 mm. Orsacetophenone is reduced to 5-methyl-4-ethylresorcinol, $+1.5\text{H}_2\text{O}$, m.p. 72—82°, $+0.25\text{H}_2\text{O}$, and anhyd., m.p. 75—80°. Zn for Clemmensen reductions is activated by pulverising and treating three times with hot HCl . R. S. C.

Derivatives of protocatechuic acid from saffrole; rearrangement of the acyl group. K. Ono and M. IMOTO (J. Chem. Soc. Japan., 1934, 55, 517—524).—Heating of 30 g. of saffrole with 17 g. of KOH and 30 g. of MeOH at 200—208° for 3 hr. in an autoclave gave 3 g. of isosaffrole and 27 g. of a mixture of 3:4- (I) and 4:3- $\text{C}_6\text{H}_3(\text{OH})(\text{O}\cdot\text{CH}_2\cdot\text{OMe})\cdot\text{CH}:\text{CHMe}$ (II). The Ac and Bz derivatives of (I) and (II) were prepared and their oxidation products investigated. CH. ABS. (e)

Catalytic action of Japanese acid earth. V. Action on methylcyclohexanols and menthol. H. INOUE (Bull. Chem. Soc. Japan, 1934, 9, 353—363; cf. A., 1927, 51).—Ring-fission of 2- (I), 3-, and 4-methylcyclohexanol (II) in presence of Japanese acid earth at 250—350° proceeds similarly to that of cyclohexanol, (I) giving most and (II) least cyclopentane derivatives. Menthol yields similarly at 250° methylcyclopentane, menthone (III), menthane, *p*-cymene, isopropyl- and methylisobutyl-cyclopentane (IV); at 350° cyclopentane, (III), and (IV) are the main products. R. S. C.

Aromatic alcohols and thiolacetic acid. B. HOLMBERG (J. pr. Chem., 1934, [iii], 141, 93—112).—CPhRR'·OH and SH·CH₂·CO₂H (I) in (usually) 2*N*-HCl at 100° (bath) give CPhRR'·S·CH₂·CO₂H (II) in addition to SH·CH₂·CO₂·CPhRR'; cinnamyl alcohol (III) and benzoic acid (IV) react similarly, but acids analogous to (II) are not obtained from CH₂Ph·CRR'·OH, CH₂Ph·CH₂·CH₂·OH, or mandelic acid. Thus, CH₂Ph·OH gives CH₂Ph·S·CH₂·CO₂H; CHPhMe·OH affords CHPhMe·S·CH₂·CO₂H, m.p. 64—66° [also prepared from (I) and CHPhMeBr in aq. EtOH-NaOH] [corresponding sulfoxide, m.p. 115—117° (decomp.)], and *sulphone*, m.p. 112—113°; CPhMe₂·OH yields *β*-phenylisopropylthiolacetic acid, m.p. 72—74°; CHPh₂·OH furnishes *benzhydrylthiolacetic acid*, m.p. 129—130° [Na salt (+4H₂O)]; CPh₂Me·OH gives impure CPh₂Me·S·CH₂·CO₂H; CPh₃·OH affords CPh₃·S·CH₂·CO₂H [Na salt (+5H₂O)]; (III) yields cinnamylthiolacetic acid [corresponding sulfoxide, m.p. 124—125° (decomp.) (previous sintering)]; (IV) furnishes *carboxymethylthioldiphenylacetic acid*, CO₂H·CH₂·S·CPh₂·CO₂H, m.p. 194—196° (decomp.). The following are prepared from (I) and the appropriate bromide: *β*-phenylethylthiolacetic acid (V), m.p. 56—58° [corresponding sulfoxide, m.p. 104—105° (slow) and 108—109° (rapid heating), and *sulphone*, m.p. 77—78°]; *γ*-phenylpropylthiolacetic acid, an oil [corresponding sulfoxide, m.p. 114—115° (decomp.)]; *carboxymethylthiophenylacetic acid*, CO₂H·CH₂·S·CHPh·CO₂H, m.p. 133—135°. (V) is best prepared by addition of (I) to styrene either alone or in AcOH; addition occurs slowly in C₆H₆. *β*-Phenylethylthetiacetic acid, CO<CH>S(CH₂·CH₂Ph)·CH₂·CO₂H, m.p. 112—113° (decomp.), is prepared from (V) and CH₂Br·CO₂H.

H. B.

Mechanism of deamination of amino-alcohols. I. Amino-alcohols derived from phenyl α -amino- β -phenylethyl ketone. A. K. MILLS. II. Amino-alcohols derived from α -aminopropiophenone hydrochloride. A. K. MILLS and J. GRIGOR (J.C.S., 1934, 1565—1568, 1568—1570).—I. COPH-CH₂·CH₂Ph [prepared in quant. yield by hydrogenation (Pt-black) of the chalkone in EtOH] in MeOH gives the oximino-derivative, reduced by SnCl₂ to *Ph* α -amino- β -phenylethyl ketone hydrochloride (I), m.p. 228—229° (decomp.), which with CH₂Ph·MgBr affords *β*-amino- α -*β*-dibenzyl- α -phenylethyl alcohol, m.p. 96—97° [hydrochloride, m.p. 251—252° (decomp.)]. This with NaNO₂ in cold 25% AcOH gives CH₂Ph·CHPh·CO·CH₂Ph. *β*-Amino- α -*γ*-diphenyl- α -*p*-

tolyl-n-propyl alcohol [from (I) and *p*-C₆H₄Me·MgBr], m.p. 134—135° [hydrochloride, m.p. 218—219° (decomp.)], gives on deamination CH₂Ph·CHPh·CO·C₆H₄Me-*p*; *β*-amino- α -*γ*-diphenyl- α -(*α*-naphthyl)-*n*-propyl alcohol (similarly prepared), m.p. 165—166° [hydrochloride, m.p. 229—230° (decomp.)], affords similarly *α*-naphthyl α -*β*-diphenylethyl ketone, m.p. 68—69°, also obtained from α -C₁₀H₇·CO·CH₂Ph, Na, and CH₂ClPh in EtOH. The migration of Ph in each of the above cases is contrary to the behaviour of *s*-pinacones on dehydration and indicates that org. groupings do not possess a definite "migrational aptitude."

II. α -Aminopropiophenone hydrochloride [by hydrogenation (Pd-C) of oximinopropiophenone, m.p. 113—114°, in Et₂O-HCl] and 1-C₁₀H₇·MgBr give *β*-amino- α -phenyl- α -1-naphthyl-*n*-propyl alcohol, m.p. 160° [hydrochloride, m.p. 253—254° (decomp.)], which with NaNO₂ in cold, dil. AcOH gives *α*-naphthyl α -phenylethyl ketone, m.p. 49.5—50.5° (oxime, m.p. 160.5—161.5°), also obtained from α -C₁₀H₇·CO·CH₂Ph, NaOEt, and MeI in EtOH. *β*-Amino- α -phenyl- α -benzyl-, m.p. 69.5° (hydrochloride, m.p. 235—236°), and *α*-methyl-*n*-propyl alcohol, m.p. 82—83° (hydrochloride, m.p. 244°), similarly prepared, give with HNO₂ CH₂Ph·CO·CHPhMe, b.p. 175°/12—13 mm. (oxime, m.p. 83—84°), and CHPhMe·COMe, b.p. 94—96°/12—13 mm. (semicarbazone, m.p. 172—173°). Migration of Ph is thus the normal reaction (cf. lit.).

R. S. C.

Sterol group. XIX. Constitution of ergosterol. J. L. DUNN, I. M. HEILBRON, R. F. PHIPERS, K. M. SAMANT, and F. S. SPRING (J.C.S., 1934, 1576—1581; cf. A., 1933, 1290).—Reasons (see original for details) are adduced for believing that ergosterol has the OH at position 3 and the ethylenic linkings at 5 : 6 and 8 : 9. Methoxycholestene, m.p. 82—83°, best prepared by methylation of cholestanol, with CrO₃ in AcOH at 80° gives the acid, C₂₇H₄₆O₄, m.p. 195°. *Me ergostanylzanthate*, m.p. 109—110°, [α]_D²⁰ -3.6° in CHCl₃, at 200—210°/vac. affords *ergostene*, C₂₈H₄₈, m.p. 86—87°, oxidised by CrO₃ to the acid, C₂₈H₄₈O₄, m.p. 218—219° (Me₂ ester, m.p. 82—83°). Cholestenediol diacetate (prep. from cholestanetriol diacetate), m.p. 124—125°, could not be dehydrated. Ergostadienetriol I (A) readily loses H₂O, best in Ac₂O at 100°, to give dehydroergosterol. Ergostanediol is reduced (Clemmensen in AcOH) to *ergostene*, m.p. 78°, hydrogenation of which affords *ergostane*, m.p. 82°. (A) and CrO₃ give first ergostadienediol, m.p. 249°, and then a substance, C₂₈H₄₀O₄, m.p. 204—205° (monoxime, m.p. 165—167°). Ergostadienediol and KOH-MeOH give a little (?) *ergostatrienedione*, C₂₈H₄₀O₂, m.p. 145—146°. The product, C₂₉H₄₈O₃, from methoxyergostadienediol and Pb(OAc)₄ has m.p. 130—131° (lit. 105—106°). Structures are assigned to the OH-derivatives.

R. S. C.

Chemistry of the algæ. I. Algal sterol, fucosterol. I. M. HEILBRON, R. F. PHIPERS, and H. R. WRIGHT (J.C.S., 1934, 1572—1576).—*Fucus vesiculosus* contains chlorophyll, carotenoids, *n*-C₃₁H₆₄, and two pectins, which yielded *fucosterol* (I) (0.2% of dry wt.), C₂₉H₄₈O, m.p. 124°, b.p. 220—230°/0.2 mm., [α]_D²⁰ -38.42° in CHCl₃ {acetate, m.p. 118—119°, [α]_D²⁰

—43.8° in CHCl_3 [tetra-bromide, m.p. 133° (decomp.), unstable]; propionate, m.p. 105—106°; benzoate, m.p. 120°, monotropic; digitonide, m.p. 223—225°, hydrogenated (PtO₂) in EtOAc-AcOH to fucostanol (=stigmastanol). (I) occurs, at least partly, free and contains two ethylenic linkings in the nucleus (Br and BzO₂H titrations; O₃ does not give $\text{CHMe}_2\text{-CHEt}\cdot\text{CHO}$); it occurs also in *Pelvetia canaliculata* and, with sitosterol, in *Nitella opaca*, Agh, and is probably the characteristic algal sterol. Biological relations are indicated. R. S. C.

Calosterol.—See this vol., 1276.

Diazotisation of anæsthesine (ethyl *p*-amino-benzoate). M. A. SCHWARZ (Gazzetta, 1934, 64, 518—521).—Diazotisation of $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ in dil. HCl at 2°, adding 1 mol. NaNO_2 all at once, yields $p\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ and *Et diazoaminobenzene-4:4'-dicarboxylate* (I) (yellow), m.p. 152—154°, converted by $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ and a little HCl into *Et aminoazobenzene-3:4'-dicarboxylate* (II) (red), m.p. 114°. In presence of NaOAc addition of NaNO_2 to a solution of $p\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ at 70° (then rapidly cooling) yields a mixture of (I) and (II). R. K. C.

Preparation of anæsthesine. E. A. TZOFIN and A. G. RADUSHKEVICH (Khim. Farm. Prom., 1934, No. 1, 23—25).— $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ is refluxed with EtOH and H_2SO_4 , and the product neutralised and reduced by Fe filings and AcOH. CH. ABS. (e)

Fission of disulphides by alkali. I. Behaviour of $\alpha\alpha'$ -disulphidobisphenylacetic acid. A. SCHÖBERL, E. BERNINGER, and F. HARREN (Ber., 1934, 67, [B], 1545—1550).—Treatment of $\text{CHPhCl}\cdot\text{CO}_2\text{H}$ or $\text{CHPhBr}\cdot\text{CO}_2\text{H}$ with hot aq. Na_2S_2 leads to $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, whilst in cold solution $\alpha\alpha'$ -disulphidobisphenylacetic acid (I) ($\text{CO}_2\text{H}\cdot\text{CHPh}$)₂₂, m.p. 218°, and an isomeride, m.p. (indef.) 141°, are obtained; they are also prepared by oxidation of $\text{SH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ by I. (I) is readily decomposed by alkali to $\text{SH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, H_2S , and $\text{COPh}\cdot\text{CO}_2\text{H}$ [identified as the phenylhydrazone, m.p. 163° (decomp.), and 2:4-dinitrophenylhydrazone, m.p. 194°]. Reaction is therefore: $[\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{S}]_2 + \text{H}_2\text{O} \rightarrow \text{SH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H} + \text{OH}\cdot\text{S}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$. $\text{COPh}\cdot\text{CO}_2\text{H}$ is formed from (I) by the action of O₂ in alkaline solution, but is not an oxidation product, the gas being used mainly for the conversion of Na_2S_2 into $\text{Na}_2\text{S}_2\text{O}_3$; the simultaneous production of BzOH is unexplained. H. W.

Hydrolysis of phenylalanine.—See this vol., 1314.

Synthesis of γ -chloro- α -phenyl- α -alkylbutyronitriles. R. HASTINGS and J. B. CLOKE (J. Amer. Chem. Soc., 1934, 56, 2136—2138).— γ -Chloro- α -phenyl- α -methyl-, b.p. 109—111°/3—4 mm., - α -ethyl-, b.p. 115—116.5°/3—4 mm., - α -n-propyl-, b.p. 121—123°/3—4 mm., and - α -n-butyl-, b.p. 133—135°/3—4 mm., butyronitrile are prepared by successive treatment of $\text{CHPhAlk}\cdot\text{CN}$ (from $\text{CHNaPh}\cdot\text{CN}$ and Me_2SO_4 , Et_2SO_4 , PrBr , and BuBr in Et_2O) with NaNH_2 and $(\text{CH}_2\text{Cl})_2$ in C_6H_6 ; the yields are about 22%. H. B.

Perkin's cinnamic acid synthesis. F. BOCK, G. LOCK, and K. SCHMIDT (Monatsh., 1934, 64, 399—414).—When the aldehyde (1 mol.), NaOAc (0.7 mol.),

and Ac_2O (2.1 mols.) are heated at 150° until reaction commences and then for 7—8 hr. at 180—200°, the presence of Cl in the aldehyde mol. increases the yield of the cinnamic acid in all cases, particularly when Cl is at 2 or 2 and 6. Under these conditions or at lower temp. the presence of NO_2 favours the yield. The presence of Me has the opposite effect. The influence of time, temp., and ratio of reactants in the case of PhCHO , NaOAc, and Ac_2O is described. The following cinnamic acids are described: *o*-chloro-, m.p. 211°; *m*-chloro-, m.p. 165°; *p*-chloro-, m.p. 247°; 2:5-dichloro-, m.p. 194.5° (corr.), whence β -2:5-dichlorophenylpropionic acid, m.p. 181° (corr.); 2:6-dichloro-, m.p. 196°; 2:3:6-trichloro-, m.p. 189°; *o*-nitro-, m.p. 242°; *m*-nitro-, m.p. 201°; *p*-nitro-, m.p. 288°; 2:4-dinitro-, m.p. 179° [improved prep. of 2:4-(NO_2)₂ $\cdot\text{C}_6\text{H}_3\cdot\text{CHO}$]; *o*-methyl-, m.p. 169°; *m*-methyl-, m.p. 118°; *p*-methyl-, m.p. 199°; 2:4:6-trimethyl-, m.p. 176° (*Ba* salt; *Et* ester, m.p. 40°), in very small yield by Perkin's reaction, more conveniently obtained by hydrolysis of the crude ester from mesitylaldehyde, Na, and EtOAc , and converted by Br in CS_2 or AcOH into bromotrimethylstyrene, m.p. 53°. 2:4:6-(NO_2)₃ $\cdot\text{C}_6\text{H}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ could not be obtained. H. W.

Course of the semi-hydrogenation of the acetylenic linking from the stereochemical viewpoint. E. OTT [with V. BARTH and O. GLEMSER] (Ber., 1934, 67, [B], 1669—1674; cf. A., 1927, 441).—Parallelism exists between the "activity" of a reducing catalyst and the reduction potential of metals. Reduction of $\text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H}$ (I) by Zn, dil. aq. NH_3 , and NH_4Cl gives 10% of *allo*- (II) and 90% of *trans*- (III) cinnamic acid. Mn affords mainly (II) with 4% of (III), whereas the less noble metals Mg, Ba, and Na, in accordance with Le Chatelier's principle, do not yield (III), but 50% of unchanged (I) and 50% of $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Metals nobler than Zn give (III) exclusively, as shown particularly by Cr powder and HCl-AcOH. Combination of Zn with nobler metals (Ag, Au, Cu) gives pairs occupying a place between Zn and Mn with respect to reduction potential. The phenomenon is probably analogous to overvoltage. Zn-Ag and Zn-Cu are the most active pairs, yielding 24% and 37%, respectively, of (II) from (I). The reduction potentials of the reducing catalysts Co, Ni, Pt, Pd, all lie in a very narrow region corresponding with a position intermediate between Zn and Mn in the electrochemical series. The reduction potentials of $\text{Cr}(\text{OH})_2$ (IV) and $\text{Ti}(\text{OH})_3$ (V) suspended in $\text{NH}_3\text{-NH}_4\text{Cl-H}_2\text{O}$ are of the same order of magnitude, (IV) yielding a mixture of (II) and (III) from (I), whereas (V) gives solely (II). H. W.

Synthesis of isomeric phenylbutadienecarboxylic acids. H. LOHAUS (Annalen, 1934, 513, 219—229).—*cis*- α -Bromocinnamaldehyde (I) (von Auwers *et al.*, A., 1931, 222; 1932, 271), $\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$, and piperidine or MeOH-NaOMe give *Me* (Δ^r -*cis*-) γ -bromocinnamylidenecyanoacetate (II), m.p. 133°, also obtained [together with (III)] from *Me* γ -*di*-bromo- α -cyano- δ -phenyl- Δ^r -butene- α -carboxylate, m.p. 98° [from $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Me}$ (III) and Br in CHCl_3], by spontaneous decomp. in Et_2O or by the action of $\text{Et}_2\text{O-NHET}$. (I) does not similarly condense with

$\text{CN}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$; *Et* γ -bromocinnamylideneacetate, m.p. 75° , is obtained from $\text{CHBrPh}\cdot\text{CHBr}\cdot\text{CH}\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ and $\text{Et}_2\text{O}\cdot\text{NHET}_2$. Reduction (Zn dust, 90% MeOH) of (II) gives the non-cryst. impure *Me* (Δ^7 -*cis*-)cinnamylidenecyanoacetate, decomp. about 80° (not sharp). Supplementary details are given (cf. von Auwers and Muller, A., 1924, i, 44) for the prep. of γ -bromo- β -hydroxy- γ -benzylidenebutyric and γ -bromocinnamylideneacetic acid (IV), m.p. 142° . (IV) is considered to have the Δ^a -*trans*- Δ^7 -*cis* configuration. Reduction (Zn dust, 80—90% EtOH) of (IV) (as Na salt) affords some Δ^a -*trans*- Δ^7 -*cis*-cinnamylideneacetic acid (V) (isocinnamylideneacetic acid), m.p. 128° , and (mainly) the *trans-trans*-acid (VI), m.p. 165° . Reduction (Zn dust, 90% MeOH) of the *Me* ester of (IV) gives (mainly) the *Me* ester, solidifies at -13° , of (V); hydrolysis (MeOH-KOH) of this gives (VI) and a little (V). H. B.

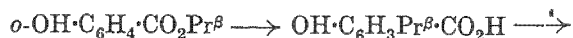
Preparation of chaulmoogra derivatives. I. Substituted amines and amides. J. H. PAYNE, R. WRENSHALL, and K. VAN H. DUKER (J. Amer. Chem. Soc., 1934, 56, 2126—2128).— β -Iodoethyl chaulmoograte [from chaulmoogryl chloride (I) and $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{OH}$ (II) at 0°] and NMe_3 in C_6H_6 at 100° (sealed tube) give chaulmoogrylcholine iodide, decomp. about 150° , which with AgCl in MeOH affords the chloride, softens and decomp. about 65° . Di-iododihydrochaulmoogrylcholine iodide, decomp. about 210° , and chloride, melts partly at 54° , decomp. $> 185^\circ$, are similarly prepared from β -iodoethyl di-iododihydrochaulmoograte [from (I), (II), and I]. Chaulmoogr-*p*-phenetide, m.p. 115° , and -*p*-carbethoxyanilide, m.p. 94 — 95° , and dihydrochaulmoogr-anilide, m.p. 94° , -*p*-phenetide, m.p. 117° , and -*p*-carbethoxyanilide, m.p. 120 — 121° , are described. H. B.

Mechanism of the formation of choleic acids. E. CHARGAFF and G. ABEL (Biochem. J., 1934, 28, 1901—1906).—Choleic acids (I) formed from deoxycholic acid and fatty acids with branched chains are much more labile than those formed from normal fatty acids. (I) from fatty acids substituted in the β -position are more stable than from α -substituted acids. If the quotient mol. wt. of longer chain/mol. wt. of shorter chain is > 6.3 , the corresponding (I) has a normal co-ordination no. Smaller quotients correspond with lower co-ordination no. Many halogenated fatty acids do not form (I). The following compounds appear to be new: methylnonylmalonic acid, m.p. 94 — 95° (*Et* ester, b.p. 147 — $148^\circ/5$ mm.), loses CO_2 to yield α -methylundecic acid, b.p. 125 — $127^\circ/6$ mm. The following are described: α -butyl-*n*-hexoic acid-tetracholeic acid, m.p. 147 — 148° ; β -methyl-*n*-nonoic acid-hexacholeic acid, m.p. 170.5° ; α -ethyl-*n*-decoic acid-tetracholeic acid, m.p. 176° ; α -methyl-*n*-undecic acid-tetracholeic acid, m.p. 179° ; α -ethyl-*n*-hexadecic acid-octacholeic acid, m.p. 178 — 179° .

A. E. O.

Organic reactions with boron fluoride. VII. Rearrangement of isopropyl salicylate and condensation of propylene with salicylic acid. W. J. CROXALL, F. J. SOWA, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, 56, 2054—2056).—Slow passage of C_3H_6 (1.25 mols.) into $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ and BF_3 in heptane and fractionation of the resulting esters gives $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Pr}^\beta$ (I), b.p. 120 — $122^\circ/18$ mm., Pr^β

3-isopropylsalicylate, b.p. 147 — $149^\circ/18$ mm. [the free acid, m.p. 72° , heated to 200° affords $o\text{-C}_6\text{H}_4\text{Pr}^\beta\cdot\text{OH}$ (II)], and Pr^β 3:5-diisopropylsalicylate (III), b.p. 163 — $165^\circ/18$ mm. (free acid, m.p. 115.2° , decarboxylated to 2:4- $\text{C}_6\text{H}_3\text{Pr}^\beta_2\cdot\text{OH}$); the following reactions occur: $o\text{-OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} + \text{C}_3\text{H}_8 \longrightarrow$



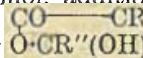
$\text{OH}\cdot\text{C}_6\text{H}_3\text{Pr}^\beta_2\cdot\text{CO}_2\text{Pr}^\beta \longrightarrow \text{OH}\cdot\text{C}_6\text{H}_3\text{Pr}^\beta_2\cdot\text{CO}_2\text{H} \longrightarrow \text{OH}\cdot\text{C}_6\text{H}_2\text{Pr}^\beta_2\cdot\text{CO}_2\text{Pr}^\beta$. (III) is obtained in almost quant. yield when the reaction is allowed to go to completion. (I) heated with BF_3 gives 3-isopropylsalicylic acid (not isolated) and a little of the 5-derivative; thermal decomp. of the mixture of acids affords (II) (and a little $p\text{-C}_6\text{H}_4\text{Pr}^\beta\cdot\text{OH}$) H. B.

Reactions of γ -ketonic acids. IV. Ketonic esters. E. P. KOHLER and W. D. PETERSON (J. Amer. Chem. Soc., 1934, 56, 2192—2197).—Bromination of β -*p*-chlorobenzoyl- α -phenylpropionic [γ -keto- α -phenyl- γ -*p*-chlorophenylbutyric] acid gives a mixture [separable as previously described (this vol., 1217) for the Cl-free analogue] of β -*Br*-derivatives, m.p. 183° (I) and 216° (II) (cf. A., 1926, 1140), esterified ($\text{MeOH}\cdot\text{H}_2\text{SO}_4$ or $\text{Et}_2\text{O}\cdot\text{CH}_2\text{N}_2$) to *Me* esters, m.p. 145° and 133° , respectively. These are converted by $\text{MeOH}\cdot\text{NaOAc}$ or $-\text{C}_5\text{H}_5\text{N}$ into mixtures (proportions varying with conditions) of *cis*- (III), m.p. 93° , and *trans*- (IV), m.p. 109° , -*Me* β -*p*-chlorobenzoyl- α -phenylacrylates. (III) and (IV) are reduced (catalytically) at the same rate, give the same dibromide, m.p. 136° [converted by aq. KI into (III)], and with $\text{MeOH}\cdot\text{NH}_2\text{OH}\cdot\text{AcOH}$ afford 6-keto-5-phenyl-3-*p*-chlorophenyl-1:2-oxazine (V) (*loc. cit.*). (III) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ in $\text{C}_5\text{H}_5\text{N}$ also give (V); (IV) similarly affords *Me* γ -oximino- α -phenyl- γ -*p*-chlorophenylcrotonate, m.p. 130° (VI) (main product) and 105° , which are probably *syn* and *anti* forms [both are hydrolysed to the same acid, m.p. about 220° (decomp.), which with $\text{MeOH}\cdot\text{H}_2\text{SO}_4$ gives (VI)]. Addition of MgMeI to (III) in cold $\text{Et}_2\text{O}\cdot\text{C}_6\text{H}_6$, and decomp. of the Mg complex with cold acid in Et_2O gives *Me* γ -hydroxy- α -phenyl- γ -*p*-chlorophenyl- Δ^a -pentenoate, m.p. 107° [oxidised (KMnO_4 , COMe_2) to BzCO_2Me (VII) and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COMe}$ (VIII)], and α -phenyl- γ -*p*-chlorophenyl- γ -methylcrotonolactone (IX), m.p. 94° [oxidised (KMnO_4 , COMe_2) to $\alpha\beta$ -dihydroxy- α -phenyl- γ -*p*-chlorophenyl- γ -valerolactone, m.p. 182° , and thence to (VII) and (VIII)]. Reduction of (IX) affords α -phenyl- γ -*p*-chlorophenyl- γ -valerolactone, m.p. 105° , also prepared (together with an isomeride, m.p. 120°) from *Me* β -*p*-chlorobenzoyl- α -phenylpropionate and MgMeI with subsequent hydrolysis ($\text{MeOH}\cdot\text{NaOH}$). MgMeI and (IV) give *Me* *trans*- γ -hydroxy- α -phenyl- γ -*p*-chlorophenyl- Δ^a -pentenoate, m.p. 105° [free acid (X), m.p. 134°], also oxidised to (VII) and (VIII). (III) and (IV) are both hydrolysed ($\text{MeOH}\cdot\text{NaOH}$ or $\text{AcOH}\cdot\text{HCl}$) to *cis*- γ -*p*-chlorobenzoyl- α -phenylacrylic acid (XI), two forms, m.p. 132° and 102° (re-solidifying with m.p. 132°), which with MgMeI affords (IX). *trans*- γ -*p*-Chlorobenzoyl- α -phenylacrylic acid (XII), m.p. 135° [which with MgMeI gives (X)], is obtained together with (XIII) (below) from β -*p*-chlorobenzoyl- α -phenyl- β -propiolactone [from (II)] and NaOAc in $\text{AcOH}\cdot\text{Ac}_2\text{O}$; (XII) is also formed similarly in small

yield from the isomeric lactone from (I). (XI) and $\text{AcOH}-\text{Ac}_2\text{O}$ give γ -acetoxy- α -phenyl- γ -p-chlorophenylcrotonolactone (XIII), m.p. 110° , also formed (at a much slower rate) from (XII). (XI) and $\text{MeOH}-\text{H}_2\text{SO}_4$ afford (III) (about 40%) and γ -methoxy- α -phenyl- γ -p-chlorophenylcrotonolactone, m.p. 73° (about 60%) [also obtained from (XIII) and MeOH]. The changes occurring in the production of mixtures of (III) and (IV) from (I) and (II) are discussed.

H. B.

Reactions of γ -ketonic acids. C. F. H. ALLEN, J. B. NORMINGTON, and C. V. WILSON (Canad. J. Res., 1934, 11, 382—394).—Reaction with RMgX has been employed to differentiate between the open-chain (1 mol. addition for each atom of active H) and lactol



(I) (2 mols. addition for each atom of active H) structures of various substituted γ -keto- α -diaryl- β -arylmethyl- Δ^a -butenoic acids, prepared by methods previously described (A., 1932, 1031; 1933, 610). The following acids, $\text{R}''\text{CO}\cdot\text{C}(\text{CH}_2\text{R}')\cdot\text{CR}\cdot\text{CO}_2\text{H}$, or lactols [as (I)] are new: $\text{R}=\text{R}'=\text{Ph}$ and $\text{R}'=\text{mesityl}$, m.p. 250° (decomp.), $p\text{-C}_6\text{H}_4\text{Cl}$, m.p. 144° (acid chloride, m.p. 150° ; reduced by $\text{Zn}-80\%$ AcOH to γ -keto- α -phenyl- γ -p-chlorophenyl- β -benzylbutyric acid, m.p. $173\text{--}174^\circ$), $p\text{-tolyl}$, m.p. 133° , and $p\text{-C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 240° (*Me* ester, m.p. 137°); $\text{R}=\text{Ph}$, $\text{R}'=\text{o-C}_6\text{H}_4\text{Cl}$, and $\text{R}''=\text{p-C}_6\text{H}_4\text{Cl}$, m.p. 147° ; $\text{R}=\text{piperonyl}$, $\text{R}'=\text{Ph}$, $\text{R}''=\text{p-C}_6\text{H}_4\text{Cl}$, m.p. 153° , and Ph , m.p. 138° ; $\text{R}=\text{anisyl}$, $\text{R}'=\text{Ph}$, $\text{R}''=\text{o-C}_6\text{H}_4\cdot\text{OMe}$, m.p. 126° , $\text{o-C}_6\text{H}_4\text{Cl}$, m.p. 154° , and $\alpha\text{-furyl}$, m.p. 121° . It is concluded that the differences are due to *cis-trans* isomerism, the *cis*-acid giving rise to esters of both open-chain and cyclic forms, the latter being impossible with the *trans*-acid. Confirmatory evidence of structure accrues from the action of AcCl , which gives chlorides with the lactols but fails to react with the open-chain acids. The same tests are applied to a series of γ -keto- α -diarylbutyric acids, $\text{R}'\text{CO}\cdot\text{CH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}$, some of which give evidence of cyclic forms, and of which the following are new: $\text{R}=\text{Ph}$, $\text{R}'=\text{p-C}_6\text{H}_4\text{F}$, m.p. 161° (nitrile, m.p. 102° ; *Me* ester, m.p. 101°), $p\text{-C}_6\text{H}_4\text{Br}$, m.p. 160° , $p\text{-tolyl}$, m.p. 152° (nitrile, m.p. 80° ; *Me* ester, m.p. 112°), *mesityl*, m.p. 172° (nitrile, m.p. $77\text{--}78^\circ$; *Me* ester, m.p. $60\text{--}61^\circ$); $\text{R}=\text{piperonyl}$, $\text{R}'=\text{p-C}_6\text{H}_4\text{Cl}$, m.p. 190° (nitrile, m.p. 129° ; *Me* ester, m.p. 109°); the *Me* esters when $\text{R}=\text{Ph}$, $\text{R}'=\text{p-C}_6\text{H}_4\text{Ph}$, m.p. 157° (nitrile, m.p. 176°), $p\text{-C}_6\text{H}_4\cdot\text{NO}_2$, m.p. 104° (nitrile, m.p. 155°), $p\text{-C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, m.p. 110° (nitrile of $\text{R}'=\text{p-C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, m.p. 239°), and 4-chloro-*m-tolyl*, m.p. 80° (nitrile, m.p. $76\text{--}77^\circ$); and when $\text{R}=\text{piperonyl}$, $\text{R}'=\text{Ph}$, m.p. 121° . With AcCl dimerides of γ -keto- α -phenyl- γ -p-chlorophenyl-, m.p. 235° , - γ -phenyl-, m.p. 295° , - γ -p-fluorophenyl-, m.p. 247° , and - γ -p-tolyl-, m.p. 270° (all decomp.), -butyric acid, are obtained. No evidence of cyclic forms of γ -keto- γ -p-chlorophenyl- (II), m.p. 131° (*Me* ester, m.p. 63°), and - γ -mesityl- $+0.5\text{H}_2\text{O}$ (III), m.p. 107° , -butyric acid, and of other derivatives of the type $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, was obtained, and with AcCl all [except (III)], which affords the *enol acetate*, m.p. $288\text{--}290^\circ$] give unsaturated lactones, (II) affording γ -p-chlorophenylcrotonolactone. With AcCl cyclohexanone gives cyclohexenyl acetate. Mechanisms are

discussed and it is considered probable that lactone formation in ketonic acids occurs by dehydration of an enolic form, and hence the formation of angelica lactones from lactic acid (IV) is not evidence for a cyclic structure, (IV) being almost certainly open-chain. The following new compounds are also prepared: 4-chloro-*m-tolyl*, b.p. $195\text{--}200^\circ/6\text{ mm.}$ (dibromide, m.p. 117°), 4-isopropyl-*o-tolyl*, b.p. $205\text{--}210^\circ/12\text{ mm.}$ (dibromide, m.p. $140\text{--}141^\circ$), mesityl (dibromide, m.p. 131°) and *p*-fluorophenyl, m.p. $76\text{--}77^\circ$, styryl ketone, and piperonylidene-*p*-chloroacetophenone, m.p. 128° ; *p*-chlorobenzoyl-3:4-methylenedioxybenzoyl-methane, m.p. 151° [*Cu* derivative, m.p. $290\text{--}292^\circ$ (decomp.)], benzoylmesitylmethane, m.p. 84° [*Cu* derivative, m.p. 185° (decomp.)], α -bromobenzylidene-2:4:6-trimethylacetophenone, m.p. 73° , 3-*p*-chlorobenzoyl-5-piperonylisooxazole, m.p. 180° , and 5-phenyl-3-mesitylisooxazole, m.p. 76° . All m.p. are corr.

J. W. B.

Phenolic acids. V. Reaction of 3:5-dinitro- β -resorcylic acid with sugars. P. P. T. SAH and K. C. MENG (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 343—346).—3:5-Dinitro- β -resorcylic acid gives a red coloration with *d*-glucose, maltose, and lactose in alkaline solution. There is no quant. relationship between the depth of colour and the concn. of the sugar.

H. N. R.

Hexahydroterephthalic acids. R. MALACHOWSKI and J. JANKIEWICZÓWNA (Ber., 1934, 67, [B], 1783—1788).— $p\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ is reduced by Na-Hg to the H_4 -stage, esterified, and the ester is hydrogenated (PtO_2) and then hydrolysed with 10% HCl . The mixture of acids [*cis*- (I) : *trans*- (II) -hexahydroterephthalic acid=5:1] is purified through the *Ca* salts giving (I), m.p. $170\text{--}171^\circ$ [*Me* ester, m.p. 14° , *Ca* (+2.5 H_2O) salt, less sol. in hot than in cold H_2O], and (II), m.p. $312\text{--}313^\circ$ [*Ca* salt (+2.5 H_2O)]. The acid, m.p. $166\text{--}167^\circ$, contains 94% of (I) and 6% of (II) and cannot be separated into its components by crystallisation from H_2O ; it differs in cryst. form from homogeneous (I). Treatment of (I) with Ac_2O at 100° affords the polymeric *cis*-anhydride (III) (?) $\text{OAc}\cdot[\text{C}_8\text{H}_{10}\text{O}_3]_n\cdot\text{Ac}$, m.p. (indef.) $105\text{--}110^\circ$, transformed at 230° into the polymeric *trans*-anhydride (IV), m.p. (indef.) $262\text{--}270^\circ$. Distillation of (III) or (IV) under diminished pressure and with very rapid cooling of the vapour gives Ac_2O and the monomeric anhydride, m.p. $150\text{--}160^\circ$, which is very unstable and polymerises when melted or warmed in C_6H_6 in presence of a trace of NaOH . Hydrolysis by H_2O or 10% HCl leads to (I).

H. W.

Preparation of phthalimido-compounds. R. WEISZ and K. LANYI (Magyar chem. Fol., 1933, 39, 153—155; Chem. Zentr., 1934, i, 2746).—Phthalimido-compounds are prepared by boiling phthalimide with EtONa in EtOH for 2 hr., and then adding the appropriate halogen derivative. Alkyl halides have no action. Aryl α -bromoalkyl ketones, $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et}$, and $\text{CHMeBr}\cdot\text{CO}_2\text{Et}$ react smoothly, but α -bromo-fatty esters containing side-chains are ineffective. *Ca* and *Mg* phthalimides give poorer yields than *Na*. Benzylphthalimide, m.p. 116° , *Ph* α -phthalimidoethyl ketone, m.p. $87\text{--}88^\circ$, *Et* phthalimidoacetate, m.p. $112\text{--}113^\circ$,

and *Et* α -phthalimidopropionate, m.p. 61—63°, are described. R. N. C.

Stereochemistry of diphenyls. XXXVII. Resolution of substituted diphenylbenzenes. A. E. KNAUF, P. R. SHILDNECK, and R. ADAMS. XXXVIII. Resolution of 2:2'-dibromodiphenyl-4:4'-dicarboxylic acid. N. E. SEARLE and R. ADAMS (J. Amer. Chem. Soc., 1934, 56, 2109—2111, 2112—2114).—XXXVII. *cis*-3:6-Dibromo-2:5-di-(3-bromo-2:4:6-trimethylphenyl)quinol (A., 1931, 348, 1049) and *l*-menthoxyacetyl chloride in C_6H_6 - C_6H_5N give a mixture (separable by fractional crystallisation from $COMe_2$) of the *dimethoxyacetates*, m.p. 141—143° and 155°, of *d*- (I), m.p. 289—290°, $[\alpha]_D^{25} +13.4^\circ$ in $EtOAc$, and *l*- (II), m.p. 290—291°, $[\alpha]_D^{25} -16.2^\circ$ in $EtOAc$, -3:6-dibromo-2:5-di-(3-bromo-2:4:6-trimethylphenyl)quinol, respectively. (I) and (II) are obtained from the esters by hydrolysis (aq. $EtOH$ - $NaOH$ in H_2), subsequent treatment with $SnCl_2$ - HCl in aq. $COMe_2$, and final crystallisation (C_6H_6). (I) and (II) are oxidised (*p*-benzoquinone in $EtOH$) to *l*-, m.p. 283—284°, $[\alpha]_D^{25} -26.5^\circ$ in $CHCl_3$, and *d*-, m.p. 284—285°, $[\alpha]_D^{25} +36.74^\circ$ in $CHCl_3$, -3:6-dibromo-2:5-di-(3-bromo-2:4:6-trimethylphenyl)-*p*-benzoquinone, respectively, which are reduced ($SnCl_2$, C_6H_5N) to (I) and (II), respectively. The *dimethoxyacetate* of *trans*-3:6-dibromo-2:5-di-(3-bromo-2:4:6-trimethylphenyl)quinol exists in 2 cryst. modifications, m.p. 167—168° (from light petroleum) and 145—146°, re-solidifying with m.p. 167—168° (both forms are obtained from $COMe_2$ or $EtOH$); hydrolysis of either form gives an inactive product. *cis*- and *trans*-2:5-Dibromo-3:6-di-*m*-4-xylylquinol (A., 1930, 1588) (*dimethoxyacetates*, m.p. 120—124° and 154°, respectively) could not be resolved.

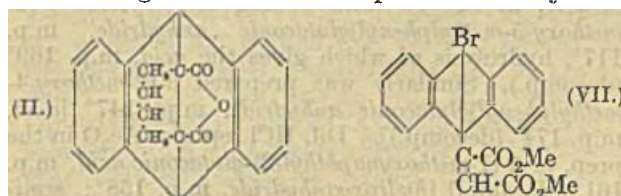
XXXVIII. Tetrazotised *Et* 2:2'-diaminodiphenyl-4:4'-dicarboxylate and $Hg(NO_3)_2$ in aq. HBr give the tetrazonium di(mercuribromide) (III). Hydrolysis (aq. $EtOH$ - KOH) of the product obtained by thermal decomp. [method essentially that of Schwechten (A., 1932, 1244)] of dry (III) in presence of dry KBr affords 2:2'-dibromodiphenyl-4:4'-dicarboxylic acid, m.p. 310—312°, which is resolved by brucine into *d*- (IV), m.p. 311—313°, $[\alpha]_D^{25}$ (in 7:3-dioxan- $MeOH$) +17.4° (max. by extrapolation) $\rightarrow 0^\circ$ [brucine salt, m.p. 210—220°, $[\alpha]_D^{25}$ (in $CHCl_3$) +27.2° (max.) $\rightarrow +1.9^\circ$, and *l*-forms (V), m.p. 311—313°, $[\alpha]_D^{25}$ (in dioxan- $MeOH$) -17.8° (max.) $\rightarrow 0^\circ$ [dibrucine salt, m.p. 197—207°, $[\alpha]_D^{25}$ (in $CHCl_3$) -15.7° (max.) $\rightarrow 0^\circ$]. (IV) and (V), obtained by decomp. of the salts with $EtOH$ -conc. HCl at -65°, racemise more readily than the corresponding I_2 -acids (A., 1933, 608). 2:2'-Dibromo-4:4'-diaminodiphenyl (*di-d*-bromocamphorsulphonate, m.p. 297—300°, and *d*-camphorsulphonate, m.p. 218—219°, which do not exhibit mutarotation at 0° or 25°, prepared from (*m*- C_6H_4Br) $_2$ (in Et_2O) and conc. HCl , could not be resolved. H. B.

Solubility relationships amongst optically isomeric salts. IV. Salts of 6:6'-dinitrodiphenic acid, a new type of resolving agent. A. W. INGERSOLL and J. R. LITTLE (J. Amer. Chem. Soc., 1934, 56, 2123—2126).—*dl*-6:6'-Dinitrodiphenic acid (I) (improved prep.; cf. Kenner and Stubbings, J.C.S., 1921, 119, 593) [*d*-, m.p. 199° (corr.), and *dl*-,

m.p. 206—208° (corr.), - α -phenylethylamine and *d*- α -tolylethylamine, m.p. 211.5—213° (corr.), salts] is resolved by *d*- α -phenylethylamine into the *d*-acid (II), m.p. 231—231.5° (corr.), $[\alpha]_D^{25} +127^\circ$ in $MeOH$ [*dl*-, m.p. 207—208°, and *d*- (+ $COMe_2$), m.p. ($COMe_2$ -free) 217—219° (corr.), - α -phenylethylamine, *dl*- α -tolylethylamine, m.p. 197.5—198° (corr.), and *dl*- α -anisylethylamine salts], and impure *l*-acid (III), m.p. 228—229°, $[\alpha]_D^{25} -111^\circ$ in $MeOH$ [*d*- α -phenylethylamine salt, m.p. 204—205° (corr.)]. (III), purified through the *l*-phenylethylamine salt, is obtained with $[\alpha]_D^{25} -126^\circ$ in $MeOH$. (I) could not be resolved by *d*- α -tolylethylamine. *dl*- α -Phenylethylamine (but not the *p*-tolyl- or anisyl-ethylamines) is resolved by (II); *dl*- α -fenchylamine is similarly partly resolved. Solubility data (cf. A., 1932, 263) for the above salts are given. H. B.

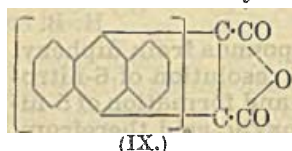
Formation of cyclic compounds from diphenyl derivatives. III. Optical resolution of 6-nitro-6'-acetamidodiphenic acid and formation of 5-nitrophenanthridone-4-carboxylic acid therefrom. S. SAKO (Bull. Chem. Soc. Japan, 1934, 9, 393—402; cf. this vol., 520).—6:6'-Dinitro-2:2'-dimethyldiphenyl is reduced by Na_2S in $EtOH$ at 50° to 6-nitro-6'-amino-2:2'-dimethyldiphenyl (I), m.p. 124—125° (lit. 122—123°), distils in vac., or by an excess of Na_2S at 100° mainly to 4:5-dimethylphenazone oxide, m.p. 153°. The *Ac* derivative, m.p. +0.5 C_6H_6 , 92°, and anhyd., 103—104°, of (I) is oxidised (aq. $KMnO_4$; $MgSO_4$; 100°) to *dl*-6-nitro-6'-acetamidodiphenic acid, decomp. 229° (sinters at 130°), giving *strychnine H* salts, of the *l*-, m.p. 273° (decomp.), $[\alpha]_D^{25} -73^\circ$ in $MeOH$, and *d*-, m.p. + $MeOH$, 175° (decomp. 273°), and, anhyd., decomp. 273°, $[\alpha]_D^{25} +36.5^\circ$ in $MeOH$, -acids, and the *distrychnine* salt, +2 $MeOH$, m.p. 174°, decomp. 207°, $[\alpha]_D^{25} +11.9^\circ$ in $MeOH$, of the *d*-acid, whence were obtained the *d*- and *l*-acids, $[\alpha]_D^{25} \pm 122.1^\circ$ in H_2O , m.p. (impure) 93° (decomp.). The NH_4 salt of the *d*-acid is stable to hot H_2O , but the acid is racemised by cold, conc. HCl . The active acid with hot H_2SO_4 slowly gives inactive 5-nitrophenanthridone-4-carboxylic acid (II), m.p. > 330°. This is not rigid proof of the planar configuration of (II), which is, however, probable on other grounds. R. S. C.

Syntheses in the hydroaromatic series. XXII. Anthracene- C_4O_3 [acetylenedicarboxylic anhydride] adduct, its use in diene syntheses, and synthesis of phthalic and dihydrophthalic acids. O. DIELS and W. FRIEDRICHSEN (Annalen, 1934, 513, 145—155).—Anthracene-acetylenedicarboxylic anhydride (I) (A., 1931, 848) and butadiene in C_6H_6 at 100° (sealed tube) give a 1:1-adduct (II), m.p. 212°, which undergoes thermal decomp. to 9:10-dihydro-



anthracene (III) and *o*- $C_6H_4(CO)_2O$. (I) and dimethylbutadiene (IV) (mixture of α - and γ -derivatives) afford a similar adduct, m.p. 197°, which when heated under atm. pressure decomposes to anthracene

(V), (III), and (after hydrolysis) a *dimethylphthalic acid*, m.p. 194° (anhydride, m.p. 124°); thermal decomp. in a vac. gives (V) and a *dimethyldihydrophthalic acid*, m.p. 145° (anhydride, m.p. 99°). An isomeric *dimethyldihydrophthalic acid*, m.p. 184° (anhydride, m.p. 100°), is prepared by hydrolysis (EtOH-KOH) of the product from equimol. amounts of (IV) and Me acetylenedicarboxylate (VI). Adducts, $C_5H_{22}O_3$, m.p. 199—200°, and $C_{23}H_{16}O_3$, m.p. 279—280°, are prepared from (I) and $\alpha\gamma$ -trimethylbutadiene and cyclopentadiene, respectively. 9-Bromoanthracene and (VI) give the *Me*₂ ester (VII), m.p. 178° {free acid, m.p. 215° [anhydride, m.p. 240°, which forms an adduct, $C_{24}H_{19}O_3Br$, m.p. 192°, with (IV)]}. 9:10-Dibromoanthracene (VIII) does not react with (VI), but with maleic anhydride gives the 9:10-endo-maleic



(IX.)

anhydride - 9:10-dibromoanthracene, m.p. 263° [converted by short heating with quinoline into (VIII)]. (I) heated in $PhNO_2$ or $PhOH$ gives CO , CO_2 , and the compound (IX), m.p. 360°, which is stable towards KOH , conc. HNO_3 , Ac_2O , NH_2Ph , and quinoline. H. B.

b-Dinitro- α -truxillic acid and the di- and tetranitro- γ -truxillic acids. F. SCHENCK (Ber., 1934, 67, [B], 1690—1695).—Treatment of γ -truxillic anhydride (I) with Ac_2O and HNO_3 (*d* 1.4) at 100° affords *pp'*-dinitro- γ -truxillic acid (II), decomp. 308—310° (*Me*₂, m.p. 196.5—197°, and *Et*₂, m.p. 147—147.5°, esters; *Me H* ester, m.p. 214—215°), oxidised to *p*- NO_2 - C_6H_4 - CO_2H in 53% yield, α -dinitro- γ -truxillic acid, decomp. 265° (corresponding anhydride, decomp. 253°), transformed by $NaOH$ - $MeOH$ into *Me H* α -dinitro- γ -truxillate, m.p. 179—180°, and thence by $MeOH$ - H_2SO_4 into *Me*₂ α -dinitro- γ -truxillate, m.p. 111—112° (from $MeOH$ - H_2O) or m.p. 136—137° (after desiccation over P_2O_5), and *b*-dinitro- γ -truxillic acid, decomp. 265° (*Me*₂ ester, m.p. about 102—104°). (III) is not identical with *b*-dinitro- α -truxillic acid, which is isomerised by boiling Ac_2O to *pp'*-dinitro- γ -truxillic anhydride, m.p. about 232°. Nitration of (I) with fuming HNO_3 and conc. H_2SO_4 under defined conditions leads to 2:4:2':4'-tetranitro- γ -truxillic acid, decomp. 238° (*Ba* salt), which is oxidised to 2:4- $C_6H_3(NO_2)_2$ - CO_2H ; the anhydride, *Me*₂, m.p. 188—189°, *Et*₂, m.p. 180—181°, and *Et H*, m.p. 207—208°, esters are described. H. W.

β -Arylglutaconic acids. I. Synthesis. G. R. GOGTE (Proc. Indian Acad. Sci., 1934, 1, (A), 48—59).—6-Methylcoumarin-4-acetic acid refluxed with 20% aq. $NaOH$ and subsequently treated with Me_2SO_4 at 80—90° and boiling Ac_2O yields β -(2-methoxy-5-methylphenyl)glutaconic anhydride, m.p. 117°, hydrolysis of which gives the acid, m.p. 169° (decomp.). Similarly was prepared β -(2-methoxy-4-methylphenyl)glutaconic anhydride, m.p. 147° [acid, m.p. 174° (decomp.)]. Dil. HCl replaces Ac_2O in the prep. of β -(1-methoxynaphthyl-2)-glutaconic acid, m.p. 161° (decomp.) [hydroxyanhydride, m.p. 158°; semianilide, m.p. 180° (decomp.); hydroxyanil, m.p. 199—200°]. Condensation of α -naphthyl Me ether with acetonedicarboxylic acid (cf. A., 1931, 1055) affords β -(1-methoxynaphthyl-4)-glutaconic acid, decomp. 199°

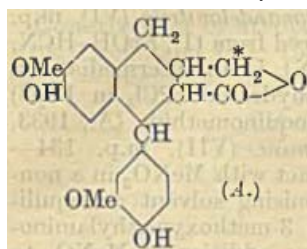
[hydroxyanhydride, m.p. 156°; semianilide, m.p. 176—177° (decomp.); hydroxyanil, m.p. 223—224°]. β -Naphthacoumarin-4-acetic acid on treatment with aq. $NaOH$, Me_2SO_4 , etc. yields two β -(2-methoxynaphthyl-3)-glutaconic acids, (a), m.p. 186° (decomp.) and (b), m.p. 162° (decomp.). Both give the same hydroxyanil, m.p. 196—197°, and, on heating, hydroxyanhydride (I), m.p. 135° (from which the semianilide, m.p. 172°, is obtained), and an isomeride of the latter, m.p. 172°; (b) with Ac_2O readily yields (I) [which on hydration readily reverts to (b)], whilst (a) is unchanged. Hence (a) is the *trans* and (b) the *cis* form of the acid. F. O. H.

Constitution of pinastric acid. M. ASANO and Y. KAMEDA (Ber., 1934, 67, [B], 1522—1526; cf. Koller *et al.*, A., 1933, 508).—*p*- OMe - C_6H_4 - CH_2 - CN , $Et_2C_2O_4$, and $NaOEt$ afford *Et* cyano-*p*-anisylpyruvate, m.p. 93—95°, converted by CH_2Ph - CN and $NaOEt$ into *p*-methoxydiphenylketipinonitrile, which is hydrolysed to *p*-methoxypulvinic anhydride (I). Treatment of (I) with KOH - $MeOH$ leads to the compound (II) *p*- OMe - C_6H_4 - $C(C(OH)(O))C(Ph)CO_2Me$.

identical with natural pinastric acid. Reduction of (II) with Zn and $AcOH$ gives *Me* γ -keto- α -phenyl- δ -*p*-anisyl-*n*-valerate (semicarbazone, m.p. 142—144°). CH_2Ph - CO_2Na , *p*- OMe - C_6H_4 - CH : CH - CHO , and Ac_2O at 150—155° give α -phenyl- δ -*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadienoic acid (III), m.p. 192—193° (*Na* and *K* salts), and α -phenyl- Δ -*p*-anisyl- $\Delta^{\alpha\gamma}$ -butadiene, m.p. 158—159°. (III) is transformed by reduction in boiling $AcOH$ - $EtOH$ with Na - Hg followed by bromination and treatment of the product with $NaOAc$ at 100° into α -phenyl- γ -*p*-methoxybenzylcrotonolactone, m.p. 115.5—116.5°, converted by KOH - $MeOH$ into γ -keto- α -phenyl- δ -*p*-anisylvaleric (*p*-methoxyhydrocornicularic) acid, m.p. 103—104° [semicarbazone, m.p. 191° (decomp.)]; *Me* ester, m.p. 56—57°, and its semicarbazone, m.p. 144—145°. Condensation of $CHPh$: CH - CHO with *p*- OMe - C_6H_4 - CH_2 - CO_2Na in presence of Ac_2O gives δ -phenyl- α -*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadienoic acid, m.p. 209—210°, whence α -*p*-anisyl- γ -benzylcrotonolactone, m.p. 102—103°, γ -keto- δ -phenyl- α -*p*-anisylvaleric (*p'*-methoxyhydrocornicularic) acid, m.p. 146—147° [semicarbazone, m.p. 146—147° (decomp.)]; *Me* ester, m.p. 63—64°, and its semicarbazone, m.p. 173—174°. H. W.

Structure of "sulphite-liquor lactone." H. ERDTMAN (Annalen, 1934, 513, 229—239).—The α -dimethyl-lactone (I), $C_{22}H_{24}O_6$ (*Br*₂-derivative, m.p. 183—184°), of Holmberg (A., 1921, i, 850) is oxidised ($KMnO_4$, aq. $COMe_2$) to 4:5:3':4'-tetramethoxy-2-benzoylbenzoic acid (II) (Haworth and Mavin, A., 1931, 954), an alkali-insol. substance, m.p. 166—167° [2:4-dinitrophenylhydrazones (?), m.p. 250—252° (decomp.)], and resinous materials. Oxidation (alkaline $NaOBr$) of (I) affords (II) [the diveratroylacetic acid of Holmberg (B., 1928, 185)], the so-called 3:4-diveratrolylfuran (*loc. cit.*), and a dibasic acid (III), $C_{22}H_{24}O_8$ (Holmberg's "dimethoxytruxinic acid"), m.p. 192—193°, [α]_D²⁰ +39.3° in $COMe_2$. Oxidation ($KMnO_4$, $COMe_2$) of (III) gives the same products as (I). (I) could not be reduced (H_2 , PtO_2 , $EtOH$ - $AcOH$). (II) is converted by conc. H_2SO_4 and fuming

HNO₃ into 2:3:6:7-tetramethoxyanthraquinone and trinitroveratrole, respectively. (III) gives an



anhydride, m.p. 204—205° (rapid heating); its *Me*₂ ester, m.p. 148—149°, is dehydrogenated

[Pb(OAc)₄ in AcOH] to *Me* 6:7-dimethoxy-1-3':4'-dimethoxyphenyl-naphthalene-2:3-dicarboxylate, m.p. 165—167°.

(III) is (probably) 6:7-dimethoxy-1-3':4'-dimethoxyphenyl-1:2:3:4-tetrahydronaphthalene-2:3-dicarboxylic acid. "Sulphite-liquor lactone" (Holmberg, A., 1921, i, 25, 849; *loc. cit.*) is probably *A* or *A* with CO and CH₂* interchanged; it does not occur as such in wood, but probably arises by cyclisation of a diarylbutene. H. B.

Imines. G. MIGNONAC (Ann. Chim., 1934, [xi], 2, 225—294).—Imines are products of hydrogenation of nitriles or oximes or of dehydrogenation (in presence of metals) of bases, but their isolation is often impossible owing to secondary reactions. One mol. of the imine, reacting as CH₂R·CH:NH, with a second mol., reacting as CHR:CH·NH₂ (imine-enamine tautomerism), forms NH₃ and substances, CH₂R·CH:N·CH:CHR, which either condense further with imine to yield, e.g., CHPh(N·CHPh)₂ (I), or may be further reduced to Schiff's bases (*A*) or sec.-amines. (*A*) may, however, also be formed (e.g., from aromatic aldimines) by hydrolysis of the imine and condensation of the resulting aldehyde with the amine formed by reduction of another portion of imine. Thus, addition of 1 mol. of H₂ to PhCN, *o*- or *p*-C₆H₄Me·CN in Et₂O in presence of Ni at room temp. gives the primary base, unchanged nitrile, a little aldehyde, and (*A*); PhCN gives also some (I). The following are incidentally described: *p*-toluylidene-*p*-methylbenzylamine, m.p. 84°, b.p. 156—157°/3 mm., and the corresponding *o*-*o*-compound, b.p. 170—171°/5 mm.; *benzylidenebenzylamine* (II), b.p. 142—143°/4 mm. Similarly, addition of 1 mol. of H₂ to CHPh·NOH in abs. EtOH in presence of Ni gives CH₂Ph·NH₂ (II), and a little PhCHO, whilst much PhCHO is formed in 50% EtOH; the PhCHO does not arise by hydrolysis of the oxime, since the catalyst is necessary for its formation. Reduction of the appropriate ketoximes led, however, to isolation of the imines themselves; thus are obtained *Ph Me ketimine hydrochloride*, cryst., hygroscopic, *Ph Et ketimine hydrochloride*, m.p. 145° (block) (*Ac* derivative of the imine, m.p. 126°) [with some of the Schiff base, CHPhEt·N:CPhEt, b.p. 170—171°/9 mm. (*hydrochloride*, m.p. 174°)], CPh₂·NH, and *Ph C₁₀H₇ ketimine*, m.p. 68—69°. *cyclohexanoneoxime* resembles the aldioximes in giving *cyclohexanone* (50—60%) and *cyclohexyliminocyclohexane*, b.p. 117—118°/9 mm. [*hydrochloride*, m.p. 180° (decomp.)].

Passage of CH₂Ph·CH₂·NH₂ (III) in N₂ over Ni at 190—230° gives H₂, NH₃, PhCN, and unchanged (III); if steam is added to the mixture, base, NH₃, and 10—15% of CH₂Ph·CHO are obtained; PrCHO (25—30%), PhCHO (40%), and *p*-C₆H₄Me·CHO (35%) are obtained similarly from the corresponding

amines; if anhyd. NH₃ is added to the mixture at 225°, there is more rapid evolution of H₂, and much CH₂Ph·CH:NH is isolated, together with unchanged (III) and CH₂Ph·CN. These results prove the existence of an equilibrium between (III), the nitrile, imine, and H₂ in presence of Ni. The imines were themselves isolated (20 and 70% yields, respectively) by passage of CHPhEt·NH₂ (at 240—250°) or CHPh₂·NH₂ (at 260°) in N₂ over Ni (no added NH₃); NH₂Pr gave only NH₃ and unidentified products. CH₂Ph·CH:NH·HCl, m.p. 180—183°, gives in air the *carbonate* (IV), m.p. 101—103°, of (III) (cf. lit.), and by dissolution in H₂O affords CH₂Ph·CN and (III). (IV) in air gives some CH₂Ph·CHO. CHPh·NH·HCl [best obtained from (I) and HCl in EtOH], m.p. 181—182°, with dry NH₃-Et₂O at room temp. or -40° give NH₄Cl and (I); the free imine could not be isolated (cf. lit.). The stability of ketimines varies greatly according to the nature of the ketone. Hydrogenation of (I) (Ni) in abs. EtOH at < 40° gives CH₂Ph·NH₂ (about 1 mol.) and (II) (about 1 mol.); the first products are, however, (II) and CHPh·NH, since in 98% EtOH the imine is partly hydrolysed and the resulting aldehyde condenses to re-form (I); this in turn is further reduced, so that the final product contains little amine and much (II). R. S. C.

Reactive methyl group in toluene derivatives. I. **Oxidation with selenium dioxide and cleavage of benzylpyridinium halides.** C. H. FISHER (J. Amer. Chem. Soc., 1934, 56, 2056—2057).—*p*-NO₂·C₆H₄·CHO is obtained in 56% yield when equimol. amounts of *p*-NO₂·C₆H₄·CH₂Br and SeO₂ in EtOH are heated at 140—150° (the EtOH is allowed to distil). CH₂PhCl (no solvent) heated with SeO₂ gives 49% of PhCHO and 3% of BzOH; CH₂Ph₂ (I) similarly affords 47% of CPh₂; CHPh₂ (II) furnishes 15% of CPh₃·OH; *p*-NO₂·C₆H₄Me (III) gives a little *p*-NO₂·C₆H₄·CO₂H (IV). (I), (II), (III), and 4:4'-dinitrodiphenylmethane are unaffected by SeO₂ in boiling EtOH. *p*-Nitrobenzylpyridinium chloride and bromide are converted by aq. NaOBr into (IV); reaction occurs very rapidly and probably proceeds through an intermediate Br-derivative. Benzylpyridinium chloride similarly gives resinous products.

H. B.

Oxidation of organic compounds as a means of investigating their constitution. II. C. CATTANEO (Gazzetta, 1934, 64, 509—517; cf. this vol., 653).—CH₂Ph·CHO and aq. H₂O₂ combine at room temp. to give the "*perhydrate*" 2CH₂Ph·CHO·H₂O₂, m.p. 69—70° (decomp.), which decomposes very slowly in presence of H₂O yielding HCO₂H, CH₂Ph·OH, and CH₂Ph·CHO by "*perhydrolysis*." At 50° the interaction of CH₂Ph·CHO and H₂O₂ yields CO₂, CO, and O₂, whilst at 95° H₂ and CH₄ are also formed, and CH₂Ph·CO₂H, BzOH, PhCHO, and HCO₂H are produced. CH₂Ph·CO₂H and aq. H₂O₂ at 95° yield CO₂, O₂, BzOH, PhCHO, and HCO₂H, and treatment of the solution with KMnO₄ yields a little BzCO₂H, indicating that OH·CHPh·CO₂H is formed by a process of α-oxidation.

R. K. C.

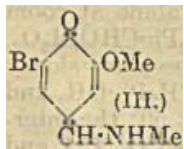
Compounds of bivalent carbon. IX. **Chlorodiphenylacetaldehyde diethylacetal and its adaptability to carbon monoxide acetal fission.** H.

SCHEIBLER and A. SCHMIDT (Ber., 1934, 67, [B], 1514—1518; cf. this vol., 1201).—Hydroxydiphenylacetaldehyde $\text{Et}_2\text{ acetal}$, b.p. $140^\circ/2\text{ mm.}$, obtained from MgPhBr and $(\text{OEt})_2\text{CH}\cdot\text{CO}_2\text{Et}$, is converted by SOCl_2 and $\text{C}_5\text{H}_5\text{N}$ into *chlorodiphenylacetaldehyde Et. acetal* (I), b.p. $136^\circ/1\text{ mm.}$, which with $\text{C}_5\text{H}_5\text{N}$ yields $\text{CHPh}_2\cdot\text{CO}_2\text{Et}$. Addition of (I) to MgPhBr in Et_2O leads to loss of PhCl and formation of a compound, $(\text{OEt})_2\text{CH}\cdot\text{CPh}_2\cdot\text{MgBr}$, which affords $\text{C}(\text{OEt})_2$ (recognised by conversion into HCO_2H) and CH_2Ph . (yield 35.7%). H. W.

Cannizzaro's reaction. G. LOCK (Monatsh., 1934, 64, 341—348; cf. A., 1933, 504).—Treatment of 3 : 4- $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CHO}$ with $\text{KOH}\cdot\text{MeOH}\cdot\text{MeI}$ gives a mixture of 3-hydroxy-4-methoxy-, (I), 4-hydroxy-3-methoxy-, and 3 : 4-dimethoxy-benzaldehyde. 2-Bromo-3-hydroxy-4-methoxybenzaldehyde (II) (simplified prep. from (I)) is very slowly transformed by 25% KOH at 100° into 2-bromo-3-hydroxy-4-methoxybenzyl alcohol (III), m.p. $151\text{—}152^\circ$ after softening, and 2-bromo-3-hydroxy-4-methoxybenzoic acid, m.p. $214\text{—}215^\circ$ (corr.). 2-Bromo-3 : 4-dimethoxybenzaldehyde, m.p. 86° , from (II), Me_2SO_4 , and KOH , similarly affords 2-bromo-3 : 4-dimethoxybenzyl alcohol (IV), m.p. 82.5° , and 2-bromo-3 : 4-dimethoxybenzoic acid, m.p. $203\text{—}204^\circ$ (corr.). (IV) is obtained also by methylation of (III). 2 : 6-Dibromo-3 : 4-dimethoxybenzaldehyde, m.p. 137.5° , is converted by 50% KOH at 100° into HCO_2H and 3 : 5-dibromoveratrole, m.p. 34° , transformed by HI ($d\ 1.7$) at 100° into pyrocatechol. H. W.

Vanillin synthesis. H. O. MOTTERN (J. Amer. Chem. Soc., 1934, 56, 2107—2108).— $o\text{-OMe}\cdot\text{C}_6\text{H}_4\cdot\text{OAc}$ and AlCl_3 at $< 5^\circ$ give 4-hydroxy-3-methoxyacetophenone, oxidised [PhNO_2 (1 mol.) and aq. NaOH (3 mols.) at 100°] to 4-hydroxy-3-methoxyphenylglyoxylic acid, which when heated with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NMe}_2$ at 170° affords vanillin. H. B.

Mechanism of condensation of aromatic hydroxyaldehydes with nitromethane in presence of organic bases. S. P. MAKAROV (J. pr. Chem., 1934, [ii], 141, 77—90).—5-Bromovanillin (I) and $\text{EtOH}\cdot\text{NH}_2\text{Me}$ (1.2 mols.) in cold CHCl_3 give 5-bromo- α -methylamino-4-hydroxy-3-methoxybenzyl alcohol (II), m.p. $93\text{—}95^\circ$ (loss of H_2O), re-solidifying with m.p. 211° , which is hydrolysed (acid; alkali) to (I), and when heated at $85\text{—}90^\circ$ in a vac. loses 1 mol. of H_2O and



affords 5-bromo-3-methoxymethylaminoquinomethide (III), m.p. 211° , decomp. $214\text{—}215^\circ$. (III) is also obtained from (I) and NH_2Me in warm EtOH . (II) does not react with cold MeNO_2 ; in the hot [whereby (III) is produced] the NH_2Me salt (IV), decomp. 150° , of 5-bromo- ω -nitro-4-hydroxy-3-methoxystyrene (V), m.p. $189\text{—}190^\circ$ (decomp.) (NH_4 , decomp. $145\text{—}150^\circ$, and *Ba* salts), results. It is probable that MeNO_2 first adds to (III) forming α -nitro- β -methylamino- β -5-bromo-4-hydroxy-3-methoxyphenylethane, which then isomerises to (IV) or gives (V) + NH_2Me . (V) is also formed from (I), MeNO_2 , and NH_2Me (trace) in EtOH at $70\text{—}75^\circ$. (II) and $\text{EtOH}\cdot\text{HCN}$ afford α -methylamino- α -(5-bromo-4-hydroxy-3-methoxy-

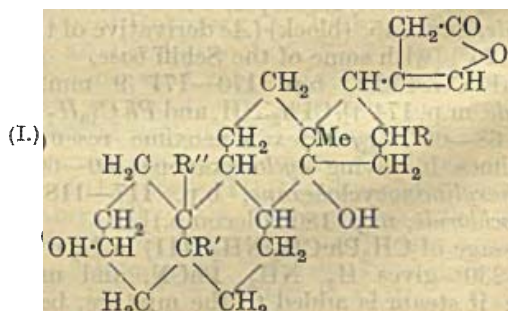
phenyl)acetonitrile, m.p. $93\text{—}94^\circ$ [formed by addition of HCN to (III)], hydrolysed (acid; alkali) to (I); 5-bromo-4-hydroxy-3-methoxymandelonitrile (VI), m.p. $106\text{—}107^\circ$ (decomp.) [prepared from (I), $\text{EtOH}\cdot\text{HCN}$, and a little K_2CO_3 or KCN], is an intermediate in the hydrolysis. (VI) is dehydrated (PCl_3 in Et_2O) to 5-bromo-3-methoxycyanoquinomethide (A., 1933, 716). *Vanillylidene*methylamine (VII), m.p. $134\text{—}135^\circ$ (decomp.), does not react with MeNO_2 in a non-ionising solvent. In an ionising solvent an equilibrium between (VII) and 3-methoxymethylaminoquinomethide (VIII) results; addition of MeNO_2 to (VIII) gives (after acidification) ω -nitro-4-hydroxy-3-methoxystyrene (*Ba* salt). (VII) and $\text{Et}_2\text{O}\cdot\text{HCN}$ afford α -methylamino- α -(4-hydroxy-3-methoxyphenyl)acetonitrile, m.p. 132° . H. B.

o -Aldehydicarboxylic acids. I. New general method of synthesising phthalonic acids. Synthesis of ψ -opianic and m -opianic acids. S. N. CHAKRAVARTI and M. SWAMINATHAN (J. Indian Chem. Soc., 1934, 11, 715—719).—Oxidation of homophthalic acids with SeO_2 in boiling xylene affords phthalonic acids in good yields. Thus 5 : 6- (I) and 4 : 6-dimethoxyhomophthalic acid afford, respectively, ψ - (II) and m -opianic acid (isolated as their NH_2Ph salts), and homophthalic acid gives phthalonic acid. When heated with 4 mols. of PCl_5 and POCl_3 at $140\text{—}150^\circ$ (I) affords 3 : 3 : 4 : 4-tetrachloro-5 : 6-dimethoxy-3 : 4-dihydroisocoumarin, m.p. 128° , hydrolysed by $\text{MeOH}\cdot\text{KOH}$ to (II). J. W. B.

Condensation of polyhydric alcohols, sugars, and hydroxy-acids with aldehydes.—See this vol., 1330.

X-Ray crystallographic measurements on derivatives of cardiac aglucones. J. D. BERNAL and D. CROWFOOT (Chem. and Ind., 1934, 953—956).—Measurements are recorded for *lactone* 135 (I), digitoxigenin (dianhydrodigitoxigenin) [II], digitoxigenin (III), gitoxigenin (IV), and digoxigenin (V). (I) is free from OH and is prepared by dehydration of digoxigenin and reduction of the product; it is therefore isomeric or identical with the lactone, $\text{C}_{23}\text{H}_{36}\text{O}_2$, of Windaus and Stein. The data obtained for (I) and (IV) exclude many of the chemically permissible configurations which might be given to the framework of the cardiac aglucones, whereas those obtained for (II), (III), and (V) supply no certain information. H. W.

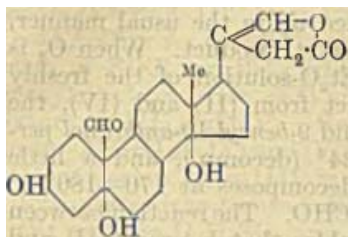
Constitution of vegetable heart poisons. R. TSCHESCHE (Angew. Chem., 1934, 47, 729—732).—A



lecture. Reasons are advanced for the constitutions I ($\text{R}=\text{H}$; $\text{R}'=\text{OH}$; $\text{R}''=\text{CHO}$) and ($\text{R}=\text{OH}$;

$R'=H$; $R''=Me$) for strophanthidin and gitoxigenin, respectively. H. W.

Constitution of strophanthidin. II. G. A. R. KON (Chem. and Ind., 1934, 956—958; cf. this vol., 1007).—Discussion of possible formulæ for stroph-



anthidin (I) in the light of the results of Bernal *et al* (see above) indicates the annexed structure as the most probable. The arguments are valid only if the formation of 3'-methylcyclopentenophenanthrene from (I) and uzarigenin can be regarded as proof of a sterol-like skeleton, and is not due to re-arrangement in the course of dehydrogenation; also that the latter does not involve the elimination or wandering of Me groups other than those attached to quaternary C atoms.

H. W.

Jute lignin. IV. Dioxymethylene group in lignin. P. B. SARKAR (J. Indian Chem. Soc., 1934, 11, 691—700).— CH_2O (I) has been obtained from five lignocelluloses (II) and from the lignins obtained from them, the $O\cdot CH_2\cdot O$ group being a common constituent of lignin (III). The best yield of (I) [determined by the dimedon method, which is the only one applicable to (III), and is shown to be trustworthy] is obtained by distillation with 28% H_2SO_4 , more conc. or weaker acids giving lower vals. The max. yield (2.78%) of (I) is obtained from (III) prepared by the action of 42% HCl at 20° for 24 hr., prolonged exposure of (II) to strong acids, higher temp., and subsequent acid boiling reducing the yield of (I), due to resin formation with phenolic substances. The reducing action of (III) is due to the two $o\text{-OH}$ groups set free during isolation. Allowing for this loss of (I) the true % is 3.61, whence the mol. wt. of (III) is 830. The presence of $O\cdot CH_2\cdot O$ in (III) is confirmed by treatment of a sample, from which (I) has been removed, with CH_2I_2 at 140—150°, the product again giving similar amounts of (I). Since (I) also gives an insol. compound with phloroglucinol the lower yield of furfuraldehyde in delignified jute [(I) having been thus removed] is explained. J. W. B.

Manufacture of cyclic α -cyanoketimines and cyclic α -cyanoketones.—See B., 1934, 953.

Ammono-ketone alcohols. I. Benzophenone-imine. G. E. P. SMITH, jun., and F. W. BERGSTROM (J. Amer. Chem. Soc., 1934, 56, 2095—2098).—The additive compound from PhCN and MgPhBr with liquid NH_3 in Et_2O gives (cf. Cornell, A., 1929, 173) $CPh_2\cdot NH$ (I) [hydrochloride, m.p. > 310°; picrate, m.p. 281—282° (slow decomp.)], which with $NHPh\cdot NH_2$ at 60—70° and NH_2Ph (excess allowed to distil) affords benzophenone-phenylhydrazine, m.p. 138—139°, and -anil, m.p. 112—113°, respectively. (I) and NH_2OH in liquid NH_3 give $CPh_2\cdot N\cdot OH$, whilst (I) and anhyd. HCN in $EtOH$ afford α -cyano-benzhydrylamine, m.p. 101—102°, which is converted by KNH_2 (1 mol.) in liquid NH_3 into (I) and KCN. N-Phenyl-N'-benzhydrylidene-carbamide, m.p. 160—162° (decomp.) [from (I) and PhNCO in C_6H_6], is

hydrolysed by repeated crystallisation from 95% $EtOH$ to $COPH_2$ and $NH_2\cdot CO\cdot NHPh$. (I) with $NaNH_2$ (1 mol.) and KNH_2 (2 mols.) in liquid NH_3 gives salts, $CPh_2\cdot NNa$ and $CPh_2\cdot (NHK)_2$, respectively, which could not be freed from NH_3 . Deep red solutions are obtained from (I) and Na or K in liquid NH_3 ; subsequent hydrolysis (H_2O) gives $COPH_2$, and $CHPh_2\cdot NH_2$ (II) [hydrochloride, m.p. 290—292° (decomp.)] (in about 50% yield, irrespective of the excess of Na used). (I) is not reduced by $MgPhBr$, probably owing to the insolubility of the resulting complex. (I) and $Mg+MgI_2$ in C_6H_6 give the complex, $(CPh_2\cdot NH)_2\cdot MgI_2$; when the reaction mixture is evaporated and then treated with liquid NH_3 , (II) and $CPh_2\cdot N\cdot CHPh_2$ are obtained. Reduction of (I) to an ammono-benzpinacol or -benzpinacolin has not been accomplished. H. B.

Side-chain chlorination of *pp'*-dimethylbenzophenone. II. 4:4'-Tetrachlorodimethylbenzophenone. E. CONNERADE (Bull. Soc. chim. Belg., 1934, 43, 447—461; cf. A., 1933, 1051).—4:4'-Dimethylbenzophenone and Cl_2 (slightly > 4 mols. at 140°) yields a product, from which MeOH isolates a Cl_4 -compound, m.p. 109.5° (probably partly nuclear-substituted). The main product, from which the Cl_5 -derivative is removed by ligroin, is 4:4'-tetrachlorodimethylbenzophenone (I), identified by hydrolysis to benzophenone-4:4'-dialdehyde. (I) with LiPh yields Ph_2 and polymeric products of the type $[CH\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CH]_n\cdot (CH\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CHO)_n$; (II), $n=3$, m.p. 190—195°; (III), $n=4$; (IV), $n=11$. These are coloured and fluorescent in solution. (I) with $AlCl_3$ yields 4:4'-dibenzylbenzophenone, as a gum (oxidised to 4:4'-dibenzoylbenzophenone, m.p. 227°), and bis-4:4'-dibenzylbenzophenone, $[CHPh\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CHPh]_2$, a gum, oxidised to triphenyl-4:4'-dimethylbenzophenone (?) and a product, $C_{54}H_{40}O_6$, m.p. 157°. (I) with $MgPhBr$ yields Ph_2 and a resin, $C_{42}H_{55}O_5$. H. N. R.

Pinacol-pinacolin rearrangement. VI. Rearrangement of symmetrical aromatic pinacols. W. E. BACHMANN and J. W. FERGUSON (J. Amer. Chem. Soc., 1934, 56, 2081—2084).—s-Pinacols, $OH\cdot CRR'\cdot CRR'\cdot OH$, prepared usually by reduction (Zn , $AcOH$; $Mg+MgI_2$; exposure to sunlight in Pr^sOH for 1—2 months) of $CORR'$ or, occasionally, from $(COR)_2$ and $MgR'X$, are rearranged by $AcCl$ in $AcOH\text{-}C_6H_6$ or (more generally) I in $AcOH$ to mixtures of $COR\cdot CRR'R'$ and $COR'\cdot CRRR'$, which are analysed by fission with $MeOH\text{-}KOH$ to $RCO_2H+R'CO_2H$. The relative migration aptitudes of the groups studied are ($Ph=1$): phenetyl 500, anisyl 500, m-anisyl 1.6 (mean val.), p- C_6H_4Cl 0.66, m- C_6H_4Cl 0; vals. previously deduced (cf. A., 1932, 515, 737; this vol., 292) for other groups are also given. The relative migration aptitudes of R and R' can be predicted from the vals. of these groups with respect to a third (mutual) group. 4:4'-Diethoxy-, m.p. 141—142°, 4:4'-diethoxy-4':-dimethyl-, m.p. 168—169°, 3:3'-dimethoxy-, m.p. 140—142° (lit. 139°), 3:3'-dimethoxy-3':3''-, m.p. 139—140°, and -4':4''-, m.p. 160—162°, -dimethyl-, 3:3'-dimethoxy-4':4''-diphenyl- (I), m.p. 172—173°, 4:4'-dimethoxy-3':3''-dimethyl-, m.p. 144—145°, 4:4'-

dichloro-4'' : 4'''-dimethoxy- (II), m.p. 181—182°, 4 : 4'-dichloro-4'' : 4'''-dimethyl-, and 3 : 3'-dichloro-4'' : 4'''-diphenyl- (III), m.p. 174—175°, -benzpinacols are described. 3-Methoxy-4' : 4''-diphenyltriphenylmethane, m.p. 149—149.5°, isolated from the fission products of the mixture of pinacolins from (I), is also prepared by reduction (HCO_2H) of the carbinol from 3-methoxy-4'-phenylbenzophenone and $p\text{-C}_6\text{H}_4\text{Ph}\cdot\text{Li}$. 4-Chloro-4' : 4''-dimethoxytriphenylmethane, m.p. 65—66°, obtained similarly from (II), is prepared by reduction (Zn dust, AcOH) of the carbinol from $\text{CO}(\text{C}_6\text{H}_4\cdot\text{OMe-}p)_2$ and $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{MgBr}$, whilst 3-chloro-4' : 4''-diphenyltriphenylmethane, m.p. 144—145° [from (III)], is obtained by reduction (HCO_2H) of the carbinol from 4 : 4'-diphenylbenzophenone and $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{MgI}$. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{COCl}$, PhOEt , and AlCl_3 in CS_2 give 4-ethoxy-4'-methylbenzophenone, m.p. 84—85°; 4-ethoxybenzophenone, m.p. 47° (lit. 38—39°), is prepared from BzCl . $m\text{-OMe-C}_6\text{H}_4\cdot\text{CN}$ with MgPhBr and $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{MgBr}$ (IV) affords 3-methoxy-, b.p. 185°/4 mm., m.p. 38—40°, and 3-methoxy-3'-methylbenzophenone, b.p. 212—213°/22 mm., respectively. $p\text{-OMe-C}_6\text{H}_4\cdot\text{CHO}$ and (IV) give 4-methoxy-3'-methylbenzhydrol, m.p. 51—52°, oxidised (CrO_3 , AcOH) to 4-methoxy-3'-methylbenzophenone, b.p. 238—240°/35 mm., also prepared from $p\text{-OMe-C}_6\text{H}_4\cdot\text{CN}$ and (IV). $m\text{-C}_6\text{H}_4\text{Cl}\cdot\text{COCl}$, Ph_2 , and AlCl_3 in CS_2 afford 3-chloro-4'-phenylbenzophenone, m.p. 106—107°; 3-chloro-4'-methylbenzophenone, m.p. 97—98°, is similarly prepared from PhMe . H. B.

Reversibility of the Friedel-Crafts condensation. Styryl methyl and distyryl ketones. C. F. WOODWARD, G. T. BORCHERDT, and R. C. FUSON (J. Amer. Chem. Soc., 1934, 56, 2103—2105; cf. this vol., 774).— p -Chlorostyryl Me ketone (I), m.p. 58—59.5° (lit. 51°), prepared by Walther and Ratze's method (A., 1902, i, 466), PhCl , and AlCl_3 in the cold give $\beta\beta$ -di- p -chlorophenylethyl Me ketone (II), m.p. 91—92.5° (semicarbazone, m.p. 180—181°), oxidised ($\text{Na}_2\text{Cr}_2\text{O}_7$, AcOH) to 4 : 4'-dichlorobenzophenone. $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{COMe}$ (III) and PhMe similarly afford $\beta\beta$ -di- p -tolylethyl Me ketone (IV), m.p. 73.5—74° (semicarbazone, m.p. 140—141.5°), whilst $\text{CHPh}\cdot\text{CH}\cdot\text{COMe}$ (V) and PhCl yield (under appropriate conditions) β -phenyl- β - p -chlorophenylethyl Me ketone (VI), b.p. 180—182°/4 mm. (semicarbazone, m.p. 155.5—157°). (I)—(VI) treated with C_6H_6 , AlCl_3 , and HCl (cf. A., 1933, 1170) give $\beta\beta$ -diphenylethyl Me ketone (VII) in 33—92% yield; (VII) and PhCl similarly afford (mainly) (VI) and (II). Interruption of the reaction between di- o -chlorostyryl ketone (VIII), m.p. 124—125°, C_6H_6 , and AlCl_3 gives β -phenyl- β - o -chlorophenylethyl o -chlorostyryl ketone (IX), m.p. 144° [also prepared from (VIII) and MgPhBr]; more prolonged reaction affords di- $\beta\beta$ -diphenylethyl ketone (X), which is also obtained from MgPhBr and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}_2$ (XI). (X) is also formed from C_6H_6 , AlCl_3 , and (IX), (XI), and distyryl, di- p -chlorostyryl, and di- p -methylstyryl ketones. H. B.

Additions to conjugated systems in anthracene series. I. Action of magnesium phenyl bromide on methyleneanthrone. P. L. JULIAN and A. MAGNANI (J. Amer. Chem. Soc., 1934, 56, 2174—

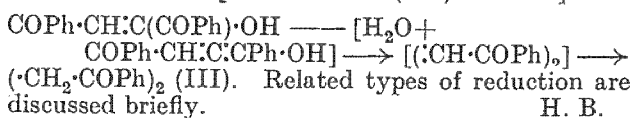
2177).—Contrary to Bergmann (A., 1930, 903), 9-benzylidenanthrone (I) (obtained by passing dry HCl into anthrone + PhCHO at 100°) and MgPhBr (II) give a compound, $\text{C}_{27}\text{H}_{20}\text{O}$, m.p. 147°, and only a little anthraquinone (III). In agreement with Bergmann (*loc. cit.*), the product from 9-methyleneanthrone (IV) and (II), when worked up in the usual manner, affords (III) as the sole cryst. product. When O_2 is passed into the moist Et_2O -solution of the freshly prepared reaction product from (II) and (IV), the fluorescence disappears and 9-benzyl-10-anthranol peroxide (V), m.p. 133—134° (decomp.), and a little (III) are isolable. (V) decomposes at 170—180° to (III), $\text{CH}_2\text{Ph}\cdot\text{OH}$, and PhCHO . The reaction between (II) and (IV) thus resembles that between (II) and $\alpha\beta$ -unsaturated ketones (Kohler, A., 1906, i, 753). Reduction (H_2 , Pd, EtOH) of (I) gives 9-benzylanthrone (VI), m.p. 91—92°, and some (III) (separates when the Et_2O -extract is kept); passage of O_2 through the freshly prepared reduced solution affords (III) and $\text{CH}_2\text{Ph}\cdot\text{OH}$. (VI) could not be prepared from the dibromide, m.p. 138° (lit. 148°), of (I) by Bach's method (A., 1890, 1144); (I) and (III) are obtained. H. B.

Condensation of phenols with unsaturated ketones or aldehydes. I. β -Naphthol and vinyl methyl ketone. S. A. MILLER and R. ROBINSON (J.C.S., 1934, 1535—1536).— $\text{CH}_2\text{:CH}\cdot\text{COMe}$, $\beta\text{-C}_{10}\text{H}_7\cdot\text{OH}$, and NaOEt or KOEt in cold, dry EtOH give β -2-hydroxy-1-naphthylethyl Me ketone (I), m.p. 84° (ferrichloride of Ac derivative, cryst.), the Me ether, m.p. 54°, b.p. 205°/10 mm., of which was also obtained by hydrogenation (Pd) in AcOH at 30—40° of 2-methoxy-1-naphthylidenacetone, m.p. 146.5—147.5°, b.p. 195—205°/1 mm. (prepared from COMe_2 and the aldehyde by NaOH). (I), best with chloranil and hot POCl_3 , gives 2-methyl-5 : 6-naphtha-(1 : 2)-pyrylium ferrichloride, m.p. 151°. R. S. C.

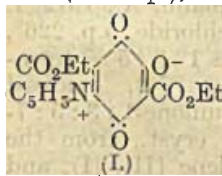
Highly activated carbonyl group. Dimesityl triketone. R. C. FUSON, J. F. MATUSZESKI, and A. R. GRAY (J. Amer. Chem. Soc., 1934, 56, 2099—2101).—Di-2 : 4 : 6-trimethylbenzoylmethane (I) is oxidised (SeO_2 , dioxan) to di-2 : 4 : 6-trimethylphenyl triketone (II), m.p. 111—112.5°, and a compound, m.p. 201—202°. (II) is also obtained (i) as a by-product in the oxidation (HNO_3) of γ -hydroxy- $\alpha\beta$ -triketo- $\alpha\delta$ -di-2 : 4 : 6-trimethylphenylbutane (this vol., 895), (ii) by the action of alkali on di-2 : 4 : 6-trimethylphenyl tetraketone (III) (*loc. cit.*), or (iii) (most conveniently) by prolonged heating of (III) in AcOH (or EtOH). (II) and $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ give mesityl-glyoxalsemicarbazone (this vol., 525); with NH_2OH , a compound, m.p. 180—181°, which appears to be isomeric with mesityl-glyoxaloxime, results. (II) is decomposed by hot 10% NaOH to 2 : 4 : 6 : 2' : 4' : 6'-hexamethylbenzil, 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}_2\text{H}$, and 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$. (I) does not react with $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{CHO}$ in aq. EtOH-NaOH . (I), $\text{Bu}^n\text{O}\cdot\text{NO}$, and HCl in Et_2O give a compound, $\text{C}_{31}\text{H}_{33}\text{O}_3\text{N}$, m.p. 153—154°, which could not be hydrolysed ($\text{EtOH-H}_2\text{SO}_4$ or $-\text{HCl}$). Cryst. products could not be obtained from (I) and $\text{Pb}(\text{OAc})_4$ in AcOH . H. B.

Reduction of α -hydroxy- $\alpha\beta$ -dibenzoylethylene and dibenzoylethylene oxide and chlorohydrin.

R. E. LUTZ and F. N. WILDER (J. Amer. Chem. Soc., 1934, **56**, 2065—2067).—Reduction ($\text{Na}_2\text{S}_2\text{O}_4$ in boiling 85% EtOH) of α -hydroxy- $\alpha\beta$ -dibenzoyl ethylene (I) or $\alpha\beta$ -dibenzoyl ethylene chlorohydrin (II) gives approx. equal amounts of $\alpha\beta$ -dibenzoyl ethane (III) and $\alpha\beta$ -dibenzoyl ethyl alcohol (IV), m.p. 87.5° (corr.) [acetate (V), m.p. 116° (corr.), obtained by the action of cold AcCl or Ac_2O at 75°; chloride, prepared by the action of SOCl_2 or BzCl (cold or at 50°)]. $\alpha\beta$ -Dibenzoyl ethylene oxide (VI) similarly affords a 2:1 mixture of (III) and (IV). Reduction [Zn dust (large excess), AcOH] of (IV) and (VI) at 35°, and the acetate of (II) at the b.p., gives (III) in each case. (IV) heated at 150° passes into *trans*- $\alpha\beta$ -dibenzoyl ethylene. (IV) or (V) with Ac_2O - H_2SO_4 and AcCl - H_2SO_4 affords 3-acetoxy- and 3-chloro-2:5-diphenylfuran, respectively. The production of (III) and (IV) from (I) is considered to involve the following reactions:



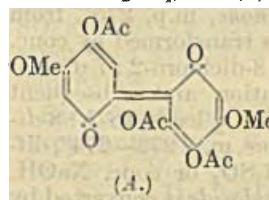
Action of pyridine on ethyl 2:5-dichloro-*p*-benzoquinone-3:6-dicarboxylate and derivatives of terephthalic acid. H. LIEBERMANN and D. LISSER (Annalen, 1934, **513**, 180—189).—Et 2:5-dichloro-*p*-benzoquinone-3:6-dicarboxylate and $\text{C}_5\text{H}_5\text{N}$ in cold COMe_2 give the *betaine* (I) of *Et 2-hydroxy-5-pyridinium-*p*-benzoquinone-3:6-dicarboxylate*, m.p. 194° (decomp.), which is formed by hydrolysis (traces of H_2O present in the reagents or formed by autocondensation of COMe_2 by the $\text{C}_5\text{H}_5\text{N}$) of the first formed di(pyridinium chloride) and subsequent elimination of HCl from the hydroxyphenylpyridinium chloride. (I) is reduced (aq.



$\text{Na}_2\text{S}_2\text{O}_4$) to *Et 2:3:5-trihydroxyterephthalate*, m.p. 116° [Ac_3 derivative, m.p. 100°; free acid, m.p. 247° (decomp.)]. The product obtained from (I) and boiling MeOH or EtOH is reduced ($\text{Na}_2\text{S}_2\text{O}_4$ in aq. COMe_2) to Et tetrahydroxyterephthalate, m.p. 178°. *Et 2-hydroxy-5-phenoxy-*p*-benzoquinone-3:6-dicarboxylate*, m.p. 128—130° [from (I) and PhOH in aq. COMe_2], is similarly reduced to *Et 2:3:5-trihydroxy-6-phenoxyterephthalate*, m.p. 128° (Ac_3 derivative, m.p. 128°; free acid, m.p. > 280°), whilst *Et 5-anilino-2-hydroxy-*p*-benzoquinone-3:6-dicarboxylate*, m.p. 160° [from (I) and NH_2Ph in aq. COMe_2], similarly gives *Et 6-anilino-2:3:5-trihydroxyterephthalate*, m.p. 102°. (I) and fuming HCl at 45° afford *Et 5-chloro-2-hydroxy-*p*-benzoquinone-3:6-dicarboxylate*, m.p. 98° [Ac derivative (II), m.p. 107°], reduced to *Et 6-chloro-2:3:5-trihydroxyterephthalate*, m.p. 110° [Ac_3 derivative, m.p. 104°; 3- Ac derivative, m.p. 85°, prepared by reduction of (II)]. 2:4:5-Trihydroxy-3:6-dicarboxyphenylpyridinium bromide, m.p. 202° (decomp. from 170°), is obtained from (I) and 48% HBr . H. B.

Dehydrogenation of phenols. IV. Reactive positions of 4:4'-dimethoxydiquinone and oxidative coupling of 4-ethylpyrogallol. H. ERDT-

MAN (Annalen, 1934, **513**, 240—250).—Prolonged treatment of 4:4'-dimethoxydiquinone (4:4'-dimethoxydiphenyl-2:5:2':5'-diquinone) (this vol., 184) with AcOH -conc. H_2SO_4 gives 2:3:6:2':3':6'-hexa-acetoxy-4:4'-dimethoxydiphenyl (I) (cf. *loc. cit.*) and (probably) 1:4:5:6-tetra-acetoxy-2:7-dimethoxydiphenylene oxide (II), m.p. 255—256°; the quinone (A) is probably an intermediate [addition of AcOH affords (I); rearrangement gives (II)]. Hydrolysis (EtOH - H_2SO_4) of (I) and subsequent methylation



(Me_2SO_4 , KOH) gives 2:3:4:6:2':3':4':6'-octamethoxydiphenyl, m.p. 146—147° (5:5'- Br_2 -derivative, m.p. 113—114°), also prepared from 4-iodo-1:2:3:5-tetramethoxybenzene, m.p. 52—53° [from 1:2:3:5- $\text{C}_6\text{H}_2(\text{OMe})_4$, I, and HgO at 70—75°], and Cu -bronze at 230°. (II) is similarly converted into hexamethoxydiphenylene oxide, m.p. 126—127.5°. (I) is unaffected by prolonged treatment with AcOH -conc. H_2SO_4 ; 6-hydroxy-2:7-dimethoxydiphenylene oxide-1:4-quinone similarly gives (mainly) the acetate and a little 1:4:6-triacetoxy-2:7-dimethoxydiphenylene oxide (*loc. cit.*).

4-Ethylpyrogallol (III) is oxidised [air in aq. $\text{Ba}(\text{OH})_2$] to 4:5:6:4':5':6'-hexahydroxy-3:3'-diethylidiphenyl, m.p. 235—237° (decomp.) (*hexa-acetate*, m.p. 168—169°), which readily absorbs O_2 in 2*N*- NaOH or KOH , converted by successive methylation and bromination into 2:2'-dibromo-4:5:6:4':5':6'-hexamethoxy-3:3'-diethylidiphenyl, m.p. 98—101°. Clemmensen reduction of 6-acetyl-4-ethylpyrogallol [from (III), AcOH , and ZnCl_2 at 145°] gives 4:6-diethylpyrogallol (*triacetate*, m.p. 106—108°), which is readily oxidised (O_2 in alkali); cryst. products could not be isolated. 1:2:3- $\text{C}_{10}\text{H}_5(\text{OH})_3$ is oxidised (O_2 in aq. MeOH - NaHCO_3 + Na_2CO_3) to an impure hydroxynaphthaquinone, m.p. 263—265° (decomp.), reductive acetylation of which affords 1:2:3- $\text{C}_{10}\text{H}_5(\text{OAc})_3$. H. B.

Preparation and properties of hexachloro-1:4-naphthaquinone. V. SCHVEMBERGER and V. GORDON (J. Gen. Chem. Russ., 1934, **4**, 695—703).—Hexachloro-1:4-naphthaquinone (I), m.p. 222—222.5°, b.p. 412—415°/758 mm., is obtained from C_{10}Cl_8 and conc. HNO_3 , or from 1:4-naphthaquinone and SbCl_5 in presence of I. Fuming HNO_3 oxidises (I) to tetrachlorophthalic acid, H_2O has no action, aq. or EtOH - KOH yields NaCl and unidentified products, PCl_3 converts (I) into C_{10}Cl_8 , and H_2SO_4 dissolves (I) but does not decompose it. R. T.

Photolysis of halogenated anthrahydroquinones. A. E. GOLDSTEIN [with J. H. GARDNER] (J. Amer. Chem. Soc., 1934, **56**, 2130—2131).—Halogeno-anthraquinones are reduced ($\text{Na}_2\text{S}_2\text{O}_4$ in 20% NaOH), the resulting solutions exposed in absence of air to light from a 500-watt lamp, and then oxidised (air); anthraquinone is thus obtained from its 1- and 2- Cl - and - Br -derivatives, whilst 1-hydroxyanthraquinone is formed from its 4- Cl -derivative. The ease of removal of halogen is: 1->2- and $\text{Br}>\text{Cl}$. H. B.

Preparations in the anthracene series. R. SCHOLL and K. ZIEGS (Ber., 1934, 67, [B], 1746—1750).—1 : 8-Dichloro-2 : 7-dimethylantraquinone (I), m.p. 196—197°, is purified with difficulty when prepared from 2 : 7-dimethylantraquinone (I), SO_2Cl_2 , and I in PhNO_2 and is better obtained by addition of the tetrazotised 1 : 8-(NH_2)₂-compound (III) to $\text{CuCl}\cdot\text{HCl}$. 1 : 8-Dichloro-2 : 7-di- ω -chloromethylantraquinone, m.p. 285°, is obtained by the action of Cl_2 on (II) in conc. H_2SO_4 containing I at 100°. 1 : 8-Dichloro-2 : 7-di- ω -bromomethylantraquinone, m.p. 275°, from (I) and Br in PhNO_2 at 170°, is transformed by conc. H_2SO_4 at 130—135° into 1 : 8-dichloro-2 : 7-dialdehydoanthraquinone. Diazotisation and subsequent treatment of (III) with $\text{KC}(\text{CN})_3$ leads to 1 : 8-dicyano-2 : 7-dimethylantraquinone, m.p. 272—274°, difficultly hydrolysed by 80% H_2SO_4 or conc. NaOH . Anthraquinone-2 : 7-dicarboxyl chloride is converted by *m*-xylene and AlCl_3 at 60—65° into 2 : 7-di-*m*-4'-xyloylantraquinone, m.p. 163—164°. Oxidation of (I) with HNO_3 (*d* 1:1) at 210—220° or by pptd. MnO_2 and conc. H_2SO_4 at 55—60° gives 1 : 8-dichloroanthraquinone-2 : 7-dicarboxylic acid, m.p. 318° (decomp.) after darkening at about 300° (*Me*, ester, m.p. 193.5—194°), slowly converted by NaOH and NH_3 into the 1 : 8-(OH)₂- and 1 : 8-(NH_2)₂-compounds, respectively. Treatment of the acid chloride with C_6H_6 and AlCl_3 leads to 1 : 8-dichloro-2 : 7-dibenzoylantraquinone, m.p. 236°, converted by $\text{NH}_3\text{--EtOH--H}_2\text{O}$ at 170—175° into 1 : 8-diamino-2 : 7-dibenzoylantraquinone, m.p. 266—267°. 1 : 8-Dianilino-, m.p. 263°, 1 : 8-di-*p*-toluidino-, m.p. about 240°, and 1 : 8-diphenoxy-, m.p. 235°, -2 : 7-dibenzoylantraquinone are described. H. W.

1 : 3 : 5 : 8-Tetrahydroxy-2-methylantraquinone. E. H. CHARLESWORTH and R. ROBINSON (J.C.S., 1934, 1531—1533).—*p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{COCl}$ and ClSO_3H give a little 4-carboxytoluene-3-sulphonyl chloride, m.p. 110°. Attempts to prepare 3 : 5-dihydroxy-*p*-toluic acid (I) by the method of Mitter *et al.* (A., 1928, 764) gave only *m*- $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$. (I) (modified prep.), +0.5 H_2O , m.p. 260°, gives ($\text{Me}\cdot\text{SO}_4$) the *Me*₂ ether, m.p. 215°, of which with $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$ and H_2SO_4 yields 3 : 5-dimethoxy-4-methyl- α -trichloromethylphthalide, m.p. 133—134°, hydrolysed by hot 20% NaOH to 3 : 5-dimethoxy-4-methylphthalide- α -carboxylic acid, m.p. 173—174°, which with Cu chromite and quinoline at 150—160° gives 3 : 5-dimethoxy-4-methylphthalide (II), m.p. 158°. 3 : 5-Dimethoxy-*p*-toluic acid, CH_2O , and HCl give a *Cl*-compound, m.p. 131°. (II) and alkaline KMnO_4 afford 3 : 5-dimethoxy-4-methylphthalic acid, m.p. 195—196° (decomp.), the anhydride, m.p. 166°, of which with *p*- $\text{C}_6\text{H}_4(\text{OMe})_2$ and AlCl_3 in CS_2 gives a product, converted directly by H_2SO_4 at 150° into 1 : 3 : 5 : 8-tetrahydroxy-2-methylantraquinone, m.p. 276—277° (*Ac*₄ derivative, m.p. 223°), not identical with catenarin. R. S. C.

Hydroxy- and chloro-derivatives of 2-methylantraquinone. G. J. MARRIOTT and R. ROBINSON (J.C.S., 1934, 1631—1635).—3 : 6-Dichlorophthalic anhydride (I), *o*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{OMe}$, and AlCl_3 give 3 : 6-dichloro-2-(4'-methoxy-3'-methylbenzoyl)benzoic acid, m.p. 182—183°, which with 10% oleum and H_3BO_3 at 130° (10 min.) or conc. H_2SO_4 and H_3BO_3 at 140—150°

(15 min.) gives 5 : 8-dichloro-2-methoxy-1-(or 3-)methyl-antraquinone, m.p. 246—247°; some demethylation also occurs to give the 2-*OH*-compound, m.p. about 298°, also obtained in poor yield from *o*-cresoldichlorophthalein, 3 : 6-dichlorophthalic acid, and H_2SO_4 at 110—115°. The above results are contrary to the statements of Walsh *et al.* (J.C.S., 1910, 97, 691). (I) and *o*-cresol with AlCl_3 give 3 : 6-dichloro-2-(2'-hydroxy-3'-methylbenzoyl)benzoic acid (II) (54% yield), m.p. 197° (*Ca* salt), and *o*-cresol-3 : 6-dichlorophthalein, m.p. 268°. (II), also obtained in 12% yield by H_3BO_3 at 160—170°, with 20% oleum and H_3BO_3 affords (max. yield 40%) 5 : 8-dichloro-1-hydroxy-2-methylantraquinone, m.p. 196—197° (*Ac* derivative, m.p. 191°). This, best (poor yield) with NaOMe in MeOH at 135—145° or with Cu-bronze at 100—105°, gives 1 : 5-dihydroxy-2-methylantraquinone, m.p. 187° (*Ac*₂ derivative, m.p. 220°), and, by the former method, also a little 1 : 5 : 6-(OH)₃-compound. Catenarin (III) with SnCl_2 gives the anthrone, $\text{C}_{15}\text{H}_{12}\text{O}_4$, decomp. 230°, the amorphous *Ac*₂ derivative of which by oxidation (CrO_3) and acetylation affords a little 1 : 8-di-acetoxy-2-acetoxymethylantraquinone, m.p. 182°. Absorption spectra (described) confirm the above structures. (III) is either 1 : 4 : 8- or 1 : 5 : 8-trihydroxy-2-hydroxymethylantraquinone. R. S. C.

Tautomerism of anthraquinone-1-carboxyl chlorides. VII. Tautomerism of anthraquinone-1 : 3 : 5 : 7- and -1 : 4 : 5 : 8-tetracarboxyl chlorides. R. SCHOLL, K. MEYER, and A. KELLER (Annalen, 1934, 513, 295—304; cf. this vol., 1104).—The $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}_2\text{H}$ obtained from *p*-xylene, ($\cdot\text{COCl}$)₂, and AlCl_3 in CS_2 at 0° (cf. Liebermann, A., 1912, 1, 464) is converted (SOCl_2) into the chloride, b.p. 226°, which with AlCl_3 at 115—120° gives 1 : 3 : 5 : 7-tetramethylantraquinone (Seer, *ibid.*, 276), oxidised [HNO_3 (*d* 1:1) at 210°] to anthraquinone-1 : 3 : 5 : 7-tetracarboxylic acid [chloride (I), cryst., from the acid and PCl_5 in C_6H_6], *m*-Xylene (II), (I), and FeCl_3 in PhNO_2 at 60—70° give 30% of 1 : 3 : 5 : 7-tetra-*m*-4'-xyloylantraquinone, m.p. > 355° (darkens at 315°), whilst (I), PhCl , and AlCl_3 at 75° afford 28% of 1 : 3 : 5 : 7-tetra-*p*-chlorobenzoylantraquinone (not investigated) and 13% of 3 : 7-di-*p*-chlorobenzoyl-9 : 10-di-*p*-chlorophenylantracene-1 : 5-dicarboxylic acid (III), m.p. > 350° (formed by reduction of the intermediate dilactone of 9 : 10-dihydroxy-3 : 7-di-*p*-chlorobenzoyl-9 : 10-di-*p*-chlorophenyl-9 : 10-dihydroanthracene-1 : 5-dicarboxylic acid). (III) is converted by conc. H_2SO_4 at 50° into the blue 5' : 5''-dichloro-3 : 7-di-*p*-chlorobenzoylheterocoerdianthrone (7' : 7'') (for structure of parent compound, see A., 1932, 617). 5 : 8-Dicyano-1 : 4-dimethylantraquinone, m.p. 309° (darkening) [from the 5 : 8- Cl_2 -derivative, m.p. 313—314° (lit. 244°), and CuCN in $\text{CH}_3\text{Ph}\cdot\text{CN}$], is hydrolysed (dil. HCl at 200°) to 1 : 4-dimethylantraquinone-5 : 8-dicarboxylic acid; with dil. HNO_3 at 200—210°, anthraquinone-1 : 4 : 5 : 8-tetracarboxylic acid [chloride (IV)] results. (II), (IV), and a little FeCl_3 give 49% of 1 : 4 : 5 : 8-tetra-*m*-4'-xyloylantraquinone, m.p. 320° (darkening), and about 35% of an inseparable mixture of lactones. 1 : 4 : 5 : 8-Tetra-*p*-toluoylantraquinone, m.p. 350° (slow decomp.), is obtained in 56% yield from (IV), PhMe , and AlCl_3 in cold PhNO_2 . The

reactions with (I) and (IV) often give inseparable mixtures of CO-, lactic, and ketolactic acids, ketolactone, tetraketone, and the original acid.

p -C₆H₄ClMe, (COCl)₂, and AlCl₃ in CS₂ at room temp. give 2-chloro-5-methylbenzoic acid (40%) [chloride, b.p. 165—167°/85 mm., which could not be converted (method: Seer, *loc. cit.*) into a dichlorodimethyl-anthraquinone] [oxidised (KMnO₄) to 4:1:3: C₆H₃Cl(CO₂H)₂] and a dichlorodimethylbenzophenone, m.p. 70°.

H. B.

Preparation of ketols by means of mixed aminomagnesium compounds. J. COLOGNE (Bull. Soc. chim., 1934, [v], 1, 1101—1114; cf. A., 1932, 499; 1933, 698, 1277).—The condensation proceeds best with 2 mols. of ketone and 1 mol. of NPhMe·MgBr (I); Mg compounds derived from NH₄Et₂ and piperidine are unsuitable. The following are described: γ -methylheptan- γ -ol- ϵ -one, b.p. 85—86°/14 mm. (semicarbazone, m.p. 124—125°), from COMeEt, β δ -trimethylnonan- δ -ol- ζ -one, b.p. 81—82°/2 mm. (semicarbazone, m.p. 135—136°), from COMeBu^s, the semicarbazone, m.p. 197°, of δ -methyl- γ -ethylheptan- γ -ol- ϵ -one from COEt₂, and $\gamma\eta$ -trimethyl- δ -ethylnonan- δ -ol- ζ -one, b.p. 104—105°/3 mm., from δ -methylhexan- γ -one. Treatment of the product from fluorenone and (I) with pinacolin, COEtBu^r, COPr^s, or COPhMe gives δ -(9-hydroxy-9-fluorenyl)- $\beta\beta$ -dimethylbutan- γ -one, m.p. 95°, δ -(9-hydroxy-9-fluorenyl)- $\beta\beta$ -dimethylpentan- γ -one, m.p. 92°, δ -(9-hydroxy-9-fluorenyl)- $\beta\delta$ -dimethylpentan- γ -one, m.p. 127°, and ω -(9-hydroxy-9-fluorenyl)-acetophenone, m.p. 112°, respectively, in yields of 60—80%. An intermediate ketone-aminomagnesium compound is formed.

F. S. H. H.

Perylene and its derivatives. A. ZINKE, F. STIMLER, and E. REUSS (Monatsh., 1934, 64, 415—425).—The yield of perylene-3:10-quinone is greatly improved by adding MnO₂ to the mixture of α -dinaphthol and AlCl₃ at 160—170° and oxidising the crude product (I) with dil. CrO₃. (I) is converted into perylene, m.p. 273°, when distilled with Zn dust. 2:11-Dihydroxyperylene-3:10-quinone (II) is obtained from β -naphthaquinone (III) and AlCl₃ at 140—150° or, similarly, from 2-dinaphthylidiquinone, m.p. 310°, prepared by warming (III) with dil. H₂SO₄ and oxidation of the product with K₂Cr₂O₇. Treatment of (II) with H₂SO₄ and MnO₂ gives phenanthrene-1:8:9:10-tetracarboxylic dianhydride. (II) and BzCl in boiling PhNO₂ afford 2:11-dibenzoyloxyperylene-3:10-quinone, m.p. 317°, whilst reduction and subsequent benzylation of (II) yields 2:3:10:11-tetra-benzoyloxyperylene, m.p. 278—279°. (II) and o -C₆H₄(NH₂)₂ in boiling PhNO₂-AcOH give the diazine, C₃₂H₁₈N₄.

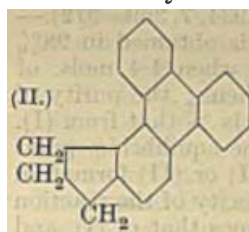
H. W.

Compounds of petroleum. III. Mode of formation of naphthenic acids. J. VON BRAUN and H. WITTMAYER (Ber., 1934, 67, [B], 1739—1746).—The possibility is discussed that naphthenic acids (I) are formed by oxidation during the refining of petroleum by acid and alkali. Petroleum is therefore exhaustively extracted with liquid SO₂ and extract (II) and residue (III) are treated separately with alkali. The ratio of (I) in (II) and (III) is 3:1, but the assumption that this is due to acids differing in kind is not warranted. The isolation of individuals from

(II) and (III) is impossible, but comparison of the acid mixtures of similar b.p. from (II) and (III) by conversion into the amines and NH₄ bases followed by degradation of the latter shows that *tert.* dimethylated amines and olefines (IV) are produced in similar amount. Oxidation of (IV) affords ketones and acids (V) in similar proportion and of like physical properties, and from (V) similar amines are derived. The pre-existence of (I) in petroleum is therefore established. Treatment of (I) from various sources with SO₂ at -10° to -20° does not lead to a clean separation into groups of constitutively closely related individuals.

H. W.

Strophanthin. XXXI. Dehydrogenation of strophanthidin. R. C. ELDERFIELD and W. A. JACOBS (J. Biol. Chem., 1934, 107, 143—154; cf. this vol., 657).—The products obtained by dehydrogenation of strophanthidin (I) depend on the conditions; caution is therefore necessary in interpreting the results. (I) with Se at 320—340° yields a hydrocarbon, C₁₈H₁₆, m.p. 125—126° (corr.) [picrate, m.p. 118—119°; C₆H₃(NO₂)₃ derivative, 148—150°; C₆H₂Me(NO₂)₃ derivative, m.p. 93—94°], identical with that isolated by Diels *et al.* (A., 1928, 169). Preliminary pyrolysis of (I) at 340—360°, followed by Se dehydrogenation at 320—340°, yields a small amount of a mixture (?) of hydrocarbons, m.p. 123—124° [picrate, m.p. 128—130°; C₆H₃(NO₂)₃ derivative, m.p. 150—152°], yielding a little of a quinone on oxidation. Dehydrogenation of (I) at 340—360° and fractional crystallisation of the product yields: (a) a



hydrocarbon, C₂₁H₁₆, m.p. 295—297°, possibly cyclopentanotriphenylene (II); (b) Diels' hydrocarbon, C₁₈H₁₆; (c) a hydrocarbon (III), C₁₆H₁₄, m.p. 124—125° [picrate, m.p. 140—141°], yielding, on oxidation, a quinone, C₁₆H₁₂O₂, m.p. 208—209° (quinoxaline, m.p. 150°); and (d) a hydrocarbon (IV), C₁₆H₁₄, m.p. 127° [picrate, m.p. 126—127°; C₆H₃(NO₂)₃ derivative, m.p. 151—153°], yielding on oxidation a quinone, m.p. 203—205° (quinoxaline, m.p. 168—171°). (III) and (IV) are regarded as di-methyl- or -ethyl-phenanthrenes; their formation, and that of (II), is discussed. *iso*-Strophanthic acid, after preliminary decarboxylation at 200°, on dehydrogenation with Se at 320—340° yields a mixture from which a hydrocarbon, C₁₆H₁₄ (?), m.p. 140—142° [picrate; C₆H₃(NO₂)₃ derivative, m.p. 128—129°], can be isolated.

H. N. R.

Grayanotoxin, the active principle of *Leucothoe grayana*. I. S. MIYAJIMA and S. TAKEI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1234—1244).—From *L. grayana*, Maxim., were isolated *p*-methoxy-cinnamic acid and grayanotoxin-I (I), m.p. 249°, -II (II), C₂₀H₃₂O₅, m.p. 190—191°, and -III (III), m.p. 210—235°. These are not alkaloids or glucosides. Deacetylation of (I), C₂₀H₃₀O₂(OH)·OAc, gives (III), C₂₀H₃₄O₆·0.5H₂O. The toxicity to fish is in the order (III) > (I) > (II), it being < that of rotenone or pyrethrin.

F. O. H.

Resins of mastic and Manila elemi. P. CASPARIS and P. NAEF (Pharm. Acta Helv., 1934, 9,

19—23; Chem. Zentr., 1934, i, 3350).— α -Masticoresin is hydrolysed by KOH-EtOH to α -masticoresinol and α -masticoresinic acid (both gums); β -masticoresin resists hydrolysis. The following are described: *menthyl*, m.p. 70—72°, and *amyrin anthraquinone-2-carboxylate*, m.p. 263—265°, and *amyrin 3:5-dinitrobenzoate*, m.p. 220—221.5° (α -naphthalide, m.p. 202—203°). H. N. R.

Use of *l*-menthoxyacetyl chloride for resolution of amino-acids. D. F. HOLMES and R. ADAMS (J. Amer. Chem. Soc., 1934, 56, 2093—2094).—*l*-Menthoxyacetyl chloride (I) and *dl*-NH₂·CHR·CO₂H (II) in 5% NaOH give mixtures (separable by crystallisation from 60% EtOH or a 3:1 mixture of high-boiling petroleum and EtOAc) of the diastereoisomeric *l*-menthoxyacetyl derivatives; subsequent hydrolysis (20% HBr-EtOH) affords *d*- and *l*-(II) (when R is Me, Pr^{*s*}, and Ph). The following are described: *l*-menthoxyacetyl-glycine, m.p. 155—156°, *d*- and *l*-alanine, m.p. 147—148° and 117—118°, respectively, *d*- and *l*-valine (III), m.p. 156—157.5° and 93—96°, respectively, *d*- and *l*-phenylglycine (IV), m.p. 162° and 113—116°, respectively, and *dl*-phenylalanine, m.p. 100—101°; β -C₁₀H₇·*l*-menthoxyacetate, m.p. 108—109.5° [from β -C₁₀H₇·OH and (I) in C-H₅N]; *l*-menthoxyacetyl-*p*-nitroanilide, m.p. 106; *l*-menthoxyacetamide, m.p. 94—95° (lit. 93°). The *l*-(II) obtained from (III) and (IV) are optically impure. H. B.

Conversion of camphene into isobornyl acetate and formate. V. E. TISCHTSCHENKO and G. A. RUDAKOV (J. Appl. Chem. Russ., 1934, 7, 369—372).—At 15—20° isobornyl acetate (I) is obtained in 98% and formate (II) in 94% yield, when 1.4 mols. of acid are taken per mol. of camphene; the purity of the isoborneol obtained from (II) is > that from (I). The reaction is reversible, and the equilibrium point is displaced in the direction of (I) or (II) formation with diminishing temp. The velocity of the reaction of formation of (II) is 10—20 times that of (I), and in both cases varies inversely with the concn. of acids. R. T.

Optical rotation. Rotatory powers of acyl-biscamphorquinonehydrazones and camphorylthiocarbamylhydrazides and attempts to prepare compounds possessing abnormal rotation. M. S. KOTNIS, B. S. RAO, and P. C. GUHA (J. Indian Chem. Soc., 1934, 11, 579—593).—Condensation of camphorquinone (I) with the dihydrazides of the dibasic acids gives *s*-carbonyl-, m.p. 225°, [α]₅₇₈₀ 288.6°, [α]₅₄₆₁ 333.4°, *s*-oxalyl-, m.p. 249°, [α]₅₇₈₀ 256.1°, [α]₅₄₆₁ 298.6°, *malonyl*-, m.p. 185°, [α]₅₇₈₀ 251.3°, [α]₅₄₆₁ 272.1°, *succinyl*-, m.p. 275°, *glutaryl*-, m.p. 219°, [α]₅₇₈₀ 213.7°, [α]₅₄₆₁ 261.2°, *adipoyl*-, m.p. 220°, [α]₅₇₈₀ 195.4°, [α]₅₄₆₁ 260.7°, *terephthaloyl*-, m.p. 279°, and *isophthaloyl-biscamphorquinonehydrazone*, m.p. 274°. The hydrazides with camphorylthiocarbimide give *carbonyl*-, m.p. 208°, [α]₅₇₈₀ 28.2°, [α]₅₄₆₁ 32.9°, *oxalyl*-, m.p. 245°, [α]₅₇₈₀ 30.4°, [α]₅₄₆₁ 50.7°, *malonyl*-, m.p. 185°, [α]₅₇₈₀ 29.8°, [α]₅₄₆₁ 50.7°, *succinyl*-, m.p. 176°, [α]₅₇₈₀ 39.7°, [α]₅₄₆₁ 50.5°, *glutaryl*-, m.p. 201°, [α]₅₇₈₀ 12.4°, [α]₅₄₆₁ 18.6°, and *adipoyl-biscamphorylthiocarbamylhydrazide*, m.p. 207°, [α]₅₇₈₀ 33.4°, [α]₅₄₆₁ 42.4°. The vals. of [α] and [*M*] and of the dispersions

are discussed and compared with the results of Frankland (J.C.S., 1912, 101, 654) and Hilditch (*ibid.*, 1909, 95, 1578). Attempts to prepare a series of compounds for which [*M*] might be exalted (cf. this vol., 659) failed. Neither (I) nor its hydrazone (II) condenses with *p*-NH₂·C₆H₄·CHO (III). (II) with *p*-NHAc·C₆H₄·CHO (IV) gives *p*-acetamidobenzylidenecamphorquinone- α -hydrazone, m.p. 232°, [α]_D 95.85° (oxime, m.p. 183°, [α]_D 546.3°; semicarbazone, m.p. 195°, [α]_D 102.4°; phenylhydrazone, m.p. 205°, [α]_D 150.9°), but on hydrolysis (KOH) this gives (IV) (oxime, m.p. 207°) and camphor or (dil. acid) azocamphane and (III). Neither deacetylation of *terephthaloyl-di-p*-acetylphenylenediamine, m.p. 350° [from *p*-NH₂·C₆H₄·NHAc and *p*-C₆H₄(COCl)₂ (V) in AcOH] nor reduction of *terephthaloyl-di-p*-nitroanilide, m.p. 295° [from (V) and *p*-NO₂·C₆H₄·NH₂] or NN'-*di-p*-azobenzene-*terephthaloyldiamide* [from (V) and *p*-NH₂·C₆H₄·N·NPh] gives the desired diamine. Reduction (Sn-HCl) of 4:4'-*dinitro-di- α -naphthylcarbamide*, m.p. 275° (from 4-nitro- α -naphthylamine and Ph₂CO₃ at 190—210°), gives the *hydrochloride* (VI) of 4:4'-*diamino-di- α -naphthylcarbamide*, which with KCNO affords 4:4'-*dicarbamidodi- α -naphthylcarbamide*. (I) does not condense with 4-*p*-aminobenzeneazo- α -naphthylamine or 2:7-diamino-9:10-phenanthraquinol (modified prep.) and with (VI) it gives tars. (All [α] are + and in EtOH.) F. S. H. H.

Essential oils from East Africa.—See B., 1934, 987, 988.

Essential oil of *Calythrix virgata*.—See B., 1934, 988.

Action of mixed organo-magnesium compounds on *N*-disubstituted amides of β -2-furylacrylic acid. N. MAXIM and I. ZUGRAVESCU (Bull. Soc. chim., 1934, [v], 1, 1087—1099).—Grignard reagents react with the above amides to give saturated *N*-disubstituted amides in yields of 70—75% (cf. A., 1906, i, 96). β -2-Furylacryloyl chloride in C₆H₆ with the corresponding *sec*-amines (2 mols.) gives the *N*-diethylamide (I), b.p. 186°/15 mm., *N*-methyl-anilide (II), m.p. 117.5°, *N*-ethyl-anilide (III), b.p. 215°/11 mm., m.p. 60°, and *N*-diphenylamide (IV), m.p. 181.5°, of the acid. (IV) with MgEtBr, MgPr^{*a*}Br, and MgPhBr gives β -(2-furyl)-valeroyl-, b.p. 253°/15 mm., *hexoyl*-, b.p. 241°/10 mm., m.p. 47°, and β -phenylpropionyl-diphenylamide, b.p. 291°/12 mm., m.p. 83°, respectively, which on hydrolysis (20% KOH) afford β -2-furyl-valeric, b.p. 145°/17 mm. (*Et* ester, b.p. 114°/18 mm.), *hexoic*, b.p. 148°/11 mm. (*Et* ester, b.p. 126°/16 mm.), and β -2-phenylpropionic acid, m.p. 105° (*chloride*, b.p. 88°/31 mm.; *amide*, m.p. 137.5°; *Et* ester, b.p. 172°/15 mm.). Similarly (I), (II), and (III) with MgEtBr yield the diethylamide, b.p. 196°/41 mm., the methyl-, b.p. 130°/3 mm., and ethyl-anilide, b.p. 211°/27 mm., of β -2-furylvaleric acid and with MgPhBr the diethylamide, b.p. 218°/23 mm., and the methyl-, b.p. 213°/11 mm., and ethyl-anilide, b.p. 236°/14 mm., of β -2-furyl- β -phenylpropionic acid, respectively. These amides cannot be hydrolysed by KOH, and acid hydrolysis gives resinous products.

F. S. H. H.

Synthesis of *p*-substituted β -furyl- β -alkyl- and β -furyl- β -aryl-propiophenones. N. MAXIM and J.

ANGELESCO (Bull. Soc. chim., 1934, [v], 1, 1128—1133; cf. A., 1933, 281).—*Furfurylidene-p-methoxyacetophenone*, m.p. 75°, with MgEtBr and MgPr·Br affords *p-anisyl β-2-furyl-n-butyl ketone*, b.p. 218°/14 mm. (*semicarbazone*, m.p. 161°), and *p-anisyl β-2-furyl-n-amyl ketone*, b.p. 220°/12 mm. (*semicarbazone*, m.p. 149°). *p-Chloro-*, b.p. 200°/10 mm. (*semicarbazone*, m.p. 122°), and *p-bromo-phenyl β-2-furyl-n-amyl ketone*, b.p. 215°/8 mm. (*semicarbazone*, m.p. 105°), *p-chloro-*, b.p. 242°/15 mm., m.p. 79°, and *p-bromo-phenyl β-2-furyl-β-phenylethyl ketone*, b.p. 268°/6 mm., m.p. 78°, and the *semicarbazone*, m.p. 125°, of *p-tolyl β-2-furyl-δ-methyl-n-amyl ketone* are described. *p*-Substituents in the C₆ ring favour the reaction in the order Me < Cl < Br < OMe. F. S. H. H.

Action of phosphorus pentahalides and thionyl chloride on saturated and unsaturated αδ-diketones and 2:5-diphenylfurans. R. E. LUTZ and F. N. WILDER (J. Amer. Chem. Soc., 1934, 56, 2145—2149).—3:4-Dichloro-2:5-diphenylfuran (I) is obtained in 35—95% yield from the following compounds and PCl₅ at 100°: 2:5-diphenyl- (II), and 3-chloro- (III), 3-acetoxy- (IV), 4-chloro-3-acetoxy- (V), and 3:4-diacetoxy-2:5-diphenyl-furan; αβ-dibenzoyl-ethylene oxide (VI); *dl*- and *meso*-αβ-dichloro-αβ-dibenzoyl-ethane; αβ-dibenzoyl-ethyl chloride; *trans*-αβ-dibenzoyl-ethylene (VII); *trans*-α-chloro-αβ-dibenzoyl-ethylene. (I) is also obtained from the following compounds and PCl₅ at 25—40°: α-chloro-β-hydroxy-αβ-dibenzoyl-ethane (VIII); CPh·CO·CH·CPh·OR (R=Me or Et); *cis*-α-chloro-αβ-dibenzoyl-ethylene (IX); α-hydroxy-αβ-dibenzoyl-ethylene (X) and its Me ether (XI); α-chloro-γδ-diketo-αδ-diphenyl-Δ^α-butene, m.p. 133—133.5° [prepared from (X) or (XI) and SOCl₂]. (IV) and PCl₅ at 25—40° give (V); αβ-dibenzoyl-ethyl alcohol (XII) and its Me ether similarly afford α-chloro-αβ-dibenzoyl-ethane (XIII), whilst *cis*- and *trans*-dibenzoyl-ethylenes give (III). 3:4-Dibromo-2:5-di-*p*-bromophenylfuran is formed from (II), (IV), (VII), and (CH₂Bz)₂ with PBr₃ at 100° and from (XI) and CPh·CO·CH·CPh·OEt at 25—40°. (I) is also obtained from (VI), (VIII), or (IX) and SOCl₂; (VII) and (XII) similarly give (XIII). (I), PCl₅, and POCl₃ give *cis*-αβ-dichloro-αβ-dibenzoyl-ethylene. H. B.

Furan dyes. I. O. ASCHAN and A. SCHWALBE (Finska Kem. Medd., 1934, 43, 48—54, and Ber., 1934, 67, [B], 1830—1833).—Furfuraldehyde and NH₂Ph·HCl give the compound, NPh·CH·CH·CH·C(OH)·CH·NPh·HCl (I), transformed by Ac₂O and NaOAc under defined conditions into *δ-acetanilido-α-acetoxy-Δ^α-pentadiene* (II), NPhAc·CH·CH·CH·C(OAc)·CH·O, m.p. 184°, and two *Ac*-aldehydes, m.p. 132° (III), and m.p. (indef.) 145° (IV), for which the respective structures, NPh·CH·CH·CH·C(OAc)·CHO and NPhAc·CH·CH·CH·C(OH)·CHO, are available. (II) gives a *semicarbazone*, m.p. 240°, and *phenylhydrazone*, m.p. 206°; with NH₂Ph·HCl in H₂O it affords the *anil hydrochloride*, NPhAc·CH·CH·CH·C(OAc)·CH·NPh·HCl, m.p. 169—170°. (III) and *p*-C₆H₄Me·NH₂·HCl or NH₂Ph·HCl yield, respectively, *dyes*, m.p. 157—160° (decomp.) and about 157° (decomp. after darkening at 140—

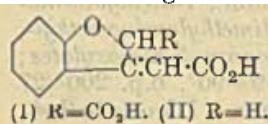
150°. A dye from (IV) and NH₂Ph·HCl is described. Direct acetylation of (I) under modified conditions gives a *product*, C₁₉H₁₉O₂N₂Cl, m.p. 154°, unchanged by boiling Ac₂O. H. W.

Carboxylated aminocoumarans. GOMEZ (J. Pharm. Chim., 1934, [viii], 20, 337—342).—By successive treatments with Br and NaOEt, *Me 2-acetoxy-3-allylbenzoate*, b.p. 187—190°/30 mm. (from the OH-ester), is converted into *Me 1-bromomethylcoumaran-6-carboxylate*, b.p. 177°/0.912 mm., which gives *Me 1-diethylaminomethylcoumaran-6-carboxylate*, b.p. 184°/ < 1 mm. [*hydrochloride*, m.p. 182°; *amide*, m.p. 113° (*hydrochloride*, m.p. 207—208°); *acid*], with NHEt₂ at 120—130°. Derivatives of the *m*- and *p*-carboxylic acids are prepared by similar methods, the following new *Me* esters being described: 3-allyloxybenzoate, b.p. 167—170°/30 mm.; 3-hydroxy-4-allylbenzoate, m.p. 61°, b.p. 195°/30 mm. (*acetate*, b.p. 93—95°/30 mm.); 1-bromomethyl-, b.p. 167°/0.992 mm., 1-diethylaminomethyl-, b.p. 167°/1.312 mm., 1-dimethylaminomethyl-, b.p. 175—180°/1.28 mm., -coumaran 5-carboxylates; 4-hydroxy-3-allylbenzoate, m.p. 89—90°, b.p. 200°/27 mm. (*acetate*, b.p. 195—196°/28 mm.), 1-bromomethyl-, b.p. 165—169°/0.976 mm., 1-diethylamino-, b.p. 158°/0.736 mm. (*hydrochloride*, m.p. 147—148°; *free acid*, m.p. 141°), -coumaran 4-carboxylates. In their pharmacological behaviour the carboxylated derivatives resemble the parent aminocoumarans, but in addition they show hyperthermic and local anaesthetic properties (cf. A., 1933, 1168). S. C.

Pyrone series. II. Chromones and coumarins derived from 2-hydroxy-4-methoxy-aceto- and -propio-phenones. I. M. HEILBRON, D. H. HEY, and B. LYTHGOE (J.C.S., 1934, 1581—1583).—NaOPr, Pr₂O, and 2-hydroxy-4-methoxyacetophenone (I) give 7-methoxy-3:4-dimethylcoumarin and a little of the 7-OH-compound, whilst NaOBu and Bu₂O with (I) form 7-methoxy-4-methyl-3-ethylcoumarin, hydrolysed to 2:4-dimethoxy-β-methyl-α-ethylcinnamic acid, m.p. 127.5°, and some 7-methoxy-2-propylchromone. NaOPr, Pr₂O, and 2-hydroxy-4-methoxypropio-phenone yield 7-methoxy-3-methyl-2-ethylchromone and some 7-methoxy-3-methyl-4-ethylcoumarin, m.p. 89°, whilst NaOBu and Bu₂O similarly afford 7-hydroxy-3-methyl-2-propylchromone, m.p. 212°, its OMe-derivative (chiefly), and some 7-methoxy-3:4-diethylcoumarin (?), m.p. 63°. The product depends on the ketone, the Me ketone giving chiefly the coumarin and the Et ketone the chromone. F. R. S.

4-Bromomethylcoumarins. Synthesis from phenols and γ-bromoacetoacetic ester. B. B. DEY and Y. SANKARANARAYANAN (J. Indian Chem. Soc., 1934, 11, 687—689).—Condensation of CH₂Br·CO·CH₂·CO₂Et with *m*-cresol in presence of H₂SO₄ affords 7-methyl-4-bromomethylcoumarin, identical with a specimen prepared by bromination of 7-methylcoumarin-4-acetic acid (see following abstract); similar condensation with α- and β-C₁₀H₇·OH gives, respectively, 4-bromomethyl-α- (*loc. cit.*) and β-naphthapyrone, m.p. 197°, hydrolysed by 2N-KOH, respectively, to α-, m.p. 162°, and β-3-naphthodihydro-furylideneacetic acid, m.p. 172°. J. W. B.

Action of chlorine and bromine on coumarin-4- and coumarin-3-acetic acids : coumarin-3- and -4-halogenoacetic acids and 4-halogenomethylcoumarins. B. B. DEY and (MISS) K. RADHABAI (J. Indian Chem. Soc., 1934, 11, 635—650).—Halogenation of coumarin-4-acetic acids in AcOH at 100° gives the 4-halogenoacetic acids together with 4-halogenomethylcoumarins, which are also obtained on heating the halogeno-acids to the m.p. Less decarboxylation occurs with the chloro- than with the bromo-acids. Addition of halogen to the double linking of the pyrone ring is observed only in the case of (XII). The position of the halogen is determined thus : (a) oxidation yields halogen-free salicylic acid derivatives ; (b) boiling alkali completely removes the halogen and gives 1-carboxy-2-coumaranylidene- (I) and 2-coumaranylidene-acetic acids (II) (isomeric with 2-methylcoumarilic acids derived similarly from the 3-halogeno-4-methylcoumarins), respectively.



The acids of type (II) are readily reduced, but could not be oxidised to the corresponding ketones. All attempts to replace halogen in 4-halogeno-

methylcoumarins by CN, OH, NH₂, or NHP, or to prepare Grignard compounds failed. 7-Methylcoumarin-4-acetic acid is converted into 7-methylcoumarin-4-bromoacetic acid (III), m.p. 223° (*Me*, m.p. 162°, and *Et* ester, m.p. 144°), and 7-methyl-4-bromomethylcoumarin (IV), m.p. 236°. (III) and (IV) give rise to 5-methyl-1-carboxy- (V), m.p. 231° (*Me*₂, m.p. 83°, and *Et*₂ ester, m.p. 118°), and 5-methylcoumaranylidene-2-acetic acid (VI), m.p. 107° [anilide, m.p. 161° (*Ba*, *Cu*, and *Ag* salts; *Me* and *Et* esters)], respectively. (VI) with H₂ and PtO₂ in EtOH gives 5-methylcoumaran-2-acetic acid, m.p. 130°. (IV) in COMe₃ is reduced (Zn-Cu) to 4:7-dimethylcoumarin, m.p. 130°, and oxidised (KMnO₄) to *m*-hydroxytoluic acid. Similarly 7-methylcoumarin-4-chloroacetic acid, m.p. 170° (decomp.) (*Me*, m.p. 160°, and *Et* ester, m.p. 158°), gives rise to 7-methyl-4-chloromethylcoumarin, m.p. 214° (V), and (VI); 6-methylcoumarin-4-bromoacetic acid, m.p. 168° (decomp.) (*Me*, m.p. 170°, and *Et* ester, m.p. 146°), gives 6-methyl-4-bromomethylcoumarin (VII), m.p. 177° 4-methyl-1-carboxy- (VIII), m.p. 244° (*Me*₂, m.p. 102°, and *Et*₂ ester, m.p. 182°), 4-methyl-2-coumaranylidene-acetic acid (IX), m.p. 104°, and *p*-hydroxytoluic acid; 6-methylcoumarin-4-chloroacetic acid (X), m.p. 162° (decomp.) (*Me*, m.p. 156°, and *Et* ester, m.p. 146°), gives 6-methyl-4-chloromethylcoumarin (XI), m.p. 149°, (VIII) and (IX) [(X), (XI), and (VIII) were incorrectly formulated by Dey, J.C.S., 1915, 107, 1606]; 7-methoxycoumarin-4-bromoacetic acid, m.p. 168° (decomp.), gives 7-methoxy-5-bromomethylcoumarin, m.p. 204°, and 5-methoxy-2-coumaranylideneacetic acid, m.p. 126°; coumarin-4-bromoacetic acid, m.p. 135° (decomp.), gives 4-bromomethylcoumarin, m.p. 176°, and 2-coumaranylidene-acetic acid, m.p. 93°; βx-5:6-naphthapyrone-4-bromoacetic acid, m.p. 190° (decomp.), gives 4-bromomethyl-βx-5:6-naphthapyrone, m.p. 197°, dihydro-βx-4:5-naphthafuranylidene-3-acetic acid, m.p. 130° (*Ag* salt), and 1-hydroxy-2-naphthoic acid. Halogenation of αβ-5:6-naphthapyrone-4-acetic acid (XII) affords 3-bromo- (XIII), m.p. 188° (decomp.) (*Me*, m.p. 172°,

and *Et* ester, m.p. 139°), and 3-chloro 5:6-naphthapyrone-4-acetic acid (XIV), m.p. 152° (decomp.) (*Et* ester, m.p. 134°), and decarboxylation of these acids gives 3-bromo-, m.p. 146° (lit. 145°), and 3-chloro-4-methyl-αβ-5:6-naphthapyrone (XV) (this vol., 1008). (XIII) and (XIV) with hot alkali give 2-carboxy-αβ-4:5-naphthafuran-3-acetic acid, m.p. 252° (decomp.) (*Me*₂, m.p. 158°, and *Et*₂ ester, m.p. 104°); (XV) gives 4-methyl-βx-2:3-naphthafuran-5-carboxylic acid, m.p. 242° (lit. 240°), and the coumarinic acid. Bromination of coumarin-3-acetic acid gives (probably) the -3-bromoacetic acid, m.p. 200° (*Me* ester, m.p. 94°), which could not be decarboxylated; alkali converts it into a substance, m.p. 142°, formulated as benzopyran-2-carboxylic acid (*Ag* salt). F. S. H. H.

Xanthen group. E. A. H. ROBERTS and R. ROBINSON (J.C.S., 1934, 1650—1651).—1:3:6:8-Tetrahydroxanthylum chloride (I) and alkaline Na₂S₂O₄ yield 1:3:6:8-tetrahydroxanthene, converted by Br into a tribromotetrahydroxanthylum bromide, but oxidised by chloranil to (I). Chloranil is useful as an oxidising agent for leuco-derivatives in the xanthylum salt and similar series. F. R. S.

Syntheses of flavones containing the methylphloroglucinol nucleus. S. FURUKAWA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1098—1107).—Methylphloroglucinol and MeCN (Hoesch) afford methylphloracetophenone (I), m.p. 211—212°, which with Bz₂O and NaOBz followed by hydrolysis gives 6(or 8)-, m.p. 251.5—252° (*Ac*₂ derivative, m.p. 180.5—181°), and 8(or 6)-methylchrysin, m.p. 308—310° (*Ac*₂ derivative, m.p. 196.5—197.5°). Similarly, (I) with anisic anhydride gives methylacetins, m.p. 190.5—191° [*Ac*₃ and (*OMe*)₃-derivatives, m.p. 234—235° and 200—201°, respectively], 293° [*Ac*₃ and (*OMe*)₃-derivatives, m.p. 198—200° and 194—195°, respectively], and 325° (decomp.) [*Ac*₃ and (*OMe*)₃-derivatives, m.p. 213—215° and 226.5—227.5°, respectively]. J. L. D.

Constitution of tannins. III. Hemlock tannin. Synthesis of bis-(7:8:3':4'-tetrahydroxy)flavpinacol. A. RUSSELL and J. TODD (J.C.S., 1934, 1506—1508; cf. this vol., 416, 1107).—Gallacetophenone tribenzoate and protocatechualdehyde dibenzoate in dry EtOAc at 0° give with HCl during 60 hr. 2:3:4:3':4'-pentabenzoyloxychalkone, m.p. 85° after sintering, hydrolysed by KOH in N₂ to 2:3:4:3':4'-pentahydroxychalkone, m.p. 233°, which is reduced (Zn-HCl) in EtOH to amorphous bis-(7:8:3':4'-tetrahydroxy)flavpinacol (I), which has the same percentage composition and properties as hemlock tannin (II) (prep. described). (II) with alkali affords no s-C₆H₃(OH)₃, which supports (I) rather than bis-(5:7:3':4'-tetrahydroxy)flavpinacol with which (I) is very similar qualitatively. J. L. D.

Synthesis of 5-hydroxyflavone. S. SUGASAWA (J.C.S., 1934, 1483—1484).—See this vol., 1107.

Attempted flavonol synthesis. E. H. CHARLESWORTH and R. ROBINSON (J.C.S., 1934, 1651—1652).—*o*-Vanillin and ω-3:4-triacetoxyacetophenone condense to 3:3':4'-trihydroxy-8-methoxyflavylum chloride (+H₂O). *o*-Vanillaldoxime with Ac₂O at room

temp. gives an *Ac* derivative, m.p. 101° (oximino-group acetylated), whilst with *AcCl* it forms a *Ac*₂ derivative, m.p. 100°. The *Ac*₂ derivative with boiling *Ac*₂O affords *o*-vanillonitrile, m.p. 61°, which does not condense with ω :4-dihydroxyacetophenone.

F. R. S.

Derivatives of hydroxyquinol, including a synthesis of pyrylium salts of anthocyanidin type. XXII. (MISS) M. HEALEY and R. ROBINSON (J.C.S., 1934, 1625—1631).—2:4:5-Trihydroxybenzaldehyde (I) gives the *Ac*₃ derivative, m.p. 115°, and a 4-*OBz*-derivative, m.p. 184°, which condenses with ω :3:4-triacetoxyacetophenone to give a flavylum salt. Hydroxyquinol (II) and methoxyacetoneitrile condense (*ZnCl*₂-*HCl*) to 2:4:5-trihydroxy- ω -methoxyacetophenone (+*H*₂O), m.p. 95°, which with *NaOAc*-*Ac*₂O and subsequent hydrolysis yields 6:7-dihydroxy-3-methoxy-2-methylchromone, m.p. 272° (decomp.) (diacetate, m.p. 129—130°; *Me*₂ ether, m.p. 185.5—186°), demethylated (III) to the 3:6:7-(*OH*)₃-compound. 2:4:5-Trihydroxy-1:3-diacetylbenzene, m.p. 186° (*Ac*₃ derivative, m.p. 144°; *Bz*₃ derivative, m.p. 140.5°), obtained from 2:4:5-*C*₆*H*₃(*OAc*)₃ and *AlCl*₃, and *CH*₂*N*₂ yield a mixture containing a homologue of hydroxydimethoxydiacetylbenzene, m.p. 89.5—90°. (II), *HCO*₂*H*, and *HCl* give 2:3:6:7-tetrahydroxyxanthylum chloride (III) (+2.5*H*₂O), the *HCO*₂*H* entering the condensation. (I) and (II) condense (*HCO*₂*H*-*HCl*) to give (III), a xanthylum salt, *C*₁₃*H*₉*O*₅*Cl*·*H*₂*O*, and a substance *C*₁₉*H*₁₅*O*₈*Cl*. (I) with ω :4-diacetoxyacetophenone similarly yields 3:6:7:4'-tetra- (+*H*₂O), with ω :3:4-triacetoxyacetophenone gives 3:4':3:6:7-penta- (+3*H*₂O or +*H*₂O), and with ω :3:4:5-tetra-acetoxyacetophenone forms 3':4':5':3:6:7-hexa-hydroxyflavylum chloride (+0.5*H*₂O) (picrate). The effect of transposition of *OH* from position 5 to 6 is to make the salts much yellower than the anthocyanins in acid and alkaline solution.

F. R. S.

Synthesis of anthocyanins. XXIII. Glucosides of petunidin chloride. (MISS) J. C. BELL and R. ROBINSON. XXIV. Cyanidin 3-biosides and a synthesis of mecocyanin. (MISS) K. E. GROVE, M. INUBUSE, and R. ROBINSON. XXV. Pelargonidin 3-galactoside. P. V. NAIR and R. ROBINSON. XXVI. Resocallistephin and reso-ænin chloride. (MISS) K. E. GROVE, L. F. LEVY, P. V. NAIR, and R. ROBINSON (J.C.S., 1934, 1604—1608, 1608—1611, 1611—1614, 1614—1619).—XXIII. ω -Diazo-3-methoxy-4:5-diacetoxyacetophenone and *HCO*₂*H* give the ω -*OH*-compound (+0.5*H*₂O), m.p. 86—87°, which with tetra-acetylglucosidyl bromide forms ω -*O*-tetra-acetyl- β -glucosidoxy-3-methoxy-4:5-diacetoxyacetophenone (I), m.p. 67—69°. (I) and 2-*O*-benzoylphloroglucinaldehyde (II) condense (*EtOAc*-*HCl*) to a benzoylhexa-acetylpetunidin monoglucoside chloride, hydrolysed [*Ba*(*OH*)₂-*MeOH*] to 3-*O*-glucosidylpetunidin chloride, isolated as the picrate. (I) and 2-*O*-tetra-acetyl- β -glucosidylphloroglucinaldehyde give 7-hydroxy-3:5-di-(*O*-tetra-acetyl- β -glucosidoxy)-3'-methoxy-4':5'-diacetoxyflavylum chloride, which with *MeOH*-*HCl* in *H*₂ yields petunidin 3:5-diglucoside chloride, which could not be separated from inorg. materials. The colour reactions, distribution no., and

absorption spectra of the mono- and di-glucoside have been determined.

XXIV. Hepta-acetylcellobiosidyl bromide and ω -hydroxy-3:4-diacetoxyacetophenone yield ω -*O*-hepta-acetylcellobiosidoxy-3:4-diacetoxyacetophenone, which with (II) in *EtOAc*-*HCl* forms 3-cellobiosidoxy-7:3':4'-trihydroxy-5-benzoyloxyflavylum chloride (+4*H*₂O), hydrolysed to 3-*O*-cellobiosidylcyanidin chloride (+4*H*₂O). Similarly ω -*O*-hepta-acetyl-lactosidoxy- (+0.5*H*₂O), m.p. 78—80°, -maltoxydoxy- (+0.5*H*₂O), m.p. 88°, and -gentiobiosidoxy-3:4-diacetoxyacetophenone (+0.5*H*₂O), m.p. 70—72°, yield the corresponding 3-*O*-lactosidyl- (+1.5*H*₂O), -maltoxydoxy- and -gentiobiosidyl-cyanidin chloride (mecocyanidin chloride, identical with the natural compound) (+3.5*H*₂O).

XXV. ω -*O*-Tetra-acetyl- β -glucosidoxy-4-acetoxyacetophenone and (II) give 3- β -glucosidylpelargonidin chloride (+2*H*₂O) (callistephin chloride), identical with the anthocyanin of scarlet carnations. ω -Hydroxy-4-acetoxyacetophenone and *O*-tetra-acetyl-galactosidyl bromide form ω -*O*-tetra-acetyl-galactosidoxy-4-acetoxyacetophenone, which with (II) leads to 7-hydroxy-3-*O*-tetra-acetyl-galactosidoxy-5-benzoyloxy-4'-acetoxyflavylum chloride (+2*H*₂O), hydrolysed to 3-galactosidylpelargonidin chloride (+4*H*₂O), isolated as the picrate. 2-*O*-(*O*-Triacetylalloyl)phloroglucinaldehyde, m.p. 148—150°, condenses with ω :3:4-trihydroxyacetophenone (III) to 5-*O*-galloylcyanidin chloride (+4*H*₂O), which with *HCl*-*EtOH* gives partly acetylated 5-*O*-galloylcyanidin chloride (+3*H*₂O). Phloroglucinaldehyde and 4-acetoxybenzaldehyde afford 2:4-di-*O*-4-acetoxybenzoylphloroglucinaldehyde (+0.5*H*₂O), m.p. 180—182°, which with (III) gives 5:7-di-*O*-4-hydroxybenzoylcyanidin chloride (+3*H*₂O).

XXVI. ω -*O*-Tetra-acetyl- β -glucosidoxy-4-acetoxyacetophenone (IV) and β -resorcyaldehyde (V) yield the penta-acetate of 7:4-dihydroxy-3- β -glucosidoxyflavylum chloride (+2.5*H*₂O), which is hydrolysed to resocallistephin chloride (+2.5*H*₂O), isolated as the picrate. Similarly the penta-acetate (+2.5*H*₂O) of 7:4'-dihydroxy-3-galactosidoxyflavylum chloride (+2*H*₂O) and the picrate are prepared. The 3-*OMe*-derivative of (IV) and (V) give a flavylum salt (+2.5*H*₂O), hydrolysed to reso-oxycoccicyanin chloride (+0.5*H*₂O), isolated as the picrate (+2*H*₂O). Condensation of (V) and the required component gives reso-ænin chloride (+2*H*₂O), hydrolysed (*HCl*) to reso-ænidin chloride (+*H*₂O), also obtained by direct condensation. 2-*O*-Benzoyl-4-*O*-tetra-acetyl- β -glucosidylphloroglucinaldehyde and ω :4-dihydroxy-3:5-dimethoxyacetophenone condense to γ - β -glucosidylmalvidin chloride. Distribution properties indicate that probably fisetin and resocallistephin are not associated in either aq. or isoamyl-alcoholic solution.

F. R. S.

Synthesis of pyrylium salts of anthocyanidin type. XXI. 6-Hydroxy-derivatives of the chief anthocyanidins. E. H. CHARLESWORTH and R. ROBINSON (J.C.S., 1934, 1619—1624).—Antiarolaldehyde (I) and ω -acetoxyacetophenone (II) condense to 3-hydroxy-5:6:7-trimethoxyflavylum chloride (+*H*₂O), demethylated to the 3:5:6:7-(*OH*)₄-compound (+*H*₂O). 2-*O*-Benzoylphloroglucinaldehyde and (II) give 5-*O*-benzoylgalanginidin chloride, hydrolysed to galanginidin chloride (+*H*₂O). (I) and ω :4-diacet-

oxyacetophenone condense to 3 : 4'-*di*hydroxy-5 : 6 : 7-trimethoxyflavylium chloride ($+H_2O$), hydrolysed to the 3 : 5 : 6 : 7 : 4'-(OH)₅-compound ($+H_2O$), whilst ω :3:4-triacetoxyacetophenone gives 3:3':4'-*tri*hydroxy-5:6:7-trimethoxyflavylium chloride ($+1.5H_2O$), demethylated to the 3 : 5 : 6 : 7 : 3' : 4'-(OH)₆-compound (quercetageninidin chloride) ($+2H_2O$). (I) and 3 : 4 : 5-tetra-acetoxyacetophenone yield 3 : 3' : 4' : 5'-tetrahydroxy-5 : 6 : 7-trimethoxyflavylium chloride [picrate ($+H_2O$)], which forms the 3 : 5 : 6 : 7 : 3' : 4' : 5'-(OH)₇-derivative ($+2H_2O$). The colour reactions and absorption spectra of the salts have been examined: they are all redder than the corresponding anthocyanins. F. R. S.

Synthesis of benzopyrylium compounds. I. M. GOSWAMI and A. CHAKRAVARTY (J. Indian Chem. Soc., 1934, 11, 713—714).—By condensation of the phenol with coumarin in presence of $POCl_3$ (A., 1933, 281) are prepared 4'-methoxy-, m.p. 125°, 3' : 4'-*di*methoxy-, m.p. 192°, 3' : 4'-*di*methoxy-4 : 7-dimethyl-, m.p. 180°, and 2' : 4'-*di*methoxy-4 : 7-dimethyl-, m.p. 150°, -2-phenylbenzopyrylium ferrichloride.

J. W. B.

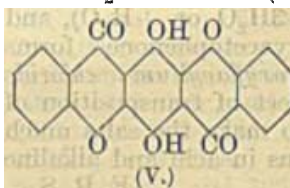
Styrylpyrylium salts. XVI. Conversion of coumarins into isospiropyran. I. M. HEILBRON and G. F. HOWARD (J.C.S., 1934, 1571—1572; cf. A., 1933, 614, 1169).—7-Methoxy-4-methylcoumarin with $MgPhBr$ in dry Et_2O at room temp., followed by treatment with dry HCl , gives some 7-methoxy-2-phenyl-4-methylbenzopyrylium chloride, but mainly 7-methoxy-2 : 2-diphenyl-4-methyl- Δ^3 -chromone, m.p. 90—91°. Similarly, 7-methoxy-3 : 4-dimethylcoumarin with excess of $MgPhBr$ in hot Et_2O gives 7-methoxy-2 : 2-diphenyl-3 : 4-dimethyl- Δ^3 -chromene, m.p. 162—163°. 7-Methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (A., 1926, 1042) and β -naphthol-1-aldehyde (I) in $EtOH$ containing dry HCl at 0° give 7-methoxy-2-phenyl-3-methylbenzo- β -naphthaisospiropyran, m.p. 166—167°, which exhibits the typical colour phenomenon (at a max. in the 7-methoxy-2 : 3-diphenylbenzo-compound below) of the *spiropyran* series with an unsubstituted 3'-position (cf. A., 1927, 884). 6-Methoxy-3 : 4-dimethylcoumarin, m.p. 177—178° (from the OH-compound and also obtained from p -OMe- C_6H_4 -OH and $CHMeAc$ - CO_2Et), with $MgPhBr$ (2 mols.) gives 6-methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (cf. A., 1931, 1070) [ferrichloride, m.p. 80° (decomp.)], which with (I) gives 6-methoxy-2-phenyl-3-methylbenzo- β -naphthaisospiropyran, m.p. 168—169°. 7-Methoxy-3-phenyl-4-methylcoumarin, m.p. 106—107° (lit., 102°) gives, as above, 7-methoxy-2 : 3-diphenyl-4-methylbenzopyrylium chloride, which with (I) gives 7-methoxy-2 : 3-diphenyl-4-(β -2'-hydroxy-1 naphthavinyl)benzopyrylium chloride (ferrichloride), hydrolysed to the isospiropyran, m.p. 173° ($+H_2O$, m.p. 126—127°), which in Et_2O gives a deep blue colour with a drop of $AcOH$. 7-Methoxy-3 : 4-diphenylcoumarin, m.p. 168° (from the OH-compound and Me_2SO_4), with $MgPhBr$ gives 7-methoxy-2 : 3 : 4-triphenylbenzopyrylium chloride [ferrichloride, m.p. 140—142° (decomp.)]. J. L. D.

Pyrylium salts with two fused benzopyran nuclei. E. KELLER and R. ROBINSON (J.C.S., 1934, 1533—1535).—7-Methoxychromanone (I) (prep. de-

scribed; cf. A., 1926, 732) and β -resorcyraldehyde in $EtOAc$ containing dry HCl afford 7-hydroxy-2 : 3-[7'-methoxychromeno-(4' : 3')]benzopyrylium chloride; reduction with $Pt-H_2$ is incomplete, but with $Zn-AcOH$ affords a dimeride (?). Similarly, (I) with *o*-vanillin gives 8-methoxy-2 : 3-[7'-methoxychromeno-(4' : 3')]benzopyrone [ferrichloride, m.p. 202° (not sharp)]. With 2-*O*-benzoylphloroglucinaldehyde and 2-hydroxy-4 : 5-dimethoxybenzaldehyde, (I) gives 7-hydroxy-5-benzoyloxy- and 6 : 7-dimethoxy-2 : 3-[7'-methoxychromeno-(4' : 3')]benzopyrylium chloride, the latter of which gives a ferrichloride identical with that of Robinson *et al.* (A., 1926, 732). (I) with 6-aminopiperonal in boiling $EtOH$ containing 20% aq. KOH affords 6 : 7-methylenedioxy-2 : 3-[7'-methoxychromeno-(4' : 3')]quinoline, isolated as the *picrate*, m.p. about 244°. J. L. D.

Formation and reactions of meso-dihydroxy-chromonoxanthenes and reactions of anthraquinone.

H. LIEBERMANN [with G. LEWIN, A. GRUHN, E. GOTTESMANN, D. LISSER, and K. SCHONDA (Annalen, 1934, 513, 156—179).— Et 2 : 5-dichloro- (I) or 2 : 5-dibromo- (II) *p*-benzoquinone-3 : 6-dicarboxylate, $PhOH$, and C_5H_5N in $COMe_2$ give Et 2 : 5-diphenoxy-*p*-benzoquinone-3 : 6-dicarboxylate, m.p. 171°, reduced ($Na_2S_2O_4$ in aq. $COMe_2$) to the Et ester, m.p. 176° (Ac_2 derivative, m.p. 168°), of 2 : 5-dihydroxy-3 : 6-diphenoxyterephthalic acid (III), m.p. 268° (darkens > 200°) [(NH_4)₂, Ag_2 , Ag_4 , Ba , and Ba_2 salts]. (III) heated with $BzCl$ and a little conc. H_2SO_4 gives the Bz_2 derivative (IV) of *ms*-dihydroxychromono-



xanthone (V), m.p. 406° (Ac_2 derivative). (IV) is converted into (V) by hydrolysis (cold conc. H_2SO_4) or by heating with NH_3Ph . KOH -fusion of (V) affords o -OH- C_6H_4 - CO_2H . Et 2 : 5-di- β -naphthoxy-*p*-benzoquinone-3 : 6-dicarboxylate, m.p. 175° [from (I) or (II) and β - $C_{10}H_7$ -OH in $COMe_2$ - C_5H_5N], is similarly reduced to the Et ester, m.p. 220° (Ac_2 derivative, m.p. 196°), of 2 : 5-dihydroxy-3 : 6-diphenoxyterephthalic acid (VI), m.p. 266° (darkens > 200°) [(NH_4)₂ salt], which with $BzCl$ -conc. H_2SO_4 gives 9 : 10-dihydroxy-1 : 2 : 5 : 6-dibenzochromonoxanthone (VII), m.p. 438° (Ac_2 derivative), after treatment of the intermediate dibenzoate with NH_3Ph . Et 2 : 5-di-*o*-, m.p. 156°, -*m*-, m.p. 162°, and -*p*-, m.p. 173°, -*tolyl*oxy-, 2 : 5-di-*s*-xylyloxy-, m.p. 147°, 2 : 5-di- α -naphthoxy-, m.p. 180°, 2 : 5-di-*p*-chlorophenoxy-, m.p. 197°, 2 : 5-di-*o*-, m.p. 143°, and -*p*-, m.p. 155°, -*methoxyphen*oxy-, 2 : 5-di-*p*-diphenyloxy-, m.p. 150°, 2 : 5-di-(*o*-*o'*-hydroxyphenylphenoxy)-, m.p. 155°, and 2 : 5-di-(*p*-*p'*-hydroxyphenylphenoxy)-, m.p. 120° (decomp.), -*p*-benzoquinone-3 : 6-dicarboxylates are similarly prepared from the appropriate $ArOH$. These are reduced to the quinol esters, which are then hydrolysed to the acids; the following are prepared: 3 : 6-di-*o*-, m.p. 250°, -*m*-, m.p. 242°, and -*p*-, m.p. 265°, -*tolyl*oxy- (Et esters, m.p. 163°, 156°, and 195°, respectively), 3 : 6-di-*s*-xylyloxy-, m.p. > 300° (Et ester, m.p. 177°), 3 : 6-di- α -naphthoxy-, m.p. 262° (Et ester, m.p. 192°), 3 : 6-di-*p*-chlorophenoxy-, m.p. > 300° (Et ester, m.p. 200°), 3 : 6-di-*o*-, m.p. 254°, and -*p*-, m.p. 275°, -*methoxy*-

phenoxy- (*Et* esters, m.p. 172° and 151°, respectively), 3:6-di-*p*-diphenylthioxy-, m.p. 290° (*Et* ester, m.p. 218°), 3:6-di-(*o-o'*-hydroxyphenylphenoxy)-, m.p. 251° (*Et* ester, m.p. 225°), and 3:6-di-(*p-p'*-hydroxyphenylphenoxy)-, m.p. > 300° (*Et* ester, m.p. 230°), -2:5-dihydroxyterephthalic acids. These are converted [as (III)] into 4:8-, 3:7-, and 2:6-dimethyl-, 1:3:5:7-tetramethyl-, 3:4:7:8-dibenz-, 2:6-dichloro-, 4:8- and 2:6-dimethoxy-, 2:6-diphenyl-, 4:8-di-*o*-hydroxyphenyl-, and 2:6-di-*p*-hydroxyphenyl-*ms*-dihydroxychromonoxanthone, respectively; the colours of these compounds in conc. H_2SO_4 are given.

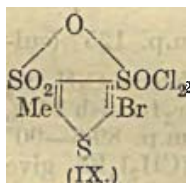
(III) heated with SOCl_2 affords [after hydrolysis (aq. K_2CO_3)] a little 5:8-dihydroxy-7-phenoxyxanthone-6-carboxylic acid, m.p. 240° (*K* salt; *Ac* derivative, m.p. 275°), also convertible into (V). (VI) similarly gives (mainly) (VII) and a little 5:8-dihydroxy-7- β -naphthoxy-3:4-benzoxanthone-6-carboxylic acid, m.p. > 300°, convertible (BzCl) into (VII). (V) heated with NH_2Ph and H_3BO_3 gives *ms*-dianilinochromonoxanthone, m.p. > 400° (*Ac*₂ derivative); *ms*-di-*o*- and -*p*-toluidino- (*Ac*₂ derivative), *ms*-di-*p*-anisidino-, *ms*-di-*p*-toluidino-4:8-dimethoxy-, and *ms*-dianilino-3:4:7:8-dibenzochromonoxanthones are similarly prepared. Anthraquinone (VIII), H_3BO_3 , SnCl_2 , and NH_2Ph afford 9:10-dianilinoanthracene, m.p. 306° [*Bz*₂, m.p. > 320°, *Ac*₂, m.p. 210° (previous sintering), and di(chloroacetyl), m.p. 296°, derivatives], also formed (in smaller yield) from 9:10-diacetoxanthracene, m.p. 270°, H_3BO_3 , and NH_2Ph . Anthraquinone-*p*-tolil, m.p. 165°, is obtained from (VIII), H_3BO_3 , and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$.

Et 2:5-diphenylthiol-*p*-benzoquinone-3:6-dicarboxylate, m.p. 146° [from (I), PhSH (2 mols.), and $\text{C}_6\text{H}_5\text{N}$ in COMe_2], is reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to *Et* 2:5-dihydroxy-3:6-diphenylthiolterephthalate, m.p. 155° [*Ac*₂ derivative, m.p. 162°; corresponding disulphone, m.p. 178° (*Ac*₂ derivative, m.p. 206°)], which is obtained directly (with Ph_2S_2) from (I) and PhSH (4 mols.) in COMe_2 - $\text{C}_6\text{H}_5\text{N}$. 2:5-Dihydroxy-3:6-diphenylthiolterephthalic acid, becomes turbid at 120° and clears at 218° (*Cd* salt), with BzCl -conc. H_2SO_4 gives the Bz_2 derivative of *ms*-dihydroxythiochromonothioxanthone (V, with $\text{O}=\text{S}$), m.p. 436° (decomp.) (also obtained directly from the acid and conc. H_2SO_4). (I), the appropriate alcohol, and $\text{C}_6\text{H}_5\text{N}$ give *Et* 2:5-dimethoxy-, m.p. 118°, 2:5-diethoxy-, m.p. 67°, and 2:5-dibenzoyloxy-, m.p. 118°, -*p*-benzoquinone-3:6-dicarboxylate. *Et* 2:5-dihydroxy-3:6-dimethoxyterephthalate, m.p. 93°, and 2:5-dihydroxy-3:6-diethoxyterephthalic acid, m.p. 196° [Bz_2 derivative, m.p. 233° (decomp.); *Et* ester, m.p. 132° (*Ac*₂ derivative, m.p. 131°)], are prepared.

H. B.

Thiophen series. XXVII. Bromo-derivatives of 2-thiotolene [2-methylthiophen]. W. STEINKOPF (Annalen, 1934, 513, 281—294).—Tri-bromo-2-methylthiophen (I) and $\text{Mg}+\text{MgMeBr}$ in Et_2O give [after treatment with the appropriate reagent (see this vol., 1108)] 3:4-dibromo-2-methylthiophen (II), b.p. 237—237.5°, m.p. 9° [5- NO_2 -, m.p. 96—99°, and 5- ClHg - (III), m.p. 215°, -derivatives], 3:4-dibromo-2-methylthiophen-5-carboxylic acid, m.p. 224°, and 3:4-dibromo-5-iodo-2-methylthiophen, m.p. 66°. (III) and an excess of NaI in COMe_2 afford *Hg* 3:4:3':4'-tetrabromo-2:2'-dimethyl-5:5'-dithienyl,

m.p. 238—240°. *Ph*, m.p. 75°, and *Me*, m.p. 115°, 3:4-dibromo-2-methyl-5-thienyl ketones are prepared (Friedel-Crafts) from (II). (II) and $\text{Mg}+\text{MgMeBr}$ give a mixture, b.p. 172—185°, of 3- (IV) and 4-bromo-2-methylthiophens (5- ClHg -derivatives, m.p. 237—239° and 165—166°, respectively). Successive treatment of 2:5-dibromothiophen with $\text{Mg}+\text{MgMeBr}$ and *p*- $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_3\text{Me}$ in Et_2O affords a little 5-bromo-2-methylthiophen (V), b.p. 171—175.5°. Contrary to Opolski (A., 1905, i, 367; 1906, i, 33), 2-methylthiophen (VI) and Br (approx. 1.5 mols.) in CS_2 give (after treatment with EtOH-KOH) a mixture of Br_1 - (A), b.p. 172—183°, and Br_2 -, b.p. 220—235°, -derivatives; (A) contains (IV) (action of HgCl_2) and (V) [since treatment with 33% oleum affords the 3:4-disulphonian anhydride (VII), decomp. 210° (darkens at 185°)]. (VI) and Br (slightly < 3 mols.) similarly give a mixture from which 3:5-dibromo-2-methylthiophen, b.p. 227.5—230°, m.p. -13° (no reaction with HgCl_2), is isolable; the Br_2 -derivative, m.p. 44—45°, of Opolski (*loc. cit.*) was never obtained. (VII), PCl_5 , and POCl_3 afford 5-bromo-2-methylthiophen-3:4-disulphonyl chloride, m.p. 174°; the diamide and dianilide (VIII) have decomp. 300° and m.p. 162°, respectively. Na 5-bromo-2-methylthiophen-3:4-disulphonate and PCl_5 give the chloride, m.p. 189° [as (IX) or with SO_2 and SOCl_2 interchanged], which reacts very slowly with $\text{C}_6\text{H}_5\text{NH}_2$ yielding (VIII). Reduction (Na-Hg , dil. NaOH) of (VII) affords 2-methylthiophen-3:4-di-



sulphonic acid [chloride, m.p. 138—139°, which with liquid NH_3 gives the diamide, m.p. 250—255° (darkens at 240°)]. 3:5-Dibromo-2-methylthiophen is converted (Grignard) into 3-bromo-2-methylthiophen, b.p. 174—176° [5- NO_2 -, m.p. 71—72°, 5- ClHg -, m.p. 237°, and 5- SO_3H (amide, m.p.

150—151°), derivatives], and 3-bromo-2-methylthiophen 5-carboxylic acid, m.p. 197—198°. *Hg* 3:3'-dibromo-2:2'-dimethyl-5:5'-dithienyl has m.p. 266°. 3:4:5-Tribromo-2-bromomethyl- (X), m.p. 86° (quaternary salt, m.p. 148°, with NPhMe_2), and -2-dibromomethylthiophen (XI), m.p. 60—61°, are prepared from (I) and Br . (X) is hydrolysed (aq. Na_2CO_3) to 3:4:5:3':4':5'-hexabromo-2:2'-dithienyl ether, m.p. 146—148°. (XI) is hydrolysed (CaCO_3 , H_2O in CO_2) to 3:4:5-tribromothiophen-2-aldehyde, m.p. 141—142°, converted by conc. KOH into 3:4:5-tribromo-2-hydroxymethylthiophen, m.p. 127—128° (previous sintering), and 3:4:5-tribromothiophen-2-carboxylic acid (*loc. cit.*).

2-Nitrothiophen forms a 1:1-compound with KOMe and 1:1- and 1:2-compounds with NaOEt ; 2:4-dinitrothiophen forms a 1:3-compound with NaOH and a 1:2-compound with KOH .

H. B.

Ring compounds and polymerides from polymethylene dihalides and dimercaptans. J. R. MEADOW and E. E. REID (J. Amer. Chem. Soc., 1934, 56, 2177—2180; cf. A., 1933, 398).—The product from *s*- $\text{C}_2\text{H}_4\text{Cl}_2$ and an excess of NaSH contains 45—55% of $(\text{CH}_2\text{S})_2$ (I), 16% of $\text{S}(\text{CH}_2\text{CH}_2\text{SH})_2$ (II), b.p. 135—136°/10 mm., m.p. -12.5° (*Ag* salt), about 1.5% of $(\text{CH}_2\text{S}\cdot\text{CH}_2\text{CH}_2\text{SH})_2$, b.p. 168—172°/10 mm., m.p. 15—17° (impure *Ag* salt), 5—6% of 1:4-dithian (III), and 10% of polymerides. $(\text{CH}_2)_3\text{Br}_2$ and EtOH-KSH

(20% excess) at room temp. give 52% of $(\text{CH}_3)_3(\text{SH})_2$ (IV), b.p. 66–68°/18 mm., m.p. $-79 \pm 2^\circ$, and 6% of $\text{S}[(\text{CH}_2)_3\text{SH}]_2$, b.p. 138–140°/6 mm., m.p. -9° to -8° (Ag salt); $(\text{CH}_3\text{Cl}\cdot\text{CH}_2)_2\text{O}$ similarly affords 30% of 1:4-thioxan, 12% of $(\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{O}$, b.p. 103–104°/18 mm., m.p. $-80 \pm 2^\circ$ (Ag salt), and 5% of $\text{S}(\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SH})_2$, b.p. 182–185°/8 mm. (Ag salt). (IV) and CH_2Cl_2 (excess) in $\text{EtOH}\cdot\text{NaOEt}$ give 15% of 1:3-dithian (V), b.p. 207–208°, m.p. 53.3° [sulphone, m.p. 307–308° (corr.)], and polymeric material [which when heated in dry HCl affords a further 32% of (V)]. (I) and $\text{CHBrMe}\cdot\text{CH}_2\text{Br}$ similarly yield 2-methyl-1:4-dithian (12.5%), b.p. 209–210°, m.p. 20°; (IV) and $\text{C}_2\text{H}_4\text{Br}_2$ furnish the disulphide, $(\text{CH}_2)_2\text{S} < \text{S} > (\text{CH}_2)_3$ (8.2%), b.p. 221–222°, m.p.

47° (sulphone, m.p. 287–288°) (cf. *loc. cit.*); (IV) and $(\text{CH}_2)_3\text{Br}_2$ give ditrimethylene 1:5-disulphide (4%), b.p. 245–246°, m.p. -15° (cf. Autenrieth and Wolff, A., 1899, i, 579) [also obtained (in 2% yield) with trimethylene sulphide, m.p. $-64 \pm 1^\circ$, from $(\text{CH}_2)_3\text{Br}_2$ and $\text{EtOH}\cdot\text{Na}_2\text{S}$], and 1% of the tetrasulphide, $\text{S} < \text{S} < \text{S} < \text{S} > \text{S}$, m.p. 46°; (IV) and $(\text{CH}_2)_4\text{Br}_2$

afford 0.6% of the disulphide, $\text{S} < \text{S} > \text{S}$, m.p. 57.5–58° [sulphone, m.p. 185.6° (corr.)], and 1.8% of the tetrasulphide, $\text{S} < \text{S} < \text{S} < \text{S} > \text{S}$, m.p. 61°

(I) and $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{O}$ yield 1.4% of the compound (VI), $\text{O} < \text{S} < \text{S} < \text{S} < \text{S} > \text{O}$, m.p. 125° (sulphone, m.p. 265–266°), also obtained from $s\text{-C}_2\text{H}_4\text{Br}_2$ and $(\text{SH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{O}$; (II) and $s\text{-C}_2\text{H}_4\text{Br}_2$ furnish 1.7% of the hexasulphide (VI with $\text{O}=\text{S}$), m.p. 89.6–90° (sulphone, m.p. $> 330^\circ$); (IV) and $(\text{CH}_2)_5\text{Br}_2$ give 1.1% of the tetrasulphide, $\text{S} < \text{S} < \text{S} < \text{S} > \text{S}$, m.p. 62° (sulphone, m.p. 260–261°). The results show that 9–11-membered rings are rarely obtained.

The above cyclic compounds are accompanied by polymerides. Polymerides containing the following structural units give the products quoted in brackets when heated in dry HCl or in a mol. still at 175–200°: $\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot$ [40–60% of (III)]; $\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot$ [30% of 1:3-dithiolan]; $\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{C}_3\text{H}_6\cdot\text{S}\cdot$ [5–10% of (III) and 5–10% of 2-methyl-1:4-dithian]; $\cdot\text{C}_3\text{H}_6\cdot\text{S}\cdot\text{C}_3\text{H}_6\cdot\text{S}\cdot$ [indefinite]; $\cdot\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot$ [10–15% of (III) and 20% of the monosulphone of (III)]; $\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot$ [5–10% of (III) and 15–20% of 1:4-thioxan]; $\cdot\text{C}_3\text{H}_6\cdot\text{S}\cdot\text{CH}_2\cdot\text{S}\cdot$ [30–40% of (V)]; $\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{C}_6\text{H}_{12}\cdot\text{S}\cdot$ [10% of (III)]; $\cdot\text{C}_2\text{H}_6\cdot\text{S}\cdot\text{C}_4\text{H}_8\cdot\text{S}\cdot$ [10% of $(\text{CH}_2)_4 > \text{S}$]; $\cdot\text{C}_3\text{H}_6\cdot\text{S}\cdot\text{C}_5\text{H}_{10}\cdot\text{S}\cdot$ [15–20% of $(\text{CH}_2)_5 > \text{S}$]. Depolymerisation does not occur unless halogen is present, thus supporting the view of Bennett *et al.* (A., 1927, 958) on inter- and intra-mol. sulphonium addition. The following results further support this view. Heptyl bromide (VII) heated with Bu_2S gives approx. equal amounts of (VII), BuBr , Bu_2S , and Bu heptyl sulphide: $\text{Bu}_2\text{S} + \text{C}_7\text{H}_{15}\text{Br} \rightleftharpoons \text{C}_7\text{H}_{15}\text{SBu} + \text{BuBr} + \text{C}_7\text{H}_{15}\text{S}\cdot\text{Bu}$. $\text{C}_2\text{H}_4\text{Br}_2$ and Bu_2S similarly afford (III) and BuBr , whilst di-*n*-amyl methylene sulphide, $\text{CH}_2(\text{S}\cdot\text{C}_5\text{H}_{11})_2$, and $\text{C}_6\text{H}_4\text{Br}_2$ give amyl bromide and 1:3-dithiolan.

H. B.

Action of amines on quinolinic acid. A. K. DAS and I. B. SARKAR (J. Indian Chem. Soc., 1934, 11, 707–710).—With NH_2Ph (I) quinolinic acid forms the NH_2Ph H salt (II), m.p. 137° with decomp. to the $(\text{NH}_2\text{Ph})_2$ salt (III), m.p. 187° (decomp.). When heated with (I) in AcOH at 100°, or by heating (II) or (III) at $> 187^\circ$, the dianilide, m.p. 225°, is obtained, converted by heating at 225–250° into the anil, m.p. 208° (lit., m.p. 248°, 251°, and 228°), which, refluxed with $\text{NH}_3\text{-MeOH}$, affords quinanilic acid, m.p. 217° (decomp.). Similarly $o\text{-C}_6\text{H}_4(\text{CO}_2\text{H})_2$ affords its NH_2Ph H salt, m.p. 158° (decomp.) (described by Zincke *et al.*, A., 1890, 784, as the anilic acid), the anil, m.p. 205°, and the anilic acid, m.p. 170° (Meyer *et al.*, A., 1899, i, 755).

J. W. B.

Condensation product of pyridine and keten. O. WOLLENBERG (Ber., 1934, 67, [B], 1675–1679).—Passage of keten into $\text{C}_5\text{H}_5\text{N}$ followed by immediate treatment of the solution with H_2O yields only a red resin and dehydracetic acid. If, however, the solution of $\text{C}_5\text{H}_5\text{N}$ in anhyd. COMe_2 , Et_2O , EtOAc , C_6H_6 , light petroleum, or dioxan is kept, a violent reaction occurs with formation of a substance (I), $\text{C}_{13}\text{H}_{11}\text{O}_3\text{N}$, m.p. 204°. (I) is hydrolysed by 0.1*N*- NaOH to an acid (II), $\text{C}_{13}\text{H}_3\text{O}_4\text{N}$, but does not yield $\text{C}_5\text{H}_5\text{N}$ with conc. HCl or molten alkali. (I) contains *tert.* N which does not unite with MeI . Since also (II) does not unite with MeI , (I) must be a lactone. (I) and (II) contain 2 and 3 active H, respectively (Zerevitinov). (I) is rapidly hydrogenated to the strongly fluorescent compound, $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}$, m.p. 242–243° (decomp.), which contains 2 active H and then more slowly to the colourless, non-fluorescent substance, $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}$, m.p. 190°; ultimately a non-cryst. *perhydro*-derivative is produced. Oxidation of (I) with KMnO_4 or CrO_3 gives $\text{H}_2\text{C}_2\text{O}_4$, AcOH , and NH_2Ac ; under milder conditions part of (I) remains unchanged, whereas the rest is completely decomposed.

H. W.

Sulphonation of pyridine in presence of mercuric sulphate as a catalyst. (Miss) A. J. P. VAN GASTEL and J. P. WIBAUT (Rec. trav. chim., 1934, 53, 1031–1036).—Sulphonation of $\text{C}_5\text{H}_5\text{N}$ with HgSO_4 as catalyst at 300–350° yields pyridine-3-, m.p. 357° (NH_4 salt, m.p. 243°), and about 2% of 2-sulphonic acid, m.p. 247–248° (NH_4 salt, m.p. 274.2–275.3°). At 225°, only the 3-acid is formed, but sulphonation does not take place below 300° without catalyst.

F. R. S.

Synthesis of N-phenylpiperazine. C. B. POLLARD and L. G. MACDOWELL (J. Amer. Chem. Soc., 1934, 56, 2199–2200).— $\text{NH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$ and $\text{NH}_2\text{Ph}\cdot\text{HCl}$ at 230–240° give about 50% of N-phenylpiperazine, b.p. 156–157°/10 mm. (*hydrochloride*), and some $\text{NH}(\text{CH}_2\cdot\text{CH}_2\cdot\text{NHPh})_2$.

H. B.

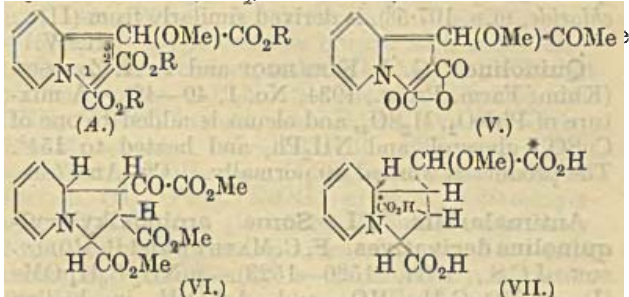
Formation of 2-phenyl- Δ^2 -tetrahydropyridine by the action of magnesium phenyl bromide on δ -bromovaleronitrile. J. B. CLOKE and O. AYERS (J. Amer. Chem. Soc., 1934, 56, 2144–2145).—Furan is reduced (H_2 , Ni, Bu°OH at 50°) to tetrahydrofuran, converted by red P and Br in H_2O into $\alpha\delta$ -dibromobutane, which with aq. $\text{EtOH}\cdot\text{KCN}$ affords δ -bromovaleronitrile, b.p. 110–111°/11 mm. This and MgPhBr give 2-phenyl- Δ^2 -tetrahydropyridine [platinichloride,

decomp. 191—192° (sinters at 190°), re-solidifying with m.p. 210—211° (lit. 202°)]. H. B.

Addition of cyanoacetamide to α -methoxybenzylideneacetophenone. C. F. H. ALLEN and J. A. SCARROW (Canad. J. Res., 1934, 11, 395—405).—Addition of $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$ to $\text{CHPh}\cdot\text{CBz}\cdot\text{OMe}$ (improved prep. of $\text{OMe}\cdot\text{CH}_2\cdot\text{Bz}$ described) in dry MeOH-trace NaOMe affords 6-hydroxy-2-keto-3-cyano-5-methoxy-4:6-diphenylpyridine (I), m.p. 241—242°, converted by Me_2SO_4 –10% NaOH into 3-cyano-2:5:6-trimethoxy-4:6-diphenyl-1:4:5:6-tetrahydropyridine, m.p. 290°, and by PCl_5 in boiling C_6H_6 into 2-hydroxy-3-cyano-5-methoxy-4:6-diphenylpiperidine (II), m.p. 318—320° (decomp.). Passage of dry HCl into a suspension of (I) in CHCl_3 affords (II) and 2-keto-3-cyano-5-methoxy-4:6-diphenyl-2:3:4:5-tetrahydropyridine, m.p. 233—235°, and treatment of (I) with AlCl_3 in boiling C_6H_6 and subsequent basification gives (II) and 6-hydroxy-2-keto-5-methoxy-4:6-diphenylpiperidine, m.p. 155°. Addition of $\text{Br}\cdot\text{AcOH}$ to (I) in boiling AcOH (+1 drop of COMe_2) affords NH_4Br and a compound, m.p. 125—130° (decomp.), decomposed by MeOH into a mixture from which (I), (II), 3-bromo-6-hydroxy-2-keto-3-cyano-5-methoxy-4:6-diphenylpiperidine (III), m.p. 292—293° (60%), and 6-hydroxy-2-keto-5-methoxy-4:6-diphenyl-1:2:5:6-tetrahydropyridine (IV), m.p. 252—253° (2—5%), were separated. Addition of Br to (I) in MeOH–NaOMe affords unchanged (I), (III), and 6-hydroxy-2-keto-5-methoxy-4:6-diphenyl-1:2:5:6-tetrahydropyridine-3-carboxylic acid, m.p. 149—150°, decarboxylated at 180—200° to (IV). When heated with $\text{Ac}_2\text{O}\cdot\text{C}_6\text{H}_5\text{N}$ (or 2 drops of conc. H_2SO_4) (I) gives 6-hydroxy-5-methoxy-2-acetyl-4:6-diphenyl-1:4:5:6-tetrahydropyridine, m.p. 126°, hydrolysed (H_2SO_4 –EtOH) with dehydration to 2-hydroxy-5-methoxy-4:6-diphenyl-4:5-dihydropyridine, m.p. 173—174°. (I) is converted by warm 33% H_2SO_4 into 2-keto-5-benzoyl-4-phenylpyrrolidine, m.p. 172° (isomeric form, m.p. 153—154°, by action of HCl –EtOH; dinitrophenylhydrazones, m.p. 205°, and a gum (V), from which were separated γ -hydroxy- γ -benzoyl- β -phenylbutyric acid and the corresponding two stereoisomeric lactones, m.p. 130° [dinitrophenylhydrazones (VI), m.p. 164°] and m.p. 98° [dinitrophenylhydrazones (VII), m.p. 192°] (Kohler, A., 1911, i, 984). Direct treatment of (V) with $\text{NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ gives (VI) and (VII), and a dinitrophenylhydrazone, m.p. 182°. With dry NH_3 –MeOH the lactone affords only (?) γ -hydroxy- γ -benzoyl- β -phenylbutyramide, m.p. 173°. Mechanisms are discussed. Condensation of α -bromobenzylideneacetophenone with $p\text{-C}_6\text{H}_4(\text{NO}_2)_2\cdot\text{CH}_2\cdot\text{CN}$ in presence of NaOMe affords a mixture of 1-cyano-2-benzoyl-1-p-nitrophenyl-3-phenylcyclopropane, m.p. 144°, and its stereoisomeride, m.p. 151°. J. W. B.

Syntheses in the hydroaromatic series. XXI. Diene syntheses with heterocyclic nitrogen compounds. VIII. Course of the diene synthesis with pyridine in methyl-alcoholic solution. O. DIELS and R. MEYER (Annalen, 1934, 513, 129—145; cf. A., 1932, 1144; 1933, 1058; this vol., 782).—Me acetylenedicarboxylate (I) and $\text{C}_5\text{H}_5\text{N}$ in MeOH at 0° give a colourless adduct (II), $\text{C}_{16}\text{H}_{17}\text{O}_7\text{N}$, m.p. 142—143°, oxidised (H_2O_2 , AcOH) to 2-carboxypyridine

1-oxide (III) and converted by Br in AcOH or MeOH into Me indolizinetricarboxylate [also obtained directly from (I) and $\text{MeOH}\cdot\text{C}_5\text{H}_5\text{N}$ in the absence of cooling]. (II) is unaffected by $\text{K}_2\text{Cr}_2\text{O}_7$ in AcOH or Et azodicarboxylate. These results are explained by assigning structure A ($\text{R}=\text{Me}$) to (II). Hydrolysis (dil. $\text{MeOH}\cdot\text{KOH}$) of (II) gives a salt, $\text{C}_{14}\text{H}_{13}\text{O}_7\text{N}\cdot\text{C}_{14}\text{H}_{15}\text{O}_7\text{NK}\cdot\text{H}_2\text{O}$, decomp. about 200°, whilst hydrolysis with 25% $\text{MeOH}\cdot\text{KOH}$ affords the tricarboxylic acid (+2 H_2O) (IV) (A , $\text{R}=\text{H}$), decomp. about 100° [K_3 salt (+4 H_2O)], which is oxidised [HNO_3 (d 1.4)] to pyridine-2-carboxylic acid and converted by Ac_2O into the keto-anhydride (V), decomp. 270°. (II) is reduced (H_2 , PtO_2 , AcOH) to a tetrahydro-derivative, m.p. 103—105°, which is oxidised



(KMnO_4 , COMe_2) to the keto-ester (+0.5 H_2O) (VI), m.p. 162—164°, and hydrolysed (30% aq. KOH) to the tricarboxylic acid (VII), m.p. 130° (decomp.) [anhydride, m.p. 154—155° (loss of H_2O between CO_2H groups marked *), formed by the action of Ac_2O]. The resinous product obtained by similar reduction of (IV) is converted by Ac_2O into the tetrahydro-derivative, decomp. 260°, of (V). (II) and dil. HNO_3 in AcOH give Me 3-nitroindolizine-1:2-dicarboxylate, m.p. 165°, oxidised (H_2O_2 , AcOH) to (III) and reduced (H_2 , PtO_2 , AcOH) to Me 3-amino-tetrahydroindolizine-1:2-dicarboxylate, m.p. 105° (Ac derivative, m.p. 167°).

Me fumarate and Me methoxyfumarate, b.p. 228—230° [hydrolysed (conc. HCl) to Me₂ oxaloacetate, m.p. 73—74°], are isolated from the mother-liquors from the prep. of (II). (II) is probably formed by addition of the residue $\cdot\text{C}(\text{CO}_2\text{Me})\cdot\text{C}(\text{CO}_2\text{Me})\cdot\text{CH}(\text{CO}_2\text{Me})\cdot\text{C}(\text{OMe})(\text{CO}_2\text{Me})\cdot$ to $\text{C}_5\text{H}_5\text{N}$ and subsequent elimination of HCO_2Me . The previously described (A., 1933, 1058) Me quinolizinetricarboxylate is probably A with $\text{OMe}=\text{H}$ and $\text{R}=\text{Me}$. H. B.

Catalytic dehydrogenation of cyclic bases. III. Behaviour of the stereoisomeric decahydroquinolines during catalytic dehydrogenation. M. EHRENSTEIN and W. BUNGE (Ber., 1934, 67, [B], 1715—1729; cf. this vol., 534).—cis-Decahydroquinoline is dehydrogenated by Pd and more rapidly by Pt, whereas the trans-form is resistant towards Pd but dehydrogenated by Pt. The corresponding 1-Me compounds behave analogously to their parents. The two decahydronaphthalenes are readily dehydrogenated, the rate of action being greater with the cis- than with the trans-compound. Pt is a more active catalyst than Pd.

Quinoline is hydrogenated (colloidal Pt–AcOH–HCl) and the crude product is passed over Pt–asbestos at

310°, thus leading conveniently to 5:6:7:8-tetrahydroquinoline, b.p. 103°/10 mm. [*picrate*, m.p. 158°; *picrolonate*, m.p. 213° (decomp.); *aurichloride*, m.p. 138.5—139°; *platinichloride*, m.p. 212.5—213°]. Hydrogenation of pure quinoline (colloidal Pt-H₂O) yields 1:2:3:4-tetrahydroquinoline, b.p. 246—247° (hydrochloride, m.p. 181°; *picrate*, m.p. 145—146°). The *phenylthiocarbamides*, m.p. 143° and m.p. 139°, respectively, and *aurichlorides*, m.p. 200° and m.p. 126°, of *cis*- (I) and *trans*- (II) -decahydroquinoline are described. (I), HCO₂H, and CH₂O at 100° yield *cis*-1-methyldecahydroquinoline, b.p. 208.5—209.5°/1 atm. (*picrate*, m.p. 199—200°; *aurichloride*, m.p. 103°). *trans*-1-Methyldecahydroquinoline, b.p. 204—205° (*picrate*, m.p. 173°; *picrolonate*, m.p. 205.5°; *aurichloride*, m.p. 107.5°), is derived similarly from (II).

H. W.

Quinoline. G. A. KIRKHOFF and V. A. ZASOSOV (Khim. Farm. Prom., 1934, No. 1, 40—42).—A mixture of PhNO₂, H₂SO₄, and oleum is added to one of CuSO₄, glycerol, and NH₂Ph, and heated to 154°. The product is worked up normally. CH. ABS. (e)

Antimalarials. XI. Some aminoalkylarylquinoline derivatives. F. C. MATHUR and R. ROBINSON J.C.S., 1934, 1520—1523).—*p*-NH₂·C₆H₄·OMe (I), *m*-NO₂·C₆H₄·CHO, and AcCO₂H in boiling EtOH afford 2-*m*-nitrophenyl-6-methoxyquinoline-4-carboxylic acid, m.p. 268—269°, which does not lose CO₂ when heated. 2-*m*-Aminophenyl-6-methoxyquinoline (improved prep.) and phthalo-*γ*-bromopropylamide (II) at 120—130° afford 2-(*m*-*γ*-phthalimidopropylaminophenyl)-6-methoxyquinoline, m.p. 149—150° (hydrobromide, m.p. 202—203°), which is converted by N₂H₄·H₂O in boiling EtOH, followed by excess of dil. HCl, into 2-(*m*-*γ*-aminopropylaminophenyl)-6-methoxyquinoline hydrochloride (+1.5H₂O, m.p. 240—241°, which is lost in vac. at 110°). *o*-Nitrocinnamaldehyde with (I) and conc. HCl at 160° affords 2-*o*-nitrophenyl-6-methoxyquinoline, m.p. 133—134°, reduced (SnCl₂-HCl) to the *amine*, m.p. 158—169°. 6-Methoxyquinaldine, *p*-NO₂·C₆H₄·CHO, and Ac₂O at 120—130° afford 2-*p*-nitrobenzylidene-6-methoxy-2-methylquinoline, m.p. 165—166°, reduced (SnCl₂ or Fe-HCl) to the *amine* (III), m.p. about 162—165° (decomp.) with softening from 130° (hydrochloride; *stannichloride*). (III) with (II) at 110—120° gives 2-*p*-*γ*-phthalimidopropylaminostyryl-6-methoxyquinoline, m.p. 191—192° (hydrobromide, m.p. 241°), converted as above into 2-(*p*-*γ*-aminopropylaminostyryl)-6-methoxyquinoline monohydrate, m.p. 156° (hydrochloride +3.5H₂O, m.p. 222—223°; the H₂O is lost in vac. at 110°). 2-*p*-Aminostyrylquinoline with (II) as before gives 2-(*p*-*γ*-phthalimidopropylaminostyryl)-quinoline, m.p. 175—176° (hydrobromide, m.p. 248—249°), converted into 2-(*p*-*γ*-aminopropylaminostyryl)-quinoline, m.p. 141—142° [hydrochloride, m.p. 269—276° (decomp.)]. Quinaldine, *m*-NO₂·C₆H₄·CHO, and Ac₂O at 110—120° afford 2-*m*-nitrocinnamylidene-2-methylquinoline, m.p. 158—159° [methiodide, m.p. 229—230° (decomp.)], reduced to the *amine*, m.p. 147° [*H* sulphate, m.p. 237° (decomp.)]. Similarly prepared, the corresponding 6-OMe-compounds have m.p. 197—198° and 139—140° (+H₂O; hydrochloride +1.5H₂O, m.p. 250—251°), respectively.

3-Nitro-*p*-anisidine, (MeCHO)₃, and conc. HCl at 100° gives 8-nitro-6-methoxy-2-methylquinoline (IV), m.p. 186—187°, converted into the *amine* (+0.25H₂O, m.p. 102°) by reduction (Pt-H₂) in EtOH-HCl. (IV) with *p*-NO₂·C₆H₄·CHO, and Ac₂O at 120° affords 2-*p*-nitrobenzylidene-8-nitro-6-methoxy-2-methylquinoline (+1.5H₂O, m.p. 182—183°). 2-*p*-Dimethylaminobenzylidene- and 2-*m*-nitrocinnamylidene-8-nitro-6-methoxy-2-methylquinoline have m.p. 204—205° and 223—224°, respectively. J. L. D.

Antimalarials. XII. Quinolines with basic side-chains. R. ROBINSON and (Miss) M. L. TOMLINSON (J.C.S., 1934, 1524—1530).—8-Amino-6-methoxyquinoline [*Ac* derivative (I), m.p. 126°] and phthalo-*δ*-bromobutylamide (II) at 130° afford 8-*δ*-phthalimidobutylamino-6-methoxyquinoline hydrobromide, m.p. 196—198° (decomp.); the base is hydrolysed (N₂H₄ in EtOH) to 8-*δ*-aminobutylamino-6-methoxyquinoline (III) [dihydrochloride +0.5H₂O, m.p. 208° (decomp.)]. 8-*γ*-Aminopropylamino-6-methoxyquinoline with phthalo-*γ*-bromopropylamide (IV) and with (II), followed by hydrolysis, give 8-*γ*'-aminopropyl- and 8-*δ*'-aminobutyl-*γ*-aminopropylamino-6-methoxyquinoline, respectively. Similarly, (III) gives 8-*γ*'-aminopropylamino- and 8-*δ*'-aminobutylamino-*δ*-butylamino-6-methoxyquinoline, respectively. The above are isolated as extremely deliquescent hydrochlorides, which have a high antimalarial activity. 8-*β*-Aminoethylamino-6-methoxyquinoline with (IV), followed by hydrolysis and prolonged interaction with *n*-octyl bromide, gives 8-*γ*'-octylaminopropyl-*β*-aminoethylamino-6-methoxyquinoline, isolated as a deliquescent hydrochloride. (I) with Cl₂ in AcOH affords 5-chloro-8-acetamido-6-methoxyquinoline, m.p. 169°, hydrolysed to the *amine* (V), m.p. 150—152° [hydrochloride, m.p. 264° (decomp.)]. Equimol. quantities of (V) and (IV) at 100° affords 5-chloro-8-*γ*-phthalimidopropylamino-6-methoxyquinoline, m.p. 153—154°; hydrolysed as above to 5-chloro-8-*γ*-aminopropylamino-6-methoxyquinoline [dihydrochloride +H₂O, m.p. 235° (decomp.)]. (I) (free base) with excess of CH₂Br·CO₂Et at 100° gives Et 6-methoxyquinolyl-8-aminoacetate [hydrobromide, m.p. 203° (decomp.)], and with CH₂Cl·CH₂·OH, an impure substance, C₁₄H₂₀O₃N₂Cl₂. 4-Hydroxy-6-methoxyquinaldine with (IV) and K₂CO₃ at 140° affords 4-*γ*-phthalimidopropoxy-6-methoxy-2-methylquinoline, m.p. 197°, hydrolysed to 4-*γ*-aminopropoxy-6-methoxy-2-methylquinoline (VI), m.p. 170° [dihydrochloride, m.p. 215° (decomp.)]. (VI) and (IV) at 120° affords 4-*γ*-phthalimidopropyl-*γ*-aminopropoxy-6-methoxy-2-methylquinoline hydrobromide +H₂O, m.p. 200—202°, hydrolysed and then converted into 4-*γ*'-aminopropyl-*γ*-aminopropoxy-6-methoxyquinaldine trihydrochloride +2H₂O, m.p. 145° (decomp.). Me *β*-6:7-dimethoxyquinaldine-4-propionate (VII) (this vol., 83) with boiling *β*-diethylaminoethanol (VIII) affords *β*-diethylaminoethyl *β*-6:7-dimethoxyquinaldine-4-propionate, isolated as the dihydrochloride (*picrate*, m.p. 186° after sintering at 175°). The azide of (VII) with warm (VIII) affords *β*-diethylaminoethyl *β*-6:7-dimethoxyquinaldyl(4)ethylcarbamate (*picrate*, m.p. 187°; very deliquescent hydrochloride). The azide from anishydrazide with (VIII) at 100° gives *β*-diethyl-

aminoethyl *p*-anisylcarbamate (*picrate*, m.p. 150—152°; hydrochloride). MgEtBr with 6-methoxy-tetrahydrocarbazole in Et_2O containing BzCl gives 9-benzoyl-6-methoxytetrahydrocarbazole, m.p. 134°, which is nitrated ($\text{HNO}_3\text{-AcOH}$) at room temp. to a 5(or 7)-mononitro-derivative, m.p. 150°, which is not hydrolysed (KOH) to 8-5-methoxy-2-aminobenzoyl-valeric acid (cf. J.C.S., 1923, **123**, 676). 2-Nitro-4-methoxyaniline (diazonium compound) with $\text{SnCl}_2\text{-HCl}$ gives 2-nitro-4-methoxyphenylhydrazine, m.p. 127°, which with cyclohexanone at 100° gives a hydrazone, m.p. 69°, converted by boiling 18% H_2SO_4 into 8-nitro-6-methoxytetrahydrocarbazole, m.p. 136°; reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to the NH_2 -compound (IX), m.p. 149°. (IX), 6-amino-, 6-amino-9-acetyl-, and 6-amino-9-methyl-tetrahydrocarbazole, and 3:6-diaminocarbazole afford no cryst. products with (IV). 6-Nitro-9-acetyltetrahydrocarbazole in boiling EtOH with Fe-HCl gives the amine, m.p. 140°, the diazonium compound of which with $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ gives an azo-derivative, m.p. 195°. Neither 6-chloro-7-nitro- nor 6-chloro-5-nitro-tetrahydrocarbazole condenses with NH_2Me , phthalimide, or $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NH}_2$. 2-Nitro-5-methoxyphenol with (IV) and K_2CO_3 at 145° affords 2-nitro-5-methoxy- γ -phthalimidopropoxybenzene, m.p. 178°, reduced (Fe-HCl) to the NH_2 -compound, m.p. 94—96° (with Zn in AcOH it affords a compound, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, m.p. 162—164°), which cannot be converted into a quinoline or a tetrahydrocarbazole. 4-Iodo-2-nitroanisole, 3-nitro-*p*-anisidine, K_2CO_3 , and Cu at 110° give 2:2'-dinitro-4:4'-dimethoxydiphenylamine (X), m.p. 218° [*Ac* derivative (XI), m.p. 134—135°] (also a compound, $\text{Cu}_2\text{I}_2\text{C}_8\text{H}_8\text{N}_2\cdot 3\text{H}_2\text{O}$, from crystallisation mother-liquors), also obtained from 4:4'-dimethoxydiphenylamine with HNO_3 in AcOH . Neither (X) nor (XI) can be converted into an acridine. (X) with CH_3O in conc. H_2SO_4 gives a compound, $\text{C}_{16}\text{H}_{13}\text{O}_8\text{N}_3$, m.p. 223—224°, converted by boiling Ac_2O into a substance, $\text{C}_{20}\text{H}_{17}\text{O}_{10}\text{N}_3$, m.p. 219—221°. 2-Bromo-3-nitrobenzophenone with *m*-nitro-*p*-anisidine, K_2CO_3 , and Cu at 150° affords 2:2'-dinitro-4-methoxy-6'-benzoyldiphenylamine, m.p. 175°, converted by Ac_2O containing ZnCl_2 into 1:9-dinitro-3-methoxy-5-phenylacridine, m.p. 272°, reduced ($\text{Na}_2\text{S}_2\text{O}_4$) to an amine [*Ac* derivative, m.p. 258°; hydrochloride, m.p. 245° (decomp.)]. J. L. D.

3:6-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups attached to the 9-carbon atom. I. Introduction and synthesis of 3:6-dialkoxyacridones and 3:6-dialkoxy-*N*-alkylacridones. II. Synthesis of 3:6-dialkoxy-9-chloro-10-alkylacridinium chlorides. K. ISHIIHARA (J. Chem. Soc. Japan, 1934, **55**, 458—470, 557—564).—I. Improvements in the synthesis of 9-amino-3:6-methoxyacridinium-methyl chloride are described.

II. The OMe - and OEt-Me and -Et derivatives of chloroacridinium chloride have been synthesised (m.p. 221°, 190—191°, 197—204°, 181°, respectively).

CH. ABS. (e)

Preparation of antipyrine. G. M. NIKOLAIEV (Khim. Farm. Prom., 1934, No. 1, 35—38).—Phenylmethylpyrazolone is methylated with PhSO_3Me .

CH. ABS. (e)

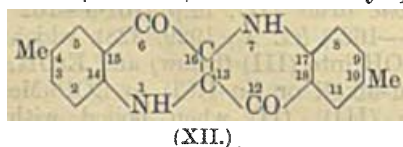
Stereochemistry of diphenyls. XXXVI. Preparation and resolution of dipyrrolylbenzenes. C. CHANG and R. ADAMS (J. Amer. Chem. Soc., 1934, **56**, 2089—2092).—4:6-Dinitro-*m*-xylene (modified prep.; cf. Errera and Maltese, A., 1904, i, 307) is reduced (H_2 , PtO_2 , EtOH) to the $(\text{NH}_2)_2$ -derivative, m.p. 104—105°, which with $\text{Et } \gamma\text{-keto-}\alpha\text{-acetylvalerate}$ (I) at 110—120° gives [after hydrolysis (EtOH-KOH)] a mixture of *cis*- (II), m.p. 260—262° (*brucine*, m.p. 172—177°, *strychnine*, m.p. 178—185°, and *cinchonine*, m.p. 154—160°, salts), and *trans*- (III), m.p. 305° (decomp.), -4:6-di-(3-carboxy-2:5-dimethyl-1-pyrrolyl)-*m*-xylene. (II) and (III) are meso and racemic forms, respectively. (III) is resolved by *brucine* into *d*-, m.p. 275—276°, $[\alpha]_D^{25} +172.2^\circ$ in $\text{C}_6\text{H}_5\text{N}$ (*brucine* salt, m.p. 186—190°), and *l*-forms, m.p. 275—276°, $[\alpha]_D^{25} -165.8^\circ$ in $\text{C}_6\text{H}_5\text{N}$ (impure *brucine* salt, m.p. 152—159°), which racemise partly in boiling *N*- NaOH but not in boiling $\text{C}_6\text{H}_5\text{N}$. 2-Acetamido-*p*-xylene and HNO_3 (*d* 1.42) in cold conc. H_2SO_4 give the 5- NO_2 -derivative, m.p. 167—169° (lit. 166° and 192°); hydrolysis ($\text{EtOH-conc. H}_2\text{SO}_4$) and subsequent reduction (H_2 , PtO_2 , EtOH) gives 2:5-diamino-*p*-xylene. This and (I) afford 2:5-di-(3-carboxy-2:5-dimethyl-1-pyrrolyl)-*p*-xylene, m.p. 150—157°, separable (with difficulty) by fractional crystallisation (EtOH) into *cis*-, m.p. 158—160°, and *trans*-, m.p. 183—185°, -forms. The corresponding *cis*-, m.p. 419—422°, and *trans*-, m.p. 455—460° (Maquenne block), -acids are racemic and meso forms, respectively; alkaloidal salts could not be prepared. (II) and *m*-di-(3-carboxy-2:5-dimethyl-1-pyrrolyl)benzene, m.p. 273—274° [from $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and (I) at 80—100° in N_2 , followed by hydrolysis], could not be resolved.

H. B.

Complex salts of 2:2'-dipyridyl with bivalent copper.—See this vol., 1317.

Epindoline group. I. Trial of various methods for the synthesis of epindolidiones. A. D. AINLEY and R. ROBINSON (J.C.S., 1934, 1508—1520).—Isatin [*Na* derivative (I)] with $\text{CH}_2\text{X}\cdot\text{CO}_2\text{Et}$ ($\text{X}=\text{Br}$ or Cl) in dry C_6H_6 (room temp.) affords *Et isatin-N-acetate*, m.p. 129—130° [different from the product, m.p. 114°, of Putochin (A., 1929, 74)], hydrolysed to an acid, m.p. 206—207° (cf. A., 1928, 771), the chloride of which, m.p. 139—140° (previous softening), gives no definite product with $p\text{-C}_6\text{H}_4\text{Me}\cdot\text{NHAc}$. (I) with CH_2BzBr in C_6H_6 at room temp. affords a product, $\text{C}_{16}\text{H}_{14}\text{O}_2\cdot 2\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}$, and *isatylideneacetophenone oxide* (II), m.p. 161.5—162° (+ EtOH , m.p. 161—162°) (cf. A., 1929, 328), which is converted by NaOH into (III) (below) and EtOH , and is reduced (Zn-alkali or Zn-HCl) to COPhMe more readily than (III). (II) when boiled with EtOH-NaOH affords *benzoylformylloxindole* (III), m.p. 178.5—179.5° (*phenylhydrazone*, decomp. at 165° after sintering at 160°, exhibits colour changes in various solvents, and probably has the $\text{NHPh}\cdot\text{N}$ residue on the C adjacent to Ph), which is hydrolysed by AcOH-HCl to oxindole, and couples with diazonium chlorides to give sparingly sol. alkali salts (cf. A., 1918, i, 229). (I) with $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ in C_6H_6 as above gives *isatylidene-o-nitroacetophenone oxide* (IV), m.p. 207—208° (decomp.), converted by boiling

NaOH-EtOH into *o*-nitrobenzoylformyloxindole (V), m.p. 239° (decomp.). Reduction of (IV) by many methods gives indirubin, m.p. 345–347°; the yield is improved by reducing (V). (III) with boiling 10% NaOH affords BzCO_2H and 2-benzoylindole-3-carboxylic acid (?), m.p. 230–231° (decomp.), converted by fusion with KOH into indole. (III) with boiling NaOH containing Zn gives mandeloyloxindole (VI), m.p. 164–165° [also contained by reducing (II)], which is fairly stable to boiling 40% KOH. Diazonium derivatives of (VI) with alkali give PhCHO, as does (VI) with Br followed by NaOH. (II) with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ in AcOH-EtOH at 100° affords a substance, m.p. 200–201°. Similarly, (III) affords a quinoxaline (?), m.p. 255°, the structure assigned to which is in accord with its somewhat anomalous properties. *N*-Benzoyl-4-ketotetrahydroquinoline (cf. A., 1924, i, 1103) with an equimol. amount of $\text{o-NO-C}_6\text{H}_4\text{CO}_2\text{Et}$ at 100° affords a product, $\text{C}_{22}\text{H}_{20}\text{O}_5\text{N}_2$, m.p. 99.5–100.5°, converted by boiling H_2O into a product, m.p. 106–109°. The same reactants in boiling EtOH containing Na_2CO_3 afford a substance, m.p. 253.5–254° [probably a compound of (VII) and its Et ester], 3-*o*-carboxyanilino-4-hydroxyquinoline (VII), m.p. 255° (decomp.) (Et ester, m.p. 274.5–275°), which is not cyclised to an epindolidione. Similarly, α -tetralone gives 2-*o*-carbethoxyanilino- α -naphthaquinone + $0.5\text{H}_2\text{O}$, m.p. > 280°, and an acid, $\text{C}_{24}\text{H}_{16}\text{O}_5\text{N}_2 \cdot 2\text{H}_2\text{O}$, m.p. 244° (decomp.). ω -Chloro-2-amino-5-methylacetophenone (cf. A., 1900, i, 663) with $\text{CO}_2\text{Et} \cdot \text{COCl}$ in boiling Et_2O affords ω -chloro-2-ethoxalylamino-5-methylacetophenone, m.p. 144–144.5°, the I-analogue of which reacts with $p\text{-C}_6\text{H}_4\text{Me} \cdot \text{NH}_2$ in boiling COMe_2 to give ω -*p*-tolylamino-2-ethoxalylamino-5-methylacetophenone (VIII), m.p. 140.5–141°. The unsubstituted compound is not prepared because ω -bromo-*o*-nitroacetophenone does not condense with NH_2Ph . Boiling EtOH-NaOH converts (VIII) into 3-*p*-tolylamino-4-hydroxy-6-methylquinoline-2-carboxylic acid (IX), m.p. 237–238° (decomp.) [Ac_2 derivative + $0.5\text{H}_2\text{O}$ (X), m.p. 217° (decomp.)], which with boiling $\text{MeOH-H}_2\text{SO}_4$, or with CH_3N_2 in dry Et_2O at 0° affords *Me* 3-*p*-tolylamino-4-keto-6-methyl-1:4-dihydroquinoline-2-carboxylate (XI), m.p. 227–228° (decomp.). (IX) with CH_3N_2 in MeOH at room temp. affords (XI) and some *Me* 3-*p*-tolylamino-4-keto-1:6-dimethyl-1:4-dihydroquinoline-2-carboxylate, m.p. 246°. (X) with AcCl followed by AlCl_3 in PhNO_2 at room temp. gives the Ac_2 derivative (infusible) of 4:10-dimethylepindolidione; also an



(XII).

dolidione (XII) (infusible), which possesses weakly basic and acidic properties, and is not reduced by alkaline $\text{Na}_2\text{S}_2\text{O}_4$ in $\text{C}_5\text{H}_5\text{N}$ or EtOH. J. L. D.

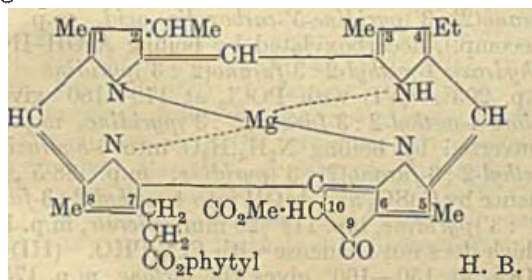
Synthesis of polymethine dyes. T. OGATA (J. Chem. Soc. Japan, 1934, 55, 394–436; cf. this vol., 422).—The prep. and properties of a large no. of cyanine dyes are described. Vals. for the sensitising max. of these dyes are recorded. CH. ABS. (r).

Residual affinity and co-ordination. XXXV. 2:2':2''-Tripyridylplatinum salts. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1934, 1498–1500; cf. this vol., 1113).—2:2':2''-Tripyridyl (=trpy) with K_2PtCl_4 in H_2O at 90° affords 2:2':2''-tripyridylchloroplatinous platinumochloride (I) [$\text{Pt trpyCl}_2\text{PtCl}_4$, bis-2:2':2''-tripyridyltriplatinous hexachloride (II), and 2:2':2''-tripyridylplatinous chloride trihydrate (III), [$\text{Pt trpyCl}_2\text{Cl}_3\text{H}_2\text{O}$ (red)], converted by keeping over H_2SO_4 , or by EtOH, or by HCl, into the dihydrate (IV) [also obtained from the black form of (III) with H_2O or acid]. Prolonged action of tripyridyl on (I) or (II) in H_2O , or Ag_2O followed by HCl on (I), gives (IV). (III) with K_2PtCl_4 in cold H_2O gives (I), whereas with aq. NH_3 it gives 2:2':2''-tripyridylamminoplatinous chloride hydrate (V), which readily reverts to (III) by loss of NH_3 . (III) or (I) with warm $\text{Ag}_2\text{O-H}_2\text{O}$ gives 2:2':2''-tripyridylplatinous hydroxide, [$\text{Pt trpyOH}_2\text{OH}_2\text{H}_2\text{O}$, which with acids gives the bromide and iodide dihydrates, also prepared from (III) with the appropriate halides. (III) with Cl_2 affords 2:2':2''-tripyridyltrichloroplatinic chloride dihydrate, [$\text{Pt trpyCl}_3\text{Cl}_3\text{H}_2\text{O}$, desiccated over H_2SO_4 to a monohydrate, which is reconverted in air into (III). (I) with hot conc. NH_3 gives the plato-salt (VI), [$\text{Pt trpyNH}_3\text{PtCl}_4$ (black)] [converted into (I) with warm HCl], also obtained by interaction of (V) with K_2PtCl_4 . Tripyridyl in hot 2*N*-HCl with K_2PtCl_4 affords 2:2':2''-tripyridyl platinumochloride, $\text{trpyH}_2\text{PtCl}_4$, which is unchanged by boiling H_2O , but when heated at 230–260° for 5 hr. affords some 2:2':2''-tripyridyl hydrochloride, the black form (VII) (probably a dimeride) of (III) [plato-salt converted into (I) with HCl; is converted by hot 2*N*-HCl or boiling H_2O into (III)], and a product of indefinite composition. J. L. D.

Constitution of the purine nucleosides. II. J. M. GULLAND, E. R. HOLIDAY, and I. F. MACRAE (J.C.S., 1934, 1639–1644).—Methylation of xanthosine (I) with CH_3N_2 gives a mixture of methylated purines and methylriboside, hydrolysed to 1:7-dimethylxanthine, 1:7:9-trimethyluric acid (?), ribose (as furfuraldehyde), and 3-methylxanthine (cf. Levene *et al.*, A., 1925, i, 1463). Comparison of absorption spectra of (I), isocaffeine, and caffeine, 9-, 7-, 1-, and 3-methylxanthine, and theophylline-*d*-glucoside (II) and -*l*-araboside (III) indicates that (I) is probably xanthine-9-riboside and that (II) and (III) are γ -substituted xanthines. Methylation (MeI) of xanthosine Ag gives 7-methylxanthine and ribose derivatives containing OMe but no N. F. R. S.

Chlorophyll. I. Structure of chlorophyll *a*. H. FISCHER and J. HASENKAMP (Annalen, 1934, 513, 107–129).—Chlorin *e* (I) contains the isoporphin ring since it undergoes the "oxo-reaction" (this vol., 420) to give a mixture (30% yield) of oxochlorophorphyrin e_5 (II), $\text{C}_{33}\text{H}_{32}\text{O}_6\text{N}_4$, m.p. > 305°, and small amounts of oxochlorophorphyrins e_4 and e_7 . (II) heated with HCO_2H or 60% H_2SO_4 gives oxorhodophorphyrin (III). Short treatment of (II) with $\text{Et}_2\text{O-CH}_3\text{N}_2$ in $\text{C}_5\text{H}_5\text{N}$ affords a *Me*₁ ester, decomp. 260°; with MeOH-HCl , (II) affords a *Me*₂ ester, (?) $\text{C}_{35}\text{H}_{36}\text{O}_7\text{N}_4$, m.p. 288° (oxime, sinters at 268°). Chlorin *e*₄ is converted by cold HI-AcOH into 35–40% of oxochlorophorphyrin *e*₄

(IV), $C_{33}H_{34}O_5N_4$, m.p. $> 300^\circ$ (Me_2 ester (V) (CH_2N_2), m.p. 288° [oxime (VI), decomp. 260° ; Cu salt, m.p. 260°]). Oxophylloporphyrin is formed when (IV) is heated to 309° ; (III) is similarly obtained from (V) at 310° . (III) heated to 311° gives oxopyrroporphyrin. Oxophylloerythrin ester dioxime and Ac_2O at 100° (bath) afford a Ac_2 derivative, decomp. 208° , which when heated at 130° in a high vac. is converted into an isomeric compound [hydrolysed (20% HCl) to a new porphyrin]. The Ac derivative, decomp. 230° , of (VI) exhibits an analogous behaviour. Oxophylloerythrin (VII) is converted by conc. HCl at 190° and subsequent esterification into (mainly) *de-ethylphylloerythrin* ester, $C_{32(33)}H_{32(34)}O_5N_4$, m.p. 261° (Cu , m.p. 266° , and Fe , m.p. 320° , salts), which with Br in $CHCl_3$ gives a compound, also obtained from (VII) and Br in HCO_2H . (VII) and conc. HCl at 200° afford *de-ethylpyrroporphyrin* (8% yield), the Me ester, m.p. 215° (Br - and Br_2 -, m.p. 268° , -derivatives), of which is identical with 1:3:5:8-tetramethyl-4-ethyl-7- β -carbomethoxyethylporphyrin (synthesis to be described later). (VII) and $AcOH-HBr$ at 190° give (after esterification) *de-ethyldeoxophylloerythrin* Me ester, m.p. 252° , the constitution of which is established by its synthesis (details to be published later). The above results can be explained satisfactorily only by assuming that chlorophyll derivatives which undergo the "oxo-reaction" contain a $CHMe$ group. Oxo-derivatives contain an Ac and not a formyl group (cf. *loc. cit.*); their formation involves the following reactions: $CHMe:C \rightleftharpoons CHIme:CH \rightleftharpoons CHIme:Cl \rightleftharpoons OH:CHMe:Cl \rightleftharpoons OH:CMe:C \rightleftharpoons COMe:C \rightleftharpoons C<$ is C_2 of the porphin structure. Structures are suggested for (I), (II), and methylphæophorbide *a*. Chlorophyll *a* is now assigned the following constitution.



Chlorophyll series. XIII. Nuclear isomerism of porphyrins. E. M. DIETZ and T. H. WERNER. **XIV. Potentiometric titration in acetic acid solution of basic groups in chlorophyll derivatives.** J. B. CONANT, B. F. CHOW, and E. M. DIETZ (J. Amer. Chem. Soc., 1934, 56, 2180—2184, 2185—2189).—**XIII. isoRhodoporphyrin (I)** (A., 1933, 403) is converted (to the extent of about 50% in 48 hr.) into rhodoporphyrin (II) by treatment with cold 50% H_2SO_4 in O_2 or N_2 ; conversion is also effected with conc. or 75% H_2SO_4 (with some decomp.), conc. HCl , and $MeOH$ -, $CHCl_3$ -, or $AcOH-HCl$ and $-HBr$, but in some cases an unidentified porphyrin is also formed. Pyrochloroporphyrin (III) is similarly converted by 50% H_2SO_4 into phylloporphyrin (IV). The changes (I) \rightarrow (II) and (III) \rightarrow (IV) are considered to be isomerisations (prototropic) and not reductions. The Zn salts of the Me_2 esters of (I)

and (II) are not identical (cf. *loc. cit.*) and regenerate the original porphyrins; the Fe complexes differ also. Interconversion of (I) and (II) (or their salts) could not be effected by mild dehydrogenating agents, heating in various solvents, or exposure to light (white or ultra-violet) in various solvents. Verdoporphyrin could not be prepared from phæophytin by Treibs and Herrlein's method (A., 1933, 1173); (I) is obtained. The nos. quoted after the following compounds are the no. of mols. of H_2 absorbed on reduction with PtO_2 and Pt -black, respectively, in $AcOH$ (cf. Fischer *et al.*, A., 1930, 932; 1933, 1308): phylloporphyrin Me ester, 4, 3-3; pyrochloroporphyrin Me ester, —, 4-1 [oxidation of the leuco-compound gives (IV)]; pyrroporphyrin Me ester, 3-6—4, — (re-oxidation gives 60—65% of original material); rhodoporphyrin Me_2 ester, 3-7—4-1, 3-1 (re-oxidation affords 60—65% of original material); isorhodoporphyrin Me_2 ester, 4-8—5-4, 4 [re-oxidised to (II) (about 57%)] ; chlorin *f* Me_2 ester, 4-4—4-6, 3-2—3-3 [re-oxidised to (II) (about 50%)] ; chlorin *e* Me_3 ester, 3-7—4-2, 3-2. These results indicate that isoporphyrins are dehydrogenation products of true porphyrins. Little importance is attached to the hydrogenation results and the isomerism of the true and isoporphyrins is maintained.

XIV. Potentiometric titrations of various pyrroles and chlorophyll derivatives with $HClO_4$ in $AcOH$ at const. ionic strength, using a chloranil electrode, are carried out using the procedure previously developed (A., 1931, 40; 1933, 1121). Porphyrins, chlorins, and rhodins all contain 3 basic groups; the titration curves, however, show marked characteristic differences. Revised structures, which are consistent with the data obtained, are assigned to chlorin *f* and rhodin *l*.

H. B.

Porphyrins. XXX. Synthesis of 2-(β - β -dicarboxyethyl) - 4 : 6 : 8 - tri - (β - carboxyethyl) - 1 : 3 : 5 : 7 - tetramethylporphyrin (isoconchoporphyrin I) and deuteroporphyrin (II). H. FISCHER and E. VON HOLZ (Z. physiol. Chem., 1934, 227, 124—144; cf. A., 1932, 285).—2:4-Dimethyl-3- β -carboxyethylpyrrole and 4-bromo-5-aldehydo-3-methylpyrrole-2-carboxylic acid in $AcOH$ yield the carbinol base, which with HBr gives 3-bromo-5-carboxy-4:3':5'-trimethyl-4'- β -carboxyethylpyrromethene hydrobromide (I), m.p. $< 290^\circ$. With Br in CCl_4 , (I) affords 3:5-dibromo-4:3':5'-trimethyl-4'- β -carboxyethylpyrromethene hydrobromide (II), m.p. $< 290^\circ$. Fusion of (II) containing perbromide and 5-bromo-4:3':5'-trimethyl-3:4'-di-(β -carboxyethyl)pyrromethene hydrobromide in citric acid (240°) gives a mixture of porphyrins (15—20% yield), separated by bromination into coproporphyrin I (Me_4 ester, m.p. 246°) and 2-bromo-1:3:5:7-tetramethyl-4:6:8-tri-(β -carboxyethyl)porphyrin (III), m.p. $< 290^\circ$ [Fe salt, m.p. $< 290^\circ$; Me_3 ester, m.p. 203 — 204° (Fe , m.p. 230 — 231° , Cu , m.p. 316 — 317° , Zn , m.p. 235 — 236° , salts)]. Debromination of (III) Me_3 ester by Busch's method (A., 1925, ii, 823) gives 1:3:5:7-tetramethyl-4:6:8-tri-(β -carboxyethyl)porphyrin (IV), m.p. $< 270^\circ$ (Fe salt, m.p. $< 300^\circ$), as Me_3 ester, m.p. 195 — 196° (Fe , m.p. 225 — 226° , Cu , m.p. 189 — 190° , salts). The Fe salt of (IV) with CH_2ClOMe and $SnCl_4$ yields, as Fe salt, 1:3:5:7-tetramethyl-4:6:8-tri-(β -carboxy-

ethyl)-2-hydroxymethylporphyrin, which with Et potassium-malonate yields 1 : 3 : 5 : 7-tetramethyl-2-($\beta\beta$ -dicarboxyethyl)-4 : 6 : 8-tri-(β -carboxyethyl)porphyrin (isoconchophyrin I), isolated as the Me_5 ester, m.p. 172°. Fusion of (II) containing perbromide in succinic and citric acids (205°) affords deuteroporphyrin II (V), m.p. < 300° [Me_5 ester, m.p. 286° (Fe, m.p. 296°, Cu, m.p. 302—303°, salts)]. A similar fusion (240°) gives monobromodeuteroporphyrin II Me_5 ester, m.p. 243—244°. Bromination of (V) Me_5 ester in AcOH yields dibromodeuteroporphyrin II, m.p. < 270°, as the Me_5 ester, m.p. 303—304° (Cu, m.p. 309—310°, Fe, m.p. 285—286°, salts). Bromination of 5-formyl-2 : 3-dimethylpyrrole and opsopyrrolecarboxylic acid gives 4 : 5 : 3'-trimethyl-4'- β -carboxyethylpyrromethene hydrobromide, m.p. 202°, which on bromination and fusion with succinic acid (180—190°) affords (V).

J. H. B.

Crystalline stercobilin and urobilin. See this vol. 1386.

α -isoOxazolehydrazide. M. FRERI (Gazzetta, 1934, 64, 644—649).—*iso*-Oxazole-5-carboxylhydrazide (cf. A., 1932, 1145) (I) with HNO_2 in AcOH gives di(isooxazole-5-carboxyl)hydrazine, m.p. 212°, which is also formed from (I) and isooxazole-5-carboxyl chloride. Acids hydrolyse it to (I) and N_2H_4 . (I) condenses with $BzCl$, $PhCHO$, $COPh_2$, and o - $C_6H_4(CO)_2O$ to benzoylisooxazole-5-carboxylhydrazine, m.p. 192—193°, benzaldehyde-, m.p. 193—194°, and benzophenone-isooxazole-5-carboxylhydrazine, m.p. 190°, and phthalylisooxazole- α -carboxylhydrazine, m.p. 204—205°, respectively.

R. N. C.

4-Hydroxy-3 : 5-diphenylisooxazole. A. H. BLATT and W. L. HAWKINS (J. Amer. Chem. Soc., 1934, 56, 2190—2191).— $CHBz_2 \cdot OAc$ and $NH_2OH \cdot HCl$ in aq. EtOH give 4-hydroxy-3 : 5-diphenylisooxazole (I), m.p. 122—123° (decomp.) (acetate, m.p. 103°; benzoate, m.p. 157—158°; *Me* ether, m.p. 69—70°), oxidised (alkaline $KMnO_4$) to a bimol. compound, m.p. 110—112°, and converted by I in AcOH into an isomeride (II), m.p. 151° (decomp.). Acetylation of (II) and subsequent hydrolysis affords (I). (I) heated to 135° gives CO , $PhCN$, and $PhCHO$, whilst (I) and Br in $CHCl_3$ at 0° afford [after hydrolysis (H_2O)] $PhCN$ and $BzOH$.

H. B.

Amine oxides of the novocaine series. J. LAUER (Bull. Soc. chim., 1934, [v], 1, 857—860).—*N*-Oxides of the following are prepared: novocaine, m.p. 181—182° (hydrochloride, m.p. 136—137°; picrate, m.p. 165—166°); butelline, m.p. 126—127° [hydrochloride, m.p. about 129° (decomp.)]; pantocaine, m.p. 87° (hydrochloride, m.p. 146°; picrate, m.p. 144—145°); $N(C_2H_4 \cdot OH)_3$, m.p. 106° (hydrochloride, an oil); *N*- β -hydroxyethylmorpholine, cryst., hygroscopic (hydrochloride, an oil); β -hydroxyethyldiethylamine and diethyl- δ -hydroxy- $\beta\beta$ -dimethylbutylamine, oils (hydrochlorides, oils).

R. S. C.

Derivatives of 3-ethylpyridine and 2 : 3-furano(2' : 3')pyridine. R. ROBINSON and J. S. WATT (J.C.S., 1934, 1536—1543).— $\beta\beta'$ -Dihydroxydiethylamine with PCl_5 in $CHCl_3$ affords $\beta\beta'$ -dichlorodiethylamine, m.p. 45°, converted by KCN in boiling MeOH into $\beta\beta'$ -dicyanodiethylamine, m.p. 81°, which

does not cyclise and is stable to basic catalysts. *Et* γ -phenoxy- α -acetylbutyrate (I), b.p. 195°/30 mm., is hydrolysed to γ -phenoxypropyl Me ketone (cf. A., 1932, 288), which with $Et_2C_2O_4$ gives α - β -phenoxyethylcyclopentane-1 : 3 : 4-trione-2-oxalate, m.p. 145° (cf. A., 1906, i, 438), hydrolysed to 5- β -phenoxyethylcyclopentane-1 : 3 : 4-trione, m.p. 119.5°, the enol form of which is the more stable. (I) or $CH_3Ac \cdot CO_2Et$ (Na derivatives) with β -carbomethoxypropionyl chloride in dry Et_2O , followed by hydrolysis, affords no derivatives of succinacetic ester. *Et* α -cyano- γ -phenoxybutyrate, b.p. 190—195°/14—15 mm. (cf. A., 1924, 261) [Na derivative (II)] with Et β -chloroglutarate (cf. J.C.S., 1923, 123, 2964) gives a product, b.p. about 200°/0.2 mm., but nothing cryst. on hydrolysis. (II) with Et muconate (cf. A., 1931, 1037; 1930, 1163) in boiling EtOH- Et_2O gives *Et* α -cyano- α - β -phenoxyethyl- β -carbomethoxymethyladip- $\gamma\delta$ -enolate, b.p. 212°/0.2 mm., hydrolysed (KOH-MeOH) to an acid, $C_{17}H_{17}O_7N$, m.p. 137—138°. (II) with Et β -chloroglutaconate (J.C.S., 1922, 121, 1642) in hot EtOH gives $OPh \cdot C_6H_4 \cdot CH(CN) \cdot C(CH_2 \cdot CO_2Et) \cdot CH \cdot CO_2Et$, b.p. about 210°/0.2 mm., hydrolysed (boiling HCl) to 2 : 6-dihydroxy-3-(β -phenoxyethyl)pyridyl-4-acetic acid (an oil) [hydrochloride, m.p. 146° (decomp.)], which with Br gives a mixture of Br_3 - and Br_4 -compounds, m.p. 187—188° (decomp.); 2 : 6-Dihydroxy-4-methylpyridine (J.C.S., 1905, 87, 1685) with maleic acid in conc. H_2SO_4 at 100° gives the lactone (III), m.p. 295—296°, of β -(2 : 6-dihydroxy-4-methyl-3-pyridyl)acrylic acid [*Bz* derivative (IV), m.p. 209°]; this [or (IV)] with Br in AcOH gives an α : 5- Br_2 -derivative (V), m.p. 298° (decomp.). (V) with boiling EtOH-KOH rearranges to 5-bromo-6-hydroxy-4-methyl-2 : 3-furano-(2' : 3')pyridine-5'-carboxylic acid, decomp. at 245°, and is reduced ($Zn-NaOH$) to 6-hydroxy-4-methyl-2 : 3-furano(2' : 3')pyridine-5'-carboxylic acid, m.p. 278° (decomp.), decarboxylated by boiling AcOH-HCl to 6-hydroxy-4-methyl-2 : 3-furano(2' : 3')pyridine (VI), m.p. 203°. (VI) with $POCl_3$ at 170—180° gives 6-chloro-4-methyl-2 : 3-furano(2' : 3')pyridine, m.p. 45°, converted by boiling $N_2H_4 \cdot H_2O$ into 6-hydrazino-4-methyl-2 : 3-furano(2' : 3')pyridine, m.p. 88.5°, and thence by $CuSO_4$ and AcOH into 4-methyl-2 : 3-furano-(2' : 3')pyridine, b.p. 118°/20 mm. (picrate, m.p. 151°), which does not condense with $CCl_3 \cdot CHO$. (III) with $POCl_3$ at 150—160° gives the lactone, m.p. 175°, of β -(2-hydroxy-6-chloro-4-methyl-3-pyridyl)acrylic acid, reduced (HI-red P) to β -(2-hydroxy-4-methyl-3-pyridyl)propionic acid, m.p. 214° [$Zn-HCl$ reduces it to β -(6-chloro-2-hydroxy-4-methyl-3-pyridyl)propionic acid, m.p. 204—206°], which with $POCl_3$ at 210° gives β -(2-chloro-4-methyl-3-pyridyl)propionic acid, m.p. 128°.

J. L. D.

Preparation of 4-phenyl-1 : 4-thiazan. A. OKAČ (Chem. Listy, 1934, 28, 227).— $S(CH_2 \cdot CH_2Cl)_2$ and NH_2Ph in boiling EtOH containing NaOAc and Na_2CO_3 give 4-phenyl-1 : 4-thiazan, b.p. 203—204°/13 mm.

R. T.

Syntheses and transformations of natural substances under physiological conditions (biogenesis of natural substances). III. Biogenesis of isoquinoline alkaloids. Synthesis of 6 : 7-dihydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydro-

isoquinoline under physiological conditions. C. SCHOPF and H. BAYERLE (Annalen, 1934, 513, 190—202; cf. A., 1932, 1046).— β -3:4-Dihydroxyphenylethylamine hydrobromide (I) (0.04*M*) and MeCHO (II) (0.08*M*) in aq. solution at p_H 5° and 25° give (after 3 days) a good yield of the *hydrobromide*, m.p. 184—186°, of 6:7-dihydroxy-1-methyl-1:2:3:4-tetrahydroisoquinoline (III) [picrate (+H₂O), m.p. 205—206° (decomp.) (sinters at 125°), m.p. (anhyd.) 205—206°]. Preliminary experiments with (I) and (II) (leading to the adoption of the above conditions) are described briefly. 6:7-Dihydroxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline [picrate (+H₂O), m.p. 92°] is similarly obtained from β -3:4-dihydroxyphenylethyl-*N*-methylamine hydrobromide, m.p. 169—171°, and (II) at p_H 4. These results support the view (cf. *loc. cit.*) that biosynthesis of isoquinoline alkaloids occurs in the absence of enzymes.

Acet- β -3:4-dimethoxyphenylethylamide is converted (method: Spath and Polgar, A., 1929, 578) into 6:7-dimethoxy-1-methyl-3:4-dihydroisoquinoline, m.p. 101°, reduced (H₂, PtO₂, MeOH) to the 1:2:3:4-tetrahydro-derivative (picrate, m.p. 189°), which is demethylated (HBr) to (III). H. B.

ind-N-Methylharmine. V. V. S. IYER and R. ROBINSON (J.C.S., 1934, 1635—1637).—Methylharmine and Me₂SO₄ give dimethylharmine methosulphate (I) [iodide, m.p. 285° (decomp.)], the corresponding chloride on thermal decomp. giving ind-N-methylharmine, m.p. 114—118° (+2H₂O) and 124—125° (anhyd.) [hydrochloride, m.p. 280° (decomp.); *H* nitrate, m.p. 242—243° (decomp.); picrate, m.p. 249—250° (decomp.)]. This combines with Me₂SO₄ and MeI to give (I) and the iodide, respectively. The Me is thus ejected from the N with the cationic charge.

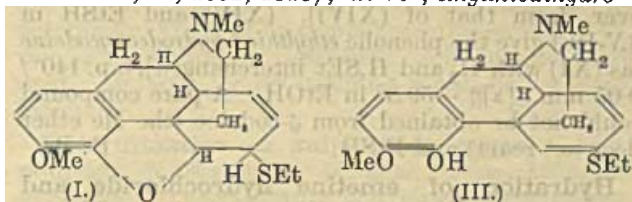
F. R. S.

Retamine. H. WUNSCHENDORFF and P. VALIER (Bull. Sci. pharmacol., 1933, 45, 601—604; Chem. Zentr., 1934, i, 2452).—Retamine, C₁₅H₂₆ON₂, m.p. 168°, prepared from *Retama sphaerocarpa*, Boiss., is dextrorotatory in EtOH, gives no colour reaction with Froehde, Mandelin, or Marquis and Lafon reagents, ppts. hydroxides from salts of Fe^{III}, Cu^{II}, Mn^{II}, Ni^{II}, and Co^{II}, liberates NH₃ from NH₄ salts, forms salts with acids, and acts as reducing agent.

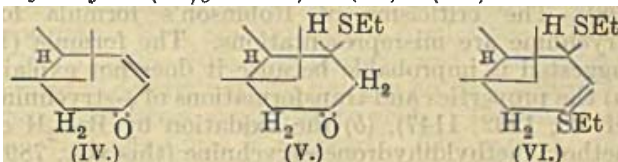
A. G. P.

Ethylthiocodides. D. E. MORRIS and L. SMALL (J. Amer. Chem. Soc., 1934, 56, 2159—2166).— α -Ethylthiocodide (I), m.p. 77—79° and 86—87° (stable), [α]_D —344.6° in 95% EtOH (sulphate, m.p. 185—190°), prepared by Pschorr and Rollet's method (A., 1910, i, 419), is reduced (Na, EtOH) to the same dihydrothebainol (II), m.p. 142°, as is obtained by reduction (Na—Hg) of dihydrothebainone (Kondo and Ochiai, A., 1929, 1088) or dihydrocodeinone. Catalytic reduction of (I) could not be accomplished owing to liberation of EtSH. β -Ethylthiocodide (III), m.p. 144—146°, [α]_D —49.9° in EtOH (improved prep.; cf. *loc. cit.*), formed by rearrangement of (I) with NaOEt, is also reduced (Na, EtOH) to (II); it is undoubtedly formed in the above reduction of (I). (III) is also reduced (H₂, Pd—BaSO₄, EtOH) to tetrahydro- β -ethylthiocodide, distills in a high vac., [α]_D +15.3° in EtOH. (III) is converted by boiling 2*N*-HCl into thebainone

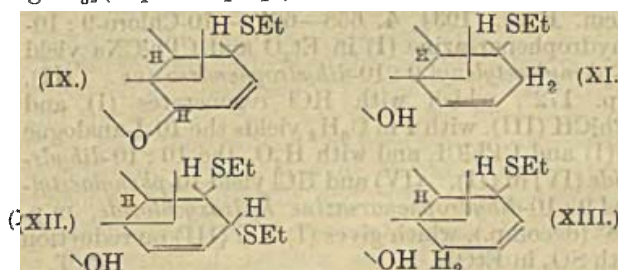
(IV) [hydrochloride, m.p. 254—256° (decomp.)] (Schöpf and Hirsch, A., 1931, 1313); at 70°, ethylthiodihydro-



thebainone (V), m.p. 181—182°, [α]_D +55.4° in COMe₃, [the "thio ketone" of Pschorr (A., 1910, i, 421)], results. The formation of (V) from (III) involves the following reactions: (i) (III) is partly hydrolysed to (IV) and EtSH; (ii) addition of EtSH to (III) gives dihydro- β -diethylthiocodide (VI) (proved experimentally); (iii) (VI) is hydrolysed to (V). (V) is also hydrolysed (20% NaOH) to (IV). (III) and MeI in



75% EtOH at 100° (sealed tube) give (cf. Pschorr, *loc. cit.*) the methiodide of (IV). (IV) and CH₂N₂ afford a small amount of a substance, C₁₉H₂₃O₃N, m.p. 142—144° (sinters at 125°). β -Methylthiocodide (VII) (Pschorr, *loc. cit.*) is hydrolysed to methylthiodihydrothebainone (VIII) (+H₂O), m.p. 95—97° (sinters at 90°), decomp. 110°, m.p. (anhyd.) 138—140° and 164—166°. The formation (Pschorr, *loc. cit.*) of methylthiodihydro- β -ethylthiocodide [from (III) and MeSH or (VIII) and EtSH] and of isomeric ethylthiodihydro- β -methylthiocodide [from (VII) and EtSH], is explained; the former is hydrolysed (2*N*-HCl) to (VIII). The γ -ethylthiocodide of Pschorr (*loc. cit.*) is now shown to be the sulphoxide of (III); it is obtained by oxidation (O₂) of (III) in EtOH at 38—40°, and it does not accompany (III) when this is prepared in H₂. δ -Ethylthiocodide (IX), distills in a high vac., [α]_D +57.7° in EtOH [perchlorate (X), m.p. 223—224°; 1:1-compound, m.p. 176—180° (decomp.), with AgNO₃] (improved prep.), is reduced (Na, EtOH) to the



phenolic dihydro- δ -ethylthiocodide-B (XI), distills at 140°/high vac. (malonate, m.p. 170.5—171.5°), and a mixture of the phenolic dihydrodeoxycodines-B and -C (this vol., 1117). (X) and EtSH in 6*N*-HCl give the phenolic dihydro- δ -diethylthiocodide (XII), m.p. 125—126°, [α]_D —100° in EtOAc. Electrolytic reduction of (X) affords the phenolic dihydro- δ -ethylthiocodide-A (XIII), m.p. 156—157°, [α]_D +167.6° in EtOH [benzoate (+H₂O), m.p. 151—154° (decomp.)], and a dihydrodeoxycodine [hydrochloride, m.p. 157—

159° (decomp.) [which has the properties of deoxycodine-*C* (XIV); the de-*N*-Me derivative differs, however, from that of (XIV)]. (XIV) and EtSH in 6*N*-HCl give the phenolic *ethylthiodihydrodeoxycodine* [as (XI) with H₂ and H₂SEt interchanged], b.p. 140°/0.05 mm., $[\alpha]_D^{25}$ -59.8° in EtOH. A pure compound could not be obtained from ψ -codeine (the Me ether does not react) and EtSH. H. B.

Hydration of emetine hydrochloride and codeine phosphate. H. WALES (J. Amer. Pharm. Assoc., 1934, 23, 879—882).—V.-p. curves at 25° give no evidence of a hydrate of emetine hydrochloride; the H₂O present is adsorbed. Codeine phosphate has 1.5H₂O. C. G. A.

Strychnine and brucine. XXX. Comments on a memoir of M. Kotake and T. Mitsuwa. R. ROBINSON (J.C.S., 1934, 1490—1491; cf. this vol., 908).—The criticisms of Robinson's formula for strychnine are misrepresentations. The formula (I) suggested is improbable because it does not explain (a) the properties and transformations of ψ -strychnine (cf. A., 1932, 1147), (b) the oxidation by BzO₂H of methoxymethyldihydroestrychnine (this vol., 789), (c) or the fact that (I) requires the ready loss of 2H from the dihydroindole nucleus. Gentle hydrolysis of Tafel's base gives hydroxymethyldihydroestrychnine (?), m.p. 219° (this vol., 908; A., 1932, 527), which, when heated with H₂O, forms a quaternary NH₄ hydroxide. J. L. D.

Reaction between organo-metallic compounds and certain dihydrophenarsazine derivatives. G. A. RAZUVAIEV (J. Gen. Chem. Russ., 1934, 4, 629—631).—10-Formyl-9:10-dihydrophenarsazine with HgPh₂ yields 10-phenyl-9:10-dihydrophenarsazine (I), Hg, CO₂, and C₆H₆; with PbEt₄ it yields 10-ethyl-9:10-dihydrophenarsazine (II) and (HCO₂)₂Pb (III), and with PbPh₄ it yields (I) and (III). 10-Chloro-9:10-dihydrophenarsazine yields (I) and PbPh₂Cl₂ with PbPh₄ in C₅H₁₁·OH, (II) and PbEt₂Cl₂ with PbEt₂, and (I) and HgPhCl with HgPh₂. R. T.

10-Phenylacetylenyl-9:10-dihydrophenarsazine and its properties. V. SCHPANSKI (J. Gen. Chem. Russ., 1934, 4, 658—661).—10-Chloro-9:10-dihydrophenarsazine (I) in Et₂O and CPh·CNa yield 10-phenylacetylenyl-9:10-dihydrophenarsazine (II), m.p. 172°, which with HCl regenerates (I) and CPh·CH (III), with I in C₆H₆ yields the 10-*I*-analogue of (I) and CPh·Cl, and with H₂O₂ the 10:10-dihydro-oxide (IV) of (II). (IV) and HCl yield 10-phenylacetylenyl-9:10-dihydrophenarsazine hydroxychloride, m.p. 148° (decomp.), which gives (I) and (III) on reduction with SO₂ in EtOH. R. T.

Organic gold compounds. V. Auration of aromatic nitriles. M. S. KHARASCH and T. M. BECK (J. Amer. Chem. Soc., 1934, 56, 2057—2060; cf. A., 1931, 1172).—The following are obtained from anhyd. AuCl₃ and an excess of the appropriate RCN (alone or, if solid, in presence of PhNO₂) and subsequent dilution with Et₂O: *Au cyanophenyl* (I), m.p. 168° (decomp.), 3-cyano-4-, m.p. 147—148° (decomp.), and -6-, m.p. 170—171° (decomp.), -methylphenyl (converted by Br into 4-bromo-*o*- and 2-bromo-*p*-toluo-

nitrile, respectively), α - and β -cyanonaphthyl, m.p. 161—162° (decomp.) and 127° (decomp.), respectively (from α - and β -C₁₀H₇·CN, respectively), 6-bromo-3-cyanophenyl, m.p. 172° (decomp.) (converted by Br into 3:4-C₆H₃Br₂·CN), *m-nitrocyanophenyl*, m.p. 185—187° (decomp.) (from *m*-NO₂·C₆H₄·CN), *cyanomethylphenyl*, m.p. 127—128° (decomp.) (from CH₂Ph·CN), and *p-nitrocyanomethylphenyl*, m.p. 140—142° (decomp.) (from *p*-NO₂·C₆H₄·CH₂·CN), *dichlorides*. Thermal decomp. of (I) gives Au, HCl, PhCN, and 2:5-C₆H₃Cl₂·CN. (I) does not react with Br at 25°; at 100°, polybromo-compounds are formed. The rate of formation of the above dichlorides varies with the electronegativity of the aryl group. The relative stability of these compounds suggests that an electron pair is shared by the Au and N atoms. *o*-C₆H₄Me·NO₂ and AuCl₃ give *Au 3-nitro-4-methylphenyl dichloride* (+H₂O), converted by Br into 4-bromo-2-nitrotoluene. EtCN (slight excess) and AuCl₃ give a compound, EtCN, AuCl₃, m.p. 85—89° (decomp.); other aliphatic nitriles generally form additive compounds. H. B.

Simple mercuri-organic derivatives of phenol. A. N. NESMEJANOV and E. M. TOROPOVA (J. Gen. Chem. Russ., 1934, 4, 664—668).—*m*-OH·C₆H₄·HgCl (I) (*Ac* derivative, m.p. 199—200°) is obtained in 43% yield from *m*-OH·C₆H₄·N₂Cl, HgCl₂, and Cu in EtOH at room temp. (I) is converted by Na₂S₂O₃ into *Hg*(C₆H₄OH-*m*)₂ (II) (*Ac*₂ derivative, m.p. 161°), decomp. at 315°. The *Br*-, sintering at 240°, sintering at 200°, *CN*-, m.p. 186—188°, and *CNS*-, m.p. 175—176°, analogues of (I) are prepared by heating (II) with the corresponding Hg halide. R. T.

Constitution of proteins. A. BONOT (Bull. Soc. chim., 1934, [v], 1, 1017—1025).—A lecture.

Oxidation of caseinogen. I. S. JAITSCHNIKOV (J. Gen. Chem. Russ., 1934, 4, 662—663).—Certain of the oxidation (KMnO₄) products of caseinogen (I) are acidic, do not give the xanthoproteic, Millon's, and cysteine reactions, and absorb less I than did the original (I). R. T.

Clupein. II. Electrometric titration. K. E. RASMUSSEN and K. LINDERSTRØM-LANG (Z. physiol. Chem., 1934, 227, 181—212; cf. this vol., 1015).—The titration curves of clupein fractions and unfractionated clupein resemble those of aliphatic (NH₂)₁-acids. The logarithms of the acid and basic dissociation consts., *P*_A and *P*_B, are 2.9—3.3 and 7.4—8.0, respectively, on the assumption that each clupein prep. is composed of a homogeneous unbranched polypeptide with terminal CO₂H and N groups. The calc. mol. wt. is 4000—4100, corresponding with a content of 19—20 arginine and 7—8 (NH₂)₁-acid groupings. J. H. B.

Polysaccharoproteins. III. Compounds of myosin with polysaccharides. S. J. VON PRZYŁECKI and R. MAJMIN (Biochem. Z., 1934, 273, 262—272; cf. this vol., 961).—Myosin (I) forms well-defined compounds (II), stable at *p*_H 3—10, with dextrin, glycogen, and starch, each mol. of (I) being united with 1 to > 10 mols. of polysaccharide (III). The proportions in which the constituents unite depend on [H⁺], purity of (I), nature and amount of (III), and on

the presence of salts in the absence of which practically no combination occurs. The amount of (III) in (II) is the greater the higher is the mol. wt. of (III).

W. McC.

Cysteine from cystine by hydrolysis. P. HOLTZ (Klin. Woch., 1933, 12, 1876; Chem. Zentr., 1934, i, 532).—Ultra-violet irradiation of egg-white (I) produces reversibly oxidisable substances. Hydrolytic fission products are probably concerned. On warming (I) with 0.01*N*- or 0.1*N*-NaOH sulphide-S is liberated. Cystine is hydrolysed by heating for 30 min. at 100° with *N*-NaOH; cysteine is formed.

A. G. P.

Partial fission of silk fibroin. T. UCHINO (J. Biochem. Japan, 1934, 20, 65—130).—Hydrolysis of silk fibroin by glycerol (cf. A., 1925, i, 1109) yields a product, extraction of which by EtOAc affords glycyl-alanine anhydride and tyrosine-containing compounds contaminated with melanins. Hydrolysis at low temp. with 70% glycerol- H_2SO_4 is > that with 70% aq. H_2SO_4 , which, in turn, is > that with conc. H_2SO_4 . Data from degradation with varying concs. of H_2SO_4 and NaOH are given. With 0.175*N*- H_2SO_4 for 10 hr. at 170° and subsequent fractional extraction with solvents, anhydrides of glycyl-tyrosine and -alanine (but not that of alanyltyrosine) are obtained. Diketopiperazine derivatives yielded by hydrolysis with glycerol are probably not preformed, but are products of the reaction. The results generally support Fischer's acid amide linking theory of protein structure.

F. O. H.

Polypeptide constitution and proteolytic enzymes. J. MATSUI (J. Biochem. Japan, 1934, 20, 141—145).—*Et* $\alpha\beta$ -dichloroacetamidopropionate, m.p. 88—89° [from abs. EtOH-HCl and the acid (A., 1932, 304)], with EtOH-NH₃ at room temp. and treated with Ag₂SO₄ followed by CO₂ yields *glycyl(glycyl-di-aminopropionyl) anhydride carbonate* [2:5-diketo-3-(glycylaminomethyl)piperazine carbonate], $\text{C}_8\text{H}_{15}\text{O}_2\text{N}_2\text{CH}_2\text{NHCOCH}_2\text{NH}_2\cdot 0.5\text{H}_2\text{CO}_3$ (I), m.p. 144—145°. Trypsin (with and without enterokinase), but not pepsin or erepsin, hydrolyses (I). The action of enzymes on diketopiperazine derivatives is discussed.

F. O. H.

Enzymic hydrolysis of peptides from aspartic and glutamic acids.—See this vol., 1403.

Crystalline progestin.—See this vol., 1268, 1412.

Titration of protein with trichloroacetic acid. R. K. SCHOFIELD and L. W. SAMUEL (Nature, 1934, 134, 665).— $\text{CCl}_3\cdot\text{CO}_2\text{H}$ can be used for the rapid determination of titratable NH₂-groups. Edestin added to 0.1*M*- $\text{CCl}_3\cdot\text{CO}_2\text{H}$ gives, after centrifuging, a clear liquid which contains only a trace of the added N, and can be sharply back-titrated.

L. S. T.

Catalytic determination of carbon and hydrogen in organic substances. A. CONTARDI and C. FERRI (Atti R. Accad. Sci. Torino, Cl. Sci. fisich., 1932—1933, 68, 181—189; Chem. Zentr., 1934, i, 2165—2166).—Separated layers of PbO₂ (at 160°) and MnO₂ (at 390—400°) are employed for the combustion. Hg, if present, is held in a layer of Ag foil, 3—4 cm. long.

H. J. E.

Semimicro-combustion by the contact process. K. H. SLOTTA and J. MÜLLER (Chem.-Fabr., 1934, 7, 380—383).—Apparatus and modified technique for determining C and H by combustion in a stream of O₂, using Pt-asbestos, are described. A 30-mg. sample is used. Methods for determining S and halogens are indicated.

E. S. H.

Determination of sulphur in organic compounds. N. MELNIKOV (Z. anal. Chem., 1934, 98, 412—414).—The substance is oxidised destructively, forming SO₄²⁻, by addition of KMnO₄ to its H₃PO₄ solution at 70—140°.

J. S. A.

Kuttner-Lichtenstein microcolorimetric method for determining organic phosphorus. D. GLICK (J. Lab. Clin. Med., 1934, 19, 1012—1013).—Excess of H₂O₂ is removed by heating for 3 min. at the b.p. of H₂SO₄.

CH. ABS. (p)

Determination of bromine number of acid products. S. I. SCHODTZEY (J. Appl. Chem. Russ., 1934, 7, 605—608).—McIlhiney and Johannsen's method of determining the halogen no. of unsaturated compounds is not applicable to acids. The following universal procedure is proposed. The sample, dissolved in 10 ml. of CCl₄ and treated with excess of 0.2*N*-Br in CCl₄, is left in diffused light for 10—15 min., after which 10—15 ml. of H₂O are added, and 0.5% PhOH drop by drop to almost complete decolorisation of the CCl₄ layer, when 1% aq. PhOH containing Me-orange is added to the appearance of a red coloration in the aq. layer. 10 ml. of conc. HCl and excess of Cl₂-H₂O are now added, followed by 10 ml. of *N*-KCN; air is aspirated through the solution for 5 min., 2 g. of KI are added, and the liberated I is titrated 20 min. later. The Br no. is given by $0.7992(v_1 - v_2)/w$, where v_1 and v_2 are, respectively, the no. of ml. of 0.1*N*-Na₂S₂O₃ equiv. to the Br used, and to the I liberated, and w is the wt. of the sample.

R. T.

Distillation with mercury vapour and the formation of hydrocarbon dross. H. DECKER (Ber., 1934, 67, [B], 1636—1640).—The volatilisation of hydrocarbon dross during the distillation of bituminous idrialite suggests distillation with Hg vapour as a method of purifying difficultly-volatile hydrocarbons etc. Distillation is carried out in Anschütz flasks of Jena glass which are about 1/4 filled with Hg; 5—10 g. of substance are added and the mixture is heated over a free flame. Bumping is prevented by Cu turnings and the cork stoppers are protected by asbestos or metal foil. The method has been applied successfully to indigotin, chrysene, pyrene, fluoranthene, 2-phenylquinoline, phenanthrene, and anthracene.

H. W.

Determination of formaldehyde by aniline. G. TOUSSAINT, J. DÉTRIE, and M. VERAÏN (Compt. rend. Soc. Biol., 1934, 117, 193—194).—Measurement at 15—20° of the optical densities of aq. solutions of NH₂Ph to which CH₂O is added may be used to determine CH₂O.

A. L.

Analysis of mixtures of acetone, acetaldehyde, and acetic acid. M. S. PLATONOV and V. A. PLAKIDINA (J. Gen. Chem. Russ., 1934, 4, 472—476).—AcOH is determined by titration with standard Ba(OH)₂ (phenolphthalein), COMe₂ + MeCHO by adding NH₂OH, HCl and titrating the HCl liberated, and

COMe₂ iodometrically after oxidising MeCHO with KMnO₄, excess of which is removed by adding H₂O₂.

R. T.

3-Nitrobenzhydrazide as reagent for the identification of aldehydes and ketones. K. C. MENG and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 347—351).—*m*-Nitrobenzhydrazide, from *m*-NO₂·C₆H₄·CO₂Et and N₂H₄·H₂O in EtOH, m.p. 151—152°, is recommended as a reagent for CO-compounds. *m*-Nitrobenzoylhydrazones of the following compounds are described: MeCHO, m.p. 160—161°; EtCHO, m.p. 153—154°; PrⁿCHO, m.p. 138—139°; PrⁱCHO, m.p. 141—142°; heptaldehyde, m.p. 118—119°; PhCHO, m.p. 207—208°; *m*-, m.p. 251—252°, and *p*-, m.p. 261°, -NO₂·C₆H₄·CHO; *o*-OH·C₆H₄·CHO, m.p. 244°; furfuraldehyde, m.p. 197—200°; COMe₂, m.p. 151—152°; COMeEt, m.p. 112°; Me hexyl ketone, m.p. 100°; 2-furfurylideneacetone, m.p. 186—187°; COPh₂, m.p. 156—157°; pinacolin, m.p. 165—166°; styryl Me ketone, m.p. 168—169°; COPhMe, m.p. 194°; *m*-nitro-, m.p. 248—249°, *p*-methyl-, m.p. 194—195°, *p*-methoxy-, m.p. 199°, and *p*-bromo-acetophenone, m.p. 210°; CH₃Ac·CO₂Et, m.p. 103—104°; Et lævulate, m.p. 136°, and lævulic acid, m.p. 185—186°. H. N. R.

***o*-Chlorobenzhydrazide as reagent for the identification of aldehydes and ketones.** T. H. SUN and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 359—363).—*o*-C₆H₄Cl·CO₂Et and N₂H₄·H₂O in EtOH solution yield *o*-chlorobenzhydrazide (I), m.p. 117—118°. The hydrazones formed from (I) and CO-compounds are, in general, more sol. and of lower m.p. than those from the *p*-isomeride. *o*-Chlorobenzoylhydrazones of the following are described: MeCHO, m.p. 145°; EtCHO, m.p. 151—152°; PrⁿCHO, m.p. 141°; heptaldehyde, m.p. 129°; COMe₂, m.p. 110—111°; COMeEt, m.p. 81—82°; pinacolin, m.p. 125—126°; styryl Me ketone, m.p. 128—129°; COPhMe, m.p. 135—136°; *m*-nitro-, m.p. 212—213°, *p*-methyl-, m.p. 127—129°, and *p*-methoxy-acetophenone, m.p. 125—126°; PhCHO, m.p. 162°; *m*-, m.p. 178—179°, and *p*-, m.p. 219—221°, -NO₂·C₆H₄·CHO, *o*-OH·C₆H₄·CHO, m.p. 165°; furfuraldehyde, m.p. 162—163°; lævulic acid, m.p. 215°; Et lævulate, m.p. 99—100°, and COPh₂, m.p. 142°. H. N. R.

***p*-Chlorobenzhydrazide as reagent for the identification of aldehydes and ketones.** C. SHIH and P. P. T. SAH (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 353—357).—*p*-Chlorobenzhydrazide, m.p. 162—163°, prepared from *p*-C₆H₄Cl·CO₂Et and N₂H₄·H₂O in EtOH, is recommended as a reagent for CO-compounds. *p*-Chlorobenzoylhydrazones of the following are described: MeCHO, m.p. 180—181°; EtCHO, m.p. 163—165°; PrⁿCHO, m.p. 142—143°; PrⁱCHO, m.p. 153—154°; PhCHO, m.p. 227—229°; *m*-, m.p. 213—215°, and *p*-, m.p. 246—248°, -NO₂·C₆H₄·CHO; *o*-OH·C₆H₄·CHO, m.p. 214—217°; furfuraldehyde, m.p. 210—212°; COMe₂, m.p. 169—171°; COMeEt, m.p. 161—162°; Me hexyl ketone, m.p. 121—122°; COPhMe, m.p. 175—177°; *m*-nitro-, m.p. 240—242°, *p*-methyl-, m.p. 213—215°, and *p*-methoxy-acetophenone, m.p. 190—192°; COPh₂, m.p. 137—139°; styryl Me ketone, m.p. 197—199°; pinacolin, m.p. 197—199°; CH₃Ac·CO₂Et, m.p. 98—

99°; lævulic acid, m.p. 135—137°; Et, m.p. 106—108°, and CH₂Ph, m.p. 131—132°, lævulate. H. N. R.

Hydrazines. IV. β -Naphthylhydrazine as reagent for the identification of aldehydes and ketones. H. H. LEI, P. P. T. SAH, and C. H. KAO (Sci. Rep. Nat. Tsing Hua Univ., 1934, 2, 335—341).— β -Naphthylhydrazine (prep. described; *picrate*, m.p. 176.5°) is recommended as a reagent for CO-compounds. β -Naphthylhydrazones of the following compounds are described, some of which may be further characterised by conversion into their *picrates* and titration with alkali: *o*-OH·C₆H₄·CHO, m.p. 186—187°; *m*-NO₂·C₆H₄·CHO, m.p. 201—202°; furfuraldehyde, m.p. 134—135° (*picrate*, m.p. 118°); 2-furfurylideneacetone, m.p. 163—164° (*picrate*, m.p. 118—119°); COPh₂, m.p. 127—128° (*picrate*, m.p. 157—158°); styryl Me ketone (*picrate*, m.p. 124—125°); *m*-nitroacetophenone, m.p. 143—144° (*picrate*, m.p. 161—162°); CH₃Ac·CO₂Et, m.p. 107—108° (*picrate*, m.p. 160—161°). The β -naphthylhydrazones of PhCHO, m.p. 194—195°, *p*-NO₂·C₆H₄·CHO, m.p. 233—234°, COPhMe, m.p. 157—158° (*picrate*, m.p. 153—154°), lævulic acid, m.p. 143—144° [*picrate*, m.p. 176° (decomp.)], and Et lævulate, m.p. 138—139° (*picrate*, m.p. 152—153°), were also prepared. H. N. R.

Application of quantitative spectrum analyses to binary mixtures of common carotenoids. E. S. MILLER (Plant Physiol., 1934, 9, 681—684).—Over a limited range of concn. binary mixtures of carotenoids obey Beer's law. Spectrum analysis permits determinations with approx. 1% error. A. G. P.

A. Liebermann-Burchard reaction with compounds containing five-membered monoheterocyclic rings. V. E. LEVINE and E. RICHMAN. **B. Liebermann-Burchard reaction with carotene.** V. E. LEVINE and G. E. BIEN (Proc. Soc. Exp. Biol. Med., 1934, 31, 582—584).—A. The Liebermann-Burchard (I) reagent reacts with thiophen, furan, and many of its derivatives, as well as with cholesterol (II).

B. The (I) test for (II) will detect 0.01 mg. of carotene (III) dissolved in CHCl₃. The green colour with (III) reaches a max. intensity rapidly and fades in 2 min. to a yellow-brown. The green colour with (II) reaches a max. in 15 min. (III) does not interfere with the determination of (II) in blood. CHCl₃ extracts (II) from blood and from plaster of Paris mixture, but does not remove (III). CH. ABS. (e)

Determination of tyrosine by bromination. M. BONICATTI (Boll. uff. R. Staz. sperim. Seta, 1933, 3, 66—69).—The solution is acidified with HCl, and 5 c.c. of 20% NaBr are added followed by 0.1N-NaBrO₃ until the solution is deep yellow. After 2 hr. excess of KI is added and the mixture titrated with 0.05N-Na₂S₂O₃. A. G. P.

Tryptophan reaction of Adamkiewicz and Hopkins. S. WINKLER (Z. physiol. Chem., 1934, 228, 50—60).—Since small amounts of Cu greatly increase the intensity of the colour, addition of Cu makes the detection of tryptophan in proteins by means of CHO·CO₂H much more certain. The Cu addition also facilitates an exact colorimetric determination of tryptophan. J. H. B.

Determination of ecgonine. A. GORIS, A. CHALMETA, and C. CHALMETA (Bull. Sci. Pharmacol., 1933, 40, 641—650; Chem. Zentr., 1934, i, 2171).—In de Jong's method (A., 1923, ii, 798) the extraction

of ecgonine is not always complete. Hydrolysis with HCl requires at least 3 hr. The use of more conc. acid may cause partial transformation into anhydro-ecgonine. A. G. P.

Biochemistry.

Changes in the respiratory characteristics following respiration of mixtures with low concentrations of oxygen. R. MARGARIA and C. TALENTI (Atti R. Accad. Sci. Torino, 1933, 68, 483—491).—Inspiration of mixtures containing < 15% O₂ produced an increase of ventilation and velocity of inspiration; frequency of inspiration increased only slightly. On re-establishment of normal conditions all the respiratory characteristics fell temporarily to vals. < normal. The blood-*p_H* in hypoventilation (I) from anoxæmia decreased by 0.03—0.10 according to the magnitude of (I); the increase in respiration is therefore attributed to increased [H⁺] of the nerve centres. R. N. C.

Influence of respiration on the oxygen-saturation of arterial blood. K. MATTHES (Arch. exp. Path. Pharm., 1934, 176, 683—696).—Spectrophotometric determinations of oxygenated and reduced hæmoglobin indicate that the blood of experimental animals, whether narcotised or not, has an O₂-saturation (I) of 94—98%, the val. falling to 80% with certain types of narcosis; the deficiency disappears on administration of O₂. (I) varies by approx. 0.5—5% when the respiration (II) is fast and slow, respectively. The types of (II) due to injection of adrenaline or picroton and to vagal stimulation are correlated with the changes in (I). F. O. H.

Spectroscopic comparison of foetal and maternal blood in the rabbit and goat. F. G. HALL (J. Physiol., 1934, 82, 33—37).—The O₂-dissociation curves for foetal (I) and maternal hæmoglobin (II) show that in all cases and at all periods of gestation, (I) has a greater affinity for O₂ than (II). The difference in the goat is > in the rabbit, whilst in the latter case at *p_H* 7.4 it is > at 6.8. Foetus and mother probably have a sp. difference in their hæmoglobins. R. N. C.

Blood-volume and oxygen-capacity of the foetal blood of the goat. R. H. ELLIOT, F. G. HALL, and A. ST. G. HUGGETT (J. Physiol., 1934, 82, 160—171).—The O₂-capacity (I) of the foetal blood rises during the first half, and is steady during the second half, of pregnancy, at which stage the total (I) of the circulation also becomes const., and the corpuscular carrying-power for O₂ increases and remains high until birth. R. N. C.

Effect of blood transfusion on the condition of the receiver's blood, and of the withdrawal of blood on the donor's gas metabolism. M. NAKANISHI (Nagoya J. Med. Sci., 1934, 7, 202—205).—Receiver's blood after transfusion shows temporarily increased sugar and lowered Ca and N contents; that of the donor has increased O₂ consumption.

CH. ABS. (p)

Changes in hæmoglobin concentration of blood of growing rats. E. V. ENZMANN (Amer. J. Physiol., 1934, 108, 373—376).—Neither Ponder's nor Drastich's suggested formula for relating hæmoglobin (I) to erythrocyte vol. is applicable throughout life. Both are low during the first six weeks of life, i.e., during the period of physiological anæmia, but fairly const. after the adult level of (I) is attained.

NUTR. ABS. (b)

Hæmoglobin and erythrocyte differences according to sex and season in doves and pigeons. O. RIDDLE and P. F. BRAUCHER (Amer. J. Physiol., 1934, 108, 554—566).—In both species and all races studied hæmoglobin (I) and erythrocyte count (II) in males were > in females; (I) in winter was >, and in summer <, in the other seasons; (II) was highest in autumn and lowest in summer. (I) and cell count were not necessarily parallel. Both (I) and (II) were slightly higher in adolescent than in adult birds.

NUTR. ABS. (b)

Rôle of erythrocytes in protein metabolism. I. Exchange of amino-nitrogen between erythrocytes and plasma *in vitro*. B. I. SBARSKI and L. SUBKOVA (Biochem. Z., 1934, 273, 279—283).—*In vitro* erythrocytes (I) always have an NH₂-acid (II) content > that of the surrounding plasma (III). (I) take (II) from (III) or give up (II) to (III) according as the (II) content of (III) rises or falls. W. McC.

Microdetermination of protein and protein fractions in serum and plasma without distillation. F. RAPPAPORT and G. GEIGER (Klin. Woch., 1934, 13, 563—564).—The NaOBr method for determining non-protein-N is adapted for the determination of fibrinogen, albumin, globulin, and globulin fractions. The fibrinogen-N is determined in the ppt. itself, otherwise Howe's method is followed. 0.2 ml. of serum or plasma is necessary. NUTR. ABS. (m)

Serum-albumin and -globulin of new-born, premature, and normal infants. D. C. DARROW and M. K. CARY (J. Pediat. St. Louis, 1933, 3, 573).—Total protein decreases in all infants, the decrease being due chiefly to globulin (I). The decrease in (I) is greatest in premature infants. *Post-mortem* serum of small foetuses showed essentially the same albumin : (I) ratio as that of full-term infants. Both premature and normal infants may show an increase in (I) during infection. The low (I) in infants may indicate the lack of the usual stimuli that give rise to (I) production in adults. NUTR. ABS. (b)

Chemistry and spectroscopy of serum-globulin. J. GRÖH and M. WELTNER (Biochem. Z., 1934, 273, 389—395).—The chemical (tyrosine and tryptophan contents) and spectroscopic properties of the globulin fractions (I) obtained from dil. blood-serum (II) (horse, man) by pptn. with aq. (NH₄)₂SO₄

suggest that there is a relationship between (I) and the kind of haemagglutinin which (II) contain. Hence there may be also a connexion with the blood-groups.

W. McC.

p_H of serum inactivated by heat. P. L. DU NOUY (Nature, 1934, 134, 628—629).—The p_H of mammalian sera is lowered by heating for 10 min. in sealed tubes. A min. val. occurs at approx. 60°; above this temp. a tendency towards higher vals. is sometimes shown.

L. S. T.

Physical properties of blood-serum. M. DOLADILHE (Ann. Inst. Pasteur, 1934, 53, 379—403; cf. this vol., 912).—When colloids of the gamboge type are treated with increasing concn. of blood-serum (I), two zones of non-flocculation [(II) and (III), respectively] with an intermediate zone of flocculation (IV) occur. With (II) the particles are sensitised, whilst with (III) a protective action occurs. With gum and resin colloids, (I) has a marked dispersive action (V) at (III) to an extent depending on the concn. of electrolyte present, the prior treatment (e.g., heating) of (I), etc. (IV) and (V) are mainly due to the globulin and albumin-lipoprotein constituents of (I), respectively; a mutual action also occurs. The bearing of (V) on complement action in immuno-serology is discussed.

F. O. H.

Post-partum changes in blood-urea, -polypeptides, and -chlorine. E. ESTIENNY, J. LASSERRE, and P. VALDIGUIE (Compt. rend. Soc. Biol., 1934, 115, 1676).—In the *post-partum* phase, the urea content of the blood was approx. doubled and the polypeptide content multiplied 6 times; the Cl content was slightly lowered, this change occurring chiefly in the corpuscles. The kidney appeared to play little part in producing the changes in the N constituents.

NUTR. ABS. (b)

A. Changes in urea- and amide-nitrogen of the blood following injection of urease. **B. Influence of urea injection on the action of urease.** **C. Respiratory and chemical changes in exhaled air and in blood reaction following urease injection.** A. AGGAZZOTTI, G. BUCCIARDI, and B. D. MARANI (Boll. Soc. ital. Biol. sperim., 6, 597—599, 600—602, 603—605; Chem. Zentr., 1934, ii, 561).—A. The increase in amide-N and lowering of urea-N in blood following injection of urease (I) indicate that the action of (I) is not limited to blood-urea but extends to that of the tissues.

B. Injected urea is partly eliminated through the kidneys and partly stored in tissues. Stored urea is acted on by (I). After heavy administration of urea injection of (I) is fatal.

C. No definite relationships were observed.

A. G. P.

Determination of blood-urea by the urease aeration-titration method. W. W. KAY and H. L. SHEEHAN (Biochem. J., 1934, 28, 1784—1794).—The method has been modified to give an accuracy of 0.4 mg. per 100 c.c. of blood, but shows only 96% of the urea, the proportion of the NH_3 removed by the aeration.

H. G. R.

Glutathione content of blood. R. O. BOWMAN (Proc. Soc. Exp. Biol. Med., 1934, 31, 616—617).—A modification of the IO_3^- titration method of Hess has

been applied to the determination of reduced glutathione in the tungstic acid filtrates of blood. An accuracy of 7% is claimed. No relationship was found between glutathione content and clinical condition, exercise, diet, age, sex, or colour. NUTR. ABS. (b)

Tryptophan content of blood-serum. A. T. BRICE, jun. (J. Lab. Clin. Med., 1934, 19, 1113—1115).—Dil. serum (1:10) is treated with glyoxylic acid and H_2SO_4 . The colour is compared with standard dye tints.

CH. ABS. (p)

Acetylcholine in ox and dogs' blood. G. H. ETTINGER and G. E. HALL (J. Physiol., 1934, 82, 38—40).—Very small quantities of acetylcholine (I) were found in ox and dogs' blood; the yield was greater if the blood was collected in EtOH than MeOH, and was not affected by the presence or absence of $H_2C_2O_4$, or by keeping the blood. (I) was best extracted from blood with EtOH; MeOH gave unsatisfactory results. (I) added to dogs' blood could be recovered quantitatively.

R. N. C.

Alleged occurrence of acetylcholine in normal ox-blood. J. V. LOACH (J. Physiol., 1934, 82, 118—120).—Attempts to extract acetylcholine (I) from normal ox-blood as aurichloride proved unsuccessful, although (I) added before extraction could be recovered as (II). The Au salt obtained when (I) had not been added was identified as choline aurichloride.

R. N. C.

Phosphoric acid compounds in blood after injection of lecithin. Y. SUBYOSHI and T. OKONOGI (J. Biochem. Japan, 1934, 19, 489—494).—Ingestion of lecithin by rabbits has little influence on the inorg. (I) and acid-sol. P level (II) of the blood. Intravenous injection increases (I) and (II) [mainly in the corpuscles (III)] and the lipin-P [both in (III) and plasma].

F. O. H.

Lipin-chlorine in serum. J. P. PETERS and E. B. MAN (J. Biol. Chem., 1934, 107, 23—34).—Normal sera (I) and those from patients with nephrotic syndrome who have hyperchloræmia and hyperlipæmia (II) are treated with an EtOH-Et₂O mixture (3:1), and, after refluxing, the pptd. proteins, the light petroleum extract of the EtOH-Et₂O mixture (III), and the residue from (III) are analysed for Cl. The fatty acids, lipin-P, and cholesterol in (III) are also determined. Amounts of Cl in the lipin fraction of 2—6 and 2—10 m.-equiv. per 100 c.c. were found in (I) and (II), respectively. No Cl was found in the (III), by the same procedure, of bacon, salt butter, or serum-ultrafiltrates. The lipin-Cl of sera is sufficient to account for the observed differences in total base and acids.

H. D.

Cholesterol content of the blood of the hen. Y. KAISHIO (Proc. 5th World's Poultry Congr. Rome, 1933).—The total cholesterol (I) of the serum in fast-ing birds after a normal diet averaged 0.073%, of which 0.044% was free and 0.029% was ester-(I). Figures are also given for the plasma. The content in non-laying hens is similar to that in cocks. When the ovary contained well-developed ova, total (I) was higher than when the ovary was quiescent. The ester-(I) was lower in the former case. There was

no correlation between blood-(I) and age or egg production. NUTR. ABS. (b)

Determination of plasma-bilirubin. Comparison of the van den Bergh and the Thannhauser and Andersen methods. E. H. BENSLEY (J. Lab. Clin. Med., 1934, 19, 1122—1125).—In sera from cases of subsiding jaundice van der Bergh's method gave low results. In all other cases the method was satisfactory. CH. ABS. (p)

Blood-sugar in monkeys (*Macacus rhesus*). P. V. BOCHKAREV and O. I. NIKOLAEVA (Arch. Sci. Biol. U.S.S.R., 1933, 33, 235—236).—Fasting venous blood-sugar ranged from 43 to 147 mg. per 100 c.c. CH. ABS. (p)

Depression of blood-sugar by egg-yolk fractions. G. HOLLAND, K. HINSBERG, G. KOHLS, and V. NICKEL (Z. ges. exp. Med., 1934, 93, 62—68; Chem. Zentr., 1934, i, 2444—2445).—Active material isolated from egg-yolk contained highly unsaturated acidic substances, the action of which on blood-sugar was related to the extent of unsaturation. Oxidation destroyed the activity. A. G. P.

Increase in sugar content of blood produced by diastase. J. WEINMANN (Biochem. Z., 1934, 273, 312—316).—Diastase (I) of animal and vegetable origin and, occasionally, saliva intravenously or subcutaneously injected into rabbits cause an increase, sometimes large, in the blood-sugar. No increase results if (I) is inactivated by heat or acid. W. McC.

Colorimetric determination of fructose in blood and urine. J. H. ROR (J. Biol. Chem., 1934, 107, 15—22).—The Seliwanoff reaction is modified by using 18% HCl, alcoholic resorcinol, and warming to 80°. Proteins are removed from blood with the Somogyi reagent (A., 1930, 801); urine is decolorised with acid-washed activated charcoal at p_H 3.1. Under these conditions glucose (< 300 mg. per 100 c.c.) does not interfere; furfuraldehyde gives a green colour with the test although xylose (< 1%) does not interfere. Normal human urine secreted under fasting conditions gives a negative fructose test, whilst after a meal containing fruits and sucrose it gives a positive test. H. D.

Diacetyl and acetylmethylcarbinol (or their heat-labile precursors) in blood. H. SCHMALFUSS (Z. physiol. Chem., 1934, 227, 247—250).—Ac₂ and CHAcMe·OH were detected in fresh ox-blood and in sheep's blood. J. H. B.

Determination of oxalic acid in blood and intermediary oxalic acid metabolism. R. JURGENS and E. JUERGENSOHN (Z. ges. exp. Med., 1934, 93, 441—446).—The method of Merz and Maugeri is used, but 7% aq. CCl₃·CO₂H is used for deproteinising. Administration of 7.5—40.0 g. of malic, succinic, or tartaric acid causes no increase in the H₂C₂O₄ content of the blood. NUTR. ABS. (m)

Blood-calcium. A. A. JANSON (Illinois Med. J., 1934, 65, 91—95).—No const. relationship could be established between total and diffusible Ca or between inorg. P and Ca of blood. Normal vals. for total Ca were associated with high, normal, and low vals. for diffusible Ca, with low vals. predominating. Many

cases with low total Ca showed normal diffusible Ca and with high total, low diffusible Ca. The importance of determining diffusible rather than total Ca content of the blood is indicated. NUTR. ABS. (b)

Calcium and phosphorus content of the blood-plasma of the fasting laying hen. M. LASKOWSKI (Biochem. Z., 1934, 273, 284—290).—The P content of the blood-plasma (I) of laying (II) is 3.5 times that of (I) of non-laying (III) hens. No increase in the Ca and P contents of their (I) results from feeding diet rich in Ca and P to fasting hens. 2—4 days' fasting does not interrupt the laying, and the Ca and P contents of (I) remain at the normal val. for (II). 4—6 days' fasting interrupts laying for several days, and the Ca and P contents of (I) fall to the val. characteristic of (III). There is no relation between the Ca and P contents of (I). W. McC.

Escape of potassium from rabbit's red cells into hypotonic solutions. E. PONDER and E. J. ROBINSON (Biochem. J., 1934, 28, 1940—1943).—When rabbit's red cells are suspended in hypotonic NaCl, K is lost from the cells, probably during the 15 sec. in which swelling to equilibrium takes place, in sufficient quantity to account for the observed vol. changes. A. E. O.

Sulphur content of pancreatic blood and thoracic lymph. II. S. KUMAMI (J. Biochem. Japan, 1934, 19, 457—467; cf. A., 1933, 965).—The total S levels of the pancreatic venous blood (I) and thoracic lymph (II) of dogs transiently increase after injection of glucose or stimulation of the vagus. The increase is at least partly due to increased secretion of insulin, which is therefore transported by both (I) and (II). Intravenous injection of aq. NaCl diminishes the S content of (II). F. O. H.

Normal bromine cycle in blood. H. FLEISCHHACKER and G. SCHNEIDER (Klin. Woch., 1933, 11, 1550; Chem. Zentr., 1934, i, 3502).—Roman's method is not applicable to determinations of small amounts of Br' in blood. A. G. P.

Determination of iodine [in blood]. D. R. McCULLAGH (J. Biol. Chem., 1934, 107, 35—44).—Blood is heated with saturated aq. KOH in a Ni crucible until foaming ceases, and then heated at 250° for 30 min. H₂O is added, the paste extracted with 95% EtOH, and the extract evaporated to dryness. The residue is heated at 385° for 10 min. in a stream of O₂. The ash is dissolved in H₂O and filtered and 50% H₂SO₄, 10% Fe₂(SO₄)₃, and 30% H₂O₂ are added. The solution is distilled into a mixture of aq. H₂SO₄ and 10% NaHSO₃ for 30 min. After boiling the distillate for 3 min. KOH is added and the solution is conc. Br is added to the slightly acid solution and after further concn. KI is added and the liberated I is titrated with Na₂S₂O₃. H. D.

Water content of the blood of the silk-worm (*Bombyx mori*, L.) during development. K. KURODA (Keijo J. Med., 1934, 5, 151—164).—The H₂O content of the blood shows complex variations during the life cycle; these are completely different from those obtaining in the mouse, chicken, and salmon, and bear no relation to the H₂O intake. P. G. M.

Mitogenetic spectrum of circulating blood. K. P. GOLUISHEVA (Aroh. Sci. Biol. U.S.S.R., 1933, 33, 107—113).—Spectrographic measurements indicate the spectral regions of glycolysis, oxidation, hydrolysis of hexose phosphate and creatine phosphate, and deamination of peptides. CH. ABS. (p)

Relations between immunity-hæmolysis and diet in the rat. A. FORSSBERG (Z. Immunität., 1933, 80, 16—27; Chem. Zentr., 1934, i, 2304—2305).—Rats were given a synthetic basal diet of varying composition, immunised against sheep-serum, and the hæmolytic titres (I) estimated. Antibody formation was lowered by vitamin deficiency only for vitamin-A. Increase of fat in the diet raised blood-cholesterol, and lowered hæmolysin (II). Substitution of gelatin for caseinogen, ovalbumin, or glutinin in the diet reduced the (I), the fall being considerable if albumin was entirely absent. Addition of lecithin or choline increased the production of (II). R. N. C.

Absorption of simple lysins at cell interfaces. E. PONDER (Proc. Roy. Soc., 1934, B, 116, 282—295).—The "initial" and "delayed" absorption at red-cell surfaces does not correspond with the adsorption postulated by other investigators (cf. Reiner, this vol., 551). H. G. R.

Hæmostatic possibilities of snake venom. R. G. MACFARLANE and B. BARNETT (Lancet, 1934, 227, 985—987).—The venom of *Vipera russellii* contains a coagulant which, in high dilutions *in vitro*, rapidly clots normal and hæmophilic blood. L. S. T.

Effect of snake venom on hapten antibody reaction. W. SCHEPERS (Z. Immunität., 1933, 80, 395—411; Chem. Zentr., 1934, i, 883—884).—Cobra venom (I) inhibits the coagulability of haptens, and even of organ-sp. EtOH brain extracts, group-sp. human blood-A extracts, and species-sp. organ extracts. The same inhibition also occurs with lecithin or organ extracts after boiling. There was no indication of the conversion of hapten into hemi-hapten, the production of non-sp. inhibitions by the action of (I) on the lipin vehicle of the hapten function appearing the most probable explanation. Experiments with *Daboia* venom suggested a parallelism between lecithin cleavage and the inhibition of flocculation. The hæmolytic products of snake venoms and lecithin show the same inhibitory action. R. N. C.

Chemistry of immunity. F. HAUROWITZ (Med. Klin., 1933, 29, 936—939; Chem. Zentr., 1934, i, 3484).—From the use of chemically-known antigens and analysis of their reaction products with antibodies it is concluded that the antigen disturbs globulin (I) formation in the reticulo-endothelial cells, the NH_2 -acids, oriented by polar attraction, combining to form the antibody-(I), which does not differ chemically from serum-(I). R. N. C.

Chemo-immunological studies of conjugated carbohydrate proteins. VIII. Influence of the acetyl group on specificity of hexoside-protein antigens. W. F. GOEBEL, F. H. BABERS, and O. T. AVERY (J. Exp. Med., 1934, 60, 85—94).—Introduction of a simple chemical group (e.g., Ac) induces a new specificity in carbohydrates. CH. ABS. (p)

Immunological specificity of the thyroglobulins. M. ADANT and P. SPEHL (Compt. rend. Soc. Biol., 1934, 117, 230—231).—Sheep antithyroglobulin immune serum (I) and ox (I), whilst having a high pptn. activity with respect to the corresponding antigens, have very little activity towards the thyroglobulins (II) of the pig and the ox, and (II) of the pig and the sheep, respectively. A. L.

Immunological comparison of iodised protein and thyroglobulins. M. ADANT and P. SPEHL (Compt. rend. Soc. Biol., 1934, 117, 232—233).—Thyroglobulin (I) immune sera have a slight pptn. activity towards iodised serum-protein (II) when (I) and (II) are derived from the same species of animal. There is no activity, however, when (I) and (II) are derived from different species. A. L.

Avidity of concentrated and unconcentrated sera. F. MODERN (Anal. Asoc. Quím. Argentina, 1934, 22, 33—40).—The serum ratio (I) of an unconc. diphtheria antitoxin (II) varies with the serum, but is < 1 . The conc. (II) has (I) approx. 1. The time of flocculation varies considerably with the serum. The L_5 of diphtheria toxin in guinea-pigs usually requires 1.5—1.7 units of (II) for neutralisation. The dilution ratio is slightly higher in unconc. than in conc. (II). Conc. of normal sera lowers the (I) slightly. R. N. C.

Precipitin production in rabbits following intramuscular injection of antigen adsorbed on aluminium hydroxide. L. HEKTOEN and W. H. WELKER (J. Infect. Dis., 1933, 53, 309—311).—Precipitin production following injection may continue for several months. $\text{Al}(\text{OH})_3$ is gradually replaced by connective tissue. Antigens adsorbed on $\text{Al}(\text{OH})_3$ retain precipitinogenic properties for at least 1 year. CH. ABS. (p)

Complexes of iron with various biological materials. S. L. TOMPSETT (Biochem. J., 1934, 28, 1802—1806).— Fe^{+++} but not Fe^{++} forms complexes with the non-diffusible P of biological materials, such as lecithin, egg-white, and milk, but not with simple proteins. It is liberated on reduction by thiolacetic acid and $\text{Na}_2\text{S}_2\text{O}_4$, and by $\text{Na}_4\text{P}_2\text{O}_7$ with formation of a non-ionised $\text{Fe}_2\text{P}_2\text{O}_7$. In the blood-corpuscles some Fe^{++} is present. Cu does not form these complexes. H. G. R.

Distribution of vanadium in organisms. A. P. VINOGRADOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 454—458).—Various terrestrial and marine animals and plants contain V in concns. of about 10⁻⁵%, but certain species of *Holothuria* and of *Ascidia* contain much higher concns. The ashes of certain species of *Ascidia* contain up to 1.5% of V. W. O. K.

Phosphatic calculi in Silurian polyzoa. K. P. OAKLEY (Proc. Roy. Soc., 1934, B, 116, 296—314).—The calculi were probably formed in the coelomic fluid, due to a rise in p_{H} during degeneration of polypide structures. H. G. R.

Calcium content of frog nerve. S. R. TIPTON (Amer. J. Physiol., 1934, 109, 457—466).—The Ca content of the sciatic nerves of winter frogs averages 0.735 ± 0.0937 milli-equiv. Ca per 100 g. wet wt. Immersion of the nerve in Ringer's solution of varying

[Ca⁺⁺] until equilibrium between Ca inside and outside the nerve has been established produces changes in nerve-Ca, indicating that 55% of the nerve is involved in the diffusion process. If the outside solution (I) contains no Ca, 60% of the nerve-Ca does not diffuse out. As [Ca⁺⁺] or [PO₄^{'''}] in (I) is increased, at a certain concn. there is a sudden increase in nerve-Ca, the concn. at which this occurs apparently depending on the factors governing Ca₃(PO₄)₂ pptn. in (I). At a const. [Ca⁺⁺] in (I) the magnitude of the increase depends somewhat on [PO₄^{'''}] in (I). The increase occurs even when (I) contains no PO₄^{'''}. Ca diffusion is scarcely affected by varying [K⁺] or the *p*_H of (I). Low *p*_H tends to involve a greater % of the nerve in the diffusion process. R. N. C.

Biochemistry of the brain. A. PALLADIN (Bull. Soc. Chim. biol., 1934, 16, 1193—1210).—A lecture.

Citric acid in tissues. C. L. GEMMILL (Skand. Arch. Physiol., 1934, 67, 201—210; Chem. Zentr., 1934, i, 3363).—Citric acid was found in frogs' liver and muscle under anaerobic conditions, and in rabbits' normal resting muscle, liver, brain, and kidneys. It was not present in normal and excited frogs' muscle. R. N. C.

True sugar and glycogen of tissues. Micro-determination. N. DOI (J. Biochem. Japan, 1934, 19, 469—488).—The importance of parallel determinations of free sugar (I) and glycogen (II) in the study of carbohydrate metabolism of tissues is emphasised. Micro-methods for 0.2—0.5 g. of tissue, based on hydrolyses with acid and alkali and subsequent yeast-fermentation and (I) determination, are given. The action of strong acids or alkalis increases the non-fermentable (I) by 30—50%. The liver and muscle of rabbits vary greatly in their contents of (II), whilst those of (I) (1.068—1.342 and 0.092—0.168%, respectively) are more const. F. O. H.

Coccids produced in Japan. VI. Nitrogen compounds and mineral matter in *Pulvinaria horii*, Kuw. M. KONO and R. MARUYAMA (J. Agric. Chem. Soc. Japan, 1934, 10, 360—367).—Analytical data are recorded. CH. ABS. (p)

Human epidermis. I. Amino-acid content of the stratum corneum and its comparison with other human keratins. V. A. WILKERSON (J. Biol. Chem., 1934, 107, 377—381).—Analysis of the stratum corneum of human epidermis (I) indicates that during the course of specialisation of nail and hair from (I), the mol. ratios of histidine, lysine, and arginine are not significantly altered. A. E. O.

Solubility of the stereoisomerides of cystine with a note on the identity of stone and hair cystine. H. S. LORING and V. DU VIGNEAUD (J. Biol. Chem., 1934, 107, 267—274).—The solubilities at 25° are *l*-, 0.108; *d*-, 0.108; *dl*- 0.049; *meso*-cystine, 0.056 g. per litre. *dl*-Cystine is a racemic compound and not a mixture. *d*- and *l*-Cystine may form more sol. compounds with *meso*-cystine. Stone- and hair-cystine have the same solubility, which is not increased on mixing, proving their identity. C. G. A.

Creatine, creatinine, iron, and fat contents of fish muscle. S. NAMIKI (Nagoya J. Med. Sci., 1934,

7, 206—207).—The ratios of creatine, creatinine, and fat in white and in red muscle are 2:1, 1:1, 1:7, respectively. The amounts of Fe are, respectively 0.67—1.04 and 4.44—7.19 mg. per 100 g.

CH. ABS. (p).

Fatty acids of pig liver. II. Octadecenoic acids and the desaturation theory. H. J. CHANNON, E. IRVING, and J. A. B. SMITH (Biochem. J., 1934, 28, 1807—1811).—Oxidation of the octadecenoic acids of pig liver by the method used by Hartley (A., 1909, ii, 597) confirms the original finding (this vol., 913) that the chief constituent is oleic acid and not the Δ¹ isomeride. A. E. O.

Occurrence of highly unsaturated fatty acids in oils of common fowls and animal fats. J. B. BROWN and C. C. SHELTON (J. Amer. Chem. Soc., 1934, 56, 2149—2151).—Various oils [goose (I), chicken, duck, turkey] are shown [by conversion (methanolysis) into Me esters and subsequent bromination in cold Et₂O] to contain 0.2—1.16% of (mainly) arachidonic acid (II). Two specimens of (I) contained linolenic acid but no (II). The traces of Me ester polybromides similarly obtained from animal fats (beef, calf, lamb, reindeer) have m.p. >238°, indicating the presence of acids either more unsaturated or of higher mol. wt. than (II). H. B.

Highly unsaturated C₂₄-acid in herring, cod-liver-, pilot-whale, and aburazame liver-oils. Y. TOYAMA and T. TSUCHIYA (J. Soc. Chem. Ind. Japan, 1934, 37, 530—534B).—The fraction, b.p. <240°/10 mm., of the Me esters of the fatty acids of each of these oils is hydrolysed; the COMe₂-sol. portion of the Na salts of the resulting acids is converted into Me esters, the portion, b.p. <215°/2 mm., of which by hydrolysis affords *nisinic acid*, C₂₄H₃₈O₂, an oil (*dodecabromide*, decomp. about 240°), affording *n*-tetracosic acid by hydrogenation. R. S. C.

Gadoleic acid in sei-whale and humpback-whale oils. Y. TOYAMA and T. ISHIKAWA (J. Soc. Chem. Ind. Japan, 1934, 37, 534—536B).—Isolation of the acid is recorded. R. S. C.

New eicosenoic acid from pilot-whale oil. Y. TOYAMA and T. ISHIKAWA (J. Soc. Chem. Ind. Japan, 1934, 37, 536—537B).—The body oil of this whale yields *gondoic acid*, C₂₀H₃₈O₂, m.p. 23.5—24°, giving by oxidation a (OH)₂-acid, m.p. 126.5—127°, and by reduction arachidic acid. R. S. C.

Millipede oil. S. UENO and R. YAMASAKI (J. Soc. Chem. Ind. Japan, 1934, 37, 507—510B).—1 kg. of *Strongylosoma tamberum*, Attems (I) (235 g., when dried), gave 5.01 g. of oil (*n*_D²⁰ 1.6285; acid val. 69.7; sap. val. 175), which yielded 21.4% of unsaponifiable matter (II) and 76.3% of fatty acids (III). (I) contains free EtCO₂H and oleic acid. (III) is mainly palmitic with some myristic acid. (II) contains *yasudesterol*, C₂₄H₄₆O, m.p. 134—135° (*digitonide*; *acetate*, m.p. 123—123.5°), and a mono-unsaturated *alcohol*, C₁₈H₂₈(OH)₂, an oil, which by hydrogenation (Pd-black), followed by oxidation, gives a *ketone* (*phenylhydrazone*, amorphous). R. S. C.

Cholesterol deposition in the tissues of rats. I. Differences in the liver-lipins of males and

females. R. OKEY, H. L. GILLUM, and E. YOKELA (J. Biol. Chem., 1934, 107, 207—212).—The fatty acid content of livers from females is slightly > that from males, whilst the total cholesterol (I) is lower, the difference being due to esterified (I), which is almost entirely absent in the case of females on a (I)-free diet.

C. G. A.

Pigment content of hen's eggs. T. RADEFF (Arch. Geflügelkunde, 1934, 8, 47—51).—The pigment content of Bulgarian market eggs determined colorimetrically by comparison with aq. $K_2Cr_2O_7$ averages 2.25 mg. per yolk, or 13.41 mg. per 100 ml. of yolk.

NUTR. ABS. (m).

Carotenoid from the scallop, *Pecten maximus*. E. LEDERER (Compt. rend. Soc. Biol., 1934, 116, 150—153).—The chemical and physical consts. of a new carotenoid, *pectenoxanthin* (I), isolated from the genital organ of the scallop, *Pecten maximus*, are described. (I) appears to resemble xanthophyll and phytoanthin in constitution.

NUTR. ABS. (b).

Carotenoid content of some invertebrates. H. VON EULER, H. HELLSTRÖM, and E. KLUSMANN (Z. physiol. Chem., 1934, 228, 77—89).—The carotenoids of *Calanus finmarchicus*, *Daphnia magna*, *Volsella modiolus* (testes and ovary), ant's eggs, and *Coregonus albula* (eggs) were examined spectroscopically. Acid keto-carotenoids such as astacene are widely distributed in Crustacea and molluscs, and probably in invertebrates. Asteric acid (this vol., 544) recalc. to C_{40} is $C_{40}H_{56}O_6$, i.e., it contains 2 mols. of H_2O > astacene.

J. H. B.

Astacene from shells of fresh-water crayfish [*Potamobius (Astacus) fluviatilis*, L.]. H. WILLSTAEDT (Svensk Kem. Tidskr., 1934, 46, 205—208).—Astacene (I) has been isolated from the shells, and from its chromatic behaviour and that of its reduction products in various solvents it is concluded that (I) is 4:5:4':5'-tetraketocarotene. Reduction of (I) with Zn is irreversible, and (I) is not recovered when the solution is treated with KOH in EtOH. (I) is changed by $SbCl_3$, the bluish-violet solution in $CHCl_3$ being converted by aq. HCl into a raspberry-red solution not identical with the yellowish-red solution of (I).

S. C.

Lipochrome and lyochrome pigments in the skin of the frog and cod. M. VAN EEKELLEN (Acta Brev. Neerland., 1934, 4, 65—66).—Spectroscopical investigation of the light petroleum fraction of extracts of the skin of *Rana temporaria* (I) and *R. esculenta* (II) shows that carotene and xanthophyll are present. A yellow-green H_2O -sol. pigment apparently related to the dye-component of Warburg's yellow oxidising enzyme, and a urochrome pigment are obtained from the skin of (I) and in very small amounts from (II). The same carotenoids and fluorescent pigments are found in the skin of the cod.

NUTR. ABS. (m).

Flavin and a blue-fluorescing substance in the retina of the eyes of fish. H. VON EULER and E. ADLER (Z. physiol. Chem., 1934, 228, 1—12).—The flavin content of the pigmented epithelium of the fish's retina varies from < 0.2 to 87×10^{-6} g. per eye. Wide variations are shown between species of the same genus. In some species, e.g., *Labrus bergyltra*, a blue-

fluorescing substance (I) is present, resembling flavin in its solubility, but differing in its p_H relations. The fluorescence of (I) disappears at p_H 3.0—3.5, but is stable in alkaline medium. Illumination under conditions which produce lumiflavin from lactoflavin converts (I) into a $CHCl_3$ -sol. violet-fluorescing substance, very stable to reducing agents. In other organs of fish and marine animals and in plants the flavin content is relatively low.

J. H. B.

Free and combined (enzyme-)flavin in animal tissues and fluids and in yeast. H. VON EULER and E. ADLER (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 28, 6 pp.).—Extraction and dialysis methods for the free (I) and total flavin (II) contents give the vals. [$\times 10^{-4}$ % for (II)]: dried bottom yeast, 18—21; apozymase prep., 16—20; ox liver, 9—18; ox kidney, 8—16; ox corpus luteum, 4—8; pressed bottom yeast, 7; egg-yolk, 5—6; egg-white, 4—5; cow's milk, 2—3; man's brain, 2; man's urine, 0.3—0.5. Excepting with urine [totally (I)], 70—100% of the flavin of the remainder is combined.

F. O. H.

Golgi apparatus of the adrenal gland. G. BOURNE (Austral. J. Exp. Biol., 1934, 12, 123—139).—Histological. In the adrenal cortex probably both the Golgi apparatus and vitamin-C are concerned in the formation of the lipid droplets, which may contain a cortical hormone.

W. O. K.

Colour reaction in cocoons treated with formaldehyde. G. COLOMBO (Boll. uff. R. Staz. sperim. Seta, 1933, 3, 63—64; Chem. Zentr., 1934, ii, 635).—The colour obtained by the action of conc. HCl on cocoons (I) treated with CH_2O is ascribed to the presence of tryptophan. Washing of (I) with warm H_2O prevents the reaction, which is then favoured by presence of oxidising agents.

A. G. P.

Cerebrospinal fluid-sugar determinations in experimental hypoglycæmia in dogs. R. DAVIS and H. BROWN (J. Lab. Clin. Med., 1934, 19, 1049—1053).—The decreased glucose (I) content of cerebrospinal fluid (II) in dogs after administration of insulin is often relatively > that of the blood. Intraspinal injection of (I) during hypoglycæmia causes only a temporary improvement. Intravenous injections of (I) rapidly enter (II). A high concn. of (I) in (II) without correspondingly high concn. in blood will not preserve life.

CH. ABS. (p)

Diastase in cerebrospinal fluid. F. EOKARDT (Jahrb. Kinderheilk., 1933, 141, 195—204; Chem. Zentr., 1934, i, 3478).—The presence of diastase is recorded.

A. G. P.

Lipins of the thoracic duct lymph in fasting. B. MORTIMER and A. O. TISOHER (Proc. Soc. Exp. Biol. Med., 1934, 31, 553—554).—A table shows the range and average vals. for the lipin-P and I, and sap. vals. of the lipins of thoracic duct lymph of dogs after fasting 4—7 days. The I val. and the content of unsaponifiable matter for lymph-fat agree closely with the vals. for faecal fat.

NUTR. ABS. (m)

Permeability of blood capillaries to lipins. A. MARBLE, M. E. FIELD, C. K. DRINKER, and R. M. SMITH (Amer. J. Physiol., 1934, 109, 467—474).—The peripheral lymph of normal fasting dogs on the average contained 56 mg. of cholesterol (I), 239 mg. of fatty

acid, and 305 mg. of total lipin (II) per 100 c.c., these being, respectively, 41%, 54%, and 52% of the corresponding vals. for plasma from the same dogs. Intravenous injection of fat-laden chyle or fat emulsion caused a slight rise in lymph (II), but no change in (I), suggesting that the capillary walls are slightly permeable to lipins other than (I), but more so than to (I) itself.

R. N. C.

Composition of gastric juice. I, II. G. V. RUND (Med. J. Austral., 1934, i, 431—436, 455—463).—Methods of analysis for acidity, Na, K, NH_4 , Ca, Mg, Cl, PO_4''' , HCO_3' , urea, and protein are described. The bases of the "neutral chloride" (I) in human gastric juice are Na, K, Ca, Mg, and NH_4 . Some of the base is secreted by the parietal cells in the form of (I). The concn. of HCl in the parietal secretion (II) varies. It is doubtful whether the total Cl' of (II) is const.

NUTR. ABS. (m)

Acidity of the gastric juice and contents of the fasting stomach. W. N. BOLDYREFF (Acta Med. Scand., 1934, 82, 111—125).—Strongly acid solutions (0.5% HCl) introduced into the isolated stomach of the dog or into gastric pouches are not neutralised, but in the normal stomach are rapidly neutralised by regurgitation of pancreatic juice. Thus neither gastric mucus nor pyloric juice is capable of causing effective neutralisation. The gastric glands always secrete a juice of the same degree of acidity, 0.56—0.59% HCl. Hyperacidity of the gastric juice does not exist; hypersecretion may occur. Secretion of neutral chlorides does not occur.

NUTR. ABS. (m)

Relation of acidity of gastric juice to the rate of its secretion. M. M. GORBUNOVA, S. I. LEBEDINSKAYA, and V. V. SAVICH (Arch. Sci. Biol. U.S.S.R., 1933, 33, 515—521).—The acidity of the juice was largely controlled by its mucin content.

CH. ABS. (p)

Secretory work of gastric glands during prolonged effect of sodium chloride. O. F. SHAROVATOVA-ZAVALISHINA (Arch. Sci. Biol. U.S.S.R., 1933, 33, 471—479).—The effects of NaCl were independent of the nature of the diet and caused an increase in total acids, free HCl, and total Cl' in gastric juice.

CH. ABS. (p)

Influence of combinations of basal foodstuffs (chiefly proteins and carbohydrates) on gastric and pancreatic secretions. M. L. EIDLINOVA (Arch. Sci. Biol. U.S.S.R., 1934, 34, 113—122).—The combination of any two foods may increase or decrease the rate of secretion as compared with each component fed separately. Changes in acidity were paralleled by the vol. secreted, but enzyme activity was not.

CH. ABS. (p)

Bile analysis. F. BREUSCH (Z. physiol. Chem., 1934, 227, 242—246).—Bile (5—10 c.c.) is treated with 50 c.c. of EtOH to remove protein, the filtrate is evaporated, and the residue dissolved in 20 c.c. of H_2O is treated with 2 c.c. of 5% aq. Na_2CO_3 . Extraction with CHCl_3 removes phosphatides. The aq. portion is heated for 6 hr. after addition of 5 c.c. of 30% KOH to hydrolyse coupled bile acids. Acidification and extraction with Et_2O removes all the acids, leaving the bilirubin. The residue from the Et_2O is subjected to

sublimation for 3 hr. in vac. at 150° (bath temp.)/ ≥ 2 mm., the process being repeated if necessary. The fatty acids sublime, the residue consisting of bile acids.

J. H. B.

Separation of principal constituents of bile. R. U. HARWOOD (J. Lab. Clin. Med., 1934, 19, 1003—1007).—Pigments are absorbed on aq. $\text{Zn}(\text{OH})_2$. The supernatant liquid is heated with KOH, acidified, and treated with K_2CO_3 to give a clear solution. Cholesterol is extracted with petroleum, and bile salts with abs. EtOH.

CH. ABS. (p)

Micro-determination of cholic acid in bile. K. LANG and B. LUEKEN (Biochem. Z., 1934, 273, 446—451).—The method (I) is based on the pptn. of cholic acid (II) by I in aq. KI, a compound (III) of 1 mol. of (II) with 2I being produced. (III) is dissolved in AcOH and, after dilution, titrated with 0.005N- $\text{Na}_2\text{S}_2\text{O}_3$. Other bile acids do not interfere. ≤ 0.25 mg. of (I) can be determined. (I) cannot be applied to the determination of (II) in blood and liver.

W. McC.

Determination of cholesterol and cholesteryl esters in dog's bile. I. A. WRIGHT (J. Exp. Med., 1934, 59, 407—410).—Elman and Taussig's method for the determination of total cholesterol in dog's bile (I) is accurate. A method of determining cholesteryl esters is described and their absence from normal (I) demonstrated.

NUTR. ABS. (m)

Toad bile. II. Trihydroxybufostercholeonic acid from winter bile.—See this vol., 1219.

Changes in composition and secretion of bile during the action of certain internal secretions and vegetative poisons. S. M. LEITES and R. M. IZABOLINSKAYA (Arch. Sci. Biol. U.S.S.R., 1933, 33, 417—431).—Bile secretion was decreased by subcutaneous injection of adrenaline (I), parathyroid extract (II), thyroxine (III), and atropine (IV), increased by insulin (V) and histamine (VI), and unchanged or irregularly affected by pituitary preps. (VII) and ergotamine. The concn. of bile acids was unchanged or increased by (I), (VII), and (V), unchanged or lowered by (IV) and (VI), and unchanged or variably influenced by (II) and (III). The cholesterol concn. was affected only by (III). In no case were $[\text{Na}']$ and $[\text{K}']$ changed.

CH. ABS. (p)

Effect of thyroid gland on secretion and cholesterol content of bile. V. P. BEZUGLOV and L. M. TUTKEVICH (Arch. Sci. Biol. U.S.S.R., 1933, 33, 411—416).—Administration of thyroxine lowers the secretion of bile and the excretion of cholesterol. The effects were intensified by thyroidectomy.

CH. ABS. (p)

Bile-stimulating action of *Curcuma domestica* (Temoe Lawak). F. GRABE (Arch. exp. Path. Pharm., 1934, 176, 673—682).—The bile-stimulating action of extracts and of the essential oil and its vac. distillation fractions of rhizomes of *C. domestica* (tumeric) indicates that the principle concerned is α -n-tolylethyl alcohol (cf. A., 1932, 1178; 1933, 876).

F. O. H.

Influence of bile acids on biliary salt excretion. IV. Ammonium salts. V. Alkali salts. Y. KAWADA (J. Biochem. Japan, 1934, 20, 43—50, 51—

57).—IV. The bile- NH_3 in dogs with biliary fistulae is increased by oral administration of cholic acid (I). Simultaneous administration of yeast-nucleic acid enhances this effect and also increases the vol. of bile secreted.

V. The vol. and K and Na contents of the bile are increased by oral administration of (I), but diminished by subcutaneous injection of atropine. (I) probably has a vago-stimulatory action. F. O. H.

Statistical investigations on milk. B. ROSS-MANN (Z. Unters. Lebensm., 1934, 68, 279—293).—The seasonal variations in fat content of milk from 7 districts in the Merseburg area are analysed. E. C. S.

Rapid simultaneous refractometric determination of fat and lead acetate serum of milk. W. LEITHE (Z. Unters. Lebensm., 1934, 68, 293—297; cf. B., 1934, 602).—The milk is treated with $\text{Pb}(\text{OAc})_2$ and petroleum (b.p. 90—100°), emulsified, and centrifuged. The clear petroleum and aq. layers are together transferred to the refractometer cup, and their n successively determined. Fat in milk can be determined to within 0.1%. E. C. S.

Influence of inheritance and environment on milk production and butter-fat percentage in Jersey cattle. J. W. GOWEN (J. Agric. Res., 1934, 49, 433—465).—Approx. 50% of the variation in milk yield and 80% of that in butter-fat are traced to inheritable factors. A. G. P.

Cholesterol content of human milk. O. MUHLBOCK (Z. Kinderheilk., 1934, 56, 303—306).—Mixed samples of human milk taken between the 4th and 10th days of lactation have an average total cholesterol (I) content of 26 mg. per 100 ml., most of which is free. The milk-fat contains on an average 1% of (I). Samples taken from one individual show no definite variation between the 12th and 47th day. Cow's milk has an average (I) content of 9.18 mg. per 100 ml., practically all being free. There is no (I) in separated milk. NUTR. ABS. (m)

Milk secretion in relation to blood composition. Urea contents of blood and of milk-serum. G. L. PESKETT (Biochem. J., 1934, 28, 1657—1658).—In the cow, whole blood (mammary, venous, or arterial) and the fat-free serum of milk have the same urea contents irrespective of the rate of milk secretion. Urea is not conc. by the mammary gland. A. E. O.

Tryptophan in cow's milk. D. TUKOV and M. ZAKOMORNY (Rocz. Nauk. rol., 1934, 31, 366—382).—The tryptophan (I) content of milk from different cows is not const., but varies < do other milk constituents. It varies considerably over a lactation (II), being highest in colostrum and at the end of (II). (I) is thought to be produced by a sp. enzyme, the activity or quantity of which is greatest early and late in (II). NUTR. ABS. (m)

Maturation of cheese. I. Proteases, diketopiperazine, and proline peptides. E. PARISI and G. DE VITO (Atti R. Accad. Lincei, 1934, [vi], 20, 44—51).—Ripe cheeses contain proline peptides and diketopiperazine, which resist attack by proteases. The extent to which the casein of cheese is broken

down appears to be related closely to the % of proline compounds present. T. H. P.

Lane-Eynon volumetric method for determination of lactose in milk. F. T. ADRIANO, S. B. OLIVEROS, and L. G. MIRANDA (Philippine J. Sci., 1934, 54, 83—89).—The max. difference between results obtained by volumetric and gravimetric methods is 0.1%. The optical method gives variable results. P. G. M.

Vitamin-A in milk. W. C. RUSSELL (New Jersey Agric., 1933, 15, 3).—Of the vitamin-A fed as dried lucerne and maize silage < 5% appears in milk. CH. ABS. (p)

Resistance of vitamin-C in milk to vacuum pasteurisation. G. RUNDBERG (Acta paediat., 1934, 15, 357—373).—The milk from a single cow, maintained on pasture, was pasteurised and freed from air, but failed to protect guinea-pigs from scurvy in the largest dose administered (50 ml. daily), even when raw. NUTR. ABS. (b)

Determination of sulphur in pig's milk. F. LACHMANN (Bied. Zentr. [Tierernähr.], 1934, B, 6, 421—424).—The sample is evaporated in a vac. over P_2O_5 and the product digested with fuming HNO_3 in a sealed tube. S is determined as BaSO_4 . A. G. P.

Differences in the phosphorus and sulphur content of human and cow's milk. F. STEFFEN and H. SULLMANN (Schweiz. med. Woch., 61, 114; Chem. Zentr., 1934, i, 2988).—Vals. for S and all fractions of P are considerably higher in cow's milk. A. G. P.

Spectrum analysis of milk ashes. W. F. DREA (J. Nutrition, 1934, 8, 229—234).—Ag and Mo occurred in milk of cows drinking H_2O containing these elements. Mn and F, although present in H_2O and in lucerne supplied, were not detected. A. G. P.

Mitogenetic radiation. VI. Secondary radiation. L. K. WOLFF and G. RAS (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 430—455).—Mitogenetic radiation (Gurwitsch) emitted by milk, pasteurised at 37°, to which rennet has been added, has been passed through a culture contained in a cryst. SiO_2 vessel, and the secondary radiation (a) has been studied. (a) is transmitted also by the medium of the culture, from which cells have been removed, but not by pure medium, or boiled cultures. (a) is more intense than the incident radiation. The effect of (a) when the bacterial detector is contained in a SiO_2 vessel is > for glass or paraffin, owing to reflexion at the walls. Similarly, powdered SiO_2 and air bubbles in the detector increase the influence of (a). Experiments show that (a) polarised by reflexion, or by Iceland spar, is more effective than the unpolarised rays. A plate of amorphous SiO_2 between emitter and detector has no effect, but cryst SiO_2 , topaz, and other minerals accelerate the influence on the detector. The walls of the vessel also influence the induction period for the multiplication of bacteria in a dil. culture (6000—20,000 per c.c.). R. S. B.

Composition and f.p. of cow's colostrum. G. D. ELSDON (Analyst, 1934, 59, 665—666).—

Analytical data on 9 consecutive samples from each of two cows are given. E. C. S.

Composition of "witch's" milk. R. G. LINTON (Vet. J., 1934, 90, 213—215).—The milk secreted by two foals, 2 and 4 days old, respectively, was lower in total solids, protein, and ash than was the milk of the respective dams. In one case the fat and lactose contents were higher, in the other case they were lower, in the foal's milk than in the dam's. When one foal was 8 days old its milk contained the following percentages: total protein, 3.58, caseinogen, 2.03; globulin, 0.86; albumin, 0.69; ash, 0.58; Cl, 0.230; CaO, 0.041; MgO, 0.014; and P_2O_5 , 0.079.

NUTR. ABS. (m)

Diastase in the urine of infants and children. F. ECKARDT (Jahrb. Kinderheilk., 1934, 142, 319—343).—In infants the urinary diastase (I) is low, but increases with age to reach a more or less steady level in childhood. The excretion of (I) is fairly const. for the individual. No significant differences are observed between the sexes. (I) excretion is increased during starvation and fever, diminished in pylorospasm, in acute digestive disturbances, and in diabetes mellitus, and unaffected in rickets and tuberculosis.

NUTR. ABS. (m)

Urinary excretion of rennin in infants. J. SURANYI and L. VESZELSZKY (Le Nourrisson, 1933, 21, 296—300).—The urine (especially night urine) of artificially fed (I) but not that of breast-fed infants contains the precursor of rennin (II). In (I) there is over-production of (II), the surplus being excreted.

NUTR. ABS. (m)

Urinary compound of albumin, Bence-Jones protein pseudoglobulin, and an unknown antigen. W. H. WELKER and L. HEKTOEN (J. Infect. Dis., 1933, 53, 165—168).—The protein could not be separated from the compound by boiling or crystallisation. Precipitins in rabbit serum prepared against the compound were removed by sp. adsorption.

CH. ABS. (p)

Trimethylamine oxide in human urine. W. LINTZEL (Klin. Woch., 1934, 13, 304; Chem. Zentr., 1934, i, 2777).—Administered NMe_3 is excreted largely as NMe_3O . A. G. P.

Trimethylammonium bases. III. In human urine. W. LINTZEL (Biochem. Z., 1934, 273, 243—261; cf. A., 1931, 1178).—Urine is made alkaline with $Ba(OH)_2$, Na_2CO_3 , or MgO , CH_2O is added, and air is passed through. The only base then expelled is NMe_3 , which is determined by trapping in excess of 0.02N-HCl and titrating with 0.02N- NMe_3 . NMe_3O is determined in the same way after reduction with Devarda alloy + HCl [choline (I), betaine (II), γ -butyrobetaine (III), and carnitine (IV) do not interfere]. Total NMe_3 bases (V) are determined as is NMe_3 after treating the urine at 120° for 4½ hr. with KOH, Zn dust, and a little H_2O . The N of (V) in 1 day's normal urine is distributed thus: free NMe_3 , 1.0; NMe_3O , 12.4; other (V), 22.4 mg. Orally administered NMe_3 is excreted almost quantitatively as NMe_3O , but a small part appears unchanged. NMe_3O given orally is excreted almost quantitatively unchanged and at the same time the excretion (VI) of

free NMe_3 is slightly increased. A diet of sea fish results in greatly increased (VI) of NMe_3O and slightly increased (VI) of NMe_3 . Administration of (II) leads to no increase of (VI) of (V), that of (I) leads to increase, most of (I) being destroyed in the body, part being unchanged, and part appearing as NMe_3O . (III) appears chiefly unchanged, there being no increased (VI) of NMe_3O . After giving (IV) there is no appreciable increase in (VI) of (V), but after meat extract there is an increase. The production of NMe_3O from (V) results, to some extent, from the action of intestinal bacteria.

W. McC.

Determination of urinary ammonia. P. FLEURY (J. Pharm. Chim., 1934, [viii], 20, 319—326).—Mestrezat and Janet's modification of Schlösing's method (A., 1922, ii, 453) is further modified so that urine- NH_3 is determined in 3 hr. at 20° or in 45 min. at 37°.

F. O. H.

Clearance of creatine in dog and man. R. F. PITTS (Amer. J. Physiol., 1934, 109, 532—541).—Clearance of creatine (I) in the dog is a function of the plasma concn. (II). At low (II), urine is (I)-free, but as (II) rises, clearance rises sharply. At (II) of 15—120 mg. per 100 c.c., the (I) clearance in the dog is intermediate between the xylose (or sucrose) (III) and creatinine (IV) clearances. In man, between 6 and 40 mg. per 100 c.c. of plasma-(I), the clearances of (I) and (III) are equal, but < the (IV) clearance. Administration of Na_2HPO_4 does not affect (I) excretion, but glycine raises (III) clearance relatively more than that of (I).

R. N. C.

Clearance of creatine in the phloridzinised dog. R. F. PITTS (Amer. J. Physiol., 1934, 109, 542—549).—Creatine clearance in phloridzinised dogs is a function of plasma-creatine concn. (I) below 5 mg. per 100 c.c.; between 20 and 130 mg. it is independent of (I). Administration of phloridzin does not affect xylose clearance, but creatine and creatinine clearances fall, and glucose clearance rises, to the xylose level, all four agreeing within an average of $\pm 5\%$.

R. N. C.

Diffusion equilibria for isolated frog's kidney. E. J. CONWAY and F. KANE (Biochem. J., 1934, 28, 1760—1768).—The concn. of $SO_4^{''}$ in the blood-plasma of the frog is 6.2 mg. S per 100 ml. The concn. in the urine is approx. 33% of this and of the kidney (I) 40%. $SO_4^{''}$ passes freely into and out of (I), the equilibrium concn. (II) being attained in 15 min. The (II) for active (I) is 41% of the external $SO_4^{''}$ and for inactive (I) (CN'), 58%. (II) for muscle (III) is 25%, and for liver (IV) sections 29%, CN' causing a slight reduction. The rate at which (II) is attained is the same for active or inactive (I), (III), and (IV).

C. G. A.

Colorimetric determination of sulphate in serum and urine adaptable to determination of sulphate clearance. T. V. LETONOFF and J. G. REINHOLD (Amer. J. Med. Sci., 1934, 188, 142).—The method is based on the colour reaction between benzidine sulphate and Na β -naphthaquinone-4-sulphonate in the presence of $Na_2B_4O_7$ -NaOH buffer solution. Addition of $COMe_2$ after the reaction is complete reduces the colour of the reagent. Protein and $PO_4^{''}$ are removed by U acetate.

CH. ABS. (p)

Determination of total and neutral sulphur in urine. A. FRIEDRICH and E. BAUER (Z. physiol. Chem., 1934, 228, 61—76).—A volumetric micro-method is described, the benzidine method for $\text{SO}_4^{''}$ being employed, since it does not necessitate removal of $\text{PO}_4^{'''}$. Ashing is performed by means of Br-HNO_3 . The vals. obtained for neutral S are low owing to loss of a volatile S compound on acid hydrolysis, unless the urine is first treated with dil. NaOH . J. H. B.

(a) Excretion of salt by the human kidney.
(b) Thirst and potassium overdosage. F. ARDEN (Austral. J. Exp. Biol., 1934, 12, 111—120, 121—122).—a: After oral administration to man of 15 g. of NaCl (10% solution) diuresis took place accompanied by increase of Cl' in the urine for about 4 hr. up to 0.3—0.4*N*, Cl' thereafter remaining approx. const., although the vol. of urine decreased. Administration of H_2O caused no extra diuresis, but a second dose of NaCl increased the vol. of urine, but had little effect on $[\text{Cl}']$. Similar results were obtained with KCl , the diuresis being somewhat greater, whilst the administration of NaHCO_3 (30 g.) produced corresponding effects, the max. $[\text{HCO}_3']$ in the urine being 0.318*N*. Urinary Cl' did not entirely disappear.

b. KCl does not produce thirst as does NaCl in corresponding quantities. Thirst is probably due to the presence in the tissues of an excess of salt and especially of Na^+ . W. O. K.

Organic acids in urine. W. MECKE (Z. ges. exp. Med., 1934, 92, 688—691; Chem. Zentr., 1934, i, 1666).—The acids fall into two groups, the dissociation consts. of which lie approx. between 10^{-3} and 10^{-4} or 3×10^{-3} and 10^{-8} . L. S. T.

Urinary pigments and their composition. M. WEISS (Klin. Woch., 1933, 11, 1817—1820; Chem. Zentr., 1934, i, 1516).—Normal urine contains a series of yellow to red pigments, chromogen, and, in certain physiological conditions, coproporphyrin and bilirubin. The existence of Heilmeyer's urochrome-B is doubtful. In pathological conditions the pigment content may increase, and new pigments, e.g., urobilin and a melanogen, may occur. A. G. P.

Crystalline urobilin. I. Crystalline stercobilin and its absorption spectrum. II. Crystalline urobilin from urine and its identity with crystalline stercobilin. L. HEILMEYER and W. KREBS (Z. physiol. Chem., 1934, 228, 33—46, 46—49).—I. Cryst. stercobilin (I), probably $\text{C}_{33}\text{H}_{42}\text{O}_6\text{N}_4$, m.p. begins 110° , complete 130° (decomp.), was obtained from faeces. In contrast with Watson's (I) (A., 1932, 296), it gave absorption curves identical with non-cryst. (I) from faeces, urine, and from mesobilirubinogen, but showed const. absorption relations. This prep. is probably "native faecal (I)."

II. Cryst. urobilin from urine and (I) from faeces agree in solubility, light absorption, and crystallographic behaviour, and are regarded as identical. On keeping, the crystals undergo spontaneous change (pseudomorph formation) making recrystallisation impossible. J. H. B.

Sterol secretion and coprosterol formation. R. SCHOENHEIMER and W. M. SPERRY (J. Biol. Chem., 1934, 107, 1—4).—The faeces of dogs with bile fistulae

fed on a lipin-free diet contain coprosterol (I) and dihydrocholesterol; hence (I) is formed from the cholesterol secreted by the intestinal mucosa. H. D.

Chemical ideas in medicine and biology. H. H. DALE (Science, 1934, 80, 343—349).—A lecture. L. S. T.

Respiration and glycolysis of red corpuscles in allergic and anaphylactic animals. M. AXST-ANEFF (Z. ges. exp. Med., 1933, 90, 643—650; Chem. Zentr., 1934, i, 2444).—Mature red corpuscles of the guinea-pig, without nuclei, showed no O_2 consumption. Respiration (I) was slightly raised by horse-serum, fivefold by liver extract (II) from guinea-pigs, and further on addition of anaphylactogen to sensitised erythrocytes (III). (II) had no action on (III) after anaphylactic shock (IV), or on animals killed by (IV), although it raised the (I) of normal guinea-pigs. (I) is increased in (III) of tuberculous animals. "Old tuberculin" (V) has no effect *in vitro* or *in vivo*, but in large quantities reduces (I). Addition of tissue extracts raises the (I) of tuberculous cells. The (I) of liver sections of tuberculous animals treated with (V) is raised 100—150% of the val. for untreated tuberculous animals. R. N. C.

Active allergic substance in the hop. M. J. GUTMANN (Heil- u. Gewürz-Pflanzen, 1933, 15, 89—92; Chem. Zentr., 1934, i, 2159).—The allergic reaction is due to lupulone. Humulone and hop-resin gave weak reactions in isolated cases; the hop essential oils and hop-protein were without effect. R. N. C.

Preparation and standardisation of pollen extracts for the treatment of hay fever. R. A. COOKE (J. Allergy, 1933, 4, 87—91).—Defatted pollen is extracted with a solution containing 0.5% NaCl , 0.275% NaHCO_3 , and 0.4% PhOH . The sterilised extract is standardised by determining the protein-N pptd. by phosphotungstic acid. CH. ABS. (p)

Standardisation of pollen extracts proposed by Cooke and Stull. A. F. COCA (J. Allergy, 1934, 4, 354—362).—The N precipitable by phosphotungstic acid is dialysable and therefore not albumin. There is no parallelism between loss of activity and loss of precipitable N (cf. preceding abstract). CH. ABS. (p)

Allergen content of pollen extracts. Determination and deterioration. A. STULL, R. A. COOKE, and J. TENNANT (J. Allergy, 1933, 4, 455—467).—The activity of pollen (I) extracts as determined by protein-N (II) varied with the condition of (I) and age of extracts. Deterioration was prevented by storing dry (I) in sealed containers. Alkaline salt extracts lost 50% activity in 1 year's storage. Repeated filtration decreased activity and (II) proportionally. CH. ABS. (p)

[Pollen] allergen. H. WEYLAND and O. RIPKE (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, 2, 244—252; Chem. Zentr., 1934, i, 3362).—The albuminoid nature of the hay-fever-exciting allergen of grass-pollen is confirmed. R. N. C.

Urinary proteoses in bronchial asthma. A. TRASOFF (J. Allergy, 1933, 4, 136—140).—Urine of asthmatic patients contained a substance resembling

Oriel's "protease," but showing no sp. skin reactions or therapeutic results.

CH. ABS. (p)

Serum-lipins in anæmia. R. GANTENBERG (Deut. Arch. klin. Med., 1934, 176, 343—347).—Total cholesterol (I) usually rises in pernicious anæmia during successful stomach or liver treatment from low to markedly increased vals. The behaviour of the serum-(I) has a certain diagnostic val., since variations from the above indicate complications. The (I) rise depends on increased function of the blood-forming apparatus, probably of the reticulo-endothelial system. In secondary anæmias the behaviour of (I) is much less regular. In both forms of anæmia the (I) ester plays a greater part than free (I) in the rise that takes place. The total (I) in the serum moves parallel as a rule to the total fats in the serum, but the phosphatides show no regular relation to the other serum-lipins. NUTR. ABS. (b)

Anæmia caused by deaminised caseinogen. A. G. HOGAN and W. S. RITCHIE (J. Biol. Chem., 1934, 107, 179—189).—Gelatin and gliadin together were an adequate source of protein for growth, but the addition of deaminised caseinogen was followed by an anæmia. This did not develop if caseinogen was added to the diet, and no effect on the rate of growth was noted. H. G. R.

Effects of various colloidal and crystalloidal metallic compounds in nutritional anæmia in the rat. H. L. KEIL and V. E. NELSON (J. Lab. Clin. Med., 1934, 19, 1083—1088).—The min. requirements of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and colloidal $\text{Fe}(\text{OH})_3$ necessary to raise the hæmoglobin (I) content in anæmic rats to normal val. were 0.002 and 0.10 mg. per day, respectively. Mn cannot replace Cu in the synthesis of (I). Cu is utilised in the form of Cu_2O , CuS , $\text{Cu}(\text{OH})_2$, CuI , and colloidal Cu. Intraperitoneal injection of Fe citrate temporarily increases (I) formation. Zn and Hg salts have no influence.

CH. ABS. (p)

Factors influencing the utilisation of the iron and copper of egg-yolk for hæmoglobin formation. W. C. SHERMAN, C. A. ELYEHJEM, and E. B. HART (J. Biol. Chem., 1934, 107, 289—295).—The incomplete hæmoglobin regeneration in anæmic rats fed with egg-yolk (I) is due not to the unavailability of the Fe in (I), but to a retarded utilisation of Cu, possibly due to formation of insol. CuS in the digestive tract. A. E. O.

Nature of hæmopoietin, the anti-anæmic substance in hog's stomach. II. Production of a thermostable hæmopoietically active substance similar to or identical with the anti-anæmic principle of liver by the action of the thermolabile hæmopoietin on beef. L. KLEIN and J. F. WILKINSON (Biochem. J., 1934, 28, 1684—1692; cf. A., 1933, 641).—When concentrates containing the enzyme-like hæmopoietin (I), with or without pepsin, are incubated *in vitro* with beef-muscle at 37°, thermostable hæmopoietically active material is obtained resembling the anti-anæmic principle (II) from liver. It can also be obtained free from protein in a form suitable for intramuscular injection. It is considered that (I) acting, in the

stomach of normal individuals, on an unknown substrate in beef yields (II), an end-product ultimately stored in the liver until required by the body for the production of red blood-corpuscles. A. E. O.

Ascorbic acid content in mouse cancer. B. BORCHI and R. DEOTTO (Z. Krebsforsch., 1934, 40, 293—297; Chem. Zentr., 1934, i, 3488).—Administration of tumour extracts prolongs the life of young scorbutic guinea-pigs only insignificantly, and scarcely hinders loss of wt. Mouse tumours do not require ascorbic acid for their metabolism. R. N. C.

Cathepsin in rats with transplantable cancer. A. PURR (Biochem. J., 1934, 28, 1907—1910).—Rats into which cancers (I) have successfully become transplanted, and rats which have resisted efforts to transplant (I), both show a high concn. of cathepsin (II) in the liver, and a significant concn. in the muscle, which in normal rats is free from (II). A. E. O.

Effect of heavy water on viability of mouse sarcoma and melanoma. K. SUIGIURA and L. C. CHESLEY (Proc. Soc. Exp. Biol. Med., 1934, 31, 659—661).—Proliferation capacities were unaffected.

CH. ABS. (p)

Chromium. I. Determination of chromium in human tumours. A. DINGWALL, R. G. CROSEN, and H. T. BEANS (Amer. J. Cancer, 1934, 21, 606—611).—The tissue is ashed and the residue fused with Na_2CO_3 and KClO_3 . The aq. extract of the melt is warmed with HCl to expel CO_2 and treated with a solution of diphenylcarbazide in EtOH-AcOH . The % transmission vals. for $\lambda\lambda$ 5045 and 5710 Å. are compared with those for standard Cr preps. Results varied from 0.001 to 0.25 mg. Cr. per 100 g. of ash.

CH. ABS. (p)

Vitamin-D [and dental caries]. E. C. McBEATH (Amer. J. Publ. Health, 1934, 24, 1028—1030).—Avitaminosis-D appears to be a factor in the incidence of dental caries in children. F. O. H.

Osteodystrophic diseases of domesticated animals. I. Structure of bone; atrophy; osteoporosis; osteomyelitis. II. Rickets and osteomalacia. A. THEILER (Vet. J., 1934, 90, 143—158, 159—175).—I. Dietary requirements of Ca and P are examined.

II. With a sufficiency of solar radiation, rickets developed in bovines and ovines under conditions of simple P-deficiency.

CH. ABS. (p)

Factors influencing malformation of the leg bones of growing chickens. T. T. MILBY (Iowa Agric. Exp. Sta. Res. Bull., 1934, No. 172, 223—252).—With otherwise normal rations excess of P is the primary cause of slipped tendons (I). Leg bones of affected chickens have ash contents substantially the same as those of normal birds. Rice bran and, to a smaller extent, wheat middlings contain a substance counteracting the tendency towards (I). Incorporation of 3% MgCO_3 in the ration prevented (I), somewhat reduced the growth rate of chickens, and lowered the ash content of the fat-free femurs. A. G. P.

Crystalline lens. Fate of glutathione in parathyroid cataract. E. I. EVANS (Proc. Soc. Exp. Biol. Med., 1934, 31, 603—605).—The normal glutathione content of the lens (0.385%) in dogs decreased

by 50—70% after parathyroidectomy, and before there was appreciable deposition of Ca in the cataract. Free cystine was absent from the lens filtrates.

CH. ABS. (p)

Crystalline elements of stomach lavage of patients with cholelithiasis. H. A. RAFSKY (J. Lab. Clin. Med., 1934, 19, 959—962).—Appreciable amounts of cholesterol, carbonates, and Ca bilirubate were identified.

CH. ABS. (p)

Vitamin-A and colds. E. L. GARDNER and F. W. GARDNER (Amer. J. Dis. Children, 1934, 47, 1261—1264).—Administration of vitamin-A diminished the incidence and severity of colds.

CH. ABS. (p)

Changes in the carbohydrate metabolism of the heart following coronary occlusion. H. E. HIMWICH, W. GOLDFARB, and L. H. NAHUM (Amer. J. Physiol., 1934, 109, 403—408).—Coronary occlusion (I) in dogs was followed by a decrease in the glycogen of the infarcted area, part of the glycogen appearing as increased sol. carbohydrate and lactic acid (II). Before (I), the heart absorbed (II) from the blood-stream, but (I) usually resulted in a release of (II) by the heart, probably due to the diminished O₂ supply to the cardiac tissues. Glucose was absorbed from the blood both before and after (I).

R. N. C.

Renal function in diabetes. G. FERRO-LUZZI and A. SALADINO (Arch. Farm. speriment., 1934, 58, 107—130).—The amount of glomerular filtrate (I) in diabetes is slightly raised by administration of H₂O, and decreased when liquid food is withheld. Variations of (I) and polyuria are not dependent on corresponding oscillations of hydræmia. Hypercreatininæmia and hyperazotæmia, the latter sometimes due to resorption, have been noted.

R. N. C.

Clinical experiments with carbohydrate-free meal in diabetics. E. EGEDY (Klin. Woch., 1934, 13, 334; Chem. Zentr., 1934, i, 3363).—Tresfarin, containing gluten without starch, sugar, or other carbohydrates harmful to diabetics (I), does not raise the blood-sugar when consumed in large quantities at a time, or in small quantities over long periods, either in normal persons or (I). The characteristic sp. dynamic effect for protein (II) is marked, and on account of its high (II) content (61.5%), the meal can be used as a foodstuff.

R. N. C.

Use of synthalin in diabetes mellitus. L. K. CAMPBELL (J. Lab. Clin. Med., 1934, 19, 1067—1073).—After administration of synthalin for 4—6 days, glucose was absent from urine for several days.

CH. ABS. (p)

Essential fructosuria. S. SILVER and M. REINER (Arch. Int. Med., 1934, 54, 412—426).—Fructosuria (I) is thought to be due to an error of metabolism localised in the liver resulting in a loss of ability to fix fructose as glycogen, the metabolism of other carbohydrates being unaffected. Administration of fructose (II) after injection of insulin prevents hypoglycæmia in such cases by the replacement of glucose in the blood by (II), and the increased glycogenolysis caused by adrenaline does not alter the (II) tolerance. Sorbitol administered to a (I) patient caused hyperglycæmia with an increase in blood-(II), and half as much (II) was excreted from a dose of sorbitol

as from an equal dose of (II). Formation of 1 mol. of glucose and of (II) may therefore be an intermediate stage in the metabolism of 2 mols. of sorbitol.

A. L.

Influencing of diphtheria-immunity in guinea-pigs by vitamin feeding and ultra-violet irradiation. C. K. CHOUN (Z. Immunität., 1934, 81, 432—444; Chem. Zentr., 1934, i, 2608).—Animals on a vitamin diet (I) showed a stronger resistance to diphtheria toxin than with normal feeding; ultra-violet irradiation (II) with normal feeding gave the same result, but not so strong. The combined (I) and (II) had no effect, as the rays apparently destroyed the vitamins. Animals with normal feeding showed no change when kept in either the light or dark; with (I), resistance to the toxin was increased by exposure to sunlight.

R. N. C.

Presence of arsenic in the brain and its relation to pericapillary hæmorrhages or so-called acute hæmorrhagic encephalitis. A. E. OSTERBERG and J. W. KERNOHAN (Amer. J. Clin. Path., 1934, 4, 362—369).—Following administration of org. As compounds, As is found in the central nervous system (I) and may cause hæmorrhagic encephalitis (II). Ingestion of inorg. As also results in the presence of As in (I), but rarely causes (II).

CH. ABS. (p)

Calcium treatment of milk-fever. O. STINSON (Vet. Rec., 1934, 14, 1244).—Milk-fever was cured by subcutaneous injection of a 10% solution of Ca gluconate in a newly-calved cow.

R. N. C.

Prolan elimination in essential hypertonia. Ætiology of high pressure. E. KYLIN (Deut. Arch. klin. Med., 1934, 176, 301—310; Chem. Zentr., 1934, i, 3481).—Prolan elimination in the urine was frequently increased in hypertonics.

R. N. C.

Hypoglycæmia hypophysiopriva. W. MAHONEY (Amer. J. Physiol., 1934, 109, 475—482).—The cachexia hypophysiopriva (I) following hypophysectomy (II) is accompanied by hypoglycæmia (III), administration of glucose resuscitating puppies in an advanced state of (I). In fasting puppies, the physical signs of (III) appear 24—36 hr. after (II) at a blood-sugar level of 50 mg., after which the blood-sugar falls rapidly to zero. Repeated administration of carbohydrates prevents (I) following (II). The low glucose combustion curves indicate a high tolerance. (III) is suggested as an explanation of fatalities following (II).

R. N. C.

Infection and the tolerance for glucose. E. G. SCHMIDT, J. S. EASTLAND, and J. H. BURNS (Arch. Int. Med., 1934, 54, 466—481).—Of 73 cases of infection subjected to the glucose tolerance test, 36 had pyogenic infection (I) and of these 29 gave pathologic glycaemic curves, the highest being from cases of cellulitis. Glycosuria, however, was found in only 4 of these. Disappearance of the infection resulted in normal blood-sugar curves. Both *Streptococci* and *Staphylococci* produced disturbances in the carbohydrate mechanism. 9 patients with non-pyogenic febrile conditions (II) also gave abnormally prolonged blood-sugar curves. Of 28 patients with arthritis (III) and rheumatoid conditions, 15 gave diabetic-like

blood-sugar curves. After fasting, the curves in (I), (II), and (III) were, in general, normal. A. L.

Radiothorium in leucæmic myelosis. I, II. I. ZADEK (Folia hæmatol., 1933, 49, 287—340; 50, 369—409; Chem. Zentr., 1934, i, 3227).—I. Cases of leucæmic myelosis (I) have been cured by administration of large quantities of Rd-Th, combined with Th-X and X-rays.

II. Symptomatological description of the action of Rd-Th. Th-X accelerates the release of cells from the bone-marrow into the blood-stream. Rd-Th accumulates in the liver and spleen, Th-X in the bone-marrow. Administration of CaCO_3 causes an increased excretion of Th-X in the urine, suggesting that Th-X affects the Ca metabolism. R. N. C.

Chemotherapy in acute pancreatic necrosis. J. BAUMANN (Sitzungsber. Ges. Beford. ges. Naturwiss. Marburg, 1933, 68, 59—74; Chem. Zentr., 1934, i, 2443).—In pancreatic necrosis the organ undergoes autodigestion by trypsin (I), which has been activated in the gland by enterokinase. There is also a considerable excretion in the urine of activated (I) which apparently passes through the blood-stream in the active state. Quinine does not inhibit (I), but activates it still further. (I) is inhibited by rivanol, trypaflavin, and particularly by insulin. R. N. C.

Composition of œdema fluid and lymph in œdema and elephantiasis resulting from lymphatic obstruction. C. K. DRINKER, M. E. FIELD, J. W. HEM, and O. C. LEIGH, jun. (Amer. J. Physiol., 1934, 109, 572—586).—The œdema fluid from dogs with complete lymphatic obstruction in the hind leg was studied over a long period. Proteins reached a concn. of 4—5%; the albumin-globulin ratio was slightly > that in blood. The proteins of lymph and œdema fluid when examined together were fairly similar. R. N. C.

Creatine-creatinine metabolism in infantile paralysis and the effects of glycine. I. W. GROS (Z. klin. Med., 1933, 126, 152—160; Chem. Zentr., 1934, i, 1517).—Administration of glycine in poliomyelitis increased the excretion of creatine without affecting that of creatinine. A. G. P.

Effect of hyperpyrexia on phosphorus partition of whole blood in paresis. D. SACKETT and A. W. TURNER (J. Lab. Clin. Med., 1934, 19, 1045—1049).—Treatment of paresis by hyperpyrexia results in conversion of acid-sol. P of blood into lipin-P. The total P content is unchanged. CH. ABS. (p)

Significance of the inorganic sulphate clearance in renal disease. J. W. MACY (Arch. Int. Med., 1934, 54, 389—404).—The excretion of inorg. SO_4 (I) by fasting subjects remains fairly const.; with normal food intake, however, the variations are considerable and > those in the serum-(I) vals. The concn. of (I) in the urine is < that of the urea (II) or creatinine (III), and the clearance vals., whilst being more const. than those for (II) and (III), are scarcely affected by the vol. of the urine. Where renal insufficiency exists, the (I)-clearance val. is reduced in most cases, and in 12% of the subjects examined (I) vals. indicated impaired renal function when other tests gave normal results. A. L.

Treatment of schistosomiasis with acridine compounds. M. KHALIL and M. SALAH (Lancet, 1934, 227, 862—863).—Trypaflavine and allied compounds have no curative effect on schistosomiasis due to *Schistosoma hæmatobium* or *S. mansoni*.

L. S. T.

Effect of dinitrophenol on metabolism in schizophrenic patients. J. M. LOONEY and R. G. HOSKINS (New Engl. J. Med., 1934, 210, 1206—1213).—Administration of 2:4-dinitrophenol (3—4 mg. daily for 6 weeks) had no harmful effects. Basal metabolic rates were increased. Non-protein-, urea-, and uric acid-N in blood increased gradually, but tended to regain normality as treatment continued.

CH. ABS. (p)

Experimental scurvy. XIX. Urine- and blood-lactic acid in scorbutic guinea-pigs. J. SHIMADA (J. Biochem. Japan, 1934, 20, 147—159).—The incidence of scurvy in guinea-pigs does not produce an increase in the urine-lactic acid, whilst the blood level varies within normal limits (0.030—0.076%) (cf. A., 1928, 544). An occasional decrease in blood-lactic acid is probably due to inanition.

F. O. H.

Relation of avitaminosis-C to blood-clotting. A. K. PRESNELL (J. Nutrition, 1934, 8, 69—74).—Blood from scorbutic guinea-pigs has a longer clotting-time, smaller no. of platelets and red cells, and less hæmoglobin than that of normal animals. A. G. P.

Resistance of capillaries. I. Decreased resisting power through lack of vitamin-C, and through other conditions in hospital patients. P. SCHULTZER (Acta Med. Scand., 1934, 81, 113—132; Chem. Zentr., 1934, i, 2611).—Administration of vitamin-C generally restored the resisting power of the capillaries in scorbutic patients, but was ineffective when the decreased resistance was due to infection or chronic kidney disease. R. N. C.

Incidental hyperguanidinæmia as a cause of clinical tetany. K. DODD and A. S. MINOT (Amer. J. Dis. Children, 1934, 47, 948—962).—Tetany associated with alimentary intoxication in infants, and with post-influenzal pneumonia, is caused by the presence of increased amounts of guanidine in the blood. Guanidinæmia may be caused by increased autolysis of tissues, marked dehydration, or a disturbed Ca : P balance. Blood-Ca remains normal.

CHEM. ABS. (p)

Iodine content of blood and of urine and the basal metabolic rate; their value in the diagnosis of the function of the thyroid gland. A. W. ELMER and M. SCHEPS (Acta Med. Scand., 1934, 82, 126—136).—In cases of different diseases with normal thyroids and normal or low basal metabolic rate and in cases of non-toxic goitre, vals. for blood-I of $8—19 \times 10^{-6}$ g. per 100 ml. were found. The urinary I excretion for 24 hr. in these cases varied from 16 to 32×10^{-6} g. In cases of exophthalmic goitre, blood-I was $20—112 \times 10^{-6}$ g. per 100 ml. Urinary I excretion was greatly increased in severe cases, $96—136 \times 10^{-6}$ g. per 24 hr. Typical cases of myxœdema had blood-I of $4—6 \times 10^{-6}$ g. Excretion was within normal limits except in one case, in which it was low. NUTR. ABS. (b)

Calcium and phosphorus metabolism in diseases of the thyro-parathyroid apparatus. I. Calcium, phosphorus, and total metabolism in hyperthyroidism. Rôle of the parathyroid glands. F. S. HANSMAN and F. H. WILSON (Med. J. Austral., 1934, i, 37—66).—Hyperthyroidism alone has no effect on Ca and P metabolism. If there is disturbance of the latter there will be some degree of associated hyperparathyroidism.

NUTR. ABS. (m)

Effect of toxæmia on the tolerance for glucose and on the action of insulin. II. J. S. SWEENEY, N. BARSHOP, L. C. LOBELLO, and R. A. ROSENTHAL (Arch. Int. Med., 1934, 54, 381—388).—Previous findings (this vol., 799) are confirmed, viz., the amounts of insulin (I) necessary to dispose of quantities of glucose injected with (I) into normal rabbits are inadequate in the case of animals injected with diphtheria toxin.

A. L.

Vitamin therapy in pulmonary tuberculosis. VI. Effect of viosterol on the carbon dioxide content, hydrogen-ion concentration, chlorides, glucose, and urea-nitrogen of the blood, and protein, calcium, and phosphorus of the serum. Effect of physiological saline on these constituents during hypercalcaemia. P. D. CRIMM and J. W. STRAYER (J. Lab. Clin. Med., 1934, 19, 966—971).—Administration of viosterol sufficient to produce hypercalcaemia in tubercular patients causes an increase in the P, total protein, and albumin contents of serum, and in the urea-N of the blood, and a decrease in serum-globulin and blood-Cl'. Intravenous injection of physiological saline reduces the concns. of Ca, P, and total protein. CH. ABS. (p)

Gastric ulcer. Rôle of cathepsin in ulcer formation. H. TAMESUE (Z. Chirurg., 1934, 242, 706—713).—Autolysis of gastric mucosa (I) is most marked in rabbits at p_H 4.0—5.0, in man [(I) obtained at operation] at 4.0 and 8.0. The presence of excess of O_2 in the environment inhibits, and of excess of N_2 promotes, autolysis. KCN, reduced glutathione, and hexose phosphate accelerate autolysis and activate the cathepsin in (I). The production of gastric ulcer is attributed to circulatory disturbance leading to increased glycolysis in (I), formation of lactic acid, increase in acidity, and O_2 deficiency.

NUTR. ABS. (m)

Gaseous metabolism of tissues *in vitro*. VI. Determination of tissue respiration and glycolysis by evolved ammonia. Y. OGATA (J. Biochem. Japan, 1934, 19, 377—390).—The evolution of NH_3 by tissues necessitates a correction to the Warburg formulæ. The solubility of NH_3 in Ringer's solution, and the max. tension and vol. which can be neglected in metabolic experiments, are determined. The application of the findings to data of the respiration of rabbit's kidney medullary tissue is given.

F. O. H.

Tissue metabolism of warm-blooded animals at normal and at febrile temperatures. M. E. MARSH (Amer. J. Physiol., 1934, 109, 502—514).—The average increase in O_2 consumption per 1° rise in temp. of liver and kidney tissues of the rat, rabbit, cat, and dog was fairly uniform in all the series under the

same conditions. In Ringer's PO_4''' -glucose solution, equilibrated with O_2 , the Q_{10} vals. averaged 1.7 for the first hr., but the accelerated decline in metabolism at the higher temp. made them of little significance. With serum and air, the metabolism at febrile temp. was maintained for several hr. at a rate parallel to the normal rate and slightly higher, the average Q_{10} being 2.0, which compared more favourably with that found in intact animals.

R. N. C.

Oxygen consumption of large-mouth black bass (*Huro floridiana*) fingerlings. A. H. WIEBE and A. C. FULLER (Trans. Amer. Fish. Soc., 1933, 63, 208—214).—The O_2 consumption is not related to the O_2 tension or p_H of the H_2O .

CH. ABS. (p)

Metabolism of the frog's egg in course of development. I. Respiration and glycolysis from segmentation to hatching. J. BRACHET (Arch. Biol., 1934, 45, 611—728).—Anaerobic conditions have no effect on segmentation (I) of developing frogs' eggs, but gastrulation (II) is impeded and neurulation (III) inhibited entirely. Reduced methylene-blue is oxidised in certain parts of the egg in anaerobiosis (IV), max. oxidation occurring in the sub-equatorial regions with $rH > 14$. O_2 consumption in (I), (II), and (III) is inhibited by 0.001M-KCN in the order of 85—100%, the inhibition falling to approx. 50% as growth proceeds. $NHPh \cdot CO_2Et$ in 0.001—0.002M concn. inhibits (I) and (III) and arrests (II). $CH_2I \cdot CO_2H$ has no action in presence of air; in (IV) it inhibits (III). The R.Q. of the eggs rises steadily through (I) and (II) to a max. at (III), when it falls slightly, then remaining const. until hatching occurs. Lactic acid, absent from the new-laid eggs, appears at the beginning of (I) and rises to a max. after (III), afterwards falling. (IV) is accompanied by the formation of considerable quantities of acid at the commencement of development. In more or less complete (IV) the eggs continue to produce CO_2 , which in complete (IV) is still approx. 50% of its aerobic val. Pulped eggs contain indophenol-oxidase (V), and also reducing substances (VI). Pulpung is followed by a momentary increase of O_2 consumption that may reach 800%; it is inhibited by KCN, but not by $p\text{-}C_6H_4(NH_2)_2$ or $CH_2I \cdot CO_2H$. The cause of this is probably connected with (V). R.Q. of tadpoles falls on pulpung. (VI) decolorise methylene-blue in absence of air; one or more of them are thermolabile at 52° , and all at 100° ; they are inhibited to a small extent by $NHPh \cdot CO_2Et$. They probably consist partly of dehydrogenases. The pulped eggs show no trace of either cytochrome or hæmatin spectra, although both are to be found in frogs' spermatozoa. Iodometric determinations indicate the possible presence of traces of glutathione, which, however, certainly plays no part in the respiration of the eggs. The reducing action of extracts of the pulped eggs suggests the possibility of ascorbic acid being one of the (VI).

R. N. C.

Synthesis of thymonucleic acid in the development of the trout's egg. M. VAN DER GHINST (Arch. Biol., 1934, 45, 729—734).—Thymonucleic acid is absent from the new-laid egg, but is synthesised progressively in the cellular portion of the egg as it develops.

R. N. C.

Fish metabolism under increasing temperature. R. C. CLAUSEN (Trans. Amer. Fish. Soc., 1933, 63, 215—219).—The daily rhythm of O_2 consumption (I) corresponds with the activities of the fish. (I) varies irregularly with rising temp., showing peak vals. at 12° and 20°. CH. ABS. (p)

Basal metabolism of old people. Y. KISE and T. OCHI (J. Lab. Clin. Med., 1934, 19, 1073—1079).—Between the ages of 50 and 93 years the metabolic rate declines 3—5% for each 10-year period. CH. ABS. (p)

Growth and basal metabolism. I. Basal metabolism of pre-school children. I. NAKAGAWA (Amer. J. Dis. Child., 1934, 47, 963—969).—The basal metabolic rate for Japanese children is > the Benedict-Talbot standards. CH. ABS. (p)

Blood-pigment and the living cell. I. Hæmoglobin decomposition in tissue cultures. II. Bilirubin formation *in vitro*. III. Formation of a yellow pigment in tissue cultures. L. DOLJANSKI and O. KOCH (Virchow's Arch., 1933, 291, 379—389, 390—396, 397—400; Chem. Zentr., 1934, i, 882).—I. Tissue cultures, especially from connective tissue (fibroblasts), liver, and spleen, transform added hæmoglobin (I) more rapidly and markedly than do the tissue extract controls. Addition of embryonic extracts to a blood-pigment (II) solution results in a decomp. of (I). In presence of the living cell the fission of the Fe-containing group from (I) does not occur.

II. Tissue cultures from spleen, fibroblasts, and liver formed no bilirubin (III) from added blood-pigment, whilst in the controls, which contained no living tissue and only tissue extract, (III) was detected.

III. Tissue cultures treated with (II) contained, besides methæmoglobin, another pigment which must be related to the decomp. of (I). Solubility and spectrum data indicate that the pigment is xanthorubin. L. S. T.

Site of bilirubin formation from experiments on angiotomised dogs. I. E. S. LONDON and L. J. KRYZANOVSKAYA (Z. physiol. Chem., 1934, 227, 229—232).—Blood samples were drawn from the venae lienalis and hepatica and the femoral vein and/or artery after production of hæmolysis by injection of H_2O into the jugular vein. The samples were analysed for bilirubin (I). The formation of (I) from hæmoglobin occurs chiefly but not entirely in the spleen. After splenectomy the femoral and hepatic veins showed a very small (I) content, indicating that the reticulo-endothelial system is not involved in (I) production. J. H. B.

Nutritional requirements of brook trout. A. V. TUNISON and C. M. McCAY (Trans. Amer. Fish. Soc., 1933, 63, 167—177).—Milks dried by various processes had equal food vals. Peanut and cottonseed meal were equally well utilised. The thermolabile factor *H* can be preserved by drying meat in a vac. in inert gas. The difficult digestion of fat by trout is not entirely due to the physical state of the fat at H_2O temp. Hg_2Cl_2 , $C_{10}H_7\cdot OH$, and CCl_4 were effective in freeing trout from *Octomitus salmonis*. CH. ABS. (p)

Nutritive value of whale-liver. T. OSEKI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1160—1165).—Liver-proteins of finback- (I) and sei-whale have a high nutritive val. and contain vitamin-A, but no -B. (I) contains some -E. J. L. D.

Alimentary value of soya beans. M. LIGORI (Arch. Farm. sperim., 1934, 58, 142—148).—Rats on a diet of soya beans show limited rates of growth, due to deficiencies of salts and vitamin-A and -D. Addition of 2% of cod-liver oil or butter resulted in the death of most of the animals, but the survivors showed a considerable improvement in growth and general condition. R. N. C.

Nutritive value of canavanine. I. M. OGAWA (J. Agric. Chem. Soc. Japan, 1934, 10, 225—231).—Canavanine is non-toxic; 0.01—0.1 g. per kg. per day promotes the growth of mice. CH. ABS.

Digestion and nutrition of heated cow's milk. J. OKADA and T. SANO (Jap. J. Exp. Med., 1934, 12, 169—198).—Heated milk has a lower nutritional val. and digestibility than raw milk. Effects of additions of gelatin, peptone, $Na_4P_2O_7$, and $CaCl_2$ are recorded. CH. ABS. (p)

Fish-meat powder as a substitute for horse-meat protein in synthetic diets used for feeding experiments. M. MATSUOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 335—340).—The nutritive val. of the proteins of fish-meat (I) is nearly the same as that of horse-meat powder. Albino rats died within 98 days on a vitamin-A-free diet containing (I), many exhibiting xerophthalmia. J. L. D.

Nitrogen balance of laying hens. J. S. WILLCOX (J. Agric. Sci., 1934, 24, 636—648).—Variations in the N retention of hens are not related to the output of egg-N or with the no. of eggs laid. The N required for egg production can be obtained mainly, if not entirely, from the food supply during the laying period. A. G. P.

Factors determining renal weight. XVI. Nature of the protein intake. E. M. MACKEY and L. L. MACKEY (J. Nutrition, 1934, 8, 187—195).—The influence of increased protein (I) intake by rats on the renal wt. varied with the nature of (I) in the order gelatin > ovalbumin > caseinogen. A. G. P.

Experiments on nutrition. XIII. Relative values of proteins. R. H. A. PLIMMER, J. L. ROSEDALE, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1934, 28, 1863—1886).—The proteins (I) in common foodstuffs were fed to chicks in conjunction with the carbohydrates of various cereals (II), the biological val. of (I) being given by (increase in wt.)²/time × (I)-consumption. Animal (I), such as egg-white, egg-yolk, caseinogen, and fish-meal, are far superior to vegetable (I) in pulses (III), grass, and lentils. When chicks were fed on (II) or (III) alone, the best results were obtained with buckwheat, barley, oatmeal, and wheat or maize in that order. The inferior val. of (III) is due to their low cystine content. A. E. O.

Feeding experiments with mixtures of highly purified amino-acids. IV. Supplementing effect of caseinogen fractions obtained by carbamate procedure. V. Additional pro-

properties of unknown growth-factor present in proteins. C. T. CALDWELL and W. C. ROSE (J. Biol. Chem., 1934, 107, 45—55, 57—72; cf. A., 1932, 83).—IV. Caseinogen (I) was refluxed with aq. H_2SO_4 and neutralised with $\text{Ba}(\text{OH})_2$; the filtrate was concn. in vac. Addition of $\text{Ba}(\text{OH})_2$ pptd. Ba aspartate, which was discarded. After further concn. 95% EtOH was added and the Ba salts of the dicarboxylic acids were converted into their acids. The filtrate was fractionated by the Ba carbamate procedure of Kingston and Schryver (A., 1925, i, 89). Rats fed on a diet containing purified NH_2 -acids as sole source of N showed greatest growth recovery when fed with the NH_2 -acids pptd. by EtOH. Several of the other fractions were also effective to a smaller degree. Glycine may be removed from the growth-stimulating factor (II) by the relative insolubility of its carbamate in ice-cold H_2O .

V. The hydrolysed (I) was fractionated by the Cu salt procedure (Town, A., 1928, 1148). From growth curves of rats (II) is absent from the H_2O -insol. Cu salt fraction, and is very slowly extracted with MeOH from the H_2O -sol. salts. None of several synthetic products similar to proline, valine, and isoleucine had growth-promoting powers. H. D.

Tryptophan deficiency. R. S. ALCOCK (Biochem. J., 1934, 28, 1721—1728).—Partial replacement of hydrolysed caseinogen by zein affords an improved tryptophan (I)-deficient diet on which rats lose but little wt. Rats on this diet, injected with (I), failed to grow, but showed increased growth when injected with anterior pituitary hormone. The rat can synthesise sufficient (I) for maintaining wt. C. G. A.

Utilisation of energy-producing nutriment and protein as affected by individual nutrient deficiencies. I. Effects of cystine deficiency. R. W. SWIFT, O. J. KAHLENBERG, L. VORIS, and E. B. FORBES (J. Nutrition, 1934, 8, 197—219).—Deficiency of cystine (I) in the diet of rats had an adverse effect on appetite, but no definite influence on the digestibility of dietary protein. Supplementary feeding with (I) improved growth and increased the storage of N and of energy. The C:N ratio of the urine (2.0) was not significantly affected.

A. G. P.

Metabolism of *l*- and *dl*-cystine in adult dogs maintained on a protein-free diet. J. A. STOKOL (J. Biol. Chem., 1934, 107, 225—228).—*dl*-Cystine, in contrast to *l*-cystine, is only partly retained by animals, 40% of the S being excreted in the urine as inorg. SO_4^{2-} and neutral S. The S of *d*-cystine is not used by dogs to replace tissue waste. C. G. A.

Site of deamination of amino-acids from experiments on angiotomised dogs. I. E. S. LONDON, A. M. DUBINSKY, N. L. VASSILEVSKAYA, and M. J. PROKHOROVA (Z. physiol. Chem., 1934, 227, 223—228).—Blood samples from the portal and kidney veins and the femoral artery of fasting dogs were examined for NH_3 , O_2 , CO_2 , and AcCO_2H (I), before and after injection of *d*-alanine (II) or *l*-aspartic acid into the femoral vein. Deamination of NH_2 -acids under physiological conditions occurs principally in the intestinal wall. The deamination of (II) is accompanied by increased O_2 uptake, (I) being

formed. Deamination also occurs in the kidney; the increased O_2 uptake again indicates (I) production. No increase of (I) (but often a decrease) is, however, observed in the kidney vein, presumably owing to its removal by the kidney. J. H. B.

Oxidation of tyrosine and phenylalanine by the livers and kidneys of certain animals. F. BERNHEIM and M. L. C. BERNHEIM (J. Biol. Chem., 1934, 107, 275—282).—Tyrosine (I) is oxidised by broken cell suspensions of the livers (II) of the rat, guinea-pig, rabbit, cat, and dog; phenylalanine (III) is also oxidised by these preps., but in some cases very slowly. Preps. of the kidneys (IV) oxidise (III) but not (I). Oxidation of 1 mol. of (I) requires 2O_2 and of (III), 0.5O_2 . (I) is not deaminated, but tyramine and (III) are. $0.005M$ -KCN inhibits oxidation of (I) but not (III). (III) but not (I) reduces methylene-blue. C. G. A.

Influence of temperature on protein metabolism. III. Hexone bases of toad's liver during winter. H. MAKINO (J. Biochem. Japan, 1934, 20, 1—3).—The hexone base fraction from toad's liver during winter contained 0.0439% of cadaverine and 0.0934% of choline, but no lysine, arginine, or histidine (cf. this vol., 321). F. O. H.

Perfusion of the stomach. IV. Perfusion with urea. S. SUMIDA (J. Biochem. Japan, 1934, 19, 449—456; cf. A., 1933, 745).—Blood containing added urea perfused through the isolated dog's stomach (I) experiences an increase in $\text{NH}_3\text{-N}$ which, however, is only approx. 1/6 of the decrease in urea-N. The $\text{NH}_3\text{-N}$ levels of the contents and muscular and mucosa layers of (I) are increased, whilst the corresponding urea-N levels are practically unchanged. The catabolism of urea in (I) is discussed. F. O. H.

Participation of ornithine, citrulline, and arginine in the normal process of urea formation in the liver, using angiotomy. I. E. S. LONDON, A. K. ALEXANDRY, and S. V. NEDSVESKI (Z. physiol. Chem., 1934, 227, 233—241).—Ornithine (I) injected into the portal vein together with NH_4Cl gives a greater increase in the urea in the liver vein than NH_4Cl alone. (I) alone gives a considerable increase. (I) injected with NH_4Cl into the peripheral veins does not cause an increase in the urea in the arterial blood over that produced by NH_4Cl alone. Citrulline and arginine disappear from the blood much more slowly than NH_4Cl ; the production of urea is also slower. No support is found for Krebs' proposed scheme for urea production in the liver based on *in-vitro* experiments (A., 1932, 1059). J. H. B.

Non-enzymic uricolysis in animal tissue. D. MICHLIN and A. RYZOVA (Biochem. Z., 1934, 273, 354—358).—In the presence or absence of O_2 added uric acid is partly or wholly destroyed by fresh or dried, boiled or unboiled extracts of the mammary glands of cows or of rat or rabbit kidney. Haemoglobin has no effect (cf. Gomolinska, A., 1928, 1269) on the process, which is accompanied by production of urea but not of allantoin. No glycine is produced. W. McC.

Fate of carotene introduced into the circulation. J. C. DRUMMOND, H. P. GILDING, and R. J. MACWALTER (J. Physiol., 1934, 82, 75—78).—Carotene introduced into the blood-stream as a colloidal suspension in aq. solution was taken up very rapidly, principally in the liver, which, however, could absorb only a limited amount, excess being retained by the lungs. The liver showed carotene granules in the Kupffer cells, suggesting that it was absorbed from the circulation by the reticulo-endothelial system.

R. N. C.

Is cholesterol absorbed by the mucous membrane of the gall-bladder? B. VARELA, J. VILAR, and A. TERRA (Compt. rend. Soc. Biol., 1934, 115, 1652—1656).—Results of previous workers were confirmed. The ratio of cholesterol to bilirubin in bile secreted by the gall-bladder was < in duodenal juice or hepatic bile, collected simultaneously. The differences observed are not attributed to any special function of the mucous membrane of the gall-bladder.

NUTR. ABS. (b)

Spleen and cholesterol metabolism. F. GOEBEL (Compt. rend. Soc. Biol., 1934, 116, 233—236; J. Physiol. Path. gén., 1934, 32, 59—61).—In normal dogs, subcutaneous injection of cholesterol (I) produced hypercholesterolemia of about 30 min. duration, often followed by slight hypocholesterolemia. After removal of the spleen (II) the rise in blood-(I) lasts at least 24 hr. (II) probably produces (I), removes excess of it from the blood, and stores it.

NUTR. ABS. (m)

Diagnostic value of blood-cholesterol determination after peroral loading with cholesterol. P. BARREDA (Klin. Woch., 1934, 13, 290—292; Chem. Zentr., 1934, i, 3081).—Attempts to confirm Bürger's observations of the regular appearance of alimentary hyperglycemia in metabolic recovery after peroral loading with cholesterol (I) lead to a reverse result. The results are not considered sufficient evidence from which to deduce any far-reaching conclusions on (I) metabolism.

R. N. C.

Physiology of phospholipins. R. G. SINCLAIR (Physiol. Rev., 1934, 14, 351—403).—A review.

CH. ABS. (p)

Action of phosphoaminolipins in fat assimilation. I. Injection of iodised fats. C. ARTOM (Boll. Soc. ital. Biol. sperim., 7, 126—129; Chem. Zentr., 1934, i, 2449).—Shortly after injection fat constituents appear in the liver in the form of COMe₂-sol. compounds. Blood also contains a part of the iodised fat.

A. G. P.

Significance of the liver in metabolism of lipins. III. Changes in lipins in blood and bile when various kinds of bile acids are administered. Y. ASODA (Jap. J. Gastroenterol., 1934, 6, 1—6).—Feeding of Na salts of bile acids to rabbits caused a temporary increase of blood-lipins and a decrease in bile-lipins.

CH. ABS. (p)

Liver-lipins during the intake of neutral fat. C. ARTOM (Boll. Soc. ital. Biol. sperim., 7, 133—136; Chem. Zentr., 1934, i, 2449).—After administration of fats to fasting dogs, the fatty acids and P of phosphoaminolipins, the CHCl₃-sol. P, and the P pptd. by COMe₂ increase proportionally. Total and non-

phosphatide fatty acids also increase. The dry matter and unsaponifiable fraction vary irregularly.

A. G. P.

Fatty acids produced by the metabolism of nematodes. J. WAECHTER (Z. Biol., 1934, 95, 497—501).—The Et₂O-sol. material from 1% aq. NaCl (saturated with CO₂) in which *Ascarides* have been kept at 37° for 72 hr. yields on fractional distillation *n*- but not *iso*-valeric acid (cf. A., 1902, ii, 155).

F. O. H.

Fat metabolism. IV. Bi-lateral β -oxidation of the dicarboxylic acids arising by ω -oxidation of saturated fatty acids. P. E. VERKADE and J. VAN DER LEE (Z. physiol. Chem., 1934, 227, 213—222).—After administration of triundecoin to man, undecanedicarboxylic, pimelic, and azelaic acids are excreted in the urine, and after tridecain, sebacic, adipic, and suberic acids. Thus both β - and ω -oxidation occur.

J. H. B.

Relation between surface tension of solutions and solubility of physiologically important fatty acids.—See this vol., 1304.

Good growth of albino rats fed on a polished rice diet. M. MATSUOKA (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1139—1154).—Growth is rapid when polished rice is the source of carbohydrates if the other necessary dietary constituents are present in adequate amount.

J. L. D.

Stereochemical constitution and selective [animal] resorption of carbohydrates. G. MALYOTH (Klin. Woch., 1933, 12, 1930—1933; Chem. Zentr., 1934, i, 2308).—A dextrin-maltose mixture partly fermented (50%) by *Aspergillus* to produce a preponderance of α -compounds increased the live wt. of piglings to an extent > that produced by the untreated mixture.

A. G. P.

Rate of absorption of glucose from the intestine of the dog. H. C. TRIMBLE and S. J. MADDOCK (J. Biol. Chem., 1934, 107, 133—142).—The max. rate of absorption is 0.92 g. per kg. per hr. The optimal concn. for absorption of 13.5% was not confirmed.

H. G. R.

Metabolism of galactose. P. DE LUCIA and M. TORELLI (Boll. Soc. ital. Biol. sperim., 7, 250—251; Chem. Zentr., 1934, i, 2449).—Administration of 1 g. of galactose (I) per kg. live wt. to fasting dogs was followed by 70% utilisation of (I) within 72 hr. The balance appeared in the urine. A. G. P.

Metabolism of fructose. IV. Hepatic influence on utilisation of galactose and fructose. A. W. ROWE, M. A. McMANUS, and A. J. PLUMMER (New. Engl. J. Med., 1934, 210, 1163—1169).—Utilisation of fructose (I) and galactose (II) is influenced by hepatic disturbance, which lowered the tolerance for (I) and (II) in most cases.

CH. ABS. (p)

Fate of dulcitol and dulcitan in the animal body. C. J. CARR and J. C. KRANTZ, jun. (J. Biol. Chem., 1934, 107, 371—376).—Dulcitol (I), but not its anhydride dulcitan (II), can be stored as glycogen (III) in the liver of white rats. Each tends to reduce tissue storage of (III). Neither (I) nor (II) affects the R.Q., or is effective in relieving insulin shock or in

raising the blood-sugar of rabbits when administered orally. A. E. O.

Utilisation of blood-sugar and formation of lactic acid by the lungs. C. L. EVANS, F. Y. HSU, and T. KOSAKA (J. Physiol., 1934, 82, 41—61).—Perfusion of blood through exsected dog's lungs causes conversion of the blood-sugar into lactic acid (I). The rate for the first hr. is about 100 mg. of glucose (II) per 100 g. of lung, forming 50 mg. of (I), and slows down as perfusion proceeds. After all the (II) has been removed, (I) shows a slight fall. Ventilation of the lungs with CO_2 reduces the rate of glycolysis, which rapidly becomes normal on resumption of air supply. Perfusion with serum alone shows the same results. Blood-(I) of heart-lung preps. (III) is formed partly by glycolysis in the blood-stream and partly by the lungs, as is the (I) consumed by the beating heart in (III). R. N. C.

Metabolism of lactic and pyruvic acids in normal and tumour tissue. I. Methods and results with kidney cortex. K. A. C. ELLIOTT and E. F. SCHROEDER (Biochem. J., 1934, 28, 1920—1939).—Lactate is slowly metabolised by slices of rabbit-kidney cortex (I), but less rapidly than pyruvate, which in turn is oxidised less rapidly than succinate, fumarate, malate, and oxaloacetate, none of which is converted into glycogen by (I). Acetate is also fairly rapidly metabolised, but β -hydroxybutyrate does not appreciably affect the respiration of (I). β -Carboxylase, but not α -, is present in (I). After mincing the tissue, only succinic dehydrogenase, fumarase, and (to a slight extent) β -carboxylase remain active. Formate is not oxidised by (I). A. E. O.

Intermediate metabolism of endocrine organs.

II. Glycolysis in adrenals and corpus luteum.

III. Glycolysis and proteolysis in adrenals during increased production of hormone. A. UTEVSKI, S. EPSTEIN, V. OSSINSKAJA, and E. MIMA (Biochem. Z., 1934, 273, 359—361, 362—364).—II. The medullary and cortical regions of the adrenal glands (I) and the corpus luteum (II) of the cow are rich in preformed lactic acid (III), the amount of which increases on autolysis. Addition of glycogen (IV) or AcCO_2H does not stimulate production of (III) in (I) or (II). Alanine slightly stimulates production of (III) in (II) but not in (I), and glucose stimulates it slightly in (I) but not in (II). 100 g. of (I) contain 40 mg. and of (II) 150 mg. of (IV).

III. In dogs electrical stimulation (V) of the splanchnic nerve leads to increase in the sugar and (III) contents of the blood and in the (IV) content of (I). The (III) content of (I) decreases. (V) has no effect on the N content of (I) (cf. this vol., 102). W. McC.

Chemistry of anaerobic recovery in muscle. J. K. PARNAS and P. OSTERN (Nature, 1934, 134, 627).—Three intermediate reactions in the conversion of glycogen into lactic acid are proposed. L. S. T.

Disappearance of hexose monophosphate from muscle under aerobic and anaerobic conditions. G. T. CORI and C. F. CORI (J. Biol. Chem., 1934, 107, 5—14).—The leg muscles of frogs are analysed for hexose phosphate (I) and lactic acid (II) during re-

covery from tetanic stimulation (III) and adrenaline treatment (IV) under aerobic (V) and anaerobic (VI) conditions. The rate of disappearance of (I) under (V) after (III) is uninfluenced by the presence of (II) and \propto the concn. of (I); in 30 min. of recovery 77 mg. per 100 g. disappear, reaching the basal val. in 2 hr. Under (VI) decreases of 49, 63, and 78 mg. per 100 g. occurred in 60, 90, and 120 min., respectively. After (IV) the rate of disappearance of (I) under (V) is uninfluenced by changed p_{H} or addition of MgCl_2 , (II), PO_4''' , and KCl, and it occurs thrice as rapidly as under (VI). After (III) and (IV) the disappearance of (I) under (VI) was accompanied by equiv. (II) and inorg. P formation. H. D.

Phosphagen in plain muscle. M. G. EGGLETON (J. Physiol., 1934, 82, 79—87).—The ratio (I) of phosphagen (II) to the sum of (II) and inorg. PO_4''' in the resting aerated muscle of *Mytilus edulis* is 0.8; fatigue induced by intermittent contractions reduces it to 0.45, and that from a tetanus to 0.6. The muscle at rest recovers its original (II) content under aerobic, but not under anaerobic, conditions; thus (II) plays the same part in plain as in skeletal and cardiac muscles. The hydrolysis const. of the *Mytilus* (II) in 0.01N-HCl at 28° is similar to that of argininephosphoric acid (III); the effect of MoO_4'' on the rate of hydrolysis is also the same for both substances. (III) can be determined rapidly by separating it from $\text{P}_2\text{O}_7'''$ and PO_4''' as sol. Ba salt and then hydrolysing. Both $\text{Na}_4\text{P}_2\text{O}_7$ and muscle " $\text{P}_2\text{O}_7'''$ " are slightly hydrolysed in 0.05N-acid at 28° , the latter twice as fast as the former. R. N. C.

Transparency and action-metabolism of muscle. E. VON BABYER (Klin. Woch., 1933, 12, 1278—1279; Chem. Zentr., 1934, i, 2783—2784).—

The intensity of the transmitted light through frogs' sartorii was measured under varied conditions. The course of the colour curve was not essentially altered in any case, but there was a parallel shifting of the intensity. In the breakdown of creatinephosphoric acid the extinction (I) by the muscle decreased; in lactic acid formation it increased in presence of Ringer's solution, a swelling generally taking place. It has not been definitely proved that the changes in (I) are dependent on p_{H} , and the nature of the optical changes is still unknown. R. N. C.

Effect of prolonged hard muscular work on sulphur and nitrogen metabolism. H. E. C. WILSON (J. Physiol., 1934, 82, 184—188).—The excess N excretion during and after the riding of a bicycle-ergometer for a prolonged period increases with the protein intake during the work period; S excretion runs on similar lines. The excess S tends to precede the N in excretion, the S output returning to its basal val. before the N. The S:N ratio of the total excess of each experiment does not show that the excess is derived from any one tissue-protein. R. N. C.

Efficiency and performance of a vegetarian racing cyclist under different dietary conditions. G. M. WISHART (J. Physiol., 1934, 82, 189—199).—The best performance is obtained on a high-cal. diet rich in animal proteins (I). The gross efficiency (II)

is > that on (I)-poor diets; the lower (II) is not explained by the higher sp. dynamic action of the (I).

R. N. C.

Chemico-physiological basis of muscular fatigue. H. RIGLER (Med. chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1933, 198—206; Chem. Zentr., 1934, i, 2444).—Theoretical. R. N. C.

Effect of varying sugar intake on nitrogen, calcium, and phosphorus retention of children. R. B. HUBBELL and M. KOEHNE (Amer. J. Dis. Children, 1934, 47, 988—992).—Addition to diets of girls (7—11 years) of sugar sufficient to raise the caloric val. (I) by 6% did not affect the retention of N, Ca, or P. An increase of 16—18% in (I) caused an increase in the N and P, and a decrease in Ca, retained.

CH. ABS. (p)

Influence of various additions to the ration, of potassium, calcium, magnesium, and iron on the mineral status of these elements in the blood of cattle during stall feeding and pasturage. E. BERNDT and H. BETHMANN (Bied. Zentr. [Tierernähr.], 1934, B, 6, 292—350).—The relative effects of electrolyte ions on blood functions are in accordance with the Hofmeister series, especially in relation to antagonism. The K content of blood in old cows was > that in younger animals. Vals. fluctuated between 27.7 and 78.6 mg. per 100 c.c., and were increased during pasture feeding. Blood-Ca (I) in all animals showed approx. const. mean vals. These were lower during pasturing than during stall feeding and were influenced by the Ca content of the ration. Feeding of sugar-beet leaves caused a marked increase in (I). Blood-Mg was not affected by the Mg content of the food during either indoor feeding or pasturing. Blood-Fe was higher in animals at grass, but otherwise was unrelated to the Fe content of the food.

A. G. P.

Influence of the addition to rations of chlorine, sodium, phosphorus, and protein on the mineral status of these elements in blood of cattle during stall feeding and pasturage. E. BERNDT and G. F. BAUMGARTEN (Bied. Zentr. [Tierernähr.], 1934, B, 6, 351—397).—Blood-Cl' was higher in old than in young cows, was not affected by the amounts fed, but was higher during stall feeding (I) than in pasturage (II). Variations in blood-Na were small. The Na : K ratio widened with increasing age and also increased in spring at the transition period from (I) to (II). Blood-PO₄''' varied considerably and was directly affected by the PO₄''' content of the ration. During (I) blood-protein (III) increased with age, but the digestible protein of the food bore no relationship to (III).

A. G. P.

Mobilisation of calcium during development. O. GLASER and E. PUEHLER (Biol. Bull., 1934, 66, 351—356).—The % of Ca in hen egg-shell during incubation was const., but the total Ca declined by approx. 150 mg. in 21 days.

CH. ABS. (p)

Effect of carbon dioxide on calcium and phosphorus retention. J. C. FORBES (J. Biol. Chem., 1934, 107, 283—287).—CO₂ in concn. up to 12% of the air breathed has no significant effect on the retention of either Ca or P by young rats. C. G. A.

Nitrogen and salt metabolism in monkeys. P. V. BOCHKAREV and N. P. KOROTKOVA (Arch. Sci. Biol. U.S.S.R., 1933, 33, 255—261).—N and mineral balances are examined.

CH. ABS. (p)

Salt requirements of *Ligia* in Bermuda. T. C. BARNES (Biol. Bull., 1934, 66, 124—132).—Longevity of *L. baudiniana* in air, sea-H₂O, and NaCl solutions is examined.

CH. ABS. (p)

Relation between the spleen and sulphur metabolism, especially the effect of various endocrine glands thereon. I. Effect of removal of spleen on sulphur metabolism. II. Effect of thyroid glands on sulphur metabolism of splenectomised dogs. III. Effect of insulin and glucose on sulphur metabolism of splenectomised dogs. IV. Effect of adrenaline on sulphur metabolism of splenectomised dogs. S. NISHIKORI (Folio Endocrinol. Japan, 1933, 9, 5—6, 6—7, 17—18, 18—19).—I. During 7—35 days after splenectomy the total N and S excreted decreased considerably, although the N : S ratio increased. The % of SO₄''' fell, but the proportion of total S appearing as SO₄''' increased. The proportion of alkylsulphuric acid was unchanged. Neutral S decreased.

II. Feeding of thyroid gland to splenectomised dogs (I) produced the same effect on N and S metabolism as on normal animals.

III. Administration of insulin to (I) increased the total N and S excreted without affecting the N : S ratio; inorg. S decreased and neutral S increased. Simultaneous injection of glucose accentuated these effects.

IV. Injection of adrenaline into (I) increased the excretion of total N and S, inorg. S, and neutral S.

CH. ABS. (p)

Bromine metabolism in the human organism. P. SERBESCU and G. A. BURRU (Bull. Acad. Med., 1934, 111, 232—238; Chem. Zentr., 1934, i, 3489).—Human blood contains > 0.1 mg. of Br per 100 c.c. The pituitary does not control Br metabolism, since no Br can be detected in it. The thyroid (I) always contains Br, and possibly controls both I and Br metabolism. Br introduced into the blood is taken up by the tissues, since it is eliminated only very slowly. (I)-Br appears to decrease with age.

R. N. C.

Effect of water drinking, mineral starvation, and salt administration on the total osmotic pressure of the blood in man, chiefly in relation to the problems of water absorption and water diuresis. E. J. BALDES and F. H. SMIRK (J. Physiol., 1934, 82, 62—74).—H₂O drinking lowers the blood-osmotic pressure (I), but any changes in the urine flow that follow are not dependent on the lowering of (I). The time of absorption of H₂O can be determined by observation of (I). A diet deficient in salts lowers (I) to a new level, without causing diuresis (II). Administration of salt to normal subjects raises (I); subsequent administration of H₂O causes (II), even if (I) has not been lowered to its normal val., showing that the onset of (II) is not dependent on the initial level of (I).

R. N. C.

Physiological importance of nickel and cobalt. G. BERTRAND and H. NAKAMURA (Ann. Inst. Pasteur,

1934, 53, 371—378).—The addition of small amounts of NiCl_2 and CoSO_4 to a diet of starch, lactose, caseinogen, and mineral salts (containing only traces of Ni and Co) increases the max. wt. attained and the survival period (the latter by approx. 17%) of mice.

F. O. H.

Iron metabolism of the growing organism. F. THOENES and R. ASCHAFFENBURG (Abh. Kinderheilk. Grenzgeb. No. 35, 1—103; Beih. Jahrb. Kinderheilk., 1934, 141; Chem. Zentr., 1934, i, 1668—1669).—A monograph on the Fe economy and the intermediate Fe metabolism in children, together with fresh investigations concerning normal and pathological vals. of serum-Fe, the effect of exogenous and endogenous Fe on serum-Fe, and the influence of bacterio-toxins.

L. S. T.

Iron and copper retention in young children. A. L. DANIELS and O. E. WRIGHT (J. Nutrition, 1934, 8, 125—133).—The Fe retention (I) ranged from 0.12 to 0.25 mg. per kg. and was met by rations containing 0.6% of Fe. Larger amounts of dietary Fe did not increase (I). Cu retention averaged 0.026 mg. per kg. Suitable diets should contain \leq 0.1 mg. Cu per kg. body-wt.

A. G. P.

Iron and copper metabolism in the developing chick embryo. W. D. MCFARLANE and H. I. MILNE (J. Biol. Chem., 1934, 107, 309—319).—Determinations of the daily changes in Fe and Cu contents of the livers (I) and of the body-tissue (II) of chick embryos indicate that although the abs. amount of Fe in the liver increases steadily up to hatching time, the % Fe and % Cu per unit dry tissue decreases in inverse ratio to the dry wt., although remaining const. in (II). 50—60% of the Fe in (I) before hatching is non-hæmatin-Fe.

A. E. O.

Analysis of oxidation and reduction of indicators in living cells. R. CHAMBERS (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 205—213).—Aerobic reducing intensities, which express an average of the relative velocities of the reducing and oxidising reactions within the cell, have been measured.

CH. ABS.

Reactions of oxidation-reduction indicators in biological material, and their interpretation. B. COHEN (Cold Spring Harbor Sympos. Quant. Biol., 1933, 1, 214—223).—The reducing intensity of sol. indicators injected into various plant and animal cells under aerobic and anaerobic conditions was approx. the same for the same indicators.

CH. ABS.

Determination of ethyl alcohol in brain. R. J. ABERNETHY, E. R. RUSSELL, and C. H. THIENES (J. Lab. Clin. Med., 1934, 19, 1014—1018).—Brain-tissue is distilled in steam, and the distillate oxidised with $\text{K}_2\text{Cr}_2\text{O}_7\text{--H}_2\text{SO}_4$. AcOH produced is separated by distillation and determined volumetrically. In very small samples the product of oxidation is treated with Ca(OH)_2 and distilled in steam a second time to prevent volatilisation of org. acids.

CH. ABS. (p)

[Effect of] nembutal (pentobarbital sodium). M. W. HEMINGWAY, J. VAN DE ERVE, and J. D. BOOTH (J. Lab. Clin. Med., 1934, 19, 738—742).—In nembutal anaesthesia (dogs) blood-sugar is slightly

raised, but -urea-N, -non-protein-N, and serum-protein are unaffected.

CH. ABS.

Diazo-reaction for detection of certain local anaesthetics in urine and tissues. W. E. GIBB and W. M. DEAN (J. Lab. Clin. Med., 1934, 19, 1018—1019).—Riegel and Williams' technique is applied to detect procaine and aminobenzoic acid derivatives.

CH. ABS. (p)

Effect of anaesthetics on the surface precipitation reaction. L. V. HEILBRUNN (Biol. Bull., 1934, 66, 264—275).—Anaesthetics, including Mg, inhibit the formation of a ppt. on the surface of extruded protoplasm of *Stentor* and *Arbacia* eggs.

CH. ABS. (p)

Retention of caffeine in the animal organism. A. KRUPSKI, A. KUNZ, and F. ALMASY (Biochem. Z., 1934, 273, 317—320).—The caffeine (I) content of guinea-pigs (II) which have received a single oral dose of (I) decreases in about 47 hr. to 0.1 of the amount administered, about 20% being excreted in urine and faeces and 70% degraded. After about 130 hr. (II) contain no more (I). In a goat, (I) orally administered became regularly distributed throughout the whole organism within 2 hr.

W. McC.

Pilocarpine and gastric anacidity in monkeys. J. H. FERGUSON, J. MCGAVRAN, and E. R. B. SMITH (J. Physiol., 1934, 82, 1—10).—Pilocarpine on injection into monkeys produces complete disappearance of free acid and a fall in total acidity of the gastric contents, without affecting total Cl' .

R. N. C.

Effect of morphine on secretory processes of the intestinal tract. M. M. GORBUNOVA-NIKOLAEVA (Arch. Sci. Biol. U.S.S.R., 1933, 33, 509—513).—Morphine abolished the stimulatory effects of Hg_2Cl_2 and HCl .

CH. ABS. (p)

Physiological action of *l*- and *d*-derivatives of morphine alkaloids. T. TAKEBE (Kitasato Arch. Exp. Med., 1934, 11, 48—63).—The action of various morphine derivatives depended on their configuration.

CH. ABS. (p)

Relation between liver-glycogen and liver function. T. IKUSHIMA (Japan. J. Gastroenterol., 1934, 6, 349—356).—Rabbit liver-glycogen (I) is reduced by strychnine, by phloridzin, or by hunger. Lowered (I) is probably unfavourable to excretion of dyes.

CH. ABS. (p)

Bile acids and carbohydrate metabolism. XXIX. Influence of cholic acid and spleen on the sugar excretion threshold. C. TATEISHI (J. Biochem. Japan, 1934, 19, 409—423).—Subcutaneous or oral administration of Na cholate to rabbits lowers the sugar excretion threshold to an extent \propto the dose. Splenectomy has a similar effect, subsequent administration of spleen extract or Na cholate causing a return to normal vals.

F. O. H.

Bile acids and carbohydrate metabolism. XXX. Influence of bile acids on glycogenesis from liver-fatty acids. I. OKII. XXXI. Liver-glycogenesis on administration of pituitary extracts and cholic acid. K. OHASHI (J. Biochem. Japan, 1934, 20, 37—42, 59—63).—XXX. Liver-glycogenesis (I) in rabbits due to oral administration

of stearic, palmitic, or oleic acid is enhanced by simultaneous administration of Na cholate (II).

XXXI. (I) due to intravenous injection of glucose is enhanced by subcutaneous injection of pituitrin and, to a greater extent, by that of pituitrin+ (II).

F. O. H.

Influence of bile acids on the digestion of nucleins. II. Hydrogen-ion and phosphate concentrations of intestinal juice. III. Sodium, potassium, calcium, and magnesium levels of intestinal juice. T. KURAMOTO (J. Biochem. Japan, 1934, 19, 425—436, 437—448; cf. A., 1932, 1287).—I. In dogs with duodenal fistulae, parenteral or, more especially, oral administration of Na cholate (I) increases the vol., sp. gr., p_H , and total and inorg. PO_4 levels of the intestinal secretion.

III. (I) increases the Na^+ , K^+ , and Mg^{++} levels of the intestinal juice; that of Ca^{++} is lowered. The action of (I) on the secretion of Na, K, Mg, and Ca into the intestine occurs after their absorption. The bearing of the data on nuclein catabolism is discussed.

F. O. H.

Influence of bile acids on urinary and gastric acidity. I. Urinary excretion of sodium chloride, sodium, and potassium. T. HASEGAWA (J. Biochem. Japan, 1934, 19, 403—407).—Intravenous injection of Na cholate into dogs diminishes the urinary excretion of NaCl and K^+ and increases that of Na^+ .

F. O. H.

Influence of bile acids on the synthesis of phenylsulphuric acid in the animal organism. I. OKI (J. Biochem. Japan, 1934, 20, 31—35).—Subcutaneous injection of PhOH into rabbits increases the urinary excretion of ethereal SO_4 , an effect enhanced by subcutaneous or oral administration of Na cholate. Hence bile acids increase the detoxifying action of the liver by increasing the glycogenesis.

F. O. H.

Pharmacology of tannic acid. I. Coagulant action on proteins of egg-albumin. U. SAMMARTINO (Arch. Farm. sperim., 1934, 58, 131—141).—The proteins are pptd. fractionally. Viscosimetry is recommended for demonstrating the physico-chemical modifications preceding and following the pptn. of natural proteins by drugs.

R. N. C.

Significance of phenol-indole metabolism. VI. Latent phenol-indole intoxication and adrenal hypertrophy. M. BIEBL (Z. ges. exp. Med., 1933, 91, 622—637; Chem. Zentr., 1934, i, 2941).—Rabbits fed for long periods with doses of PhOH or cresol developed a latent intoxication which was often followed by hypertrophy of the adrenal cortex, suggesting that this tissue acts as a detoxicator of phenol and indole derivatives.

R. N. C.

Action of dinitro-compounds on sea-urchin eggs. G. H. A. CLOWES and M. E. KRAHL (Science, 1934, 80, 384—385).—At 21° , optimum concns. of 4:6-dinitro-*o*-cresol stimulate O_2 consumption by 400% in fertilised, and by 600% in unfertilised, eggs of *Arbacia punctulata*. Cell division (I) is simultaneously suppressed. KCN antagonises the stimulation of respiration (II), but supplements suppression of (I). The NO_2 -substituted mol. is responsible for suppression of (I), and the optimum concn. for (II)

is a crit. concn. for (I). In the case of NO_2 -compounds (I) and (II) decrease with a decrease in ability to penetrate the cell.

L. S. T.

Pharmacodynamic action of nitrophenols. An agent accelerating cell oxidation: 2:4-dinitrophenol (Thermol). I. General effect of 2:4-dinitrophenol poisoning. II. Effects of 2:4-dinitrophenol poisoning on the principal processes of nutrition. Effect on carbohydrate status. III. The non-lethal dose, chronic poisoning and tolerance. H. MAGNE, A. MAYER, and L. PLANTEFOL. IV. Analytical data of dinitrophenol and derivatives. Detection of these substances in urine, organs, and blood. M. GUERBET. V. Presence of dinitrophenol and derivatives in organs and body fluids during poisoning. Elimination in urine. M. GUERBET and A. MAYER. VI. Glycuronic acid content of urine after injection of 2:4-dinitrophenol. J. GEORGESCU. VII. Action of 2:4-dinitrophenol on cell respiration and plant tissues. L. PLANTEFOL. VIII. Pharmacological action of various nitrophenols. Comparison of 2:4-nitrophenol with other nitrophenols. H. MAGNE, A. MAYER, and L. PLANTEFOL. IX. Action of nitrophenols on haemoglobin. A. MAYER and F. VLES (Ann. Physiol. Physicochim. Biol., 1932, 8, 1—50, 51—69, 70—91, 92—116, 117—121, 122—126, 127—156, 157—175, 176—194; Chem. Zentr., 1934, i, 2614—2615).—I. In all conditions examined poisoning was accompanied by rise in temp. and a marked increase in O_2 consumption.

II. Glycogen in liver and muscle is increased and changes in N elimination indicate protein decomp.

III. Solubility data, reactions, and analysis of 2:4-dinitro- (I), 4-nitro-2-amino- (II), 2-nitro-4-amino- (III), 2:4-diamino-phenol, picric (IV) and picramic acid (V) are given.

V. (I) and (IV) are reduced within the organism. Products include (II), (III), and (V) probably combined with glycuronic acid (VI) or as nitro-uramidophenols.

VI. Urinary (VI) increases.

VII. (I) is more toxic to *Aspergillus niger* than are tri- or mono-nitrophenols. Toxicity of the latter is in the order $o < m < p$.

VIII. Toxicity to higher animals is in the order $p > m > o$ -nitrophenol and among dinitrophenols, 2:4-, 2:5-, and 2:6- $>$ 3:5-, 3:4-, and 3:2-.

IX. Effects of mono-, di-, and amino-nitrophenols are compared.

A. G. P.

Effect of histamine on jejunal secretion. A. L. BERNDT and I. S. RAVDIN (Amer. J. Physiol., 1934, 109, 587—591).—Injection of histamine diphosphate produced a temporary increase in the rate of secretion of juice from an isolated jejunal loop. There was no apparent effect on the production of enzymes by the loop.

R. N. C.

Protein therapy and glycæmia. R. V. ULLOA and C. M. DOMINGO (Kitasato Arch. Exp. Med., 1934, 11, 78—86).—Injection of caseinogen caused, in nearly all cases, an immediate hyperglycæmia, followed by hypoglycæmia within 30 min.

CH. ABS. (p)

Physiological effect of the active principles of *Solanum tuberosum* on the larvæ of *Leptinotarsa decemlineata*. B. TROUVELOT, M. RAUCOURT, and J. CASTETS (Compt. rend., 1934, **199**, 684—686).—When the active extract is offered simultaneously with other nutriment, the extent to which each is attacked by the larvæ is a function not only of its concn. and intrinsic activity, but also of the activities of the other nutriment. A. E. O.

Yew poisoning in domestic animals. J. A. NICHOLSON (Rep. Cambridge Inst. Animal Path., 1932—1933, 169—199).—Taxine (I) contents of fresh female leaves are: *T. baccata* var. *fructu luteo* 0.24, *T. canadensis* 0.12, *T. cuspidata* 0.22, *T. baccata* var. *barroni* (young) 0.29, (old) 0.33%. The prep. of (I) is described, and m.l.d. recorded. Aq. (I) hydrochloride is rendered non-toxic by heating for 1 hr. at 60° or 10 min. at 100°. (I) (1 : 100) does not affect the digestion of fibrin by pepsin. CH. ABS.

Histological changes in the bone marrow of the dog following amidopyrine administration. D. K. MILLER (Science, 1934, **80**, 320).—Oral administration of amidopyrine to dogs exerts a toxic effect on bone marrow, with little or no evidence of the effect in the circulating granular elements of the blood. L. S. T.

Ascaricidal action of sodium santoninate in oral and subcutaneous administrations. R. E. S. SCHULTZ and K. I. ABULADZE (Khim. Farm. Prom., 1934, No. 2, 21—26).—Na santoninate is no less efficient than santonin. CH. ABS. (p)

Irritant constituent of anti-leprotic oils. H. PAGET, J. W. TREVAN, and A. M. P. ATTWOOD (Int. J. Leprosy, 1934, **2**, 149—158).—Fractionation of the acids of sapucainha oil yields chaulmoogric (I), hydnocarpic (II), and palmitic acids, two fractions containing unsaturated and keto-acids, respectively, and a fraction (III) of tarry acids giving Cu salts insol. in COMe_2 and Et_2O . (III) is highly irritating, and may be identical with the irritating substance derived from (I) and (II) on exposure to light and air. W. O. K.

Lipæmia caused by absorption of products of intestinal putrefaction of proteins and effects thereon of hormones. I. Influence of thyroid gland. II. Effect of adrenaline. M. MITANI (Folia Endocrinol. Japan, 1932, **8**, 47—48).—I. Administration of tyramine (III), indole, PhOH , NaOBz , or histamine results in increased fat (II) and lipin (I) (notably cholesterol) contents of blood. If thyroid powder is also given, these changes are restricted. In thyroidectomised animals administration of the above increases total fatty acids, but not (I).

II. Injection of adrenaline (IV) causes a temporary increase in (I) and (II). Lipæmia caused by (III) is increased by (IV). Prolonged administration of (IV) reduces blood-(I) and -(II) and also checks (III)-lipæmia. CH. ABS. (p)

Influence of monobromoacetic and hydrocyanic acids on ciliary and vibratory motion. E. WERTHEIMER (Pflüger's Archiv, 1933, **231**, 155—168).— $\text{CH}_2\text{Br}\cdot\text{CO}_2\text{H}$ (I) inhibits the motion of muscle, heart-auricle, -ventricle, vibratory epithelium of

tracheal mucosa, and also the isolated spermatozoa (II) of guinea-pigs. Halogen derivatives of homologues of AcOH are without effect. The effect of (I) is inhibited by lactic (III) and pyruvic acid (IV), but not by AcCHO (V), dihydroxyacetone (VI), or the Robison (VII) and Neuberg hexose monophosphoric ester (VIII). The motion of (II) is inhibited irreversibly by 0.001*N*- NaCN . *Paramecia* are not affected by (I) or NaCN , or the two together. Glucose in concn. 0.00025% is antagonistic to NaCN in its action on (II), fructose in higher concns., galactose still higher, whilst (III), (IV), (V), (VI), (VII), (VIII), arabinose, and glucosamine are practically without effect. R. N. C.

Physiological and thermal investigations on taste-affectors. S. MICHAEL and G. LIMMER (Pflüger's Archiv, 1933, **233**, 645—651).—An apparatus is described which imitates and measures the thermal effects of taste-affectors (I) on the tongue, and can be used to correlate these with their thermal data. The gradation of their temp. effects on the tongue is the same as that of their effects in solution in the apparatus. The temp. effects of all (I) on their heats of dissolution in the same vol. of H_2O . R. N. C.

Diffusion rates of anions and urea through tissues. E. J. CONWAY and F. KANE (Biochem. J., 1934, **28**, 1769—1783).—The diffusion coeff. (I) of $\text{SO}_4^{''}$, Cl' , $\text{PO}_4^{'''}$, and lactate through frog's sartorius is $6.0 + 1.5 \times 10^{-5}$ sq. cm. per min. The vals. for muscle, liver, and kidney for $\text{SO}_4^{''}$ are the same. The ratios of the equilibrium concn. in isolated muscle to the external concn. are 0.30, 0.25, and 0.29 for Cl' , $\text{SO}_4^{''}$, and $\text{PO}_4^{'''}$, respectively. (I) for urea through muscle or kidney is 1.1×10^{-5} . Urea in freshly excised kidney, blood, and sartorius is 85, 45, and 41 mg. per 100 g., respectively. H. G. R.

Ion effects on ion permeability of *Fundulus* chorion. M. SUMWALT (Biol. Bull., 1933, **64**, 114—123). CH. ABS.

Biological significance of certain ions. VII. Production of ammonia in nerve tissue with various stimulations as a general law. V. V. PRAVDICH-NEMINSKIĬ (Arch. Sci. Biol. U.S.S.R., 1933, **33**, 121—144).—Changes in NH_3 content following stimulation by electric currents, osmotic effects, chemicals, and temp. are examined. CH. ABS. (p)

Effect of hypertonic solutions on tissue respiration. II. Sodium salts of univalent anions. B. KIRSCH (Biochem. Z., 1934, **273**, 324—337; cf. this vol., 918).—The restriction of respiration of tissues (I) at p_H 7.4 by 0.2*M* solutions of NaF , NaCl , NaBr , NaI , NaNO_3 , and NaCNS varies in a manner similar to that described for the cations, the effect of NaF being particularly strong. The extent to which (I) are supplied with nutrient material also affects the results. W. McC.

Effect of calcium lack on tissue respiration. B. KIRSCH (Biochem. Z., 1934, **273**, 338—344).—Lack of Ca causes restriction of respiration in some tissues, but increase in others, and results also vary according to the kind of nourishment supplied. W. McC.

Effect of fluoride on tissue respiration. B. KISCH (Biochem. Z., 1934, 273, 345—348).—The powerful inhibitory effect of 0.2*N*-NaF on tissue (rat kidney) respiration (I) is counteracted by addition of Ca salts (II) or by removal of NaF even in absence of (II). At least part of the Ca compounds (III) of tissue cannot be pptd. as CaF₂. Very dil. (0.002—0.00143*N*) aq. NaF stimulates (I). (I), which is increased by addition of lactate (IV), is inhibited by NaF despite simultaneous addition of (IV). The action of NaF is partly due to its action on (III) and partly sp. W. McC.

Influence of neutral sodium salt solutions on chemical stimulation. I. CHAO (Amer. J. Physiol., 1934, 109, 550—560).—The relative effectiveness of isotonic solutions of Na salts in sensitising curarised frogs' sartorii to chemical stimulation follows the order of the Hofmeister series for anions. The increased sensitivity is a direct function of the concn. of the salt, the min. concn. necessary to produce a given increase depending on its position in the series. The change of irritability increases rapidly with the duration of immersion in the solution, the rapidity in reaching the max. response depending also on the position of the salt in the series. The effect of any given Na salt is antagonised by HCl and alkaline-earth chlorides, the antagonising effects increasing in the order SrCl₂ < MgCl₂, CaCl₂ < HCl. The min. concn. of any of the salts required depends also on the position of the Na salt in the series. Skeletal muscle is more susceptible to chemical stimulation at low temp., and the sensitising action of every Na salt except NaCl shows a negative temp. coeff. The stimulating solution (0.005*N*-KCl in isotonic NaCl solution) exerts a double stimulation—a primary stimulation followed by inhibition due to K⁺, and a secondary stimulation due to exchange of anions. R. N. C.

Cold stimulation and influence of neutral sodium salts on cold stimulation. I. CHAO (Amer. J. Physiol., 1934, 109, 561—568).—Frogs' muscles sensitised in isotonic solutions of Na salts are stimulated by sudden exposure to lower temp. The contraction depends on the fall in temp., the initial temp., the concn. of the Na salt, and the duration of immersion in the sensitising solution. The relative effectiveness of Na salts on cold stimulation increases in the order of the Hofmeister series. CaCl₂ antagonises their action, but produces contraction if used as the cold solution. R. N. C.

Physiological effects of high altitudes. K. M. BUIKOV and E. E. MARTINSON (Arch. Sci. Biol. U.S.S.R., 1933, 33, 147—187).—Hyperventilation lowers the CO₂ tension and alkali reserve in the blood, and is followed by an increase of urinary Cl⁻, and, to a smaller extent, of bases. The org. acids excreted are unchanged. CH. ABS.

Action of poisonous gases on the liver and kidney function. M. YAGATA (Japan. J. Gastroenterol., 1934, 6, 280—314).—Excretion through kidneys (I) and liver (II) of rabbits of phenolsulphonephthalein, azocochineal, azorubin-S, and eosin-A is decreased by inhalation of CO. HCN and Cl₂ act more

strongly on (I) than on (II). COCl₂ destroys (I) function in dye excretion. CH. ABS. (p)

Lead poisoning. Detection in the ash of the corpse. H. JESSER (Suddeut. Apoth.-Ztg., 1934, 74, 65—66; Chem. Zentr., 1934, i, 2628).—The ash is treated with dil. HCl, 30 c.c. of 0.5% aq. CuSO₄ are added, and H₂S is passed to ppt. Pb and Cu. Pb is then determined as PbSO₄ or by electroanalysis as PbO₂. H. J. E.

Rôle of lead poisoning in the etiology of gastric ulcer. Effect of lead poisoning on the external secretion of the pancreas. S. D. REISELMAN (Arch. Sci. Biol. U.S.S.R., 1933, 33, 221—234).—Administration of Pb(OAc)₂ to dogs with a pancreatic fistula disturbed the parallelism of amylase, lipase, and trypsin. CH. ABS. (p).

Effect on the iodine content of the thyroid glands and blood of wethers and ewes when dosed with potassium iodide. M. C. FRANKLIN (Rep. Cambridge Inst. Animal Path., 1931, 134—142).—Weekly administration of KI (40 mg. per day) increased blood-I from 0.0008—0.0040 to 0.0480—0.0800 mg. per 100 c.c.; thyroid-I increased from 0.144—0.224 to 0.212—0.355%. CH. ABS.

[Physiological] action of alkali iodides. J. J. WESTRA (Amer. J. Physiol., 1934, 109, 450—456). R. N. C.

Effect of potassium cyanide poisoning on the respiration of tissues, especially the influence of different hormones on the action of potassium cyanide. I. Effect of insulin, thyroid substance, and adrenaline. II. Effect of genital glands. III. Effect of extract of adrenal cortex and of thyroidectomy. K. MIZUTANI (Folia Endocrinol. Japan, 1932, 8, 33—3, 636—37, 42—43).—Injection of KCN in rats increased the O₂ consumption of heart muscle and decreased this in liver (I), kidney, and skeletal muscle, thyroid (II), and spleen (III). The respiratory disturbance was reduced by simultaneous injection of insulin or of extracts of adrenal cortex [except in (II)] or corpus luteum and was increased by thyroidectomy [except in (III)] and by simultaneous injection of adrenaline or of extracts of testicles or of thyroid [except in (I)]. CH. ABS. (p).

Effect of injection of potassium cyanide on the oxygen dissociation curve of blood, especially with respect to the effect of the cyanide on the activity of various hormones. I. Effect of injection of small doses of insulin and of insulin and glucose. II. In relation to the thyroid gland. III. Effect of genital glands on the action of potassium cyanide. IV. Effect of adrenal cortex and adrenaline on the action of potassium cyanide. V. Effect of castration. VI. Effect of extirpation of spleen. T. FUKUI (Folia Endocrinol. Japan, 1933, 8, 94—96).—I. The lowering of the O₂-dissociation curve (*D*) following injection of aq. KCN is checked by previous injection of glucose and still more by insulin.

II, III. Large doses of thyroid gland or of extracts of genital glands increased, and smaller doses decreased, the fall in *D* following KCN injection.

IV. Single administrations of extract of adrenal cortex with aq. KCN reduced the decline in *D* produced by the latter. Repeated injection or oral administration had the reverse effect. The action of adrenaline was similar.

V. The action of KCN is increased.

VI. The decline in *D* is < normal. CH. ABS. (p)

Methæmoglobin and methylene-blue as cyanide antagonists. O. M. SOLANDT, D. V. SOLANDT, E. ROSS, and R. W. GERARD (Proc. Soc. Exp. Biol. Med., 1934, 31, 539—541).—For *Venus mercenaria* methylene-blue acts as substitute for a cyanide-poisoned respiratory catalyst. Addition of sufficient methæmoglobin reverses CN' inhibition.

CH. ABS.

Mechanism of the antidotal action of methylene-blue in cyanide poisoning. W. B. WENDEL (Science, 1934, 80, 381—382).—Mainly critical (cf. this vol., 912). It is probable that the binding of cyanide by methæmoglobin accounts for most of the action of the dye.

L. S. T.

Pharmacology of the rare earths. I. Anti-emetic effect. II. Hæmolytic action and simultaneous protective action of some members of the group. III. Preparation of rare-earth calcium gluconates. P. M. NICCOLINI (Boll. Soc. ital. Biol. sperim., 1931, 6, 202—204, 204—206; 1932, 7, 14—17).—I. Subcutaneous injection of SmCl_3 in the dog produced protection against the emetic action of apomorphine. Oral administration of SmCl_3 retarded the vomiting and rendered it incomplete, but did not prevent it. Injection of $\text{Nd}_2(\text{SO}_4)_3$ also retarded vomiting.

II. Red corpuscles were suspended for variable periods in isotonic solutions of PrCl_3 , NdCl_3 , and SmCl_3 , and then transferred to solutions of concns. 0.1—0.9%. Partial hæmolysis occurred in all solutions, but it was not complete even in distilled H_2O .

III. Nd and Sm form double gluconates with Ca, which are prepared by treating a solution containing 3.1738% Ba gluconate and 0.742% Ca gluconate with a saturated solution of $\text{Nd}_2(\text{SO}_4)_3$ and $\text{Sm}_2(\text{SO}_4)_3$, respectively, until the Ba is pptd. The resultant solutions contain 2% of the rare-earth gluconate and 1.53% of Ca gluconate, and have p_H and mol. concns. similar to those of plasma. The presence of Ca has no effect on the physiological action.

R. N. C.

Chemical changes accompanying the reabsorption of irradiated tissue. J. LOISELEUR (Compt. rend., 1934, 199, 686—688).—During the reabsorption of irradiated thymus (I), PO_4''' is liberated (from tissue-nucleins) and the Cl' content of the cellular residues from (I) increases. In the blood, the alkaline reserve and p_H both increase, and the urea content of erythrocytes diminishes while their Cl' content increases. The PO_4''' and Cl' contents of the urine show a considerable increase and decrease, respectively.

A. E. O.

Ultra-violet light and blood-iodine. Bioclimatology. C. BENNHOLDT-THOMSEN and M. WELLMANN (Klin. Woch., 1934, 13, 800—803).—One group of male white rats, kept in complete darkness for 4 months on a diet of bread and skim milk, was

irradiated with a quartz lamp for 15 min. and another group was given 0.05 ml. of vigantol daily. The thyroids of untreated rats contained less colloid and were more active than those of the treated groups and the average I content was 211×10^{-6} g. per 100 mg. of dry substance as compared with 167 for the vigantol and 112 for the irradiated rats. Blood-I varied inversely with thyroid-I, the vals. being 40.5, 31.0, and 25.2×10^{-6} g. per 100 ml.

NUTR. ABS. (b)

Concentration of eosin and the photodynamic effect on tentacles of a terebellid worm. J. H. WELSH (Biol. Bull., 1934, 66, 346—350).—Stimulation of tentacles of *Terebella magnifica* in sea- H_2O by light was increased by the presence of eosin. The survival period was shortened.

CH. ABS. (p)

Influence of α -, β -, and γ -rays of radium on the aerobic respiration of animal organisms. J. STOKLASA (Strahlenther., 43, 685—700; Chem. Zentr., 1934, i, 2305).—The intensity of respiration of both fish and guinea-pigs is raised considerably by α -rays (I), slightly by γ -rays (II); it is lowered by β -rays (III) and (II) together, as is also that of plants. (II) lower CO_2 -production in plants, but raise it in animals. (I), (II), and (III) over long periods depress anaerobic respiration and lactic acid increases in the lungs, and inhibit the other respiratory enzymes.

R. N. C.

Reversible dehydrogenase systems. III. Carrier-linked reactions between isolated dehydrogenases. D. E. GREEN, L. H. STICKLAND, and H. L. A. TARR (Biochem. J., 1934, 28, 1812—1824).—Purified dehydrogenases isolated from cells together with the appropriate substrate (e.g., formic dehydrogenase+formate) do not react with positive enzyme systems (I) (e.g., nitrates+nitrate) except in the presence of an added indicator (II) of suitable potential. (II) functions even at dilutions at which its colour cannot be detected, is continuously reduced by the negative and re-oxidised by the positive (I), and is most efficient as a catalyst in (I) in which it is reduced and re-oxidised at comparable rates. The reaction between formate and nitrate, linked by Nile-blue, proceeds linearly. An acidic (II), being reduced much more slowly than a basic (II), is a less efficient H carrier. The kinetics of such linked reactions is discussed. None of the known natural hydrogen carriers, e.g., glutathione, ascorbic acid, cytochrome, lactoflavin, with the single exception of pyocyanine, is effective as a link in any of the (I) studied, and attempts to extract natural carriers from cells failed. Considerations of potential show that intact cells of *B. coli* must contain at least two such carriers, since they catalyse the reaction succinate-nitrate as well as H_2 -pyruvate.

A. E. O.

Biological reduction. V. Specificity of lactic acid dehydrogenase. I. YAMAMOTO (J. Biochem. Japan, 1934, 20, 23—30).—The lactic acid (I) dehydrogenase system of washed pig's heart muscle and co-enzyme (A., 1932, 537) rapidly oxidises (dehydrogenates) α -OH-acids, e.g., malic (II), tartaric (III), hydroxyglutaric, fumaric (IV), maleic (V), citric, etc. With (I), the *d*- but not the *l*-isomeride is oxidised, the reverse being true for (III); both forms of (II) are oxidised. (IV) and (V) are equally good H₂-donators,

the presence of co-enzyme being dispensable only with the latter. Et lactate is unaffected. F. O. H.

Cozymase and the dehydrogenating enzyme system in milk. B. ANDERSSON (Arkiv Kemi, Min., Geol., 1934, 11, A, No. 17, 9 pp.).—Cozymase (I) does not promote the dehydrogenation of xanthine, and it inhibits the dehydrogenation of MeCHO. Decomposition products of (I), such as adenylyl pyrophosphate, muscle-adenylic acid, and adenosine, do not act as inhibitors. Heat and alkali [which deactivate the promoting power of (I) for fermentation] increase its inhibiting power for dehydrogenation. R. P. B.

Relation of iron and copper to cytochrome and oxidase content of animal tissues. E. COHEN and C. A. ELVEHJEM (J. Biol. Chem., 1934, 107, 97—105).—Cytochrome (I) is determined spectroscopically after reduction of the tissue with NaHSO_3 ; haemoglobin (II) is converted into methaemoglobin by treatment with $\text{K}_3\text{Fe}(\text{CN})_6$ after poisoning the oxidase (III) with KCN. CO or KCN intensifies the band of the A component (IV) of (I). The heart, brain, and liver of rats contained all four bands of (I), whilst in the medulla of the adrenals the C component was in high concentration and A and B were absent. (IV) is absent from the hearts of severely anæmic rats (V). (V), fed with Fe and Cu for 6 weeks, have normal (I) spectra. In (V) given Cu alone the (IV)-band appeared earlier, but B and C were reduced. (III) tests by the "Nadi" reagent (Keilin, A., 1929, 470) were feeble in the livers of rats fed on milk alone or milk supplemented with Fe. With Cu and Cu+Fe good (III) tests were obtained. The (III) test is independent of the (II) response, but directly dependent on the level of Cu intake; a close relationship exists between (III) and (IV). A very active reducing system is present in the livers of (V) fed on milk alone or milk and Fe.

H. D.

Spectroscopic examination of cytochrome preparations. Absorption bands in the red. E. J. BIGWOOD, J. THOMAS, and D. WOLFERS (Compt. rend. Soc. Biol., 1934, 117, 220—222).—The two absorption bands, given by yeast cytochrome (I) preps. in alkaline solution, and situated at 675 and 640—645 μ , are unaffected by oxidation and reduction of (I). The red fluorescence of (I) preps. is not due to a free porphyrin, either originally present in the yeast, or formed during the concentration of (I).

A. L.

Oxidation of cytochrome-c. E. J. BIGWOOD, J. THOMAS, and D. WOLFERS (Compt. rend. Soc. Biol., 1934, 117, 222—224).—KCN has no action on the rate of reoxidation by O_2 of aq. solutions of cytochrome reduced by evacuation, although the presence of indophenol-oxidase increases the rate. A. L.

Distribution of peroxidase in animal tissues. G. BANCROFT and K. A. C. ELLIOTT (Biochem. J., 1934, 28, 1911—1919).—Neither alkaline phosphate nor 50% glycerol solution removes peroxidase (I) completely from tissue, and attempts to remove catalase (II) without affecting (I) failed. The method of Willstätter and Stoll (A., 1918, i, 555) for the determination of (I) was modified so that (I) and (II) could be determined separately. Spleen and lung tissues show true (I)-activity; liver and kidney show

slight (I)-activity probably due to haemoglobin (III) and removable by perfusion; most other tissues contain no (I). Among haematin derivatives, only the $\text{C}_5\text{H}_5\text{N}$ - and nicotine-haemochromogen have (I)-activities > those of (III) derivatives. A. E. O.

Catalase determination in faeces, urine, and gastric juice. J. KRETZ and A. F. PELLEGRINI (Wien. klin. Woch., 1934, 47, 388—391; Chem. Zentr., 1934, i, 3093).—The catalase reaction (I) does not give the same indications as the guaiacum or the benzidine reaction. The latter is invariably positive where blood-pigment or Fe-containing derivatives occur (cooked meat, absorbed blood, etc.) in which cases (I) is negative. A. G. P.

Influence of reductone and thiol compounds on catalase. H. VON EULER and H. LARSSON (Arkiv Kemi, Min., Geol., 1934, 11, A, No. 13, 7 pp.).—Glutathione increases the reaction coefficient of barley catalase (I)- H_2O_2 systems, probably due to combination with the small amount of destructive metals in the enzyme prep. Ascorbic acid and reductone (A., 1933, 937) destroy (I), whilst cysteine activates or protects (I) from inactivation. Liver-(I) resembles barley-(I).

F. O. H.

Immunological action of tyrosinase from mealworms. W. L. DULIERE and M. C. ADANT (Biochem. J., 1934, 28, 1659—1664).—Injection of an active tyrosinase prep. (I) into rabbits yields a serum which inhibits an active (I), but reactivates a feebly active (I). A serum prepared against the latter has no effect on an active (I), but reactivates a feebly active (I). It is suggested that two antibodies are formed, sp. to the enzyme and to an antagonistic factor in (I), respectively. A. E. O.

Inhibition of the "dopa reaction" by vitamin-C. H. SCHROEDER (Klin. Woch., 1934, 13, 553—554; Chem. Zentr., 1934, i, 3488).—Frozen sections of human skin or that of guinea-pig's ear were treated with a 1% solution of "dopa" (3:4-dihydroxy-phenylalanine) (I). The development of the brown coloration in the cells was hindered by addition of 1 pt. of ascorbic acid (II) per 100 pts. of (I). Inhibition of oxidation of adrenaline by (II) was also observed.

R. N. C.

Carboxylase. II. W. LANGENBECK, H. WREDE, and W. SCHLOCKERMANN (Z. physiol. Chem., 1934, 227, 263—276; cf. this vol., 110).—Acetoin was determined in presence of MeCHO as Ni dimethylglyoxime by evaporating the oxime-dioxime mixture in presence of NiSO_4 , since acetaldoxime, which interferes, is readily volatile. The "carbolicase quotient," C.Q. (mols. of acetoin/mols. of CO_2), increases with increasing MeCHO and decreases with increasing AcCO_2H . The enzymic nature of acyloin formation is confirmed. The identity of carbolicase and carboxylase is probable, since in a no. of purified enzyme preps. the two effects could not be separated.

J. H. B.

Emulsin in certain marine invertebrates and micro-organisms. D. L. FOX (Biochem. J., 1934, 28, 1674—1677).—The California mussel (*Mytilus californianus*) (I) excretes an emulsin (II) independently of the presence of micro-organisms (III).

PhMe-preserved extracts of the viscera or cryst. style of (I) also contain (II). Many marine moulds, yeasts, actinomyces, and bacteria produce HCN from nutritive media containing amygdalin (IV), usually after a long period of incubation, but cultures killed by PhMe or CHCl_3 are inactive. No (IV) has so far been detected in any marine plant, including (III).

A. E. O.

Action of emulsin. II. S. VEIBEL (Biochem. J., 1934, 28, 1733—1745).—For *d*- and *l*- α -methylamyl- β -*d*-glucoside, $k_d = 1.75 \times 10^{-2}$ and $k_l = 0.51 \times 10^{-2}$, respectively. The equilibrium is at approx. 95% hydrolysis. For the γ -methylamyl- β -*d*-glucosides the vals. are 0.16×10^{-2} , 0.15×10^{-2} , and 96%, respectively.

C. G. A.

Emulsin. XVI. Fission of β -*d*-xylosides by almond emulsin. B. HELFERICH and U. LAMPERT (Ber., 1934, 67, [B], 1667—1669).—*o*-Cresol- β -*d*-xyloside, m.p. 161—162.5° after softening at 159°, $[\alpha]_D^{25}$ —51.7° in H_2O (obtained by the action of NaOMe in MeOH on *o*-cresol- β -*d*-xyloside triacetate, m.p. 116.5° (corr.), $[\alpha]_D^{25}$ —52.3° in CHCl_3 , prep. from β -*d*-xylose-tetra-acetate, *o*- $\text{C}_6\text{H}_4\text{MeOH}$ and *p*- $\text{C}_6\text{H}_4\text{MeSO}_3\text{H}$ at 100°), is readily hydrolysed by emulsin from sweet almonds. The increased ease of fission, in comparison with phenol- β -*d*-xyloside, is the same as for the glucosides within the experimental limits. Parallelism exists between ease of hydrolysis and purity of enzyme prep. in the case of β -*d*-xylosides and β -*d*-glucosides. Hence there is no reason to assume that different enzymes are involved in the respective hydrolyses.

H. W.

Diastase in blood. G. KATSCH (Münch. med. Woch., 1934, 81, 505—507; Chem. Zentr., 1934, i, 3092—3093).—Diastatic activity of blood as determined by hydrolysis of glycogen (Otterstein) is either abnormally high or very much depressed in pathological cases.

A. G. P.

Chemistry of enzymes of cereals. I. Starch-liquefying enzyme in rice. II. Starch-liquefying enzyme in polished rice. G. YAMAGISHI (J. Agric. Chem. Soc. Japan, 1934, 10, 496—501, 502—509).—I. The enzyme in aq. extracts of unhulled and unpolished rice showed optimum activity at p_H 4.1—4.3 and 36—42°. It was absent from polished rice (P).

II. The aq. extract of a mixture of P and papain liquefies starch. Zymogen may occur in P.

CH. ABS. (p)

Effect of temperature on the digestion of starch by amylase. S. TRAUTMANN and L. AMBARD (Ann. Physiol. Physicochim. Biol., 1933, 9, 707—712; Chem. Zentr., 1934, i, 3353).—The increase in the rate of starch hydrolysis with rising temp. is related to changes in the concn. of co-enzyme (I) (H^+ or Cl^-). The increased rate per 10° (Q_{10}) is small (1.02) for the transition of (I), considerable (2.2) for the amylolytic action.

A. G. P.

Influence of temperature on amylases of cold- and warm-blooded animals. L. C. CHESLEY (Biol. Bull., 1934, 66, 330—338).—The time of inactivation (I) with rising temp. was in the order fish > terrapin > human amylases. (I) probably results from protein coagulation.

CH. ABS. (p)

Content of amylase in the organs of fed and starving animals. W. SEYFARTH (Arch. exp. Path. Pharm., 1934, 176, 745—750).—Of the liver (I), kidney (II), and heart (III) of normal rats, (II) has the highest content (per g.) of amylase (IV). Starvation diminishes the (IV) content of (II) and (III), whilst an exclusively fat diet does not influence that of (I), (II), or (III). Phloridzin poisoning lowers the (IV) level of (II) and, when the fat content is high, of (I) and (III). (I), (II), and (III) in the same rat have a parallel content (i.e., high or low) of (IV).

F. O. H.

Preparation of highly active yeast invertase. J. G. LUTZ and J. M. NELSON (J. Biol. Chem., 1934, 107, 169—177).—A highly active prep. (time val. 0.102 min.), sol. in saturated $(\text{NH}_4)_2\text{SO}_4$, was obtained by adsorption on kaolin and $\text{Al}(\text{OH})_3$.

H. G. R.

Determination of the activity of commercial invertase. C. E. PRÉLAT (Anal. Assoc. Quim. Argentina, 1934, 22, 73—75).—The method of Gore is recommended.

R. N. C.

Role of active acidity of the medium in the enzymic inversion of sucrose. S. M. KOBRIN (J. Gen. Chem. Russ., 1934, 4, 477—486).—The $[\text{H}^+]$ remains const. during the enzymic hydrolysis of sucrose, pointing either to non-participation of H^+ in the enzyme-substrate complex, or to the very low concn. of the latter.

R. T.

Effect of very high pressures on enzymes. M. MACHEBOEUF, J. BASSET, and G. LEVY (Ann. Physiol. Physicochim. Biol., 1933, 9, 713—722; Chem. Zentr., 1934, i, 3352).—Pressures of 5000—6000 atm. did not affect enzymic activity. Partial inhibition occurred in some cases with 9000 atm., the effect being influenced by external conditions (e.g., p_H), but not by the rate at which pressure was raised or lowered. Pressure-resistance of enzymes is > that of ultravirus or bacteriophage, but < that of bacterial spores.

A. G. P.

Osmotic pressure and rate of enzymic reactions. S. MARDASHEV and M. MOGILEVSKI (Biochem. Z., 1934, 273, 430—434).—Rate of fermentation (arginine by arginase, sucrose by invertase) markedly although not proportionally decreases as the (potential) osmotic pressure of the solution is increased by increasing the concn. of electrolytes (KCl , KNO_3 , NaCl , NaNO_3) or non-electrolytes (urea). There may also be sp. ionic effects.

W. McC.

Fate of enzymes in the digestive tract. W. HEUPKE and H. WIRTZ (Klin. Woch., 1933, 12, 1866—1867; Chem. Zentr., 1934, i, 2297).—Myrosin, emulsin, urease, and catalase remain active in the large intestine, but zymase and peroxidase are destroyed.

A. G. P.

Activation of enzymes. II. Papain activity as influenced by oxidation-reduction and by the action of metal compounds. L. HELLERMAN and M. E. PERKINS (J. Biol. Chem., 1934, 107, 241—255).—Papain (I) is reversibly inactivated by catalysed (Cu^{++} or Fe^{++}) oxygenation, I, benzoquinone, and $\text{Fe}(\text{CN})_6^{3-}$, activity being restored by many reducing substances. Cu_2O and mercurials of the type RHgX (which give mercaptides) completely inactivate (I), elimination of the metal restoring activity, suggest-

ing that this depends on the presence of free $\cdot\text{SH}$ in (I). C. G. A.

Inhibitors of milk-curdling enzymes. H. TAUBER (J. Biol. Chem., 1934, **107**, 161—168).—Urease inhibits the milk-coagulating power of pepsin (I) and trypsin (II), but not the protease activity of (II). Rennin (III) and (I) are distinct entities, and there is no (III) in the stomach of adult mammals. Gastric proteases of animals differ with the species.

H. G. R.

Pepsin and rennin activity of preparations from dried stomach substance from the cardia, fundus, and pyloric regions of pig's stomach. E. MEULENGRACHT and E. SCHIÖDT (Ugeskr. Laeger, 1934, **96**, 187—190; Acta Med. Scand., 1934, **82**, 375—383).—Pepsin and rennin activity is greatest in preps. from the fundus. The location of the anti-anæmic substance is different from that of pepsin. These substances are therefore physiologically and anatomically separated in the mucous membrane of the stomach.

NUTR. ABS. (m)

Biochemical micro-methods. IV. Nephelometric determination of pepsin. B. J. KRIJGSMAN (Z. physiol. Chem., 1934, **227**, 251—262; cf. this vol., 337).—Nephelometric determination of the residual (protein) substrate is recommended for following enzymic hydrolysis and is applied to the fission of serum-proteins, edestin, and caseinogen by pepsin.

J. H. B.

Rate of liberation of amino-acids and ammonia in tryptic hydrolysis. T. TOMIYAMA and S. SHIGEMATSU (J. Biochem. Japan, 1934, **20**, 131—140).—The rates of liberation of NH_2 - and NH_3 -N on digestion of the proteins of sardine muscle (I), silk-worm pupæ, and soya bean (II) by trypsin+enterokinase do not conform with a unimol. reaction: that of NH_2 -N (as % of total N or NH_2 -N) is greatest with (I), whilst that of NH_3 -N (as % of total N but not NH_2 -N) is greatest with (II).

F. O. H.

Activation of pancreatic juice by acidification. M. LISBONNE and A. FRANK (Ann. Physiol. Physicochim. Biol., 1933, **9**, 723—732; Chem. Zentr., 1934, i, 3354).—Liberation of trypsin from pancreatic juice by small amounts of acid is confirmed. The action is slower than that of kinase, max. activity being attained in 24—30 hr. at room temp., more quickly at 42—45°, but ceasing at 60°.

A. G. P.

Micro-methods for the detection of proteases and amylases. G. E. PICKFORD and F. DORRIS (Science, 1934, **80**, 317—319).—For detecting proteases in biological liquids one drop of buffered fluid or extract is placed on the gelatin surface of an unexposed photographic plate which has been cleared with aq. $\text{Na}_2\text{S}_2\text{O}_3$. After about 2 hr. at $\geq 20^\circ$, the slide is fixed in aq. CH_2O , washed, and stained in either acid fuchsin or Delafield's hæmatoxylin. A clear spot appears when digestion is complete, a clear ring when it is only partly complete. For amylases, a thin starch film on glass replaces the gelatin and digestion is allowed to proceed at 39° . When this is complete the plate is rinsed with dil. I, and a clear spot is obtained. With partial digestion the spot is only partly cleared and is often reddish. The method can detect 1 in 0.5×10^6 of Merck's pancreatin.

Pyrex glass, but not soft glass or quartz, inhibits trypsin and amylase.

L. S. T.

Proteases of the frog. S. R. MARDASCHEV (Biochem. Z., 1934, **273**, 321—323).—As regards the effect on it of temp. and $[\text{H}^+]$ the tryptase (I) of frog pancreas does not differ from (I) of warm-blooded animals. Frog liver contains a peptidase exhibiting max. activity at p_{H} 8.1 and a catheptic protease (II) most active at p_{H} 4. (II) is activated by H_2S .

W. McC.

Proteolytic enzymes of seeds. A. V. BLAGOVESHCHENSKI and R. M. MELAMED (Biochem. Z., 1934, **273**, 435—445).—The proteolytic enzymes (I) (cathepsin, catheptic polypeptidase, dipeptidase) of seeds from different species of plants exhibit specificity as regards their activity. Sometimes (I) from a particular seed act more powerfully on the protein of the same seed than on that of any other seed.

W. McC.

Stability of the dipeptidase in extracts of the muscles of the serpent, *Natrix annularis* (Hallowell). M. SATO (Mem. Fac. Sci. Agric. Taihoku, **9**, No. 1).—The decomp. of leucyl- and of alanyl-glycine by the extracts are probably independent processes, effected by two different enzymes. The stability of extracts made with aq. glycerol (I) increases with their (I) content.

CH. ABS. (p)

Specificity of dipeptidases. Enzymic hydrolysis of peptides from aspartic and glutamic acids. W. GRASSMANN and F. SCHNEIDER (Biochem. Z., 1934, **273**, 452—462).—Glycine Et ester (I) reacts with the α - CH_2Ph ester of carbobenzyloxy-aspartyl chloride (cf. Bergmann *et al.*, A., 1933, 1149) to give the compound $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m.p. 101° . The corresponding acid, m.p. 144 — 145° , yields β -glycylasparagine, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (II), m.p. 153° $[\alpha]_{\text{D}}^{25} + 7.2^\circ$ in $\text{H}_2\text{O} + 1$ mol. of HCl , on reduction (H_2 -Pd-black). Carbobenzyloxy-L-aspartic anhydride with (I) in CHCl_3 gives the compound $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m.p. 113° ; the corresponding acid, m.p. 160° , is converted (H_2 -Pd-black) into α -glycyl-L-asparagine (III). Carbobenzyloxy-L-aspartic acid with PCl_5 yields the dichloride, m.p. 46° , which gives the $(\text{CH}_2\text{Ph})_2$ ester (IV), m.p. 164° , of the corresponding diglycyl derivative on treatment with glycine CH_2Ph ester. Hydrolysis of (IV) gives diglycyl-L-asparagine (V). Carbobenzyloxy-L-glutamic anhydride and (I) give the Et α -glycylcarbobenzyloxy-L-glutamate, m.p. 122° ; the corresponding acid, m.p. 143° , with H_2 -Pd-black yields α -glycyl-L-glutamic acid (VI), m.p. 180° , $[\alpha]_{\text{D}}^{25} + 80.3^\circ$ in H_2O . (III), (V), and (VI) but not (II) are hydrolysed by dipeptidase from yeast and by extracts of intestine or kidney. Amino-polypeptidase does not attack (II), (III), (V), or (VI). Dipeptidases hydrolyse the $\text{CO}\cdot\text{NH}$ linkings (VII) of appropriate natural NH_2 -acids only when a free α - NH_2 and a free CO_2H are in the neighbourhood of (VII).

W. McC.

Micro-titration in enzymic peptide and protamine synthesis. H. VON EULER and B. SJÖMAN (Arkiv Kemi, Min., Geol., 1934, **11**, A, No. 16, 8 pp.).—Using a micro-technique (A., 1931, 1455), peptide

synthesis by pig's intestinal mucosa preps. was detected with *D*-alanine (I)+glycine, (I)+*L*-histidine (II). (I)+*D*-arginine, and with (I) or (II) alone in 0.5*M* solution (containing glycerol) at p_H 7.5—8.0; with periods of up to 6 days, approx. 20% synthesis (as dipeptide) occurs. On dilution almost total hydrolysis of the formed peptide occurs. F. O. H.

Influence of carotene on the guanase content of rat's spleen. I. RYDH-EHRENSVARD and G. SCHMIDT (Z. physiol. Chem., 1934, 227, 177—180).—Absence of vitamin-A from the diet produces a decrease in guanase (I) content in rat's spleen and a change in the time-action curve, the effects being nullified by carotene administration. In the spleen of rats with Jensen sarcoma, the (I) activity is considerably > in normal animals. J. H. B.

Specificity of arginase. H. O. CALVERY and W. D. BLOCK (J. Biol. Chem., 1934, 107, 155—160).—The CO_2H of arginine (I) is probably a point of attachment of arginase (II) before hydrolysis, since (II) will hydrolyse argininic acid (III), but not the Me ester of (I) or the Et ester of (III). (I) and (III) probably exist in solution as stable ring structures. H. G. R.

Activators of arginase. F. LEUTHARDT and F. KOLLER (Helv. Chim. Acta, 1934, 17, 1030—1047).—At p_H 9.2 and 38° the action of arginase (I) does not conform to the unimol. law and is never complete owing to inactivation of the enzyme, which occurs more rapidly with extracts of dry materials than with those of fresh organs. Inactivation is partly due to air, and in this respect the sensitiveness of liver-arginase of different animals differs widely. The activation of (I) by cysteine (II) is due in part to the absorption of mol. O_2 by the latter, which thus creates anaerobic conditions, but other factors appear also to be operative. The degree of activation of (I) by (II) in the organs of different animals was parallel with their sensitiveness to O_2 . Ascorbic acid (III) absorbs O_2 more rapidly than does (II), but is not a more powerful (frequently less powerful) activator, since it is too rapidly consumed; its action is not generally enhanced by the presence of Cu. The action of (II) is increased by Fe^{2+} ; this is not necessarily due to a (II)- Fe^{2+} complex, since (II) shields Fe^{2+} from oxidation and reduces Fe^{3+} and also retains $Fe(OH)_3$ in solution. Ca^{++} activates fresh rat liver. Sections of tissue do not give reproducible results, probably owing to variations in thickness. Since activation is produced by such widely-differing substances as (II), (III), and $N_2H_4 \cdot H_2O$, it is more probably due to the reducing power of the compounds, independent of their mol. structure, rather than to a sp. chemical action. H. W.

Optimum buffer p_H for hydrolysis of urea by urease, and the preparation of stable urease powder. W. W. KAY and M. A. H. REID (Biochem. J., 1934, 28, 1798—1801).—An initial p_H of 6.6—7.0 for >6 mg. of urea is recommended. Urease powder is prepared by granulating a conc. aq. jack bean extract with $COMe_2$. H. G. R.

Reaction between crystalline urease and antiurease. J. S. KIRK and J. B. SUMNER (J.

Immunol., 1934, 26, 495—504).—A definite compound is formed. CH. ABS. (p)

Influence of different cations on the growth of yeast cells. A. LASNITZKI and E. SZORÉNYI (Biochem. J., 1934, 28, 1678—1683).—Alkali cations, in 0.01*N* concn., favour growth (I) of baker's yeast on a synthetic medium containing glucose, tartaric acid, asparagine, $MgSO_4 \cdot 7H_2O$, and $(NH_4)_2HPO_4$, their effects agreeing with their positions in the Hofmeister series. Thus Rb^+ and K^+ show a large, Na^+ and Cs^+ a moderate, and Li^+ a small (I)-promoting effect. Mg^{++} (but not Ca^{++}) also exerts a marked (I)-promoting effect in a medium containing K^+ . $MgSO_4$ acts more strongly than $MgCl_2$, but the difference cannot be ascribed to the (I)-promoting action of SO_4^{--} . A. E. O.

Growth of yeast below zero. J. A. BERRY (Science, 1934, 80, 341).—Of the several strains of yeast isolated from fermented cider one in particular is able to increase at -2.2° ; it ferments glucose, fructose, and sucrose, but not maltose or lactose. L. S. T.

Influence of shaking on yeast. T. M. KONDRATEVA (Bull. Acad. Sci. U.R.S.S., 1934, 653—668).—When suspensions of *Saccharomyces cerevisiae*, Race XII, *Schizosaccharomyces Pombe*, *Nadsonia fulvescens* (I), *Monilia variabilis*, and *Endomyces vernalis* are shaken in a machine, the cell-structure is modified. Vacuolisation becomes more marked, the vacuoles change their form, increase in no., and diminish in size, the homogeneity of the plasma disappears, and the amount of fat present increases; the form and size of the cells remain unchanged. With (I) the glycogen decreases in amount. These changes are accentuated by prolonging the shaking and are reversible, but the most pronounced alterations were transmitted, although only to the first generation of the first culture made. Shaking impairs the multiplication of the cells by budding or scission to an extent increasing with the period of shaking. The course of fermentation and the final products are unaffected. With (I) the sexual process and spore formation are accelerated. T. H. P.

Action of cocaine on yeast. N. N. STADNITSCHENKO (Bull. Acad. Sci. U.R.S.S., 1934, 669—684).—Cocaine (I) is weakly toxic to yeast, the cells being killed after several hr. in a solution containing <5% of (I). In concn. of 0.05—0.1%, (I) serves as a nutrient for certain yeasts. With *Saccharomyces cerevisiae*, spore formation is unaffected. Asporogenous yeasts undergo morphological and physiological changes, giving variants of the saltant type. Cell multiplication is influenced by <0.1% of (I); with >0.5% it is transitorily increased, such increase being specially marked in media containing 0.2%. The fermentative functions are impaired only by distinctly toxic doses (<3%) of (I). No stimulating effect of (I) on the fermentative activity of *S. cerevisiae*, Race XII, was detected. The action of (I) yields new strains of *S. cerevisiae*. T. H. P.

Preparation of a new type of compound from yeast. K. MYRBACK (Svensk Kem. Tidskr., 1934, 46, 211—219).—The cozymase of yeast (I) consists

of adenylic acid (II) united to another component (III) through a P atom. (I) contains only one free acidic OH, but on deactivation by heat another appears, as in (II). (III) probably contains one N, and it has reducing powers like the sugars; the reducing power \propto the enzymic activity of the sample. It was not possible to isolate (III) from the products of hydrolysis of (I), but an acid has been isolated having reducing powers like (III), but containing no N. R. P. B.

Equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid. III. Fixing the triosephosphoric acid with hydrogen sulphite. Distribution of zymohexase in different cells. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1934, 273, 413—418; cf. this vol., 1261).—A procedure for the almost quant. enzymic conversion of Na hexosediphosphate into dihydroxyacetonephosphoric acid (I) [fixed as the NaHSO₃ compound (II)] described. No glyceraldehydephosphoric acid is produced. (II) is converted into the Ba salt of (I). The zymohexase (III) content of muscle (IV) is twenty times that of yeast. Heart, brain, retina, blood-corpuscles, spleen, and carcinoma (mouse) contain smaller amounts, and liver and kidney almost none. (III) from (IV) is much less sensitive to temp. changes than is (III) from other organs.

W. McC.

Mannose monophosphate. II. Fermentation of mannose by dried yeast. C. M. JEPHCOTT and R. ROBISON (Biochem. J., 1934, 28, 1844—1853; cf. A., 1933, 316).—In the fermentation of glucose (I), fructose (II), and mannose (III) by dried yeast in presence of PO₄^{'''}, mannose monophosphate (IV) may in all cases be isolated from the monophosphate fractions, either as the sparingly sol. cryst. Ba salt (+2H₂O), or, with greater certainty, as the *phenylhydrazine* salt of mannose monophosphatephenylhydrazone, m.p. 144—144.5°, which, by the action of PhCHO, yields (IV). The yield of (IV) from (III) is > from (I) and (II) both at 25° and, more especially, at 38°, when (IV) forms the chief part of the total hexose phosphates formed from (III). Reconsideration of the scheme previously put forward (*loc. cit.*) for the initial stage in the fermentation of (I), (II), and (III) is necessary. In aq. solution (IV) exists in two forms, only one of which is rapidly oxidised by (I).

A. E. O.

Course of oxygen consumption in aerobic glucose fermentation. LAZZARI and G. SCOZ (Boll. Soc. ital. Biol. sperim., 7, 247—250; Chem. Zentr., 1934, i, 2438).—In PO₄^{'''}-buffer solutions at p_H 5.6 the O₂ consumption reached a max. after 20 min. and then declined slowly. For 1 mol. of glucose utilised, 6 equivs. of O₂ were consumed in the principal fermentation, and 2 equivs. at the later stage.

A. G. P.

Malarial pigment (hæmozoin). I. Action of solvents on hæmozoin, and spectroscopical appearances observed in the solutions. J. A. SINTON and B. N. GHOSH. II. Reactions of hæmozoin to tests for iron. B. N. GHOSH and J. A. SINTON (Rec. Malaria Survey India, 1934, 4, 15—42, 43—59).—I. Hæmozoin (I) peptised with NaOH or KOH, and alkaline solutions of hæmatin

(II) or of pigment isolated from parasites by papain digestion does not dialyse through parchment. (I) is sol. in (NH₄)₂S, AcOH, HCO₂H, and butyric acid; H₂SO₄ affords hæmatoporphyrin. (I) dissolves slowly in NH₂Ph, C₆H₅N, and 4% quinine-CHCl₃. The spectra of (I) solutions are identical with those of (II). NH₂Ph solutions of (I) and (II) afford *aniline-p-hæmatin*.

II. (I) contains non-ionisable, but not ionisable, Fe. CH. ABS.

Nitrogen content of *Aspergillus niger* in relation to the salt content of the culture medium. G. ROSSI and G. SCANDELLARI (Biochem. Terap. sperim., 19, 92—98; Chem. Zentr., 1934, i, 559).—Absence of NO₃['] or PO₄^{'''} from media has harmful effects. MgSO₄ is not essential for growth, but has a favourable influence. High salt concns. are harmful. Small proportions of MnSO₄ facilitated N accumulation.

A. G. P.

Production of citric acid by *Aspergillus niger*. E. SOTNIKOV (Compt. rend. Acad. Sci. U.R.S.S., 1934, 3, 544—547).—Growth of mycelium on four successive changes of medium gave the following approx. yields of citric acid calc. on the sugar consumed: sterile medium in flasks, 70%; unsterile medium in loosely covered dishes, 60%; unsterile medium in open dishes, 20%.

L. D. G.

Gluconic fermentation. X. Influence of iron on gluconic fermentation by *Penicillium luteum-purpuregenum*. A. ANGELETTI and L. MERLO (Annali Chim. Appl., 1934, 24, 468—472).—On addition of small amounts of Fe (0.01145 g. per litre) as FeCl₃, the gluconic fermentation of a nutrient solution containing 20% of glucose is at first retarded, but the yield of gluconic acid obtained in 20 days is increased by about 11.5%.

T. H. P.

Alleged stimulation of moulds by paraffin in heavy water. S. L. MEYER (Nature, 1934, 134, 665).—A reply to criticism (this vol., 1035). L. S. T.

Assimilation of nitrites by micro-organisms.

I. Culture solution for moulds containing nitrites as nitrogen source. K. SAKAGUCHI and W. Y. CHANG (J. Agric. Chem. Soc. Japan, 1934, 10, 459—476).—The optimum [NO₂[']] in media for growth of various moulds was 0.1—0.25%. Neutral or slightly alkaline media are preferable. The utilisation of NO₂['] by moulds is followed by formation of NH₃, but not of NO₃[']. Yeasts and bacteria assimilating NO₃['] grow easily on NO₂['].

CH. ABS. (p)

Energy and wave-length limits of mitogenetic rays. R. RUYSSSEN (Acta Brevia Neerland. Physiol., 1933, 3, 141—142; Chem. Zentr., 1934, i, 1204).—The effect of radiation on the growth of *Staphylococcus* cultures has been examined. With 2500 Å. a 30—100% increase was observed, 3000 Å. had no action, and at 2600—2900 Å. there was an intermediate effect.

H. J. E.

Action of a filterable staphylococcal toxin on kidneys of normal rabbits. R. H. RIGDON, A. L. JOYNER, and E. T. RICKETTS (Amer. J. Path., 1934, 10, 425—433).—Animals showing kidney lesions

after injection of the toxin had high blood-N without a corresponding increase in uric acid content.

CH. ABS. (p)

Reversible inactivation of pneumococcal hæmolysin. Effects of oxidation and reduction and of metal compounds. H. SHWACHMAN, L. HELLERMAN, and B. COHEN (J. Biol. Chem., 1934, 107, 257—265).—Hæmolysin (I) extracted from type II pneumococci is reversibly inactivated by O_2 , I, $Fe(CN)_6^{3-}$, H_2O_2 , SeO_2 , azochloroamide, Cu_2O , and organomercurials. Reactivation is effected by H_2S , $Na_2S_2O_4$, reduced glutathione, thioglycolic acid, $NaCN$, cysteine, and ascorbic acid. The effects are analogous to those with urease and papain (A., 1933, 1332; this vol., 1402).

C. G. A.

Serological specificity of bacterial carbohydrates with special reference to type II pneumococcus and a heterophile strain of *B. lepi-septicum*. J. H. DINGLE (Amer. J. Hyg., 1934, 20, 148—168).—Sp. carbohydrate materials are isolated from types of various bacteria. Serological reactions are described.

CH. ABS. (p)

Respiration mechanism of pneumococcus. III. M. G. SEVAG and L. MAIWEG (J. Exp. Med., 1934, 60, 95—105).—Transformation from a virulent (I) into an avirulent form causes a large but temporary increase in O_2 consumption, followed by a decline to vals. < that of (I).

CH. ABS. (p)

Physical method of deproteinisation. Separation of carbohydrates from egg-proteins and pneumococcus. M. G. SEVAG (Biochem. Z., 1934, 273, 419—429).—The material [egg-white (I), pneumococcus (II)] is repeatedly frozen with liquid air and allowed to thaw, shaken with a mixture of H_2O , $CHCl_3$, and amyl alcohol (III), and centrifuged. Almost all of the protein (IV) is thus pptd. The supernatant liquid which contains the carbohydrate (V) is freed from (IV) by shaking with $CHCl_3$ + (III). (I) contains 16% of non-(IV), half of it being sol. in EtOH. Part of (V) from (I) is immunologically active, contains 11.5% N, has $[\alpha]_D^{25} -6^\circ$ (+25° after hydrolysis), and reduces Fehling's solution. It contains no S. Dried virulent (II) yield 5.5% of (V) which contains about 7% N, has $[\alpha]_D^{25} +22^\circ$ (+54° after hydrolysis), contains 8% Ac, and is immunologically active.

W. McC.

Comparison of the combining, antigenic, and toxic properties of chemically altered diphtheria toxoid and toxin. L. REINER (J. Immunol., 1933, 24, 213—220).—Conversion of the toxoid into azo-dye by coupling with diazotised arsanilic acid results in loss of antigenic power, but not of combining power (Ramon test), of sp. toxic action, or of ability to give non-sp. reactions. The toxoid dye has a high As : N ratio.

CH. ABS. (p)

Adsorption of diphtheria toxoid by cellulose derivatives and ferric hydroxide gel. L. REINER (J. Immunol., 1933, 24, 221—227).—Adsorption of the toxoid by cellulose nitrate (I) is > by the acetate and is favoured by an acid reaction and low temp. Toxoid can be obtained in a purified form by elution of the adsorbate from (I) or $Fe(OH)_3$ gel at p_H 7.6—7.8.

CH. ABS. (p)

Antigenic power of a mixture of diphtheria toxin and vitamin-C. E. HARDE and M. PHILIPPE (Compt. rend., 1934, 199, 738—739).—The effect of diphtheria toxin on guinea-pigs was reduced if ascorbic acid (I) was added to it before injection, and to a smaller degree when it was diluted with saline, or when (I) was injected separately into the animals.

R. N. C.

Decomposition of citric acid by *B. aertrycke*. W. F. BRUCE (J. Biol. Chem., 1934, 107, 119—129).—Aerobic cultivation of *B. aertrycke* (I), on a citrate medium, yields HCO_2H , AcOH, succinic acid, and CO_2 . The rough form of (I) produces more HCO_2H and AcOH, less succinic acid and CO_2 , than the smooth, and small amounts of lactic acid.

H. G. R.

Immunising fractions isolated from *B. aertrycke*. H. RAISTRICK and W. W. C. TOPLEY (Brit. J. Exp. Path., 1934, 15, 113—129).—The presence of a phosphatide and a polysaccharide is indicated.

CH. ABS.

Blood-sugar changes and toxic effects produced in rabbits by certain fractions derived from *B. aertrycke*. M. E. DELAFIELD (Brit. J. Exp. Path., 1934, 15, 130—137).—Polysaccharide fractions produce hyperglycaemia.

CH. ABS.

Toxicity for mice of certain fractions isolated from *B. aertrycke*. A. R. MARTIN (Brit. J. Exp. Path., 1934, 15, 137—142).—The toxic substance is probably present in the fractions which induce an active antibacterial immunity.

CH. ABS.

Content of specific antigenic polysaccharide substance in *B. aertrycke*. A. BOIVIN, L. MESROBEANU, and I. MESROBEANU (Compt. rend. Soc. Biol., 1934, 117, 271—273).—The method of extraction (this vol., 929) of the sp. polysaccharide complex (I) is modified by a preliminary digestion of the bacteria with trypsin before the $CCl_3 \cdot CO_2H$ extraction. (I) is present to the extent of 10% of the dry wt.

A. L.

Hyperglycaemic action of the specific toxic and antigenic complex isolated from *B. aertrycke*. A. BOIVIN and L. MESROBEANU (Compt. rend. Soc. Biol., 1934, 117, 273—275).—Aq. solutions of the sp. preps. from *B. aertrycke* injected intraperitoneally into rabbits have a considerable hyperglycaemic action.

A. L.

Metabolism of the strict anaerobes (genus *Clostridium*). I. Chemical reactions by which *Cl. sporogenes* obtains its energy. L. H. STICKLAND (Biochem. J., 1934, 28, 1746—1759).—Washed suspensions of *Cl. sporogenes* activate H donation by the naturally occurring isomerides of alanine (I), valine, and leucine, and H acceptance by glycine (II), proline, and hydroxyproline. (I) is deaminated in the first stage of the oxidation. Any of these donors will react with any of the acceptors, e.g., (I) will reduce 2 mols. of (II): $NH_2 \cdot CHMe \cdot CO_2H + 2NH_2 \cdot CH_2 \cdot CO_2H + 2H_2O \rightarrow 3AcOH + 3NH_3 + CO_2$. The rates of these reactions are of the same order as those of aerobic oxidations by other bacteria.

C. G. A.

Bacterial anaerobiosis. III. Oxidation-reduction potential of the butyric bacillus in presence of thiol compounds. W. A. MESSING (Biochem. J., 1934, 28, 1894—1900).—SH-compounds

(I) promote the growth (II) of *B. saccharobutylicus*, (II) being initiated prior to, but subsequently being accompanied by, a lowering of the redox potential of the medium (III). (III) containing (I) does not acquire a negative potential in absence of bacteria.

A. E. O.

Occurrence of *B. aerogenes* in sewage and faeces. N. ATKINSON (Austral. J. Exp. Biol., 1934, **12**, 141—149).—In crude sewage (I) and sewage effluent (II) *B. aerogenes* (III) was present in considerable quantities and the proportion to the total lactose fermenters was approx. the same for (I) and (II). (III) was commonly found in human faeces (about 5% of the total lactose fermenters). It therefore appears unnecessary to differentiate (III) from *B. coli* in testing H_2O for faecal pollution. W. O. K.

Nuclease activity of *B. subtilis*. D. A. MACFADYEN (J. Biol. Chem., 1934, **107**, 297—308).—*B. subtilis*, *B. mesentericus vulgatus*, and *B. megatherium* rapidly decompose yeast nucleic acid (I), particularly at p_H 6.6, at both low and normal O_2 tensions. The liberated nucleotides (II) are further broken down, mainly to ribose phosphate and nitrogenous bases. UO_2Cl_2 in $CCl_3 \cdot CO_2H$ ppts. (I) at p_H 1.5—2.0, and (II) at p_H 3.0—7.0. A. E. O.

Innate individuality of the bacteriophagous properties of three bacteriophages isolated from canal-water. P. C. FLU (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 417—423).—Three strains of bacteriophage isolated from Leiden canal- H_2O have been tested over a no. of years on plague (I), Shiga (II), and coli bacteria and it is concluded that each bacteriophage is a substance independent of the microbe undergoing lysis. Under certain conditions each colony can be caused to lose its lysogenic properties for (II), but a rapid recovery occurs by transmission through (I). S. C.

Bacteriophage of *Bacterium megatherium*; origin of the bacteriophage. P. C. FLU (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 423—429).—Non-lysogenic strains of *B. megatherium* can be infected with *B. megatherium* phage and then develop into resistant spore-bearing varieties, in which the phage is preserved after heating for 1 hr. at 80° . The latter is not necessarily a product of the bacterium undergoing lysis. S. C.

Chemical composition of bacteriophage. M. SCHLESINGER (Biochem. Z., 1934, **273**, 306—311; cf. A., 1933, 1084).—Qual. and quant. (C 42, H 6.4, N 13.2, P 3.7%, and S) examination indicates that bacteriophage consists chiefly of protein. Fat is also present, but probably no polysaccharide. The content of dry matter exceeds 50%. W. McC.

Hydrogen-ion concentration as a factor in the toxicity of amines for *Amoeba proteus*. R. B. HOWLAND and A. BERNSTEIN (Biol. Bull., 1934, **66**, 276—285).—In the p_H range examined amine solutions at p_H 7.8 were the most toxic. The order of toxicity of amines was $NH_2Me > NH_2Et > NH_2Bu > NH_2Pr$, and $NH_2Me > NHMe_2 > NMe_3$.

CH. ABS. (p)

Protective action of pure proteins in photodynamic phenomena. O. JIROVEC and Z. ZIEGLER

4 Y

(Z. ges. exp. Med., 1933, **90**, 651—660; Chem. Zentr., 1934, i, 1664).—The effect of proteins on the toxicity and the sensitising power of rose-Bengal, erythrosin, eosin, and pyronin has been investigated with *Paramecium aurelia* and *Colpidium colpoda*. The protective action against photodynamic action is in the order serum-albumin > ovalbumin > peptone.

L. S. T.

Biliary antiseptics. R. OTTENBERG (J. Infect. Dis., 1933, **53**, 29—44).—Of substances examined, mercurochrome and salyrgan were promising. Flumerin (a Hg-fluorescein derivative) gave best results.

CH. ABS. (p)

Mercuric phenyl nitrate. K. E. BIRKHAUG (J. Infect. Dis., 1933, **53**, 250—261).— $HgPhNO_3$ produces bacteriostatic effects in biliary, cerebrospinal, genito-urinary, and vascular tracts. CH. ABS. (p)

Mode of action of antiseptics. R. FREUND (Biochem. Z., 1934, **273**, 365—380).—Urea and bile (ox) greatly increase the bactericidal efficiency of antiseptics (rivanol). Since adsorbent materials on which very finely-divided Ag has been deposited act in the same way, oligodynamic factors are probably involved. W. McC.

Comparison of the antiseptic power of hexamethylenetetramine and the hydriodide of hexamethylenetetramine-ethyl alcohol. G. TOUSSAINT, R. GÖTZ, and M. VERAÏN (Compt. rend. Soc. Biol., 1934, **117**, 194—196).—At p_H 4—8, the antiseptic power of the hydriodide of $(CH_2)_6N_4 \cdot EtOH$ towards *B. coli* is > that of $(CH_2)_6N_4$. A. L.

Action of sodium hypochlorite, chloramine-T, and azochloroamide on organic substrates. A. F. GUITERAS and F. C. SCHMELKES (J. Biol. Chem., 1934, **107**, 235—239).—The loss of available Cl to org. substrates increases in the order azochloroamide (I) (this vol., 993), chloramine-T, NaOCl, (I) being very inactive over a p_H range 3—11. This property is important in connexion with germicidal val.

C. G. A.

Spirochaeticidal action of bismuth. C. LEVADITI and Y. MANIN (Compt. rend., 1934, **199**, 739—741).—Syphilitic rabbits were injected with basic Bi β -methyl- α -carboxyethylnonoate (bivatol). The variations of the syphilomatous Bi during 12 days were quite independent of the corresponding Bi variations in kidney, spleen, and blood. The spirochaeticidal action of Bi is therefore catalytic, like that of Te, As, V, and Au. R. N. C.

Autocoid function of parasympathetic nerves. A. B. L. BEZNAK (J. Physiol., 1934, **82**, 129—153).—The moving-surface curve of the decrease in the heart's action by acetylcholine (I) is a hyperbola; the equation of the (I) concn.-decrease curve corresponds with that of the Freundlich adsorption isotherm. The inotropic effects on the frog's heart in Ringer's solution of tissue extracts (II) decrease rapidly on dilution compared with that of a pure (I) solution giving the same effect, suggesting that (I) is not the active substance in the tissues. The reaction of the heart to (I) is not altered by changes in osmotic pressure or histamine; choline in amounts > 0.1 mg. decreases the effect, whilst fall of p_H generally increases it.

Evidence is given that (II) contain a substance inhibiting the effect of (I). The effect of (I) on the frog's rectus (III) and leech (IV) increases to a max. on repeated treatment with the same concn. of (I); it is decreased by raising the total [NaCl] of the Ringer's solution. The optimum p_H is 6.8 for (III), and 7.8 for (IV). (III) and (IV) are both sensitive to K^+ , a $[K^+]$ of 0.20% being toxic to (III); the effects of small concns. of (I) and K^+ together are mutually increased. Choline increases the effect of (I) on both (III) and (IV). Parasympathetic stimulation does not alter the total choline ester content (V) of (II). Degenerative chorda section does not alter submaxillary (V). Perfusion of the frog's heart with Ringer's solution containing excess H^+ or K^+ causes an increase in (I) similar to that from vagus stimulation. The (I) of the press-juice from frogs' hearts obtained in presence of eserine increases on incubation at 37°.

R. N. C.

Chemical transmission of secretory impulses to the sweat glands of the cat. H. H. DALE and W. FELDBERG (*J. Physiol.*, 1934, 82, 121—128).—Stimulation of the sympathetic nerve supply to the sweat glands results in the appearance of acetylcholine in the venous fluid.

R. N. C.

Acetylcholine: a peristaltic hormone. F. T. HARVEY (*Vet. Rec.*, 1934, 14, 1219—1221).—A description of the action of acetylcholine on intestinal peristalsis, and its use in the treatment of ileus in horses.

R. N. C.

"Fat metabolism hormone" and hyperglycaemia. B. HARROW, I. M. CHAMELIN, and A. MAZUR (*Amer. J. Physiol.*, 1934, 109, 436—439).—To obtain an extract of "fat metabolism hormone" (I), male urine is acidified with AcOH, and BzOH in EtOH added slowly; the ppt. is treated twice with 95% EtOH to remove BzOH, and extracted with aq. NH_3 , and the extract is kept alkaline until required for testing. Injection of (I) into rabbits causes large increases in blood-sugar, -ketones, and -lactic acid; CO_2 -combining power is decreased, and carbohydrate and fat metabolism undergo a profound disturbance.

R. N. C.

Inactivation of callicrein. II. E. WERLE (*Biochem. Z.*, 1934, 273, 291—305; cf. A., 1930, 1624; this vol., 224).—The inactivating material (I) occurs in blood-serum but not in corpuscles, does not pass through semi-permeable membranes (high mol. wt.), and is destroyed by papain. (I) is destroyed by heating (completely in 45 min. at 58°) and hence inactivated callicrein (II) can be reactivated by heating to 58°. The rate of inactivation depends on the temp., concn. of (I) and (II), and $[H^+]$ (optimum at 7.5, quite inactive at 4 and 11). Horse-serum contains also a second (I) which has an additional optimum at p_H 5.5. These two (I) exhibit differences with regard to sensitivity to the action of heat. As regards inactivating power sera from various animals form the series man > ox > dog > horse > pig. The effects of (I) are counteracted by germanin and novocaine. There seems to be an equilibrium, governed by the mass action law, between (I), (II), and a compound of (I) with (II).

W. McC.

Action of insulin on the heart and blood-pressure. R. K. PAL and S. PRASAD (*J. Physiol.*, 1934, 82, 154—159).—Insulin in small doses causes slowing of the heart rate with some irregularities, and in larger doses complete stoppage of the heart, the action being physiologically antagonistic to that of atropine. Blood-pressure also falls after insulin.

R. N. C.

Effect of insulin in conjunction with posture on blood concentration in depancreatized dogs. A. M. WATERHOUSE and E. P. RALLI (*Amer. J. Physiol.*, 1934, 109, 422—429).—Administration of hypoglycaemic doses of insulin to depancreatized dogs kept on their backs caused increase of blood concn. This did not occur when the animals were kept upright, or on their backs without insulin.

R. N. C.

Effect of insulin and glucose on the metabolism of amino-acids. J. P. BOUCKAERT, P. P. DE NAYER, and W. CASSEMAN (*Compt. rend. Soc. Biol.*, 1934, 117, 257—258).—The blood of rabbits injected simultaneously with insulin, amounts of glucose sufficient to maintain the normal amount of blood-sugar, and glycine (I) shows an increase in the NH_2 -acids as compared with that of animals receiving (I) only.

A. L.

Effect of insulin on the blood amino-acid level. R. MARTENS (*Compt. rend. Soc. Biol.*, 1934, 115, 752—754).—In the depancreatized dog the NH_2 -acid content of liver, muscle, and blood is high and is reduced by insulin (I). From comparisons of the NH_2 -N of femoral vein and artery, and hepatic and portal veins in normal and depancreatized dogs before and after (I) it is deduced that (I) reduces loss of NH_2 -acids from muscle and liver; (I) is therefore thought to inhibit proteolysis and favour synthesis.

NUTR. ABS. (b)

Effect of insulin and adrenaline on carbohydrate metabolism in hyperglycogenæmia. H. BIEDERMANN and W. HERTZ (*Deut. Arch. klin. Med.*, 1934, 176, 272—280; *Chem. Zentr.*, 1934, i, 3077).—Blood-sugar of persons with hyperglycogenæmia scarcely reacts to adrenaline, but shows great sensitivity to insulin.

R. N. C.

Glycaemic curve of adrenaline and insulin in castrated animals. G. B. CONTARDO (*Boll. Soc. ital. Biol. sperim.*, 1932, 7, 98—101).—Castration (I) is followed by a fall in blood-sugar and an increase in the hyperglycaemia due to adrenaline (II) or the hypoglycaemia due to insulin (III). Before puberty, (I) does not produce these effects. The actions of (II) and (III) are influenced in similar ways by the ovarian hormone.

R. N. C.

Effect of adrenaline on liver-glycogen in adrenalectomized rabbits. J. ASAEDA and P. T. SHEN (*J. Biochem. Japan*, 1934, 19, 391—401).—Bilateral adrenalectomy in rabbits diminishes the blood-sugar (I), liver-glycogen (II), and, to a smaller extent, muscle-glycogen (III). Subsequent administration of adrenaline increases the survival period and (I) but not (II) or (III).

F. O. H.

Adrenaline, lymphatic extract, and hyperglycaemic reaction. M. COPPO (*Boll. Soc. ital. Biol. sperim.*, 6, 378—381; *Chem. Zentr.*, 1934, i,

560).—Thymus extract causes hyperglycemia and reduces or prevents adrenaline-hyperglycemia (I). Lymphatic extracts behave similarly, but are less effective in respect of (I). A. G. P.

Determination of adrenaline in blood. G. VIALE (Compt. rend. Soc. Biol., 1934, 117, 267—268).—A reply to criticisms. A. L.

Influence of adrenals on the function of muscle, particularly on its metabolism. G. KUSCHINSKY and D. NACHMANSOHN (Klin. Woch., 1934, 13, 265—266; Chem. Zentr., 1934, i, 3077).—The gastrocnemius of an adrenalectomised guinea-pig (I) when stimulated produces more phosphagen (II) than that of a normal animal (III) equally stimulated, and is sooner fatigued. Lactic acid (IV) formation in (I) is diminished or prevented; in (III) it supplies energy for the resynthesis of (II). Administration of adrenaline (V) restores the activity of the muscle, (V) therefore playing an important part in the resynthesis of (II) and in (IV) production. R. N. C.

Effect of fluid deprivation and fluid intake on the revival of dogs from adrenal insufficiency. Effect of sodium chloride administration on adrenalectomised dogs not receiving extract. Relation between blood-pressure, blood-urea-nitrogen, and fluid balance of the adrenalectomised dog. W. W. SWINGLE, J. J. PFIFFNER, H. M. VARS, and W. M. PARKINS (Amer. J. Physiol., 1934, 108, 144—150, 159—167, 428—437).—As the blood-pressure falls the blood-urea rises. Adrenalectomised dogs lose a greater proportion of H_2O than do normal dogs and correspondingly there is retention during treatment with extract. NUTR. ABS. (m)

Influence of various internal secretion glands on the formation of indican in the organism. Influence of (i) thyroid, (ii) insulin and adrenaline, (iii) testicles, (iv) ovaries, (v) spleen; relation between spleen and thyroid in indican formation. S. SHINGU (Folia Endocrinol. Japan, 1932, 8, 17—18, 18—19, 21, 21—22, 22—23).—(i) In normal rabbits 15% of injected indole (I) appeared in urine as indican (II). Feeding with powdered thyroid increased, and thyroidectomy decreased, urinary (II).

(ii) Excretion of (II) was increased by injection of insulin or of glucose and further increased by injection of both. Adrenaline reduced the (II) eliminated.

(iii) Feeding powdered testicle increased and castration decreased elimination of (II).

(iv) The (II) in urine decreased after ovariectomy or feeding powdered corpus luteum and increased after feeding follicular fluid containing powdered connective tissue.

(v) Spleen extirpation increased (II) in urine. Removal of spleen and thyroid caused a return to normal (II) excretion. CH. ABS. (p)

Adrenal capsules and electrolyte metabolism. IV. Influence of adrenaline, choline, and cortical substance of adrenal capsules on potassium and calcium contents of skeletal muscles. S. SUGIMOTO (Folia Endocrinol. Japan, 1932, 8, 23—24).—In 30 min. after injection of adrenaline the K content of muscle had increased and that of Ca decreased. After 2 hr. the changes were re-

versed. Injection of choline chloride increased K. Feeding of cortex increased K and decreased Ca.

CH. ABS. (p)

Influence of hormones on hydrogen-ion concentration of blood-plasma. I. Influence of thyroid and of insulin. N. NAKATSUGAWA (Folia Endocrinol. Japan, 1932, 8, 39—40).—Feeding of thyroid powder lowered, and thyroidectomy raised, the blood- p_H . Injection of insulin (I) caused a temporary decrease followed by a transition to an alkaline period. On simultaneous injection of glucose with (I) the acid change is less marked, but the alkali phase is prolonged. Large injections of (I) produce marked acidosis.

CH. ABS. (p)

Reduction of blood-lipase by thyroxine and its prevention. J. BAUER and L. FEIL (Wien. med. Woch., 1934, 84, 566—568).—Thyroxine does not produce a general reduction of activity of lipolytic enzymes, but affects only blood-lipase. Lipase is reduced in the liver, but not in the kidney. The reduction of serum-lipase is attributed to lowered production in the liver. NUTR. ABS. (m)

Effect of thyroxine and antithyroid substances on the serum-lipase. M. H. HOFFMANN (Arch. Int. Med., 1934, 54, 427—435).—The reduction in serum-lipase (I) after thyroxine (II) injection as a means of studying antithyroid substances is applied to the blood-extract (III) of Anselmino and Hoffmann (A., 1933, 754) and to olive oil (IV). Both substances inhibit the reduction of (I), (III) being twice as active as (IV). Injection of insulin before the (II) did not protect (I). A. L.

Investigation of the thyroid-liver effect by continual examination of the complement content of the serum. Examination of antithyrotropics by this method. F. FISCHER and W. LOEW (Med. Klin., 1934, 30, 200—203; Chem. Zentr., 1934, i, 2149).—Injection of thyroxine (I) in guinea-pigs causes a fall in serum complement, which can be used as a test for thyroid effect, and depends on the influence of (I) on the liver function. The effect is inhibited by di-iodotyrosine, cholesterol, the Hoffmann-Anselmino serum extract, and insulin. R. N. C.

Concentration of thyroxine in the blood of man and animals. A. W. ELMER, Z. LUCZYNSKI, and M. SCHEPS (Compt. rend. Soc. Biol., 1934, 115, 1714—1716).—By a modification of Leland and Foster's method it was found that the thyroxine content of human blood was in two cases 0.0394 and 0.0482 mg. per litre; in the blood of a horse it was 0.029 and of a dog 0.034 mg. This represents 25—32% of the total I and 40—60% of the org. I.

NUTR. ABS. (b)

Extrathyroid origin of iodine compounds with action resembling that of thyroxine. I. ABELIN (Klin. Woch., 1934, 13, 940—942).—One of the fractions obtained by the hydrolysis with aq. $Ba(OH)_2$ of iodised protein has an action similar to that of thyroxine on the metabolism of rats, the depigmentation of feathers of fowls, and the McCN resistance test.

NUTR. ABS. (m)

Functional inter-relationship between the adrenal and parathyroid glands. J. M. ROGOFF (Science, 1934, 80, 319—320). L. S. T.

Variations in blood- and bile-calcium following injections of calcium gluconate and parathyroid extract. M. CHYRAY, A. MARCOTTE, R. LE CANUET, and P. FIRMIN (*Presse med.*, 1933, 41, 2109—2111).

NUTR. ABS. (b)

Detoxicating principle in the organism. I. Extraction of the active principle of the liver. II. Complementary experiments and investigation of the active principle in various organs and tissues. A. DE BARBIERI (*Boll. Soc. ital. Biol. sperim.*, 1931, 6, 196—197, 197—199).—I. An EtOH extract of the liver was adsorbed with kaolin, the adsorbate eluted with H₂O, extracted with Et₂O, repeatedly treated with PhMe, decolorised with animal C, extracted again with EtOH, and finally dissolved in H₂O. Guinea-pigs injected subcutaneously with this extract (I) were not killed by quantities of NH₄Cl that proved fatal to untreated animals.

II. Frogs injected with (I) and NH₄Cl in the dorsal lymphatic sac remained in normal condition, whilst those injected with NH₄Cl alone developed muscular paralysis and tetanic convulsions. Extracts similar to (I) in effect were obtained from muscle and kidney. Positive results were also obtained from serum, suggesting that the active principle is hormonal.

R. N. C.

Action of tonephin or pitressin and orasthin in increasing blood-sugar and antagonising insulin. H. SCHROEDER (*Klin. Woch.*, 1933, 12, 1766—1768; *Chem. Zentr.*, 1934, i, 560).—Injection of pituitary extracts increases blood-sugar (I) by approx. 20%. Components affecting the uterus do not influence (I). The antagonistic action of pitressin towards insulin (II) is not brought about by restriction of resorption of (II).

A. G. P.

Biological determination of anti-diuretic activity of posterior pituitary extracts. H. PÉNAU and H. SMONNET (*J. Pharm. Chim.*, 1934, [viii], 20, 304—319).—Modified technique using dogs is described. Results of Molitor (*cf. A.*, 1932, 885) are confirmed.

F. O. H.

Action of pituitrin [on urinary excretion]. S. BIANCARDI (*Boll. Soc. ital. Biol. sperim.*, 1931, 6, 227—231).—Injection of pituitrin (I) into fasting animals to which H₂O had been administered produced a marked reduction of diuresis. Administration of dil. NaCl solution instead of H₂O reduced the vol. of urine; this masked the reduced diuresis from (I), but the blood-chlorine was unaffected.

R. N. C.

Corticotropic hormone of the anterior pituitary. K. J. ANSELMINO, F. HOFFMANN, and L. HEROLD (*Klin. Woch.*, 1934, 13, 209—211; *Chem. Zentr.*, 1934, i, 3223).—To obtain an extract of the hormone, fresh ox anterior pituitary is dried with COMe₂, powdered, and agitated for 1 hr. with H₂O; the solution is freed from other hormones by ultrafiltration at p_H 5.0—5.5. The hormone is sol. in H₂O, but insol. in EtOH, COMe₂, Et₂O, and CHCl₃; it withstands boiling for 15 min., and is stable to dil. acids and alkalis. It is not adsorbed by animal C. It can be ultrafiltered through collodion, and is consequently not associated with protein.

R. N. C.

Determination of the [pituitary] anterior lobe hormone in human urine, and its importance in

the recognition of the functioning conditions of different endocrine glands. M. ARON (*Bull. Acad. Méd.*, 1934, 111, 273—275; *Chem. Zentr.*, 1934, i, 2442).—In primary hyperthyroidism the thyroxine of the urine is diminished; in primary hypothyroidism it is increased. This fact is applied in determining whether thyroid abnormalities are primary or secondary.

R. N. C.

Effects of anterior pituitary extracts of cattle on carbohydrate metabolism in the guinea-pig. R. F. HOLDEN, jun. (*Proc. Soc. Exp. Biol. Med.*, 1934, 31, 773—776).—In the male guinea-pig, repeated injections of an extract (I) of the anterior pituitary of the cow cause a diminution in liver-glycogen which reaches a min. in 6 days and is thereafter restored despite continued injections. The min. val. varies with the dose. These observations accord with the view that (I) increases the activity of the thyroid gland.

NUTR. ABS. (m).

Effect of operative interference with the anterior pituitary on the metabolism of diabetic dogs. H. LUCKE, E. R. HEYDEMANN, and O. BERGER (*Z. ges. exp. Med.*, 1933, 92, 711—723; *Chem. Zentr.*, 1934, i, 2148).—Depancreatised dogs were given sufficient insulin (I) to prevent glycosuria (II), and the anterior pituitary (III) was cauterised. The carbohydrate metabolism was considerably improved, and after the effect of (I) had worn off, (II) did not appear at once. In some cases the destruction of (III) resulted in a rapid and heavy fall of blood-sugar, ending in death from hypoglycæmic shock. Dogs treated in this way were unusually variable in blood-sugar retention, suggesting an increased sensibility to hypo- and hyper-glycæmic substances. (III) probably secretes a hormone necessary for the control of carbohydrate metabolism.

R. N. C.

Effect of intermedin and the thyrotropic substance from the anterior pituitary on the adrenaline and ascorbic acid content of the adrenals. A. G. HOLMQUIST (*Klin. Woch.*, 1934, 13, 664—666).—Extracts from the intermediate and anterior lobe of the pituitary, although producing hypertrophy of the adrenal cortex when injected into guinea-pigs, did not affect the adrenaline or ascorbic acid content of the gland.

NUTR. ABS. (b)

Solubility of anterior pituitary substances in solutions of different p_H . R. MÜLLER (*Endokrinol.*, 1934, 14, 1—12; *Chem. Zentr.*, 1934, ii, 626).—The optimum p_H for dissolution of thyrotropic hormone was 12.7 and for the gonadotropic hormone 8.7.

A. G. P.

Thyrotropic substance of the anterior pituitary gland. I. II. Metabolic relation to other organs of internal secretion. A. LOESER (*Arch. exp. Path. Pharm.*, 1934, 176, 697—728, 729—739).—I. The thyrotropic principle (I) (*A.*, 1932, 970) has a max. stability at p_H 9; at p_H 1—3, 7, and 13, decomp. at room temp. is complete in approx. 6 days. With rats, rabbits, and guinea-pigs, the blood-level of (I), which normally has a low val., rises after thyroidectomy and falls after hypophysectomy. Intravenously injected (I) is rapidly excreted unchanged in the urine, no accumulation occurring in the liver,

spleen, kidney, thyroid gland (II), or muscle. (I) is relatively stable in blood *in vitro*. The action of (I) is independent of the nervous system, but dependent on the activity of (II); thus it is diminished by thyroxine, di-iodotyrosine, 3:5-di-iodothyronine, or KI+I, but not tyramine, tyrosine, or thyronine. The relation between the activity of (II) and that of the pituitary gland is discussed.

II. The metabolic activity of (I) is related to the functioning of the ovary and adrenal glands (III). Thus ovariectomy in guinea-pigs produces an increased secretion of (I) which influences (II). The changes in (III), which occur mainly in the cortex, are not directly due to hormonal influence, but are probably caused by the metabolic disturbance due to (I) and (II).

F. O. H.

Thyrotropic hormone of the anterior pituitary. E. M. ANDERSON and J. B. COLLIP (J. Physiol., 1934, 82, 11—25).—The metabolic rate (I) of the rat or guinea-pig is increased by injection of extracts of the thyrotropic hormone (II) of the anterior pituitary. Hypophysectomised animals (III) are more sensitive to (II) than normal animals. A prolonged series of injections results in a fall of (I) to the level of (III); the antithyrotropic hormone causing this is not produced in the pituitary, since (III) also develop the same resistance. (I) rises very steeply in goitrous animals injected with (II). Purified extracts of (II) are prepared by concn. in vac. of the $\text{Ca}_3(\text{PO}_4)_2$ filtrates from the original extracts, saturation with $(\text{NH}_4)_2\text{SO}_4$, filtration and extraction of the ppt. with H_2O twice, pptn. with EtOH and dissolution in H_2O twice, and repeated pptn. from EtOH or COMe_2 . The adrenotropic hormone can be separated from (II) in the filtrates from the last pptns. by isoelectric pptn. (II) is stable for long periods in the cold in aseptic conditions, but is destroyed by boiling.

R. N. C.

Hypoglycæmic action of the thyrotropic hormone of the anterior pituitary. E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1934, 117, 262—264).—Intravenous injection of the thyrotropic hormone of the anterior pituitary gland into dogs causes a decrease in blood-sugar due to increased insulin secretion.

A. L.

Thyrotropic activity of anterior pituitary extracts. I. W. ROWLANDS and A. S. PARKES (Biochem. J., 1934, 28, 1829—1843).—The thyrotropic activity of anterior pituitary extracts was tested by their capacity to increase the wt. of the thyroids of immature female guinea-pigs. A curve for response/dose has been constructed, and a provisional unit adopted. It is probable that a clean and simple separation of the growth hormone and prolactin from the thyrotropic and gonadotropic substances may be effected by $\text{C}_5\text{H}_5\text{N}$ extraction, only the latter being sol. in aq. $\text{C}_5\text{H}_5\text{N}$.

A. E. O.

Mechanism of action of the insulin-antagonistic hormones of the anterior pituitary. II. Anterior pituitary, adrenal insufficiency, and carbohydrate metabolism. III. Anterior pituitary, adrenal denervation, and carbohydrate metabolism. H. LUCKE, E. R. HEYDEMANN, and H. HAHNDEL (Z. ges. exp. Med., 1933, 94, 483—491,

492—501; Chem. Zentr., 1934, i, 2148).—II. In adrenalectomised dogs, injection of the insulin-antagonistic hormones (I) (fresh anterior lobe preps.) produces no rise of blood-sugar.

III. (I) have no hyperglycæmic effect in dogs with denervated adrenals. The hyperglycæmia is therefore due to a stimulation of the adrenal nerves.

R. N. C.

Influence of anterior pituitary on bile secretion. G. BALTACÉANO, C. VASILIU, and M. H. PARASCHIV (Compt. rend. Soc. Biol., 1934, 117, 279—283).—Anterior pituitary preps. injected into dogs increase the quantity of bile (I) secreted. The amount of salts in (I) is increased, the cholesterol content diminishes, and the pigments remain unchanged.

A. L.

Anterior pituitary hormones. VI. Comparison of the effect of the different hormones on deamination processes. R. AGNOLI (Boll. Soc. ital. Biol. sperim., 6, 754—756; Chem. Zentr., 1934, i, 560).—The lipin hormone (Agnoli) and prolactin (Zondek) intensify deamination.

A. G. P.

Pituitary and fat-accumulation following castration. K. W. SCHULTZE (Arch. Gynakol., 1934, 155, 327—334; Chem. Zentr., 1934, i, 2938).—Injection of the Anselmino-Hoffmann extract of the anterior pituitary into rats raises the blood-ketones. The active substance (I) can be detected in human blood after a meal of fat. In persons with fat-accumulation following castration or climacteric, there is no diminution below the normal of the blood-(I). The ketonæmia induced by injection of the anterior pituitary extracts is probably the result of an increased fat exchange.

R. N. C.

Extraction of gonad-stimulating substances of the anterior pituitary. A. E. MEYER and H. L. FEVOLD (Proc. Soc. Exp. Biol. Med., 1934, 31, 570—571).—Almost complete extraction is obtained with 5% aq. $\text{C}_5\text{H}_5\text{N}$, 6% BuOH, or 3% *n*-amyl alcohol.

CH. ABS. (p)

Bio-assay of the anterior pituitary-like sex-hormone (antuitrin-S). L. W. ROE, A. SIMOND, and W. O. NELSON (J. Amer. Pharm. Assoc., 1934, 23, 882—891).—Using 26-day-old rats and examining for corpora lutea gives a method accurate to 10—20%. 1 mouse unit is equiv. to 4 rat units. The rabbit ovulation unit is equiv. to 1 rat unit per kg. body-wt. of the rabbit.

C. G. A.

Effect of pineal extracts on the action of the anterior pituitary hormone. P. ENGEL (Klin. Woch., 1934, 13, 266—267; Chem. Zentr., 1934, i, 3076).—In mice and rabbits injected with anterior pituitary hormone (I) and then with an extract of the human pineal gland (II), the stimulating effect of (I) on the ovary did not appear. A human (II) contained enough active material to inhibit the action of 30 rat units of (I).

R. N. C.

Demonstration of an oestrus-inhibiting substance in the pineal gland of young female rats. W. FLEISCHMANN and H. GOLDHAMMER (Klin. Woch., 1934, 13, 415; Chem. Zentr., 1934, i, 3076).—Attempts to inhibit the action of the anterior pituitary by implantation (I) of pineals (II) in young animals

failed; the implants also did not antagonise injected folliculin. (I) of two (II) from young female rats in mice suspended oestrus (III), often for 4–6 weeks. The inhibitory effect was max. when the (I) took place at the height of (III). After the effect had subsided, (III) occurred normally again. R. N. C.

Elimination of prolan in the urine in the involution period and in age. H. SAETHRE (Klin. Woch., 1933, 12, 1727–1729; Chem. Zentr., 1934, i, 3481).—Prolan elimination (I) in the urine of women in the climacteric and post-climacteric stages was always increased. No increased (I) was established in pre-puberty or puberty. R. N. C.

Complete recovery of gonadotropic substances from the urine of pregnant women. L. DAVY (Endocrinol., 1934, 18, 1–17).—Acidified urine is shaken with Lloyd's reagent, which is dried, eluted with 50% C_6H_5N , and the active substance pptd. with 95% $COMe_2$. CH. ABS.

Action of ovarian extract on the alkali reserve of castrated rabbits. G. B. CONTARDO (Boll. Soc. ital. Biol. sperim., 1932, 7, 102–104).—Injection of ovarian extract or folliculin in castrated rabbits shows no effect on the alkali reserve (I). The increase in (I) on castration is probably due to the activity of other endocrine organs. R. N. C.

Preparation of the female [sex] hormone, and a new phenomenon of the hormone. M. IRO and S. HAYAZU (Münch. med. Woch., 1933, 80, 1969; Chem. Zentr., 1934, i, 3222).—Mare's urine is acidified with HCl, filtered through kieselguhr, the hormone adsorbed on C, and the C washed with dil. alkali and EtOH and extracted with aq. PhOH, the PhOH being distilled off in steam. The solution is evaporated, the residue dissolved in aq. EtOH, and boiled with 10 vols. of C_6H_6 . The yellow C_6H_6 layer is washed with 2% aq. Na_2CO_3 until colourless, conc., and then shaken with 4% NaOH; this extracts 90–95% of the hormone, which is pptd. on neutralisation. By repeated saponification of the ppt. with 5% NaOH, followed by extraction with Et_2O and evaporation, 60% of the hormone is obtained as crystals, m.p. 254°. Analysis indicates the formula $C_{18}H_{22}O_2$; the mouse unit is 0.07×10^{-6} g. 100 litres of urine yield 640 mg. of crystals. The same crystals are obtained from urine of pregnancy. The hormone content of these extracts increased slowly, in one case from 7 to 60 million units in one year, suggesting that a prohormone was being converted slowly into the hormone. R. N. C.

Theelin prepared from human and mare's urine and from theelol. Preparation of theelin from mare's urine. J. M. CURTIS, D. W. MACCORQUODALE, S. A. THAYER, and E. A. DOISY (J. Biol. Chem., 1934, 107, 191–205).—There is no evidence of the existence of α - and β -isomerides of theelin (I). (I) is obtained from mare's urine by pptn. with BzOH in acid solution and purified by the usual methods. < 0.1% of the activity is due to a less active form, if this is present. H. G. R.

Influence of folliculin on the flowering of plants. R. HARDER and I. STORMER (Jahrb. wiss. Bot., 1934, 80, 1–19).—The hormone had no effect

on the rate of growth or period of flowering of any plant species examined. A. G. P.

Action of oestrin on the coagulating glands and on certain vestigial structures in the mouse (*Mus musculus*). H. BURROWS (Nature, 1934, 134, 570).—The changes described indicate that oestrin may have a sp. action on structures derived from the Müllerian apparatus. L. S. T.

Crystalline progesterin. O. WINTERSTEINER and W. M. ALLEN (J. Biol. Chem., 1934, 107, 321–336).—From the cryst. fraction containing progesterin previously isolated from corpus luteum extracts (A., 1933, 194) four cryst. substances have been isolated by fractionation from C_6H_6 and light petroleum. The chief constituent is a substance, $C_{21}H_{34}O_2$ (or less probably $C_{22}H_{36}O_2$) (I), m.p. 190°, a saturated hydroxy-ketone [phenylurethane, m.p. 214.5°; p-nitrobenzoate, m.p. 216°; semicarbazone, m.p. 248–249° (decomp.)] devoid of progesterin activity. The mother-liquors from (I) contain an active substance, $C_{21}H_{30}O_2$ (II), m.p. 128°, an unsaturated diketone [dioxime, m.p. 238° (decomp.); semicarbazone, amorphous, m.p. 280° (decomp.)], exhibiting selective absorption at 240 μ , together with a second very similar active substance, $C_{20}H_{28}O_2$ (?), m.p. 120–121°, which may consist of mixed crystals of (II) with small amounts of impurities. A second inactive substance, m.p. 74°, was also isolated in minute amount. The above results are in good agreement with those of Butenandt (this vol., 1039) and of Slotta *et al.* (*ibid.*, 931). Oxidation of (I) by CrO_3 yields a diketone, m.p. 191–194°, not identical with pregnandione. A. E. O.

Hormones of the corpus luteum. K. H. SLOTTA, H. RUSCHIG, and E. FELS (Helv. Chim. Acta, 1934, 17, 1361–1362).—The cryst. hormone of Hartmann *et al.* (this vol., 1039) is a mixture of 75% of luteosterone-A and 25% of luteosterone-C (I) + -D. Their dioxime is probably derived from (I). H. W.

[Hormones of the corpus luteum.] M. HARTMANN and A. WETTSTEIN (Helv. Chim. Acta, 1934, 17, 1363–1364).—A reply to Slotta *et al.* (preceding abstract) and Butenandt *et al.* (this vol., 1039). A bibliography is appended. H. W.

Corpus luteum hormones. II. M. HARTMANN and A. WETTSTEIN (Helv. Chim. Acta, 1934, 17, 1365–1372; cf. this vol., 1039).—Preliminary enrichment is effected by the method of Corner *et al.* (Amer. J. Physiol., 1929, 88, 326). After freezing from dil. MeOH, partition between 80 vol.-% EtOH and light petroleum (I) causes the active material to remain in the EtOH while much inactive material passes into the (I). The EtOH is diluted to 33% and shaken with (I), into which the corpus luteum hormones pass, whilst the follicular hormone and ballast remain in the EtOH- H_2O . Purification can also be effected by adsorbing the hormones from anhyd. (I) or CS_2 by fuller's earth followed by elution with boiling EtOH; the method is particularly applicable to ox corpus luteum. A third method consists in extracting the C_6H_6 solutions with 75% H_2SO_4 , diluting the extract to 20%, and extraction with Et_2O . The quant. separation of diketones and OH-ketones in the

products thus obtained is effected by use of more freely sol. ketonic products; thus the *dioximes*, $C_{21}H_{30}(N\cdot OH)_2$, m.p. 269° (corr.) and m.p. 251° (corr.), respectively, have been obtained. Further, the OH-compounds may be removed by treatment with $o\text{-}C_6H_4(CO)_2O$ in C_5H_5N ; the non-reactive portion yields homogeneous hormones, m.p. 129° (corr.) and m.p. 120° (corr.), respectively, whilst the H phthalate fraction is hydrolysed to a OH-ketone, m.p. $196\cdot5\text{--}197\cdot5^\circ$ (corr.). H. W.

Effect of the male sex hormone on the genital tract of the female. S. SKOWRON (Nature, 1934, 134, 627).—Female rabbits give a macroscopic positive reaction after subcutaneous injections of the male hormone of the rabbit. L. S. T.

Standardisation of the male hormone. R. FUSSGANGER (Med. chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1933, 213—226; Chem. Zentr., 1934, i, 2440—2441).—The comb method is recommended, the unit being the amount of hormone which after five daily injections into the castrated cock produces a comb-growth of 30% in seven days from the beginning of the experiment. R. N. C.

Colour test for vitamin-A. J. ROSENTHAL and J. ERDELYI (Magyar Orvosi Arch., 1934, 35, 232—237).—5% guaiacol (I) solution produces with vitamin-A the same red-violet colour as does 5% pyrocatechol. The stability of the colour renders the (I) test suitable for quant. purposes. NUTR. ABS. (m)

Colour reaction for carotene. V. E. LEVINE and G. E. BIEN (Proc. Soc. Exp. Biol. Med., 1934, 31, 581—582).—Carotene (I) in $CHCl_3$ reacts with CH_2O in H_2SO_4 (1 vol. of 40% CH_2O in 50 vols. of acid) to form a deep violet zone between the layers. The violet zone, on shaking, spreads through the acid layer, leaving the $CHCl_3$ colourless. Addition of Ac_2O causes a transitory blue to appear in the acid layer if the concn. of (I) is sufficiently high. NUTR. ABS. (m)

Liebermann-Burchard reaction with carotene. V. E. LEVINE and G. E. BIEN (Proc. Soc. Exp. Biol. Med., 1934, 31, 804—808).—Carotene (I) can be detected by means of Ac_2O and conc. H_2SO_4 , in concns. of $< 0\cdot01$ mg. of (I) in 10 ml. of $CHCl_3$. The reaction resembles the Liebermann-Burchard test for cholesterol (II) except that the green colour is more rapidly formed and much more transitory. (I) does not interfere with the determination of (II) in blood. NUTR. ABS. (m)

Storage of vitamin-A in cattle. H. R. GUILBERT and G. H. HART (J. Nutrition, 1934, 8, 25—44).—Carotene in adipose tissue may be withdrawn during vitamin-A (I) privation without the withdrawal of the fat. The premature expulsion of the foetus resulting from (I)-deficiency is examined. The liver-tissue of mature beef cows reared under favourable conditions contained (I) in amounts approximating to that of cod-liver oil. The (I) in livers of newly-born calves from well-fed cows was relatively low. A. G. P.

Vitamin-A storage in livers of turkeys and chickens. H. R. GUILBERT and W. R. HINSHAW (J. Nutrition, 1934, 8, 45—56).—Storage of vitamin-A (I) in chicken livers is directly related to the (I) content

of the ration. The influence of age on the (I) reserves of chicken and turkeys is examined. A. G. P.

Cholesterol and vitamin-A content of the human liver. G. L. MULLER and M. M. SUZMAN (Arch. Int. Med., 1934, 54, 405—411).—The cholesterol content (I) of livers obtained at autopsy was $0\cdot098\text{--}1\cdot003\%$ (average $0\cdot301\%$). (I) was $<$ average in cases of death from infectious and $>$ average in death from arterial hypertension. No relation could be established between (I) and the vitamin-A content of the liver or the sex or age of the patient. A. L.

Vitamin content of the pituitary. E. VOGT (Med. Klinik, 1933, 29, 1734—1735; Chem. Zentr., 1934, i, 880).—Normally the pituitary (I) of adults under 50 possesses a definite vitamin-A (II) content. In chronic, exhausting illnesses (II) gradually disappears completely. With malignant tumours, especially of the quick-growing type, the (II) of (I) can be $<$ normal. Only in the final stages of the disease does (I) become deprived of (II). L. S. T.

Carotene, vitamin-A, and vitamin-C in cow's milk. J. C. H. VAN WIJNGAARDEN (Acta Brev. Neerland., 1934, 4, 49—52).—Vitamin-A and carotene, determined after saponification of the milk, by means of the $SbCl_5$ test and Lovibond tintometer, respectively, are low in the milk of cows kept in stall on a diet of hay and oil-cake, or hay and mangolds, but higher on pasture or when silage is given. The same variation of conditions produces little change in the vitamin-C content of the milk. NUTR. ABS. (m)

Carotene and vitamin-A in human milk with special reference to colostrum. M. VAN EEKELLEN and J. H. DE HAAS (Acta Brev. Neerland., 1934, 4, 52—54).—The carotene and vitamin-A contents are very high for the first week after parturition, but decline gradually until after some weeks the vals. are about one sixth of the initial figures and approach the vals. for cow's milk. NUTR. ABS. (m)

Effect of prolonged feeding of raw carrots on vitamin-A content of liver and kidneys in the dog. R. G. TURNER (Proc. Soc. Exp. Biol. Med., 1934, 31, 866—868).—The vitamin-A content of the liver and kidneys of dogs fed on fresh carrots is $>$ that of dogs on a meat or boiled rice diet. NUTR. ABS. (m)

Relation between effects of vitamin-A and -D and amount of calcium salts and phosphates in food. H. MØLLGAARD (Ugeskr. Laeger, 1934, 96, 565—570).—Dietary promotion of rapid growth in the pig without too great accumulation of fat greatly strains growth capacity and makes great demands on the vitamin supply and the amount and composition of mineral salts in the food. Administration of vitamin-A (I) and -D (II) produces different effects according to the Ca and P content of the food, and overdosage of these vitamins depends not only on the size of the dose, but also on the composition of the diet. Administration of (II) or of (I) + (II) causes tetany and osteoporosis when the Ca is low. Human beings should never be treated with highly conc. preps. of (II) or (I) + (II) unless the diet contains sufficient Ca. NUTR. ABS. (m)

Calcium and phosphorus metabolism. II. Influence of carotene and gallosterol on blood-calcium and -phosphorus. III. Influence of carotene on organ- and tissue-calcium. I. ISHIDA (J. Biochem. Japan, 1934, 20, 5—16, 17—22; cf. this vol., 323).—II. Rabbits fed on barley and vegetables show an increase in blood-Ca (I) which is diminished by repeated bleeding. Administration of gallosterol (vitamin-A-choleic acid) or β -carotene (II) increases the blood-inorg. and -org. P, but decreases (I).

III. Subcutaneous injection of (II) increases the Ca content of muscle, bone, liver, and kidney by 26.87, 14.27, 10.99, and 5.15%, respectively; that of lung and heart diminishes by 34.05 and 6.21%, respectively.

F. O. H.

Nutritional significance of vitamin-A throughout the life cycle. E. L. BATCHELDER (Amer. J. Physiol., 1934, 109, 430—435).—Rats on diets containing variable quantities of vitamin-A as butter-fat (I) showed significant differences in their life-cycles. The rate of growth and wt. of young at 28 days declined with the (I) in the diet when (I) was < 4%. The no. of young reared decreased below 2% of (I), and no. of young born, duration of reproductive life, and length of life, below 1%; on this diet fourth generation rats were born, but only a few were reared. R. N. C.

Metabolism of carotene. B. AHMAD, K. S. GREWAL, and K. S. MALIK (Indian Med. Gaz., 1934, 69, 320—323).—Carotene (I) suspended in aq. glucose given to rats intravenously does not relieve the symptoms of vitamin-A (II) deficiency, and does not cause the storage of detectable amounts of (II) in the liver. Similar experiments with dogs fail to show any transformation of injected (I) into (II). The liver of the rabbit, however, seems able to make (II) from this source. NUTR. ABS. (m)

Influence of the solvent on the biological effect of carotene and vitamin-A. K. C. LATHBURY and G. N. GREENWOOD (Biochem. J., 1934, 28, 1665—1673).—Different batches of arachis oil and of coconut oil vary in their suitability as solvents for the biological testing (I) of vitamin-A or carotene, on account of an unknown factor not arising by deterioration of the solutions on keeping. Quinol does not render an inferior oil suitable for (I). A. E. O.

Influence of vitamin-A, -B, and -C and Collip's hormone on the development of tadpoles after treatment with irradiated ergosterol. P. COCCHERI and G. ROSSI (Boll. Soc. ital. Biol. sperim., 6, 750—753; Chem. Zentr., 1934, ii, 562).—Large amounts of irradiated ergosterol (I) were injurious, but smaller proportions stimulated the growth (II) and metamorphosis (III) of tadpoles. III effects of (I) were counteracted by vitamin-A in respect of (II), but (III) was only slightly influenced. Vitamin-C restricted the injurious action of (I). Collip's hormone acts similarly to small amounts of (I) and accentuates the injurious effect of (I) when administered simultaneously. A. G. P.

Fatty constituents of marine plankton. I. Biology of the plankton. E. R. GUNTHER. II.

General character of the plankton oils. G. COLLIN, J. C. DRUMMOND, T. P. HILDITCH, and E. R. GUNTHER. III. **Vitamin-A and -D content of the oils.** J. C. DRUMMOND and E. R. GUNTHER (J. Exp. Biol., 1934, 11, 173—197, 198—202, 203—209).—I. The representative occurrence of different species of organisms in zoo- (I) and phyto-plankton (II) was studied in relation to the yield of oil obtained from different samples. In plankton giving a high yield, the *Copepoda*, particularly *Calanus finmarchicus*, were predominant. The plankton oils resemble fish oils of the Clupeoids and Gadid liver oils, which are probably therefore derived ultimately from the plankton.

II. Methods of extraction and examination of the oils are given, with analyses of samples of (I) and (II) oils, and of the unsaponifiable fraction of (I) oil. The presence of an unsaturated C_{20} alcohol of the oleyl or eicosenyl type is recorded.

III. Colorimetric and biological tests indicated that vitamin-A was present in (II) oil, but probably absent from (I) oil. (I) oil has some small vitamin-D activity, but (II) oil is inactive. NUTR. ABS. (b)

Influence of vitamins on the catalase content of blood. II. H. J. JUSATZ (Klin. Woch., 1934, 13, 727—728).—Administration of carrots or of vitamin-A (I) causes no rise in the catalase content (II) of the blood of rabbits maintained for two months on a diet devoid of (I). Administration of 100 mg. of ascorbic acid daily, orally or intravenously, raises (II) of the blood of rabbits maintained on a scorbutic diet. NUTR. ABS. (m)

Vitamin-D content of eggs. H. D. BRANION (Canad. Pub. Health J., 1934, 25, 171—174).—Egg-yolk is a rich source of vitamin-D (I), of which a store is laid up in summer, the vals. being lowest in February and March. Addition of 2% of cod-liver oil (II) to the diet of the laying hens increased the amount of (I) in the egg-yolk 7.5 times; it also increased the no. of eggs laid and of chicks hatched from fertile eggs. With 2% of viosterol of strength comparable to (I), the (I) content was again raised 7.5 times; with viosterol 10 times as strong the increase was 15-fold; with viosterol 10,000 times as strong the increase was about 6000-fold, but with this last amount no chicks could be hatched from the eggs. Exposure of the hens daily for 20 min. to ultra-violet light slightly increased the (I) content in the yolk. Eggs kept in cold storage for several months did not deteriorate in (I). NUTR. ABS. (b)

Accuracy of biological determinations of vitamins. K. H. COWARD (Analyst, 1934, 59, 681—685).—Biological tests for vitamins are exceedingly sensitive. Assuming that the vitamin-D of cod-liver oil (I) and of butter (II) is calciferol, 0.0001 mg. can be detected in any wt. of (I), (II), or other foodstuff that can be given to a rat in 10 days. Thus the concn. of -D in (I) may be 1 in 2×10^5 , and in (II) 1 in 4×10^7 parts. In any other foodstuff it is less. The accuracy of the tests is discussed. E. C. S.

Vitamin-D assay of the "reference cod-liver oil." L. L. LACHAT and H. A. HALVORSON (Science, 1934, 80, 342).—A statement of the problem of

reducing the chick assay of antirachitic supplements to terms of International rat units (I). Each chick requires 80—135 (I) to produce satisfactory calcification (normal growth and average bone-ash content >45%). The view that the vitamin-D requirement of the chick is very large when compared with that of the rat for the antirachitic substance in cod-liver oil is supported. L. S. T.

A. Role of bile in the absorption of vitamin-D in the rat. B. Action of viosterol in jaundiced rachitic rats. J. D. GREAVES and C. L. A. SCHMIDT (Univ. California Pub. Physiol., 1934, 8, 43—48, 49—60).—A. Healing of rickets due to loss of wt. makes the direct assay of vitamin-D (I) absorption in icteric rachitic rats (II) unfeasible. By feeding Et₂O extracts of the livers of jaundiced (II) receiving viosterol to other (II), it was shown that (I) is stored in the liver of icteric rats when subcutaneously, but not when orally, administered. The presence of bile in the intestinal tract is, therefore, essential for absorption of (I).

B. Viosterol given orally or subcutaneously to jaundiced (II) raised the level of inorg. PO₄''' in the blood, but did not aid calcification. There was no definite evidence of injury to the osteogenic cells. Phosphatase activity was decreased in the livers and kidneys of icteric rats and slightly increased in the bones. NUTR. ABS. (b)

Lung and vitamin-D. G. A. METZ and P. A. COPPENS (Nederland. Tijdschr. Geneesk., 1934, 78, 769).—In the dog, orally administered irradiated ergosterol is destroyed in the lungs.

NUTR. ABS. (b)

Solar irradiation of children with special reference to hypervitaminosis-D. E. C. DODDS, J. D. ROBERTSON, and H. J. ROCHE (Arch. Dis. Childhood, 1934, 9, 91—103).—Hypervitaminosis was not observed. Blood-Ca and -inorg. P were increased by exposure to sunlight. CH. ABS.

Vitamin content of Philippine foods. III. Vitamin-B in various fruits and vegetables. A. J. HERMANO and G. SEPULVEDA (Philippine J. Sci., 1934, 54, 61—71).—Himbaba-o, cauliflower, and tamarind are excellent sources of vitamin-B₁, as are mango, pineapple, melon, and many other both immature and ripe fruits; bananas contain none. P. G. M.

Effect of X-rays on the vitamin-B content of wheat seedlings. K. SUGIURA (Radiology, 1933, 21, 438—448).—Treatment with X-rays caused only a small decrease in the "vitamin-B" content of whole, dry wheat grains as tested by the growth method with rats. If the wheat was soaked and allowed to germinate, its "vitamin-B" content increased, but at the same time it became more vulnerable to X-rays. Irradiation of dry seeds, before germination, with massive doses of X-rays inhibited subsequent growth of the plant > did irradiation of the growing seedlings. This effect was reversed with small doses of X-rays.

NUTR. ABS. (b)

Isolation of oryzanin (antineuritic vitamin). III. S. OTAKE (J. Agric. Chem. Soc. Japan, 1934, 10, 409—416).—Dry yeast was extracted with 60% EtOH. Vitamin-B₁ was pptd. by Ba(OH)₂ and

AgNO₃ at *p*_H 4.5—6.8. After repptn. with phosphotungstic acid -B₁ was obtained as cryst. hydrochloride, identical with that from rice bran. CH. ABS. (p)

Antineuritic vitamin. III. A. WINDAUS, R. TSCHESCHE, and R. GREWE (Z. physiol. Chem., 1934, 228, 27—32; cf. A., 1932, 310).—Oxidation of the nitrate of the vitamin with conc. HNO₃ at 60°, removal of SO₄'' (equiv. to 20% of the total S) with Ba(OH)₂ and of HNO₃ in vac., treatment of the residue with EtOH, and addition of 3 vols. of Et₂O, filtration, and evaporation of the filtrate in vac. affords a cryst. substance (I), C₇H₁₁O₅N₃, decomp. 146—153°, which is a nitrate and Et ester of C₅H₉O₂N₂. This is apparently not a glyoxaline derivative, but is possibly a dihydroxymethylpyrimidine. The residues from the prep. of (I) gave at 160°/12 mm. a cryst. *sublimate* (II), C₅H₉O₂NS, reddens at 200°, decomp. > 250° [Me ester (with CH₂N₂), m.p. 73—74°, giving a *phosphotungstate*]. (II) probably contains a free ·CO₂H and a C·S or C·SH group. It gives the pyrrole reaction when heated with Zn dust. J. H. B.

Effect of the Clayton process on the vitamin-B₁ content of rice. A. G. VAN VEEN and M. T. KOKS (Geneesk. Tijdschr. Ned.-Ind., 1934, 74, 482—485).—The Clayton process (action of SO₂ up to 3—4.5% concn. for about 3 hr.) caused a loss of vitamin-B₁ (I), depending on the H₂O and degree of milling of the rice and on the method of packing. When the rice was packed in small sacks the loss of (I) in dry paddy could just be detected, that in slightly milled ("silver-skin") rice was > 30%, and that in half-milled rice about 50%. With rice packed in large sacks the loss in "silverskin" rice was negligible. Pure (I) withstood aq. SO₂ at *p*_H 3—7, but was slowly destroyed in more conc. solution. NUTR. ABS. (b)

Use of unwashed, slightly milled rice as food. A. G. VAN VEEN (Geneesk. Tijdschr. Ned.-Ind., 1934, 74, 672—680).—All methods involving washing seriously diminish the vitamin-B₁ content of rice, whatever the degree of milling; steaming, in which the loss is relatively small, even with highly milled rice, is the preferable method of cooking. NUTR. ABS. (b)

Lactoflavin (vitamin-B₂) from liver. R. KUHN and T. WAGNER-JAUREGG (Ber., 1934, 67, [B], 1770—1773).—The flavin from ox-liver (isolation described) has m.p. 276° (Berl; decomp.) after darkening, [α]_D²⁰ -118°±10° in 0.05*N*-NaOH. In composition, m.p., mixed m.p., [α]_D, and spectroscopic behaviour it is indistinguishable from lactoflavin (I). Since it is also hydrolysed by alkali to 4 : 5-diamino-o-xylene it is regarded as identical with (I). H. W.

Liberation of vitamin-B₂ adsorbed on acid earth by the action of pancreatin. W. NAKAHARA, F. INUKAI, and S. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 325—334).—Vitamin-B₂ (I) in liver extract is adsorbed completely on acid earth (II) and partly eluted (> 66%) by 1% aq. pancreatin at *p*_H 7.6 during 24 hr. at 32°. Pepsin has no eluent action. The eluent relieves symptoms of (I)-deficiency in a rat, the eluted (I) being more easily utilised by the animal than when fed adsorbed on (II). J. L. D.

Flavins and vitamin-B₂. I. H. VON EULER, P. KARRER, and E. ADLER (Arkiv Kemi, Min., Geol.,

1934, 11, B, No. 33, 6 pp.).—Ovoflavin, administered to animals simultaneously with yeast-juice [vitamin- B_4 (?) (I)], induces no growth with doses $< 20 \times 10^{-6}$ g. With pure (?) lactoflavin, doses of 2×10^{-6} g. effect growth, whilst with preps. adsorbed on C or PbS and eluted with aq. C_6H_5N or hot H_2O , $5-15 \times 10^{-6}$ g. produces initial but not permanent growth; fractionally eluted preps. also differ from each other. The data confirm the chemical but not biological identity of flavins, and also indicate a possible lack of (I) or some other factor from basal diets used. The purity of flavin preps. and their relation to vitamin- B_2 are discussed (cf. A., 1933, 522, 847). F. O. H.

Action of flavins on growth. H. VON EULER, P. KARRER, E. ADLER, and M. MALMBERG (Helv. Chim. Acta, 1934, 17, 1157—1165).—The growth-promoting action of flavins is definitely established and quant. agreement is observed in the effects produced by lactoflavin, ovoflavin *e*, hepaflavin, and the flavin from egg-yolk. The complex, non-dialysable flavin from liver and that from grass exert a B_2 action analogous to that of other flavins. H. W.

Effect of heat on vitamin- B_2 potency of desiccated yeast. F. C. BING and D. G. REMPE (Proc. Soc. Exp. Biol. Med., 1934, 31, 624—626).—Dried yeast, heated for 2 weeks at 105° , showed no significant loss of vitamin- B_2 (I) when tested by wt. changes and production of dermatitis on mice 3 weeks old receiving a diet deficient only in (I). When heated at 150° activity was completely lost in 2 weeks. The dose of dried yeast was 1.5 g. per head per week.

NUTR. ABS. (b)

Vitamin- B_2 concentration and possible supplementary relationships with the vitamin- B_2 -deficient diet. J. W. PAGE, jun. (Proc. Soc. Exp. Biol. Med., 1934, 31, 779—783).—Extraction of skim-milk powder with hot EtOH removed half the vitamin- B_2 (I), the conc. extract yielding a product ten times as active as the original powder. Pptn. of the extract with Et_2O resulted in loss of activity from both fractions. There was evidence of a variant of (I) when the preliminary depletion period was extended from 28 to 56 days. For the longer period EtOH-extracted milk powder was inadequate as a source of (I), but the Et_2O ppt., either alone or as a supplement to the extracted milk powder, enabled growth to be maintained.

NUTR. ABS. (b)

Determination of vitamin- B_2 by fluorescence. F. H. COHEN (Acta Brev. Neerland., 1934, 4, 46).—For the determination of vitamin- B_2 by means of its fluorescence, Kleinmann's nephelometer is used with light from a Hg lamp, filtered through a screen of Ni oxide.

NUTR. ABS. (b)

Fluoroscope for the assay of vitamin- B_2 . B. JOSEPHY (Acta Brev. Neerland., 1934, 4, 46—47).—In this apparatus the fluorescence of an unknown solution can be compared with that of a solution of Na fluorescein in monochromatic light. 2 ml. of material suffice.

NUTR. ABS. (b)

Vitamin-C content of body-fluids. M. VAN EEKELLEN, A. EMMERIE, B. JOSEPHY, and L. K. WOLFF (Klin. Woch., 1934, 13, 564—565; Chem. Zentr., 1934, i, 3229; cf. A., 1933, 1090).—The

vitamin-C reaction with 2:6-dichlorophenol-indophenol is also given by cystine and ergothionine, but these substances may be separated by pptn. with $Hg(OAc)_2$. In aq. humour and cerebrospinal fluid, ultra-violet absorption spectra show max. absorption with the same wave-length as pure vitamin-C and extinction vals. corresponding with ascorbic acid.

A. G. P.

Distribution of vitamin-C in the organism. A. GIROUD, C. P. LEBLOND, and M. RABINOWICZ (Compt. rend. Soc. Biol., 1934, 115, 1088—1091).—The wide distribution suggests that the vitamin plays an important part in general metabolism.

NUTR. ABS. (b)

Vitamin-C in the pituitary. A. GIROUD and C. P. LEBLOND (Compt. rend. Soc. Biol., 1934, 116, 629—631).—Staining with $AgNO_3$ (acidified with AcOH) is believed to indicate the distribution of ascorbic acid in the pituitary, and it is suggested that the vitamin may be concerned with the function of this organ.

NUTR. ABS. (b)

Vitamin-C in the lens. F. P. FISCHER (Klin. Woch., 1934, 13, 596—597).—Conditions in the lens are optimal for production of vitamin-C (I) because normal aq. humour is very rich in lactose, whilst that of the lensless eye (which shows practically no O_2 consumption) reaches the blood level. The lens-sugar is partly oxidised and partly glycolysed; part, however, is utilised differently. The lens has a high cystine content, and 1 mol. of sugar in presence of 2 mols. of cystine gave rise *in vitro* to 1 mol. of ascorbic acid and 4 of cysteine. The lens capsule has a peculiar selective permeability; (I) always passed through the capsule even when Fe salts and the $\cdot SH$ group were retained. Lenses with cataracts allowed diffusion of all the (I) except a residue, which was retained in the capsule and subepithelial layer where the glutathione colour reaction (with CN') was negative and yet strongly reducing properties were present. Derangement in any of the factors in the respiration of the lens leads to cataract. Whether faulty (I) formation leads to cataract or is only an associated condition is uncertain.

NUTR. ABS. (b)

Vitamin-C content of fruit. J. BECKER (Mezög. Kutat., 1934, 7, 12—23; Chem. Zentr., 1934, i, 2779).—The vitamin-C contents of a no. of Hungarian and foreign fruits are recorded.

R. N. C.

Isolation of vitamin-C from vegetables, and the relations between vitamin-C and ascorbic acid. S. MARUYAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 287—303).—Ascorbic acid (I) is isolated from *Rhapanus sativus*, L. (radish), and from the juice of *Citrus aurantium*, L. (a Japanese lemon), by a modification of Szent-Gyorgyi's method (A., 1929, 98). Japanese green tea also contains (I).

J. L. D.

Antiscorbutic value of lemon juice in relation to preserving media. Comparison of Tillmans' chemical method and the biological method for determining vitamin-C. R. CULTRERA (Ind. ital. Conserve aliment., 1934, 9, 1—8; Chem. Zentr., 1934, i, 1668).—The methods give vals. which are in good agreement. Preservation with 0.35% SO_2 destroys.

the vitamin-C almost completely in 98 days, but sterilisation by Matzka's method left 70% after 180 days.

L. S. T.

Biological and titrimetric determination of vitamin-C. H. LUND, B. SPUR, and L. S. FRIDERICIA (Biochem. J., 1934, 28, 1825—1828).—Assays of vitamin-C (I) by biological and titrimetric methods [Tillmans' method (A., 1932, 310) slightly modified] yield results in fairly good agreement. For the guinea-pig, the necessary daily addition of (I) to a (I)-free diet is about 0.7 mg. Dried hips contain 1.5% of (I). Lemon juice is unsuitable as a (I) standard.

A. E. O.

Effect of chemico-physical agents on the Szent-Gyorgyi and Tillmans reducing factor. R. CULTRERA (Ind. ital. Conserve aliment., 1934, 9, 9—18; Chem. Zentr., 1934, i, 1668).—Ultra-violet light quickly destroys the reducing factor (I). H_2O_2 has a strong oxidising action, but nascent H does not reduce. A rise in temp. destroys (I): at 1.4—5.2 the decomp. proceeds relatively slowly; it is quicker at p_{H} 6.7, and at >7 it occurs at room temp.

L. S. T.

Determination of vitamin-C in animal tissues by a modification of the silver method. E. HARDE (Compt. rend. Soc. Biol., 1934, 116, 153—155).—MeOH extracts of various tissues of normal and scorbutic guinea-pigs, and of rats and mice on normal and vitamin-C-free diets reduced AgNO_3 . The distribution of this AgNO_3 -reducing substance in the bodies of these animals agreed with that recorded for ascorbic acid (I), with which it is concluded to be identical. A similar extract of tumour tissue, which reduced indophenol, also reduced AgNO_3 , but it is doubted whether, in this case, reduction was due to (I).

NUTR. ABS. (b)

Effect of ageing on potency of spray-dried antiscorbutic material. H. J. GERSTENBERGER, D. N. SMITH, and G. L. HACKER (J. Pediat. St. Louis, 1933, 3, 93).—Fresh orange juice (I), spray-dried as a constituent of a lactose-(I) mixture, retains its antiscorbutic potency undiminished for at least 15 months. Scorbutic guinea-pigs were cured by the daily administration of an amount of the prep. equiv. to 3 ml. of (I), and a human infant by a daily dose equal to 45 ml. of (I). Fresh lemon juice, spray-dried as a constituent of an acid protein milk to which are added at the time of manufacture 20 ml. of lemon juice per litre, was adequate to cure scurvy in scorbutic infants 5—23 months after its manufacture.

NUTR. ABS. (b)

Assay of ascorbic acid with respect to its effect on oxygen consumption in young guinea-pigs. N. TÖRNBLÖM (Skand. Arch. Physiol., 1934, 68, 171—180; Chem. Zentr., 1934, i, 3488).—A daily dose of 9 mg. of ascorbic acid (I) per kg. protects young guinea-pigs on an otherwise vitamin-C-free diet against scurvy (II). No marked difference was found in the O_2 consumption (III) from that of animals receiving standard lemon juice instead of (I). Animals on a vitamin-C-free diet showed, towards the end of (II), a somewhat reduced (III) compared with both of the above groups.

R. N. C.

Origin of vitamin-C in the mouse. E. HARDE and J. WOLFF (Compt. rend. Soc. Biol., 1934, 116, 288—290).—The intestinal mucosa of the mouse, maintained on a vitamin-C-free diet, possessed a substance which reduced both AgNO_3 and indophenol. Its concn. here was $>$ in the liver, but, in the absence of biological tests, it could not be definitely identified with ascorbic acid.

NUTR. ABS. (b)

Protection of ascorbic acid from oxidation by animal tissue. L. DE CARO and M. GIANI (Z. physiol. Chem., 1934, 228, 13—24).—Aq., EtOH, or $\text{CCl}_3\cdot\text{CO}_2\text{H}$ extracts of tissue (guinea-pig) inhibit atmospheric oxidation of ascorbic acid *in vitro*. The aq. extract preserves this power in the filtrate after pptn. with Pb or Hg salts. Ringer's solution and its salt constituents at 0.1M concn. show marked inhibition. Glucose, fructose, and sucrose are inactive, glycine and alanine have a weak, yeast-adenylic acid a stronger, cysteine and glutathione, even in oxidised form, a very strong inhibitory action comparable with that of KCN.

J. H. B.

Colour reaction of isoascorbic acid (iso-vitamin-C). M. BACHSTETZ and G. CAVALLINI (Z. physiol. Chem., 1934, 228, 25—26).—Aq. isoascorbic acid (1%), when made slightly alkaline and treated with 2 drops of 10% $\text{UO}_2(\text{OAc})_2$, gives a weak brownish colour which becomes deep brown-red but with no formation of ppt. on addition of conc. NaOH. With ascorbic acid similarly treated, conc. NaOH causes disappearance of the colour and formation of a ppt.

J. H. B.

Occurrence of vitamin-E in soya-bean oil. U. SUZUKI, W. NAKAHARA, and Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 283—286; cf. this vol., 705).—The vitamin-E (I) content is low, since pregnancy in female albino rats with soya-bean oil as sole source of (I) is frequently terminated by abortion.

J. L. D.

Growth factor in liver. O. L. KLINE, C. A. ELVEHJEM, J. A. KEENAN, and E. B. HART (J. Biol. Chem., 1934, 107, 107—118).—A growth factor for chicks has been demonstrated in liver (I). It is stable to heat and insol. in H_2O , but sol. after mild hydrolysis of (I), when it is slightly sol. in Bu^nOH . It is destroyed by autoclaving at p_{H} 9 for 5 hr. at 1 atm.

H. G. R.

Synergistic and antagonistic behaviour of vitamins in the organism. H. J. JUSATZ (Z. Vitaminforsch., 1934, 3, 268—279).—A review.

Long and short wave-length limits of photosynthesis. G. R. BURNS (Plant Physiol., 1934, 9, 645—652).—Leaves of white pine and Norway spruce utilised all the visible spectrum except part of the blue and all the violet range.

A. G. P.

Assimilation of carbon dioxide by plants. P. KLASON (Svensk Kem. Tidskr., 1934, 46, 208—211).—A discussion of the origin of xylose and lignin in photosynthesis.

R. P. B.

Carbon dioxide storage. VI. Lowering the acidity of fungal hyphae by treatment with carbon dioxide. VII. Changes in flower colour as evidence of the effectiveness of carbon dioxide

in reducing the acidity of plant tissue. N. C. THORNTON (Contr. Boyce Thompson Inst., 1934, 6, 395—402, 403—405; cf. B., 1933, 1032).—VI. In cultures of *Sclerotinia fructicola* exposure to CO₂ increased the p_H of the hyphae to extents which retard growth. The action of CO₂ at 2° was > that at 15° or 28°.

VII. Colour changes of the anthocyanin pigment in petals of rose, verbenia, peony, and iris, confirmed by direct p_H determinations, indicate the action of CO₂ in increasing the p_H of living plant tissues.

A. G. P.

Colonial formation of unicellular green algæ under various light conditions. F. E. MEIER (Smithsonian Miscell. Coll., 1934, 92, No. 5, 14 pp.).—The effect of lighting on growth, chlorophyll (I) formation, etc. is recorded for 18 species. The majority form (I) even in continuous darkness. L. D. G.

Effects of intensities and wave-lengths of light on unicellular green algæ. F. E. MEIER (Smithsonian Miscell. Coll., 1934, 92, No. 6, 27 pp.).—Intermittent illumination is the most favourable to growth. Between the limits of 3.76 and 10.20 microwatts per sq. mm. increase in no. of cells \propto intensity of light for 12 out of 16 species tested. *Stichococcus bacillaris* grows well at a wide range of red and infra-red from 0.6 to 1.4

L. D. G.

Effect of alkyl halides on the respiration of potato tubers. L. P. MILLER (Contr. Boyce Thompson Inst., 1934, 6, 279—296).—The increase in CO₂ output of tubers was approx. the same following treatment with Et, Prⁿ, Buⁿ, *n*- or *iso*-amyl bromide (0.05 c.c. per litre), and considerably smaller for Pr² and *sec*-Bu compounds. The efficacy of Bu bromides was in the descending order, *n*, *iso*, *tert*, *sec*. At similar concns. the activity of bromides and iodides was approx. the same and > that of chlorides. In general, the effect of the halides increases with the dosage. The action of these substances on respiration is unrelated to that on dormancy.

A. G. P.

Effect of X-rays on growth and respiration of wheat seedlings. D. S. FRANCIS (Bull. Torrey Bot. Club, 1934, 61, 119—153).—Exposure to radiation retarded fresh- and dry-wt. production and, except in very young seedlings, depressed respiration. The effects varied with dosage and time. Sensitivity was greatest in lateral roots and least in coleoptiles.

Ch. Abs. (p)

Distribution of activity in the chemistry of higher plants. A. TSCHIRCH (Helv. Chim. Acta, 1934, 17, 992—996).—Evidence is adduced that chemical reactions in higher plants occur in the cell-sap colloid and in the intercellular material as well as in the plasma. Electro-chemical work in plants is due to the morphology of the participating bio-colloids.

H. W.

Action of certain salts on the germination of grain embryos outside the grain. G. DRAGONE-TESTI (Atti R. Accad. Lincei, 1934, [vi], 20, 59—63).—The growth of grain embryos on Knop's solution is stimulated by addition of various salts, notably by borax and ZnSO₄.

T. H. P.

Chemical changes in carrots during growth. H. PLATENIUS (Plant Physiol., 1934, 9, 671—680).—

With advancing growth carrots do not deteriorate in quality or in food val. Older carrots have higher sucrose and carotene and lower crude fibre contents. Roots, but not tops, contain small amounts of starch.

A. G. P.

Influence of dyes and hormones on the growth of plants. J. SELLEI (Arch. Pharm., 1934, 272, 737—743).—Addition of eosin, quinine, or methylene-blue to the soil hinders the development of wheat grains. Various animal hormone extracts have similar effects, but ovarian and testicular hormones cause an increased growth at a relatively late stage.

R. S. C.

Potentially unlimited growth of excised tomato root tips in a liquid medium. P. R. WHITE (Plant Physiol., 1934, 9, 585—600).—Root tips appeared capable of indefinite growth in culture solutions in which sucrose provides carbonaceous matter normally supplied by the aerial parts of the plant.

A. G. P.

Effects of clipping the tops on root development of lucerne (*Medicago sativa*, L.). H. G. THORNTON and H. NICOL (J. Agric. Sci., 1934, 24, 532—539).—Clipping lucerne plants did not affect the no. or size of nodules formed, or the N content of the whole plants. Root-N, however, was reduced by 40%.

A. G. P.

Test method for rhizocalin, the root-forming substance. F. W. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 445—455).—Etiolated pea (*Pisum sativum*) shoots are cut off just above the first node and the tip is removed below the third node. The cut plants are placed with their bases in H₂O (4 hr.) and then in 0.05% aq. KMnO₄ (4 hr.). The apex of the shoot is slit and the plants are inverted in the rhizocalin (I) solution under test (15 hr.), a set of controls being placed in H₂O. The test plants and controls are then placed with their bases in 2% sucrose (6 days) and finally in H₂O (7 days) and the no. of roots (II) is counted. A linear relationship exists between the concn. of (I) and (II) and the amount of (I) is calc. (in root units) from concns. giving suboptimal root formation. The very few roots grown on controls are due to small amounts of (I) stored in the nodular scales.¹ The polar transport of (I) is due to p.d. inside the pea shoot. A paste of (I) in lanolin is suggested as suitable for inducing root formation in practice.

S. C.

Chemical nature of the root-forming hormone. K. V. THIMANN and F. W. WENT (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 457—459).—The root-forming hormone is an unsaturated acid, pK 4.5 approx., oxidised by H₂O₂, neutral KMnO₄, and I but not by BzO₂H, very similar to but not identical with auxin. Root-producing and growth-promoting activities of hormones from various sources including Kogl's auxin-*a* and-*b*, heteroauxin, and conc. rhizocalin preps. from urine and *Rhizopus suinus* are recorded.

S. C.

Plant growth-substances. XI. Auxin ("hetero-auxin") from urine. XII. Influence of auxins on root-growth and chemical nature of the auxin of grass coleoptiles. F. KÖGL, A. J.

HAAGEN-SMIT, and H. ERXLEBEN. XIII. Hetero-auxin as metabolic product of the lower plant organisms. Isolation from yeast. F. KOGL and D. G. F. R. KOSTERMANS (Z. physiol. Chem., 1934, 228, 90—103, 104—112, 113—121; cf. this vol., 1332).—XI. A substance, having similar growth-stimulating properties to auxin-*a* (I) and -*b* (II), isolated from human urine proved to be β -indolylacetic acid, now termed "hetero-auxin" (III). Indole-2- and -3-carboxylic and β -3-indolylpropionic acids are physiologically inactive. (III) as isolated showed optical rotation due to an isomorphous substance, m.p. 167°, $[\alpha]_D -34.3^\circ$ in EtOH, which was separated by chromatographic analysis.

XII. (III) inhibits the growth (in length) of the roots of oat plants when present in the H₂O in which the plants are grown in concns. of 0.01—1 mg. per litre. In this respect it behaves like (I) and (II). The mol. wt. of the growth-substance in the growing tip by the diffusion coeff. method (Went technique) is 300—400, which agrees with (I) or (II) but excludes (III). The activity of the maize-tip auxin is destroyed by 0.5*N*-KOH at 100° (3.5 hr.) but unchanged by 5% HCl at 100° (3 hr.). This excludes (II) and (III) but agrees with the properties of (I), which is therefore most probably the growth hormone present in plant tips.

XIII. The plant growth-substance present in yeast was isolated from an autolysate after preliminary enrichment by Et₂O extraction. Its identity with (III) was confirmed by m.p., sensitivity to acid and alkali, and mol. wt. by diffusion coeff. The growth-substance produced by *Rhizopus nigricans* and *Aspergillus niger* when grown on substrates containing org. N is also (III). J. H. B.

Influence of growth-promoting substances on barley mutants. I. H. VON EULER, D. BURSTRÖM, and M. MALMBERG. II. H. VON EULER, D. BURSTRÖM, and H. LARSSON (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 38, 6 pp., No. 39, 5 pp.).—I. Bios preps. from malt (this vol., 696) have a slight growth-promoting action (I) (indicated by dry wt. and length of root) on seedlings of normal and chlorophyll-defective Albina barley mutants; the content of bios is not changed either in the nutrient media or in the roots. Neither inositol (A., 1928, 1152) nor folliculin (II) (this vol., 224) has any marked (I); most of (II), however, disappears from the medium.

II. Pike eggs are rich in bios but poor in flavins, whilst hen's egg-yolk has high contents of bios, vitamin-B₂, and flavins. Birch and elm pollen contain little bios, whilst 9 × 10⁻⁴% of flavins occurs in the former. Neither ZnCl₂ nor ZnCl₂ + bios has any (I) on the mutants. ZnCl₂ inhibits yeast fermentation and accelerates the reduction of methylene-blue or (II) (to testicular hormone) by barley roots. F. O. H.

Nature of indole base from barley mutants Albina 1 and 3. H. VON EULER, H. HELLSTRÖM, and J. HAGEN (Arkiv Kemi, Min., Geol., 1934, 11, B, No. 36, 6 pp.; cf. A., 1933, 877).—Extraction of the chlorophyll-defective mutant Albina 1 with EtOH followed by Et₂O and aq. HCl digestion gives an aq. layer with absorption bands (I) at 270 and 325 m μ and a weaker one at 288 m μ , the latter being also found in

Et₂O extracts. Adsorption on acid clay and elution with C₆H₅N yield solutions with (I) of 330 m μ max., stable to aq. NaOH. On keeping, aq. extracts acquire (I) between those of C₆H₆ and PhMe. This Ph derivative is not volatile in steam and is derived from the indolyl base by bacterial action. The base is not a growth-promoting factor for yeast. F. O. H.

Vegetative and reproductive responses associated with fruit development in the cucumber. J. P. MCCOLLUM (Cornell Univ. Agric. Exp. Sta. Mem., 1934, No. 163, 27 pp.).—The inhibitive effect of the development of fruits on the general growth of plants is not related to mineral nutrition or to carbohydrate accumulation within the plant. The presence of a growth-regulating substance in the fertilised ovary is indicated. A. G. P.

Accumulation of tannin in the cells of chestnut wood. M. QUENDIAC (Compt. rend., 1934, 199, 799—801).—In early spring tannins are localised in areas in which sap flow is restricted, notably in the parenchyma of the sap wood. In May accumulation zones extend towards the extremity of branches. Subsequently the sapwood develops two distinct regions, one normal and one with tannin accumulations corresponding with the zone of transition between heart- and sap-wood. A. G. P.

Growth and elasticity of cell walls in the hypocotyl of *Helianthus*. F. GESSNER (Jahrb. wiss. Bot., 1934, 80, 143—168).—Elasticity of cell walls (I) decreases with rising temp. and is not influenced by variations in the H₂O content within vital limits. Elimination of "growth substance" by decapitation causes a decline in (I). In NaOAc solutions (I) varies with [H⁺] in the range p_H 5.5—4.0. (I) is not altered by changes in lighting, but decreases on exposure to ultra-violet light. Living cells only are affected. Reduced (I) and growth restriction are not necessarily parallel phenomena. A. G. P.

Seasonal cycles of nitrogenous and carbohydrate materials in fruit trees. I. Seasonal cycles of total nitrogen and of soluble nitrogen in wood, bark, and leaf portions of terminal shoots of apple trees under two cultural systems—grass *plus* annual spring nitrate, and arable without nitrogenous fertiliser. D. V. KARMARKAR (J. Pomology, 1934, 12, 177—221).—Well-defined cycles in the total sol. matter, total N (I), protein- (II), and various fractions of non-protein-N (III) of wood and bark are established. Max. vals. for wood-N occur in June. In bark, peak vals. for (I), (II)-, humin-, and imide-N appear during dormancy, and those for (III), basic, and residual N at the beginning of the dormant period (November). The N cycle in leaves is different in character. (I) and (II) decline, especially in autumn, with a corresponding increase in (III) in leaves and in (I), (II), and (III) in bark. (I) and the % of (II) in (I) increase in the order, wood < bark < leaves. In manured grass plots the % of (II) and (I) in bark and wood is > that in arable. The distribution of the fractions of (III) is not greatly affected by differences in the method of culture. A. G. P.

Effect of ethylene, ethylene chlorohydrin, and ultra-violet light on carbohydrate content of stored apples. R. B. DUSTMAN (Plant Physiol., 1934, 9, 637—643).—None of these treatments affected the composition of the fruit or the p_H of expressed juice. C_2H_4 hastened the colour change and accelerated the softening of the fruit. A. G. P.

Metabolism of citric, sulphuric, and nitric acids in the potato tuber. Explanation for the high p_H of the juice of tubers treated with ethylene chlorohydrin. J. D. GUTHRIE (Contr. Boyce Thompson Inst., 1934, 6, 247—268).—The expressed juice of tubers treated with $CH_2Cl \cdot CH_2 \cdot OH$ shows decreased contents of SO_4^{4-} , NO_3^- , citrate, Ca, Mg, and total ash. The increased p_H is < that anticipated as a result of the above changes. Three days after treatment the juice has less buffer power on the acid side (probably due to loss of citric acid), but regains normal val. after 6 days as a result of the appearance of amphoteric substances (NH_2 - and other non-amide forms of N). Buffers occurring in juice include NH_2 -acids and asparagine (p_H 8—10), and these together with citric and malic acids in the range p_H 8—3. Phosphates exert buffer effects between p_H 8 and 6. A. G. P.

Carbohydrate and nitrogen relations in wheat plants with reference to type of growth under different environmental conditions. A. M. HURD-KARRER and A. D. DICKSON (Plant Physiol., 1934, 9, 533—565).—Leaves of plants grown with short-period lighting (8 hr.) (I) had higher N and lower carbohydrate contents than those with prolonged lighting (17 hr.). Supplementary lighting of high intensity induced higher proportions of acid-hydrolysable matter (II) and lower % N than weaker lighting without affecting the rate of growth or external appearance. Growth on limed soils (p_H 8.1) produced lower proportions of sugar and higher (II) than did that on neutral soils. (II) was not affected by temp. (I) and low temp. are associated with high p_H in the plant juice. The latter was not appreciably influenced by the intensity of light or by soil reaction. A. G. P.

Separation of cellulose particles in membranes of cotton fibres by treatment with hydrochloric acid. W. K. FARR and S. H. ECKERSON (Contr. Boyce Thompson Inst., 1934, 6, 309—313).—Treatment of mature fibres with HCl (d 1.19) for periods up to 5 days removed non-cellulose constituents, without affecting the essential characteristics of the cellulose. A. G. P.

Starch determination methods involving solubility in acids. F. E. DENNY (Contr. Boyce Thompson Inst., 1934, 6, 381—393).—Low vals. obtained by Rask's method (B., 1927, 311) are not due to hydrolysis of starch (I) during contact with HCl, but probably to incomplete extraction of (I) by the procedure adopted. From solutions in HCl, after 1 hr. at 20—25° (I) may be recovered almost completely by coagulation in EtOH. H_2SO_4 may similarly be used. Repeated extraction of tissues with acid removes all (I), but the ppt. obtained with EtOH may be contaminated with foreign substances. Determination of (I) in the ppt. by hydrolysis leads to vals. comparable with those of other methods. The taka-diaxase

method gives higher results than other methods in some cases, owing to hydrolysis of non-starchy constituents to give Cu-reducing substances. A. G. P.

Pectic constituents of citrus fruits. L. W. GADDUM (Florida Agric. Exp. Sta. Bull., 1934, No. 268, 23 pp.).—In orange, grapefruit, and kumquat the % of total pectic material (I) in the albedo and in the pulp remains const. through a considerable part of the growth period. The H_2O -sol. pectins (II) rise to a max. val. immediately prior to the decline in (I), and subsequently decrease. The degree of methylation (M) of (II) is < that of acid-extracted pectins (III). With advancing maturity the M of (II) declines but that of (III) remains approx. const. The M of pectins from various sections of the fruit increases in the order juice, pulp, albedo. The M of (II) is closely related to their viscosity. The Ca content of the various pectates approached a mean val. between 7.4 and 7.6%. A. G. P.

Determination of sugar in plant-saps by means of Fehling's solution. P. CRISCI (Atti Congr. naz. Chim., 1933, 4, 705—714; Chem. Zentr., 1934, i, 2322).—Clarification with $Pb(OAc)_2$ if prolonged > 30 min. may lead to low vals. for sugar. A. G. P.

Synthesis of sucrose in plant tissue. A. I. VIRTANEN and M. NORDLUND (Biochem. J., 1934, 28, 1729—1732).—Leaves of red clover and wheat, deprived of starch by storage in the dark, synthesise sucrose from both glucose and fructose, to the extent of 6% of the dry wt. of the leaf, when kept in a 10% solution of the sugar in the dark for 24 hr. C. G. A.

Glucoside from madder. R. HILL (Nature, 1934, 134, 628).—A yellow cryst. glucoside of ψ -purpurin (I), named *galieide* (II), m.p. indefinite (decomp.), has been prepared from the roots of wild madder (*Rubia peregrina*) and the yellow bedstraw (*Galium verum*). (II) appears to be a 1-monopentoside of (I), and is easily hydrolysed. (II) is responsible for the dyeing properties of the above plants. L. S. T.

Glucoside of *Bryonia dioica*. A. ANGELETTI and D. PONTE (Gazzetta, 1934, 64, 569—577).—The roots of *B. dioica* ("stabilised" by inactivating the enzymes) contain KNO_3 , a small amount of essential oil, an amorphous alkaloid, and the amorphous glucoside brionin, $C_{48}H_{66}O_{18}$, which yields on hydrolysis 1 mol. of glucose, 1 mol. of briogenin, $C_{30}H_{46}O_8$, and a resinous substance, $C_{12}H_{12}O_8$ (?) (cf. Power and Moore, J.C.S., 1911, 99, 937). R. K. C.

Bitter glucoside of the olive. W. V. CRUESS and C. L. ALSBERG (J. Amer. Chem. Soc., 1934, 56, 2115—2117).—Details are given for the extraction and purification of the glucoside (oleuropein) (I) (C 53.65, H 6.51, O 39.84%), M 433 (f.p. in AcOH), 470 (b.p. in EtOH), $[\alpha] -145^\circ$ to -148° in H_2O (cf. Bourquelot and Vintilesco, A., 1908, i, 904), which reduces Fehling's solution (reducing power 0.47; glucose 1) and aq. $KMnO_4$ (reducing power 0.45; tannin 1). When an aq. solution of (I) is boiled, an insol. resin, $[\alpha]^{20} -116.8^\circ$ in EtOH, is pptd.; this is probably a "phlobaphen" similar to that obtained from o - $C_6H_4(OH)_2$ -tannins. (I) is hydrolysed slowly by emulsin (not by invertase) and rapidly by "pectinol" (a mould enzyme prep.).

Hydrolysis (2% H_2SO_4) of (I) gives glucose and a bitter ester, which is readily hydrolysed by alkali with loss of the bitter taste. Cold dil. NaOH converts (I) into a non-bitter glucoside; 3% NaOH or 4% $\text{Ba}(\text{OH})_2$ at 80–100° gives 3:4-($\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$, whilst energetic alkaline hydrolysis affords a little unidentified phenol, m.p. 91.5°. The amounts of (I) in different varieties of olives are determined. H. B.

Presence of urson in *Arbutus unedo*, L. A. SANNA (Atti Congr. naz. Chim., 1933, 4, 595–596; Chem. Zentr., 1934, ii, 622).—Urson, obtained from the EtOH extract from crushed leaves of *A. unedo* (I), has m.p. 278° (Ac, m.p. 264°, and Bz derivative, m.p. 214°). With Ac_2O and a trace of H_2SO_4 , a violet colour is produced. Arbutin and methylarbutin also occur in (I). A. G. P.

Organic principle in *Eupatorium ayapana*, Vent. N. C. NAG and K. N. BOSE (Trans. Bose Res. Inst., 1932–1933, 8, 195–198).—The syrupy residue from a hot H_2O extraction of the dried leaves is extracted with 5 vols. of 91% EtOH. After filtration from inorg. salts, the EtOH is removed and the residue shaken with light petroleum, which affords a cryst. substance, $\text{C}_{12}\text{H}_{10}\text{O}_4$, m.p. 110–112°, giving a violet colour with conc. H_2SO_4 . P. G. M.

Constituents of miso. IV. Acids. Y. SAKURAI (J. Agric. Chem. Soc. Japan, 1934, 10, 486–495).—AcOH, lactic and succinic acids are identified. Amounts of Et₂O-sol. free acid were small. Acidity is probably due to acid phosphates. CH. ABS. (p).

Formation of phenols in plants. T. K. GAPONENKOV (J. Gen. Chem. Russ., 1934, 4, 466–471).—Thymol, carvacrol, and other phenols originate probably by oxidation of *p*-cymol, and terpenes (phellandrene) by reduction. The thymol content of Ash-gon plants increases with their stage of maturity; that of the seeds increases on storing, but falls on germination. R. T.

Formation of terpenes. G. V. FIGULEVSKI (J. Gen. Chem. Russ., 1934, 4, 603–609).—The view that essential oils (I) arise from the decomp. of resin acids is supported by the co-existence in natural (I) of different compounds of the same general structure and of the same type of mol. asymmetry. R. T.

Chemical examination of *Celastrus scandens*. N. WAKEMAN (J. Amer. Pharm. Assoc., 1934, 23, 873–874).—Leaves (I), stem (II), root (III), and fruit (IV) were separately submitted to successive extraction with light petroleum, Et₂O, and EtOH. (I) gives chlorophyll, sterols (V), and a white cryst. non-reducing substance (VI), m.p. 182°, yielding galactose on hydrolysis. (II) gave (V) and (VI) together with a substance, m.p. 186°, resembling dulcitol. The red bark of (III) yields β -carotene and an orange powder. C. G. A.

Constituents of *Ginkgo biloba*, L., fruit.—See this vol., 1345.

Preparation of humate-iron and other humate-metals. C. K. HORNER, D. BURK, and S. R. HOOVER (Plant Physiol., 1934, 9, 663–669).—Synthetic and natural humates containing Fe, Al, Mn, Zn, Ni, Cu, and other metals have been prepared.

Small applications of humates to plant culture media normally supply sufficient metal for entire growth requirements. The compounds are stable in alkaline, neutral, and moderately acid media and are not pptd. by PO_4^{3-} . A. G. P.

Characteristics and composition of coffee-bean oil. H. A. SOHUETTE, M. A. COWLEY, and C. Y. CHANG (J. Amer. Chem. Soc., 1934, 56, 2085–2086).—The oil (I) extracted from green Santos beans (freed from wax with $\text{C}_2\text{H}_2\text{Cl}_4$) by light petroleum has d_{25}^{25} 0.9653, n_D^{25} 1.4790, I val. (Wijs) 100.72, sap. val. 195.53, Reichert–Meissl val. 0.36, Polenske val. 0.4, acid val. 7.05, OH val. 22.82, and contains 12.63% of unsaponifiable matter (I val. 153.8). (I) gives oleic (12.36%), linoleic (25.66%), myristic (2.19%), palmitic (20.17%), stearic (9.13%), and arachidic acid (2.11%) (cf. Heiduschka and Kuhn, this vol., 465; Bengis and Anderson, *ibid.*, 710). Data previously reported (lit.) for (I) refer (usually) to the wax-containing oil. H. B.

Embryo and testa of kaoliang (*Andropogon sorghum*, Brot.). I. Oils. R. YAMAMOTO and M. NINOMIYA. II. Decomposition of oil. R. YAMAMOTO, M. NINOMIYA, and A. OTAKA (J. Agric. Chem. Soc. Japan, 1934, 10, 248–256, 257–264).—I. The embryo oil (I), m.p. –17° to –21°, d 0.8964–0.9263, n 1.4566–1.4735, has I val. 115.10–124.10, sap. val. 179.7–192.0, Reichert–Meissl val. 0.18–0.81, acid val. 3.11–21.21, and unsaponifiable matter 2.57–3.43%. Testa oil (II), m.p. 60–62.5°, n 1.4570, has I val. 110.8, sap. val. 185.8, Reichert–Meissl val. 0.73, Ac val. 18.8, Hehner val. 90.01, Polenske val. 0.46, acid val. 96.47, unsaponifiable matter 8.04%.

II. Acid vals. of (I), and particularly (II), increase *in situ*. The lipase in the embryo bud has optimum p_H 4.2; it is inactivated in 1 hr. at 90° or 3 hr. at 60°.

CH. ABS.

Sicilian sumach-seed oil. G. A. BRAVO (Annali Chim. Appl., 1934, 24, 427–430).—On extraction with light petroleum, the seeds of *Rhus coriaria* yield about 14% of a yellowish-brown oil, d 0.9128, n_D^{20} 1.4772, optically inactive and not fluorescent, acid val. 9.6, sap. val. 191.9, I val. (Hubl) 97.5, Reichert–Meissl val. 1.2, unsaponifiable matter (containing phytosterol and a resin) 1.63%. The colour reactions of the oil and properties of its fatty acids are given. The % composition is calc. on the assumption that the only glycerides present are triolein, trilinolein, tristearin, and tripalmitin. D. R. D.

Oils from leguminous pulses. H. N. BANERJEE (Trans. Bose Res. Inst., 1932–1933, 8, 199–210). Et₂O-extraction of green moog gave 0.5% of oil, sap. val. 171.2, I val. 111.9, unsaponifiable matter 12.3% from which phytosterol was obtained. Vitamin-A and -D were present in the oil obtained from *Kabuli chhola*, sap. val. 185.3, I val. 72.44, unsaponifiable matter 3.4%; phytosterol was also isolated. P. G. M.

Resin from *Achras zapota*, Linn. (Sawo Manila), fruit. A. J. ULTEE (Pharm. Weekblad, 1934, 71, 1152–1154).—The resin (ash 0.86, proteins 1.8, aq. extract 11.14, EtOH extract 84.03, gutta-percha 9.19%), gave 1% of γ -chicle-alban and consisted mainly of β -amyrin; α -amyrin and lupeol were not

detected. Hexoic acid was isolated from the hydrolysed material. S. C.

Effects of potassium on the growth of sugar cane and on the absorption and migration of ash constituents. C. E. HARTT (Plant Physiol., 1934, 9, 399—452).—In sand cultures K deficiency was marked by depressed growth, leaf discoloration, die-back of leaf tips, and reddening of midribs. The latter is attributed to the presence of phloroglucinol (I) and sufficient SO_4^{2-} in the plants. (I) is probably derived from decomp. of tannic acid as a result of K deficiency. Plants deprived of K and Na were not inferior to those receiving Na but no K. Those previously deprived of Na and K recovered after K additions, more rapidly than those previously deprived of K only. In nearly all cases, all organs contained more K than Na even when Na was supplied in relative excess. Absorption of K during the first month \propto the size of the plant, but at later stages \propto the amount supplied. Addition of K to K-deficient plants was followed by rapid absorption and increased growth, but the intake of Mg and P was depressed. K absorption was not affected by light. Deficiency of K is associated with increased intake of P, Fe, Ca, Mg, and Si during the first few months of growth, and with nodal accumulations of Fe. The latter was translocated to leaves after replenishment of the K supply. A. G. P.

Effects of potassium on the amounts of protein- and amino-nitrogen, sugars, and enzyme activity of sugar cane. C. E. HARTT (Plant Physiol., 1934, 9, 453—490).—The expressed juice of K-deficient plants (I) had similar p_H , titratable acidity, and buffer systems to that of controls (II). After 2 months' growth blades and stems of (I) had more NH_2 - and less protein-N than (II). The relationship was reversed in stems at a later stage. K starvation restricts both synthesis and translocation of K, but reduction of NO_3^- remains normal. The total sugars of leaf blades were not appreciably affected by the K supply, but reducing sugars were higher and sucrose was lower in (I). In stems a positive correlation was observed between the K supplied and the total sugar stored. Optimum invertase (III) activity occurred at p_H 4.4. K is not essential for the formation of (III), but is a sp. activator. Amylase activity (IV) in blades was optimum at p_H 5.9; that in stems was little affected by $[\text{H}^+]$. (IV) was higher in (I) than in (II). Optimum p_H for the ereptase (V) of blades and roots was 4.9, and that of stems, 5.9. K deficiency affected (V) only in roots, in which activity increased. A. G. P.

Influence of potassium on the nitrogen and carbohydrate metabolism of plants. T. W. TURTSCHIN (Z. Pflanz. Düng., 1934, A, 35, 343—357).—Deficiency of K retards assimilation of mineral N, and, when the latter is in the form of NH_4^+ , leads to toxic accumulation of NH_3 within the plant. High Ca or Na in association with insufficient K causes accumulation of non-protein-N and in some instances of glucose. The unfavourable effects of excessive Cl^- in fertilisers result from the formation of CaCl_2 in soil (by base exchange), the subsequent increased intake of Ca by plants, and the disturbed metabolism due to high Ca : K ratio. K fertilisers counteract the injurious effects of heavy NH_4^+ manuring. A. G. P.

Cuticular excretion of leaves. K. ARENS (Jahrb. wiss. Bot., 1934, 80, 248—300).—The excretion is alkaline and contains K, Ca, Mg, P, and org. matter. The total ash of leaves may be reduced by 50% by washing with distilled H_2O for 24 hr.

A. G. P.

[Composition of] dandelions. G. E. YOUNGBURG (Science, 1934, 80, 337; cf. this vol., 1275).—The P content is given.

L. S. T.

Use of tartrazine in the determination of chlorides in biological material. W. L. FEARON and W. A. GILLESPIE (Biochem. J., 1934, 28, 1629—1630).—Tartrazine is recommended as an indicator in this determination. Proteins interfere and an indirect procedure, for use in their presence, is described.

H. N. R.

Micro-determination of bromine in biological fluids. T. LEIPERT and O. WATZLAWEK (Z. physiol. Chem., 1934, 226, 108—115).—The material (blood, milk, urine) is oxidised with $\text{Ag}_2\text{SO}_4\text{--CrO}_3\text{--H}_2\text{SO}_4$ and the liberated Cl_2 and Br are retained by NaOH. The NaBr and NaOBr are oxidised by NaOCl to NaBrO_3 , which is determined iodometrically after addition of KI.

J. H. B.

Colorimetric micro-determination of arsenic. G. TAUBMANN (Arch. exp. Path. Pharm., 1934, 176, 751—756).—The material (containing 0.1—0.4 mg. As), e.g., blood, is digested with $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ and treated by the Marsh method. The AsH_3 evolved is passed through aq. AgSO_4 , excess of AgSO_4 removed, the dissolved As_2O_3 oxidised by Br, and As_2O_5 determined colorimetrically (A., 1932, 963).

F. Ö. H.

Biological method for the determination of calcium-ion concentration. F. C. McLEAN and A. B. HASTINGS (J. Biol. Chem., 1934, 107, 337—350).—The isolated frog's heart is sensitive to changes in $[\text{Ca}^{++}]$ (I) but not to non-ionised Ca, the criterion for equal (I) being equal amplitude of contraction of the ventricle. A sensitivity to differences of (I) of 1 mg. per litre has been demonstrated.

A. E. O.

Determination of nitrate-nitrogen by the Devarda process. Application to biological media. D. BACH (Bull. Sci. pharmacol., 1933, 40, 459—470; Chem. Zentr., 1934, i, 1679).—Reduction of NO_3^- to NH_3 in $< 0.05N\text{--NO}_3^-$ solution with $0.2N\text{--NaOH}$ and 0.05 g. of Devarda alloy per c.c. at 70° is complete in 10 min. The reduction and NH_3 distillation are carried out as previously described (A., 1933, 921). There is a systematic error up to 0.02 mg., due to NH_3 from the alloy. With glycine, urea, urine, meat broth, and *Aspergillus* culture liquids there is an error of 0—1.94%, blood-serum 2.31, asparagine 2.48, and peptone 5.02%. This is remedied by removal of protein from the serum or by dilution. Li_2CO_3 , Ba^{++} , Ca^{++} , Mg^{++} , Zn^{++} , Mn^{++} , Co^{++} , Ni^{++} , Fe^{++} , Cu^{++} , PO_4^{3-} , AsO_3^{3-} , and BO_3^{3-} inhibit reduction, and extra NaOH is required. $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^- , and ClO_3^- are also inhibitors. Hexoses, pentoses, and polyalcohols, but not bioses, interfere and must be diluted to a concn. of 2%. $\text{CCl}_3\text{--CO}_2\text{Na}$ and polyphenols interfere, but not PhOH and $\text{C}_{10}\text{H}_7\text{--OH}$.

L. S. T.